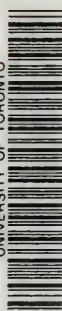


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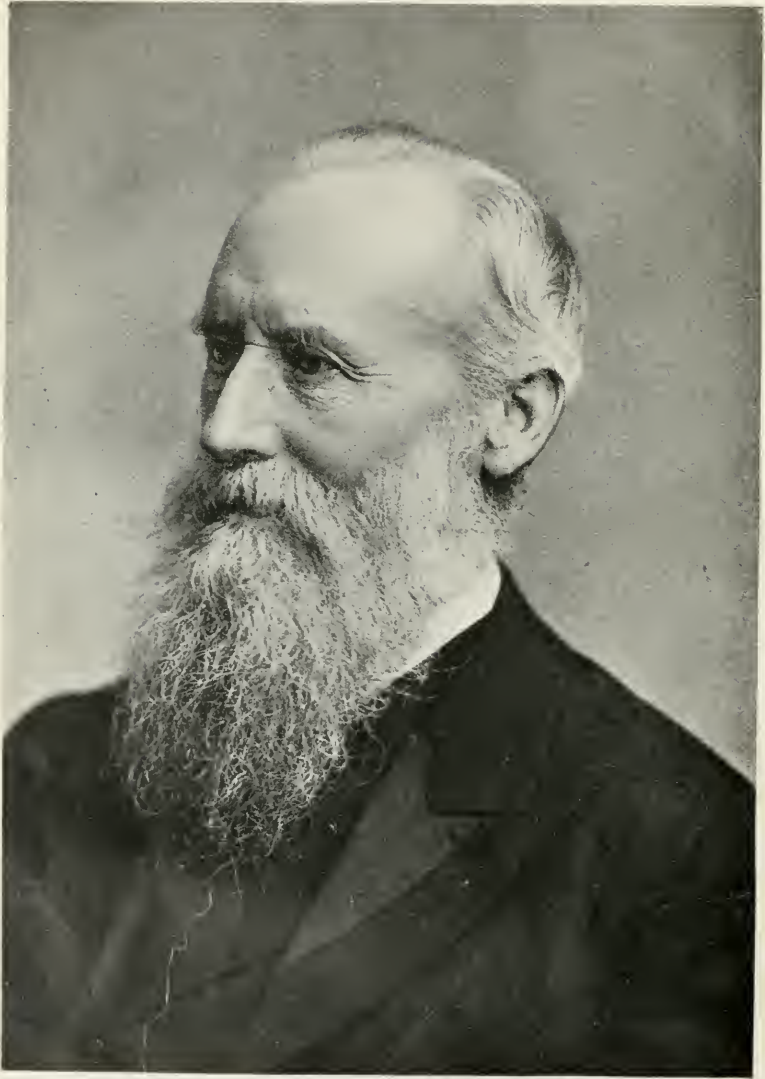
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*Elliott & Fry*

JAMES CAMPBELL BROWN, D.Sc., LL.D.



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A

# HISTORY OF CHEMISTRY

FROM THE EARLIEST TIMES

BY THE LATE

JAMES CAMPBELL BROWN,

D.Sc. (LOND.), LL.D. (ABDN.),

*Professor of Chemistry in the University of Liverpool*

WITH A PORTRAIT AND ONE HUNDRED AND SIX  
ILLUSTRATIONS

SECOND EDITION

EDITED BY

HENRY HILTON BROWN,

*Procurator Fiscal of Midlothian*



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## PREFACE TO FIRST EDITION

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THE late Dr. Campbell Brown was accustomed, as part of his Chemical Course at Liverpool University, to deliver a series of Lectures on the History of Chemistry. These lectures were to him a labour of love, and were prepared after much research into the original authorities, including many old and rare treatises. It was his intention, when release from the duties of his Chair should have afforded him the necessary leisure, to revise the lectures and to put them into shape for publication. Death put a sudden term to his labours before the period of leisure arrived, and the lectures were left in the form of manuscript notes, more or less complete, but not in that perfect shape which Dr. Campbell Brown would have wished if the History were to be published.

Mrs. Campbell Brown and the friends of the Author considered that it would be matter for deep regret if his intention of publishing the History were not carried into effect, and the material which he had collected with so much labour made available to students and others interested in the subject. For reasons which need not be mentioned here, it seemed good to Mrs. Campbell Brown to entrust the writer with the duty of editing the manuscripts and passing the work through the press. In discharging the duty thus entrusted to him, he has endeavoured to present the substance of the lectures as nearly as possible in the shape in which Dr. Campbell Brown used to deliver them, subject to such verbal alteration as was requisite in changing them from addresses intended to be spoken to the form of a book intended to be read. Unfortunately, the oral

additions and comments, with which their author was wont to supplement the written notes. have been for the most part lost, and although the Editor has tried so far as he could to supply the want by reference to other writings of Dr. Campbell Brown and such sources of information as were available, it cannot be doubted that the work is in consequence less complete than it would have been had Dr. Campbell Brown finished it himself.

For the division into chapters the Editor alone is responsible. At first he tried to make a chapter coincide with a lecture, but a little experience showed that this was impracticable. The lectures had been prepared with the object of filling a definite time in delivery. Sometimes they coincided with a logical division of the subject, but more frequently they either passed beyond or fell short of a division. The Editor, therefore, found it necessary to subdivide the lectures and to arrange the History in chapters, each of which deals with a logical section of the subject.

The Editor has to express his indebtedness to Mr. William Henry Roberts, M.Sc., F.I.C., Public Analyst for the City of Liverpool, who was for fifteen years Chief Assistant to Dr. Campbell Brown, and who has revised the manuscript and given most valuable aid in preparing the lectures for the press.

The whole book has been carefully checked by the Editor, and every effort has been made to attain accuracy. In a work of such magnitude, embracing an enormous amount of detail, it is possible that slips may have occurred, and it may be that in some instances the notes of Dr. Campbell Brown have been misunderstood. If in spite of all the care taken, some errors have been committed, the Editor, knowing the extreme accuracy of the Professor, requests that such slips may be attributed, not to the Author, but to himself.

HENRY H. BROWN.

8, ABERCROMBY SQUARE,

LIVERPOOL,

January, 1913.

## PREFACE TO THE SECOND EDITION



THE Second Edition is a reprint of the First. A few passages have been slightly altered, and a few slips have been corrected, but the book is substantially the same. It has been thought better to preserve Dr. Campbell Brown's work as nearly as possible in the shape which he wished it to take. The Index has been enlarged.

HENRY H. BROWN.

8, ABERCROMBY SQUARE,  
LIVERPOOL,  
*February, 1920.*





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## BIOGRAPHICAL NOTE

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“Nor love thy life, nor hate ; but what thou livest  
Live well ; how long or short permit to Heaven.”—MILTON.

IN an old Northern churchyard, in the shadow of the firwoods, lie the remains of a race who spelt their names anciently *Bronnie*, subsequently *Browne*, and finally *Brown* — the Browns of Fordell and Cluny. A stern and hardy race they were, staunch Tories in matters of Church and State, and firm adherers to duty. As one sits on the low wall that bounds the burying-ground and considers the old moss-grown tombstones, he can easily realise for himself some of the factors which went to the making of the men to whose memory they were erected. Nature in the North of Scotland is no kindly nurse. The man who seeks to wrest a living from the land must rise early and retire late, must not be easily discouraged, and must be prepared to wage an unending battle with the soil and the elements. Such a strife makes resolute warriors, and such it made the Browns of Fordell and Cluny.

Of this old family James Campbell Brown was born at Aberdeen, on January 31st, 1843. His father was at that date resident in Aberdeen, but soon removed to London as principal partner of the Bow Common Alum Works. Here the future chemist grew to boyhood amongst surroundings which familiarised him with some of the most beautiful processes of chemistry, and inspired that love of the science which ultimately caused him to devote his life to it.

His father placed him at the Gymnasium of Old Aberdeen under the tuition of Dr. Anderson, whose name was then a household word to all the teachers in the North of Scotland. Proceeding to the Marischal College in 1857, he took the classes

which formed the curriculum for the first part of the Medical Course, like so many of the chemists whose names appear in his *History of Chemistry*. His fondness for science, however, soon determined him in a different direction, and in 1863 he proceeded to the Royal College of Chemistry at London, where he studied under Tyndall and Hofmann, at the same time matriculating at London University. There, in 1867, he graduated Bachelor of Science with First Class Honours, being also awarded the University Scholarship in Chemistry, and in 1870 crowned his distinguished career as a student by obtaining the degree of Doctor of Science. Then, as always, he might have assumed as his motto the words of the Lycian prince in the Iliad—

“To stand the first in worth as in command.”

With a clear perception of whatever object he had for the time being set before him, with indomitable courage to fight against a delicate constitution and indifferent health, and with a determination which would be satisfied with no half-measures, but would insist that whatever was done should be rightly done, he was a true representative of a family which has produced its own share of good citizens and distinguished men.

From 1864 to 1866 he acted as Assistant to the Professor of Chemistry at Aberdeen, but the first step towards his life-work was his appointment in 1867 to be Lecturer in Experimental Science and Toxicology at the Liverpool Royal Infirmary School of Medicine. Thenceforward his biography is mainly a history of that institution and University College in which it was merged. His marriage in 1872 to Miss Ellen Fullarton, only daughter of John Henderson, Esq., of Quarrylodge, Aberdeenshire, secured for him the assistance and support of one who stood loyally by him in the great work of his life, and whose share in that work is only known to those who were intimately associated with him in its performance. But before entering upon an account of the long struggle which resulted so triumphantly in the establishment of the

University of Liverpool, there is room for a few words of a personal nature.

Like all his family Dr. Campbell Brown was a staunch Conservative in politics. In private life he was a man of many interests. He thoroughly enjoyed good literature and music, and it was said of him by old friends that "his conversation was illumined by flashes of humour that indicated the deeper current of his life." He did not restrict himself to one branch of science. His knowledge of botany was such that, if he had chosen, he might have attained distinction as a botanist. As it was, he made a special study of "alpines" and formed a valuable collection of these in the grounds of his house at Wedderhill, near Stonehaven, where they still flourish in an ideal environment.

One of my earliest recollections of my cousin, who was my senior by thirteen years, is of wandering with him in a field searching for a bulbous crowfoot which he wished to show me. The search, I remember, was prolonged, for by some perversity the buttercups in that particular spot were not of the species he sought, but he did succeed in the end, and it says much for his powers of tuition even then, that although I was little more than four years old, and had never heard of a bulbous crowfoot, I still remember the name and what he said about the plant. Perhaps I may be permitted to add that at a later date it was on his initiative, and with his assistance and encouragement, that I began the amateur study of chemistry from which I acquired a knowledge of its practice and principles sufficient to enable me to undertake the editing of the present work.

Liverpool was the sphere in which Dr. Campbell Brown found full scope for his energy. Educational and scientific matters in that city provided for him a field of usefulness in which he was occupied for the greater part of his life, and to which he devoted all his gifts of organisation, hard work, and self-denial. He has himself given us in a pamphlet published in 1892, "The First Page of the History of University College, Liverpool," an outline of the events which led up to the

ultimate establishment of the institution, and from that essay it is possible to condense an account of the matter, which will at least show the difficulties that had to be overcome.

Dr. Campbell Brown sets down as his opening words a passage which may serve as a text for the discourse :—“The desire to retain a body of men who should devote themselves to the task of keeping Liverpool on the crest of the wave of advancing knowledge, appeared very early in the nineteenth century, and made itself manifest at sundry times and in divers manners during seventy-five years, before the great effort which gave birth to University College.” The Royal Institution of Liverpool was the result of a movement set on foot in 1814 to form a fund for the remuneration of men of learning, who should fix their residence in the city, and deliver lectures and instruction in different branches of literature and science. For many years this body was the centre of a great educational work, but as time passed, changes in the city due to removal of the population and to altered conditions of living rendered the Institution less able to maintain the efficient position which it originally held.

Queen's College, Liverpool, an institution affiliated to the University of London, and partly the outcome of the Mechanics' Institution, did a great deal of good, and carried on a species of higher education for a time. It was, however, seriously hampered by the lack of endowments sufficient to render the teachers practically independent of the fees received from the pupils.

Another teaching body in Liverpool was the School of Medicine, which, having been first established in connection with the Royal Institution, was taken under the protecting care of the Royal Infirmary, and acquired a degree of efficiency and a reputation which rivalled the Medical Schools of Manchester and Leeds. It was to this Institution, as already stated, that Dr. Campbell Brown owed his introduction to Liverpool. An effort had been made in 1857 to effect a union between



Queen's College and the Royal Infirmary School of Medicine, but the negotiations broke down, and when Dr. Campbell Brown tried in 1872 to bring about a coalescence of the two bodies so as to form a complete college, he discovered that it would be very difficult to adjust questions of precedence, and to acquire the buildings and ground belonging to the Royal Infirmary, and the constitution and name vested in Queen's College, on any terms which either body was likely to accept. So the scheme dropped.

An endeavour to utilise the School of Science, which conducted evening classes in connection with South Kensington, and the Cambridge University Extension Lectures, has to be mentioned, because these two attempts, although they produced little direct fruit, led to the first step in the great scheme.

The increased requirements of the University of London necessitated an appeal to the public for funds to endow a Lectureship on Experimental Science, and Dr. Campbell Brown suggested that advantage should be taken of the opportunity to press definitely upon the attention of the citizens the need which so many people in Liverpool vaguely felt of a College for the cultivation and practical teaching of the higher branches of knowledge. November 1st, 1877, was an important date in this matter. On it was held a meeting of the Royal Infirmary School of Medicine, at which Dr. Campbell Brown presided, and it was resolved that a preliminary conference should be held with the Cambridge Science Lecturers and with the Association for the Promotion of Higher Education in Liverpool. The upshot was the formation of a committee for the purpose of arranging a plan for bringing under the notice of the public the desirability of establishing in the city a College of Science.

A scheme was drawn up, and a deputation waited upon the Mayor to ask him to take the first step for the establishment of a College of University character by calling a town's meeting to consider how that object might be attained. The Mayor having desired a formal requisition, Dr. Campbell

Brown was entrusted with the duty of procuring the necessary signatures. Three months were busily occupied in this duty, in interviewing everybody likely to sympathise with the movement, in removing scruples and objections, and in urging the necessity for a strong and representative meeting. The work was entirely successful, and a town's meeting was convened by the Mayor in response to an influential requisition. This meeting, one of the most numerous and influentially attended of any in the history of the City, was held on May 24th, 1878. A committee was formed to take the necessary steps, and Dr. Campbell Brown and Mr. W. J. Stewart were appointed Honorary Secretaries. A long course of hard work ensued, mostly done at Dr. Campbell Brown's house, or under his superintendence. Contributions were collected by personal canvass, a site was obtained on land formerly occupied by the Lunatic Asylum, and at last in 1881 the University College was regularly constituted. Of the part in this work which was taken by Dr. Campbell Brown, none can speak save those who shared it with him, but it may be truly said that he was the life and soul of the movement.

In the new College he occupied the Chair of Chemistry, and found a fresh field of work in organising the duties of the Chair, and planning and equipping the classrooms and laboratories which were essential for their performance. The Chemical Laboratories were built in 1884 and extended two years later, while in 1896-7 the William Gossage Laboratory was opened and rooms were added for Metallurgy, Electro-Chemistry, and Gas Analysis. The whole forms one of the most perfect installations for the teaching of chemistry, which is to be found in this country.

But the constitution of a new University, and the teaching of a large class, although both involved a vast amount of hard work, were not sufficient for the energies of Dr. Campbell Brown. He was in 1872 appointed Public Analyst for Liverpool under the Act relating to the adulteration of food and drugs, and received a similar appointment for Lancashire in 1875. He had

to create the organisation necessary for carrying out the purposes of the Act. Laboratories had to be planned and built, and a regular system had to be devised for obtaining samples. During thirty-five years' tenure of the Liverpool office, and thirty-two years' of the Lancashire, he supervised the detailed analysis by specially trained assistants of 120,000 samples. His method was to have every analysis repeated in its essential portion by a second operator, and, where possible, by a different process.

In addition, he was analyst to the Water Committee for the City of Liverpool, and to all the Local Authorities in the administrative county of Lancashire, and was frequently consulted in reference to large schemes of public water supply, both at home and abroad.

He took a particular interest in his work in connection with the City of Liverpool Water Works. His first report was made with reference to an investigation to determine the action upon lead piping of water from Rivington and from the Corporation Wells. For many years he made regular periodical analyses of all the sources of supply, analysing every week a sample of water from each. He also periodically tested the quality of the water in the covered service reservoirs at Liverpool. In 1875 and 1876 he made an examination of samples of water from the Lake District, and three years later from the River Vyrnwy. He also reported on the treatment of organisms found in unfiltered water between Lake Vyrnwy and Oswestry. How his services were appreciated by those who were associated with him in the Water Undertaking, may be estimated from the following extract from the Report of Mr. Joseph Parry, the Water Engineer, for the year 1910 :—  
“ He was a rigid guardian of the purity of the supply, and it was an enormous advantage to the Corporation to have the professional assistance of one who had attained to such eminence and influence as a chemist.”

He was skilled in forensic chemistry, and was engaged in a number of criminal cases involving the use of poisons. His experience in the matter of arsenic poisoning was unique.

He was one of the original members of the Society of Chemical Industry, and as the result of a long series of experiments in the analysis of soils and examination of tea-plants, devised a fertiliser for use in tea plantations in India. Where it was adopted, this fertiliser raised the tea production from 397 to 494 pounds per acre, and it is characteristic of him that he refused to receive any pecuniary return from its very extensive use.

He prepared and read a large number of papers to scientific societies, the most important of which are enumerated in the list which follows this note, and which shows the breadth of his scientific attainments. His "Practical Chemistry" is now in its sixth edition.

He made several ingenious inventions. An apparatus for the direct determination of the latent heat of evaporation was awarded two gold medals at the Franco-British Exhibition at London in 1908. By special request this apparatus was exhibited at the Japan-British Exhibition in 1910, and along with it another invention—an apparatus for fractional distillation of fats and fatty acids in the vacuum of the cathode light. Both of these exhibits were again shown in 1911 at the Coronation Exhibition in London.

On June 25th, 1902, the General Council of Medical Education and Registration of the United Kingdom appointed him Visitor of the Examinations in Chemistry, Physics and Biology, held by the Conjoint Board of the Royal College of Physicians of London and the Royal College of Surgeons of England.

The honourable recognition which his work and his services to science received may be briefly mentioned. The University of Aberdeen in 1907 conferred upon him the Degree of Doctor of Laws. In 1908 he was elected Vice-President of the Chemical Society of London, an office which he held at the time of his death. The Council of the Institute of Civil Engineers awarded to him in 1904 the Mamby Premium for a paper on "Deposits in Pipes and other Channels conveying potable water." He was a member or an honorary member

of numerous scientific bodies, and was regarded by his contemporaries as a man of great attainments and accurate knowledge.

The end came with startling suddenness. He had suffered from an attack of influenza similar to many which he had previously had, and not giving cause for any special anxiety. But heart failure ensued and he died at half-past ten o'clock in the morning on Monday, March 14th, 1910. It was probably the end which he would have chosen himself. His work was up to date, his affairs were in perfect order, and he was called away without the trial of a lingering illness. He died in harness, for he was giving instructions to his secretary about examinations, and signing certificates, till within ten minutes of the end.

Such is a very inadequate account of the life of Dr. Campbell Brown. To render it complete would necessitate my entering into numerous details that would be irrelevant to my present purpose, which is simply to give an indication of the character and attainments of the author of this book for the information of those readers to whom he is unknown. I have failed in my purpose, if I have not made plain two points—his devotion to duty, and his thoroughness. He took life at a gallop; he never spared himself when duty was to be done; and he was not satisfied with any attainment short of absolute precision and completeness. In that single sentence his biography is comprised.

HENRY H. BROWN.





## LIST OF PUBLICATIONS BY DR. CAMPBELL BROWN

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1870.

1. On the Artificial Formation of Organic Compounds (Trans. Lit. and Phil. Soc., Liverpool, Vol. 24, pp. 48-57).

2. On the Chemical Composition of the Bones of General Paralytics (*Chem. News*, Vol. 22, p. 206).

1871.

3. Analytical Tables for Students of Practical Chemistry (now in its sixth edition). It was afterwards called "Practical Chemistry."

1873.

4. On the Cause of Explosion in Flour Mills (Trans. Lit. and Phil. Soc., Liverpool, Vol. 27, pp. 301-305).

5. A Table for the Examination of Butter (*Chem. News*, Vol. 28, p. 1)

6. A Comparison of Butter with other Fats (*Chem. News*, Vol. 28, p. 39).

1874.

7. On Butterine (*Chem. News*, Vol. 29, p. 223).

1875.

8. On the Agricultural Chemistry of the Tea Plantations of India (Trans. Chem. Soc., Vol. 28, p. 1217). (For a discussion on this paper at the Chemical Society, see *Chem. News*, Vol. 31, p. 256.)

9. On the Minimum of Solids in Milk (*Chem. News*, Vol. 30, p. 266).

10. On Electricity compared with Heat as a Source of Motive Power (Trans. Lit. and Phil. Soc., Liverpool, Vol. 30, pp. 93-102).

1877.

11. On Salt in Beer (*The Analyst*, Vol. 2, p. 182).

1878.

12. On the Composition of Honey (*The Analyst*, Vol. 3, p. 267).

1879.

13. On Electric Lighting (Trans. Lit. and Phil. Soc., Liverpool, Vol. 33, p. lxii.).

1880.

14. On the Classification of the Chemical Elements and Mendeléeff's Periodic Law (Trans. Lit. and Phil. Soc., Liverpool, Vol. 34, pp. 283-299).

1883.

15. Analytical Tables for Students of Practical Chemistry, 2nd ed.

1884.

16. On the Yellow Pigment found in the Intestines in cases of Arsenical Poisoning (by J. C. B. and Ed. Davies) (*Lancet*, March, p. 421).

1886.

17. On Technical Education—Chairman's opening address to the Liverpool Section of the Society of Chemical Industry (*Journal*, Vol. 5, p. 572).

1887.

18. Chairman's Address to the Liverpool Section of the Society of Chemical Industry (*Journal*, Vol. 6, p. 706).

19. On Poivrette (*The Analyst*, Vol. 12, p. 23).

20. Further Note on Poivrette (*The Analyst*, Vol. 12, p. 47).

21. On Poivrette, Caution to Analysts (*The Analyst*, Vol. 12, p. 72).

22. On Long Pepper (*The Analyst*, Vol. 12, p. 67).

23. Another new Pepper Adulterant (*The Analyst*, Vol. 12, p. 89).

1891.

24. Justus von Liebig—an Autobiographical Sketch (Trans. by J. C. B.) (*Chem. News*, Vol. 63, pp. 265, 276).

1892. \*

25. The First Page of the History of University College, Liverpool.

1898.

26. A French View of German Industries (*Journal of the Society of Chemical Industry*, Vol. 17, p. 305).

1903.

27. A Direct Method for Determining Latent Heats of Evaporation (Trans. Chem. Soc., Vol. 83, p. 987).

28. On the Nature and Quality of some Potable Waters in S.W. Lancashire (*Engineering*, Vol. 76, p. 472).

1904.

29. Deposits in Pipes and other Channels conveying Potable Water (Proc. Inst. Civil Engineers, Vol. 156, pp. 1-17). (For the discussion on this paper, see pp. 45-75.)



1905.

30. The Latent Heat of Evaporation of Benzene and some other Compounds (Trans. Chem. Soc., Vol. 87, p. 265).

31. A Precise Method of Determining the Organic Nitrogen in Potable Waters (Trans. Chem. Soc., Vol. 87, p. 1051).

32. On the Removal of Colour from so-called Peaty Waters used for Public Supply.

1906.

33. The Critical Temperature and Value of  $\frac{ML}{\theta}$  of some Carbon Compounds (Trans. Chem. Soc., Vol. 89, p. 311).

1907.

34. Some Double Ferrocyanides of Calcium, Potassium and Ammonium (Trans. Chem. Soc., Vol. 91, p. 1826).

1908.

35. Obituary Notice: Sir David Gamble, Bart., K.C.B. (Trans. Chem. Soc., Vol. 93, p. 2279).

1910.

36. An Apparatus for the Distillation of Fats and Fatty Acids in the Vacuum of the Cathode Light (by J. C. B. and J. S. Thomas) (Proc. Chem. Soc., Vol. 26, pp. 149, 188).



## UNPUBLISHED LECTURES

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“The History of Chemistry,” delivered to the Literary and Historic Society, University College, Liverpool, May, 1895.

“Hofmann—Personal Reminiscences,” delivered to the Students’ Chemical Society, University College, Liverpool, March, 1899.

“The Use and Abuse of Hypotheses,” delivered to the Students’ Chemical Society, University College, Liverpool, April, 1900.

“Chemistry in Liverpool 100 Years Ago,” delivered to the Students’ Chemical Society, University College, Liverpool, 1901.

“Chemistry as a Profession,” delivered to the Students’ Chemical Society, The University, Liverpool, 1904.

“Science applied to the Detection of Crime,” delivered to the Chemical, Physical and Legal Societies, The University, Liverpool, 1908.

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NOTE.—A selection from the unpublished writings of Dr. Campbell Brown has now been published under the title of “Essays and Addresses” (J. and A. Churchill, London, 1914).



# HISTORY OF CHEMISTRY

## PART I ANCIENT HISTORY

### CHAPTER I

#### THE EARLY WORKERS

*(From Prehistoric Times till 1500 B.C.)*

CHEMISTRY as a science is essentially a thing of the present, or rather of the present and the future. Its progress has been so rapid, and often so sensational, and it has so frequently revolutionised industry and trade, or modified civilization by the introduction of new and widely-used comforts, that its votaries are apt to forget that it has a past. They forget that many chemical facts, products, and processes have been known from a period considerably earlier than any of which we have a historic record. As a true science, indeed, chemistry is only between one and two hundred years old, just as astronomy is less than three hundred, but, like astronomy, it has been known and practised as an art continuously since prehistoric times. The skilled, and often royal or priestly, artisans handed down its secrets in the shape of workshop traditions, from the earliest ages till the present day, without any greater break than migration from one centre of civilization to another, as war or other causes moved intellectual and artistic culture from country to country. And just as astronomy had its false philosophy, and was by astrologers

associated with superstition, so the greatest philosophers taught false doctrines concerning chemistry, and alchemy was associated with superstition in the hands of magicians, practitioners of the Black Art, and transmuters of metals.

The origin of the science of chemistry must, therefore, be sought in the art of alchemy. The professors of that art were mistaken in many of their ideas, and engaged themselves in a search for what was by them unattainable, yet in the course of their labours they gained much definite information regarding the properties of metals and other substances, devised the necessary apparatus and processes for chemical operations, and laid a foundation upon which later investigators have built up the modern science. It is thus necessary that we should in the first instance trace out the records of the Alchemical Period, and this part of our subject may with propriety be called "The Ancient History of Chemistry."

The term "alchemy," or, as it was spelt until the nineteenth century, alchymy, derived from the Arabic, is said to have come originally from a Greek word (*chyma*) signifying things melted and poured out. It is more probably derived from *Khem*, "the land of Egypt," which was so named from the dark colour of its soil, composed of crumbling syenite. Alchemy, according to this derivation, is the "art of the black country," the *Black Art*. In Egypt it was carried to a high degree of development, and this theory of the origin of the name receives support from the philological character of the derivatives—*al*, the Arabic definite article, and *Khem*, dark—because the term first came into use when the Arabian Mohammedans dominated Egypt, learned the secrets of the temple laboratories, and spread throughout the civilized parts of Western Europe the knowledge they had thus acquired.

The application of the term has frequently, but wrongfully, been restricted to the pretended arts of making gold and silver, and the more profitable arts of adulterating and of imitating gold. It had, however, a wider application, and ought to be regarded as including all the arts known in ancient

times, which dealt with things now comprehended in the science of chemistry. The extent, variety, and importance of those arts will be apparent from the following summary of their principal objects.



FIG. 1.—Fusion and Weighing of Gold in Egypt.



FIG. 2.—Egyptian Furnace and Blowpipe.

In ancient times, besides the precious metals, gold and silver, and their alloy *electrum*, five metals were known and worked. The metallurgy of these was an important branch of chemistry at that period as at the present day (Figs. 1 and 2).

The use of the expression "chemist" to indicate a druggist reminds us of another branch of alchemy, the art of making

drugs, which received much attention in Ancient Egypt, and probably in other eastern countries, and was combined with the art of preparing poisons and their antidotes.

At the present time from 300 to 400 varieties of glass have been made, differing from each other in chemical composition and properties. The ancient Egyptians of those remote ages in which the pyramids and tombs were constructed and filled, had a profound knowledge of the art of making, tinting, and working glass. Closely connected with this was the art of imitating precious stones and making enamel. The composition of some of their enamels remains a mystery, but the secrets of glass-tinting, after being lost, have been re-discovered in Europe.

The arts and industries of dyeing, painting, and staining were known and practised in eastern lands in very ancient times. As evidence we may refer to the dyeing of skins and garments, which is mentioned in most writings of antiquity. The colours used in early Egyptian art remain bright and clear in the tombs, as can be seen in numerous specimens preserved in the British Museum, and in the national museums of other countries. Remains found in Chaldea include coloured articles, as well as articles made of metal.

We are apt to suppose that the use of antiseptics is of modern origin, but that is not so. Not only did the Hebrews and the Greeks employ antiseptics in their religious rites, but in Egypt a very high degree of skill must have been attained in their preparation and use, before the body of King Rameses (1300 B.C.) and hundreds of others, could have been preserved for between three and four thousand years so perfectly that features and other details have been made out and photographed, as clearly as if those great men had been dead but a week.

The development of the paraffin and other hydrocarbon industries during the present generation may make us fancy that this is a modern discovery; but it is the fact that the fire on the Hebrew altar, fed by the Jewish priests, was our



familiar petroleum, and was called "naphthar" or "nephi," a Hebrew word signifying purification (2 Macc. i. 36).

Lastly, the art of making soap is a very old one, and was undoubtedly practised much earlier than the earliest record of it which we possess.

All these, and other departments of chemical science, are branches of alchemical knowledge, although the word "alchemy" is, as we have said, more especially used in reference to the manufacture, or rather we should say, to the sophistication, of silver and gold. With such manufacture and sophistication were associated in the Middle Ages two philosophical follies of the schoolmen—the search for the philosopher's stone and for the elixir of life.

There have been many histories of alchemy written during the last two hundred years, of which the following are the most important :—

1. Olaus Borrichius, *De Ortu et Progressu Chemiæ*, 1678.
2. Du Fresnoy, *Histoire de la Philosophie Hermetique*, in three volumes, 1742. This work contains a catalogue of ancient writings.
3. Thomson, *History of Chemistry*, in two volumes, 1830.
4. Kopp, *Geschichte der Chemie*, in four volumes, 1843-47.
5. Hoefer, *Histoire de la Chemie*, in two volumes, 1866.

In treating this subject, therefore, we shall only refer to such portions of the information contained in these and similar books, as we may find to be essential for incorporating insight more recently attained, or for making the whole a connected story.

There exists a considerable body of legendary lore, devised to account for the origin of human knowledge. Of these fables the *Book of Enoch* is one of the most important collections. It was written in the first or second century B.C., but was alleged to have been orally handed down from Enoch, the father of Methuselah (3317 B.C.). It professes to tell how the fallen angels, who had married the fair daughters of men, made them acquainted with astrology and other heavenly

secrets, and how Azazel taught men arts and manufactures, the making and use of bangles and jewellery, and the value of "precious stones, dye-stuffs, and the metals of the earth."

Books of the second century relate how the angels, wishful to please their human wives, displayed to them the interior of the globe, with all its treasures of gold, silver, and iron, and showed them how to adorn themselves with precious stones, and with garments dyed in various colours. The record adds that, for their pains, "*damnati a Deo sunt, ut Enoch refert.*"

Zosimus, a writer of whom we shall hear more in the sequel, wrote an epistle, quoted by Georgius Synkellus, in which he speaks of old and sacred writings that narrate how the angels, attracted by the beauty of woman, and fallen to the earth, instructed men in the works of Nature. He says that the first book on these arts was called *Chema*, and that from this the term *Chemia* was derived (Boerhaave, *Elementa Chemicæ* (1732), p. 6).

Lastly, there is a document purporting to be a letter written by the goddess Isis to her son Horus, in which she says that before accepting Annael as her lover, she stipulated that he should teach her the secret of making gold and silver.

Of these legends we need only remark that they exhibit the invariable tendency of the human mind to ascribe to a supernatural origin everything for which it cannot account.

Apart from these mythical tales, a large amount of definite information is to be obtained from writers, to many of whom we shall afterwards have occasion to refer. It will therefore be convenient if, for the sake of future reference, we set down here a list of the names which form the principal links in this historical chain:—

1. *Chaldean.*  
No names recorded.
2. *Egyptian.*  
Cheops or Sopes.  
Hermes Trismegistus.

Anonymous MSS.

Papyrus Ebers (found at Thebes), fifteenth century B.C.

Pebechius.

Petasius.

Pammenes.

Pauscris.

Greek letter of Isis to Horus.

3. *Grecian.*

Asclepias or Aesculapius.

Homer, about 1000 B.C.

Solon, 600 B.C.

Thales, 600 B.C.

Anaximenes, sixth century B.C.

Pythagoras, 550 B.C.

Heraclitus, 500 B.C.

Hippocrates, 400 B.C.

Leucippus, fifth century B.C.

Democritus of Abdera, 490 B.C.

Herodotus, 440 B.C.

Plato, 427—347 B.C.

Aristotle, 384—321 B.C.

Theophrastus, 300 B.C.

Dioscorides, first century A.D.

Claudius Galenus, 130—201 A.D.

Africanus, third century A.D.

Various pupils of an Alexandrian School who wrote  
under the name of Democritus, about fourth century.

Iamblichus, 350.

Synesius, 360.

Zosimus, fifth century.

Agatharchides.

Olympiodorus.

Cosmas.

Blemmydes.

Michael Psellus.

4. *Byzantine (Greek).*

Stephanus, 620.

Christianus the philosopher, fifth or sixth century.

Many anonymous commentators.

5. *Roman.*

Lucretius, 95 B.C.

Diodorus Siculus, 30 B.C.

Pliay, 23 A.D.

Aurel Cornel Celsus, second century.

6. *Persian.*

Ostans.

Sophar.

Calia.

It must be confessed that while many of these names are of world-wide celebrity, others are totally unknown to the ordinary student, and a few are undoubtedly apocryphal. Still, it is possible, by careful examination and comparison, to glean from writings ascribed to them facts which contribute to our knowledge of the history of chemical science. But we are not limited to written records for such information. Valuable hints are to be gained from the results of excavations, from ancient drawings, from inscriptions, and from remains left by those old peoples who laid the foundations of science.

While it cannot be doubted that it was from Egypt that the great mass of early alchemical learning came to Western Europe, through the Arabs and the Moors, it would be a mistake to suppose that alchemy had its birth-place, or even its earliest home, in that country. Evidence has indeed been procured by excavation of an extremely old and advanced civilization in Egypt, extending far beyond the furthest historical antiquity, but by the same process of excavation evidence has been obtained of nations still more ancient. Cities, temples, and remains of a higher antiquity have been unearthed, which show that in Chaldea a civilized people lived, and built, and worshipped, and warred, and collected taxes, many centuries before there is any trace of an Egyptian civilization. And yet this is not the most distant date to which civilization may be carried back.

In the earliest period of which we have knowledge, both in Chaldea and in Egypt, we discover the existence of metals, pigments, and architectural materials. Now, much previous work and growth of skill must be assumed before the production of these things, often so perfect of their kind, could

have reached such a stage of development and finish as to make it possible for them to subsist and to be visible to us, after the lapse of something like sixty centuries. Moreover, there were no mines and little fuel in Chaldea, and so this knowledge and skill must have been slowly acquired by some other nation, domiciled in a metalliferous and fuel-growing country, and from that nation must have spread into Chaldea, either by emigration or by conquest. There is every reason to believe that this earlier people was a Turanian race.

Development of this sort required time, and therefore the birth of alchemy is thrown back to a date anterior to that which used to be assigned for the creation of Adam, and to a time at which our worthy grandfathers believed that the earth was yet "without form and void."

Of Chaldean alchemy no written record has been discovered, although numerous traces of its influence are to be perceived in the history of the art. Thus, we are aware that the number "7" was greatly respected in Chaldean philosophy and religion. It represented one-fourth of the number of days in a revolution of the moon. The Chaldeans recognised seven visible planets, seven gods of the heaven, seven gods of the earth, and seven devils. Seven platforms of different colours and materials constituted the ascent to one of their temples, and another instance of the use of this number is to be observed in an archæological discovery made by M. Place in 1854.

This discoverer found under one of the stones of the palace of the Chaldean monarch Sargon a box containing votive tablets with euneiform inscriptions, which were intended to commemorate the foundation of the building in 706 B.C. Five tablets were found, but an inscription indicated that there had been seven. Four of them are now in the Louvre Museum at Paris. The tablets found were of gold, silver, copper, lead, and tin. The material of the missing two is not known, but the determinative of the words indicates stone of some sort, probably marble and alabaster. An account of the construction of the palace is given in the tablets, and the materials of



which these were composed are interesting from a chemist's point of view. The gold and silver tablets are pure; the copper is much oxidised, and contains 10 per cent. of tin; the fourth, supposed to be tin, is quite oxidised, and has subsequently been found to be crystallised carbonate of magnesia. As magnesia was not known until a much later date, there is no doubt that this tablet was erroneously believed to be composed of a simple, definite substance.

Another peculiarity of the Chaldean philosophy was the connection of the properties of the metals with the influence of the planets, and both with the functions of organs of the

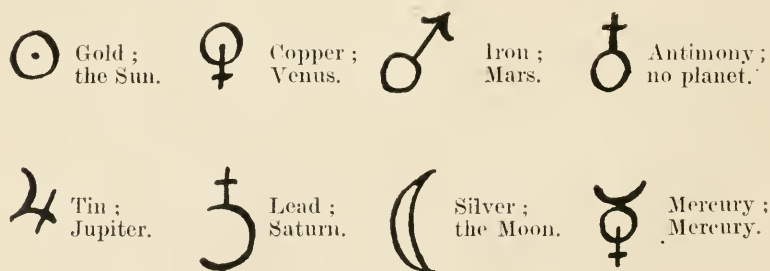


FIG. 3.—Symbols representing both Metals and Heavenly Bodies.

human body, and the destiny of individual men. This conception may be exhibited in tabular form thus:—

The Chaldean *Bel* corresponds with the metal *tin* and the planet *Jupiter*.

The Chaldean *Bilati* corresponds with the metal *copper* and the planet *Venus*.

The Chaldean *Camoth* corresponds with the metal *lead* and the planet *Saturn*.

The Chaldean *Nebo* corresponds with the metal *mercury* and the planet *Mercury*.

At Pompeii there is a painting representing the seven planetary deities, which indicates the extent to which these peculiar ideas had spread through the ancient world.

The influence of both these doctrines, the importance of the number seven, and the connection between metals and

planets, can be distinctly traced in mediæval alchemy. They had been handed down from the star-gazers of Babylonia and Persia, through the great Sabæan School of Harran in Mesopotamia, where the remains of Chaldean culture had a home from the fifth to the eleventh centuries A.D. In the writings of mediæval alchemists seven metals and seven heavenly bodies were represented by the same seven symbols, as can be perceived by an examination of Fig. 3.

An illustration of the deep impress which these old doctrines made on mediæval thought occurs in a place where we might not have expected it—in certain lines of Chaucer :—

“ Sol gold is, and Luna silver we threpe,  
Mars iron, Mereury quicksilver we clepe,  
Saturnus lead, and Jupiter is tin,  
And Venus copper, by my father’s kin.”

But many remnants of that philosophy are fossilised in our








	<i>nub</i>	.	Gold.
	<i>asem</i>	.	Electrum.
	<i>hat</i>	.	Silver.
	<i>χomt</i>	.	Copper.
	<i>men</i>	.	Iron.
	<i>teht</i>	.	Lead.
	<i>chesbel</i>	.	Blue Stone, or Enamel, or Sapphire.

FIG. 4.—Egyptian Symbols for the Metals. (Lepsius.)

own language and in the current phrases of our everyday life. We trace such remnants in the "lunatic" whose brain has been injured by the malign influence of the moon; in "lunar" caustic, which is nitrate of silver; in the "saturnine" disposition of a man whom we do not like; in the "saturnine" medical prescriptions composed of salts of lead; and in the "martial" preparations, which are not intended for war, but are compounds of iron still administered by the family doctor to those who have not iron constitutions.

From the Chaldeans alchemy passed to the Egyptians. Much information, obtained from hieroglyphics on Egyptian monuments, in respect to the ancient names of the metals, and the hieroglyphs by which they were represented, is contained in a treatise on *Metals in Egyptian Inscriptions* by Lepsius, the German Egyptologist and archæologist (1810-84). The names and symbols of the seven metals, according to that author, are exhibited in Fig. 4, and some specimens of general hieroglyphics are shown in Fig. 5, to which we shall have again to refer when discussing the philosopher's stone.

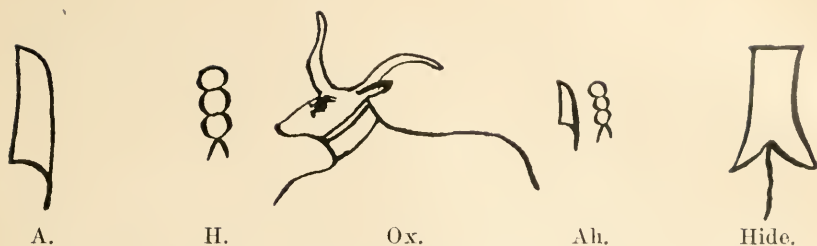
The Egyptians appear to have recognised eight metals or precious minerals, and we find these named in inscriptions, in the following order, from the Theban Dynasties down to the time of the Ptolemies:—

<i>Nub</i>	.	.	Gold.
<i>Asem</i>	.	.	Electrum, an alloy of gold and silver, in use up to the seventh century A.D.
<i>Hat</i>	.	.	Silver.
<i>Chesbet</i>	.	.	A blue mineral, like sapphire or lapis lazuli.
<i>Mafek</i>	.	.	A green mineral, like emerald.
<i>Chomt</i>	.	.	Copper or bronze.
<i>Men</i> or <i>Tehset</i>	.	.	Iron.
<i>Tcht</i>	.	.	Lead.

Although quicksilver played an important part in alchemy, the ancient Egyptians were not acquainted with it, as it was not discovered till a much later date.

The information which we possess on the subject is not





The one determinative sign is an Ox, and the other a Hide—the symbol of all quadrupeds.



. Determinative of trees.



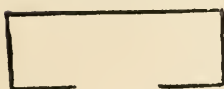
. Determinative of minerals.



. Determinative of stone.



. Determinative of plants.



. Determinative of houses.



. The letter "n."



. Water; also determinative of liquids.



. Introduced after the letters signifying "drink," "wash," "thirst," "river," etc.

FIG. 5.—Egyptian Hieroglyphics.

extensive, but from the facts which have come to our knowledge it is apparent that the Chaldeans were merely the pioneers of alchemical science ; it was the Egyptians who made the greatest advance in practical chemistry. Abraham, who came out of Ur of the Chaldees, brought with him a higher religion, a higher theology, and a higher philosophy than was then current, even among the most civilized races. No doubt, therefore, he had some knowledge of the chemical arts of the Chaldeans, but it was only after a long sojourn in Egypt, and a special education in Egyptian temple laboratories, that his great descendant, Moses, was able to lead forth the oppressed people, and conduct them triumphantly through a journey of forty years in the wild country between Egypt and Palestine. There he found them water to drink by boring the rock, and manna to eat by collecting an exudation from a tree ; there he adorned the tabernacle with skins and curtains, dyed in various hues ; and there he comminuted gold and rendered it soluble, by fusion with an alkaline or alkaline-earthly sulphide (probably polysulphide of calcium), so that the insoluble metal of the golden calf was dissolved in water, and effectually brought into contempt as a false god, through the solution being drunk by the offending people.

All these things imply a knowledge of chemical processes, which at that date could only be gained in the laboratories of the royal and priestly race, who ruled in the temple seminaries and workshops, as well as on the throne of the Pharaohs.

## CHAPTER 11

### THE EARLY WRITERS

(From 1500 to 500 B.C.)

LEAVING the Chaldean and earliest Egyptian periods, of which we have remains but no record, and from which no names of either chemists or philosophers have come down to us, we now approach the Historic Period, when books were written, not at first upon parchment or paper, but upon papyrus.

A series of early Egyptian books is attributed to Hermes Trismegistus, who may have been a real *savant*, or may be a personification of a long succession of writers. Albertus Magnus (1193—1282) tells us that Alexander the Great discovered the tomb of Hermes full of golden treasures, “not indeed metallic, but in writings on an emerald or smaragdite tablet.” Many similar fables are told of him by the Arabian philosopher Avicenna and others. He is identified by some with the Greek god Hermes,



FIG. 6.—Hermes Trismegistus.  
(Temple of Pselcis.)

Thoth or Tuti, who was the moon-god, and is represented in ancient paintings as ibis-headed with the disc and crescent of the moon. The Egyptians regarded him as the god of wisdom, letters, and the recording of time. It is in consequence

of the great respect entertained for Hermes by the old alchemists that chemical writings were called "hermetic," and that the phrase "hermetically sealed" is still in use to designate the closing of a glass vessel by fusion, after the manner of chemical manipulators. We find the same root in the hermetic medicines of Paracelsus, and the hermetic freemasonry of the Middle Ages.

Whoever Hermes may have been, there certainly existed in the early historic period of Egyptian greatness a number of Hermetic books, of which in the second century A.D. there are said to have been forty-two. At the latter date their author received the title of *Trismegistus*, or "Thrice-greatest." His works included ten books of the Prophets, ten of Stolistes, ten of Hierogrammatists, four of Horoscopus, two of Chanter, and six of Pastophorus or Medical Science. Most of these writings were lost, but a few passages quoted by Zosimus have been preserved.

One of these books, giving an account of the proceedings of the soul after death and of the rites connected with the burial of the dead, was transcribed upon papyrus and illuminated beautifully by the priestly scribes. Copies were buried with the mummies of kings, priests and their relatives, as well as with the chief scribes of the temple. Of these many have been recovered, and from their perusal a clear idea may be obtained of the ancient Egyptian religion. It was a much higher type of monotheism than succeeding generations supposed, but it was understood only by the few—the royal family, who, as priests or students, were trained in the temple schools. Specimens of these papyri, containing what is known as the *Book of the Dead*, are preserved in the British Museum.

In the "Kitab-al-Fihrist," an Arabic work which we shall have repeatedly to mention, the following passage occurs: "The people who practise alchemy, that is those who make gold and silver out of other metals, assert that the first who has spoken of the science is Hermes the Sage (*Trismegistus*), a native of

Babylonia, who established himself in Misr (Egypt) after the dispersion of the people from Babel. He reigned in Misr, and was a sage and a philosopher. He succeeded in practising the work, and composed on this subject a certain number of treatises. He studied the properties of bodies and their spiritual virtues, and thanks to his researches and his labours the science of alchemy was constituted.''

A remarkable papyrus was discovered by the late Georg Ebers, the eminent Berlin Egyptologist, in a terra-cotta vessel between the legs of a mummy, buried at a depth of ten feet, among some ruins near the pyramid of Sokara at Memphis. Here, according to Galen, there was once a medical library of some fame. The Papyrus Ebers consists of twenty pages on ten leaves. It is actually a copy of one of the six Pastophori of Hermes, and dates from 1550 B.C., that is, almost from the time of Moses. Another copy of the same work was probably studied by Moses; for being brought up as Pharaoh's grandson, he would naturally be educated in the temple.

This Papyrus Ebers is a very curious book, full of allusions to animal, vegetable, and mineral products and their uses in medicine. It is, in fact, a text-book of *Materia Medica*. The names of the substances mentioned in it are not fully understood, but if a medical man, resident in Egypt, were to establish friendly relations with the Copts and learn the names given by them to natural objects and products, he would, in all probability, be able even at this date to identify many of those ancient medicines. Honey figures as frequently in this treatise as it did in the British Pharmacopœia down to the last generation, while sugar and other things that we deem of modern manufacture were also employed at that ancient date. The book directs the medical attendant to use certain incantations and formulæ in administering the dose, and directs him to invoke the aid of the god. Similar incantations and invocations were common in more recent times, and in our own day an English doctor invokes Jupiter by using his symbol every time he writes a prescription.

As an example of this ancient pharmacy we shall extract a prescription for stomach-ache, which may with advantage be kept in remembrance at Christmas and other festive seasons: "Take of cummin one sixty-fourth part, of bird's oil one eighth part, and of milk one part; boil, filter through linen, and drink." We also find many magic formulæ, as well as directions for perfumery, for curing headache, and for keeping serpents in their holes.

There exists no other papyrus actually transcribed at a date approaching that of the Papyrus Ebers, but there are many copies more recently made of ancient manuscripts, which had their origin in the earlier Egyptian temple workshops and schools. We learn from these the character and extent of much of the knowledge and literature that existed for hundreds of years prior to the birth of Christ. We have in these writings to distinguish two sorts of chemical learning—vague and obscure pseudo-philosophical theories, and the real knowledge of the artificer and laboratory-worker. The latter class possessed true knowledge, the former little or none, and did not understand the little they had. We may perceive at the present day a similar difference between the man who has read books and committed to memory information sufficient to enable him to pass a written examination, and the man who has worked for years in a laboratory, and can not only perform difficult operations, but invent new ones.

Some of the more ancient manuscripts were translated into Greek, at the time when Egypt was ruled by Greeks. These were copied and distributed over Europe, and copies are to be found in the museums and libraries of many of the capital cities and universities, particularly in the Vatican at Rome and the Sultan's Museum at Constantinople.

The MS. of St. Mark, which is written in Greek and preserved at Venice, is perhaps the earliest as regards the date of its transcription. It was copied in the tenth century A.D. and is evidently transcribed from a far older writing, because there are



mistakes in it, committed by the copyist, which do not occur in other extant copies of the same original.

This manuscript contains : (1) a list of alchemical treatises ; (2) the treatises of Cleopatra on Chrysopoeia, on Distillation, and on Weights and Measures ; (3) the treatise of Christianus ; (4) of Ostances ; (5) of Zosimus ; (6) of Olympiodorus ; (7) of Sergius ; (8) the letter of Isis to Horus ; (9) the treatise of Democritus ; (10) of Stephanus ; (11) of Synesius ; and (12) a few anonymous treatises. It includes several figures and diagrams, which are of consequence, as they appear to have been repeatedly copied and so handed down from a remote period of Egyptian civilization. Some of them are seen in Arabic and later manuscripts, now in libraries at Paris, the Vatican, Leyden, and elsewhere. They also occur in printed books of the seventeenth century. M. Berthelot reproduces from the MS. of St. Mark a number of these figures, a few of which we shall have to consider, because their repetition in manuscripts of a later date constitutes one of the strongest arguments in support of the theory that the alchemical knowledge introduced into Western Europe by the Moors was really founded upon the wisdom of Egypt.

The first diagram which we shall examine is the *Chrysopoeia of Cleopatra*. This woman was not the celebrated queen. The name Cleopatra was common in Egypt. It is inscribed on the coffin of a mummy in the British Museum. The authoress of the *Chrysopoeia* was an earnest student of chemistry, who at a very early date wrote on gold-making, on distillation, and on weights and measures. The *Chrysopoeia* (Fig. 7) represents in the lower right hand 'an apparatus for fixing or transmuting metals, consisting of a double alembic heated upon a water-bath or *Bain Marie*. At the side is the serpent biting its tail (*Ouroborus*), which was the symbol of philosophic knowledge. The three Greek words in the centre of the ring formed by the serpent, signifying "one is all," refer to the belief in the unity of matter, which was a fundamental idea in alchemical theories. Above the serpent are several

small figures, representing the philosopher's egg (the symbol of creation) and pieces of apparatus. Two concentric circles are drawn in the upper left-hand corner, bearing inscriptions in Greek, which may be thus interpreted; the *inner*, "the serpent is one who has the poison (*i.e.*, the philosopher's stone) after two emblems"; and the *outer*, "one is all, and by it all, and to it all, and if one does not contain all, all is nought." The

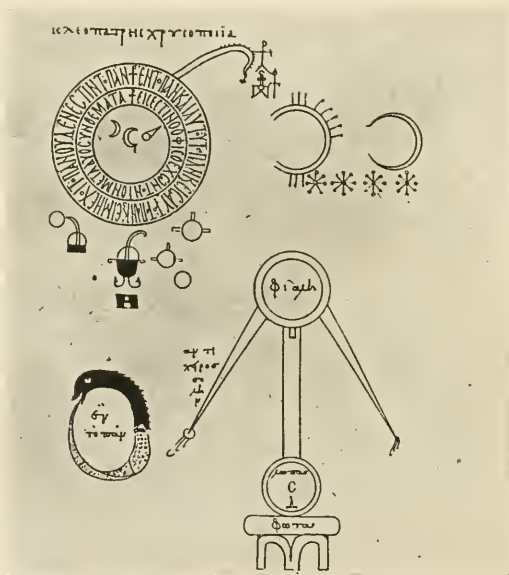


FIG. 7.—The Chrysopoeia of Cleopatrâ. (Greek MS.)

tail projecting from the double circle indicates that the whole is part of the mystic serpent, and both symbol and words imply a belief in the unity of all things. In the middle of the double circle are the most ancient symbols for mercury, gold, and silver. To the right is a very peculiar sign, termed *the sign of the Crab*, consisting of two curved lines with a number of filaments attached, like the antennæ of an insect. This was the symbol of the process of fixation, *i.e.*, transmutation, and in this instance signified the operation of calcining and transforming lead into



silver, the latter metal being indicated by the crescent moon. The diagram is a beautiful illustration of the symbolic method of the ancient alchemists, who never expressed anything by words which could be shown to the initiated by signs.

Another apparatus for fixing metals is shown in Fig. 9. It includes an alembic on a tripod matrass, and a receiver. Then in Fig. 10 we have two alembics. The matrass is called *lōpas*, and the words "*theiou apyrou*" (unburnt sulphur) are added, the text explaining that sulphur was placed in the matrass. The upright tube is marked *sōlēn ostrakinos*, "the tube of terra



FIG. 8.—The Serpent Ouroboros. (Greek MS.)

cotta," while the head is called *bikos*, "a retort or flask," instead of *phiale*, as usual. Each of the two receivers is named *bikion*, and an inscription in Greek is added to the effect that "(the flask) is placed upon the square tablet in which flows the water of sulphur." This apparatus, therefore, was designed for making what was called "water of sulphur." In the lower figure the word *phōta* is replaced by *kaustra*, meaning a combustion furnace, and sulphur is not mentioned.

A drawing of a *tribikos*, or triple alembic, is shown in Fig. 11. The parts are named *lichanos sōlēn*, "direct upright tube," and *anticheiros sōlēn*, "inverted tube."

In the rough sketch (Fig. 9) is a water-bath for digestion marked *palaistikion kaminion*. This apparatus was first heated

by hot ashes or sand. The palette above was heated in the middle, and on it reactions were performed. It was termed *pharmakou kēratokēs*. The hollows below the *kēratokēs* were

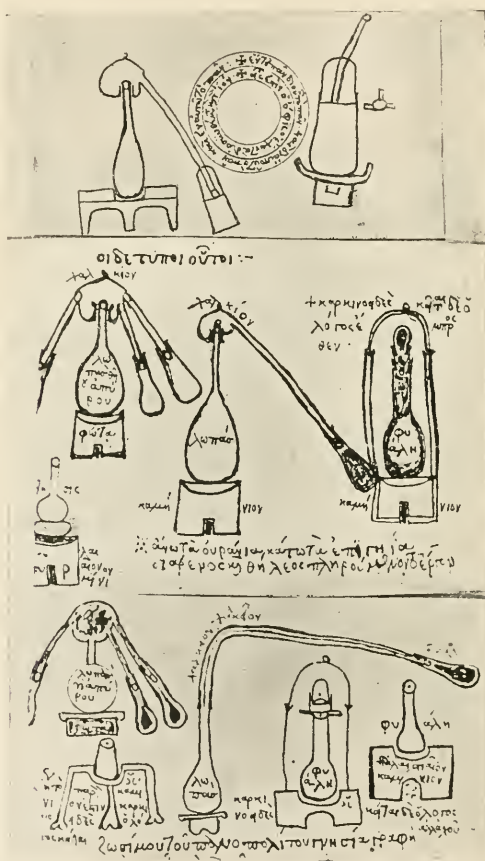


FIG. 9.—Ancient Apparatus. (Greek MS.)

meant to receive the molten metal, while the sublimed products were collected in the heads. A rough drawing of a bath for a *kēratokēs* is shown in Fig. 12, while Fig. 13 is the palette or *kēratokēs* itself. Instead of a palette we now use a platinum spatula.

We see another form of bath for a *kēratokēs* in Fig. 14. This is termed the furnace of Mary, from a celebrated Jewess in Egypt, who was an eminent alchemist, and invented this form of heating apparatus for the laboratory. It is a curious fact that in its modern shape, the water-bath, this invention retains the name of its discoverer, being still called "Bain Marie," Mary's bath.

Such are a few examples of the diagrams and drawings which have come down to us from the ancient Egyptians. Whoever wishes further information on the subject is referred to Berthelot's *Introduction à l'Etude de la Chimie des Anciens et au Moyen Age*.

An instructive illustration of alchemical nomenclature is

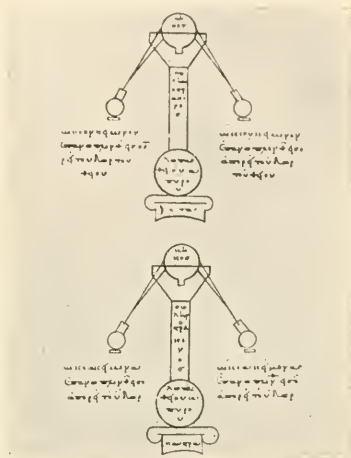


FIG. 10.—Ancient Alembics.  
(Greek MS.)

afforded by the substance, of which we have just spoken, and to which the name "water of sulphur" was applied. In the mystic phraseology, in which everything relating to alchemy was obscured, this was also termed "serpent's bile," and it played a great part in alchemical work. In the *Alchemical Lexicon* the name is attributed to Petasis. In the *Leyden Papyrus X*, recipe No. 89 gives its preparation, and it is evidently polysulphide of calcium. There is thus ample justification for

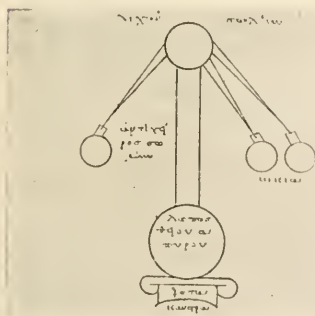


FIG. 11.—A Tribikos.  
(Greek MS.)

the suggestion, which we have made, that Moses by means of this polysulphide reduced the golden calf to powder. In Zosimus, when treating of this substance, the following words occur: "On uncovering the alembic, you will stop your nose on account of the odour." This points to the disengagement of sulphuretted hydrogen ( $H_2S$ ), which would be one of the substances produced in the course of the operation. Water of sulphur was a powerful reagent, and consequently the old

alchemists distinguished it by giving it a name reminiscent of the mystic serpent.

At the head of the MS. of St. Mark there is placed an alchemical bibliography of the period at which it was copied, which has great interest from a historical point of view. The list names Theodorus, Harachus, the Emperor Justinian, Heleodorus, Theodosius, Synesius, Theophrastus, Pelagius, Zosimus, Democritus,

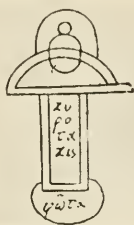


FIG. 12.—Bath for Kēratokēs.  
(Greek MS.)

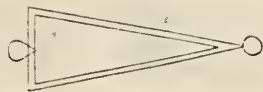


FIG. 13.—A Kēratokēs or Palette.  
(Greek MS.)

Olympiodorus, Christianus, Cleopatra, and others. We can infer from this list that there were then in existence numerous treatises on alchemy, many of which are now lost. In this bibliography are introduced a dialogue between the philosophers and Cleopatra, and a treatise by a certain Moses (not the great law-giver of Israel) on the diplosis or doubling of gold. This process was neither more nor less than a method of increasing the bulk and weight of gold by adulteration with some inferior metal, but the philosophy of that age induced the operators to regard the morality



can afford to overlook the debt which chemistry owes to these men, who may be said to have laid its foundations, and who were the first to grasp the conception that beneath its varied and complex phenomena lay certain elementary principles, which might be discovered by patient research.



## CHAPTER III

### THE GREEK PHYSICIANS AND PHILOSOPHERS

(From 400 B.C. to 100 A.D.)

We have seen that the first period into which the history of chemistry naturally divides itself is that during which a number of chemical facts were known, but not understood or explained. These facts were not correlated, nor was the subject studied with scientific purpose and method, consequently during this period chemistry was not a science. Hitherto we have been considering such traces of the knowledge of chemical facts as are left to us in the remains and manuscripts of Chaldea and Egypt. We have now to note the progress made by human wisdom and learning under the fostering care of the Greek writers on philosophy and medicine. These men, although they did much for the advancement of knowledge and the encouragement of thought, did little for chemistry. The Greeks were no chemists. The bent of their mind was not towards natural science ; few observations or experiments were made by them, and they preferred to argue from general principles to particulars, rather than from particular observations to general principles.

The earliest Greek writers, such as Homer (1000 B.C.), knew no facts save those which were familiar to the Egyptians, and which had probably come to Greece either directly from Egypt or through the Phœnicians. It was not till the time of Hippocrates that the Greeks began to study medicine in an intelligent manner, and thus to take the first steps towards a higher chemical knowledge.

Hippocrates was born in the island of Cos about 460 B.C. He was a member of the Asclepiadæ, a family of priest-physicians, and counted himself seventeenth or nineteenth in direct



descent from Aesculapius. On his mother's side he claimed kindred with Hercules. He spent his life teaching and practising medicine in Thrace, Thessaly, Delos, Cos and Athens, and died at Larissa in Thessaly. He was the first to discard superstition, and to base the practice of medicine on the principles of inductive philosophy. It is said that in the hospitals where he was trained there existed a system of case-books in the shape of votive tablets left by the patients, on which were recorded the symptoms, treatment, and result of each case. His knowledge of anatomy, physiology, and

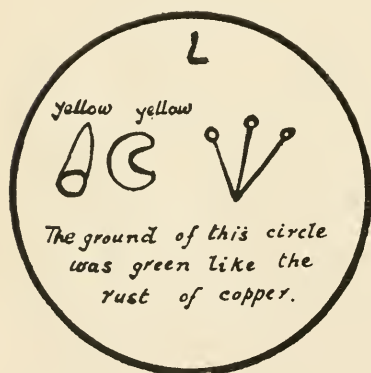


FIG. 15.—First Firmament.  
(Book of Crates.)

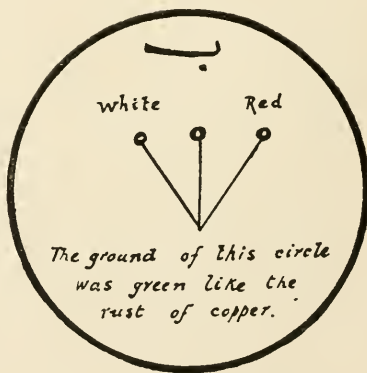


FIG. 16.—Second Firmament.  
(Book of Crates.)

pathology was hampered by the reverence with which the Greeks regarded the dead body; but he was a great clinical physician who founded his practice on the management of the *vis medicatrix naturae* (*physis*). Although no empiric, he considered that the art of medicine could only be learned from experience.

His contemporary, Leucippus, the founder of the Greek theory of atoms, has left us no extant writings, but his philosophy has been handed down by his pupil Democritus. According to his doctrine, all things are ultimately constituted of empty space and atoms, a *space* of infinite magnitude, and

atoms of infinite number, indivisible, and with only quantitative differences amongst each other. For him there is no such thing as a qualitative change. All growth and decay are merely the compounding and separation of atoms which are perpetually in motion; thus worlds are continually in the process of birth or destruction. The soul consists of spherical atoms; sensation and thought are caused by the entrance of external images.

The philosopher Democritus of Abdera is one of the earliest Greek writers on chemistry, of whom we know much, and of



FIG. 17.—Third Firmament.  
(Book of Crates.)

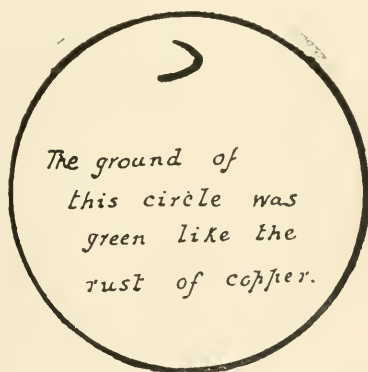


FIG. 18.—Fourth Firmament.  
(Book of Crates.)

whose writings any knowledge is extant. He was a contemporary of Socrates, having been born between 460 and 494 B.C. in Abdera, a Thracian colony. His father was sufficiently wealthy to entertain Xerxes, the son of Darius, and his army, as they returned home after the battle of Salamis. On coming into his inheritance, Democritus travelled in Egypt, Chaldea, and Persia, and studied science in these countries. Pliny and later writers assert that he also prosecuted researches into magic and other secret arts. Hippocrates was his doctor, and he had interviews with Leucippus, and doubtless influenced, and was influenced by, the theories of both. He lived upwards

of ninety years, and died about 370 B.C. Like Hippocrates, he recognised the value of the experimental method.

He appears to have imbibed much of the knowledge then possessed by the priestly cult in Egypt. Synesius, writing in the fourth century A.D., says that Democritus was initiated into the Egyptian mysteries by Ostanes, the priest, in the temple at Memphis, and that he wrote four books treating of colours, of gold, silver and precious stones, and of purple.

Democritus himself says that he saw in a miraculous opening of a pillar of the temple at Memphis the words, "Nature

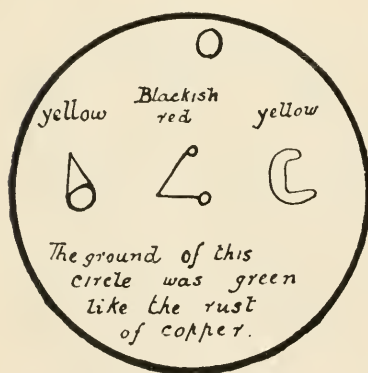


FIG. 19.—Fifth Firmament.  
(Book of Crates.)

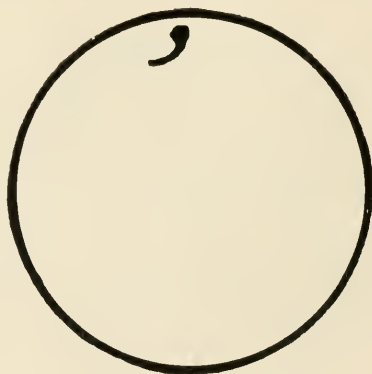


FIG. 20.—Sixth Firmament.  
(Book of Crates.)

delights in Nature," "Nature conquers Nature," and "Nature rules Nature." These words were impressed so deeply upon his mind, that he constantly introduced them as mottoes, or conclusions of periods, in his books. Of these he wrote seventy-two, but only fragments of them remain. They were written in Ionic Greek, and Cicero considered the style equal to that of Plato.

As an example of his method, we shall extract one of his prescriptions for making gold. "Take quicksilver, fix it with magnesia, or Italian antimony (*stummi*, possibly equivalent to *stibium*), or unburnt sulphur, or *aphroselmia*, or burnt lime, or *stypteria* of *Milos* (alum), or arsenic, or whatever else you please ;

throw in the white earth of copper and you obtain bright copper. Throw in the golden yellow earth of (or upon) silver, and you obtain gold. From gold comes *chrysocorallos*; sandarach (realgar) gives yellow red, and also prepared arsenic, and entirely transformed cinnabar. Bright copper one only obtains by means of quicksilver. For Nature conquers Nature."

In another passage he says: "Direct also silvery *marcasite* (pyrites), which they also call *siderite*, and make it in such a way that it can be dissolved; it liquefies either by golden or white litharge, or in Italian antimony; purify with lead"; and so he proceeds, with frequent repetitions of the phrases which flashed upon him from the pillar at Memphis. The term "*Marcasite*" used in this passage, generally regarded as meaning pale iron pyrites, is said by M. Berthelot to have been applied by the alchemists of the Middle Ages to the sulphides of all the metals properly so called.

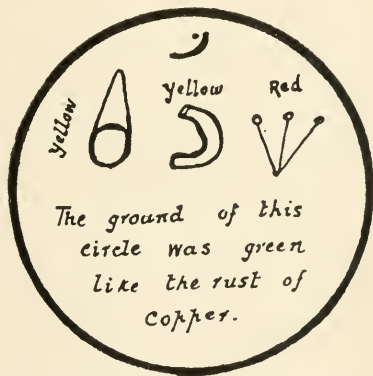


FIG. 21.—Seventh Firmament.  
(Book of Crates.)

Democritus adopted some of his theories of the universe from Leucippus, and his philosophy has retained a permanent place among Greek materialistic doctrines. According to him the universe consists of vacuum and atoms. Of matter and spirit alike atoms are the ultimate constituents; they vary in shape and are invisible, but they have extension and weight: they are impenetrable and have existed from eternity without cause. These atoms are in motion, which motion is also eternal, and regulates the world and all that is in it. The atoms of soul and fire are small, smooth and round, and by inhaling and exhaling them life is sustained.

From every object images (*eidola*) are given off continually

in all directions. These *eidola* being perceived by the organs of sense cause sensations, and sensation is our only source of knowledge. Apart from sensation there is no mental faculty. "There is nothing true, and if there is, we do not know it." Democritus rejected the popular mythology, believing that the motions of atoms which produced men produced also the higher beings who appear in dreams and influence human affairs.

Some of the writings of Democritus, or of his pupils, have been translated into Arabic, and the following passage occurs in one of the later Arabic translations :—

The *Book of Crates* (probably a corruption of Democritus) begins : "In the name of mild and merciful God" (this is an ordinary Mussulman formula) "I have accomplished the study of the stars, of the surface of the earth, of its position, and of its various elements. . . . Then I saw an old man, the most beautiful of men, seated in a chair. He was clothed in white garments, and held in his hand a board of the chair on which was placed a book. Before him were vases, the most marvellous that I had ever seen. When I asked who this old man was I was told, 'It is Hermes Trismegistus, and the book which is before him is one of those which contain the explanation of secrets which he has hidden from men. Remember well all that you see, and all that you will read or hear, so that you may be able to describe it to your fellows after you. But do not go beyond what will have been ordained, when you explain things to them. This will serve their interests, and show your good-will to them.'"

In Figs. 15 to 21 will be found drawings of the seven firmaments seen in this vision and represented in the *Book of Crates*. These consisted of circles, surrounded by inscriptions, and containing alchemical symbols which are the same as those of the Greeks ; *e.g.*, those representing gold, silver, arsenic or chryseletrum, and (probably) those of copper, tin and mercury. These are the only symbols which have as yet been found in an Arabic alchemical manuscript, for the Mohammedians had a religious objection to figures or drawings of objects, as tending to idolatry. Symbols passed from the Greek to the Syriac



writers, but not to the Arabic, and do not reappear until the fifteenth century, when they were again copied from the Greeks.

The manuscript from which we have been quoting is full of Græco-Egyptian reminiscences, and mentions Christianity and the Arabic dynasties of Syria and Egypt down to the ninth century. In addition to copies of genuine translations from the original Greek, there are passages which savour of the style and subjects of a later date. The following extract has this character, its ideas being more consistent with a period subsequent to Democritus, although the conception of mixing the properties of separate materials, and getting a combination

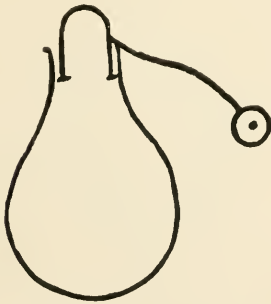


FIG. 22.—An Alembic.  
(Book of Crates.)

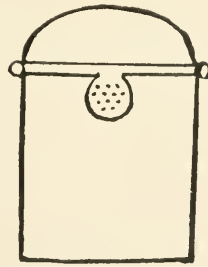


FIG. 23.—Apparatus  
for Kēratokēs.  
(Book of Crates.)

of these properties in one body, pervades alchemy for more than a thousand years.

“ This is the definition of the stone which is not a stone, nor of the nature of stone. It is a stone which is engendered every year. Its mine is found on the summit of the mountains. It is a mineral contained in sand and in rocks of all hills ; it is found also in colouring matters, in the sea, in trees, in plants, in waters, *et cetera*. As soon as you have recognised it, take it and make a *calx* of it ” (in other words, calcine it and reduce it to an oxide). “ Extract its soul, body and spirit, separate each of these things, and place it in the special vase which is set apart for it. Mix the colours, as painters do for black, white, yellow, and red, and as doctors do in their mixtures, where

enter the moist and the dry, the warm and the cold, the soft and the hard, in such a way as to obtain a well-balanced mixture, favourable to the bodies. This is done by the aid of determined weights. Then are united in one their diverse qualities.”

In Figs. 22 to 25 are shown drawings of apparatus from the *Book of Crates*, consisting of an alembic, an apparatus for *kēratokēs*, a furnace for digestion, and a flask in a bath of sand or ashes. They correspond with the figures which were found in Greek manuscripts. Some of the recipes are almost literal

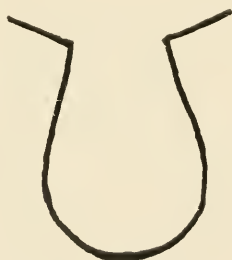


FIG. 24.—Apparatus for Digestion.  
(Book of Crates.)

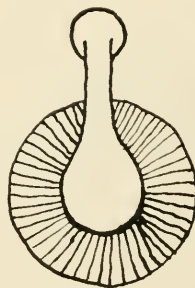


FIG. 25.—Flask in a Bath of Sand or Ashes.  
(Book of Crates.)

translations from the original Greek manuscripts, which are still extant.

The philosopher Plato was born at Athens in 427 B.C., about the date of the death of Pericles. By his father he was descended from Codrus, and by his mother from Solon. In early life he was a poet, but becoming a pupil of Socrates at the age of thirty, thenceforward devoted himself to philosophy. The search for knowledge led him through Egypt, Sicily, and Asia, and amongst Hebrews, Babylonians, and Assyrians, even to the Greek cities of lower Italy. Twelve years after the death of Socrates, he returned to Athens, and taught gratuitously, mostly in the form of dialogue, in the Academy avenues and gymnasium. He died at the age of eighty, in 347 B.C.



The tendency of the Greek mind was towards metaphysics, and their practice leant strongly to art, rather than to inductive philosophy and accurate experiment. Although Aristotle took the view that facts should lead up to theories, and that such facts should be established by repeated observations, these principles were not put in practice. It is clear from examples which have come down to us that small value was placed on research, that experiments were made with little care, and that such facts as the Greeks discovered were due to chance observations. Hence we find Plato attributing the conversion of iron into rust to the loss of something, and Aristotle giving it as the result of accurate research, that a pot filled with ashes takes as much water as an empty one. The fact that no scholar amongst the Greeks did anything to advance chemistry or the sciences related to it is due to their endeavouring to explain by means of uncertain and often obscure philosophy questions which can only be answered by experiment and observation.

Acting upon this principle of deductive philosophy Thales, who was born at Miletus about 600 B.C., and who may be regarded as an advanced thinker for his time, seeing that he furnished some of the earliest geometrical proofs, and even predicted an eclipse, named *water* as the fundamental element of all bodies, from which they are formed, and to which they return.

Then Anaximenes, also a native of Miletus (557 B.C.), evolved out of his own inner consciousness the belief that *air* is not only the source of life, but at different degrees of density the source of all things. Eternal movement pervades it, and it gives rise to every phase of existence, under the influence of heat which expands and cold which contracts it.

Heraclitus, on the other hand, deemed *fire* to be the fundamental principle. He was born at Ephesus about 535 B.C., and lived till about 475 B.C. He was of a patrician family, and became one of the profoundest metaphysicians of ancient Greece. The doctrine of Continuity was his conception. He

denied that things exist, saying that "everything is and is not"; and declared "becoming," or eternal change, to be the sole actuality. Hence he naturally selected fire, the most complete embodiment to him of the process of becoming, as the principle of existence, out of which all things, even the soul, grow by condensation, and into which all things must be again resolved. Only one fragment of his works, *Peri Physeos*, has been brought down to us.

The most influential exponent of Greek deductive philosophy was Aristotle. His influence extended far beyond the period which we are now considering, and his philosophy, profoundly affecting the progress of thought during the Middle Ages, was productive of the foolish aims and futile researches of the alchemists and others, until it was superseded by the inductive method of Bacon. Aristotle was therefore the forerunner of modern science, and it may be said of him, that if his doctrines conduced to many errors of thought, to him is due the credit of having saved man from relapsing into barbarism.

This great philosopher was born in 384 B.C. at Stageira, a Greek colony near Pella, the residence of Amyntas, King of Macedon. Nicomachus, the father of Aristotle, who like Hippocrates was a member of the Aselepiadae, became a physician to Amyntas. At the age of seventeen, Aristotle came to Athens to study under Plato, and twenty years later hoped to succeed him as the head of the Academy, but on account of his philosophical differences, being more scientific and less mystical than Plato, he was disappointed in his expectation. He then returned to Asia Minor, where he married the niece of Hermeias, ruler of Atarneus, who had become his patron. On the death of Hermeias he retired to Mitylene, where, in his forty-second year, he received the summons of Philip of Macedon to undertake the tuition of his son Alexander, afterwards universally known as "the Great." When his pupil succeeded to the throne of his father, Aristotle removed to Athens, and for thirteen years taught in the walks of the Lyceum of Apollo. He is said to have written a hundred and

forty-six books, and there is a tradition that Alexander supplied him with funds for his physical and zoological researches.

Although his physical investigations are not characterised by accuracy, or his conclusions by profundity, his zoological researches were both minute and exact. Coming of a family, the members of which were trained in dissection as regularly as others learned to read or write, his dissection of animals, both marine and terrestrial, would be creditable to a modern zoologist. It is doubtful whether he dissected the human body; probably, for the reason already mentioned, he did not.

But the Athenians, although they were fond of novelty, were always ready to raise the cry of "impiety," and Aristotle was no more able to evade it than Soerates two generations before him. He had to flee to Chaleis in Euboea, where he died in 322 B.C.

To Aristotle is due the discovery of the laws of deductive reasoning and the establishment of the syllogism, but he had no idea of the inductive method of arriving at general laws, which are finally established by systematic verification. While he was anxious to make fact the basis of every theory, his great want was experiment. He made many accurate observations in natural history, but the art of experimenting had not yet been developed, nor had any exact quantitative record of observations been made. Being thus destitute of facts, he could only in a slight degree modify the child-like views of the Greeks, and had to rest content with such unverified hypotheses as seemed to him best to cohere and to explain the nature of things. Like others before him, he argued from general principles to particular instances, instead of founding his general principles upon experimental particulars.

Aristotle developed the existing ideas of Greek philosophy, and taught that there were four elements, of which all things consist, but he did not use the term "element" in the sense in which we understand it; that is, he did not imply that all kinds of matter can be subdivided or simplified into these

four. He rather understood the term "element" as signifying a fundamental property. The four elements were :—

1. Fire, the property of dryness and heat ;
2. Air (or steam), the property of wetness and heat, or of gaseousness ;
3. Water, the property of wetness and cold ; and
4. Earth, the property of dryness and cold, or of solidity.

Everything contained one or more of these fundamental constituents, which imparted to the compound its or their properties. He also recognised a fifth element, "Ether" or "Essence," from which the term "Quintessence," used by his later followers, was derived.

Theophrastus, who was born in 371 B.C., was a native of Eresus in Lesbos. He was originally directed to philosophy by the writings of Leucippus, and afterwards went to Athens and attached himself at first to Plato, and latterly to Aristotle. When the latter left Athens, he succeeded him as head of the Lyceum. He wrote chiefly on philosophy, but also on the warm and the cold, on water, on fire, on the sea, and on coagulation and melting. He did especially good work in continuing the labours of Aristotle on Natural History, writing ten books on botany and on stones and metals, or rather minerals. He died in 286 at Athens, leaving behind him the earliest work on mineralogy that is known to us, in which he mentions coal, cinnabar, and arsenic sulphide, and describes the preparation of white lead and litharge.

If you consult a Greek dictionary in regard to any Greek scientific term, or the name of a substance, you will almost invariably find that the word was used by Dioscorides. This philosopher was born in Anazarha in Asia Minor, and probably lived a little later than Pliny ; that is to say, in the first century A.D. He was the author of a treatise in five books on Materia Medica, upon which subject, and upon botany, his authority was undisputed for many centuries. He described all the substances then used in medicine, giving an account of their

properties, or supposed properties, and virtues. He accompanied the Roman armies in Asia, and there made himself acquainted with the preparation of medicines, and with chemical manipulation. Amongst other things he describes the process of distillation, and explains the preparation of mercury from einnabar and the roasting of antimony sulphide. He seems also to have known lime-water, zinc oxide, sulphate of copper, white lead, and sugar.

Before leaving the consideration of the Greek writers, it is necessary to allude to the works attributed to Hermes Trismegistus, of whom we gave some account in the preceding chapter. It is sufficient here to say that much attention was given to these writings during the period of which we are speaking. The later treatises on Neo-Platonic philosophy, religion, and alchemy have been classed, along with these older works, under the general term of "Hermetic Books."

In some respects Asclepiades and Galen ought to be included in this chapter, but they are so intimately associated with the Roman School of Medicine that we shall defer an account of them till the next. Indeed, there is no sharp line of demarcation between the Greek and Roman periods, and the one merges into the other, naturally and gradually.



## CHAPTER IV

### THE ROMAN, ALEXANDRIAN, AND BYZANTINE SCHOOLS

(From 100 B.C. to 1000 A.D.)

WE now pass from the knowledge of the Greeks to that of the Romans. The latter adopted their philosophy from the former, and like their teachers made little progress in chemical theory. Having extended their empire till it included a greater number of nations, they necessarily learnt a greater number of facts, but their writers relate these without any originality, and without any attempt at generalisation.

The first great Roman physician whom we shall name, and whose practice in many points conformed to that of modern doctors, was Asclepiades or Asclepias, a native of Prusa in Bithynia, and a contemporary of Cicero in the first century B.C. According to him, diseases result from an inharmonious action of the corpuscles of the body. Hence he sought to restore harmony by change of diet, exercise, bathing, and massage. He employed emetics and stimulants, and occasionally resorted to bleeding, but his knowledge of anatomy was slight. He founded the school termed "methodical," and adopted the agreeable maxim, that a physician ought to cure swiftly, surely, and pleasantly.

Caius Plinius Secundus, commonly called Pliny the Elder, was a distinguished philosopher. He was born at Verona in 23 A.D., and before he was killed by the eruption of Vesuvius in 79 A.D., wrote thirty-seven volumes of a comprehensive *Historia Naturalis*. In this work he gives in the last five volumes an account of the chemical knowledge of his time. His books resemble those of Dioscorides in being compilations, and are partly copied from that author and Theophrastus. It must be remembered in reading the works of Pliny and other

classical writers, that the names of things are not applied as in modern practice. For example, *minium* meant cinnabar, not red lead; in Pliny, *molybdaena* signified litharge, and *aes* sometimes copper and sometimes brass. We do not know exactly what he intended by *stannum*, *alumena*, *nitrum*, and several other terms.

The Romans in the first century of the Christian era were acquainted with gold, silver, copper, tin, lead, and iron, with their alloys. Quicksilver is mentioned for the first time in that century, although not as a new discovery, having been known before 300 B.C. They knew the alloys of zinc, but not the pure metal. Pliny does not tell us much about the extraction of these metals from their ores, but more about the countries from which they came. The Romans also understood the process of gilding with gold amalgam, and had determined the melting points of the different metals, and some of their properties. They were able to effect changes in metal, such as the conversion of iron into steel, and the formation of iron rust, and of some oxides of lead and copper, but they comprehended nothing of the nature of those changes.

It will be convenient, as summarising the chemical knowledge of the first century, if we note here a list of the principal substances, other than the six metals, known to the Romans, according to Pliny: White lead, verdigris, carbonate of copper (which they called *chrysocolla*, and used as a pigment), silicate or carbonate of zinc (which they used for making brass), blue vitriol, green vitriol, common salt, potash, and possibly soda, vinegar, sulphurous acid (used for bleaching wood), soap, lead plaster, sugar, starch, spirits of wine, murexide purple, indigo, and oil of turpentine.

Probably the greatest of the Roman philosopher-physicians was Claudius Galenus, familiarly called Galen (130—201 A.D.). He was a native of Pergamus, and first studied medicine in that city, afterwards prosecuting his studies in Smyrna, Corinth, and Alexandria. He then returned to his own city, where he was appointed physician to the school of gladiators. Thence he went to Rome in 164 A.D., and was offered but declined the



somewhat perilous position of physician to the Emperor, but after another sojourn in Pergamus, finally returned to Rome and accepted the post of physician to Marcus Aurelius. There he wrote some of his most important books, probably in the Greek language. In these works he confines himself to the medical properties of substances, and gives no idea of their chemical properties, or of the chemical action of medicines. His medical theory assumed that four grades of properties, corresponding to the four elements of Aristotle, when mixed in proper proportions, constituted health, but in abnormal proportions constituted sickness, which was to be corrected by medicines supplying the opposite property to that which in the patient was abnormal.

The Alexandrian Academy, founded by Ptolemy I. between 301 and 284 B.C., at length became the principal seat of Greek and Roman scientific and medical knowledge. When Christianity replaced the old heathen religions, the scientific secrets which were the property of the priests of the Egyptian temples became more widely known, especially in Greece, and the Alexandrian School, from its being placed at the seat of the Egyptian religion, became the main source of scientific progress. But as the wild tribes from the north began to invade and disturb the Empire, knowledge declined in the west, and Byzantium, afterwards Constantinople, was recognised as the chief seat of European learning.

In the Alexandrian School was a pupil of the famous Hypatia named Synesius of Cyrene (360—415 A.D.). He is one of the oldest commentators on Democritus known to us. Becoming a Christian, he was made bishop of Ptolemais, but is best remembered by his writings. A Neo-Platonist at heart, his works are tinged with the spirit of the doctrine of Iamblichus: "The world is a single animal, whose every part, whatever the distance, is united to every other part in a necessary manner." This was one form of expressing the pervading idea of the unity of matter and the influence of each part on each other part, an idea which was a powerful factor in

producing the alchemical belief in the possibility of transforming one metal into another. The first perception of this unity arose with the recognition of the regular revolution of the stars, in which men began to seek an explanation of every variation alike of metallic properties and of human destiny. It was the *catena aurea* of the Middle Ages, which bound all human beings. These principles, tallying with those of the Persian fire-worshippers, had their origin in Babylon or Chaldea, the earliest home of astronomy. The number seven, as formerly mentioned, had a mystic importance in Chaldea, and the Sabacans worshipped as deities the seven heavenly bodies, each of which had a temple containing a statue made of the metal corresponding to it.

Although the Greeks had not originally this idea of seven, they adopted it from the Chaldeans and extended it in new directions. Accordingly, we find in the Alexandrian School the seven planets associated with the seven metals, while the Neo-Platonists taught that each metal was engendered in the earth by the influence of the corresponding heavenly body. With these planets and metals were also associated, as has been already explained, certain deities of Greece and Rome, and there is some trace of a similar connection in the Chaldean remains at Khorsabad.

Of the Græco-Egyptian Schools which existed towards the end of the reign of the Ptolemies, in the first and second centuries B.C., one issued its writings under the honoured name of Democritus. One treatise that has reached us, the *Physica et Mystica*, is composed of several fragments—one on magic, another on dyeing in purple, and the third on the manufacture or imitation of gold and silver. The recipes in this last part are similar to, and some of them identical with, those in the best of the Leyden Papyri (marked X.), which was copied in the third century, but they are mixed up with mystical interpretations.

The Pseudo-Democritan School of Egypt created a scientific tradition, especially in alchemy, which continued down to the

seventh century, supported by a series of original writings and commentaries, which have supplied the greater part of existing collections of alchemical manuscripts. The later authors were gnostics, pagans and Jews, who tended more and more to the development of a mystical symbolism.

Of those writings which have survived, the principal are the work of Zosimus. He seems to have written about the end of the third century a sort of Encyclopædia of Chemistry, in which he reproduces the treatises of Cleopatra on distillation, and of Mary the Jewess on apparatus for digestion. Africanus was another writer of this period, but his books are all lost, and we know nothing of him except a few fragments quoted in alchemical texts. There were also astrological and other

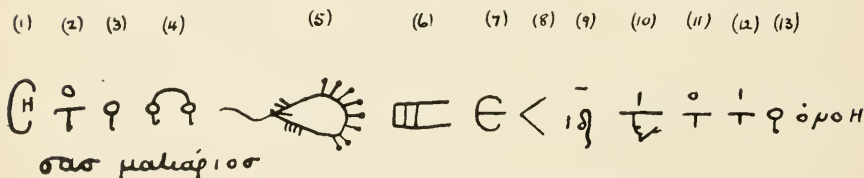


FIG. 26.—Formula of the Crab. (Memoirs of Zosimus.)

manuscripts in circulation under the names of Sophes (Cheops), Zoroaster, Manethon, and Pythagoras.

At the end of the memoirs of Zosimus occurs an interesting symbolic instruction, called the Formula of the Crab. A drawing of it is shown in Fig. 26. It was reported to contain the secret of the transmutation of metals, and is preserved in a manuscript in the museum at Leyden. In the margin of the MS. of St. Mark, already mentioned, there is a note in a more recent handwriting (fourteenth century), which professes to furnish the interpretation of the symbols.

There is first a description written in barbarous Greek of a process for the treatment of scorïæ or dross. It was apparently intended to change black metallic scorïæ, such as lead sulphide, into white, such as lead carbonate or sulphate, under the influence of water or air. The pious reflection follows:

“This has been accomplished with the aid of God and the practice of Justinian.”

Then comes the word “*tutie*.” This was an impure oxide of zinc, mixed with lead or copper. The word is followed by the magic formula recited at the moment of treating the “*tutie*” employed in the operation of the transmutation of zinc into gold. This formula consists of seventeen utterly unintelligible words in Greek letters, out of which it is impossible to make sense; but while these words are no more than nonsensical magic, the part of the formula which is in symbols appears to bear a different character. It is thought to be composed of signs intended to indicate to the initiated workman the materials and operations necessary for the process it conceals. These signs may be regarded as a sort of shorthand notes designed to supplement the traditional instructions, and were so expressed in order that they might convey no meaning to the uninitiated. The following interpretation of the symbols shown in Fig. 26 is taken from the note on the MS. of St. Mark :

1. The first sign implies “*Nota Bene*,” and is equivalent to the words “Important; begin; attention.”
2. *To pan*, the all. This also means a mixture of lead and copper (*molybdochalkos*).
3. *Chalkou ios*, rust of copper, *i.e.*, verdigris. This would introduce more copper to the *tutie*, and impart a yellower shade resembling gold.
4. These are two signs for copper joined by the sign for lead, *molybdochalkos kekarmenos*, *i.e.*, burnt copper-lead.
5. The sign of the crab or scorpion with eight anterior claws. The words are *argyrochalkos kekaumenos kai pepegmenos*. In some MSS. the scorpion’s tail is barred and in some a semicircle. It signifies “silver-copper burnt and fixed.”
6. The word “fixed.”
7. *Emeritos*, “divided up.”
8. *Dragmai*, “weights.”
9. Implies the number “14.”
10. This is an abbreviation for *titanos chalkos to pan ostrakon*, *i.e.*, calx of copper is the whole shell, or oyster, or philosopher’s egg. A “calx” meant a metal calcined and reduced to its oxide.

11. *To pan ostrakon* repeated.
12. *Titanos*, calx, repeated.
13. *Chalkou*, "of copper."
14. *Ho Noesas makarios*, "blessed is he who understands."

The initiate who understood the full signification of these symbols would be able so to colour his lead and zinc, or his more or less spurious metal, white-metal, or silver, by the addition of a copper compound, as to obtain a good imitation of gold. In this formula we have the last remnant of an ancient symbolism, that was quite meaningless without *viva voce* exposition. The method of working was in this manner handed down from one generation of craftsmen to another.

We have already mentioned the sign or symbol of the Crab (see p. 20). That symbol signified the process of fixation, that is, the transmutation of copper into silver by amalgamation or by being arseniated or otherwise treated. The philosopher's egg, referred to in the foregoing interpretation, alluded to the process of doubling gold.

Symbols similar to those which have been here explained were inscribed upon *steles*, after the Egyptian manner. There were also texts written upon papyrus, of which the originals are lost, but which are quoted in more recent writings, and so are available to us. One of these, which had been translated into Greek and copied in a papyrus, was found at Thebes. It is now preserved in the Leyden collection, where it is marked "V." It was written in the demotic character, the popular cursive writing of Egypt, and also in Greek, about the third century A.D. This practice of writing the magical recipes and formulæ in a precise and detailed manner became common at the commencement of the Christian era, when the Alexandrian School was in its prime.

There were originally a great number of such papyri, but most of them were systematically destroyed by the Romans in the time of Diocletian (300 A.D.) and Theodosius (346—395) for the purpose of preventing the enemies of Rome from making use in time of war of this source of wealth. It is clear, however,



that some of the recipes in later manuscripts still extant in the great libraries of Europe, referring to *asemos* and other substances, are workmen's traditional formulæ and probably belong to the same epoch. The treatise on emeralds and vitrified stones quoted from the *Book of the Sanctuary*, and another on pearls which we have under the name of the Arab Salmanas, who was probably its last editor, are without doubt reproduced from ancient texts, the products of technical traditions.

It was probably about the same period that first editions of the technical treatises on glass, artificial pearls, the tempering of metals, and allied subjects were issued. These texts belong to a much more ancient tradition, but they have been reproduced at various times in the course of centuries.

The most philosophic work of the whole series, the *Commentary of Synesius on Democritus*, was written about the time of the Emperor Theodosius, at the end of the fourth century; later came the group of scientific poets. But at the same period science and art sustained a disastrous blow in the destruction of the temples by order of the Emperor, among them the temple of Serapis, which had been the centre of culture in Egypt. With the destruction of the temples and their laboratories, experiments ceased, and the final stroke came with the burning of the library of Alexandria.

The scientific succession was maintained for some centuries by philosophers who were commentators rather than original writers and experimenters. The persecutions, which followed the rise of the Christian religion in Egypt, partly account for the practice adopted in these treatises of concealing the true name of the writer and assuming that of an ancient philosopher or royal personage. Such were the works of Olympiodorus, Christianus, Stephanus of Alexandria, and the Arab editions of the pseudonymous treatises of Heraclius and Justinian. Towards the seventh or eighth century there appears to have been formed round the *Commentary of Stephanus* a great collection of writings, including works of the Democritan

School, and of the early commentators, as well as the chemical poets.

Collections of Greek manuscripts had been made by Zosimus in the third century and Heraclius in the seventh. Of these specimens are preserved in the works of Synesius and Olympiodorus. It was the principal labour of the alchemists of the Byzantine School, when the seat of civilization and learning was transferred to Constantinople, to edit and re-comment on these works. The commentaries were written during the eighth and tenth centuries, and apart from them the Byzantine School did little for chemical knowledge.

On a review of the period embraced in this and the preceding chapter, we perceive that there was little advance in chemical science. Human thought had been active, but it had pursued its course along tracts which tended to draw it further and further from inductive philosophy. There had been, indeed, a great advance in general knowledge. The extensive conquests of Rome had enlarged the field of observation, and afforded to the learned definite information respecting a larger portion of the earth's surface and a greater number of its products, but these discoveries did not lead to a corresponding increase of scientific knowledge. The philosophers of the day had no conception of the true method of considering the facts thus ascertained, of correlating them, and of drawing conclusions from them. The genius of Aristotle had defined the laws of deductive reasoning, but the effect of his philosophy was in the first instance adverse to natural science. It encouraged men to employ processes of subjective analysis and deductive reasoning, and to neglect experiment and accurate observation. So long as this mental attitude persisted, there could be no science of chemistry.



*Regraded*

CHAPTER V

THE ORIENTALS

(From 500 to 1500 A.D.)

SUBSEQUENT to the conquests of Alexander and the foundation of the great Greek cities, Hellenic culture had spread in Syria and Mesopotamia, from the Mediterranean to the Tigris. Schools of philosophy sprang up in many places, to which students flocked to hear and to learn the new doctrines. But the progress of learning received a check. In 489 A.D. the Emperor Zeno destroyed the Alexandrian Academy, and at a later date Justinian closed the famous school of that city, and persecuted the philosophers, who were the heirs and upholders of the pagan culture. Teachers and pupils alike were scattered. The Syrian fugitives took refuge in Persia, and under the protection of the Sassanid kings revived the School of Nisibis and founded that of Gandisapora. In addition to these, there was a celebrated Sabaeen School at Harran, the home of the star-worshippers, the last inheritors of Babylonian learning.

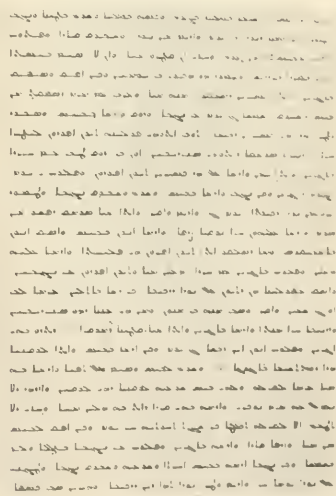


FIG. 27.—Specimen of Syriac Text.

The Syrian schools, between the fifth and eleventh centuries,

studied the Aristotelian science and medicine, and made new translations from the Greek. The Christian sect of Jacobites or Monophysites, rivals of the Nestorians, had their headquarters at Resaena and Kinnesrim in Syria, and their leader, the bishop-doctor Sergius, whose name occurs in the Greek alchemic treatises collected by Christianus, flourished in the sixth century, and dedicated his works to Theodorus. Syrian alchemists and not the Greeks invented Greek fire, and Syrian

sages acted as intermediaries between the Persian kings and the Emperors at Constantinople.



FIG. 28.—Apparatus for Digestion.  
(Syriac MS.)

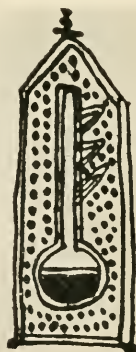


FIG. 29.—Digestion Flask  
with Bell Cover.  
(Syriac MS.)

In the seventh century an event took place which changed the history of the eastern world, the Hegira of Mohammed in 622 A.D. Arab hordes, fired by the fanaticism of Islam, overran Syria and Persia and subdued these countries. Syrian scholars were then employed by the Caliphs in such places of importance as demanded wisdom and judgment, as physicians, engineers, astrologers, treasurers, and governors of cities, and many Greek books were translated into Syriac, and from that into Arabic, the latter soon superseding the former.

The Abbasid Caliphs, in the eighth century, founded the Academy of Bagdad, where a vast number of translations were made. Amongst these were the works of the mathematicians Euclid, Archimedes, Apollonius; of the astronomer Ptolemy; and of the naturalists Hippocrates, Dioscorides, Aristotle, Galen, Theophrastus, Orbesus, Paul of Aegina, and Alexander of Aphrodesia. Besides these works there were translated books and commentaries on the *Chrysopoeia* and *Argyropoeia* of Pseudo-Democritus, the works of Zosimus, and the letters of Pebechius. But after the ninth century the Syrian schools languished, and were finally destroyed by Mussulman fanaticism in the eleventh and twelfth



FIG. 30.—Chamber for Roasting. (Syriac MS.)

centuries. After that date Arabic translations superseded the Syriac.

Two of these Syriac manuscripts may be here mentioned. One in the British Museum (No. 1007 of the 1872 Catalogue) is a copy made about the sixteenth century from an original text belonging to the period of the Abbasid Caliphs, and closely allied to the tradition of the Greek alchemists of Egypt and Constantinople. It has been published by Berthelot with a French translation (*La Chimie au Moyen Age, Vol. ii.*).

This manuscript contains a regular treatise in Syriac in ten books called "The Doctrine of Democritus." Its

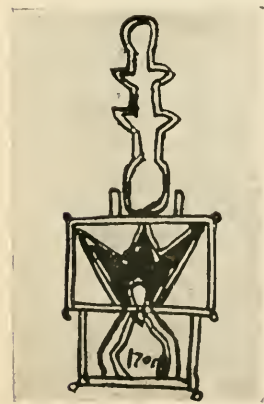


FIG. 31.—Flask for Digestion and Successive Condensation. (Syriac MS.)

origin is betrayed by its being full of Greek words in Syriac characters applied to minerals and drugs, with a few phrases from the Arabic. It begins with a preliminary notice of its object, and then indicates the general properties of substances,

with lists of symbols, notations, names, and nomenclature, necessary to the right understanding of the book. This is characteristic of the Syriac writers, for neither the Latin nor the later Arabic writers have transmitted to us any similar lists.



FIG. 32.—An Alembic.  
(Syriac MS.)

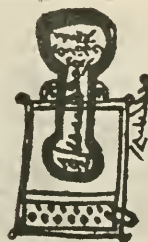


FIG. 23.—Vessel for Digestion.  
(Syriac MS.)

The following is a summary of the contents of the manuscript :—

Book I.—Chrysopocia, literally translated from the Greek Chrysopocia of Pseudo-Demoeritus.

Book II.—Argyropocia, similarly translated, but with omissions. There is an appendix, not identical with the Greek alchemical writings, on the philosopher's stone, mercury, minium, dyeing of wool, colouring lead, tin and silver, *adapta* or coloured glass, and artificial precious stones.

Book III.—On preparations of cinnabar, burnt copper, golden malachite, vinegar, the mixing of colours, and dyes. These recipes recall the Greek manuscripts of Zosimus in the Leyden Papyrus.

Book IV.—On the treatment of arsenic (male) and mercury (female); colouring tin and copper; whitening and yellowing pyrites, and the fusion of Indian iron.

Book V.—Preparation of philosophic elixir by means of

eggs, half real and half symbolie and mystic, like the Greek alchemy, but more positive and precise.

Book VI.—Diplosis of gold and silver ; elixirs ; oil and lime from eggs ; magnesia ; arsenious acid ; burnt lead, tin and copper ; mercurial sublimate, and other substances. This book resembles the Chemistry of Moses the Alehemist.

Book VII.—New reeipes on Argyropocia.

Book VIII.—Chrysopocia ; colouring lead, silver, copper and tin, to make them like gold, a series of sophistications recalling the *asemus* of the Leyden Papyrus.

Book IX.—This is the only theoretical book, and contains mystical doctrines, somewhat akin to those of Synesius, followed by practical reeipes for the use of sulphur.

Book X.—Technical preparations of various positive substances.

The manuscript also contains figures of apparatus for distillation, sublimation, and digestion, copies of which are shown in Figs. 28 to 51.



FIG. 34.—Water-bath for Digestion.  
(Syriac MS.)

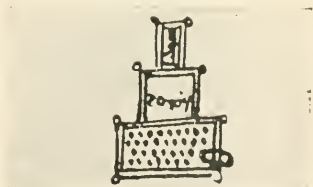


FIG. 35.—Apparatus for Sublimation.  
(Syriac MS.)

There is a list of the seven planets with their symbols, which has considerable importance, as it resembles that in the collection of Greek alchemists. These symbols date from the fifth century, but the association with them of the names of Babylonian divinities points to their origin in the Sabaeau school of Harran :—

Bel	Tin	Jupiter
Bilati	Copper	Venus
Camoch	Lead	Saturn
Nebo	Mercury	Mercury



The four elements have the symbols of four planets, but not the symbols appropriated to them in Greek alchemical writings.

Another alchemical manuscript in Syriac belongs to the University of Cambridge. It contains 148 pages, and is in the handwriting of the fifteenth century, but is in bad condition, written on paper and faded. It is, however, an important manuscript, for it has



FIG. 36.—Apparatus for Digestion in Small Chamber. (Syriac MS.)



FIG. 37.—Round-bottomed Flask. (Syriac MS.)

preserved some very old alchemical texts translated from the Greek. The following is a summary of its contents :—

1. Two books of recipes, several of which are identical with those in the Leyden Papyrus, treating of colours, and of gold, silver, tin, and other metals.
2. The treatise of Zosimus in twelve books, giving an account of work on "Egyptian silver" (that is, *asemus*), and recipes for colouring silver in various shades, black, wine-colour, yellow, rose, green and blue, as well as for gilding it, and instructions for diplosis, or doubling the precious metal.
3. The treatise of Democritus.
4. An extract called "Of Democritus."
5. A treatise of Democritus in three books, containing technical recipes.
6. The Book of Esdras, containing technical recipes.
7. A book of Zosimus on earths and minerals.
8. Letters of Pebeehius to Osrion the Magus on the Book of Ostanas.



9. Mystical fragments, concluding with a book on the union of gold and silver.
10. Magical formulæ and conjurations from the Egyptian.
11. Technical recipes on beads, pearls, and tinting metals.
12. Mystical fragments on Ostanes, Hermes, and others.
13. Technical recipes.

A fresh impulse was given to alchemical research by the Arabian alchemists. The Arabs under Omar took Alexandria in 641 A.D., and before 700 they had conquered the whole of the Byzantine part of Africa. They absorbed and extended the alchemical knowledge which they derived indirectly from the Greeks and directly from the Egyptians. Later, the Berbers and the descendants



FIG. 38.—Apparatus for Roasting. (Syriac MS.)



FIG. 39.—Apparatus resembling Greek Keratokēs. (Syriac MS.)

of the Carthaginians, Greeks, and Romans resident in Africa amalgamated with the Arabs under the general name of Moors. In 711 they crossed into Spain and in 755 founded the Caliphate of Cordova, bringing into western Europe eastern civilisation of a high order. From the eighth to the fourteenth centuries the Moorish Academies of Cordova and Granada furnished to the rising schools of Roman Europe and Germany, teachers of mathematics, philosophy, chemistry, and the arts. When at length the power of the Moors dwindled, and was finally destroyed with the conquest of Granada by the Christians under Ferdinand and Isabella in 1492 (contemporary with the discovery of America by Columbus),

Moorish manuscripts were translated into Latin, copied, and distributed throughout Europe.

Few Arabic manuscripts are extant. Like the Syriac, they contain many Greek words, and are often adapted from known Greek originals. But they also contain unmistakable Chaldean terms, and traces of Chaldean astronomy, such as was cultivated by the Sabaeans at Harran (see Fig. 52).



FIG. 40.—An Alembic.  
(Syriac MS.)

The Arabic writers were chiefly medical men, often physicians to the caliphs, and worked in chemistry mainly to study drugs, and to seek the elixir of life. As civilization and wealth moved from one centre to another, the artificers in gold and silver, precious stones, coloured glass, enamels, and dye-stuffs migrated

also, and handed down by the tradition of the workshops

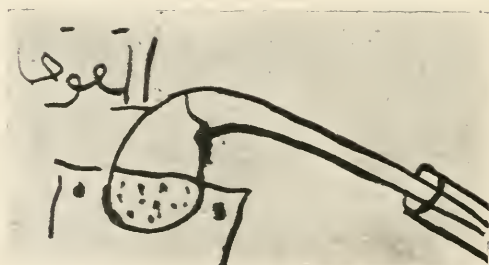


FIG. 41.—Retort and Receiver. (Syriac MS.)

many technical recipes used in their handicrafts. These recipes perpetuated a knowledge far more real and accurate than that to which the alchemy of the philosophers ever attained.

The following is a list of the notable Arabic writers :—

1. Ibn Beithar.
2. Ibn Khaldoun.
3. Ibn Khallikan.
4. Khaled ben Yezîd ibn Moaouïa.
5. Imam Djafer (Eç Çadeq) or Adfar of Alexandria.
6. Abu Abdallah Jaber ben Hayyâm al-Kufi (Geber).
7. Djou'n-Noun El-Misrî.
8. Maslema ben Ahmed El-Madjriti (of Madrid).
9. Abu Bakr Mohammed ibn Zakariya el-Râzi (*Rasès* or *Rhases*).
10. Ibn Ouahchiya.
11. El-Ikhmimi the Egyptian.
12. Abu Quirân of Nisibis.

All these are Sabaeans, that is, had the Babylonian traditions.

13. Stephanus, Monk of Mossoul.
14. Es-Saih El-'Alori.
15. Dobeïs, Pupil of El-Kindi.
16. Ibn Soleïmân.
17. Ishaq ben Noair.
18. Ibn Abi El-'Azaqir.
19. Abul Hasan Ahmed El-Khenchelil.
20. Abu Abdullah Mohammed.
21. Joghrayi (died in 1122).
22. Ibn Amyal El-Temimi.
23. Abu Casba ben Temman El-Iraqi.
24. Cadiq Mohammed.
25. Imam ibn Hasan Ali.
26. Djeldeik.
27. El-Ghazzâli
28. Ibn El-Moghreïrebi
29. Abu Nasr El-Farabi
30. Abu-'Ali-ibn-Abdallah-ibn-Sina (Avicenna).

} Alchemical Poets.

Of this long list of names it may be questioned whether many represent real personages. A number of Arabic works, in the shape of Latin translations, are to be seen in the great libraries of Europe, and a few have been printed—*Theatrum Chemicum* (1602), *Bibliotheca Chemica* (1702), *Artis Auriferæ quam Chemicam vocant* (1572), and *Artis Chemiæ Principes* (1572). Many of these books, such as the *Turba Philosophorum*, Rosinus

(i.e., Zosimus) Moricius, and Avicenna, are imitations from the Arabic, if not translations; others are mere fabrications.

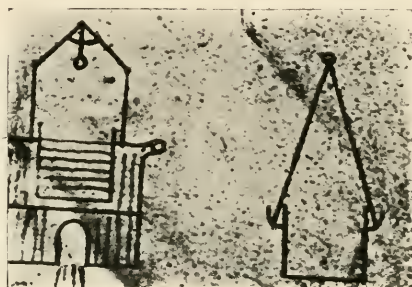


FIG. 42.—Apparatus for Sublimation and an Aludel.  
(Syriac MS.)

The *Book of Crates* already mentioned is reminiscent of the Greek manuscripts, but it also closely resembles the earliest of these Latin texts, which profess to have been translated from the Arabic in *Turba Philosophorum*. These last are full of passages which have been derived from the Greeks. The writings under the name of Marie in *Theatrum Chemicum*, and the small treatise of Synesius, published at Paris in 1612, are more modern productions of writers in the twelfth and thirteenth centuries, who adopted ancient names, yet they still retain some reminiscences of Greek alchemy, obscured and mingled with later ideas.

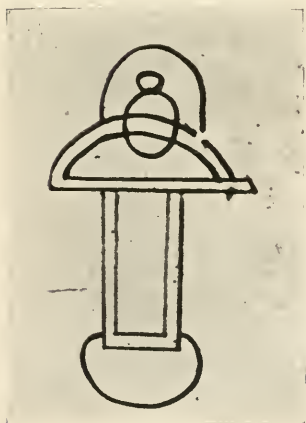


FIG. 43.—Bath for Kēratokēs.  
(Syriac MS.)

The *Book of El-Habib* is, as usual with Arabic works, preceded by a Mussulman preamble, but is clearly derived from the Greek alchemists. It names Hermes, Horus (Aros), Marie, Zosimus, Agathodemon, Archelaus, Plato, Pythagoras, Aristotle, Chymes,

Theosebius, and Justinian, and contains in an obscure form passages that resemble the work of the Byzantine alchemists, Comarius, Stephanus, and others. There are many phrases

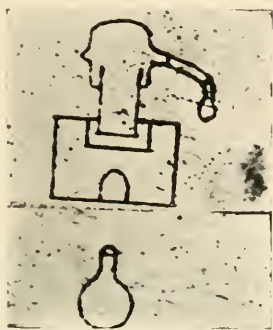


FIG. 44.—Alembic and Flask for Distillation *per Descensum*. (Syriac MS.)

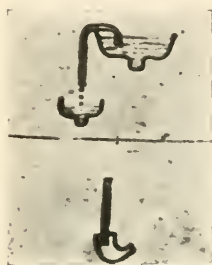


FIG. 45.—Apparatus for Decantation and Filtration, and a Spatula. (Syriac MS.)

taken from Greek manuscripts and similar to others in the *Turba Philosophorum*.

In the libraries of Paris and Leyden is a treatise entitled

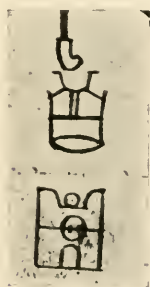


FIG. 46.—Heating Apparatus and Furnace for Calcination. (Syriac MS.)

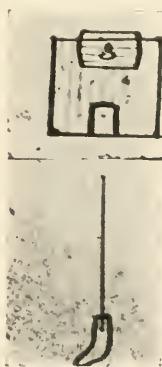


FIG. 47.—Sand-bath and Rod for Projection. (Syriac MS.)

“The Book of Twelve Chapters of Ostances the Sage on the Science of the Illustrious Stone.” It opens with a solemn invocation



of the name of God, and proceeds : "The wise Ostanès says." At the end we are told that Abu Cheddad Khalid ibn El-Yezid Aros, struck with admiration after a perusal of the book, translated it from the original language into Greek ; that Abdallah ibn Ahmed ibn Hindi re-translated it into Persian ; that Djafar Mohammed ibn Amr El-Faresi turned it into the dialect of Khorasan ; and lastly, that Abu Bekr ibn Gahia ibn Khalid El-Ghassani El-Khorasani translated it into Arabic, adding two sections. From all which we may estimate the vicissitudes

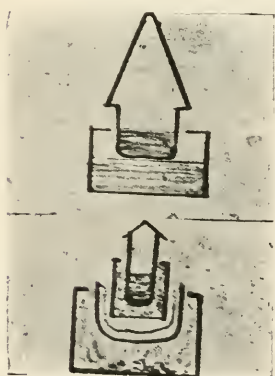


FIG. 48.—Vessels for Sublimation of Sal Ammoniac and Mercury. (Syriac MS.)

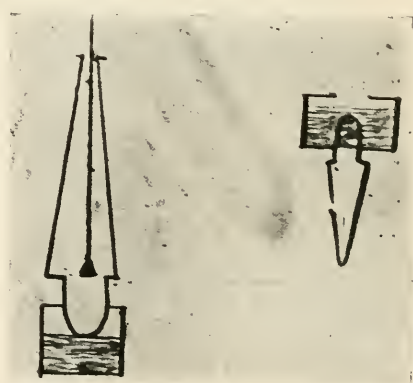


FIG. 49.—Apparatus for Fixation of Mercury and Sublimation *per Descensum*. (Syriac MS.)

through which manuscripts may have to pass before they reach us. This book mentions many Greek authors, and also Rhases, so that the compiler, whoever he was, must have lived after the twelfth century. A chapter on secret signs or symbols is important, because no purely Arabic work contains these.

Of all the Arabian alchemists the most famous and most venerated in the Middle Ages was Abu Abdallah Jaber ben-Hayyâm al-Kufi, more familiarly known as Geber (pronounced Jaber). The reputation of that sage, however, has suffered some severe criticism at the hands of M. Berthelot, and the whole question of his writings and their importance is so



complicated, that we shall defer the consideration of this subject to a separate chapter.

Next in importance to Geber, and in the medical schools even more renowned, was Abu-'Ali-ibn-Abdallah-ibn-Sina, known in the West as Avicenna (980-1036). Whewell describes him as "at once the Hippocrates and the Aristotle of the Arabians, and certainly the most extraordinary man that the nation produced." He was born at Bokhara, and received a good education from his father, Ali of

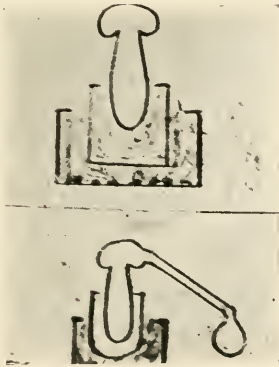


FIG. 50.—Apparatus for Sublimation with Strong Fire, and an Alembic. (Syriac MS.)



FIG. 51.—Apparatus for Distillation *per Descensum*. (Syriac MS.)

Balkh. Afterwards he studied medicine at Bagdad, and resolved to devote himself to science. At the early age of sixteen he had gained a high reputation as a physician. After wandering from city to city he filled for a time the post of Grand Vizier at Hamadan, where he died at the age of fifty-six, just thirty years before the Norman Conquest of England. His treatise, called the *Canon of Medicine*, was the leading text-book in European Universities, until its authority was challenged by Paracelsus about four centuries ago.

In his time a controversy arose as to the reality of alchemy.

Ibn Ycimiya and Ya'goub El-Kindi contested its truth, which was defended by El-Razi (Rhases) and Yoghrayi of Bagdad. Avicenna supported the attack, and was opposed by El-Farabi, whereupon Ibn Kaldoun remarked that the former was a Grand Vizier and had much riches, while the latter was poor and had not always enough to eat. The sage does not explain whether he meant to infer that the possession of wealth tends to clear or to obscure the judgment. The arguments on both sides will be found in the Latin version of Avicenna's works.

Although Avicenna was most distinguished as a physician, his chemical knowledge was not to be despised. His alechemical tracts are called in Latin *Porta Elementorum* and *Dictiones*. In the former he discourses of the Aristotelian elements, fire, air, water and earth, and their usual properties, and also about honey, milk, cheese, and similar products. In the main he retails the ideas of the Greek philosophers. The *Dictiones* contain allusions to the philosopher's stone, the elixir of life, copper and its medicinal properties, lead, tin, iron, brass, gold, silver, marcasite, antimony sulphide (which he called alcohol), soda (which he said was the juice of a plant named "sosa"), saltpetre, salt, sulphur, vitriol, orpiment, sal ammoniac, aurum vivum, hair, urine, eggs, blood, glass, white linen, horse dung, and vinegar, and to the processes of calcination and sublimation.

Another great Arab, whose writings are frequently mentioned by the alchemists of the Middle Ages, was Rhases or Rhazes (circa 850—900). His full name was Abu Bakr Mohammed ibn Zakariya el-Râzi. The latter portion of his name suggests that he was of Hebrew extraction, and this supposition is borne out by the facts that his father was a merchant at Ray in the province of Irak, Khorasan, and that he himself in his youth carried on the business of a money-changer.

Becoming attracted towards philosophy, he went to Bagdad and studied under Ibn Zein al-Taberi. On completing his studies, he was for a time Director of the Hospitals at Ray and at Bagdad, and so keenly did he study the phenomena of

Nature, that he obtained the name of "The Observer." His chief medical work, "El Mansuri," was dedicated to a powerful prince named El-Mansur, to whom he also presented his compendium of chemistry. His patron asked him to perform some of the experiments mentioned in the work. He tried to do so, but, like modern demonstrators, found that an

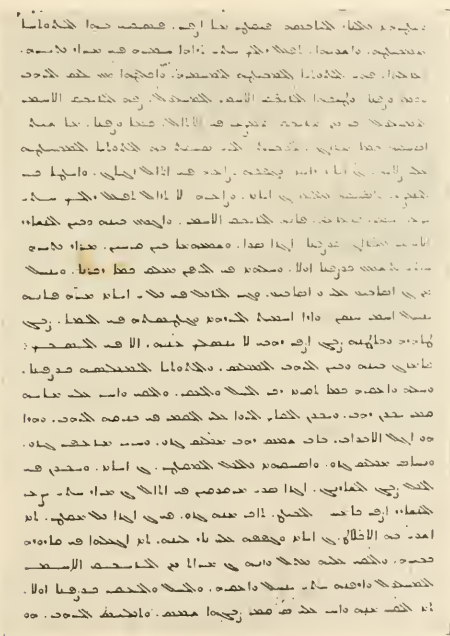


FIG. 52.—Specimen of Arabic Text.

experimenter cannot always command success, when success is most desired. The experiments failed, and the prince in a rage struck the philosopher across the face with a whip, and so injured one of his eyes that he ultimately became blind.

Many quotations ascribed to Rhases occur in mediæval treatises, and four works on chemistry have been attributed to him, called in the Latin translations, *Perfectionis Liber*, *Duodecim Libri de Arte Chemica*, *Liber Lapidis Minor*, and

*Confirmatio Artis Chemiae.* Difference of opinion exists as to the authenticity of these books and as to their value. Some authorities say that nothing remains of the chemical books save a few scattered quotations; others that the four books are in the main genuine. In the same manner, some assert that Rhases was a clear thinker, a ready operator, and a man of remarkable foresight and proved experience, while others maintain that he was a barbarous eclectic, and a physician whose only claim to remembrance rests upon his description of the small-pox. Between such discordant opinions we shall not presume to judge. One point at least may be placed to his credit—he was the first to declare that “he who knows no chemistry does not deserve the name of a philosopher.”

And, after all, this was perhaps the greatest benefit which the Oriental sages conferred on chemistry. They sought out the hidden alchemical wisdom of the Greeks and Egyptians, translated it into their own languages, demonstrated its extent and importance, and spread it over Western Europe. In this way they gave an impulse to chemical study, which led to the discoveries of modern science.

*Degraded Pseudo. (Don't kid yourself)*

## CHAPTER VI

### THE PSEUDO-GEBER

(Probably 750 to 800 A.D.)

As stated in the last chapter, we propose to devote this one to a consideration of the writings of the famous Geber. We have called the chapter "The Pseudo-Geber," because there is good reason to believe that the works upon which Geber's reputation rested in the Middle Ages were not written by him, but were forgeries of the thirteenth century.

Of the man himself we know almost nothing. Any little knowledge we possess is derived from the *Kitab-al-Fihrist*. His name is written in many ways. At full length (or nearly so, for some versions are even longer) it reads Abu-abdallah-Jaber - ben - hayyâm - al - Kufi ; more concisely Djaber-ben-Hayyâm or Jabir-ibn-Hayyâm ; and popularly Geber or Jaber. He probably lived at Kufa about the end of the eighth century, although various writers place him at the close of the ninth. Some say that he was a native of Khorasan, others that he was a Sabaeen of Harran. At Kufa he is said to have prepared the "elixir" or powder of transmutation. The writer of the *Kitab-al-Fihrist* says that he had been assured that Geber only wrote one book, and was even told that no such person had existed ; but these suggestions he laughs to scorn, declaring that he knew of nearly five hundred treatises ascribed to the famous philosopher. Apart from his writings, or reputed writings, this is really all that we know about Geber. Yet his works had a great repute, because most of the alleged discoveries of the Arabian alchemists were attributed to him on the authority of Latin treatises purporting to be translations of his Arabic texts.

There are six sets of these writings :—

1. *Summa Perfectionis Magisterii.*
2. *De Investigatione Perfectionis.*
3. *De Inventione Veritatis.*
4. *Liber Fornacum.*
5. *Testamentum Geberi Regis Indiae.*
6. *Alchemia Geberi.*

Reprints of these works are comprehended in a publication entitled *Artis Chemiae Principes* issued at Basle in 1572. Anticipating what we are about to explain in detail, we may state that M. Berthelot was of opinion that Nos. 5 and 6 were absolutely spurious, being of a later date ; that Nos. 2, 3, and 4 were mere summaries of No. 1 ; and that the *Summa Perfectionis Magisterii* contained no indication of Arabic origin, but was probably written by a Latin author or authors at the end of the thirteenth century, who issued the treatise under a name which would command veneration and respect. On the other hand, M. Berthelot was of opinion that *The Book of the Seventy* of Johannis was a translation of a genuine Arabic manuscript composed by Geber.

From an examination of these writings we infer that the Pseudo-Geber was acquainted with alum, green vitriol, saltpetre, sal ammoniac, aqua fortis and aqua regia, for the use of all which he gave directions. He extracted and purified his substances by the processes of distillation, sublimation, crystallisation, and filtration. Oil of vitriol must have been known to him, and he prepared mercuric oxide and corrosive sublimate.

M. Berthelot, having examined all the Latin translations purporting to have been made from Arabic originals and comprehended in the *Artis Chemiae Principes*, proceeded to translate a series of Arabic texts which he was inclined to regard as the actual composition of Geber or of some Arabic writer who wrote between the eighth and eleventh centuries. These texts were :—

1. *The Book of Royalty.*



2. The Little Book of Pity.
3. The Book of Balances.
4. The Book of Pity.
5. The Book of Concentration.
6. The Book of Eastern Mercury.

The manuscripts of the first two are preserved at Paris ; those of the remainder at Leyden.

In these works Geber begins in Mohammedan fashion by invoking the name of God, and then advises his readers to keep their knowledge secret. He furnishes a symbolic definition, in the form of a parable, of the philosopher's stone, and an emblematic dream in the style of the more ancient writers. After this are certain mystic doctrines such as the following :—  
 “Combine the cold and moist elements with the warm and moist elements first, and then with the warm and dry elements, and you will have the ‘imam.’” The fabrication of gold and silver he likens to the creation by God of the sun, in which heat and dryness predominate, and the moon in which cold and humidity prevail. It is necessary, he maintains, to have the elixir of the two colours which correspond with the two stars and the two metals.

The contents of these books are mystical and obscure. The Greek names of writers are disfigured. The author sets forth the doctrine of the four elements and the four qualities, so far following Aristotle, but asserts that everything consists in the equilibrium of these qualities and natures. Astrological knowledge, he says, is necessary, because of the influence of the stars on phenomena. He then states the alchemical symbolism of soul and body, and of the various parts of the philosophic egg, adding the old axiom, taken from the Greek, that “man engenders man, and gold engenders gold.” There must be suitability between the soul and the body. It is in alchemy as in the animal world. As the body of a man does not receive the soul of a bird, so the soul of the metal mercury cannot enter into a body such as glass or salt, but only into a metallic body.

The Arabic texts contain certain precise doctrines about the constitution of metals, which also occur in Latin texts purporting to be translated from Avicenna and Rhases, in the writings of Vincent de Beauvais and Albertus Magnus, and in the Latin Pseudo-Aristotle and Pseudo-Geber. But they entirely want other doctrines which are to be found in the more modern period.

Thus, in the *Book of Concentration* we find the theory of "occult qualities." The author says that the external qualities of a substance differ from the internal, and from this deduces the proposition that it is possible to complete the imperfect external qualities of lead, and to eliminate its imperfect internal qualities, so as to convert it into gold. He sums up his theories in the saying, "The elements are the same in different bodies, but the proportion of them is different."

This doctrine is here alluded to in the same terms as are found in the writings of mediæval alchemists and of Greeks such as Synesius and Olympiodorus; but, on the other hand, the Arabic texts make no mention of the doctrine of the generation of the metals by sulphur and mercury, a theory usually attributed to the Latin Geber, who would have added arsenic to these two elements. They give no recipe for the preparation of metals, salts, or other substances, while the Latin Geber furnishes a few. They are expressed in language that is vague and allegorical, and in its symbolism and declamation reminds us of the alchemical writers of the Byzantine School, such as Stephanus and Comarius. They mention the name of no alchemist, but refer to *The Book of the Seventy*, a work of a similar character and apparently written by Geber. The Latin writings, on the contrary, are especially modern in style,—methodical in composition, systematical in the description of substances and operations, and strictly conformed to the argumentative customs of the schools.

We shall take as an illustration a passage from the *Summa Perfectionis Magisterii*, a book which professes to have been written in the eighth or ninth century. In it there is a refuta-

tion of those who deny the reality of the art of transmutation expressed in the regular logical form common in the twelfth and thirteenth centuries. Now, the Greek alchemists would not have imagined that a doubt could be raised, as regards the principle at least of transmutation, neither did the Syrians, nor the oldest Arabic writers, such as the true Geber. The doubt first arose, as we mentioned in the last chapter, in the Arabico-Latin works attributed to Avicenna, and among Arabian alchemists of the same epoch. A logical discussion of these doubts does not find a place in any writer prior to the pretended Latin Geber, but it continues in most of the original works of mediæval alchemists down to the seventeenth and eighteenth centuries, when scepticism became universal.

If the Arabic manuscripts published by Berthelot are, as he seems to have established, the genuine work of the Arab Geber or one of his contemporaries or successors, they indicate that their author accepted without reserve the influence of the stars on the production of the metals; whereas the works in Latin attributed to Geber exhibit an advanced rationalism in contesting this doctrine, such as we find in the *De Nullitate Magiæ* of Roger Bacon.

An important point of evidence is the absence in the Arabic texts of the new and original facts recorded in the Latin, particularly the discoveries, such as nitric acid, aqua regia, oil of vitriol, silver nitrate, and others. Further, the ideas in the Arabic manuscripts are far-fetched, the doctrines are lacking in clearness, and the style of composition is entirely different. There is not a single passage in the Latin Geber that can be recognised as directly translated from the Arabic Geber. Berthelot quotes for comparison an Arabic work of the fifteenth century written in Spain by Abu Bekr ibn Beehrom, a pupil of Maslema. Its theories are those of Geber, but much more methodical and clear. "Three things," he says, "have to be regarded for the elixir or the philosopher's stone—whether it is possible to make it; with what matter; and how. As to the first point, it need not be discussed, for I have sent you a

specimen of the elixir. The work resides in everything, for everything consists of combinations of the four natures (elements) and is resolved into them. The manipulations are as follows—resolution (decomposition), mixture (combination), purification, calcination, maceration, and transmutation. There are decomposable things which are susceptible of passing from the power to the action, and indecomposable things. You will have to know the mode of its action, the weight, the hours, the manner in which the spirit is combined with it, how the soul is introduced, and whether fire has power to detach it from the spirit already combined. Gold, iron, and copper resist fire better than sulphur, mercury, or other spirits (*i.e.*, volatile bodies). . . . Bodies begin by being spirits. . . . When the fire is very intense they are reconverted into spirit.”

Another fact of considerable moment must be kept in mind. The alchemists of the twelfth and the early part of the thirteenth centuries, such as Albertus Magnus and Vincent de Beauvais, although they quote freely from others, never quote from the Latin Geber. This fact by itself would lead us to believe that the Latin Geber was not in existence at the period when these men wrote.

There are in the National Library at Paris copies of the *Summa Perfectionis Magisterii* of date 1300. From an examination of these we find that it is a methodical work, composed in a more scholarly style, and in a more logical arrangement, than books of earlier date. Mohammedan formulæ and allusions are absent, and, as we said before, for the first time the arguments of those who denied the truth of alchemy are stated and refuted. All this is foreign to the writings of Greek, Syriac, and Arabic alchemists, and there is nothing similar in the Arabic manuscripts.

Many such comparisons made by Berthelot tend to show that the Arabic Geber of the eighth or ninth century was less advanced than Avicenna, and had but a vague reminiscence of the Græco-Arabic doctrines; while the writings attributed

to the Latin Geber were the composition of one or more persons, who used the name of the ancient alchemist, and utilised the more modern style and knowledge of the thirteenth century, but did not translate their writings from any Arabic work. The Pseudo-Geber made certain statements to serve his own ends, and they have done so only too well, since they were credited for seven hundred years.

Gibbon in his *History of the Decline and Fall of the Roman Empire* ascribes to the Arabs the credit of being the originators and improvers of chemistry. Such was the opinion of his day, but it was an opinion formed upon insufficient information. A careful consideration of the facts set forth in this and the preceding chapter leads to the inevitable conclusion that the origin of chemistry was not due to the Arabs, and that they did little to extend or improve chemical knowledge. What they did know they derived partly from Hellenic culture through Syriac sources, and partly from the temple laboratories of Egypt. Much of their knowledge they did not understand, and they involved it in a mystical confusion, which for centuries hindered the progress of the science. It is not to the Arabs that the real credit is due, but to the clear thinkers and observers of Western Europe.



## CHAPTER VII

### THE TECHNICAL TRADITIONS

(From 1500 B.C. to 1300 A.D.)

Up to this point we have been tracing the history of the great schools of alchemy and philosophy, and of the distinguished men who were leaders in each. But, as we have from time to time reminded the reader, along with the philosophical literature there was growing up a series of technical traditions bearing on the practical operations of the laboratory or the workshop. Those traditions must now receive attention.

The most ancient Latin treatise of this class is named *Compositiones ad Tingenda*, a manuscript of the time of Charlemagne, the end of the eighth century, and *Mappae Clavicula*, a manuscript of the tenth. These transmit to us the traditions and writings on this subject which existed during the last period of the Roman Empire. The *Clavicula* gives recipes on the precious metals and for dyeing, and describes the hydrostatic balance for proving the quality of metals. There are other four collections of recipes entitled *De Artibus Romanorum*, *Schedula Diversarum Artium* (by the monk Theophilus), *Liber Diversarum Artium*, and *De Secretis* (by various authors). These six manuscripts show a continuity between the knowledge of the Græco-Egyptian period and that of subsequent ages, extending down to the twelfth and thirteenth centuries.

When we approach the consideration of such writings, we become aware of a great contrast between technical treatises and other books connected with *practical* work, and the purely *theoretical* treatises of the philosophers. For example, the methods of gilding are the same in the most ancient Greek manuscripts, in the Syriac, in the Arabic, and in the Latin,



down to the nineteenth century when the art was revolutionised by the electrolytic deposition of the metal. The philosophical writings, on the other hand, which began by attributing everything to the stars, to the gods, and to other superstitious causes, became more mystical and religious in form, the further they drifted from contact with practical work. Even the workers in mediæval alchemical laboratories, who often made an attempt to employ in the service of man the material forces of Nature, and to conduct inquiries into the causes of natural phenomena, were impeded, and their work was rendered futile, by the use of methods founded on old superstitions and mystical ideas, and a false system of philosophy.

Nevertheless, in fairness it ought to be said that, after allowing for all their shortcomings, the writings of the philosophical alchemists are not such nonsense as they seem to a modern student. We have lost the key to much of their symbolism, and the mysterious allusions with which they are filled no longer appeal to scientific thinkers. To us, therefore, they have little to say; but it was not so in the Middle Ages. Then they were studied not only by quacks, who sought to discover in them modes of enriching themselves at the expense of others, but also by earnest men, whose work resulted in a gradual improvement in chemical processes, and a steady, if slow, increase in the number of chemical compounds produced.

The volume of *Compositiones ad Tingenda* includes such recipes as a master-workman would possess for colouring stones for mosaics, and for gilding, silvering, and polishing them; for making coloured glass and enamels in different shades; for dyeing skins in various colours; and for staining wood, bone, and horn. It also contains lists of minerals, drugs, metals, earths, and oxides employed in goldsmith's work.

In this treatise appears for the first time, in a manuscript of the eighth century, the word "vitriol," and in another of the twelfth the term "alcohol." The property of this spirit which first impressed the discoverer was the fact that it burned without setting fire to the substance on which it was placed.

Certain alloys are mentioned—brass, white copper, and golden copper. There are separate articles on making parchment and varnish, and chapters on gilding, soldering, and cementing. The preparation of military and incendiary combustibles occupies an important place. From internal evidence one can infer that these recipes were first written in Greek and then transcribed in Latin, thus betraying their Byzantine origin, while the whole bears a close resemblance to, and some parts are almost literally translated from, recipes in Greek manuscripts from Thebes now preserved in the Leyden Library.

It must be apparent from what has been said, that the tradition of ancient chemistry passed to the Middle Ages by two streams—the one theoretical, and the other practical—

1. The theoretical ideas of the Greek alchemists passed through the schools of Alexandria, and through the Syrians of Mesopotamia in the time of the early Caliphs, and were carried by the Arabs or Moors into Spain. They were then translated into Hebrew, or the languages of Castille or Provence, and simultaneously into Latin, in Italy and France, at the end of the twelfth and beginning of the thirteenth centuries. For example, in the *Turba Philosophorum* and in Rosinus there are Latin translations of Arabian alchemical authors, in which are found the ideas, and even the words, of the Greek alchemists.
2. The practical work of the metallurgists, goldworkers, painters, scribes, architects, and china and glass-makers, whether they were employed in Egypt, in the East, or among the Greeks and Romans, has been handed down without any break in its continuity, from workshop to workshop, first described in Greek by the Hellenic authors, and afterwards translated into Latin, in the time of the Roman Empire. This fact is shown by the appearance of the Greek recipes contained in the Leyden Papyrus and the chemistry of Moses, in the *Compositiones*

*ad Tingenda* of the eighth century, and the *Mappae Clavicula* of the tenth. Berthelot has even identified some of these with recipes of Heraclius and Theophilus.

In a similar way, in medical history, we learn that therapeutic recipes and materia medica were preserved by practice and translated from the Greek in the time of the Roman Empire, compiled from the first to the seventh century, and transmitted from land to land, being frequently recopied.

The conclusion, therefore, at which we have arrived is this, that the alchemical collections until the thirteenth century were made up of knowledge derived through both the channels we have named—translations of old theoretical treatises, and practical traditions reduced to written recipes, some of which last we shall now examine.

The *Liber Ignium ad Comburandos Hostes* of Marcus Graecus has been preserved in a Latin manuscript of the thirteenth century. Berthelot, from an examination of the book, infers that it had been compiled from different treatises, giving details under different heads, but all mainly transmitted from the Greek through the Arabic. The following are its principal contents :—

1. Recipes on military fires, certainly from the Greek, some of them drawn from Eneus the Tactician (fourth century B.C.), and some from other Greek authors down to Julius Africanus (third century A.D.). One recipe for a spontaneously inflammable mixture is, "sulphur, salt of the mountain (saltpetre), *cindus*, exploding stone, pyrites; take of these equal parts, powder at midday, mix with bitumen to a paste, and add a little quick lime." Many similar mixtures of sulphur, quick lime, and organic matter are mentioned in manuscripts.
2. Phosphorescent matters.
3. Compositions for rendering things and persons incombustible, e.g., "take 1 lb. of tale, 1 lb. gum arabic, 4 lbs. red clay, as much as you please of white farina of Hauran, white of egg, and 6 lbs. urine: add vinegar of wine." These recipes are drawn from old Greek sources through the Arabic.

4. Composition for Greek fire. The recipes under this head contain saltpetre, and are of more modern origin. The ancients applied the term "nitrum" to various substances, and were unacquainted with the deflagrating properties of saltpetre. The earliest mention of the substance occurs in Latin translations from the Arabic made in the thirteenth and fourteenth centuries.
5. Recipes for something resembling gunpowder, which is also described by Marcus Graecus, Roger Bacon, and others, about the same period. All include *sal petersum* in the composition.
6. Description of a lamp which was provided with a reservoir to feed it slowly.

The *Mappae Clavicula* contains an excellent description of a process for testing metals by the hydrostatic balance. The ancients, even before the time of Hero, King of Syracuse, knew how to assay gold by cupellation, but this method and others of the same sort involved the destruction of the article as a work of art. Hence Archimedes was led to adopt the system of testing by specific gravity. The earliest account of this mode is given by Vitruvius (*De Architectura*, lib. IX., cap. III.). The method described is very clumsy, but Galileo mentions a more refined process by means of the hydrostatic balance, and says that Archimedes must have employed some similar device. The *Carmen de Ponderibus* of Priscian, a poem on weights and measures, written about the fourth or fifth century A.D., furnishes a full description of this balance, with directions to an artisan for its use, and attributes the discovery to Archimedes.

A most interesting account of the hydrostatic balance, as known and used by the ancients, is given in *The Book of the Balance of Wisdom*, written by an Arabian physiologist named Al-Khazini or Alhazan, in 1121-22 A.D. This work was fully discussed in an essay by Dr. Bolton read before the New York Academy of Science in 1876. Al-Khazini ascribes the invention of the instrument to Archimedes, and tells us that rules for its use were devised by the mathematician Menelaus (98-117 A.D.).

Tables of specific gravities were drawn up by means of it, which, as regards the metals and precious stones, coincide in a wonderful way with modern determinations. In many instances the difference lies only in the second place of decimals. Thus, lead is said in the old tables to have specific gravity 11·33, while in modern tables it is stated as 11·34.

The chief interest which this matter has for the student of chemical history is the fact that it demonstrates that the Orientals had attained to the art of exact experiment, which is the first step towards real scientific knowledge. Prior to this invention, as was mentioned when considering the work of Aristotle, the ancients possessed no means of making accurate observations in which weight was an element, or of preserving a record of the results. It was now possible to ascertain specific gravities and other matters which are determined by weight, and to prepare tables of these which would be available to others.

That its inventors were well aware of the uses and advantages of the hydrostatic balance is proved by the following extract from Al-Khazini's treatise :—" These advantages are (1) exactness in weighing ; this balance shows variations to the extent of a mithkal, or of a grain, although the entire weight is a thousand mithkals, provided the maker has a delicate hand, attends to the minute details of the mechanism, and understands it ; (2) that it distinguishes pure metal from its counterfeit, each being recognised by itself without any refining ; (3) that it leads to a knowledge of the constituents of a metallic body without separation one from another : (4) that it shows the superiority in weight of one of two metals over the other in water, when their weight in air is the same, and conversely ; (5) that it makes the substance of the thing weighed to be known by its weight ; and the gain above all others, that it enables one to know what is a genuine precious stone such as a hyacinth or ruby, or emerald, or fine pearl ; for it truly discriminates between these and their imitations or similitudes in colour, made to deceive."



Dr. Bolton's essay describes and figures the apparatus according to Al-Khazini, with tables of the specific gravities determined by him, and we refer to it any reader who desires further information upon this curious and interesting subject.

The *Liber Sacerdotum* of Johannes is a work derived from old Egyptian tradition, containing a collection of recipes for preparations in mineral chemistry, transmutation of metals, and the manufacture of colours and precious stones. In date it is a little more recent than the *Mappae Clavicula*. Its formulæ are similar to, but not exact translations of, those in the Leyden Greek manuscripts. The treatise is taken from an Arabic text of the tenth century, and is full of Arabic words, including two Latin-Arabic directions. The *Book of the Seventy* is a theoretical work, probably founded on some translation of a treatise of the Arab Geber, but developed and altered by the copyists. The *Liber Sacerdotum* contains no alechemical symbol, but there are in it cryptograms, and the words "Sun," "Moon," "Mars," and "Venus" are made use of to represent the metals gold, silver, iron and copper, thus reminding us of the practice of the Sabaeans already explained. Its contents may be briefly summarised thus :—

1. Forty-eight recipes for transmutation of metals; some only colouring the surface; some making gold "which will not resist the test"; and others professing to make gold which "will resist the test."
2. Recipes for soldering metals.
3. Preparation of metallic compounds, some of which are said to have been derived from the Romans.
4. Transmutation and the philosophic egg (an alechemical symbol).
5. Practical recipes for making a red dye, preparing ink, and gilding.
6. Tinting glass.

An Arabic-Latin lexicon is here placed between two sets of recipes.

7. Making precious stones and preparing bronze.

A careful examination of these technical traditions in the form of written recipes, and a comparison of them with those



contained in the more ancient writings to which we have already referred, will fully establish two points which we have endeavoured to bring out in this chapter, and which are of importance. It is, in the first place, certain that the practical workers had attained to a considerable measure of definite and exact knowledge in regard to the substances known to them, both as to their properties and the methods by which they could be treated. It is equally clear, in the second place, that this knowledge was a direct inheritance from the priestly workers in the temple laboratories of Egypt, which had been improved and extended by the labours of their successors, whether Greek or Syrian, Roman or Arabian.

## CHAPTER VIII

### THE ALCHEMICAL TREATISES OF THE MIDDLE AGES

THE works of the Greek writers on mathematics, astronomy, physics and medicine, with such ideas of theoretical and practical chemistry as they possessed, were not directly known in Western Europe until after the Renaissance. Greek science reached Latin Europe in the first instance through the medium of Arab or Moorish and Hebrew authors, writing in Arabic, about the time of the Crusades. But such learning was not recognised as Greek, because Arab writers got the credit of being the discoverers of that of which they were mainly transcribers and translators. Their works were made available through Latin translations, some of which are genuine, but others are undoubtedly forgeries.

The earliest of the translations are in manuscripts of the thirteenth and fourteenth centuries, and many others have been preserved in printed collections of a later date :—

1. *Artis Aurifera quam Chemicam vocant*, 2 volumes, 1572.
2. *Artis Chemicæ Principes*, 1572.
3. *Theatrum Chemicum*, 1659–61.
4. *Bibliotheca Chémica Curiosa* (of Manget), 1702.

These books profess to render in Latin the treatises of Hermes, Ostones, Plato, Aristotle, Morienus, Geber, Rhazes, Bubear, Alpharabi, and Avicenna. Some of them have been composed in Spain, as, for example, *Tolitanus Philosophus* (*Bibl. Chem.*, Vol. II., p. 118), which is betrayed by its name. The oldest of the manuscripts is not earlier than 1300, and the later copies contain treatises with variations, practically the same as those which appear in the printed collections of the sixteenth and seventeenth centuries.

The various Latin translations, although corresponding to

Arabic texts, go back to an earlier period than any manuscript now in our possession. They are anonymous, but belong to the same family of Arabian writers on medicine, philosophy, and mathematics which we know to have produced works that were translated in the twelfth and thirteenth centuries—for example, the treatise of Morienus, translated by Robertus Castrensis in 1182. The works were translated mostly from Arabic or Hebrew sources, but these were doubtless destroyed when the Moorish libraries in that country were burned. We are assisted in fixing an approximate date by the occurrence of quotations from these authors in the books of Albertus Magnus and Vincent de Beauvais.

The *Rosarium Philosophicum* (*Bibl. Chem.*, Vol. II., p. 87) must have been written by an assiduous reader of Arabic and other Semitic treatises, since he cites and comments on Stephanus, Geber, Rhazes, Avicenna, Pseudo-Aristotle, Morienus and Khalid. He also cites Latin alchemists such as Albertus Magnus, Arnoldus Villanovanus, Raymond Lully, Vincent of Beauvais, Thomas Aquinas, and Garlandus. This last is the most recent writer quoted in the *Rosarium*, hence its date was probably the middle of the fourteenth century. The translator of Morienus Romanus, a pretended hermit of Jerusalem, gives his name as Robertus Castrensis, and has been identified as Robert of Retinus, a translator from Arabic into Latin of many philosophical works, who wrote prior to 1182. He is one of the earliest Arabico-Latin translators. The date of these translations can thus be fixed within a period extending from the twelfth to the fourteenth centuries.

The translations are of two classes :—

1. Didactic and methodically arranged treatises ; and
2. Confused collections of facts and theories without method, written in allegorical language, often charlatanesque, and purporting to be made from Arabic or Hebrew.

Of the latter class the most ancient, and hence the nearest to the old tradition, are Morienus or Morianus, Khalid, the Pseudo-Plato, the Senior Zadith Filius Hamuelis, the *Clavis Sapientiae*

(attributed to Alphonso the Wise), *Tractatus Moreris suo discipulo Mirnefindo*, and above all the *Turba Philosophorum*. There are also the *Rosarium Philosophicum* already mentioned, and the *Clavis Majoris Sapientiae* of Artephius, which is probably of a similar character, and is quoted by Roger Bacon. All these books are printed in Latin in the *Theatrum Chemicum*, in the *Bibliotheca Chemica*, and in the collections of the sixteenth century.

When we examine the *Book of Crates*, the *Book of El Habib*, and other treatises published by Berthelot from the manuscripts preserved in the museums of Leyden and Paris, we find that they cite textually the names, phrases, and doctrines of known Greek alchemical writings. On the other hand, they are of the class to which the *Turba Philosophorum* belongs—that is, unmethodical collections of facts and theories. While most of the Latin writings become more and more vague, and do not reproduce the Greek texts with precision, yet they are more systematic in their methods than the older works, and their style conforms to the logical system of the schoolmen, which was held in honour in the twelfth and thirteenth centuries. This is a clear proof of their more recent origin. We infer that the writers were the authors, not translators, of the books, and had only a dim reminiscence of the primitive treatises.

The most modern of the didactic treatises, arranged by subject matter, have a scientific value, in spite of their errors and illusions. Of this sort are most of the writings attributed to Avicenna, those bearing the name of Pseudo-Aristotle (*e.g.*, *De Perfecto Magisterio*), and the Latin works placed by their editors under the name of Geber.

In the Latin books purporting to be translated from the Arabic we discover many traces of Greek alchemical writers. The most certain of these is the work of Morienus (otherwise spelt Marianos or Murianos), a Greek or Syriac monk. His pupil Khalid died about 708, and his book is quoted by Arabic authors, and as already mentioned, was translated by Robertus Castrensis in 1182. The date 708 is consistent with the state-

ment that Morienus became a monk or hermit four years after the death of Heraclius. He attributes the origin of his scientific knowledge to a perusal of the alchemical writings of Hermes Trismegistus, which he says were rediscovered by Adfar of Alexandria, who was probably Imam Djafer Eç Çadeq. In support of this assertion he quotes Heraclius the Wise, king and philosopher, whose name he mis-spells "Hercules," and refers to Marie Africanus, and Zosimus (Oziambes). These and other allusions place him in the Græco-Syriac period, and prior to the Arabic. It is only the earliest copy of Morienus that contains such statements. Later copies in the Paris Library want the biographical introduction, which is replaced by a scholastic dissertation on the nature and object of the art of alchemy, with arguments for and against its reality, indicating a more modern interpolation.

The *Tractatus Aristotelis alchymistae ad Alexandrum Magnum de Lapide Philosophico* professes to be translated from Hebrew into Latin by a certain Greek by order of Pope Honorius. It contains disfigured Greek traditions. There is a letter with a similar title in the Syriac Library of Assemani, and another in the *Artis Auriferae* (Vol. I., p. 382). In fact, there were several such letters composed about the eighth century and down to the fourteenth on different subjects, Latin translations of which were also made.

The *Senioris Libellus* (*Bibl. Chem.*, Vol. II., p. 216; *Theat. Chem.*, Vol. V., pp. 193, 215) is attributed to Zadith, son of Hamuel. It is full of parables, commentaries, and mystical figures. The author quotes Marie, Hermes, Khalid, Aron (Horus), Plato the Alchemist, Solomon, and Marcus (probably Marcus Græcus). The writers Theodora, Rosinus, Averrhoes, and Avicenna are also named, but no one of later date. Many passages resemble Greek manuscripts, such as: "Copper is like a man; it possesses a spirit, a soul and a body"; "three and three are one, and all results in unity"; "take the body of magnesia."

Another treatise, entitled *Consilium Conjugii seu de massa*

*Solis et Lunae, Libri III.* (*Bibl. Chem.*, Vol. II., pp. 235-41), belongs to the fourteenth century, and is Christian in doctrine. It professes to be *ex Arabico in Latinum Sermonem reductum*. As it quotes Morienus and Rhazes, it must be of later date than these writers. "Massa" means "metallic ferment," and the title therefore signifies, "three books on the ferment of gold and silver," the precious metals being represented by the sun and moon. This idea of a ferment which converted inferior metals by a purifying decomposition into precious metals (gold and silver) is very old, occurring in Zosimus, Pseudo-Moses, and a Greek papyrus in the Leyden Museum.

In *Artis Auriferae*, Vol. I. (p. 267 in 1572 edition, and p. 246 in 1593 edition), there is a treatise said to be that of Rosinus or Rubinus, probably an Arab corruption of Zosimus. It is in all likelihood a production of the thirteenth century, altered from previous manuscripts. It quotes Mohammed, Geber, Sarracenus, Morienus, and Rhazes. It may be a re-editing of the book of Zosimus, with alterations, translated first into Arabic, and then into Latin. This view is supported by the circumstance that it contains several unmistakable Oriental words. It is full of interpolations, glosses, and additions made by successive copyists.

A portion of this treatise called "*Rosinus ad Euthicium*" resembles the work of Zosimus dedicated to Eusebia or Theosebia, and quotes Horus, Marie, Hermes' *Clavicula Philosophorum*, Bilonius (Apollonius of Tyana), Agadamon (Agathodemon), Democritus and his *Chrysopeia*, and Synas, who may be Synesius. Another portion, *Rosini ad Sarratantum Episcopum*, is obviously the work of a Christian author using the name of Rosinus.

In the so-called treatises of Rosinus we find many things which suggest a Greek origin. "*Aqua Sulphuris*" in these manuscripts corresponds with the "*hydor theiou*" of the Greek manuscripts and papyri (*supra*, p. 21). The words do not occur either in the *Turba Philosophorum* or in Latin authors. The "*Venenum ignis*" attributed to Marie is



evidently meant for the "fiery remedy" mentioned in Greek copies of Marie. "The blade formed of two metallic bodies" is the "leaf formed of two metals" described by Marie, and alludes to the blade or sheet of the *kēratokēs* connected with the water-bath or Bain Marie (*supra*, p. 22 and Fig. 13). "The bright preparation equal to marble" is a quotation from Democritus. The instruction "take quicksilver and fix the body of the magnesia" corresponds to the end of the *Chrysopoeia* of Democritus, while such phrases as "Nature rules Nature," "Nature conquers Nature," or "Nature delights in Nature" are common expressions of that philosopher and of Ostances (*supra*, p. 30). There are also many axioms identical with those in Greek manuscripts, such as "one stone has body, soul and spirit," which was an expression applied to the metals and occurs in Artephius Longaevus.

The *Turba Philosophorum* forms the commencement of the *Artis Auriferae* (1572 and 1593 editions), and reappears in the *Theatrum Chemicum* and in the *Bibliotheca Chemica* of Manget (1702). These are all reprints. It is a compilation of quotations from ancient philosophers and alchemists of various periods. These quotations are similar in character to an opening passage of Olympiodorus, who quotes the Ionic and naturalistic philosophers Thales, Parmenides, Heraclitus, Hippasus, Xenophanes, Melissus, Anaximenes, Anaximander, and others. He also refers to their opinions on the principles and elements, and those of the alchemists Hermes, Agathodemon, Chymes, and Zosimus. Olympiodorus wrote in the fifth century, as formerly mentioned.

We infer that the *Turba* was written first in Arabic or Hebrew. This is indicated by its peculiarly Semitic deformations of Greek names, and its replacing of Greek words by Semitic when naming certain substances. Its quotations attributed to the philosophers are purely imaginary, and the two versions which we possess are Latin translations from two Arabic originals. One version is given in the *Theatrum Chemicum* and *Bibliotheca Chemica*, and in it the opinions

quoted, Nos. 1 to 72, are called “*sermones*” ; the other appears in the *Artis Auriferae*, and in it the opinions, Nos. 1 to 78, are termed “*sententiae*.” It is possible to conclude from internal evidence that the author was a monotheist and apparently a Christian. He quotes Parmenides, Pythagoras, Socrates, Democritus, Anaxagoras, Plato, Anaximenes, Anaximander (often mis-spelt), Hermes, Agathodemon, Lucas, Archelaus, Theophilus, and Ostanus. Many other names are so defaced by copyists that it is impossible to identify them with certainty. Among the commentaries are Stephanus and Heraclius, but no Arab, neither Morienus, Geber, Rhazes, nor Avicenna. On the other hand, the *Turba* is quoted from the twelfth century downwards by Latin authors such as Vincent de Beauvais, Arnoldus Villanovanus, Albertus Magnus, the *Consilium Conjugii*, and the *Rosarium*. Thus, the original text from which it was first translated must be the earliest of which we have knowledge. The commentaries which accompany it, called Allegories and Enigmata, are of more recent date, but yet early enough to be quoted by Geber and Morienus.

The *Turba* is given as the work of Arisleus or Aristanes, a Pythagorean, and pupil of Hermes. He is called the son of Abladus. According to the narrative of the work, he assembled the philosophers or alchemists, and each gave his ideas on the formation of the world, and on the philosopher's stone and transmutation. The title “*Assembly*” of the philosophers occurs among the Greek manuscripts translated by Berthelot, who has detected a number of passages where the Greek version and that of the *Turba* are identical. We shall note a few of these passages.

Stephanus says in one of the Greek manuscripts : “Copper is like man ; it has a soul and a body ; the soul is the most subtle part, that is to say, the tinctorial spirit ; the body is the heavy material earthy thing, endowed with a shadow.”

Now, the *Turba* uses almost the same words : “Copper has been whitened and deprived of shadow, . . . being despoiled of its black colour, it has abandoned its thick and heavy body.

Copper is like man. . . . The sages have said that copper has a body and a soul ; its soul is a spirit ” (*i.e.*, volatile) ; “ its body is a dense thing ” (*i.e.*, fixed).

In the *Turba* Democritus is represented as saying that “ it is necessary to employ our copper to obtain silver ; silver to obtain gold ; gold to obtain the shell of gold ; and the shell of gold to obtain the saffron of gold.” With the exception of the last words, this is a literal translation from the Greek.

Entire pages of the *Chrysopoeia* and *Argyropoeia* of the Pseudo-Democritus are transcribed in the *Turba*. For example, the following passage is termed “ recited by Parmenides ” :— “ Take quicksilver ; coagulate it with the body of magnesia (meaning magnetite, sulphide of antimony, sulphide of lead, sulphide of tin, or pyrites), or with kuhul (*i.e.*, sulphide of antimony, or unburned sulphur), render its nature white and put it on our copper, and it will whiten the copper. If you render the mercury red, the copper will redden, and if one then heats it, it will become gold. I say that it reddens also the male [arsenicon ?] itself, and chrysocolloa of gold. And know that gold does not take its red tint except by the action of permanent water. It is thus that Nature delights in Nature.”

So far the *Turba* ; now let us look at the old Greek manuscript version : “ Take mercury ; fix it with the metallic body of magnesia, or with the metallic body of Italian antimony, or with incombustible sulphur, or with selenite, or as you please. Put this white earth (*i.e.*, the mercurial paste thus made) on copper, and you will have copper without shade ; add yellow silver (electrum) and you will have gold ; with gold metallic chrysocorallos. The same effect is obtained with yellow arsenic and sandarach. Nature conquers Nature.”

On a comparison of the two passages we perceive that the Greek text is more intelligible. It is a clear and definite method for superficially whitening copper with mercury coloured by various substances, and for giving a golden hue to the metal which had first been whitened. It was, in short, an ordinary jeweller’s process. This and similar instances give

us a clue to the origin of the conception of the philosopher's stone. The ancients had methods of superficially tinting metals, and for alloying them with other metals, and thus producing imitations. In the hands of ignorant workers, and under the influence of mystic writers, this became a pretended process of transmutation. The same influence has changed the real meaning of the *Chrysopoeia* and *Argyropoeia* of Democritus and others, and the technical books. All had at first a technological meaning, but by successive translations from Greek, Arabic, and Hebrew into Latin the original text has been obscured and transformed. We shall, however, discuss this more fully in a subsequent chapter.

There also occurs in the *Turba* a declamatory passage: "O celestial natures multiplying true natures by divine will," which resembles a passage in Stephanus' Commentary on Pseudo-Democritus, thus still more clearly indicating the Greek origin of the work.

The *Turba* suppresses most of the *Chrysopoeia* to come to the *Argyropoeia* of the Pseudo-Democritus, and gives extracts without perceiving that these preserve the original definite meaning. Thus, in *Theatrum Chemicum*, Vol. V., p. 10, we find a statement of Lucas to the following effect:—"Take quicksilver which is male, and coagulate it in the usual manner. . . . place it upon iron, or tin, or treated copper, and the metal will be whitened. Similarly, magnesia will be whitened, and the male changed with it (her). Since the magnet has a certain affinity for iron, therefore Nature takes delight in Nature. Take then the cloud which our predecessors have prescribed, and cook it with its own body until it forms tin. According to usage, purify it from its black colour, wash and cook it on a regulated fire till it whitens. Quicksilver suitably treated whitens all bodies, for Nature transforms Nature."

Compare this with the ancient Greek text of the Pseudo-Democritus, from which it is plainly extracted: "Fix according to usage mercury drawn from arsenic" (arsenic is often called the male and some other substance the female, hence the

confusion in the *Turba*), "project it on copper, or on iron, treated with sulphur, and the metal will become white. The same effect is produced by whitened magnesia" (this is elsewhere shown to be mercury amalgamated) "by transformed arsenic, cadmium, etc., you will soften iron by adding to it magnesia, or sulphur, or the magnetic stone, for the magnetic stone has an affinity for iron. Nature delights in Nature. Take the vapour previously described. . . . This preparation whitens all sorts of metallic bodies. Nature conquers Nature."

Here again the Greek has a practical sense, which disappears in the Latin, after passing through three languages successively, yet the Latin has plainly descended from the Greek. The original Greek text, and still more the earlier technical manual in the Leyden papyrus, enables us to catch the meaning of these incoherent phrases, but it was the mutilated and false version which formed the groundwork of the studies and meditations of the mediæval alchemists. Can we wonder that their studies brought forth a rich crop of nonsense?

The *Turba* approximates more nearly to the Greek manuscripts than any other Latin treatise or translation of the Middle Ages, but bears evidence of its passage through an Arabic or Hebrew medium, or perhaps both, in the corruption of the names of the philosophers to whom it attributes the quotations, and in the Semitic words which it introduces. The original compilation may indeed have been made in Greek, but whoever the compiler was, he did not understand the root of the matter, that is to say, the practices, whether real or illusory, of the ancient experimenters.



## CHAPTER IX

### THE ALCHEMISTS OF THE TWELFTH AND THIRTEENTH CENTURIES

IN the two preceding chapters we have considered the principal sources of information which were available to the early mediæval alchemists. In doing so we have shown that the fountain from which this knowledge flowed was Hellenic culture based upon Egyptian wisdom. This was not, however, the opinion of the time. The mediæval alchemists recognised their indebtedness to Moors and Hebrews, but were quite ignorant of what they owed to the Greeks. In explanation of this fact it must be borne in mind that although the earliest Latin translations or imitations of Arabic and Hebrew treatises, such as the *Turba Philosophorum*, contain fragments of authentic Greek originals, yet these originals themselves were not translated into Latin until the sixteenth century and later. We have an example of such a translation in the *Pseudo-Democritus* of Pizimentius published in 1573.

Nevertheless, there were Latin writers in the twelfth, thirteenth and fourteenth centuries, whose writings contain aphorisms and doctrines borrowed from Greek alchemists; for example, the books attributed to—

Albertus Magnus, 1193—1282 (doubtful).

Vincent de Beauvais, 1190—1264 (authentic).

Thomas Aquinas, 1227—1274 (fictitious).

Roger Bacon, 1214—1284 (authentic).

Arnoldus Villanovanus, 1235—1312 (authentic).

Raymond Lully, 1235—1315 (fictitious).

In all these writings, whoever their authors may have been, the borrowed aphorisms and doctrines are not given as translations, or even as the doctrines of Democritus and others who figure in the *Turba*, but are vaguely attributed to "*Philosophi*," or



to Latin translations of the writings of Arabs, such as Morienus and Avicenna.

Thus we read in the *Thesaurus Thesaurum* of Arnoldus Villanovanus such phrases as these: "The magnesia of the philosophers from which they draw the gold concealed in its body"; "When the philosophers have named quick-silver and magnesia, saying it solidifies the mercury with the body of magnesia"; "Transmute the natures and you will find what you seek"; "Copper is like a man; it has a body and a soul." The last passage he quotes from the *Turba*.

In Roger Bacon's *Speculum Alchymiae* we read: "The precursors in this divine art say, 'Nature conquers Nature' and 'Nature delights in meeting an identical Nature.'" These are both sayings of Democritus (*supra*, p. 30), but Roger Bacon names no author. Vincent de Beauvais in like manner cites the Arabico-Latin writings of Avicenna, Rhazes, and the Pseudo-Aristotle, and has evidently no first-hand knowledge of the Greek alchemists, yet there is the same resemblance in doctrine. And so with Raymond Lully.

There is a treatise published in the *Theatrum Chemicum*, Vol. V., p. 855, entitled *Liber Philosophiae Occultioris*, and attributed to Alphonso X., King of Castille, "*Sapientissimus Arabum*." It is a remnant of the learning of the Moors, but develops in an indefinite manner the same theory of the dry and the humid, the warm and the cold, and so forth, that we find in Arnoldus Villanovanus, Vincent de Beauvais, and Raymond Lully. This is, in each instance, a corruption of the old Greek doctrine.

Keeping these facts in mind, we shall now briefly examine the work done by some of the principal Latin alchemists of the twelfth and thirteenth centuries who carried on the tradition of the Orientals. Of these it has to be remarked as a general characteristic that they called themselves "philosophers," taking all knowledge for their province, and although they dabbled more or less in the Black Art, their philosophic interest

had a much wider field, embracing the entirety of human knowledge, as it then existed.

We have few particulars respecting Artephius Longaevus, an adept of the twelfth century. He wrote *The Secret Book*, and *Clavis Sapientiae* about 1130, and of him John Pontanus said that he was the only writer from whom he had really learned anything of the philosophic work. He claimed to be a thousand years old, and for obvious reasons was not contradicted.

Another twelfth century writer Johannes Garlandus or Hortulanus, translated into Latin the *Tabula smaragdina* of Hermes Trismegistus (*supra*, p. 15). The date of translation and the language from which it was translated are uncertain. He explained the action of the philosopher's stone as "fermentative," and was one of the first alchemists to use the term "tartarus," which survives in cream of tartar and tartaric acid. The following is a translation of the thirteen sentences on the smaragdite table of Hermes Trismegistus, according to Garlandus :—

- " 1. I speak not fictitious things, but that which is certain and most true.
- " 2. What is below is like that which is above, and what is above is like that which is below, to accomplish the miracles of one thing.
- " 3. And as all things were produced by the one word (mediation) of one Being, so all things were produced from this one thing by adaptation.
- " 4. Its father is the sun, its mother the moon ; the wind carries it in its belly, its nurse is the earth.
- " 5. It is the father of all perfection throughout the world.
- " 6. The power is vigorous (perfect) if it be changed into earth.
- " 7. Separate the earth from the fire, the subtle from the gross, acting prudently and with judgment.
- " 8. Ascend with the greatest sagacity from the earth to heaven, and then again descend to the earth, and unite together the powers of things superior and things inferior. Thus you will obtain the glory of the whole world, and obscurity will fly far away from you.

- “ 9. This has more fortitude than fortitude itself; because it conquers every subtle thing and can penetrate every solid.
- “ 10. Thus was the world formed.
- “ 11. Hence proceed wonders, which are here established (produced in this way).
- “ 12. Therefore I am called Hermes Trismegistus, having three parts of the philosophy of the whole world.
- “ 13. That which I had to say concerning the operation of the sun is completed.”

The words within brackets are alternative renderings. What is meant by the second paragraph is the ancient doctrine that things terrestrial are copies of things celestial. This theory and the principle that “one is all” are apparently the fundamental truths which the tablet was meant to record.

One of the most celebrated of the mediæval philosophers was Albert Groot, otherwise Albertus Magnus, called the Universal Doctor. His real name was Albert von Bollstadt. Born of a noble family some say in 1193, others 1206, he was no precocious scholar, being at first dull and slow. He studied science at Padua, taught as a monk at Cologne and later at Paris, travelled in Germany as Provincial of the Dominican Friars, and was at one time Bishop of Ratisbon, but retired to a cloister at Cologne, where in 1282 he ended his days in study. He knew all that was known in his time. A theologian, physician, astronomer, alchemist, and man of the world, he did not think it derogatory to his learning to pay attention to magic and



FIG. 53.—Albertus Magnus.

necromancy. He digested the works of Aristotle and his commentators, and his knowledge of physical science was, for his age, extensive and accurate. His alchemical writings are mostly reprinted in the *Theatrum Chemicum*, and include :—

1. De Rebus Metallicis et Mineralibus.
2. De Alchymia.
3. Seculorum Tractatus.
4. De Ortu Metallorum.
5. Concordantia Philosophorum de Lapide.
6. Compositum de Compositis.
7. Liber Octo Capitem de Philosophorum Lapidi.

They have the merit of being at least intelligible.

Albertus Magnus describes the chemical operations of sublimation, distillation, and others in use at his date, and apparatus such as aludels, alembics, and water-baths. He furnishes an account of all the chemical substances then known, and the method of obtaining them. According to his theory metals are composed of philosophical sulphur and mercury, and instead of each metal being a distinct and elementary body, were produced by mixtures of their constituents in different proportions, and by variations in the purity of the component parts. The term "affinitas" was used by him as by us to designate the cause of the combination of sulphur with silver and other metals. Sulphate of iron he named "vitriol," and he described the preparation of nitric acid, its action on the various metals, and its use in separating silver from gold. Cinnabar had long been known, but he was the first to explain the process of preparing it by subliming mercury and sulphur in combination. He was a great scholar, and his shrine and relics are to this day shown in the Church of St. Andreas at Cologne.

Another distinguished philosopher of the period was Vincent de Beauvais (1190—1264), named in Latin Vincentius Bellocensis. Like most learned men of his day he was a monk, a French Dominican. He was appointed tutor to the sons of Louis IX., commonly called Saint Louis. For some time he

occupied the post of reader at the royal monastery of Royaumont, where he was patronised by the enlightened and saintly monarch, who is said to have provided him with funds for the purchase of manuscripts to aid in the preparation of his great work, the *Speculum Majus*. This is an encyclopaedia of the entire knowledge of his times, written in Latin, consisting of 80 books and 9,885 chapters, and containing references to more than 450 writers. Its chief value for us consists in the light it throws on the extent of the learning of his age, and in the quotations and references to older authors with which it is filled. It was a gigantic undertaking; probably nothing like it has ever been effected by a single man. Every branch of knowledge is treated, and it takes the form of an exhaustive commentary on the Creation as set forth in the first chapter of Genesis. The *Speculum* was printed in 1473, about two centuries after his death.

Thomas Aquinas or Thomas of Aquin (1227-74), like his teacher Albertus Magnus, was a nobleman, a scholar, and a member of the Dominican Order. He was a theologian rather than an alchemist, but wrote *Thesaurum Alchymiae Secretissimum*, *Secreta Alchymiae*, and *De Esse et Essentia Mineralium*, books which are quite unintelligible. He "converts" copper into silver by first whitening it with arsenic and then melting it with half its weight of silver—an operation which reminds us of the old Greek and Syriac manuscripts. He made artificial topaz by smelting aloes-wood (*agallochum*) in glass: he employed the term "amalgam"; and obtained a lead acetate (*Lac virginis*) by dissolving lead in acetic acid and mixing it with an alkali.

Our own Roger Bacon (1214-84) was the first English alchemist with whom we are acquainted. He was born in Somerset, studied at Oxford (where his house is still shown) and at Paris, and became a Cordelier Friar. He was learned in mathematics, optics and astronomy, and wrote eighteen books on alchemy. He devoted himself to research in private, but his discoveries were so important that they became known.



and he was accused of necromancy and cast into prison. He wrote a pamphlet in his own defence, showing the non-existence of magic. In this paper he pointed out the absurdity of magic charms, and demonstrated that things are deemed to be supernatural merely through ignorance of natural philosophy. He denied the theory of transmutation of metals, although he is alleged to have said that with a certain amount of the philosopher's stone he could transmute a million times as much base metal into gold. To save his life, however, he had to recant his opinions. Having picked up some information from the Arabs during his travels in the East, he described in an obscure way the composition of gunpowder, which was first used in war by the English in 1327, forty years after his death. That air is the food of fire he proved by placing a lighted lamp in a closed vessel, and showing that under these conditions the flame was extinguished.

The following is a list of his principal chemical writings:— (1) *Speculum Alchymiae*; (2) *Epistola de Secretis Operibus Artis et Naturae et de Nullitate Magiae*; (3) *De Mirabili Potestate Artis et Naturae*; (4) *Medulla Alchymiae*; (5) *De Arte Chemiae*; (6) *Breviorium Alchymiae*; (7) *Documenta Alchymiae*; (8) *De Alchymistarum Artibus*; (9) *De Secretis*; (10) *De Rebus Metallicis*; (11) *De Sculpturis Lapidum*; (12) *De Philosophorum Lapide*; (13) *Opus Majus* or *Alchymia Major*; (14) *Breviarium de Dono Dei*; (15) *Verbum Abbreviatum de Leone Viridi*; (16) *Secretum Secretorum*; (17) *Tractatus Trium Verborum*; and (18) *Speculum Secretorum*. A transcript of the last of these, dated 1290 to 1299, is one of the oldest manuscripts in the British Museum, where there are many extracts from his works, but no signature or specimen of his hand-writing.

What gives Bacon supreme importance in the history of his times is the fact that he was no mere schoolman with his mind cramped and fettered by logical quibbles and the rules of deductive philosophy, but a thinker of the modern type with a wonderfully just and clear conception of the principles



of science. In his experimental method we see the beginnings of the inductive philosophy associated with his greater namesake Francis Bacon, which is the only foundation upon which the natural sciences can be built. In his own day he was overshadowed by more popular names, but his reputation as a scientist is now receiving more adequate recognition.

The remarkable man who was known alternatively as Raymondus Lullius, Raymond Lully, or Raimon Lull (1235—1315), is the hero of many romantic stories, some of which seem to be authentic. He was the pupil and friend of Roger Bacon. He came of an illustrious Catalonian family, and was born in Majorca, where his father had profited through the expulsion of the Saracens by the King of Arragon. In 1281 he obtained the rudiments of *The Secret* from Arnoldus Villanovanus in Paris, and is said to have written many books on alchemy, but these are now believed to be apocryphal. At the time they were received as genuine and were quoted long after his death. They are mostly unintelligible. His *Testamentum*, *Codicillus seu Vade-mecum*, and *Experimenta* are of early, but uncertain date, probably about the close of the thirteenth century. To him is ascribed the saying, “*mare tingerem si mercurius esset*,” “I would colour the sea if it were mercury.” In his *Ultimum Testamentum* he alleged that he had converted fifty thousand pounds’ weight of base metal into gold. The story goes that he was employed by Edward I. of England to make gold for minting, and that he had a laboratory for this purpose at Westminster; but analysis of the coins of that king does not bear out the tale, for they are found to be pure gold, not gold of the philosophers.

Arnoldus Villanovanus or Arnold of Villanova (1235—1312) is one of the few Latin alchemists whose extant writings are genuine. He was probably born at Villeneuve in Provence, and studied at Paris, but spent some time in Spain, where he acquired the learning of the Moors. He had a great reputation as a physician. He wrote *Rosarium Philosophorum*, a compendium of the alchemy of his time, and treatises *De Vinis*

*De Venenis*, and *Antidotarium*. His books are rather less obscure than those of his contemporaries. He was condemned as a heretic, but the protection of the pope John XXII., who was his pupil, secured him against the consequences. Being an astrologer he ascribed many of his successes in chemical operations to the position of the planets and to prayers. He was one of the earliest of the many who have ventured to predict the end of the world, which event, he said, would occur in 1335. The external application of the compounds of mercury, and other uses of chemical preparations in medicine, were introduced by him. He obtained by distillation oil of turpentine, oil of rosemary, and spirit of rosemary (famous as "Hungary water"), and recognised the combustible properties of spirits of wine, and the poisonous character of decaying animal matter. Like others of his age he deemed a solution of gold the most perfect medicine, calling it *aurum potabile*, for gold and health are both perfect. This "drinkable gold" was a necessary constituent of the Elixir Vitæ. Sulphur, arsenic, mercury, and sal ammoniac were, he maintained, the souls of metals, because they were given off during calcination.

The period which we have been considering was, on the whole, an unsatisfactory one from a chemist's point of view. Instead of prosecuting researches into the qualities and combinations of the metals and other substances known to them, most of the philosophers of the twelfth and thirteenth centuries were drawn aside into the pursuit of vain and foolish phantoms. They were, however, the less to blame, since the alchemical works which they possessed, and which were the only source from which they could hope to learn the wisdom of their predecessors, were corrupt translations of old manuscripts, which the translators were unable either to translate or to understand. Doctrines, principles, and recipes were alike mixed up and garbled, and such portions as the translators failed to comprehend were supplied by pages of mystic nonsense. Philosophy was still deductive, not inductive. Men sought to lead thought outwards from some general principle

to its particular effects, rather than to lead it inwards from ascertained particular facts to the general principle to which these ought to be attributed. The most hopeful sign of the times was the impulse given to original research by Roger Bacon and a few others. The dawn was at hand, and the mysteries and confusion of the schoolmen were but the mists that preceded the rising of the bright light of science and the gradual disclosure of the secrets of Nature.

## CHAPTER X

### THE ALCHEMISTS OF THE FOURTEENTH CENTURY

THE fourteenth century was a period of transition. The Dark Ages were drawing to a close, and the light of the Renaissance had not yet arisen. It is therefore a convenient point at which to note the general condition of mankind, and to examine the state of alchemical science in its later phases.

William with his Normans had conquered England; the arrogant feudal nobility and the gentler Saxons, whom they had enslaved, had begun to amalgamate; a growing intercourse with the East had been initiated by the peace which Richard Cœur de Lion had made with his noble Mohammedan antagonist Saladin. The Magna Charta of our liberties had been granted by King John, and the foundations of the British Constitution were being laid. The Wars of the Roses, with all their disturbing influences, were still in the future; the Plantagenets were on the throne of England; the Scots were successfully asserting their determination to remain a free people; but Ireland was a chaos.

In the Far East Jenghiz Khan had just made a great Mongolian empire extending from China to Russia and India, with its centre in the Asiatic highlands of Afghanistan. In Europe, Frederick Barbarossa had not long ago compelled the Pope to crown him Emperor in Rome. The Hapsburg family of Austria was rising into power; and the Swiss Confederation was about to spring into existence. The first German Empire was now the principal power on the Continent, where Frederick II. and his son Conrad IV. were struggling successfully with the Popes, while Gregory IX. and Innocent IV. retaliated with the old papal weapon of excommunication. In

France the Capets had already founded their kingdom, and reduced the great vassals to subjection to the throne.

The Order of the Knights Templars, the Knights of St. John, and the German Order had been constituted ; and the Crusades had brought the West into contact with the East. Trade and trading societies were beginning to flourish, and the Hans towns were on the verge of constitution. Everywhere was a growing interest in art and industry ; the soil was already broken that was to receive the wisdom of the East.

The Mohammedan power had been carried westward with irresistible force. The Moors had crossed into Spain, bringing with them Chaldean and other traditional knowledge from the extreme east, the learning of Egypt, translations from the Greek writers of the Alexandrian School, and the books of the great authors of Syria and Arabia. Greek culture had long ago crossed from Egypt to Byzantium, but the eastern empire was tottering, and the western dominion of Rome was making Latin the universal language of scholars. Printing had not yet been invented, and books were circulated in manuscript, either on papyrus or parchment.

Alchemy had reached an unsatisfactory stage in its development. Misled by corrupt translations of ancient writings, and confused by the mysticism and symbolism of Arabic authors, alchemists devoted themselves to operations for transmutation of the baser metals into gold. The lust for gold soon brought its usual accompaniments—charlatanism, trickery, and fraud. The art of alchemy and its practitioners acquired a doubtful reputation, and the latter became objects of suspicion as either rogues or fools. At such a period it is not to be expected that many famous names should be associated with the art, but the roll of alchemists still contained a few distinguished men.

Undoubtedly the most conspicuous figure of the time was the mysterious Nicolas Flamellus (1330—1418), the French alchemist who was born at Pontoise, five miles from Paris, and became scrivener to the university of that city. During his



earlier years Flamel accumulated a very considerable fortune, some said by the practice of his art, others, probably with more reason, by fortunate speculation. Flamel won his alchemical reputation by giving out that he had bought for a couple of florins an old book on the subject by Abraham the Jew, written on the bark of trees, which actually taught the transmutation of metals. Unfortunately, however, this work, though it depicted and figured the *materia prima*, made no attempt to



FIG. 54.—Nicolas Flamellus.

explain it, an omission which cost Flamel twenty years of fruitless labour. He was indeed on the verge of despair when, as he returned from a chance journey in Spain, he fell in with a Christian Jew, by name Canches, who explained the whole process to him. Flamel devoted himself to his researches for another three years, and at the end of that time asserted that he had actually been enabled to transform mercury into gold. It is scarcely necessary to say that this interesting story was utterly exploded within a

century of its perpetration; but its disappearance has bereft us of information of any kind as to its distinguished hero. Beyond a couple of volumes of highly doubtful authenticity in the Paris Bibliothèque, our knowledge of Nicolas Flamel is practically *nil*.

An alchemist of whom little is known apart from his writings was Joannes de Rupescissa. He was of a noble family, and was imprisoned in 1357 by Pope Innocent VI. He wrote *Liber de Consideratione Quintessentia Rerum Omnium* and the *Secret Chemistry*, and claimed the gift of prophecy. His works are



rather obscure, but we owe to him the following definite instructions for the preparation of a compound, which, if it were not the true philosopher's stone, behaved like it. Quick-silver is distilled with saltpetre and Roman vinegar. The residue is thrown into *aqua fortis* to which sal ammoniac has been added. A white product results, which is sublimed and again treated with *aqua fortis* and sal ammoniac, and the whole operation is repeated. Sulphur *vivum et invisibile* is added, and the mixture distilled. From the distillate is obtained a black precipitate, with a "putrid animal spirit." This precipitate changes iron, lead, copper, and tin into silver; but, more remarkable still, being roasted becomes first white and then red, and being treated with mercury changes that metal into gold. This was drawing very near to the philosophorum lapis, if it were true.

Of Adolph Mentha, who appeared about 1318, we know nothing. Isaacus Hollandus, an alchemist of Stolk, and said to be the first Dutch alchemist, wrote in the latter half of the century *Tractatus de Lapide Philosophico, Opera Mineralia, Opera Vegetabilia et Quintessentia*, and *De Spiritu Urinae*; while a younger of the same name, Joannes Isaacus Hollandus, at the close of the century, was the author of *Opera Mineralia* and *Opus Saturni*.

A vague and uncertain personality usually assigned to this period was Abraham Eleazar. He is best known by a work called "*Donum Dei Samuelis Baruch*," which contains fifteen symbolic designs drawn upon eight plates. This is the book from which Nicolas Flamel professed to have gained his alchemical knowledge, and it is said that Abraham derived his information from copper tables engraved by Tubal Cain. Whatever be the source of the work, it is a remarkable example of hermetic symbolism. Modern criticism inclines to the view that it was written at a later date and based upon the description of Flamel. Dr. Kopp (*Die Alchemie*, Vol. II., pp. 314-17), after a careful study of the treatise, pronounces it spurious.

Antonius d'Abbatier, a monk of Pavia, who probably lived about the middle of the fourteenth century, wrote a series of alchemical epistles, and is said to have been a successful adept. A quotation from Augurello, who flourished at the beginning of the sixteenth century, casts doubt on the antiquity of his writings, but it is possible that the quotation is an interpolation by a later editor. Certainly Baumer is wrong when he assigns d'Abbatier to the end of the sixteenth century, for he calls him Tholusanus Archipresbyter, and evidently confuses him with the physician d'Abbatier of Toulouse.

Little is known about Guido de Montanor or Guido Magnus de Monte, except that he probably belonged to the fourteenth century. George Ripley calls him the "sapient Guido," and says "his fame goeth wide," but we do not know exactly when or where he lived. He wrote "*Scala Philosophorum*," "*Decreta Chymica*," and "*De Arte Chymica Libellus*," works which were translated into German in 1623, under the title of "The Long-hidden Treasure of Chemistry."

There are a few alchemists who wrote in the fifteenth century, who may be considered in this chapter because they are strongly imbued with the spirit of the fourteenth. The first of these is a person or persons (for two men seem to have been confused under one name) called Trevisan, or Bernard of Trèves or of Trevisa (1406-90). It has as yet been found impossible to disentangle the confusion created by the early writers, and it is customary to group the writings together under the name of Bernhardus, and to distinguish them as "de Trèves" or "de Trevisa," without saying whether these designations belong by right to one man or two. Bernhardus wrote on hermetic philosophy, and seems to have been an enthusiastic chemist. For many years he travelled in search of wisdom, and spent his fortune in the attempt. Returning disheartened to Rhodes, he devoted himself to a comparison of the different authors, and according to his own account penetrated the great secret, and succeeded in making the philosopher's stone in 1481. He did not add anything of

moment to chemical knowledge, but from a study of his writings we may gather a fair idea of the state of alchemical learning in his day.

Two of the few Englishmen who have distinguished themselves in alchemy have now to be mentioned. The first of these, George Ripley (1415-90), was one of the most remarkable alchemists of his day, and references to his writings are very numerous. He was born either in Yorkshire or Surrey, and became a canon-regular of St. Augustine's, Bridlington. He devoted himself to the study of physical science and especially of alchemy, wandering over France, Germany, and Italy in pursuit of knowledge. While at Rome in 1477 he was made chamberlain by Pope Innocent VIII. Next year he returned to England, asserting that he was in possession of the secret of transmutation. While continuing his alchemical work he is reported to have given vast sums to the Knights of St. John of Jerusalem for their warfare at Rhodes. He was a poet as well as a scholar and wrote a poem on alchemy. His theories of the composition of the metals in his "Compend of Alchemy" resemble those of an early date, and in *The Bosom Book* he sets forth his "philosophical accurtations in making the Philosopher's Mercury and Elixirs." According to him all chemical operations may be divided into twelve processes, which he likened to the gates of a castle—calcination, dissolution, separation, conjunction, putrefaction, congelation, cibation, sublimation, fermentation, exaltation, multiplication, and projection. He made no discoveries.

The other Englishman was Thomas Norton, who wrote in 1477 a treatise called *Ordinale seu crede mihi*, a work of little scientific value. It is also called *The Ordinall of Alchemie*, and is in poetry. No name is attached to it, but the authorship is disclosed in a sort of cryptogram. The initial syllables of the proem or introduction and first six chapters, and the first line of the seventh read thus :—

"Tomais Norton of Briseto,  
A parfet Master ye maie him call trowe."

He was an authority on ovens, and believed with some others that the metals grew underground, each in its own proper environment. He expressed the belief that metals remain unchanged by solution, one of the few approaches of the alchemists to the modern doctrine of the indestructibility of matter. Alchemy, he said, had to be learned from the mouth of an adept, and seemingly he himself was taught in this manner; but in whatever way he gained the knowledge (and probably he was a disciple of Ripley), it did him no good. His experiments merely served to ruin himself and such of his friends as were weak enough to trust him with money. This was a common experience of those days, when men became so engrossed in the search for hidden wealth, that they deceived not only others but themselves.

All these men wrote about the nature and art of making the philosopher's stone, and there are indications of a belief that the powder which could transmute the baser metals into gold could also prolong life. This is an earlier form of the conception of later alchemists that there is a universal medicine which will cure human diseases as well as the diseases or impurities of the metals.

The fourteenth century alchemists discoursed on the nature and composition of the metals, and on things in general. They were not so positive as their successors, some of whom asserted that they had seen the philosopher's stone, yet their language was less obscure. But it is not by reading the works of later authors that we arrive at an understanding of what the mediæval alchemists really knew or imagined. The *Artis Auriferae*, *Theatrum Chemicum*, and *Bibliotheca Chemica*, of which we have already spoken, contain collections of the treatises which existed in the fourteenth century, and from them we are better able to judge of the sources of information which were available to students of that date.

To a great extent these works are symbolical and allegorical. The art consisted in understanding the books, not in carrying out the processes. In this we see a great departure from the

practice of the early writers. The MS. of St. Mark and other old papyri demonstrate that the main occupation of the alchemist was the manipulation of metals, colours, and dye-stuffs, the making and colouring of glass, and the manufacture of artificial precious stones and pearls. All these operations were performed by the same people, associated in the same laboratories or workshops, originally those of the Egyptian temples. But the philosophical treatises derived through the Arabic are seldom practical, and one would almost fancy that their authors did not intend that the processes should be carried out. As a rule neither symbols, emblems, nor figurative language are explained. Such treatises, on the other hand, as contain workmen's directions, and works on metals or mining, are clear and precise. In short, the condition of alchemy at this date affords an excellent illustration of the futility of all attempts to build up a science by philosophical and abstract speculation apart from practical work in the laboratory.



## CHAPTER XI

### THE PROTEST OF PARACELSUS

THE art of alchemy was now to receive an impulse in a new direction. In the hands of the fourteenth century alchemists and their immediate successors, its main object had become the



FIG. 55.—Paracelsus.

discovery of that mysterious powder or elixir, which was to bring about universal perfection, to raise the baser metals to the perfect gold, and to endow human beings with eternal youth. At this stage a great, though erratic, genius appeared on the scene, and opened up a fresh channel, into which students of chemical science might thenceforth direct their energies.

Paracelsus (1493—1541), who gave his name as Philippus Aureolus Theo-

phrastus Paracelsus Bombastes ab Hohenheim, created in his day more stir than any other alchemist, for he shook the faith of the world in Galen and Avicenna, and was thus the means of introducing a new era. In that he possessed no real merit, for although there is no reason to doubt that he was gifted with original genius, there is good reason to believe that he was on the whole a vain and self-seeking quack, who neither understood the nature of chemical science, nor undertook any regular or successful investigation. But he con-



demned loudly and boldly all medical knowledge and all medical practitioners, except himself, and his own methods. By these means, and by some cures which he effected, partly by bold treatment, partly by good luck, he made such a reputation for himself that he freed the medical world from old trammels. He roused the mental energy of medical men by calling their attention to the importance of chemical medicines and chemical investigations, and in consequence, workers arose who studied the preparations and reactions of those metals which were most likely to be useful in medicine, and by their efforts the store of chemical knowledge was rapidly increased.

Paracelsus was born in 1493 at Einsiedeln or Hohenheim, a pretty educational village not far from Zürich. His father, Wilhelm von Hohenheim, was a physician and taught him alchemy, astrology, and medicine. After a short period spent at the University of Basle, he became a wandering scholar, practising medicine and



FIG. 56.—Wilhelm von Hohenheim.

picking up knowledge over the greater part of Europe, Egypt, and Tartary. He had little university training, but worked long and earnestly with the wealthy Sigismund Fuggerus of Schwartz, trying to make the philosopher's stone. Loud advertisement of the successful cures he had wrought by the use of mercury and opium raised him to such a pitch of fame that the magistrates of Basle in 1526 appointed him to the Chair of Medicine in that University.

At his first lecture he ostentatiously burned the works of Galen and Avicenna, the great medical authorities of the age. In this spirit he lectured for two years, but his vanity and

bombast disgusted and drove away his students, and his greed made him quarrel with the magistrates over his fees. In the end he suddenly quitted the town, and resumed his wandering life through Alsace and Germany.

During the latter part of his career he effected many cures, the reputation of which concealed his many failures, but his private life was disfigured by intemperance, which he indulged in the lowest company. Finally, he announced that he had discovered the Elixir Vitæ, and could extend human life for an indefinite term. Apparently, however, he was unable to conform to the maxim "Physician, heal thyself," for he was seized with a fever and died at Salzburg in 1541, at the early age of 48. His property was bequeathed to the poor.

Paracelsus did little by actual discovery to advance either science or medicine. His great work was effecting a breach with tradition, and setting physicians and alchemists free from the bondage in which they were held by convention. He borrowed his medical treatment from others—barber-surgeons, old women and quacks—and his fearless nature made him employ the powerful and dangerous medicines prepared from mercury, opium, and antimony more boldly than any before him had ventured to do. His alchemical doctrine, that everything consisted of three elements—mercury, sulphur, and salt—is adapted from old authors, but he was the first to use the word "alcahest" to indicate the universal menstruum or solvent, which at that time was a special object of research. He describes this liquor, alcahest, as having great power over the liver, comforting and confirming it, and preserving it from dropsy and other diseases that take their origin within it. He thus addresses his readers: "Wherefore it is your work who cultivate medicine, to prepare alcahest for curing many diseases arising from the liver." Unhappily, he does not give precise directions for the preparation of this invaluable remedy.

The great debt which chemistry owes Paracelsus is the influence he exerted in discarding the ideas of the ancients, and even of the more modern alchemists, and in teaching that the

object of chemistry was not to make gold but to ameliorate disease. The art of making drugs was one of the original branches of alchemy, but for many centuries this had been obscured by endeavours to effect the transmutation of metals. Paracelsus reinstated it in its prominent position. He used preparations not only of antimony, but of mercury, lead, iron, blue vitriol, and (for external use) arsenic. He said that the most energetic poisons might become precious medicines, and endeavoured to concentrate in essences, extracts, and mixtures the active principles of various drugs.

His philosophical views were peculiar. He arranged the several parts of man, his own universal elements, and the Aristotelian elements in triplets, thus :—

Soul	Spirit	Body.
Mercury	Sulphur	Salt.
Water	Air	Earth.

Having adopted the Cabala and its doctrines, he was grossly pantheistic. He thought that there was a connection between the sun and the heart, the moon and the brain (an idea still preserved in the word "lunatic"), Jupiter and the liver, Saturn and the spleen, Mercury and the lungs, Mars and the bile, and Venus and the kidneys.

As a rule his writings are full of mysticism, although there are a few grains of wheat among the chaff. Putrefaction, he declared, cannot give birth to a new body; the seed must pre-exist, and is developed during putrefaction by the power of the stars. The generation of animals is produced by the concurrence of an infinite number of seeds which detach themselves from all parts of the body, the seed of nose reproducing nose, of eye reproducing eye, and so on. He repudiates the view of Galen that fire is dry and hot, air moist and hot, earth dry and cold, and water moist and cold. He says that each of these elements is capable of admitting all qualities, so that there is a dry water and a cold fire. There is in the stomach a demon named Archaus, who presides over the chemical operations which take place in that organ, changing bread into blood, and separating

the poisonous from the nutritive. Tartar is the leading principle of the maladies which arise from the thickening of the humours. Stone in the abdominal organs is only part of it, and as tartar is deposited in wine casks, so tartar is deposited on the teeth. When tartar is increased by certain kinds of food, renal calculi are engendered. In this connection he thought it necessary to subject urine to chemical analysis.

All remedies, according to Paracelsus, are subject to the will of the stars and are directed by them, but chemistry is indispensable in the preparation of medicines. After his time the old disgusting decoctions gave place to tinctures, essences, and extracts. He even recommended quintessences, and described how they were to be made.

In chemical research he ascertained that alum contains an earth united to an acid. He mentions metallic arsenic, zinc and bismuth, but did not regard them as true metals, to which he considered malleability and ductility as essential characters. But his reputation as a chemist depends not so much upon discoveries made, as on the importance which he attached to a knowledge of the science. In consequence of his teaching chemistry became an indispensable part of the education of a medical man, and it was perceived that the true object of the science was not the discovery of the philosopher's stone, but the preparation of new medicines. He thus introduced the next period in the history of chemistry, when many medicinal and other substances were discovered in the laboratories of the chemical physicians, or *Iatrochemists*, as they were called.

As might be expected the protest of Paracelsus against ancient tradition led to a vast amount of discussion among contemporary alchemists. One of these named Gerhardt Dorn (circa 1550—1600), a pupil of Paracelsus, in his *Clavis Totius Philosophiae Chymisticae* (1567), *Artificii Chymistici* (circa 1568), and *In Aurorum Paracelsi* (1583) attempted to explain and comment upon his master. As might be expected, he only rendered obscurity more obscure.

But a strong opponent of the new doctrines arose in the person of Thomas Erastus (1523–83), a Swiss, who had a great reputation as a physician, and was professor of medicine at Heidelberg and at Basle. Unfortunately, instead of drawing his arguments from the results of experiments, he adopted the reasoning of scholastic philosophy and thus weakened the force of his attack, but he pointed out many contradictions in the writings of Paracelsus and his followers, denied the existence of the philosopher's stone, and combated the idea that mercury, sulphur, and salt are the elements of living bodies. He charged Paracelsus with bad faith. Erastus also wrote an apology for hermetic science, and treatises on the philosopher's stone and the triple preparation of gold.

The opposite side in this discussion was taken by Leonhardt Thurneisser or Thurneysser zum Thurn (1530–96), a native of Basle and a friend and pupil of Paracelsus. He had not the penetration of his master, and lived most of his life by his wits. His chief experimental work was a very incomplete investigation of the residues got by evaporating mineral waters. He wrote many books, of which may be named *Quinta Essentia* (1574) and *Magna Alchymia* (1583). The former is in verse. His father was a goldsmith, who, having need of money, sold a quantity of gilded lead as gold. This was the son's introduction to alchemy, as his father understood the art. After a visit to Germany, France, England, and the Scottish lead mines, Thurneysser started mining and sulphur-extracting in 1558 at Tarenz on the Inn. At a later date he studied under Paracelsus, and so far associated himself with the Paracelsian system that he acquired a great reputation for a time, which was heightened by his curing the wife of the Elector of Brandenburg. He was thereupon made court physician, and amassed a considerable fortune by medical practice with tincture of gold and similar medicines, but was exposed by Gaspard Hoffmann, lost his repute, and fled to Italy. His last years were devoted to transmutation of metals, and he died at Cologne.



Thurneysser's reputation is clouded by a criminal charge connected with the murder of Sebastian Siebenfreund for the sake of the transmuting powder which he was supposed to possess. It is now generally agreed that whatever delinquencies ought to be laid to his charge, he is guiltless in this matter. He was accused more appropriately of having a devil in a bottle which taught him to write in languages of which he was ignorant, a very convenient familiar, especially if we are to believe Bollenhagen, who asserted that Thurneysser's knowledge of languages was lamentably deficient. He then got into litigation with his wife, and lost the greater part of his fortune. But he was vain and affected to the last, for he specially requested that he should be buried beside the celebrated Albertus Magnus. His character is well summed up by Ferguson: "He was endowed with quickness and a powerful memory, but he tried to pass as a man of science, a learned physician, and an accurate scholar, when in reality he was a man of action with a gift for organising and commercial advertising. At the present day he might have been a successful manufacturing chemist, able to turn his raw material into gold without the red elixir."

We shall now direct our attention to some sixteenth century alchemists, who continued to work upon the old lines, without paying much heed to Paracelsus or his doctrines. Of these the first is one of the few princes whom alchemy has included among its disciples. This was Joannes Franciscus Pico, Conte della Mirandola (1469—1533), a nephew of the great Pius Mirandolanus. He led a stormy life of conflict with his relatives, his castle being taken and re-taken, but in the final assault his son and he were slain, and his wife and grandchildren made prisoners. His one alchemical work was *Opus Sane Novum ac Aureum de Auro* (1515), in which he adduced many remarkable cases of transmutation of metals, which he said he had witnessed with his own eyes.

Another alchemist who came to a violent end was Denis Zacaire or Zeccaire, otherwise Denys Zachary (*circa* 1510—50),



who was born in Guienne, educated in Toulouse, and studied alchemy in Paris. In 1550 he declared that he had succeeded in transmuting mercury into gold, and set out on a journey to demonstrate to other adepts the fact of his success. At Cologne he was murdered by his servant, who decamped with his wife and, what he would perhaps have more deeply regretted had he survived, his whole stock of powder of transmutation. His treatise, *Opusculum Tres Excellent de la Vraye Philosophie Naturelle*, was published at Lyons in 1612.

Pantheus was an instance of a churchman devoting himself to alchemy. His full name was Giovanni Agostino Pantheo (circa 1510-60), and he was a priest at Venice. He invented a curious word, "Voarchadumia," compounded, as he said, of the Chaldean word for "gold," and a Hebrew phrase meaning "out of two rubies." It meant "gold of two perfect cementations," that is, gold thoroughly refined. This word he used in the title of his books—*Ars et Theoria Transmutationis Metallicae cum Voarchadumia* (1550) and *Voarchadumia contra Alchimiā* (1530). He opposed the spurious alchemy current in his day, and treated of the purification and assaying of gold, the manufacture of white lead, and the preparation of an alloy used for making mirrors.

Three men who lived in the first half of the sixteenth century may be grouped together. Janus Lacinius, a Calabrian, was the author of *Pretiosa Margarita Novella de Thesaurō ac Pretiosissimo Philosophorum Lapide*, printed by Aldus in 1546. Giovanni Braceseo, a physician from Orici Nuovi in the Brescian district, composed a treatise on the Geberian philosophy and speculated in a tract called "*Lignum Vitae*," on the substance by means of which the patriarchs prolonged their lives. Jodolus Grewer was a priest and wrote *Secretum Nobilissimum et Verissimum*, but nothing else is known about him.

Bernardus Georgius Penotus (1520-1618) was born at Port-Sainte Marie in Guienne, studied at Basle, and first admired Paracelsus and then abused him as a plagiarist.

He wrote several books dealing with medicine and chemistry, of no great importance, squandered his means in the search for the philosopher's stone, and died in the poor-house at Yverdun, blind and in poverty. His most valuable contribution to philosophy was the bitter remark that if he had an enemy whom he dared not attack by force, but yet to whom he wished to do the greatest possible injury, he would urge him by every means in his power to study alchemy.

Before closing this chapter we must allude to a mysterious body, the Rosicrucian Order, which seems to have owed its origin to a determination to uphold the ancient alchemy in opposition to Paracelsus and all innovators. The cult is involved in mystery and doubt, and has for centuries exercised an attraction, and retained a prestige, of which it was hardly worthy. The extreme caution which was observed by its members in preserving their secrets, if they had any, and the unintelligible symbolism in which they contrived in their published writings to wrap up their meaning, have combined to render the study of Rosicrucianism extremely difficult and confusing.

The Rosicrucians seem to have existed for about one hundred years, practically coeval with the seventeenth century. They devoted themselves to the study of science, astrology, necromancy, and, it is said, some of the most debasing forms of Oriental superstition. Their energy was due to the impulse imparted to human thought by the three great events of the Middle Ages : the discovery of America, the invention of printing, and the reformation of religion. To them the Cabala was the touchstone of wisdom. They mixed the spiritual with the material, aiming at the perfection of the human body and soul, as well as at the transmutation of the baser metals into gold. Incidentally, they discovered scientific facts, but directly they sought to impress the truths that men ought to subordinate their appetites and desires to nobler aspirations, and that by the subjugation of our lower nature we actually prolong our lives.

NOTE BY THE EDITOR.—Since the death of Dr. Campbell Brown, there has been published a "Life of Paracelsus," by the late Miss Anna M. Stoddart (London, 1911). Miss Stoddart made a careful examination of original papers, and visited the spots associated with the leading events of the life of Paracelsus. As the upshot of her investigation she has come to the conclusion that he has been very much maligned, for which view she gives her reasons at considerable length. It seems to the Editor that she has proved too much. If Paracelsus was the unqualified saint that she represents him to have been, it is quite impossible to account for the undoubted facts of his life. Men become very unreasonable when their passions are aroused, but the fear of death is too great and too universal to permit them to drive from their cities without any cause a man who is able to work miracles of healing.

The fact seems to be that Paracelsus was neither a saint nor a reprobate. He has been both slandered and flattered. He lived at a period when even worthy men had no regard for truth when they were dealing with the characters of their opponents, and unfortunately he had opponents on both sides. His qualities, both bad and good, have no doubt been exaggerated, and this is the view which Dr. Campbell Brown has taken in the preceding chapter. Paracelsus was a genius, wayward and eccentric, but thoroughly in earnest, and there can be no dispute as to the great obligation under which he has laid both medicine and chemistry, by freeing them from the trammels of convention and superstition.

There is a circumstance mentioned by Miss Stoddart which is impressive. She says that the peasants to this day pray for health at the tomb of Paracelsus. We may, if we please, regard this either as ignorant superstition, or as the lingering tradition of a beneficent life. We like to think that the latter is the true explanation, and that there still subsists the memory of many years of faithful and self-denying services to the poor and needy.

## CHAPTER XII

### THE LATER MEDIEVAL ALCHEMISTS

(From 1550 to 1650 A.D.)

ALTHOUGH, as we mentioned in the last chapter, the art of alchemy received through the genius of Paracelsus an impulse in a new direction, there were still many learned men who followed the old paths. They were more or less aware of the new field which had been opened up, but they preferred to continue the search for the philosopher's stone. As some important chemical discoveries were made by them, we shall devote this chapter to a consideration of the most remarkable members of this group of philosophers, who may be called "the Last of the Alchemists."

Giovanni Aurelius Augurello (1441—1524) was born at Rimini and educated at Venice and Trèves. His reputation is mainly literary, as he was one of the greatest classical scholars of his day. Having written a poem called *Vellus Aureum et Chrysopoeia* he sent it in 1515 to the Pope Leo X. with an appropriate dedication, anticipating a handsome recompense. The Holy Father bestowed upon him a large empty purse, saying that he who knows how to make gold for himself has only need of a purse in which to put it. This poet laureate of alchemy died in poverty at Trèves at the age of eighty-three.

He is followed by a notable man, Heinrich Cornelius Agrippa von Nettesheim (1486—1535), who was born at Cologne, and carried to excess the extravagant notions of the age, giving himself out as a theologian, a jurist, a physician, and a philosopher. Not lacking ability, he became secretary to the Emperor Maximilian I., and was afterwards a captain in the army. Still later he was a professor at Pavia, held office at

Metz, was physician to Madame d'Angoulême, and councillor and historiographer to the Emperor Charles V. He spoke eight languages, and the aid of his talents was sought by the Pope, the King of England, several European Sovereigns, and various scholars. But though a man of great ability and powerful influence he was unsuccessful, and died poor at Grenoble.

In 1510 Agrippa wrote *De Occulta Philosophia*, and towards the end of his life *De Incertitudine et Vanitate Scientiarum*. Being a theosophist and a follower of the Cabala, he devoted himself to magic rather than to alchemy. He says that he found that to make gold, gold was needed, and that he had never been able with the extracted spirit of gold to make more of the precious metal than that from which the spirit had been extracted. So he died poor, and declared that alchemy was vanity.

An extract from his *De Occulta Philosophia*, regarding the use of vitriol in the preparation of the philosopher's stone, will furnish a fair sample of his style: "Roman vitriol is gently calcined and distilled. The distillate is the mercury of the philosophers. The residue is boiled out with water, filtered, and evaporated down. There remains a white earth. This is mixed with the mercury of the philosophers and the mixture digested eight days. (This is the process of *conjunctio*.) Then it is distilled to dryness, mercury again poured upon the residue, and the operation repeated until a little of the residue projected upon red-hot tinned iron entirely evaporates. During this series of digestions and distillations the mass becomes gray and black (*putrefactio*), but finally white again (*albifactio*). Now strong fire is applied; the whole mass sublimes (the white swan flies up) and becomes *terra foliata*. The *terra foliata* is again mixed with the mercury of the philosophers and heated. It melts like wax. One part of this waxy tincture added to ten parts of molten gold changes this into the philosopher's stone. If this does not succeed, the fault is the operator's."



The reader will follow this extract more intelligently if he compares it with the account which we furnish in Chapter XVI. of the process adopted in making the philosopher's stone.

We have now to consider the history of a man whose real character was a problem to his contemporaries, and is still uncertain, but who was a good example of one class of the alchemists. Edward Kelly (1555-97) was born at Worcester in the reign of Queen Mary. He received part of his education in that city, and may have spent a term at Oxford, although his name has not been traced at any of the colleges. Adopting the law as a profession, he settled in London and afterwards at Lancaster, but carrying his zeal for a client's interest so far as to forge a title to a property, he had to flee from justice. Some say he lost his ears over this affair, but in view of his subsequent career this is highly improbable. He certainly had some cause to stand in dread of the English legal authorities, since he kept carefully out of observation during the rest of his stay in England.

He told a romantic story about his discovery of a manuscript called *The Book of St. Dunstan*, and two caskets containing the red and white tinctures of transmutation, in the possession of the keeper of a lonely hostelry near Glastonbury Abbey. He seems to have been an accomplished liar, and it is more than doubtful whether his account of this matter had any foundation in truth. True or false, it imposed upon the scholar and mystic Dr. Dee, with whom he was associated during the remainder of his life. The doctor and he are said to have accomplished the transmutation of metals, and as there is no reason to doubt the good faith of Dr. Dee, we must suppose that the result of the experiments with the Glastonbury tinctures was in some way satisfactory. The upshot of the matter, however, was the issue of an attachment against Kelly on a charge of uttering base coins, a likely enough sequel to experiments in alchemy.

England having become no longer a safe place of residence, Dr. Dee and Kelly departed in 1583 for Cracovia, in company



with a Polish nobleman, Albert Alasko, in whose castle for a time they took up their abode. Thence they went to Prague, where Kelly created an immense sensation with "the Bishop's powder," as he called it, and posed as an adept in the alchemical art.

An invitation to the court of Rudolph II., King of Hungary and Bohemia, was the reward of their labours at Prague, and Kelly so impressed his royal patron that he was made a baron and marshal of Bohemia. But either the wonderful tinctures, or Kelly's powers of dissimulation, became exhausted. Neither entreaties nor threats could induce him to affect transmutation, and the disappointed monarch cast him into prison. He gained temporary liberation by undertaking to do what his patron wished, if he were sent back to Prague. Again failing, he was re-committed to prison, and detained there in spite of the efforts of Queen Elizabeth to reclaim him as an English subject. Attempting to escape, a rope broke, and in his fall he sustained such injuries as put an end to a remarkable but unworthy career.

As an alchemist Kelly is interesting from the fact that it is believed that he was in possession of certain tinctures, which approximated to the *Magnum Opus*; historically, interest is confined to his writings, which contain a careful compilation of the alchemical knowledge of his age. The following extract from one of his letters gives a fair example of his emblematic manner of writing:—

"As you are willing to take my advice, I will partially reveal to you the Arcanum, so that the field may not disappoint the hopes of the husbandmen. Open your ears. Our gold and silver, Sun and Moon, active and passive principles, are not those which you can hold in your hand, but a certain silver and golden hermaphroditic water; if you extract it from any perfect or imperfect metallic body, you have the Water of life, the Asafoetida, and Green Lion, in which are all colours, ending in two—white and red. The earth does not so much matter, only let it be fixed, for the Elixir must above all be fixed. If you are in earnest all

your thoughts must be concentrated on the fixed earth and the indestructible metallic water ; nor need you seek these in gold and silver, or in any determinate compound. It is true, however, that after the separation of this tincture from the gold, the indestructible water is fixed in its white earth ; but it is foolish to do by much what you can do by little."

The study of spirits of wine is the main source of the reputation of Philip Ulstadt of Nuremburg, another fifteenth and sixteenth century writer. He made observations on the specific gravity of this substance, and wrote in a style of classical elegance a complete treatise on distillation, entitled *Coelum Philosophorum*, which was published in 1528. The application of chemistry to medicine was the great object of his efforts, and he vaunted the properties of *aurum potabile* and of *eau de vie*. He made a vinous preparation which is the same as the cordial known as hippocras : "Take 4 lbs. white wine, 4 oz. hard white sugar, 1 oz. cannilla, 3 grains coriander, 2 grains cloves,  $\frac{1}{2}$  grain zedouir, 2 scruples pepper,  $1\frac{1}{2}$  grains ginger and grains of paradise. After allowing these substances to macerate in the wine, filter the liquor through linen." This drink was fashionable four centuries ago.

Hieronimus Cardanus of Pavia (1501-78) was a prolific and original writer. His works extend to ten folio volumes, which were collected in 1663. The principal are *De Rerum Subtilitate* and *De Rerum Varietate*. He observed the increase of weight in calcination of lead, the power of manganese dioxide (MnO) to colour or decolourize glass, the properties of the metals as such, and the characters of rectified alcohol. In a chapter on the forces and aliments of fire, he mentions "flatus," which nourishes flame and re-lights bodies which present a glowing point, and remarks that this property exists in saltpetre. This "flatus" must have been oxygen or nitrous oxide.

It is as an indefatigable compiler that Giovanni Battista Nazari (*circa* 1550-1600) is remembered. Dufresnoy says that Nazari had read an infinity of authors, many little known, and

had worked at the subject for forty years, although not practically in the laboratory ; but blames him for describing spurious operations which were calculated to ruin the persons who tried to perform them. His treatise, *Della Transmutazione Metallica*, a concordance of the philosophers, was published at Brescia in 1599. He also wrote an antiquarian work called "*Brescia Antica*," in which he recalls the glories of the ancient city.

Blaise de Vigenere (1523-96) was born at Saint-Pourcain in the Bourbonnais, studied in Paris, and held office at the French court. He travelled a great deal, and was a student of Greek and Hebrew. A number of historical works and translations from the classic authors were published by him, but though a learned man he seems to have led an immoral life, and died of suffocation in consequence of a growth in his throat. His one chemical work was translated into English with the title, "A Discourse of Fire and Salt, Discovering many Secret Histories as well Philosophical as Theological (London, 1649)."

The next alchemist was a lawyer of Padua named Carerius or Carrerius, with many other alternative spellings. Like most lawyers of that date, he was also a churchman, being Bishop of St. Andreas. His writings are of no importance.

We again meet with a doubtful personality in Quadrammi da Gubbio (*circa* 1550-1600). He appears to have been a monk, a doctor of theology, a botanist, and a chemist. His treatise on the symbolism of the alchemists, entitled *La Vera Dichiaratione di Tutte le Metafore, Similitudini et Entimmi degl' Antichi Filosofi Alchemisti, tanto Caldei et Arabi* (Rome, 1587), is of value as a means of interpreting the involved compositions of the ancient writers.

Nicolas Barnaud (*circa* 1550-1610) was a native of Dauphine. He wrote the *Quadriga Aurifera*, a book quaintly made up of four tracts called "*rotæ*" or wheels—one on the philosophy of the metals, two on works of George Ripley, and one on the *Elixir Solis* of Paracelsus.

The next alchemist is a Dutchman—Joost van Balbain, otherwise Justus, a Balbain (1550-1616). He studied in Italy

and probably took his doctor's degree at Padua. He returned to Holland and practised at Gouda. His contributions to the art were translations of the *Dicta Alani* and seven tracts concerning the philosopher's stone.

Giovanni Battista Porta (1537—1615) was a practical worker of some importance. He was a Neapolitan, and versed in mathematics, medicine, and science. He mastered the art of making glass and coloured enamels. He employed equal parts of calcined tartar or of soda and rock crystal or siliceous stones, well pulverised, levigated, and heated for six hours in crucibles at a high temperature. Carbonate of lead was then added to render the vitreous mass transparent, and metallic oxides to tint it. Burnt copper was used to imitate sapphire, and oxide of manganese to produce amethyst. Porta was also an authority on poisons, an important study in those days, and in this connection wrote of the culinary art, and of poisoning birds. He also discussed the possibility of rendering sea-water potable, of extracting water from the air, and of constructing an optical instrument similar to what we call "magic lantern."

Another experimenter was Johan Beguinus, whose date is uncertain, but we know that he published *Tyrocinium Chymicum* in 1608. He made observations on the fixed and volatile alkalis in plants, described the preparation of ammonium sulphide (called *oleum sulphuris* or *spiritus sulphuris volatilis Beguini*), of calomel, and of fulminating gold, and the product of the distillation of sugar of lead.

Athanasius Kircher (1602–80) was a Jesuit priest, an archaeologist, and professor of mathematics at Avignon. His chief writings are *Ars Magna Lucis et Umbrae* (1646), *Ars Magna Sciendi* (1669), and *Mundus Subterraneus* (1665). He thought that alchemists were in general impostors, although the transmutation of metals was sometimes possible. He divided alchemists into three classes: (1) Those who thought alchemy an impossible science—the disappointed alchemists; (2) those who gave false gold and silver for genuine—the false coiners; and (3) those who professed to make pure gold

and silver by means of the philosopher's stone—the true alchemists. His works form an encyclopædia of the sciences known in his period. He made a speaking trumpet, and carried out the idea of the magic lantern conceived by Porta. Many other discoveries in physics can be credited to him.

We have next to mention an English philosopher, Sir Kenelm Digby, of Buckingham (1603–65). He was one of the most notable men of the reigns of Charles I. and II., and one of the founders of the Royal Society. The following are the original titles of his books :—

1. A late discourse made in a sollemne assembly of nobles and learned men at Montpellier in France, touching the cure of wounds by the powder of sympathy, with instructions how to make the said powder; whereby many other secrets of Nature are unfolded. Translated from the French by R. White (third edition, London, 1660).
2. Of bodies, and of man's soul. To discover the immortality of reasonable souls. With two discourses: of the powder of sympathy; and of the vegetation of plants (London, 1669).
3. Chymical secrets, and rare experiments in physick and philosophy, containing many rare and unheard-of medicines, menstruums, and alkabests; the philosophical arcanum of Flamel, Artefius, Pontanus, and Zachary, with the true secret of volatilizing the fixed salt of tartar. Published by Geo. Hartmann (London, 1683).

His celebrated wound-salve or "powder of sympathy" seems to have been a quack nostrum, although he declares he used it to cure James Howell in 1624 of a wound in his hand, and that James I. and Dr. Mayerne were greatly impressed by its efficacy, while Francis Bacon noted it among his scientific curiosities. As we shall show afterwards, this conception of a universal salve was merely one of the aspects of the operation of the powder of perfection—the philosopher's stone.

J. F. Viganus Veronensis made various observations on antimony, described the preparation of green vitriol free from copper by precipitating that metal from the solution by means



of iron, and discussed the distillation of acetic acid, the first fraction of which he found to be inflammable.

Thomas Vaughan (1622–66), who took the name of Eugenius Philalethes, enjoyed a high reputation in his day. He wrote a treatise on *Experiments for the Preparation of the Mercury of the Philosophers*, published by Elzevir at Amsterdam in 1668, and either he or the next author published *Introitus Apertus ad Oclusum Regis Palatium* (1667), which is the most systematic work of its kind, and passed through many editions.

Confusion has been created by the circumstance that another writer, whose personality is a mystery, wrote under the name of Eirenaeus Philalethes. This person, who is believed to have been an adept in alchemy, was the source of the inspiration of George Starkey, a graduate of the University of Harvard, who published in England in 1654–5 a book called *The Marrow of Alchemy*. Whoever Eirenaeus Philalethes may have been, his writings have the merit of extreme lucidity, and were popular amongst the students of that period.

A few names may be disposed of in a single paragraph. Carlo Lancilotti, of Modena, published *Guida alla Chimica* in 1672. J. C. Orschall was the author of a treatise on the purple of Cassius, entitled *Sol Sine Veste* (1684). The *Aula Subterranea* of L. Ereker was issued in folio in 1730. None of these works is of historical consequence.

The Danish chemist Olaus Borrichius (1626–90), who took his name from his birthplace, Borsche in Jutland, was a man of originality, although not of accuracy, in the matter of chemical research. He seems to have been remarkable also for versatility, since he was professor at Copenhagen of philosophy, poetry, botany, and chemistry. Although he had little critical power, he was a diligent defender of alchemy, as is evinced in his *Hermetis Aegyptorum et Chemicorum Sapientia ab Hermannii Conringii Animadversionibus Vindicata* (1674). In this work he asserted, as the result of experiment, that 100 lbs. of snow, rain, or hail water, evaporated in a glass flask, changed into a powdery earth, which appeared to consist partly of common salt,



and that by repeated distillation water is converted into a non-volatile tasteless earth. This belief was shared by such men as Sir Isaac Newton, and was not finally discredited until Boerhaave in 1732 set the matter right. The common salt was produced by particles blown inland from the sea and dissolved by the rain, while the tasteless earth consisted of matter dissolved out of the material of the glass flask by repeated digestions and evaporations. Borrichius also observed that nitric acid caused certain oils to catch fire by its action upon them. He wrote a *Dissertatio de Ortu et Progressu Chemiæ* (1678), and after his death his *Conspectus Scriptorum Chemicorum* was published.

The opponent against whose animadversions Borrichius was moved to defend alchemy was Hermann Conring (1606–81), a native of Norden, in East Friesland. His work is called *De Hermetica Aegyptiorum Vetere et Paracelsicorum Nova Medicina* (Helmestadii, 1648). He took an iatrochemical view of the science, and bringing wide and comprehensive knowledge to the study, urged the cultivation of chemistry as useful for the perfecting of pharmacy. At the same time, he would not have the science extended to the explanation of physiological and pathological phenomena. He was not an alchemist, and while he possessed some sense and culture, and had no belief in efforts for the transmutation of metals, his aims were what we should consider narrow.

The old traditional and Aristotelian view of the elements was strongly held by Nicholas le Febvre, whose *Compleat Body of Chymistry*, a sort of course of the science, was published in English in 1670 and in German in 1683. He held that the mercury of the philosophers might be discovered by one who knew how to study. He made observations on the solubility of common salt, the gain in weight in burning antimony, the formation of ferrous sulphate by allowing iron and sulphur mixed to oxidise in air, and the solubility of tartaric acid when borax is added (*tartarus boratus*).

Subsequent to the time of Paracelsus it is not easy to draw a

line between the alchemists who adhered to the old school and the old aims, and those who more or less followed the new teaching. Accordingly, while we are aware that some of the writers named in this chapter were iatrochemists to a certain extent, we have gathered them together here, in respect that they did not distinguish themselves as leaders in the iatromedical school. We shall now proceed to consider some general questions applicable to the alchemical period as a whole, and afterwards open the second part of the history with an account of the iatrochemists.

## CHAPTER XIII

### THE PHILOSOPHY OF THE ALCHEMISTS

IT must be apparent from what has been said in the twelve preceding chapters, that the writings and labours of the alchemists were both extensive and important. It has also been shown that their studies, although misdirected, were not directed at haphazard. The alchemists had a definite, and (if their premises could be granted) a logical, system of philosophy, of which we now propose to give a general sketch. It may be summarised in the statement that they recognised—(1) the unity of matter; (2) the three principles—philosophical mercury, sulphur, and salt; (3) the four elements—fire, air, water, and earth; and (4) the seven metals—gold, silver, mercury, copper, iron, tin, and lead.

1. *The Unity of Matter*.—This was the fundamental theory of alchemy, and goes back to remote ages. It was expressed in the smaragdite tablet attributed to Hermes Trismegistus (*supra*, pp. 15 and 92): “As all things were produced by the one word of one Being, so all things were produced from this one thing by adaptation,” and we again find it in the “one is all” of the *Chrysopoeia* of Cleopatra (*supra*, p. 19).

The alchemists held that matter is one, but can take a variety of forms, and under these different forms can be combined and re-combined *ad infinitum*. The original matter, or *prima materia*, was called by various names—universal substance, seed, chaos. Although matter changes its form, it cannot be destroyed. As Hermes is alleged to have said, “Nothing in the world dies, but all things pass and change.” In its nature the *prima materia* was assumed to be a liquid, containing everything *in posse*, but nothing *in esse*.

2. *The Three Principles*.—All metals and minerals

consist of certain principles. These were at first called "mercury" and "sulphur," not the ordinary substances so named, but a philosophical mercury and a philosophical sulphur. At a later period the alchemists added a philosophical salt, or a philosophical arsenic, but they never ascribed to these the importance they attached to the other two principles. Traces of these ancient conceptions are still to be recognised in the word "quick-silver," that is living silver, a literal translation of *argentum vivum*. A term "quick-sulphur" (*sulphur vivum*) was also in use, but it has long since disappeared.

The mercury of a metal, according to general acceptation, represented its lustre, volatility, fusibility, and malleability; the sulphur of the metal, its colour, combustibility, affinity, and hardness. The salt of the metal was merely a means of union between the mercury and the sulphur, just as the vital spirit in man unites soul and body. It was doubtless devised to impart a triple form to the idea, in conformity with the method of the theological schoolmen. Mercury, sulphur, and salt were not three matters, but one, derived from the *prima materia*.

According to this theory, when an alchemist converted a metal into its oxide, or, as they expressed it, "made a calx" of it, he thought he had volatilised its mercury and fixed its sulphur. When he distilled ordinary mercury and found a solid residue in the alembic, he called it the "sulphur" of mercury; when he found a sublimed product in the receiver (mercury bichloride), he termed it the "mercury" of mercury or "corrosive sublimate."

The more logical mind of Artephius Longaevus introduced a modification of this theory. He distinguished two properties in a metal—the visible and the occult. The former, comprehending its colour, lustre, extension, and other properties visible to the eye, he called its "sulphur"; the latter, comprehending its fusibility, malleability, volatility, and other properties not visible until after the application of special treatment, he called its "mercury." Practically, however,

there was little difference in the application of these diverse theories regarding the three principles.

3. *The Four Elements.*—When discussing the philosophy of Aristotle (*supra*. p. 38) it was stated that he taught that all things consisted of four elements, or rather four elemental properties :—

1. Fire, the property of dryness and heat ;
2. Air, the property of wetness and heat, or of gaseousness ;
3. Water, the property of wetness and cold ;
4. Earth, the property of dryness and cold, or of solidity.

The alchemists adopted these four states of matter, and sought them in all substances. Everything hot was called " fire " ; cold and subtle, " air " ; moist and fluid, " water " ; or dry and solid, " earth." But, as heat changes liquids to vapour, and consumes solids, they reduced the number of visible elements to two—earth and water, which contained within themselves the invisible elements, fire and air.

They were thus able to apply the conception of the three principles to that of the four elements. Earth corresponded to philosophical sulphur, and water to philosophical mercury. Later, when they conceived philosophical salt, they devised a fifth element called " quintessence " or " ether," which corresponded to the third principle. Thus, if an alchemist distilled wood and obtained an inflammable gas, a liquid oil and a solid residue, he said that he had decomposed the wood into its elements—fire, water, and earth.

4. *The Seven Metals.*—It has already been told how the Chaldean star-gazers of Harran came to fix the number of metals at seven, and to associate them with the sun, moon, and five planets in the following manner :—

- Gold, corresponding to the sun.
- Silver, corresponding to the moon.
- Mercury, corresponding to the planet Mercury.
- Copper, corresponding to the planet Venus.
- Iron, corresponding to the planet Mars.
- Tin, corresponding to the planet Jupiter.
- Lead, corresponding to the planet Saturn.

Each metal acted under the influence of the planet with which it was associated (*supra*, p. 10).

Of these metals, they regarded gold and silver as being *perfect*, because they were unalterable by any method with which they were acquainted. The other five were deemed *imperfect*, as each could be formed into a calx or oxide, was readily attacked by acids, and could be consumed by fire ; but they deemed it possible to purify and modify the imperfect metals, so as to transmute them into the perfect.

The seven metals were, of course, derived like other substances from the *prima materia* or universal substance. They were the same in essence and differed only in form. The sulphur of a metal was its active principle ; the mercury its passive ; the salt was the link which united the other two. The sulphur, the property of dryness and heat, ultimately overcame the mercury, the property of wetness and cold, and thus changes were effected. To use another form of expression, sulphur was the father, mercury the mother, and metals were conceived between them. In this expression the *philosophical* principles are meant, not the ordinary substances called sulphur and mercury.

Without prolonging a somewhat profitless explanation, we may say that the alchemists accounted for the diversity of metals by five causes :—

1. Variation in the proportion of the principles, mercury and sulphur.
2. Variation in the purity of these principles.
3. Variation in the duration of the period of concoction to which the compound was subjected in the bowels of the earth.
4. Variation in planetary influences.
5. Variation in accidental influences.

Nature always sought to attain perfection, but was checked by these diverse causes, and instead of producing the perfect metals, gold and silver, produced imperfect metals, mercury, copper, iron, tin, or lead.



The later alchemists, who were mostly astrologers as well, laid special stress upon the influence of the heavenly bodies. The sun, they said, produced gold; the moon, silver; the planet Mercury, mercury; the planet Venus, copper; and so forth. Paracelsus even pretended to be able to calculate when and how this planetary influence took effect.

In the fifteenth and sixteenth centuries alchemy was affected by two external systems, *magic* and *religion*, both to its detriment. To astrology the alchemists added necromancy and the Cabala. The latter had really no connection with alchemy. It was a purely speculative system of numbers. By breaking up words, and adding together the numbers of their letters according to the practice of those languages which indicate numbers by letters, as Hebrew, Greek, and Latin, the Cabalistic philosophers professed to draw all sorts of inferences.

At a still later date it was argued that exact and natural sciences proceed by induction and deduction, and occult and spiritual sciences by analogy. Following out this line of thought the alchemists produced the following remarkable trilogy:—

<i>Material world</i>	: Sulphur	Mercury	Salt.
<i>Human world</i>	: Body	Soul	Spirit.
<i>Divine world</i>	: Father	Son	Holy Ghost.

Each of these was a trinity in unity, and a unity in trinity. In each world was a distinct design,—in the material, the perfection of the metals; in the human, the perfection of the soul; in the divine, the contemplation of the Deity in His splendour.

These mystic alchemists interpreted the three principles in their own fashion. Mercury, the passive and female principle, was *matter*; sulphur, the active and male principle, was *force*; and salt, the middle term in the proposition, was *movement*, which applied force to matter. Or, expressed in another shape, mercury was the *subject*; sulphur, the *cause*; and salt, the *effect*. Symbolically, the theory was represented

by an equilateral triangle, in one angle of which was the sign of sulphur or force ; in the second, the sign of mercury or matter ; and in the third, the sign of salt or movement.

Such, in brief, was the philosophy of the alchemists, and when fully considered it is by no means despicable. The knowledge which was at that period available did not permit of the practical application of this philosophy, and the sages did not rightly understand their own theories. Yet we must not forget that while there is much that seems absurd and nonsensical, there is much which is not inconsistent with recent researches and discoveries of science. These old philosophers had a wonderful grasp of general principles. It may be that those doctrines of the unity of matter and the mutation of form, which they taught in the light of deductive philosophy, will ultimately by the use of inductive methods be established as the true explanation of phenomena at present inexplicable and outside the domain of science.

## CHAPTER XIV

### THE AIMS AND METHODS OF THE ALCHEMISTS

BEFORE taking leave of the alchemical period it is proper that we should consider in detail the aims and methods of the sages who laboured and wrote during all these centuries. It was pointed out in the first chapter that the aims of the alchemists have been misunderstood. The term "alchemy," rightly considered, covers a very wide field of work (*supra*, p. 2) ; but the later alchemists lost sight of the wide significance of their art, and greatly restricted the scope of its application. In this chapter we shall set down the principal objects sought by those later workers, and the methods by which they hoped to attain success.

Francis Bacon in his *Novum Organum* well expresses the impression which abides with the modern reader after a perusal of the writings of the greater alchemists. How true is the saying of the inductive philosopher, that the alchemist lived on hope ! "Whoever sets his mind to a study of the arts commonly held more strange than sound, digging deep into the writings of the alchemists and magicians, may fall into some doubt whether such should more properly call forth a smile or a tear. For the alchemist nourished an undying hope, and where his work fell out amiss, was fain to suppose the blame to lie with errors of his own, with the self-accusing reflection that he had missed the drift of his technical terms or of his authors—wherefore he applied himself to traditions and whispered secrets ; or that he had slipped somewhere among the drachms and scruples of his own workings, which set him experimenting without end. At times among the chances of his work he came upon either the old things with a new semblance, or something of notable use ; on such tokens

he fed his heart, and made much show of them ; for the rest he lived on hope. Nor indeed can it be denied the alchemists that they hit on not a few discoveries, and gave many a shrewd device to the human race."

At the outset we are confronted by a difficult problem. In their pursuit of this hope—the great magisterium which would bring all things to perfection—had the alchemists in their mind's eye a *mystical conception* or a *material substance* ?

On this point it may be conceded that a few alchemists were mystics. When these men spoke of attaining perfection, and of purifying the baser metals and transmuting them into gold, they had in their minds the attainment of something far higher—the perfecting of the human soul, and the raising it to a higher spiritual life. This aspect of the matter is well set forth in the following extract from Whewell's *History of the Inductive Sciences* (1837), Vol. I., pp. 303–4: "Like other kinds of mysticism, alchemy seems to have grown out of the notions of moral, personal, and mythological qualities, which men associated with terms, of which the primary application was to physical properties. This is the form in which the subject is presented to us in the earliest writings which we possess on the subject of chemistry—those of Geber of Seville, who is supposed to have lived in the eighth or ninth century. The very titles of Geber's works show the notions on which his pretended science proceeds. They are 'of the search of perfection' ; 'of the sum of perfection, or of the perfect magistry' ; 'of the invention of verity, or perfection.' The basis of this phraseology is the distinction of metals into more or less perfect ; gold being the most perfect, as being the most valuable, most beautiful, most pure, most durable ; silver the next, and so on. The 'search of perfection' was, therefore, the attempt to convert other metals into gold ; and doctrines were adopted which represented the metals as all compounded of the same elements, so that this was theoretically possible. But the mystical trains of association were pursued much further than this ; gold and silver were held to be the most noble of metals ;

gold was their king, and silver their queen. Mythological associations were called in aid of these fancies, as had been done in astrology. Gold was Sol, the sun; silver was Luna, the moon; copper, iron, tin, lead, were assigned to Venus, Mars, Jupiter, Saturn. The processes of mixture and heat were spoken of as personal actions and relations, struggles and victories. Some elements were conquerors, some conquered; there existed preparations which possessed the power of changing the whole of a body into a substance of another kind; these were called magisteries. . . . When gold and silver are combined, the king and the queen are married. . . . It will easily be conceived, that when chemical operations were described in phraseology of this sort, the enthusiasm of the fancy would be added to that of the hopes, and observation would not be permitted to correct the delusion, or to suggest sounder and more rational views."

So strongly has this aspect of alchemy impressed the theosophists that they have laid claim to all alchemical treatises as being truly theosophic works, and maintain that these obscure writings have really a mystical theosophic meaning. At the root of this claim there is a small amount of truth. In every pre-Christian age the workers in metals, as well as the medical men, began their course of treatment of ores, metals, or patients by invoking the aid of the appropriate deities. The Chaldeans and Persians invoked the sun; the Egyptians, Thoth, Thuti, or Tat; the Greeks, Zeus; the Romans, Jove. Writers of books inserted these invocations along with their directions for alchemical operations, and when the mystical Greek philosophy began to exert an influence over the processes of alchemical philosophers, declamatory passages became more frequent. We find that as the writing of books more and more usurped the place of practical work, the less an author knew of laboratory processes, the more he invoked the aid of his gods, and the more he declaimed on the magnificence, the power, and the truth of alchemy. Ultimately, in many books of the Middle Ages, practical directions gave place to mystical disquisitions,



and well-arranged, but meaningless, reasonings founded upon false assumptions.

Although in Christian times many alchemical writers interspersed pious and devout remarks among their chemical disquisitions, yet no one who has waded through a number of these treatises can accept the theory that any large part of them is in any sense religious or theosophic. Mystical nonsense they often are, and one is only wearied by the foolish reasoning, philosophic in form, but hopelessly wrong in substance, that has to be passed over in the search for a few practical details.

Nevertheless, taking the art of alchemy as a whole, it is impossible to doubt that there was a foundation of scientific fact running through the work of successive generations of able and studious men, and that they had set before them the discovery of a definite material substance. Of course, when we read that Paracelsus said that he possessed a portion of this mystic substance, and had actually transmuted base metals into gold, we feel sure that he was simply telling a lie. Or when we read that Raymond Lully was presented to Edward I. by the Abbot of Westminster, and that he made gold for the king from base metals, which gold was used for making coins; and when by assays we discover that surviving specimens of these coins are composed of genuine gold, we assume that either King Edward or Raymond Lully was deceived at some point of the process. In a later century, Henry VI. of England and Charles VII. of France coined a quantity of gold made by the philosopher's stone, but that gold was undoubtedly spurious.

Many of the mediæval and later alchemists gave definitions of their art. Paracelsus defined it as the science which seeks to convert one species of metal into another. Denys Zächary said that it was a part of natural philosophy which taught the mode of perfecting the metals, imitating Nature in her methods as far as possible. Pernetys in his *Greek and Egyptian Tales* attempts to distinguish alchemy from chemistry, by asserting that ordinary chemistry is the art of destroying the compounds which Nature has formed, while hermetic chemistry is the art



of working along with Nature for their perfection. This, therefore, was the general aim of the alchemists—to carry out in the laboratory, as far as possible, the processes which Nature carried out in the interior of the earth.

Seven leading problems occupied their attention :—

1. The preparation of a compound named elixir, magisterium, medicine, or philosopher's stone, which possessed the property of transmuting the baser metals into gold and silver, and of performing many other marvellous operations. As this was the great work, the *magnum opus* of alchemy, we shall reserve for a future chapter what we wish to say on that subject.
2. The creation of *homunculi*, or living beings, of which many wonderful but incredible tales are told.
3. The preparation of the aleahest or universal solvent, which dissolved every substance which was immersed in it. *Aqua regia* and caustic potash were supposed to possess these powers, and Glauber even claimed them for sodium sulphate, a salt which bears his name to this day.
4. Palingenesis, or the restoration of a plant from its ashes. Had they succeeded in this, they would have hoped to be able to raise the dead.
5. The preparation of *spiritus mundi*, a mystic substance possessing many powers, the principal of which was its capacity of dissolving gold.
6. The extraction of the quintessence or active principle of all substances.
7. The preparation of *aurum potabile*, liquid gold, a sovereign remedy, because gold being itself perfect could produce perfection in the human frame.

In no way shall we more readily arrive at an understanding of the conceptions of the mediæval alchemists, their mixture of mysticism with scientific method, and their secretive habits, than by examining a few of their ordinary processes, as preserved for us in their writings.

In the first place we shall consider their method for the "fixation," as they called it, of sal ammoniac. It is certainly curious. "Crush sal ammoniac and mix it with its own weight

of quick lime ; pound the whole on the marble with care. Beware of the very violent odour which it exhales, and which is unwholesome." (This was, as we know, ammonia,  $\text{NH}_3$ , but to them it was only an unpleasant odour.) " Place the mixture in a glass flask well luted and let it dry. Place it on a furnace till all trace of moisture has disappeared. Close the vessel with its special cover, and lute it so that nothing may escape. Force the fire until the vessel is incandescent in the midst. Then allow it to cool. The result is *sal ammoniac fixed* (that is, coagulated). Take it out, pound it, and place it in a glass vessel, and pour on it cold water till it is dissolved. Filter it, pour more water on the residue, and repeat these operations till the residue has no longer a saline taste. Evaporate all the waters over a gentle fire until they solidify in a glass vessel, increasing the heat towards the end. The product is white, and must be enclosed (that is, kept in a glass vessel), because it very quickly deliquesces spontaneously."

This product was *chloride of calcium*. No notice was taken of the ammonia which had escaped, except as a pungent and unwholesome odour, which had better be avoided. But while thus ignorant of one of the most important products of his operation, the writer had evidently done the work, knew how to do it, and gave clear and precise directions which one can understand. Such clearness and precision are characteristic of, and found only in, those few works which contain what we may call workshop or laboratory traditions, handed down from one operator to another. We have already seen, and will hereafter see, that such writings are in marked contrast to the vague text-books and mystical treatises of the philosophical writers on alchemy.

We shall now compare this description of the treatment of sal ammoniac with another taken from an Arabic manuscript written in Syriac characters, which is in the University Library at Oxford. It is called " the preparation of the Red Eagle " :

" Take one part of sal ammoniac, pound it well ; and an equal quantity of yellow vitriol ; reduce them to powder ;

mix them, and make them rise (*i.e.*, sublime them) in a clay athal—I do not say an-athal of glass or porcelain, but of clay (earthenware). The heating will be for a whole day, working on two pounds.” [In another place instructions are given for luting the vessel with the lute of the philosophers.] “Open the vessel next day, when it is cold, and you will find the sal ammoniac coloured white, yellow, or grey, after it has gone up (*i.e.*, sublimed), and the vitriol will have remained at the bottom coloured very red. Withdraw the vitriol from the pot, and mix it ground up with the sal ammoniac in equal quantity. Light the fire as at the first time. Do this three or four times, and each time mix the vitriol with that which ascends (*i.e.*, sublimes). If the sal ammoniac becomes yellow, a bright yellow, it is right, for it becomes bright yellow after having taken the red of the vitriol. Put it on one side; it is red sal ammoniac. Whatever be the sal ammoniac you employ in the treatment, it must become like this. When it has reached this state, unite it with calx of gold and bring the whole into the consistency of wax between two caps.”

The following appears to be a recipe for a species of Greek fire :—

“Take pure sandarach (the gum, not realgar), 1 lb. ; and liquefied or molten gum ammoniac, 1 lb. ; pound them together and place them in a glazed earthenware vessel, luted with the lute of philosophers. Place fire below till they melt. When the mixture has the consistence of butter, in contact with a piece of wood, it is the sign of the right consistence of this fusible matter. Then add 4 lbs. of bitumen. This operation must not be performed under a roof on account of the danger.”

Then follow directions for using it at sea or on a river. In this class of recipes the following ingredients frequently occur : balsam, petroleum, pitch, sandarach, oil of sulphur, sulphur vivum, asphalt, and colophony.

Another recipe professed to render the human body immune to fire :—

“Take juice of double malva, white of egg, seeds of persil, and lime. Pound them together and prepare them with white of egg mixed with juice of sapin. Anoint your body or hand with this composition, allow it to dry, repeat the

anointing, and then you can boldly sustain the trial without hurt" (*i.e.*, the ordeal by fire).

A volatile fire, or fuse, was made thus :—

"Sulphur vivum, 1 lb. ; charcoal of lime or willow, 2 lbs. ; and saltpetre, 6 lbs. Pulverise very finely on a stone. Then you put the powder at will into the envelope of a fuse or petard."

This was practically gunpowder. The most important ingredient in it was saltpetre. The art of making this substance was unknown to the ancients, and was kept as a state secret by the Byzantine emperors, who used it for making Greek fire, which they employed with great effect against their enemies. The secret was after a time discovered by the Turks, who turned the weapon against the Greeks.

Directions for the preparation of saltpetre are found in a technical manuscript of the thirteenth century preserved in the Paris Library. Roger Bacon says in his epistle, *De Secretis Operibus Artis et Naturae et de Nullitate Magiae*, Hamburg. 1618, Chap. XI. :—

"Mix together saltpetre, *Luro vopo vir comutiret* (seemingly a cryptogram for some kind of charcoal), and sulphur, and you will make thunder and lightning, if you know the method of mixing them."

The proper method of mixture appears to have been discovered, because gunpowder was used by the English at the battle of Werewater in 1327, and again at Crecy in 1346.

Although it was known at an early date that wine when heated gave off a combustible spirit, the direct process for making spirits of wine seems to have been overlooked. The term "ardent spirit" was not used in the thirteenth century, nor "alcohol" until after the fourteenth. It is surprising that alchemists did not obtain this substance by distillation, as that process was described by the two Egyptian ladies, Cleopatra and Mary the Jewess (*supra*, pp. 19 and 25). The process for the preparation of alcohol is indicated in the *Mappae Clavicula* already mentioned. The ingredients are

concealed by a cryptogram, in which each letter stands for the next before it in alphabetical order :—

XKOK	VINI
QBSUF	PARTE
TBMKT	SALIS

The recipe when extended reads :—

“Mixing a pure and very strong wine with three parts of salt and heating it in a vessel designed for this purpose, we get an inflammable water which burns itself without destroying the matter on which it rests.”

We find in Marcus Graecus an instruction for the preparation of *aqua ardens* :—

“Take black wine thick and old. For every quarter of a pound add 2 scruples of sulphur vivum in very fine powder, 1 or 2 lbs. of tartar extracted from good white wine, and 2 scruples of common salt in large pieces. Place the whole in a good leaden alembic, put the top on it, distil the *aqua ardens*, and preserve it in a well-closed glass vessel.”

Alchemists were led to this discovery by early recipes for making wine burn when heated. Various recipes are given, one of which contains sulphur, one salt, and one both. The use of these substances was indicated by their theory that the wetness of wine was against its combustibility. Sulphur was associated in their minds with the properties of volatility and combustibility, and salt with earthiness or dryness. Therefore they added these ingredients to counteract the wetness of the wine and increase its combustibility.

Arnoldus Villanovanus mentions that the distillation of wine produced *vinum ardens*, which he also called *aqua vitae*, although that term was properly employed to describe the elixir which would prolong life. He describes it as the most subtle portion of wine, and as possessing virtue for the prolongation of life. Its preparation is also set forth by Raymond Lully.



The apparatus with which the mediæval alchemists performed

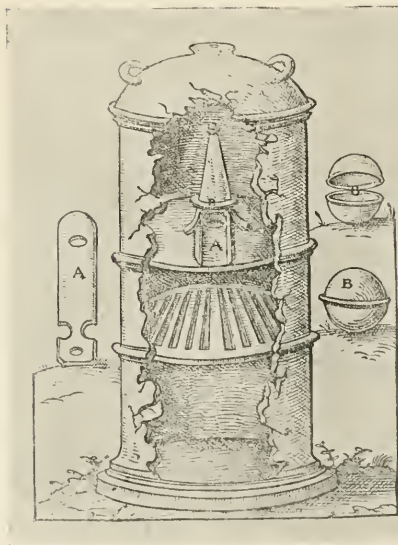


FIG. 57.—Section of Furnace. (Rupescissa.)

these processes and operations was not very different from that in use at the present day, although the more delicate experiments of modern chemistry demand instruments of a more refined character. The old alchemists tried, so far as lay in their power, to repeat in the laboratory the processes of Nature. Consequently they made use of a large quantity of material, and spread their operations over a long period of time. As the result of

these ideas, they constructed their apparatus of a greater size than is ordinarily used in modern practice.

One of the most important furnishings of a mediæval laboratory was the furnace. This assumed many forms, and a few examples are shown in Figs. 57 to 59. For distillation and sublimation the alchemists used alembics and aludels, both being apparatus



FIG. 58.—Furnace for Distillation.



adapted for catching vapours or sublimed products in one or more hoods placed above the vessel which contained the substance undergoing treatment. When they wished to heat anything for a long period at a uniform temperature they made use of an athanor, a special furnace for digestion of liquids. With this they often used a glass vessel hermetically sealed, which they called "the philosopher's egg." As there was no escape for vapour or heated air, this piece of apparatus became a sort of bomb-shell, and not infrequently exploded with results disastrous to the sage who was using it.

We show in Figs. 60 to 63 drawings of apparatus taken from the books of mediæval alchemists, and we again refer to the drawings from Syriac manuscripts

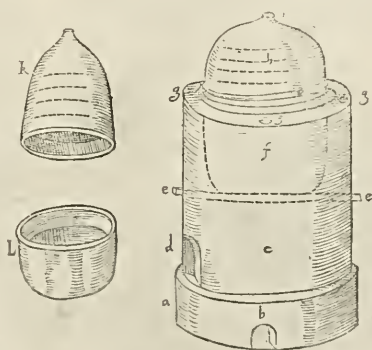


FIG. 59.—Alchemical Furnace.

(Figs. 28 to 51). These figures are inscribed in Syriac, and are rough sketches such as a student might make in his note-book. The retort and receiver (Fig. 41) is called an instrument for "making the divine water." Fig. 49, called an apparatus for the fixation of mercury, was designed for the preparation of oxide of mercury, and the same figure shows an apparatus for making arsenic *per descensum*. The old alchemists considered metallic arsenic to be a kind of mercury—that is to say, mercury from sandarach (realgar), instead of mercury from cinnabar. What they prepared by this process seems to have been arsenic trioxide ( $\text{As}_4\text{O}_6$ ), the *hutzenrauch* or "furnace smoke" of Basil Valentine, since the manuscript of Jacobus Theotonicus ends the description

of the process by saying "collect the beautiful *white arsenic*."

Of the materials upon which the alchemists exercised their art, we shall insert a few notes, in supplement of what has been mentioned in previous chapters. We have already furnished lists of the substances known to science at various periods, many of which were to the old workers little more than names.

With the exception of sulphur, the non-metallic elements were unstudied. Although carbon in its triple form was before them—diamond, graphite, charcoal—the alchemists failed to realise the relationship subsisting between these substances. The diamond was valued from a remote period, but for its rarity rather than its beauty. As the stone has little lustre until it has been cut and polished, and as the method of performing these operations was not known before the fifteenth century, the true beauty of the stone was not appreciated. Plumbago or graphite was familiar

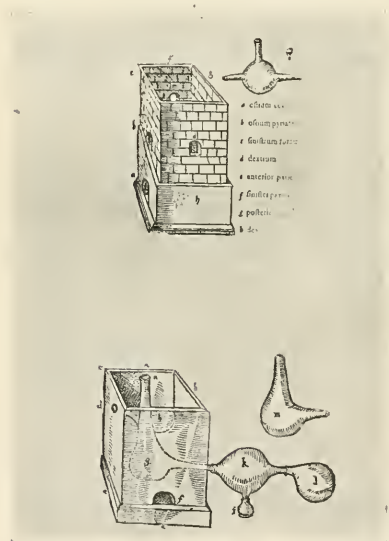


FIG. 60.—Alchemical Apparatus.

as a material which made black marks upon paper, but its chemical nature was not perceived. Charcoal was in use as a fuel, and also attracted attention on account of its insolubility. It was to be a special property of the mysterious alcahest that it could dissolve this stubborn substance, but to this day charcoal has defied solution.

Sulphur is mentioned by Dioscorides and Pliny, and Geber gives directions for preparing milk of sulphur for medicinal purposes. Vincent de Beauvais describes an acid extracted

by distillation from alum, which was probably sulphuric, and the same substance was prepared under the name of "oil of vitriol" or "spirit of vitriol" from the sulphates of iron and copper. Sulphurous acid, obtained by the combustion of sulphur under a bell-glass, was well known, and some alchemists waxed eloquent over its marvellous properties, medicinal and other. The compounds of sulphur with the various metals were familiar to the ancient workers, and were amongst the most important substances in their laboratories.

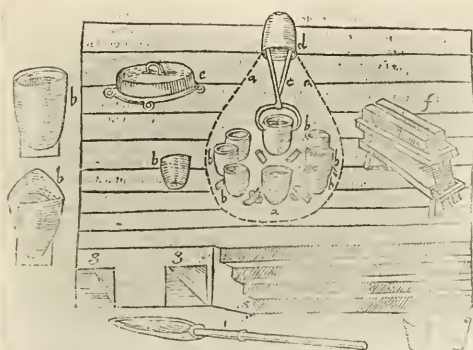


FIG. 61.—Alchemical Apparatus.

The metallic elements were more perfectly studied. Gold, the first of metals, the noblest and most perfect, has also the longest history. It was found in every country in an almost pure state, and the sands of rivers in particular yielded it in considerable quantities. Classical students will recall the golden sands of Pactolus.

The imitation, and at a later date, the preparation, of this precious metal were the grand operations of alchemy. To such an extent was the infatuation carried that the Pope in the fourteenth century, and the English Parliament in the fifteenth, had to interfere to restrain it. The English statute is a curious production, short and to the point: "None from

henceforth shall use to multiply gold or silver, or use the craft of multiplication, and if any the same do, he shall incur the pain of felony.”

Silver, being mined in a native condition, was also wrought from an early period. The Spanish mines were the most ancient source of the metal. Its alloy with gold, termed *asemus* or *electrum*, was sometimes found native, and was originally deemed to be a simple substance, not a compound. The salts of silver are mostly of recent discovery, but the nitrate and chloride are both very old preparations.



FIG. 62.—Alchemical Apparatus.

Next to the precious metals, mercury held the highest place in the mediæval laboratory. The actual date of its discovery is uncertain, but it was known in the time of Aristotle. Native mercury, which was found in liquid form in the mines of Spain, was called *argentum vivum* (living silver); mercury prepared by the sublimation of cinnabar was called *hydrargyrum* (water of silver). The red colour of cinnabar caused it to be confused with minium, and led to mistakes on the part of theoretical writers. We shall have some further remarks to make upon this metal when we refer to it in connection with the making of the philosopher's stone,

One of the baser metals much used in refining silver was lead, which is mentioned in the Bible. Of its compounds the most famous was minium or red lead ( $Pb_3O_4$ ), to which we have just referred. It was highly esteemed as a pigment, and the illuminators who used it were named *Miniatores*, a term which has descended to our miniature painters.

Tin goes back to a remote antiquity, being combined with copper to produce bronze. Since the fourth century it was called in Latin "stannum." Its salts were practically unknown till the time of Libavius, of whom we shall have to speak among the iatrochemists.

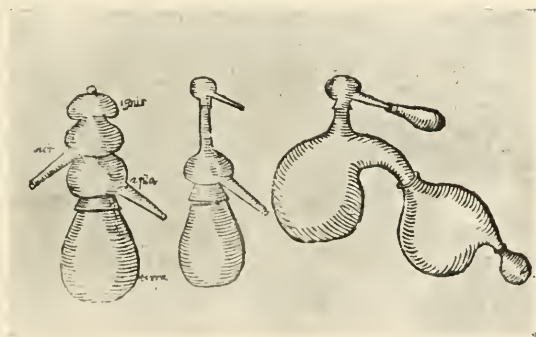


FIG. 63.—Alchemical Apparatus.

Although iron was extensively used as a metal, it was of small importance in the ancient laboratory. We often find allusions to the red oxide (rust) and to green vitriol (ferrous sulphate), but the other compounds of the metal were quite neglected.

As copper is another metal found in native purity, it has a very long history. With its alloys, bronze and brass, it was designated by the same terms—in Greek "*chalcos*": in Latin "*aes*." Our word "copper," derived from the later Latin "*cuprum*," is taken from the rich mines of Cyprus, which were extensively wrought in ancient times. The metal was used in the earliest ages in a nearly pure state, but afterwards an



alloy with tin of specific gravity 8.815 was generally used for making armour, weapons, and domestic utensils.

The two sulphides of arsenic were largely used in the ancient laboratory. One was called sandarach and the other arsenicon—the former being now usually termed realgar ( $\text{As}_2\text{S}_2$ ), and the latter orpiment, that is *auri pigmentum* ( $\text{As}_2\text{S}_3$ ). White arsenic (arsenic trioxide,  $\text{As}_4\text{O}_6$ ) was also prepared, being, as we said before, the product of the operation of preparing arsenic *per descensum*. Berthelot was of opinion that the preparation of metallic arsenic is indicated in certain fragments attributed to Zosimus, but the process does not appear to be fully described before the time of Albertus Magnus, who obtained metallic arsenic by fusing one part of orpiment with two parts of soap.

Bismuth was sometimes called marcasite, although that term was more frequently applied to the metallic sulphides, especially pale iron pyrites. Both bismuth and antimony sulphide, called stibnite, were employed from an early date, but their chemical characters were not understood. Zinc was held of small account except in the making of alloys, and was not recognised as a distinct metal until the time of Paracelsus.

The word "nitrum" often occurs in old writings, not to indicate potassium nitrate, but an impure sodium carbonate procured from six lakes lying to the west of the Nile Delta and called the Lakes of Natron, whence the term is derived. Potassium nitrate, however, was known, and as we have already said, formed an ingredient of Greek fire. Other compounds of potassium were used from the earliest times.

Common salt, sodium chloride, was found in a crude form mixed with earthy substances, which rendered it liable on exposure to become insipid, or to "lose its savour," as we read in the Scriptures.

The gases were entirely beyond the comprehension of the alchemists. Paracelsus mentions the production of an inflammable gas when iron is treated with acid in water, so he must have at least seen the flame of hydrogen; but he went no further, and it was left to Cavendish in 1766 to discover this important



element. Sulphuretted hydrogen was observed as an unpleasant odour arising in certain chemical operations, but the gas was not known.

Ammonia in its gaseous form was likewise unknown. Ammonium chloride, commonly called sal ammoniac, was studied as early as the time of Geber, and derived its familiar name from the circumstance that it was brought from the Libyan Desert, near the temple of Jupiter Ammon. By distilling hoofs and horns of animals the alchemists obtained ammonia liquor, which they termed "spirits of hartshorn," but it is doubtful whether they perceived the relation between the two substances. The gas they were unable to isolate.

It is obvious from what has been described in this chapter that the alchemists were working upon distinct if mistaken lines, and that they had in the course of their working attained to a considerable knowledge of the principal metals and of those other substances which they thought likely to be useful to them in the pursuit of their object. They had, moreover, much skill in chemical manipulation and the use of such apparatus as was at their disposal. There can be little doubt that they would have reached far greater heights of chemical knowledge had they aimed at a wider attainment, and consequently we are not surprised at the rapid advance made by chemistry so soon as the fancies of the alchemists were thrown aside, and chemists pursued the study of their science, not to make gold and silver, but to attain an understanding of the secrets of Nature.

## CHAPTER XV

### THE SYMBOLISM OF THE ALCHEMISTS

M. ALBERT POISSON, in the introduction to his *Théories et Symboles des Alchimistes* (Paris, 1891), has the following passage : “ Open one of the venerable hermetic treatises of the fifteenth or sixteenth century, and read it. If you have not made a special study of the subject, if you are not already initiated into alchemical terminology, if you have not a certain knowledge of inorganic chemistry, you will soon close the volume, disappointed and discouraged.”

The learned Frenchman does not speak by any means too strongly. The alchemists deliberately and of set purpose tried to conceal their art, their aims, and their processes, and attained a large measure of success in the attempt. It has been suggested that in doing so they were actuated by dread of the Inquisition and of a prosecution for using illegal arts, but M. Poisson demonstrates that this is an error. As a matter of fact, the alchemists were frequently charged with necromancy, and the very fact that they made use of mysterious signs and symbols, in place of aiding their defence, was brought forward as evidence in support of the accusation. But the alchemists as a rule had no need to fear an ecclesiastical prosecution. They were religious men, often monks and churchmen, and invariably prefaced their labours with prayers and the invocation of the Divine Blessing, and never failed to return thanks for any success which attended their operations.

The true motive was a desire to restrict the knowledge of alchemy to a chosen few. Apart from all other considerations, the adepts cannot have been blind to the fact that if the philosopher's stone were discovered, and the discovery made known to a large body of workers, gold would be produced in

such quantities that it would become worthless. The value of the discovery would depend upon its being confined to a few, who could be trusted to employ it with discretion.

It is much to the credit of the alchemists that they never sold their secrets, but were always ready to communicate them gratuitously to any one whom they deemed a worthy recipient. But it has also to be observed that they never communicated the whole of an operation at one time, and the same caution may be perceived in the works of alchemical writers. The different parts of the *magnum opus* have to be found by a comparison of several authors, one of whom describes the materials, another their preparation, a third their decoction, a fourth the rules for regulating the heat, and so on. This fact is one of the most serious obstacles in the way of understanding alchemical processes, but many other difficulties were raised to obstruct the uninitiated.

In the first place, the alchemists made use of an elaborate system of signs. These were introduced by the Greeks, who probably adapted them from the hieroglyphic writing of the Egyptians. Indeed, we often find the same figure adopted in both systems; as, for instance, the alchemical sign and the ideographic hieroglyph for "water," which are both parallel waved lines (see Fig. 5).

It has already been pointed out that the astrological signs for the sun, moon, and five planets were used to indicate the seven metals. In addition to these, there were signs for every important substance known to the alchemists, and for various pieces of apparatus in common use. M. Poisson, in his book already quoted, gives a list of more than a hundred signs used by the ancient authors.

To indicate operations, symbols were extensively employed. The meaning of some was obvious; for example, birds flying upwards indicated "sublimation"; flying downwards, "precipitation"; but we shall have more to say regarding obscure symbols.

A vocabulary of words taken from Greek and Arabic was

made use of, each representing an alchemical idea quite different from its meaning in ordinary speech. Unless a student was inspired with a genuine enthusiasm, this special vocabulary was enough to deter him from advancing further in the study of the art.

But, as if these obstacles were not sufficiently great, the alchemists resorted to anagrams and enigmas. As examples of the first M. Poisson gives "seganissegade" for "genie des sages," and "tripsarecopsem" for "esprit, corps, ame." Without a clue to their interpretation, such anagrams were absolutely without meaning.

The following is a specimen of an enigma:—"I have nine

letters and four syllables : the first three syllables have each two letters, the others have the remaining letters ; there are five consonants. Know me and you will have wisdom." The word is "arsenieon."



FIG. 64.—Enigma. (Basil Valentine.)

55. The first (from Basil Valentine) contains the signs of the seven metals, an eagle (symbolical of the *volatile* principle) and a lion (symbolical of the *fixed*). There are the words "Visita Interiora Terræ, Rectificando Invenies Occultum Lapidem," of which the initial letters form the word "vitriol."

The second enigma (from Kircher) is more elaborate. The words in the two outer circles are "Sola Vera Laudat Philosophia Homines Veritatis Rectæ Fiet," "Inde Xenophontis Verum Mandatum," and the initial letters read "sulphur fixum." In the inner circle are the words "Ergo Sic Tuos," "Sophos Omnes Lege," which in the same way read "est sol." The concealed phrase "sulphur fixum est sol" signifies the alchemical theory

that "fixed sulphur is synonymous with gold," the precious metal being, as usual, symbolised by "sol," the sun.

The alchemists carried symbolism to extravagant lengths. They read a hermetic meaning into the writings of Homer, Virgil, and other ancient authors, and, not content with finding allegories in the wanderings of Ulysses, or the trials of Aeneas, devised others of their own composition. We may quote a short one from M. Poisson :—" As I was setting out on a journey gold met me between two mountains, where I beheld with wonder a countryman, grave and modest in his demeanour, who was clad in a gray garment, wore a black ribbon on his hat and a white scarf about his body, was girt with a yellow belt, and shod with red boots." In this allegory are concealed the colours of the great work in their proper sequence—gray, black, white, yellow, and red (*vide* Chapter XVI.).



FIG. 65.—Enigma. (Kircher.)

In an age of cryptograms, these were, as we might expect, adopted for purposes of concealment. Words were read backwards—"zenerp al ereitam euq suov zevas" for "prenez la matiere que vous savez," or were disguised by the addition of unnecessary letters—"Pazothi adoesp uphiloqsophesa lestli pleururi inerauret" was intended to represent "Pazoth des philosophes est leur mereure."

Pentacles were drawn to exhibit at a glance the substance of a whole theory. Such diagrams served a double purpose—they aided the memory of the initiated, and hid the secrets from the uninitiated. The *Chrysopoeia* of Cleopatra (Fig. 7) is a pentacle. Another is shown in Fig. 66, which is taken from the *Gloria Mundi* in the *Museum Hermeticum*. The sage and the young



man are an adept and his pupil. The tree bearing the sun, moon, and five stars symbolises universal matter, including the seven metals. The four elements are represented thus—earth by a man and a lion; fire by a dragon; water by the sea, a dolphin and a woman; and air by a bird. The principal colours and operations in the course of the *magnum opus* are indicated by seven circles containing objects—(1) mortification and the colour black, by a crow and a skull; (2) distillation, by two crows; (3) sublimation, by three crows; (4) the end of the little magisterium and the colour white, by two birds with a crown; (5) the reign of Mars and the colour of the rainbow, by two birds and a tree; (6) the colour red, by a unicorn and a rose bush; and (7) the end of the grand work and preparation of the philosopher's stone, by a new-born infant.



FIG. 66.—Pentacle. (Gloria Mundi.)

The *purification* of metals was a work of great importance. This operation was represented by a king dressed in red (gold) and a queen dressed in white (silver). Their garments were the impurities which are usually found incorporated with the metals. The removal of the clothing of the king and queen symbolised the removal of these impurities, and the process is indicated by a bath or fountain. Antimony used in the purification of gold is shown as a wolf; lead used in purifying silver by a figure of Saturn. When the queen is drawn with flowers in her hand, these show the number of times the operation of purification has to be repeated.

Another process was *solution*. This was represented by



a lion devouring the sun, moon, or the planet which represented the metal. In fact, wherever we see in an alchemical drawing the sun or moon, Apollo or Diana, being devoured by a lion, tiger, eagle, or other fierce animal, we may read the symbol as indicating the solution of gold or silver in an acid, or in some other solvent.

The union of the great philosophical principles, sulphur, and mercury, preparatory to the *magnum opus*, was shown by what was called a hermaphrodite—a human figure with two heads, male and female. They termed this figure "Rebis," a word of disputed derivation and meaning.

The following list contains the principal symbols of operations and colours :—

*Conjunction*, symbolised by a marriage.

*Putrefaction*, a corpse, a skeleton, or a crow.

*Ablution*, a corpse or skeleton rising from the grave.

*Perfection* of the work, an infant newly born.

*Black*, a crow, Saturn, or lead.

*White*, a swan, the moon, or silver.

*Iridescence*, a peacock, Mars, or iron.

*Red*, a phoenix, Venus, or copper.



FIG. 67.—Emblematical Representation of an Alchemical Process.

In ordinary alchemical pictures these objects may be interpreted with the meanings which we have given. The same interpretation may be applied to all symbolic representations alluding to colours. Thus, when Trevisan says: "I asked him what was the colour of the king. He replied that he was dressed in cloth of gold with a doublet of black velvet, a shirt

as white as snow, but his skin as red as blood," we understand that he simply means to tell us that the materials in the course of their decoction during the preparation of the philosopher's stone assume successively the colours black, white, and red.

A few examples selected from the writings of the alchemists will illustrate the practical application of these rules.

In Fig. 67 we show an emblematic drawing, which is accompanied by the following words that read like a riddle:—"I am



FIG. 68.—The Green Lion devouring the Sun.  
(*Artis Auriferae*.)

old, infirm and debilitated; my soul and spirit (the two birds in the figure) leave me, and I become like the black crow; in my body are found salt, sulphur, and mercury." The metals are indicated in the corners by their usual signs, and the four elements are seen blowing upon the circle. The whole signifies gold being dissolved in *aqua regia*, undergoing the process

of putrefaction, and being made ready for use in the preparation of the philosopher's stone.

In Vol. II. of the *Artis Auriferae* occurs an emblem which is reproduced in Fig. 68. We are told in the heading of the chapter to which this emblem is prefixed that it treats *De nostro mercurio qui est leo viridis solem devorans*; that is, "concerning our mercury which is the green lion devouring the sun." The symbol therefore indicates mercury dissolving gold, or, as we would say, forming an amalgam with it.

Unfortunately, the symbols were not employed with a uniform signification. Nicholas le Febure (*Compleat Body of*

*Chymistry*) tells us that the "green lion" also meant tincture of vitriol, that is, sulphuric acid; but it must be borne in mind that a lion devouring the sun or moon always represented the solution of gold or silver in some solvent. Mercury and sulphuric acid were "the green lion of the philosophers"; the "green lion of fools" was green vitriol (ferrous sulphate).



FIG. 69.—Lions with Wings and without. (Mager.)

Le Febure furnishes a considerable list of symbols. He says that the ancients called *aqua fortis* "ostrich's stomach" (it was also indicated by the letters A.F.); tincture of gold, the "red lion"; corrosive sublimate, and antimony, the "two dragons";



FIG. 70.—Draco non Moritur. (Mager.)

butter of antimony, the “poisonous foam of the two dragons” ;  
tincture of antimony, “dragon’s blood” ; the same tincture



FIG. 71.—Salamander in Fire. (Mager.)

coagulated, the “wolf’s jelly” ; and the redness which appears  
in the receiver during the distillation of nitre, the “blood of

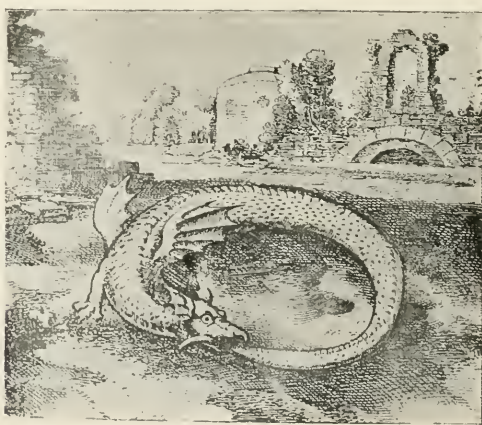


FIG. 72.—Dragon Biting its Tail. (Mager.)



the salamander." This last is probably the earliest mention of nitrous oxide.

Quite a number of symbolic terms can be gathered from the old Arabic manuscripts; for instance, *sal ammoniac* was the eagle, the vulture, the wild lion, salt of birds, the bird of Khorassan, and was called by many other names. The *two sulphides of arsenic* were the two brothers, the two caliphs, the two kings, the two crowns, the two stones, and the two sandarachs. *Asphalt* was the red of the philosophers: and *sulphur* was named the king, the two guardians, the yellow, red, or white bride, the yellow wax, the scorpion, and the earthen lion.

The following group of symbolic drawings contains some good specimens of this mode of expressing alchemical ideas:—

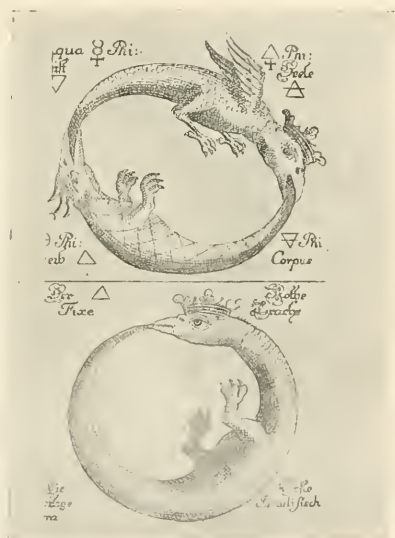


Fig. 69.—A lion with wings and another without, from the *Emblemata* of Michael Mager, a writer of the seventeenth century, represents the mercury and sulphur of the philosophers.

Fig. 73.—Two Dragons Biting their Tails. (Donum Dei.)

Fig. 70.—Entitled "*Draco non moritur nisi cum fratre et sorore sua interficiatur,*" is taken from the same, and represents mercury being combined with gold and silver in the process of making the philosopher's stone.

Fig. 71.—A salamander, from the same, indicates the element fire.

Fig. 72.—A dragon biting its tail, from the same, suggests the unity of matter.

Fig. 73.—Two dragons biting their tails, from Abraham

Eleazar, *Donum Dei*, is a more elaborate symbol. The upper pair represent the two principles mercury and sulphur, the former winged, as being female and volatile, the latter without wings, as being male and fixed.

We furnish in Figs. 74 to 85 a series of drawings which have been taken from Kelly's *Theatre of Terrestrial Astronomy*, along with the descriptions furnished by the author. They give a vague description of the philosophy of the red elixir of transmutation, and will be more readily comprehended after a perusal of Chapter XVI.



FIG. 74.—Kelly's Emblem (No. 1).

(1) *Of the Mutual Conversion of Elements.*—Fig. 74 represents a black rock, on the top of which stand black Saturn, Jupiter, the white and bright king, the red soldier Mars, Sol with golden head and red breast, Venus with green garment (pepleum), helmeted Mercury, clothed in red, green, white, yellow, purple, ochre, and black, with bright yellow, blue, and red wings, and Luna in white and black. On the black plain stand Mercury and Luna with a crescent on her head, labelled *Hermaphrodita*,



which indicates sulphur on each side of mercury. The four elements blow from the four corners upon the place where Mercury stands with Luna.

(2) *Of the Homogeneous Affinity of Metals.*—Fig. 75 represents a rock of a black colour, on which stand with joined hands the planets—black Saturn, falling down, Jupiter, Mars, many-coloured Mercury, Venus with green garment, Luna and Sol.



FIG. 75.—Kelly's Emblem (No. 2).

Lower down on the black rock stands an old man with a pickaxe, who cuts a piece out of the rock, whence Saturn falls. Near him lie as dead Jupiter and Saturn.

(3) *Of the Preparation of Mercurial Earth.*—Fig. 76 represents a glass vessel standing on a straw ring, and in it Mercury, Mars, and Saturn, lying on their backs. An old man is about to throw in Venus and Jupiter. Behind the old man on a black rock stand Luna and Sol.

(4) *Of the Conversion of Prepared Mercury into Mercurial Earth.*—Fig. 77 represents a mountain with many trees, and



*Preparatio terrae Mercurialis*

FIG. 76.—Kelly's Emblem (No. 3).



FIG. 77.—Kelly's Emblem (No. 4).

at the foot a yellow lioness suckling a green one. In front is a furnace upon which is a glass vessel, from which blue serpents ascend into an alembic, and are collected in a receiver, which is held by an old man in robes as if about to remove it.

(5) *Of the Exaltation of Water of Mercury.*—Fig. 78 represents an old man standing at a glass vessel in which a green dragon is devouring blue serpents. Above the dragon is the many-coloured symbol of Mercury. Above the vessel a green dragon



FIG. 78.—Kelly's Emblem (No. 5).

is biting its tail. In front a green lion bites the back of a red lion, so that blood runs down. To the right are woods and hills.

(6) *Of the Solution of Gold with Water of Mercury.*—Fig. 79 represents Sol in clouds surrounded by red rays, while a green lion bites the face of the sun, so that blood runs down. An old man holds a vessel, containing red liquid in which a winged figure is immersed up to his middle. Out of the vessel a green dragon is flying, which attacks Sol standing on a rock with Luna, biting his face till blood flows under the dragon into the



FIG. 79.—Kelly's Emblem (No. 6).



*Præparatione Lunæ Philosophicæ*

FIG. 80.—Kelly's Emblem (No. 7).

vessel. Under a black rock lies a green dragon, with its tail cut off, gnawing its wings.

(7) *Of the Preparation of Silver of the Philosophers.*—Fig. 80 represents a fire lighted under Sol, who is being consumed with much smoke. An old man holds a vessel, in which Luna is lying on her back under dark waves, while out of its mouth flies the green dragon, bearing in its jaws Luna held by the middle, and placing its fore-feet on a black rock. Under the rock a green dragon lies on its back dead.



FIG. 81.—Kelly's Emblem (No. 8).

(8) *Of the Conjunction of Gold and Silver.*—Fig. 81 represents Sol, very red, shedding his blood into a glass vessel. An old man pours from another vessel blood and a winged child into a third vessel, which stands in straw and contains Luna lying on her back in dark liquid. Near Sol is a jug from which white rays or drops are passing into a vessel. On the hill stands the phoenix biting its breast, from which its young receives drops of blood. Below the mountain a rustic is sowing grain in a field.

(9) *Of the Putrefaction of Gold and Silver after Conjunction.*—Fig. 82 represents Sol and Luna black. An old man with a book in his hand stands beside a furnace on a black pavement.





FIG. 82.—Kelly's Emblem (No. 9).



FIG. 83.—Kelly's Emblem (No. 10).



A vessel is in the furnace containing a black sun, and behind is a field green with barley (the symbol of fecundity).

(10) *Of the Iridescence of the Materials of the Elixir.*—Fig. 83 represents an old man near a furnace of which both towers are open, and which contains a vessel which constantly changes its colour. Behind the furnace the barley is producing ears (symbolical of ripening).

(11) *Of the Perfect Red Elixir.*—Fig. 84 represents an old



FIG. 84. —Kelly's Emblem (No. 11).

man in a tunic standing by a furnace, of which one tower is open. In the other tower is a glass vessel containing a purple Sol. We omit the symbol of the white elixir.

(12) *Of the Transmutation of Metals into Gold.*—Fig. 85 represents a king dressed in a purple garment like a pontiff, sitting on a throne, and at his feet, kneeling, are Sol, Luna, Venus, Mars, Mercury, Jupiter, and Saturn. Behind the king stands an old man with uncovered head.

Lastly, as an example of symbolic writing, we extract the



FIG. 85.—Kelly's Emblem (No. 12).

following account of antimony from Artephius Longaevus, translated by Salmon :—

“ Antimony is a mineral participating of Saturnine parts, and has in all respects the nature thereof. This Saturnine Antimony agrees with Sol, and contains in itself Argent Vive, in which no metal is swallowed up except gold ; and gold is truly swallowed by this antimonial argent vive.

“ Without this Argent Vive no metal whatsoever can be whitened ; it whitens Laton (*i.e.* Gold) ; and reduceth a perfect body into its prima Materia, or first matter (*viz.* into sulphur and argent vive), of a white colour, and out-shining a looking-glass.

“ It dissolves (I say) the perfect body, which is so in its own nature, for this water is friendly and agreeable with the metals, whitening Sol, because it contains in itself white or pure argent vive.

“ Therefore, saith the Philosopher, this water makes the body to be volatile, because after it has been dissolved in it, and in frigidated, it ascends above, and swims upon the surface of the water.

“ Take (saith he), crude leaf gold, or calcined with mercury, and put it into our vinegar, made of Saturnine antimony, mercurial, and sal armoniaek (as is said), in a broad glass vessel, and four inches high or more, put it into a gentle heat, and in a short time you will see elevated a liquor, as it were oil, swimming atop much like a scum.

“ Gather this with a spoon, or a feather, dipping it in, and so doing often times a day, till nothing more arise, evaporate away the water with a gentle heat, *i.e.* the superfluous humidity of the vinegar, and there will remain the quintessence, or powers of gold, in form of a white oil incombustible.

“ In this oil the philosophers have placed their greatest secrets. It is exceeding sweet, and of great virtue for easing the pains of wounds.

“ Our dissolving water therefore carries with it a great tincture, and a great melting or dissolving, because that when it feels the vulgar fire, if there be in it the pure or fine bodies of Sol or Luna, it immediately melts them, and converts them into its white substance, such as itself is, and gives to the body, colour, weight, and tincture.

“ In it also is a power of liquefying or melting all things that can be melted or dissolved. It is a water ponderous, viscous, precious and worthy to be esteemed, resolving all crude bodies into their prima materia or first matter, *viz.* into earth and a viscous powder; that is into sulphur and argentum vivum.

“ If therefore you put into this water, leaves, filings or calx of any metal, and set it in a gentle heat for a time, the whole will be dissolved, and converted into a viscous water, or white oil, as aforesaid.

“ Thus it mollifies the body, and prepares it for fusion and liquefaction; yea, it makes all things fusible, *viz.* stones and metals, and afterwards gives them spirit and life.

“ And it dissolves all things with an admirable solution, transmuting the perfect body into a fusible medicine, melting or liquefying, moreover fixing, and augmenting the weight and colour.

“ Work therefore with it, and you shall obtain from it what you desire, for it is the spirit and soul of Sol and Luna (*i.e.* gold and silver). It is the oil, the dissolving water, the fountain, the Balneum Mariae, the preternatural fire, the moist fire, the secret, hidden and invisible fire.

“ It is also the most acrid vinegar and the moving

instrument for putrefying, resolving and reducing gold and silver into their *prima materia* or first matter.

“It is therefore the only apt and natural medium by which we ought to resolve the perfect bodies of Sol and Luna by a wonderful and solemn dissolution with the conservation of the species, and without any destruction, unless it be to a new, more noble, and better form or generation, viz. into the perfect philosopher’s stone, which is their wonderful secret and arcanum.

“But more than that, it brings back bodies to their first original of sulphur and mercury, that of them we may afterwards in a little time (in less than an hour’s time) do that above ground which Nature was a thousand years a doing of under ground, in the mines of the earth, which is a work almost miraculous.

“He therefore that knows this salt of Sol and Luna, and its generation and preparation, and afterwards how to co-mix it, and make it homogeneous with other imperfect bodies; he in truth knows one of the greatest secrets of Nature, and the only way that leads to perfection.”

Enough has been said to indicate the general character of the symbolism of the alchemists. To protract the details would occupy space without corresponding benefit, because, after all, symbols and emblems were merely a phase of alchemy. They did not affect the art to any appreciable extent, although they had a considerable influence upon the form in which its principles were expressed. The subject is curious and rather fascinating, but in a history of chemistry unprofitable.

## CHAPTER XVI

### THE PHILOSOPHER'S STONE

WE shall close the Ancient History of Chemistry with an examination of that curious philosophical conception—the philosopher's stone. In doing so we shall endeavour to answer two questions—(1) In what manner did the old philosophers arrive at the conception of such an idea? and (2) in what manner did they attempt to impart reality to their theories? It will be necessary to repeat some things which have been said already, but it is better to risk repetition than to incur the danger of failing to make the subject comprehensible.

It may be said that all we have to do is to collate and digest the writings of the principal alchemists, and thus arrive at an understanding of their doctrine. But that is the very last thing that one should expect from the study of alchemical treatises. The authors of these treatises did not intend that the doctrines should be readily understood. This has been the experience of all who have made a thorough investigation of the subject. It is no wonder that John Pontanus complained, “after travelling through many countries that I might know the certainty of the philosopher's stone, I found many deceivers, but no true philosophers”; and again, “they have erred and they will err, because the philosophers, Artephius only excepted, have concealed the principal or proper agent, and unless I had read Artephius, and sensibly understood his speech, I had never arrived at the complement of the work” (Pontanus, *Lives of the Adepts*, p. 230).

When we refer to the writings of Artephius Longaevus, recommended by Pontanus, we do not find that they help us in our quest. The *Secret Book* and *Clavis Sapientiae* indicate various ways of getting and applying different degrees of heat, but the



directions which they contain are mainly obscure methods of dissolving gold and silver, either in mercury or in acids, mixing the product with other substances, and thus forming amalgams, alloys, or salts. We do not learn more than we do from the mediæval authors who wrote in Latin, and whose writings, as we have seen, are mystical, confused, ill-arranged, and often nonsensical.

The idea which was universal amongst the scholastic writers of the Middle Ages, that the metals are all one substance variously modified, was derived partly from the peculiar philosophical notions of the Greeks concerning the constitution of the universe, and partly from the peculiarities of the Egyptian written language. Reference has already been made (*supra*, p. 12) to the hieroglyphic writing of Egypt. In this language, besides phonetic signs representing alphabetical letters or syllables, almost every noun or word was followed by an *ideographic sign*, which was either a picture of the object named, or a conventional symbol. It represented the *class of ideas* expressed by the noun or word. In Fig. 5 some of the more common hieroglyphs are depicted. Amongst others will be seen two examples of ideographic or determinative signs—a figure of an ox, and the representation of a hide, which was the symbol of all quadrupeds. Others are shown determinative of trees, minerals, stones, plants, and houses. A series of parallel waved lines was the ideographic sign determinative of all liquids, and was introduced after the letters of words signifying drink, wash, thirst, rivers, etc.

Egyptian scholars were accustomed by the use of these words and signs to conceive that something expressed by the ideograph was present in each member of the class of things to the name of which that symbol was attached, and this conception is similar to the notion of the alchemists that there was an essence common to all metals, which was purer in the more noble metals than in the baser. We must, therefore, go back to the work of the Egyptian laboratories, as disclosed in the earliest Greek manuscripts, in order



that we may discover the original conception of the philosopher's stone.

In these papyri we have the oldest record of chemical operations of a technical character that has as yet been discovered. From them we learn what was done in the oldest workshops and laboratories of goldsmiths, silversmiths, jewellers, dyers, enamellers, and others engaged in practical work. There are many recipes for the manufacture of *asemus*; for the doubling or duplication, in other words, the sophistication, of gold, silver, and *asemus*; for rendering silver like gold; for writing in gold; for making alloys; for hardening lead, tin, etc.; for purifying metals; for whitening copper, and for the preparation and use of purple colours.

When Mr. Leemans, Director of the Antiquarian Museum at Leyden, in 1885, published a translation of these old recipe books some difficulty was caused by the occurrence in the Greek text of the word "*asemos*," a term then unknown to classical scholars. On investigation it was found to be the Egyptian "*asem*" furnished with a Greek termination, and represented an alloy which the Romans called "*electrum*." Pliny says (*Les Origines de l'Alchimie*, pp. 216—217) that gold contains silver in varying proportions, and that if the quantity of silver equals one-fifth, the substance is called *electrum*. *Asemus* or *electrum*, therefore, where it was not found as a mineral, was properly prepared by alloying gold with silver, and was an intermediate between these two metals, varying in quality. But the word soon came to be applied to a variety of compounds more or less resembling gold and silver.

Thus we discover by a comparison of the Leyden Papyrus X. and the MS. of St. Mark that *asemus* might be not only an alloy of gold and silver, but an alloy of silver and tin; an amalgam of tin; pure tin; an alloy of tin and lead; refined lead with much silver in it; an alloy of silver and lead; an alloy of tin and copper; an alloy of silver, tin, and copper; or an alloy of copper, lead, zinc, and tin. But although its

composition and mode of preparation varied, it was always supposed to be the same substance or metal, and to have one remarkable property, namely, that it could be transformed either into pure gold or pure silver, that is, *it could be made to look like either*.

Asem was, in fact, the analogue of our modern Britannia metal and German silver. Many similar compounds have been devised. Britannia metal consists of copper 80 parts, lead 4, tin 10, and zinc  $5\frac{1}{2}$ . The Chinese have from the most remote period made a material called "pakfong" or white copper, which contains copper 3 to 5 parts, zinc 1, nickel 1, and a little lead. It was also called "tutanag," a term etymologically connected with "tutie," used in the formula of the crab (*supra*, p. 45). It was probably the gong metal of the Chinese. In India an alloy was prepared composed of copper 16 parts, lead 4, tin 2, and zinc 16.

The constant recurrence in alchemical writings of recipes for the preparation of *asem* or *asemus* is remarkable. From a study of the books of practical recipes we learn that instructions for the preparation of this substance, various in form and detail, were reproduced century after century. Whether these old artificers believed that their alloys were really gold and silver of inferior quality, or whether they were deliberately cheating their customers, it is easy to perceive how there arose in their minds the idea that, if they only knew the way, it should be quite possible to manufacture from inferior materials a pure gold and a pure silver. Their handicraft mainly consisted in the manufacture from the cheapest materials that would serve their purpose, something which would pass for gold and silver. For finer purposes they had to refine their alloy more, and as they probably considered these alloys as in fact single substances, it was natural for them, after acquiring by trial and experiment a number of recipes for producing recognised substances of more or less value, to endeavour to produce from these the highest quality of the noble metals.

In considering the morality of these ancient jewellers we

must bear in mind that they believed in the unity of matter, and hence they regarded all metals as being essentially identical. Therefore, in performing the diplosis of gold by alloying it with copper and tin, they did not deem, as we would, that the gold was being falsified. Tin and copper were to them a less pure gold, and they thought they converted the less pure into a more pure gold by uniting it with the metal which we call gold. The false philosophy which characterises the theoretical writings of the alchemists was the result partly of ignorance of the real nature of the materials they were describing and the forces they wished to employ, and partly of a pagan belief in a connection between the properties of the metals and a number of deities whose good offices they hoped to secure.

The best extant definition of the philosopher's stone is probably that contained in Salmon's *Bibliothèque des Philosophes Chimiques*, a collection re-edited in the sixteenth century. It is there defined as "the universal medicine for all imperfect metals, which fixes that which is volatile, purifies that which they have impure, and gives a colour and a lustre more brilliant than Nature." In considering this subject, therefore, we must never forget that transmutation was a process for giving perfection, and that this "giving of perfection" was the constant aim of the alchemists.

We ought to note what Roger Bacon says on this subject: "Looking at the qualities of gold, we find that it is of a yellow colour, very heavy, and of a certain specific gravity, malleable and ductile to a certain degree. Those who would know the formulæ and processes necessary to produce at will the yellow colour, the great specific gravity, the ductility, etc., and those who would know the means of producing these qualities in different degrees, would use the means, and would take the measures necessary to unite these qualities in such and such bodies. Whence would result its transmutation into gold."

We can easily perceive that the belief in such doctrines led naturally to the search for the philosopher's stone. The

alchemists treated the symptoms of the metals as a doctor treats those of a sick man, when he does not know the cause of his patient's illness. They tried to remove the symptoms of illness and induce those of health, or as they said, of perfection. They thought that by altering the properties of a metal they altered its nature, and transmuted it, just as they might produce steel from iron, or bronze from copper and tin. They had various methods of altering the properties of a substance, and amongst these a very important operation was *purification*, by which they hoped to remove the imperfect qualities of the base metal.

One of the methods of purifying or perfecting silver from lead was repeated calcination, quenching in sal ammoniac or vinegar, distilling, and calcining again. Now, although it is ridiculous to suppose that calcining removed any of the impure sulphur, or the impure mercury, of the lead, leaving a purer and more noble metal, and thus effecting its transmutation into silver, the process was probably founded upon a chemical fact. Many lead ores are argentiferous, and hence much of the lead in use was also argentiferous. At some time or other an operator had calcined and treated such argentiferous lead, until most of the lead was removed, and thus he had obtained a tolerably good alloy of silver, which became the purer the more he calcined it. He was quite justified, in the light of his philosophy, in believing that he had transmuted lead into silver. Conversely, by debasing silver through alloying it again with lead, he made an inferior silver, which was still in his opinion the same substance.

The conception of the philosopher's stone, therefore, originally arose from the practical work of goldsmiths in making debased gold and silver, or spurious imitations of them. This work being confined to members of the royal and priestly house, great revenues were derived from the art. But the writers of text-books in later times, losing touch with practical men and absorbing false philosophical notions from Greek ideas, evolved from the inner consciousness of the philosophers,

and promulgated without the slightest attempt to test by experiment the truth of the assumptions, drifted further and further from a knowledge of laboratory work. The consequence was that their writings became the nonsense which we read in the books of the fourteenth century and later. Although derived from real recipes, their directions for work, when they gave any, which was seldom, were as a rule quite unintelligible. In the end, transmutation by means of a universal medicine which would heal and ennoble diseased metals was discredited by common experience, and quackery was transferred from the metallurgists to the apothecaries.

It is but just to say that not all of those who professed to transmute metals and to manufacture gold deceived themselves, or imposed upon others. Many of them were quite frank in their assertions on the subject. Thomas Aquinas candidly says that the gold of the philosophers is not the same as the gold of Nature, but only a less valuable and useful imitation.

The following recipe for the philosopher's stone, taken from Joannes Isaacus Hollandus' treatise, *Hand der Philosophen* (*supra*, p. 103), plainly indicates its character, since it is one of the few recipes which are expressed in intelligible language, and can be followed in the laboratory. It also incidentally shows what was meant by the term "projection." The word "silver?" is represented by a crescent moon:—

"Take one ounce of fine silver, dissolve it in common A.F. (aqua fortis), then add four ounces of sublimed mercury to it in a glass pot. Set it on warm sand and let it become hot, then soak it with the aqua fortis in which the silver is dissolved until it has drunk up all the aqua fortis. Then let it cool. Pound this mercury quite fine on a hard stone. Let it dissolve of itself upon the stone, then coagulate again upon a small fire in a glass. Rub it down again as before, and dissolve as before, and so on seven times. Of this elixir project (or throw) one ounce upon 31 ounces of prepared and well melted copper. So you will have fine silver, standing all tests."



Hollandus then goes on to explain that mercury alters all metallic bodies with arsenic to silver, and with sulphur to gold.

The present author prepared bars of metal according to this recipe of Hollandus, using the following formulæ :—

(1)  $\frac{3}{4}$  oz.  $\text{AgNO}_3$  and  $\text{Hg}_2\text{NO}_3$ .  
8 oz. Cu.

(2) 1 oz.  $\text{AgNO}_3$  and  $\text{Hg}_2\text{NO}_3$ .  
 $1\frac{1}{2}$  oz. Pb.  
8 oz. Cu.

(3) 1 oz.  $\text{AgNO}_3$  and  $\text{Hg}_2\text{NO}_3$ .  
 $\frac{1}{2}$  oz. Pb.  
1 oz. Sb.  
3 oz. Cu.

(4)  $\frac{1}{4}$  oz.  $\text{AgNO}_3$  and  $\text{Hg}_2\text{NO}_3$ .  
 $1\frac{1}{2}$  oz. Pb.  
2 oz. Sb.  
8 oz. Cu.

This composition (No. 4) was *rapidly cooled* by immersion in cold water.

(5) Same composition as No. 4, but *cooled slowly*.

These bars were, of course, not “pure silver standing all tests,” as Hollandus expressed it, but metallic alloys, of a more or less silvery lustre.

As indicating how the mechanical processes of gilding and silvering, and preparing imitations of gold and silver, led up to the conception of a universal elixir which would effect transmutation, we shall copy out a few recipes from the old authors.

We shall first take a Syriac version of the process for gilding silver, that is, making it look like gold (Berthelot, *Syriac and Arabic*, p. 154) :—

“ You take 10 drachms of the eagle (sal ammoniac), 10 drachms of barond (nitre), 10 drachms of verdigris, and 30 drachms of vitriol of copperas (green vitriol), in all 60 drachms, and then the total weight of virgin vinegar. Next plunge these ingredients in the vinegar, heat in a gentle fire until there remains only one part of the liquid. Filter this water separately into a clean bottle. Then take one drachm of silver filings, coat them with 3 drachms of mercury, until



they become like peas. Take next an iron spoon, place in it this mixture, and heat it on a gentle fire one whole day, until no liquid remains. Remove the mixture from the fire, and let it cool. Take 4 draehms of verdigris, and knead them with 5 draehms of water, like strong earth. Put the mixture into it, and make it into a lump like a nut. Cover with the philosopher's lute, and let it dry in the shade. Cook it on a convenient fire during the night. Urge the fire until the product melts. Then the mercury will disappear, and there remains silver coloured yellow, according to the standard of Djemâl-ed-Din."

Another recipe for the preparation of gold is from the Syriac copy of the book of Pseudo-Democritus :—

"(1) Take mercury and fix it with the body of magnesia, or with Italian antimony, or with red sulphur, or with selenite, or with lime, or with alum, or with arsenic, or how you please. Prepare two crucibles, heat and project on the mercury. Examine if the rust is red. Project it on silver and it will produce gold. If it is projected on gold, one gets the coral of gold. (2) The same result will be obtained by red sandarach and arsenic, in making them act on the body of magnesia, chrysocolla, and red ciunabar. Copper is deprived of shade only by mercury with the help of vinegar."

The recipe, " asem 1 part, or copper of Cyprus 3, gold 4 ; melt together," is simply a preparation of debased gold.

The following is given as a recipe :—

"To gild silver in an admirable manner : Take mercury and leaves of gold, and make them of the consistence of wax. Take a silver vessel, wipe and clean it with alum, and taking a little of the waxy substance rub it with the polisher, and let the substance fix itself. Do this five times. Hold the vessel with a rag of clean lincn, in order that it may not be soiled, and taking some burning coal, prepare the ashes, smooth it with the polisher. Then treat it as a gold vessel. It will stand the test for gold."

In Berthelot's *Alchemistes Grecs*, Vol. I., p. 40, we find the following recipes from a Leyden manuscript of the second century :—

"(51) *To render silver like gold* : Pound misy (basic sulphates

of iron and copper) with sandarach (realgar) and cinnabar (oxide of lead); and rub therewith the silver article. (55)  
*How to prepare golden silver*: Dilute cinnabar (oxide of lead) with alum, pour on them white vinegar, and having brought the whole to the consistence of wax, express several times, and let it stand all night."

The passage ends here, but it is plainly a recipe for making a silver article resemble gold; there is no pretence that the article is transmuted into gold. As we have already mentioned, minium was often confused with cinnabar, as in this instance.

But in the *Physica et Mystica* of Pseudo-Democritus (of the fourth century) we have practically the same process stated as a method of transmuting silver into gold:—

"Make cinnabar (oxide of lead) white by means of oil, or vinegar, or honey, or brine, or alum, and then yellow by means of misy (basic sulphates of copper and iron), or of copperas (ferrous sulphate), or of sulphur, or as you please. Throw the mixture on silver, and you will obtain gold, if you have coloured it golden. If it is copper, you will have electrum, for Nature delights in Nature."

Here, then, we find a recipe which in an ancient technical book was given for a real process, namely, gilding a silver vessel—repeated in a philosophical treatise some centuries later in more detail, but still the same recipe—as a *method of transmutation*.

Alchemists, we have said, were led to this erroneous idea by the study of Greek philosophy. They thought that the various forms of asem, although made with different metals, were merely different forms of a single substance. Now, the Greeks imagined the existence of a primordial matter, which Thales taught was water, and Anaximenes said was air. Zosimus, who had a great influence on alchemy, recognised the permanence of this primordial matter. Everything, he said, was formed from a single essence, eternal and immovable. Empedocles in the fifth century B.C. tried to reconcile the permanence of things with their continual change in appearance. He taught that the elements of which all things are composed

have four properties (called elements) which are imperishable : fire, air, earth, and water. Aristotle followed him and added a fifth element named ether, or, as it was afterwards called, quintessence. In like manner Plato and the Alexandrian School recognised the primary matter which was not composed of the four elemental properties, but which received the forms of these four properties.

According to Plato, the elements could change into each other, an idea which may have arisen from the fact that matter can exist in three forms, solid, liquid, and gaseous. The elemental property of fire was conceived to be present in all combustible substances such as carbon, sulphur, and the metals.

All these false assumptions favoured the development of the conception that metals are a single substance variously modified ; in short, in the words of the ancient alchemists, that " one is all."

On the discovery of mercury, more than 300 years B.C., it immediately took an important place in the theories of the alchemists, from its striking properties and its power of combining with most other metals. Theophrastus mentions its use in dissolving gold for gilding. Resting on the foundation of the observed qualities of metallic mercury, speculative writers raised a theory that all metals contained more or less of a volatile property, which they termed *Mercury of the Philosophers*, or Philosophical Mercury. The almost invariable use of mercury in attempts to transmute metal originated in two circumstances : its practical use as a solvent, and the false theoretical assumptions in regard to it. Hence also originated the constant efforts of the alchemists to fix mercury by imparting to it earthy properties, that is to say, the elemental property of *earthiness* or *solidity*, by treating it with substances which were rich in such properties.

But the use of mercury and also of orpiment was connected with another idea derived from a mistaken analogy with the processes of dyeing. Among the Greek alchemists there were

two fundamental operations, *leucosis* or colouring white, and *xanthosis* or colouring yellow. To these were sometimes added *melanosis* or colouring black, and *iosis* or colouring violet. They thought that by altering the colour of a metal, its properties, but not its nature, were changed, just as they might dye a skin purple, yet it would still remain a skin. As mercury whitens metals, there was another inducement to use it as a first step in transmutation. They whitened copper, then coloured it yellow, and so made what they called gold. In the words of Synesius: "Mercury whitens everything and attracts the soul of everything. . . . It changes all colours and subsists itself, while they do not subsist; and even if it does not subsist in appearance, it dwells in the bodies of things."

It has to be observed, however, that while there were many colouring matters, one for copper, one for silver, one for gold, and so forth, according to the diversity of metals, yet these were held to form but one species. From this they inferred that there was but one philosopher's stone.

After the eighth century arose the doctrine, founded solely on imagination and assumption, and without any attempt at experimental proof, that the combustible part of a metal was a species of sulphur, which all metals possessed in various quantities and of various degrees of purity. This doctrine has been attributed to Geber on the authority of Latin books purporting to be translations of his Arabic treatises. These books are forgeries, but the fraud was not discovered until long after the alchemical period, and consequently the theory of sulphur, resting upon such venerable authority, gained almost universal respect and belief.

Mercury and sulphur in their philosophical form were believed to be the elemental properties of metals, which they possessed in varying degrees of quantity and purity. Gold was formed of a purified mercury associated with a small amount of a pure sulphur. Philosophical mercury and sulphur were quintessences, much more subtle than the natural substances that bear their names.

At a later date, salt was considered essential to transmutation, not any particular salt, but salt as an earthy body possessing the property of solidity. It was designed to impart to the baser metals solid non-volatile properties, because the alchemists had observed that in the fire gold is permanent.

Having discussed the probable origin of the conception of the philosopher's stone, we shall now inquire what was the nature of that conception and in what way did the adepts proceed to carry out what they deemed their *magnum opus*.

We have already seen that the alchemists by the term elixir, magisterium, medicine, or philosopher's stone, understood a compound which was supposed to possess the power of transmuting the baser metals into gold or silver. Of this substance they recognised two sorts—a white powder transmuting metals into silver and a red powder transmuting them into gold. The Greeks expressed these processes by the words "leucosis" or whitening and "xanthosis" or yellowing, but as we have seen, these terms were at first undoubtedly working descriptions of processes for making metals look like silver or gold. As centuries passed away, the alchemists became more and more extravagant in their visions, and added to the original idea of transmutation various other powers, such as making precious stones, curing diseases, prolonging life, and controlling elemental spirits. The philosopher's stone could preserve health, raise the dead, make the old young, turn the coward into a hero, strengthen the memory, and sober the drunkard!

The materials composing this wonderful elixir have been described both theoretically and practically. As an abstract conception, the alchemists assumed that the material of the stone had—

4 angles in its virtues—fire, air, water, and earth.

3 angles in its substance—mercury, sulphur, and salt.

2 angles in its matter—the fixed and the volatile.

1 angle in its radical principle—the *prima materia*.

As the sum of those angles is 10, that number in the Cabala was held to express the material of the philosopher's stone.



These principles of deductive philosophy would have done little harm to the progress of chemistry had the alchemists not added another. The matter of the stone, they said, was mineral, animal, and vegetable. Misled by this symbolic expression, the laboratory workers, instead of prosecuting the study of metals, in which they might have hoped to make valuable discoveries, spent their time in vain distillations and examinations of all sorts of animal and vegetable matter, in the hope of discovering what was wanting to complete the material for the *magnum opus*. It is scarcely needful to say that in the ancient condition of knowledge, and with the ancient forms of apparatus, the study of organic chemistry was totally beyond their powers, and so their labours produced little fruit.

Although it was obvious that according to all the rules of their own philosophy, metals alone could produce metals, much time was wasted in this manner; but ultimately the opinion prevailed that the philosopher's stone must be produced by the union of metals, and *à fortiori* of the perfect metals gold and silver. Hermes had indicated this in the smaragdite tablet (*supra*, p. 92) when he said: "The sun (*i.e.* gold) is my father; the moon (*i.e.* silver) is my mother." To the perfect metals they added ordinary mercury, as we read in Libavius (*Paraphrasis Arnoldi*): "Gold, silver, and mercury constitute the material of the stone, after they have been prepared according to the art." The theory was that philosophical sulphur was obtained from the gold, philosophical mercury from the silver, and philosophical salt from the common mercury. By the union of these three principles they hoped to perform the great work. Gold and silver, when prepared for the *magnum opus*, were termed "gold and silver of the philosophers," and deemed to be purer than the ordinary metals, more free from dross and alloys, and more powerful in operation.

Purification was thus one of the most important operations of alchemy, as by purifying metals the alchemists deemed that they increased their perfection. Gold was purified by "cementation" or by the use of antimony; silver by cupella-



The  $\uparrow$  by the use of lead. Natural gold, such as is found in the form of gold dust, was considered sufficiently pure without further treatment. The process of cementation was performed in this way—a paste was prepared of four parts brickdust, one part of calcined ferrous sulphate (green vitriol), one part common salt, and a sufficiency of water. The gold and paste were arranged in the crucible in alternate layers, and the mass melted together.

Having purified the gold and silver, the alchemists proceeded to dissolve them. There was no point upon which they were more secretive than the nature of the *aqua vite* or solvent which they employed, but it is apparent that by the term they meant, in the case of gold, *aqua regia*, and in the case of silver, either nitric acid or sulphuric acid. The solutions were crystallised, decomposed by heat, and the product again dissolved. The ordinary mercury was used in the form of bichloride, which they called "corrosive sublimate."

There were two stages in the "work," as it was called. The small work, or small magistry, was performed by means of philosophical mercury, that is, salts of silver; the elixir was white, and had power to transmute metals into silver. The great work, or great magistry, was performed by means of philosophical sulphur and mercury, that is, salts of gold and silver; the elixir was red, and had power to transmute metals into gold. The same process produced both elixirs, but was more prolonged in the second instance.

To speak plainly, the materials for the work were gold trichloride, silver nitrate, and mercury bichloride. This mixture was enclosed in a glass matrass called the "philosopher's egg," which was hermetically sealed by fusion of the neck. The name of this vessel was no doubt derived from the idea that the philosopher's stone was hatched from it, like a chicken from an egg. Sometimes a double matrass was used, with the necks communicating but hermetically sealed together. As the materials were in the one, the vapours could escape into the other, and thus the risk of explosion was

considerably reduced. In spite of all precautions, <sup>tion, or</sup> we have done that in the great majority of cases the egg collapsed before the completion of the process. Every chemist knows how liable glass vessels are to crack or split, and when we remember that the egg was exposed to a certain degree of heat night and day for months, it is a matter for wonder that any alchemist was so fortunate as to carry on his work to the end.

The egg and its contents were placed upon a sand bath or a Bain Marie, and the whole set upon an athanor. The expression "the three vessels" means the philosopher's egg, Bain Marie, and athanor. The method by which a uniform and steady heat was maintained was most studiously concealed, but the alchemists seem to have employed an oil lamp with a wick composed of amianth or flexible asbestos. Such a lamp kept up a regular heat, which could be increased or reduced by altering the number of strands composing the wick. The heat began at 140° to 160° Fahrenheit, and was to be such that the operator might lay his hand upon the egg without burning himself. The second stage was between the boiling point of water and the melting point of ordinary sulphur; the third stage a little under the melting point of tin; the fourth stage a little under the melting point of lead. These temperatures had to be maintained for periods extending to months.

There is no unanimity among the alchemists as to the number of operations comprised in the work, but all admit at least four—(1) the preparation of the materials; (2) the decoction in the egg; (3) fixation and fermentation to impart power; and (4) transmutation. During the process of decoction certain chemical changes took place in the materials—(1) conjunction, or the union of the philosophical mercury and sulphur; (2) putrefaction, when the mass became black; in accordance with the theory that life springs from putrefaction; (3) ablution, when the mass turned white, and life was said to be restored; and (4) rubification, when the mass became red, indicating perfection.

The process had to be made to imitate as closely as possible the operations of Nature, and therefore had to be prolonged. Philalethes divides the whole into seven stages, and gives the periods as under :—

- |                                   |             |
|-----------------------------------|-------------|
| (1) The reign of Mercury . . . .  | 50 days.    |
| (2) The reign of Saturn . . . .   | 40 ,,       |
| (3) The reign of Jupiter . . . .  | 21 ,,       |
| (4) The reign of the moon . . . . | 21 ,,       |
| (5) The reign of Venus . . . .    | 40 ,,       |
| (6) The reign of Mars . . . .     | 45 ,,       |
| (7) The reign of the sun . . . .  | not stated. |

Without counting the indefinite seventh stage, the process must have occupied no less than 217 days, or over seven months !

The colours assumed by the mass in the egg were always regarded as important. The appearance of the proper colour at the right time indicated the successful progress of the work. The Greeks recognised four colours, and arranged them according to the cardinal points :—

Melanosis	Black	North.
Leucosis	White	West.
Iosis	Violet	South.
Xanthosis	Yellow or red	East.

The later alchemists grouped them according to their sequence :—

- |   |  |
|---|--|
| (1) Prior to putrefaction . . . .             | a confused mixture.                          |
| (2) At putrefaction . . . .                   | black.                                       |
| (3) Between putrefaction and ablution . . . . | gray.  |
| (4) At ablution . . . .                       | white.                                       |
| (5) Between ablution and rubification . . . . | green, blue, iridescence, yellow and orange. |
| (6) At rubification . . . .                   | red.   |

Black, white, and red were the principal colours. A fanciful attempt was made to connect the colours and the elements—

black corresponding to air, white to earth, yellow to water, and red to fire, but this scheme had little authority.

When the mass in the egg became red, perfection was held to be attained. The vessel was broken and the powder collected. It was next subjected to a peculiar operation called fixation or fermentation, designed to increase its powers and the rapidity of its action. A small quantity of gold was heated in a crucible, and a little of the powder projected or thrown upon it. This was immediately absorbed. More powder was projected and the heat forced, until the whole mass was converted into a substance resembling red lead.

The perfect philosopher's stone was a red powder, heavy and glittering, which when projected upon a plate of metal raised to a red heat, melted without producing smoke.

One part of this elixir projected upon 100 parts of pure silver was supposed to produce excellent gold. This operation was the crown of the work, and was thus performed : A quantity of base metal, lead, tin, or ordinary mercury, was heated in a crucible, and a small portion of the philosopher's stone or red elixir was wrapped in wax, and thrown upon the heated metal. On cooling, the mass was found to be an ingot of pure gold equal in weight to the base metal employed.

When we reflect upon this remarkable conception, and consider the philosophy and aims of the alchemists, we perceive how foolish it would be to attempt to sum them up in a single epithet. The men belonged to distinct classes. There were mystical or religious alchemists who made use of terms of art merely as parables, and alchemical processes as allegories. Their real subject was the human soul ; their true object the guidance of mankind to salvation. But these were few. There were philosophical alchemists, steeped in the doctrines of Aristotle, who sought by the transmutation of baser metals into gold to prove their great thesis—the unity of all things. There were scientific alchemists, whose desire was to discover the properties and combinations of metals, and the best methods for their manipulation. And there were mercenary

alchemists, who hoped to find in the philosopher's stone the key to a store of unlimited riches. Unless we keep these distinct classes in mind, and differentiate clearly between them, we shall never understand all that is implied in the title "alchemist."

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# PART II

## MODERN HISTORY

### CHAPTER XVII

#### THE IATROCHEMISTS

(From 1500 A.D. till 1700 A.D.)

#### 1. BASIL VALENTINE TO OSWALD CROLL

THE Modern History of Chemistry may be said to have begun when the alchemists altered their point of view—when they applied their minds to the search for knowledge instead of the search for gold. The peculiarity of the *Iatrochemical Period* is the tendency of chemistry towards investigating and producing new medicinal preparations by chemical means, and forming other chemical compounds in the search for new medicines, in place of a tendency towards searching for the philosopher's stone, which was the peculiarity of the *Alchemical Period*. The iatrochemists, chemist-physicians, or chemist-apothecaries, devoted themselves mainly to the attempt to discover the *Elixir Vitæ* or universal medicine, a quest as hopeless as that of their predecessors, yet they did not altogether give up the older quest, and the search for the red elixir or philosopher's stone continued to engage the attention of chemists during the whole Iatrochemical Period, which endured from the first quarter of the sixteenth century till the middle of the seventeenth, or a little later.

It must not be forgotten, when dividing the history of chemistry into periods, that the peculiarities assigned to each period are not to be regarded as being anything more than



general characteristics. Thus, alchemical ideas extended far down into the Iatrochemical Period, so that we find Van Helmont declaring that he believed in the transmutation of metals, and that he possessed a small portion of the philosopher's stone. This attitude was characteristic of those chemist-physicians of the seventeenth century who practised medicine according to the old traditions. On the other hand, those who followed Roger Bacon in the study of theoretical chemistry for its own sake, or who made technical applications of it, tended rather in the direction of our modern views, even prior to the close of what we term for convenience the *Iatrochemical Period*.

The iatrochemists carried to excess their efforts to give an explanation of everything which happened in the human body and in Nature; but their explanations were fanciful and founded either upon complete ignorance or entire neglect of facts. Their contributions to the philosophy of chemistry were meagre; their additions to our knowledge were the fruits of their practical research. In this respect the period is in marked contrast to the next, the Phlogiston Period, which is memorable for the development of a rational theory of chemistry, which, although wrong, is not so far wrong as may appear to a modern student at first sight, if he were to interpret the language of its exponents in the sense which the words bear nowadays.

Before it reached this enlightened period chemistry underwent a long process of development in the hands of the iatrochemists, whom we are now about to discuss. The following list contains the names of the most prominent of that school:—

Basil Valentine	.	.	.	<i>circa</i>	1394—1450
Francis Anthony	.	.	.	.	1550—1623
Andreas Libavius	.	.	.	.	1540—1616
Angelo Sala	.	.	.	.	1575—1640
John Baptist van Helmont	.	.	.	.	1577—1644
Daniel Sennert	.	.	.	<i>circa</i>	1575—1625
Oswald Croll	.	.	.	.	1580—1609
John Rudolph Glauber	.	.	.	.	1604—1668
Thomas Bartholin	.	.	.	.	1616—1680
Werner Rolfinck	.	.	.	.	1599—1673

Christopher A. Baldwin . . . .	1600—1682
François de la Boe . . . .	1614—1672
Otto Tachenius . . . . <i>circa</i>	1620—1690
Adrian von Mynsicht . . . .	1603—1638
Christopher Glaser . . . . <i>circa</i>	1615—1673
Johann Konrad Dippel . . . .	1673—1734
Thomas Willis . . . .	1621—1675
Johann Kunckel . . . .	1630—1715
Nicolas Lemery . . . .	1645—1715

In addition to these, several men whom we have included in the Alchemical Period were iatrochemists as well as alchemists. Of these we may mention Paracelsus (p. 108), Erastus (p. 113), who although he opposed Paracelsus was an advocate of chemical medicines, Thurneysser (p. 113), Ulstadt (p. 122), Sir Kenelm Digby (p. 125), and Hermann Conring (p. 127).

On the other hand, we mention in this chapter for the first time one who might have been included among the alchemists—Basil Valentine (*circa* 1394—1450). We have deferred consideration of this man till now, partly because his reputation rests upon his advocacy of the medicinal virtues of antimony, and partly because he is a mythical personage, and there is reason to believe that the writings attributed to him are the work of an anonymous author of the Iatrochemical Period.

Basil Valentine is said to have been born at Erfurt in Saxony, and like many another adept, to have entered the Church. He is alleged to have been a monk of the Benedictine Order in his native town, but his name has not been found in the lists of the Brethren preserved at the convent or at Rome. His biography is made up of several more or less improbable legends. Olaus Borrichius tells us that Valentine left his writings hidden in a wall or pillar of the church at Erfurt, and that they were discovered long after his death through their hiding place having been burst open by a thunderbolt. The only truth in this tale is probably the circumstance that the works were not published till 1602, or nearly two hundred years after Valentine's death, but whether they were only then discovered, or

whether they were only then written, are questions which it is now impossible to answer with confidence.

Another curious story about Valentine, which has acquired a considerable measure of belief, relates to the derivation of the name of his favourite metal—*antimony*. The story goes that some refuse antimony having been thrown to the convent pigs, the animals ate it greedily, and after the dose grew fat and throve. Thinking that what was good for the hogs would be good for his brethren, he administered a dose to the monks with serious (some say, with fatal) results. Hence the substance got the name of *anti-moine*, or monk's enemy. A little thought will show the absurdity of this derivation. Valentine was a German, not a Frenchman, and antimony was called by him "Speissglanz." Under these circumstances the point of the tale is lost.

About two dozen books stand in the name of Basil Valentine. Of these the most important is *Currus Triumphalis Antimonii* (The Triumphal Chariot of Antimony), and one of the best English editions is the translation of the work and of the notes by Theodore Kirkringuis or Kerekringuis, made by Edward Russell, in 1678. It is an excellent book, far too good indeed for the time of its reputed author. In clear and precise terms it sets down all that was known about antimony prior to the discoveries of the nineteenth century.

The writer of these books, whoever he was, had a wide knowledge of chemical compounds. He understood the preparation of hydrochloric acid, which he called *spirit of salt*, by the distillation of common salt with sulphuric acid. He knew arsenic and its sulphide, realgar; zinc in its compound, if not its metallic state; bismuth, which he sometimes termed marcasite; the red oxide, nitrate, and bichloride of mercury (corrosive sublimate); antimony and its compounds; the acetate, yellow oxide, and white carbonate of lead; and of the iron salts, ferrous sulphate (green vitriol) and the double chloride of iron and ammonium. He obtained metallic mercury by distilling corrosive sublimate with chalk. He discovered

fulminating gold. He precipitated metallic solutions by alkali ; copper by iron ; and gold by mercury. Lastly, he experimented with spirits of wine, which he combined with nitric or hydrochloric acids, and used for dissolving the caustic alkalis.

Turning to his philosophy, we find that he was as bitter against the physicians of his day as Paracelsus. He believed that there is an analogy between the purification of gold and the cure of disease, and maintained that antimony is sovereign for both. He asserted that the metals are composed of the mercury and sulphur of the philosophers, to which he added philosophical salt. The philosopher's stone, he said, is composed of the same materials.

We have devoted a considerable space to Basil Valentine, on account of the reputation which he enjoyed in the Middle Ages, a reputation second only to that of Paracelsus. But in truth his works do not merit the deference they received, and as the knowledge imputed to him is almost certainly not his, but belongs to a far later period, it is needless to enter into a more lengthened exposition of his views. The best advice which can be given to the student of chemical history is to receive with caution all that is said about Basil Valentine in text-books and histories.

Francis Anthony or Antonio (1550—1623) was an unlicensed practitioner, who advocated chemical medicines, and sold a *panacea aurea* after the fashion of Paracelsus. He strongly maintained the virtues of *aurum potabile* (liquid gold), and wrote a book entitled *Medicinae Chymicae et Veri Potabilis Auri Assertio* (1610). Another tract, *De Lapide philosophorum et Lapide Rebis*, related to the older alchemy. It will be remembered that in alchemical symbolism "Rebis" was the name given to the hermaphrodite figure representing the union of the great philosophical principles, sulphur and mercury, in the operation of making the philosopher's stone (*supra*, p. 157).

It is refreshing, among the many vain theorists and dreamers of those days, to come upon a man who was a theorist indeed, but also an acute observer and accurate experimenter.

Andreas Libavius (1540—1616) was one of the pioneers of chemical science, and the first author who wrote a really valuable text-book of chemistry. He practised medicine at Halle in Saxony and at Jena, and was a professor in the gymnasium of Coburg. As a physician he was an unflinching opponent of Paracelsus ; as a chemist he was an earnest seeker after truth. He was so far the child of his age that he believed in the possibility of the transmutation of metals and in the virtue of *aurum potabile*, but he was so far in advance of it that he was able to distinguish between the mystical and the practical, and to make discoveries which enriched the science. Much of his time was wasted in useless controversy. He thought it his duty to expose the quackery of his contemporaries, and as the quacks were numerous and vindictive, the struggle was continuous and bitter.

His *System of Chemistry*, published at Frankfort in folio in 1585, and in quarto in 1597, has the following title : “ *Alchymia e Dispersis passim Optimorum Auctorum, veterum et recentiorum exemplis potissimum, tum etiam preceptis quibusdam operose collecta, adhibitaque ratione et experientia quanta potuit esse methudo accurate explicata et in integrum corpus redacta : Accesserunt tractati nonnulli chemici item methodistici.* ” The title fairly well explains the volume, which was for long the leading text-book on the science, and contained a collection of all the chemical facts then known. He also wrote *Ars Probandi Mineralia* (1597), *De Judicio Aquarum Mineralium* (1597), *Praxis Alchymiae* (1604), *Alchymia Triumphans* (1607). They were ultimately collected as *Opera Omnia Medico-Chemica*.

Libavius was mainly interested in the preparation of chemical medicines, but some passages in his writings bear on the transmutation of metals. He observed that the fumes of sulphur blacken white lead ; he purified cinnabar by means of arsenic and lead oxide ; he made artificial rubies and other precious stones by tinting glass with metallic oxides ; he described fluor spar as a flux for metals and their oxides ; he oxidised sulphur with nitric acid ; he knew that alcohol is obtained by



distilling the fermented juice of sweet fruits ; he proved that the acid extracted from alum and from ferrous sulphate (green vitriol) is the same as that obtained by burning sulphur with saltpetre, that is to say, it is sulphuric acid ; and he discovered tin tetrachloride (stannic chloride), which is sometimes called *Liquor fumans Libavii*. It is a truly remarkable record of practical work, considering the age in which Libavius lived.

One of the most original thinkers of his day was Angelo or Angelus Sala (1575—1640). He came of a good family, was a native of Vicenza, and attained high rank as a medical practitioner. After practising in various towns (Dresden, Winterhur, and Zürich among others) he became physician to the Duke of Mecklenburg, in which office he died. He was buried in the cathedral at Gustrow. His works under the title *Opera Medico-Chemica* were published in 1647. He scouted the idea of the philosopher's stone, or of a universal medicine, and rejected *aurum potabile* for medicinal purposes. He administered gold only in the form of the fulminate.

Sala showed that sal ammoniac is obtained by treating ammonium carbonate with hydrochloric acid ; he described ammonia in wonderfully clear terms ; he observed the formation of nitric acid by the action of sulphuric acid upon saltpetre ; and he recognised that in the deposition of copper upon iron, when the latter is dipped in a solution of cupric sulphate (blue vitriol), there is no change of metal, but that the blue vitriol already contained copper. In the words of Conring (p. 127), he was "*primus chemicorum qui desinit ineptire*" (the first chemist who ceased from trifling). Whether as a critic of the old theories, or as an exponent of the new, Sala merits a distinguished place amongst the founders of chemistry.

But the greatest name of this period is undoubtedly Van Helmont. Paracelsus had discarded the disgusting decoctions of Galen and introduced chemical medicines, while Libavius and Sala had dismissed the fanatical conceptions which disfigured and almost nullified the teachings of both Paracelsians and Rosierneians, but chemists still adhered

either to the Aristotelian doctrine of the four elements, or to the later theory of the three principles (mercury, sulphur, and salt). John Baptist van Helmont (1577—1644) was the first to deny these propositions, and to begin a revolution in the philosophy of chemistry.

He belonged to a noble family and was lord of several estates in Brabant. He was born in Brussels and studied philosophy at Louvaine. At that time, however, he declined to take the usual degree. Continuing his philosophical studies under the auspices of the Jesuits, he was taught necromancy, but was soon disappointed with such useless learning. He then turned to mysticism, reading the works of Thomas à Kempis and John Tauler. His reading of these authors induced him to imitate the Founder of Christianity in works of charity and benevolence. Although a man of rank and wealth, he resigned his titles, and gave up his property to his sister. Thenceforth he devoted himself to study, and his mysticism showed itself in many ways. He professed to be guided in all the important circumstances of life by a genie who appeared to him, and he declared that in 1623 he saw his own soul in the form of a resplendent crystal.

Desiring now to practise medicine, he read Hippocrates and Galen, but detected the futility of their methods of treatment. This led him to become a disciple of Paracelsus, but having much greater knowledge than that writer he speedily discovered the ignorance and egotism which mar his writings. In 1599 he took his degree as Doctor of Medicine, and for a time travelled and practised his profession in various countries. At last he married a rich lady of Brabant, and passed the closing years of his life on his own estates at Vilvorde, chiefly in his laboratory.

Van Helmont absolutely discarded the doctrines of Aristotle and Paracelsus in regard to the four elements and the three principles. He denied the elemental character of fire, air, and earth. He disputed the material existence of fire, and asserted that earth cannot be an element, because it can be converted

into liquid. He admitted the elemental nature of water, which he deemed the fundamental principle of everything that exists. All metals and even rocks, he affirmed, may be resolved into water, and from water all animal and vegetable substances may be produced. The former proposition he based upon the fact that fish live in water; the latter he proved by a curious, but faulty, experiment. He took a willow weighing five pounds, and planted it in two hundred pounds' weight of earth carefully dried in an oven. All dust was excluded, and the plant was frequently watered. At the end of five years he weighed the plant. Its weight was one hundred and sixty-nine pounds, an increase of one hundred and sixty-four. He again dried the earth, and weighed it, when he ascertained that it had lost only two ounces. Hence, he concluded that the increase of one hundred and sixty-four pounds in the weight of the willow was derived from water alone. He was not aware that in addition to the water, the plant had absorbed a great store of carbon from the carbonic acid gas (carbon dioxide) existing in the air.

Van Helmont was the first to perceive that when a metal is dissolved in an acid it is not destroyed, but may be recovered from the solution in the metallic state by the use of suitable means. But his outstanding discovery was the discrimination of various kinds of air, which he thus proved to be no elementary substance. In this connection he introduced the term "gas." Of these gases he mentions several, but the most important were "*gas silvestre*" (i.e., the gas that is wild and dwells in out-of-the-way places) and "*gas pingue*." *Gas silvestre* was evolved from alcoholic liquor during fermentation, from burning charcoal, from marble or chalk when acidulated, and from the Grotto del Cane near Naples. It was, in fact, carbonic acid gas, or carbon dioxide ( $\text{CO}_2$ ). There is a remarkable example of the vagaries of science in connection with this discovery. It was entirely forgotten by chemists, and as we shall afterwards learn, carbonic acid gas was rediscovered by Dr. Black in the middle of the eighteenth century

under the name of "fixed air." *Gas pingue* was an inflammable air evolved from dung, and was probably impure gaseous ammonia.

He held strange notions respecting the vital functions. From his sensations on swallowing aconite he thought that the stomach was the seat of the sentient soul, which he named *Archeus*. The first digestion, he tells us, is produced in the stomach by means of an acid liquor, which dissolves the food with the assistance of *Archeus*. But there are six digestions in all, the remaining five being effected by the "vital spirits" in different parts of the body. The number seven has been chosen by Nature for the state of repose. In short, he founded his physiological system on the operation of *Archeus* and of various ferments, all mainly imaginary.

Van Helmont believed in the philosopher's stone and in transmutation, but did not waste much time upon that part of alchemy. He asserted that he had actually witnessed the transmutation of a base metal into gold, a remarkable statement from a man of his lofty character and shrewd powers of observation, which has led some to think that the adepts may have approached nearer to the *magnum opus* than is usually supposed. His chief aim, however, was the discovery of the *alcahest* or universal solvent, another of the alchemical problems, and in this line he was followed by Glauber, of whom we shall speak in the next chapter. It seems to have been thought that the *alcahest* would be a universal medicine as well as solvent. It is a curious reflection that it never seems to have occurred to Van Helmont and others to consider how they were to retain the *alcahest*, when they found it. If it were a universal solvent it would dissolve the vessel in which it was contained, and so would be lost as soon as found!

The writings of Van Helmont were collected in 1648 under the title of *Ortus Medicinæ vel Opera et Opuscula Omnia*. All honour is due to his name. In addition to his great discovery of the diversity of gases, and the distinction between

gas and vapour, he was the first to point out the imperative necessity for the use of the balance in chemical operations, and to adopt the melting point of ice and the boiling point of water as standards for the measurement of temperature. It is in his writings that the term "saturation" in its chemical sense first occurs. Altogether he was a great chemist, undoubtedly the greatest prior to Lavoisier.

Daniel Sennert (*circa* 1575—1625) is mainly notable as a professor of medicine at Wittenberg, who devoted himself to the advocacy of chemical medicines. He held to the last the erroneous doctrines of Paracelsus, especially his theory of the three principles, but he did good service to chemistry by protesting against the possibility of a universal medicine. His chief work was *Epitome Naturalis Scientiæ*, which was published at Oxford in 1664.

A more original worker was Oswald Croll (1580—1609), who won distinction as a pharmacist. His biography can be summed up in a sentence. He studied at Marburg, Heidelberg, Strassburg, and Geneva, and became physician to Prince Christian of Anhalt Bernburg. His *Basilica Chæmica*, published at Frankfort in 1608, passed through many editions, and is a treatise of some value. The English edition was entitled "Philosophy Reformed and Improved in Four Profound Tractates" (1657). He discovered, or brought into use, a number of new medicines: for example, volatile salt of amber (succinic acid); potassium sulphate; antimoniac acid; calomel; fused silver chloride (*luna cornea*), and silver chloride prepared by precipitation. Of course, he did not use the modern names of these substances, which are adopted here and in other parts of our history, for the purpose of rendering intelligible the progress of chemical discovery. Croll was a practical chemist, rather than a theorist, although the *Basilica* contains a critical study of the Paracelsian doctrines, and discusses at length both pharmacy and therapeutics, as they were understood in his day.

The death of Oswald Croll forms a convenient point at which



to break this long chapter. There is, in fact, no great difference between the doctrines of the iatrochemists who preceded Croll and those who followed him, but it will tend to clearness if we reserve for a separate chapter the consideration of Glauber and his successors.

## CHAPTER XVIII

### THE IATROCHEMISTS

(From 1500 A.D. till 1700 A.D.)

#### 2. JOHN RUDOLPH GLAUBER TO NICOLAS LEMERY

THE second portion of the Iatrochemical Period is introduced by a famous man, John Rudolph Glauber (1604—1668). This distinguished practical chemist was born in Karlstadt, spent a laborious life in Strassburg, Ritzingen (in Bavaria), Basle, Frankfort-on-Main, and Cologne, and died in poverty at Amsterdam. Much of his time was wasted in writing polemical tracts against those who still followed Galen. His anger was specially kindled against one Farner, who had worked in his laboratory, to whom he had communicated secrets, and who had not only broken his promise not to divulge these, but had boasted of them as his own discovery, and added insult to injury by decrying the skill of Glauber. The whole controversy is highly amusing to a modern unsympathetic reader. The collected works of Glauber were translated into English in 1689 by Christopher Packe.

Glauber was an alchemist and a believer in the universal medicine, but he was also an iatrochemist, and applied chemical processes to the improvement of both medicine and art. His first treatise related to philosophical furnaces, *Furni Novi Philosophici* (1648), which he described, explained, and figured. He showed how he made chemical preparations with these: for example, muriatic acid by distilling salt (sodium chloride), ferrous sulphate (green vitriol), and alum. The name "muriatic" acid, derived from "*muria*" brine, was invented by him. He made solutions of metals in this acid, calling them "oils" of the metals. The chlorides of gold, iron,

mercury, and antimony, thus prepared, he praised as medicines. Sulphuric acid he made by distilling green vitriol (ferrous sulphate), and nitric acid by distilling nitre (potassium nitrate), and alum (double sulphate of potassium and aluminium). Fulminating gold he prepared, but said it was of little use as a medicine.

In another book called "*The Mineral Work*" he explains how to separate gold from clay and other earthy substances by means of spirit of salt (hydrochloric acid). He further describes a panacea or universal antimonial medicine, consisting of a solution of oxide of antimony in pyro-tartaric acid, which he eulogised as being specially good for cutaneous eruptions. There is, however, a great deal of alchemical nonsense in this work, and it contains a curious definition of alchemy :—

"Alchemy is an intention, imagination, and studying or considering how or whereby the species of metals are transmuted from one degree and nature into another. Let, therefore, every ingenious and understanding man thoroughly consider the good art of alchemy, for he that speculates and well studies, will the sooner attain the art, and find out the truth." (*Opera*, 1689, p. 143.)

It is thus obvious that down to the age of Glauber it was recognised that the true objects of the art of alchemy were the transmutation of metals, and its necessary accompaniment, the search for the philosopher's stone.

The salt, which still bears his name, sodium sulphate, and which he called *Sal Mirabile*, is the subject of a long disquisition in his "*Miraculum Mundi*." We recognise it as useful, but Glauber maintained that it was a universal medicine and partook of the nature of the alcahest. *Secret sal ammoniac* (ammonium sulphate) is recommended in the "*Spagyricæ Pharmacopœiæ or Dispensatory*" as a substance used by Paracelsus and as the alcahest of Van Helmont. He gives a clear description of its preparation and of its conversion into ordinary sal ammoniac (ammonium chloride) by distillation or sublimation with common salt (sodium chloride).

He knew ammonium nitrate, which he termed "*nitrum flammans*." In 1648 he demonstrated the possibility of making blue vitriol (copper sulphate) by boiling copper with sulphuric acid. He prepared a vinegar, which he called *acetum lignorum*, by the destructive distillation of wood. It was what we now term pyroligneous acid. He said that by re-distillation it could be made as "virtuous" as *acetum vini*, or "common wine vinegar," a fact not unknown to those artful persons of the present day who adulterate malt vinegar. The preservative effect of wood tar did not escape his observation.

Glauber was a keen observer, a persevering experimenter, and an original genius, and he had the modesty of genius, for he says at the end of one of his discussions: "Nevertheless, I easily persuade myself that this discourse of mine will not be credited by many, which I cannot help. It contenteth me that I have written the truth, and lighted a candle to my neighbour."

Werner or Guerner Rolfinck (1599—1673) was a physician and anatomist. He was a native of Hamburg, and became successively Professor of Anatomy, Surgery, Botany, Practical Medicine, and Chemistry in the University of Jena. He has been called "the first professor of chemistry in Germany." Alchemy he determinedly opposed, and his treatise "*Chymia in Artis Formam Redacta*" (1661) methodised the science, and according to Stahl (1766), "brought chemistry into shape, deduced its operations from causes conformed to Nature and reason, and laid a foundation on which many subsequently built." So keen an anatomist was he that the verb "to Rolfinck" became a popular equivalent for "to dissect"; just as the verb "to Burke" became at a later date a synonym for "to strangle."

The author of the book *Aurum Superius* (1675), Christopher A. Baldwin (1600—1682), is memorable for a single discovery. He prepared a hygroscopic salt by treating chalk with nitric acid. This substance took up water from the atmosphere, which he distilled off, and sold under the name of "*Spiritus*

*Mundi*," using the title of an old alchemic conception. The calcined salt (anhydrous calcium nitrate), being phosphorescent in the dark, he named "phosphorus." It thus became known as *Baldwin's Phosphorus*, and created much interest, ultimately leading to the researches which enabled Brandt and Kunckel to discover the element which we now call "phosphorus."

François de la Boe or Bois, in Latin Franciscus Sylvius (1614—1672), was born at Hanau, and practised medicine at Amsterdam. A disciple of Van Helmont and Descartes, he was led to the study of those chemical compounds which we now term "salts." The first chemical laboratory in Europe was on his persuasion erected by the University of Leyden, where he became Professor of the Theory and Practice of Chemistry. He was one of the most eminent iatrochemists, was the first to prove the presence of volatile alkali in plants, and regarded all phenomena from a purely chemical standpoint, but he had wild notions of physiology. While he agreed with Van Helmont in attributing many of the operations of the human body to fermentation, he entertained a totally different idea of what fermentation was, and sometimes used the word "effervescence" to denote the process. Van Helmont recognised the acid of the gastric juice and the alkali of bile, but Sylvius appreciated the importance of the salivary secretion and the pancreatic juice. Many of the digestive processes were, he maintained, due to the saliva swallowed with the food, rather than to the ferment secreted by the stomach and other organs. Saliva caused the first stage of fermentation, and the second was due to the bile and the pancreatic juice. He identified physiological fermentation with chemical effervescence. He discarded such agencies as the demon *Archæus* of Paracelsus, and contended that although he could not explain the various processes, physiological operations were due to chemical principles, and that air inhaled in respiration acted upon and altered the blood. Illness was due to abnormal chemical reactions in the body, and could therefore be counteracted by other reactions. These theories, connecting as they did



chemistry with medicine, had a great influence on the development of the former science. He taught the use of various chemical medicines, such as silver nitrate, zinc sulphate, calomel, corrosive sublimate, and other salts of mercury. Nevertheless, he retained the old alchemical superstition regarding the transmutation of metals.

Francis Sylvius must not be confused with the anatomist Jacobus Sylvius, who was Professor of Medicine in the College of France at Paris (1550). The latter was a very distinguished man, but no chemist.

One of the best-known followers of Sylvius was Otto Tachenius (*circa* 1620—1690). Born at Herford in Westphalia, the son of an abbey miller, he settled, after many wanderings, as a physician at Venice, having graduated at Parma. He was one of the first to give quantitative data in chemistry, and greatly improved qualitative analysis. He observed the difference of colour when corrosive sublimate is precipitated by a fixed or by a volatile alkali, and noted the use of gallic acid as a test for other metals than iron.

Adrian von Mynsicht (1603—1638) was born at Otterstein in Brunswick, and practised as a physician at Helmstadt. His real name was Sumenicht or Seumenicht. He held various offices under the Duke of Mecklenburg and other German princes. He discovered tartaric acid, which he called "brechweinstein," and prepared tartar emetic from roasted antimony sulphide and cream of tartar. His principal work was his *Medico-Chemical Treasury*, published at Lubeck in 1662.

Christopher Glaser (*circa* 1615—1673), a native of Basle, was apothecary to Louis XIV. A dark stain rests upon his memory. He is said to have been an accomplice of the infamous Marchioness of Brinvilliers in her poisonings, but although he was detained for a time in the Bastille, the charge was never brought home to him. His *Traité de la Chymie* (1663) was held in much esteem. He made extensive use of what he named *Sal Polychrestum Glaseri*, which was merely potassium sulphate

( $K_2SO_4$ ). He showed that this substance could be prepared by throwing sulphur on melted nitre. The motto of his book was "*Sine igne nihil operamur*" (we can do nothing without fire). He deemed succinic acid to be a volatile alkali, and held that the adulteration of corrosive sublimate with arsenic was impossible. If he were really an accomplice of Madame Brinvilliers, his testimony on this subject may be worthy of consideration.

We now come to a man who, although an industrious student of chemistry, was in his day more famous as a theologian. Johann Konrad Dippel, or, as he called himself, Christianus Democritus (1673—1734), was born in the castle of Frankenstein, near Darmstadt. He preached in Hamburg, but he was compelled to leave the city, and was ultimately driven from Germany on account of his religious views. He will be remembered as the discoverer of *Prussian blue*, which he prepared by calcining blood with alkali and adding green vitriol (ferrous sulphate); and of the evil-smelling oil obtained by the destructive distillation of bones, which is still known as *Dippel's Animal Oil*, and from the investigation of which by modern chemists important discoveries have been made.

English chemists of eminence were not unknown even at this early period. Thomas Willis (1621—1675), born at Great Bedwyn in Wiltshire, was one of a group of men who had studied anatomy and knew how to experiment and who became the nucleus of the Royal Society of London. He received his education at Christ Church, Oxford, and, partly as the reward of his Royalist principles, was appointed Sedleian Professor of Natural Philosophy in 1660. He removed to London in 1666, where he had the highest reputation and the largest practice as a physician. He was buried in Westminster Abbey.

The opinions of Willis were founded upon those of Paracelsus, with a little matter adapted from Van Helmont and Sylvius. Consequently, he believed in the three principles—mercury, sulphur, and salt. He explained animal warmth by a theory

of respiration which brought about a true but slow combustion. He held that the decomposition arising from fermentation is contagious. He made experiments on the preparation of ether, and also on succinic acid, a substance which seems to have attracted much attention from the chemists of those days. Willis thought it contained sulphur. His writings are overloaded with verbiage and forced analogies, and do not form a solid contribution to knowledge.

Johann Kunckel (1630—1715) was the son of a trading apothecary at Hutten, near Rendsburg, and for some time followed his father's business, but paying attention at the same time to glass-making and the assaying of metals. Being an able experimenter and acute observer, he rendered excellent service to chemistry, although his books are permeated by mischievous errors based on the theories of the alchemists. He was in the service of several German princes, and finally in that of Charles XI. of Sweden, by whom he was ennobled. The place of his death is uncertain. His greatest work was the manufacture of phosphorus from urine. He was not the actual discoverer of phosphorus. That honour belongs to Dr. Brandt, of Hamburg, who discovered the substance in 1669 by distilling a mixture of sand and evaporated urine, but Kunckel made public the result of Brandt's work.

He was led into this by an investigation which he instituted respecting the so-called *Phosphorus of Baldwin*, of which we have already spoken (p. 207). Kunckel says that Baldwin made by accident the discovery of the phosphorescent properties of the solid matter left in his retort when he was distilling the water absorbed by chalk treated with nitric acid, or, as we should say, *anhydrous calcium nitrate*. Baldwin came to him (Kunckel) and told him what he had discovered. Kunckel tried to extract the secret from his friend, but only succeeded in getting a "musical evening" and a specimen of the phosphorus. Shortly after this he heard that Brandt had discovered something which glowed in the dark, and set himself to obtain possession of this secret, but Brandt was as silent as Baldwin.

So Kunckel set to work on his own account, and after some weeks succeeded in making what we now call "phosphorus," but which was then termed "the phosphorus of Brandt." His treatise of *Phosphorus* was published in 1678.

Kunckel also wrote a treatise on glass-making and five tracts on alchemical subjects. Specimens of his ruby glass are in the Green Vaults at Dresden. Many practical operations were developed by him, such as engraving, tinting, and gilding iron and silvering copper, and he drew attention to the antiseptic action of the mineral acids, more particularly in such compounds as ferrous sulphate and alum.

The first Frenchman who stripped chemistry of its mystery was Nicolas Lemery (1645—1715). He was born at Rouen, where he was placed in the shop of a druggist, but soon perceiving that there was something more in chemistry than was understood by his master, went to Paris to seek further knowledge of the science. At Paris he became a pupil of Glaser (*supra*, p. 208), with whom he resided for a short time, but quitted his house for the reason that he found M. Glaser too much absorbed in chemical studies to be an agreeable companion. If there were any truth in the Brinvilliers suspicion, there might have been another reason for Lemery wishing to avoid a more intimate association with his master than was absolutely necessary. An attempt to learn chemistry by wandering from place to place, like a German journeyman on his *wanderjahr*, did not contribute so much as he had anticipated to his knowledge of the science, and he again settled in Paris in 1672.

Lemery now became the leader of a band of young and brilliant students who had rebelled against the ignorance and prejudice that dominated the older school. He set up a laboratory in the Rue Galande, which in the picturesque language of M. du Fontenelle was "less a chamber than a cave, a magician's cave illuminated solely by the glare of furnaces." Here he delivered a course of lectures and practical demonstrations, which became the mode. The most distinguished

Frenchman of his day, fashionable ladies and students of all nationalities flocked to hear him and to witness his marvellous experiments. In a single year no less than forty Scotsmen came specially to Paris for the purpose of attending the lectures of Lemery on chemistry and of Du Verney on anatomy. One at least of his experiments is still performed. He had observed that heat is developed when iron filings are made into a paste with sulphur and water. So he took a quantity of this paste and buried it in the earth. The heat in a short time broke out in an eruption, producing a volcano in miniature. It was long thought that by this experiment the physical cause of "burning mountains," as volcanoes were then termed, had been fully explained.

Lemery was no empty theorist, but aimed at the exposition of facts by means of experiments. Yet one of his theoretical conceptions was very odd, and shows how far astray a capable man may wander, when he deserts observed facts for philosophical speculations. He thought that chemical combination between two substances, such as an acid and a base, might be accounted for by supposing that the particles of the one substance were sharp, and those of the other porous, and that combination was effected by the *fitting of the points into the holes!*

At this period he secured a great sale for a cosmetic which he called "le seul Magistere de Bismut." It is said that he maintained his large household by the profits of this *magisterium*, which was simply pearl white (bismuth oxychloride).

But apart from a little quackery, chemistry owes much to Lemery. Prior to his time it was a science in which a small portion of truth was diffused through a great quantity of falsehood, so that it had become almost invisible, and truth and falsehood were inseparable. Such is the severe censure of Du Fontenelle. To the little that he knew of natural properties each chemist added as much as he liked of imaginary attributes. That a sympathy existed between metals and



planets, and between the planets and the organs of the human body, and that an *alcahest* which no one had ever seen had power to dissolve everything, were still accepted by many chemists as fundamental principles of the science. Lemery scattered these shadows, reduced the philosophy of the science to clear and simple propositions, and abolished the useless and barbarous jargon in which the theory and practice of chemistry had for centuries been concealed.

In addition to his lectures and experiments, he published in 1675 a *Cours de Chymie*. Its success was instantaneous and enormous. It sold like a romance or a satire. Edition followed edition, and the author saw thirteen within his lifetime, while it became the standard text-book of chemistry for a century. It was translated into Latin, German, English, and Spanish. In this work he made a full disclosure of all the secrets of the science, so far as he knew them, with two exceptions, an emetic and an opiate of marvellous efficiency, which he used in his practice. Lemery says that the aim of chemistry is to attain a knowledge of the various substances which we find combined in Nature, and in classifying those substances he was the first to establish the distinction between *inorganic* and *organic chemistry*.

His Protestant religious views caused him serious trouble in 1681. Rejecting a flattering offer of a post at Berlin, he went to England, where he was held in high honour by Charles II., who would fain have retained his services. But love of country was too strong, and Lemery returned to France. The University of Caen conferred upon him with much honour the degree of Doctor of Medicine, and he practised as a physician in Paris until the revocation of the Edict of Nantes again forced him into retirement. The result of the struggle was unusual. He changed his religion, and in 1686 was received into the Roman Catholic Church. His recantation did not at once clear away all difficulties, but after a time he resumed his lectures on chemistry and his medical practice with even greater success than before.

In 1697 he published two great works, *Pharmacopée Universelle* and *Traité Universel de Drogues Simples*. The first contained an account of all the medicines described in the books of pharmacy of every country in Europe ; the latter an alphabetical list of all substances—animal, vegetable, and mineral—which were mentioned in the other volume, with their description, virtues, use, and history. M. du Fontenelle says that with such treatises one might have looked for a cure for every human ailment, but alas ! among all this body of remedies “ we have few real friends.”

Lemery's last book was *Traité de l'Antimoine* (1707), in which he examined with minute care all the compounds of that metal. After the publication of this work his vital powers began to fail. He kept up as long as possible his attendance at the Academie, but gradually declined, and an apoplectic seizure terminated his life.

Thus passed away Nicolas Lemery, the first of those eminent French chemists, who by their great technical skill, accurate observation, and clear exposition, have added lustre to the history of the science.

## CHAPTER XIX

### THE IATROCHEMISTS

(From 1500 A.D. till 1700 A.D.)

#### 3. GEORGIUS AGRICOLA AND THE METALLURGISTS

DURING the Iatrochemical Period the history of chemistry was influenced by the labours of a number of men who were strictly speaking neither alchemists nor iatrochemists, but metallurgists and mineralogists. It must be borne in mind, however, that in those days the errors of alchemy tinged all knowledge of metals and minerals, and that most of the men, whom we are about to consider, were affected, and their opinions were swayed, by the prevailing doctrines of their age.

The founder of the systematic study of mineralogy and metallurgy was Georgius Agricola or Georg Bauer (1494—1555). He was born at Glachau, and studied medicine at Leipsig and in Italy; but having spent much time as a young man in the Bohemian mountains, became so deeply interested in mines and minerals that he gave up medicine and went to Chemnitz, where he devoted himself to mineralogy and mining.

Agricola's chief work was *Libri Duodecim de Re Metallica* (1561). In this book he gives an account of machinery, implements, and all facts connected with the working of mines and metals. It is illustrated with numerous large and well-executed woodcuts, and contains a Latin-German glossary of mining terms. He also wrote (2) *De Natura Fossilium Libri Decem* and (3) *De Ortu et Causis Subterraneorum*, in both of which he touched upon geology; (4) *De Veteribus et Novis Metallis*; and (5) *Bermannus, sive de Re Metallica Dialogus*. Although he flourished in the early part of the Iatrochemical Period, there is nothing of the Paracelsian nonsense in these

writings, nor has he the vagueness and futility of the old alchemists. His statements are obviously based upon actual observation and personally ascertained facts.

He teaches the art of preparing and purifying copper and iron by means of lead, and the extraction of mercury, zinc, and bismuth from their ores. He mentions common salt, saltpetre, alum, and green vitriol. Special consideration is due to him for the discovery of bismuth, and for his classification of minerals. These he distinguished as simple and compound, dividing the former into earths, concretions, stones, and metals. He observed that minerals can be recognised by the colour of the flame produced when they are burned, and thus made the earliest suggestion of blow-pipe analysis and flame tests. Many chemical processes are described in his works, which have still interest for the chemist and mineralogist.

Georgius Agricola must not be mistaken for Daniel Agricola Philopistius (*circa* 1580—1650). The latter is the author of a curious book *Galezazeye sive Revelator Secretorum* (Cologne, 1631). This treatise contains three sections: (1) *De Lapide Philosophorum*; (2) *De Arabico Elixir*; and (3) *De Auro Potabili et Pomis Paradisi*. These are the usual alchemical literature and of little moment, but are sometimes erroneously attributed to Georgius Agricola.

Another mineralogist was Carlo Biringuccio, of Siena, of whose dates we know nothing, but who published in 1540 a book called "*Pirotechnia*." In this treatise he holds aloof from the chemical aspect of his subject, and adds nothing to our knowledge worthy of mention.

There is not very much more recorded about Lazarus Ercker (*circa* 1525—1600). He was inspector-general of the Hungarian mines in Transylvania and the Tyrol. In 1574 he published the result of his practical experience without theories and hypothesis. This work was highly prized, and was afterwards enlarged and entitled *Aula Subterranea Domina Dominantium Subdita Subditorum*. This edition was issued at Frankfort in 1672.

We are indebted to Ciriacus Schrietmann (*circa* 1525—1600) for a valuable description of the dry assay of gold and silver. In the first portion of the book there is an explanation of the balances and weights used in the process, while the subsequent parts treat of muffles, furnaces, materials, and operations. This *Probenbuchlein* was published at Frankfort in 1580.

Christopher Entzelt or Encelius (1520—1586) was a native of Saalfeld in Thuringia, and entered the Church. He is the author of a small work on metals, hypothetically dated in the British Museum catalogue 1551.

Another churchman who rendered good service to mineralogy was Alvaro Alonso Barba (*circa* 1575—1650). He was born at Lope, in Andalusia, and became a priest at Potosi in South America. While there he had special opportunities of studying at first hand minerals and mining, especially the extraction and assaying of silver. He embodied his knowledge in a book entitled "*El Arte de los Metales,*" published in 1640 at Madrid. It is a treasury of the practical and theoretical views of the time, and was long kept secret by the Spaniards, but was ultimately translated into English, German, and French.

One of the martyrs of science was Gabriel Plattes (*circa* 1575—1650). His *Discovery of Subterranean Treasure* (London, 1639) is an account of all sorts of mining, and he was one of the first to make a scientific study of agriculture. But the man who sought to increase a nation's store of food was unable to provide his own daily bread, and he died in a London street, of hunger and exposure.

John Webster or Johannes Hyphantes (1610—1682) was born at Thornton-on-the-Hill, in Yorkshire, and was for a time a schoolmaster at Clitheroe, and afterwards a chaplain and surgeon in the Parliamentary army. He was much involved in religious and educational controversy. His *Metallographia* (1671) furnishes an excellent account of the metals known and wrought in his time. He was a man of erudition and a well-trained chemist, and, as Whitaker says, "was able to keep his



head above water through all the changes of those tempestuous days."

Our next subject, Sir John Pettus (1613—1690), also came through the tempestuous days of the Civil War, but on the opposite side from Webster, and with a less fortunate event. He served under Charles I. and was knighted by him, but seems to have afterwards been on friendly terms with Cromwell, who made him deputy governor of the Royal Mines. By his expenditure on behalf of Charles II. he became impoverished and was imprisoned in the Fleet. There he wrote his treatise "*Fleta Minor*," a punning title referring to his place of imprisonment and his official occupation in the Royal Mines. His book is based upon the work of Ercker, already mentioned. He also wrote "*Fodinae Regales*," which sets forth the history, laws, and places of the chief mines in England and Wales.

Thomas Nicols (*circa* 1600—1660), a native of Cambridge, was the author of a valuable treatise on precious stones, entitled "A Lapidary" (Cambridge, 1652), in which the knowledge of his day is well explained.

A follower of Ercker was Georg Engelhard von Lohneyss, who was a nobleman of the Palatinate, and Stallmeister at the Court of the Elector Augustus of Saxony, and who published a work on metals in 1690. He designed the plates, woodcuts, and initials with his own hands, and had the book printed at his own press.

From the writings of these men it is possible to form some idea of the methods of the sixteenth and seventeenth centuries in regard to the winning and preparing of metals. These works contain minute descriptions of the technical operations. Agricola and Libavius were the first to show how it is possible to estimate the amount of metal contained in an ore, and the process of testing was gradually developed along with the working up of by-products. In this way the sulphur produced during the roasting of pyrites, and the *tutty* mixed in zinc ores, were preserved, the latter being used in the manufacture of brass.

About the middle of the sixteenth century the process of amalgamation with mercury was carried on in Mexico for the purpose of separating silver from its ore, but this method was unknown in Europe till the eighteenth century. Gold was used in the production of ruby glass. The salts of the metals were thoroughly investigated, and old theories were dispelled. The supposition that, when copper was deposited on iron plunged in a solution of blue vitriol, actual transmutation occurred, was dispelled, and it was recognised that the copper was previously existent in the solution. Steel was regarded as a very pure iron, and its production by the puddling process was first described by Agricola. In short, all the more familiar metals received attention, and greater discoveries would have been made had it not been the aim of the iatrochemists to seek subjects likely to be useful in medicine, and thus the interest of the age naturally concentrated itself upon salts or compounds of metals rather than upon the metals themselves.

Before we pass from the Iatrochemists to the Phlogistonists, we shall try to take an account of the nett gain to chemical knowledge which resulted from the accumulated experience of nearly two hundred years occupied by the Iatrochemical Period. So long time spent in experiments and study must have left its mark upon the science, and it is desirable that we should, if possible, form some idea of the nature of that impression.

Apart from the change in the attitude of chemists towards their science, and the alteration of their aims and methods, which were the peculiar features of the Iatrochemical Period, we may describe the gain to chemical knowledge through the labours of the iatrochemists as an advance made in three directions. There was an increased scepticism as regards the doctrines of the alchemists; an increased understanding of chemical compounds and reactions; and an increased appreciation of the chemistry of the human body. The change of opinion on all these points was perhaps destructive rather than constructive; there was a tendency to destroy old

theories rather than to construct new. But as the ancient philosophy was mainly erroneous, the first step towards more accurate knowledge was to sweep away the traditional myths which cumbered the ground and impeded the advance of seekers after truth.

The writings of Van Helmont shook belief in the Aristotelian doctrine of the four elements and the Paracelsian doctrine of the three principles, with a violence from which they never recovered. After his time they ceased to hold undisputed sway over the minds of chemists. A satisfactory substitute had not yet been found, but chemists no longer regarded the ancient doctrines as affording a true explanation of the phenomena of Nature.

So, too, it was with chemical compounds and reactions. When Libavius proved that the acid obtained from alum, green vitriol, and the fumes of sulphur when burned with saltpetre, was one and the same acid, or when Van Helmont demonstrated that the gas evolved from fermentation, burning charcoal, acidulated marble, and the Grotto del Cane, was one and the same gas, chemistry entered upon a new era. The marvellous phenomena produced by chemical combination and affinity were thrown open to the researches of laboratory workers. The whole teaching of the age confirmed these proofs. Sala showed that sal ammoniac, previously believed to be a simple substance, was a compound formed from ammonium carbonate and hydrochloric acid; Glauber made blue vitriol by boiling copper in sulphuric acid; and Van Helmont taught that when metals are dissolved in acids they are not destroyed, but may be recovered in their original form from the solution by the use of proper means. The way was made clear for the great reformers of the science.

Finally, the absurd conceptions of the ancients in regard to the processes and functions of the human body were totally shattered. Van Helmont, Sylvius, and Willis demonstrated that whatever might be the true cause and purpose of the processes connected with digestion, respiration, and so forth,

they were essentially chemical. Much work had still to be done before chemists could grasp the principles controlling those processes, but they were at length set upon the right track, and progress was merely a matter of time.

We have already shown that inorganic chemistry, especially the chemistry of the metallic compounds, had made the greatest advance. Van Helmont's discovery of a variety of gases, although it did not receive the attention which it deserved, introduced to the practical chemist a new series of hitherto unknown elements. To the non-metallic substances was added phosphorus, an element possessing most remarkable properties. The three acids—sulphuric, nitric, and hydrochloric—were being prepared in a variety of ways, and their properties were becoming better understood. More progress had been made in the intelligent appreciation of the metals and their salts during this period of less than two centuries than had been made during the unknown centuries of the Alchemical Period. Such is the difference between practical laboratory work and mere speculation.

Pharmaceutical chemistry is the creation of the Iatrochemical Period. The chief aim of chemistry at that time was, as we have said, the discovery of medicines, and the study of their action upon the human organism. This operated upon the history of the science in two ways. It added chemical facts to our knowledge, and it led to the establishment of drug-shops, which became schools for the training of practical men, who devoted themselves to the elucidation of chemical facts, and to the building up of the science.

The search for the *Elixir Vitæ* tended towards the discovery and use of many chemical medicines, but did not extend greatly the knowledge of organic chemistry. The reason for this was that the iatrochemists sought to discover the remedial properties of metallic preparations, and so paid little attention to organic substances. Nevertheless, some progress was made in this section of the science. Pyroligneous acid (*acetum lignorum*) was discovered by Glauber; impure pyruvic acid

(*spiritus tartari*) was obtained from tartar; and crude acetone (*spiritus ardens e Saturno*) from lead acetate, otherwise called "sugar of lead." Dippel made Prussian blue and the oil which bears his name. By heating amber, crystals of succinic acid were produced, named "*Flores succini*," and by heating gum benzoin, benzoic acid (*flores benzoin*), while by treating spirits of wine with acids, ether was discovered (*oleum vitrioli dulce*), and an alcoholic solution of ethyl chloride (*spiritus salis dulcis*). These were the principal acquisitions of organic chemistry during the Iatrochemical Period.

Improvements in chemistry also resulted from many technical processes which were introduced about this time. Amongst these was the distillation of brandy, which began to be extensively used as a beverage. Previously, it had been looked upon solely as a medicine. This trade led to improvements in apparatus for distillation, and the benefit was extended to chemical laboratories. A further advance took place in the relations of chemistry to agriculture, such men as Bernard Palissy, Plattes, and others calling attention to the importance of soluble salts as manures, and recommending the addition to the soil of marl and similar mineral substances.

But it was, of course, to the ceramic industry that Palissy gave the greatest impetus. In his work "*L'Art de Terre*," he described the preparation of enamels for earthenware vessels, especially Fayence pottery, the application of different clays, and the burning-in of colours. He was accompanied in the same direction by Porta (*supra*, p. 124). All these things called for an increased knowledge of chemical compounds.

Glass manufacture was also a stimulus to chemical research. Porta had shown what wonderful effects could be attained in the imitation of precious stones, and the lovely work of the Venetian factories spread the manufacture of glass of all colours and of different degrees of refrangibility throughout the principal nations of Europe. Antonia Neri by his work "*De Arte Vitriaria*" (1640) contributed materially to this result. One of the most important discoveries due to this art



was Cobalt blue. Christoph Schurer, a Saxon glass-blower, on fusing with glass the cobaltous residue from the manufacture of bismuth, succeeded in producing this beautiful colour, which soon became a much-prized article of commerce under the names of *zaffre* (from "sapphire") and *smalt*.

One of the results of the discovery of America and of the ocean route to the East Indies was the increased importation of indigo and cochineal. This again led to the improvement of the arts of dyeing and of fixing the colours in the cloth. Solution of tin and mordanting with alum were invented during the period of which we are speaking, and no little credit is due to Glauber for his observations on dyeing processes. The first text-book on the subject was written by a Venetian (Rosetti) in 1540.

Everything contributed to the advance and improvement of chemical knowledge. The time of mere speculation was past. In every country eager students were toiling in chemical laboratories to increase the store of observed facts and the number of recognised compounds, while their energies were being stimulated by the demands of the glass-worker, the dyer, the distiller, the agriculturist, and others engaged in technical operations, as well as by the physician and the apothecary, who sought the aid of chemistry in the preparation of medicines to meet the needs of suffering humanity.

## CHAPTER XX

### THE PHLOGISTONISTS

(From 1650 A.D. till 1775 A.D.)

#### 1. JOHANN JOACHIM BECHER TO HERMANN BOERHAAVE

THE Fourth or Phlogiston Period of the history of chemistry originated about the time when astronomy and physics had been raised to the position of sciences. This had been effected principally by the agency of three great men : Kepler (1571—1630), Galileo (1564—1642), and Torricelli (1608—1647). Chemistry also had to be freed from the trammels of superstition and made to take its place as a true science cultivated in the spirit which one of its distinguished founders, Roger Bacon, had advocated long before. This new development of the science began in the middle of the seventeenth century and lasted about a hundred and twenty years, ending in the last quarter of the eighteenth century. At that date the pneumatic trough and balance commenced to influence the study, and modern chemistry may be said to have been founded. The period was marked chiefly by the elucidation of qualitative problems (that is to say, the alteration of bodies by the action of chemical reagents), and witnessed the rise of analytical chemistry.

A great leader in what has been termed the Phlogiston Period was Johann Joachim Becher (1635—1682), who was one of the most original and remarkable men of the seventeenth century. He was the son of a learned Lutheran preacher, and was born at Spire. His father died when he was quite young, ruined by the Thirty Years War, and Becher found himself while still a boy charged with the maintenance of his mother, brothers, and himself. He applied himself to the discharge

of this duty in the most praiseworthy manner, and for several years endured a hard struggle. At length, however, he was free to pursue his own career, and, after travelling and studying, was appointed Professor of Medicine in the University of Mainz, and also physician to the Archbishop Elector. His restless ingenuity constantly involved him in fresh schemes, and more than once he had to change his place of abode on account of the ill-will engendered by his devices. In this fashion he passed through Vienna, Haarlem, Scotland (where he visited the lead mines), Cornwall, and lastly, London, where he died.

Becher is notable not only as the first suggester of a rational theory of combustion, but as a miner, metallurgist, technologist, and general projector. He was one of the first to propose a universal language, and invented ten thousand words for that purpose. Schemes practical and unpractical filled his mind. His plan for a government monopoly of the cloth manufacture and trade compelled him to fly from Munich; he was engaged in devising a method of settling a large tract of country between the Orinoco and the Amazons; and he acted as adviser in a number of German commercial undertakings.

His most important practical work in chemistry was the discovery of boric acid derived from borax, and ethylene or olefiant gas is first mentioned in his *Physica Subterranea*; but he was a theorist rather than a laboratory worker and experimenter. He wrote many books, of which the chief are: (1) *Metallurgia* (1660); (2) *Institutiones Chymicæ* (1664); (3) *Parnassus Medicinalis Illustrata*; (4) *Oedipum Chymicum seu Institutiones Chymicæ* (1663); (5) *Acta Laboratorii Chymici Monacensis, seu Physica Subterranea* (1669); (6) two supplements (1681); (7) *Trifolium Becherianum Hollandicum*; (8) *Experimentum Chymicum Novum* (third Supplement to the *Acta*, 1703); (9) *Chymischer Gluckshafen* (Chemical Luckpot); (10) *Foolish Wisdom or Wise Folly*; (11) *Magnalia Naturæ*; (12) *Tripus Hermeticus, etc.* (1689); (13) *Chemical Rose-garden* (1717); (14) *Pantalion Delarvatus*; (15) *Becheri*

*Sancilotti Epistolae Quatuor Chymicae.* In these works he propounded a theory by means of which all known chemical facts were connected together and deduced from one general principle. The theory was afterwards adopted and modified by Stahl, and forms the basis of his Phlogiston hypothesis.

Becher in his *Physica Subterranea* stated the following fundamental principle of combustion: that it is a decomposition or dissolution of the combustible body into its constituents. A simple body, which is incapable of being split up into constituent parts, cannot burn. The flame depends upon the separation arising from this dissolution, and the rarification of the combustible body. Every body which is combustible must have a cause for its combustibility. This cause he assumed to be a fatty earth, which he called "terra pinguis." Mineral substances, in so far as they are combustible, must also contain this earth, and the calcination of metals depends upon the expulsion of the *terra pinguis* by fire. In short, fire dissolves and decomposes everything which consists of heterogeneous parts, and expels the more volatile portion of metals. The use of fluids is to prevent the sulphurous parts from volatilising.

This was an improvement upon the older doctrine of the three principles. He held that the primary ingredients of every inorganic subterrestrial body were *water* and *earth*. From these were produced three earthy principles, *terra pinguis*, *terra mercurialis*, and *terra lapidia*. These terms have been variously rendered in English as the fatty or combustible, the fluid or mercurial, and the strong or vitrifiable earths. They correspond to the ancient *sulphur*, *mercury*, and *salt*, respectively. Every metal, according to Becher, consists of these three earthy principles, combined in varying proportions.

It will be seen that Becher's views did not differ greatly from those of Paracelsus, and that they have some reminiscence of ideas current in the thirteenth century; but he advanced beyond all his predecessors by being furnished with a definite

theory of combustion applying to all combustible bodies. He asserted that when the *terra pinguis* was expelled by fire, there still remained the *terra lapidia* of the metal, that is, its calx. We may compare with this doctrine the saying of Kunckel in 1670: "*Ubi ignis et calor ibi sulphur*" (there is sulphur wherever fire and heat exist).

In the opinion of Becher iron consisted of its red oxide (rust) or *terra lapidia* united with a strong but not abundant *terra pinguis* and a very little *terra mercurialis*. Copper had a redder and more dilute *terra lapidia*. Gold had a very fixed and pure *terra lapidia* and a very pure and penetrating *terra mercurialis*. Silver was composed of much white *terra lapidia*, a little *terra pinguis*, and less *terra mercurialis*. Tin had much *terra lapidia*, little *mercurialis*, and an impure and imperfect *pinguis*. Lead had a large quantity of *terra mercurialis*, little *pinguis*, and very little *lapidia*. Hence, he said, metals are always generated in the earth. He declared that the opinion of St. Augustine and others, that metals had existed from the beginning, is a mistake.

Becher's views, therefore, were essentially derived from older sources. They implied a change of terms rather than of principles. But he did generalise so far as to propound a definite theory connecting together all metals and combustible things, and giving a scientific explanation of combustion, which, although erroneous, was fruitful and enlightening.

From the earliest times men have been impressed by the phenomena of fire, combustion, and heat. Combustion was regarded as the grand and essential phenomenon of chemistry, partly on account of the utility of fire, and partly on account of its importance in producing changes in bodies submitted to it. Modern chemists still regard combustion as of the highest importance, but consider it as a purely chemical action, the result of the union of unlike bodies under the influence of affinity, attended with the evolution, always of *heat*, and sometimes of *light*. The ancients, however, took a different view. For many centuries fire was one of the elemental principles.



In the Middle Ages philosophers tried to simplify the matter by subdivision, and recognised two sorts of fire, a pure *celestial* and a gross *terrestrial*. "Air," they declared, "is the food of fire," and when they observed that a glowing coal is kindled into flame equally by a blast of air or a handful of nitre, they said: "Nitre and air are connected, for things that are equal to the same thing are equal to one another." This was a happy guess and came wonderfully near the truth, for the power of reviving flame, possessed equally by air and nitre, is due to the large proportion of oxygen contained in both. But all those vague theories were superseded in the Phlogiston Period by the conceptions of Becher and his followers, and this, as we shall afterwards perceive, was their main contribution to science.

Becher's pupil and follower, Georg Ernst Stahl (1660—1734), developed his master's views. In his *Zymotechnia* and *Pyrotechnia* he advanced his celebrated doctrine of Phlogiston, which he characterised as a general theory of fermentation. He expressed his agreement with Becher's assertion that sulphur contains the same combustible matter (*terra pinguis*) as the metals, and that sulphuric acid is the other constituent of sulphur, just as the calx of each metal is the other constituent of that metal. That this was the view of Becher may be gathered from the *Experimentum Novum*, where he explains the mode of reducing sulphuric acid to sulphur in the same way as metals are reduced from their calces, that is to say, by treatment with charcoal. He combined the acid with an alkali, reduced it with charcoal in the now familiar manner, and then obtained the sulphur from the sulphide by means of an acid.

Stahl, the greatest of the Phlogistonists, was born at Anspach. He studied medicine at Jena, and took his degree when twenty-three years of age. He began to lecture at once. At the solicitation of his friend Hoffmann, he was in 1694 appointed Second Professor of Medicine in the University of Halle, a post which he held for twenty-two years. It is remarkable

that Hoffmann and Stahl were each the founder of a medical system. In 1716 Stahl was transferred to Berlin as physician to the King of Prussia, and died there. Although he studied chemistry and wrote chemical books, he does not appear to have lectured upon that subject.

His medical system, like that of Van Helmont, resolved the cure of disease into the action of the soul, which is the regulator of the body and the restorer of functions deranged by disease. The business of the medical man is therefore to aid and guide the action of the soul, the *vis medicatrix Naturae*. The same doctrine was taught at a later date by the famous Edinburgh physician, Dr. Cullen.

Stahl's principal writings are : (1) *Zymotechnia Fundamentalis sive Fermentationis Theoria Generalis* (1697) ; (2) An edition of Becher's *Physica Subterranea* and his own *Specimen Becherianum* (1702) ; (3) *Theoria Medica Vera* (1707) ; (4) *Opusculum Chymico-Physico-Medicum* (1715) ; (5) *Chymia Rationalis et Experimentalis* (1720) ; (6) *Experimenta, Observationes, Animadversiones, Chymicae et Physicae, CCC numero* (1731) ; (7) *Fundamenta Chymiae Dogmaticae et Experimentalis* (1732).

In 1702 Stahl republished Becher's *Physica Subterranea* and added his own *Specimen Becherianum*, because he felt that his master's work had received too little recognition, but in doing so he extended his predecessor's views on the composition of the metals and on combustion. He reiterated that every calcinable metal is composed of the calx of that metal and a special combustible substance, which escapes into the air when the metal is burned. "*Ignobilia metalla continent substantiam inflammabilem, quae modo igne aperto in auras abiens, metallam in cinerem fatescens relinquit.*" The reduction of the calx is its uniting with this combustible substance. "*Metallis ita combustis non licet in metallicam suam faciem rererti, quodcunque aliud experimentum vel additamentum, nisi quod materiam talem inflammabilem illis iterum communicare atque insinuare possit.*"

This combustible substance (*substantia inflammabilis*), which had first been called "the sulphur of the philosophers," then "oleum," "pinguetudo" or "terra pinguis," and which according to Stahl is not fire, but only the principle or condition of the origination of fire, was termed by him Phlogiston.

In brief, therefore, *Phlogiston was the principle of combustibility*. Stahl did not invent the term, which was used in 1661 by Boyle; he only defined it more precisely and brought it prominently forward. He developed this theory of combustion, and his views as to the metals, in his later books, but although the exposition occupies much space, the general principles may be set out in a few paragraphs.

The property of combustion, the fundamental principle, is the same in all combustible bodies. "It is to be kept in mind," he says, "that as well in the fat with which one smears his shoes, as in the sulphur of the mines and all metals, partly or wholly combustible, there is actually the same essence (or principle) which gives and constitutes its inflammability."

It has to be observed on this passage that Stahl and all the Phlogistonists confused the idea of a property with a substance or essence possessing that property. In reading phlogistic literature the use of the word "phlogiston" to signify a substance renders these writings, reasonings, and explanations nonsensical in our modern view; but if we could read into them the idea of a *property only*, and discard altogether the idea of a concrete thing, their doctrines would not seem to us to be so far removed from those of our own day.

In burning some substances, Stahl said, the whole of the phlogiston will disappear as fire; in others partly as fire, and partly as a peculiar form of soot. This soot, in his view, was the purest possible form of phlogiston. The identity of the combustibility of metals and of vegetable matter he tried to explain by supposing that the principle is not ordinary sulphur, but a constituent of sulphur, which is a compound body. He differed from Becher in regard to the origin of metals. He thought that they had existed from the beginning, and ridiculed those who

believed that in course of time the baser metals became better, more mature, more perfect, more like the noble metals. He pointed to the tin mines. "The British Cassiterides," he said, "have been known for more than two thousand years, and the kitchen is still so badly furnished that one gives up the idea of tin ever being sufficiently cooked. It is a peculiar kind of addled egg and will not be hard-boiled."

Substances that will not burn resemble the calces of the metals. He instanced quicklime, which, if it could have phlogiston combined with it, would form a substance similar to the metals. In this illustration he foreshadowed the discovery by Davy in 1808 of the metal calcium.

Such is Stahl's theory of phlogiston. It formed the groundwork of chemical research for the next fifty years, dominated the minds of philosophers for a hundred years, and was the outstanding fact of chemical history in the eighteenth century.

In his *Fundamenta Chymiae*, a book which may have been written by one of his pupils from notes of his lectures, he followed Boerhaave in dividing the subject into two parts—a theoretical and a chemical. He constantly used symbols for words, which renders his works difficult to read. Chemistry he defined as "the art of resolving compound bodies into their constituents, and again forming them by uniting those constituents together." He agreed with Becher in believing that there are four simple principles. In the first part he treated of several matters in the following order:—

1. Mixtures, compounds, and aggregates. He related processes and described apparatus, and maintained that the first object of chemistry is corruption not generation.
2. Salts. These he defined as mixtures of water and earth, and divided them into *simple salts*, such as vitriol, alum, nitre, common salt, and sal ammoniac: and *compound salts*, such as sugar, tartar, and other substances derived from animals and plants, and quicklime.
3. Cinnabar, antimony, sulphur of vitriol, sulphur of nitre, resin, and distilled oils, *aqua humida* and *aqua secca* or

mercury. The distinction between sulphurous and sulphuric acids was first pointed out by Stahl.

4. Friable earths, metallic earths, metals, and smelting.
5. Mercuries, the philosopher's stone, and universal medicine.

This last section is history rather than his own views. In the second part of the book he discusses the nature of substances and processes and salts ; the definition of bodies ; the reduction of metallic calces ; the instruments of chemical motion, fire, air, water, and earth or salt ; and chemical generation and mixtures.

Stahl's opinions are well expressed in the following passage, which is taken from his *Specimen Becherianum* : " Briefly, in the act of composition, as an instrument, there intervenes and is most potent, fire, flaming, fervent, hot ; but the very substance of the compound there intervenes, as an ingredient, as it is commonly called, as a material principle and as a constituent part of the whole compound, the *material and principle of fire*, not fire itself. ' This I was the first to call Phlogiston.' "

He held that there is a great gulf between things having life however simple, and things not having life, however compound and complex in their phenomena. Living things, so long as they have life, are actuated by an immaterial agent, the sensitive soul ; non-living things are not so actuated. A living body, though capable of change and constantly undergoing change, maintains for a certain time an individual existence ; a non-living body has no individual existence. A phenomenon which takes place in the non-living body may not take place in the living body, for the chemical and physical phenomena of the latter are modified by the action of the living and sensitive soul.

Amongst Stahl's contemporaries Hoffmann and Boerhaave were the most conspicuous. Friedrich Hoffmann (1660—1742) was the intimate friend of Stahl. He was born at Halle, received an excellent education, and graduated as Doctor of Medicine in 1681. On this occasion he read a thesis " De Cinnabari Antimonii," which was highly admired and drew



large audiences to attend his course of chemical lectures. He began to practise as a physician at Minden, in Westphalia, and afterwards visited Holland and England. In 1693 he was appointed Primarius Professor of Medicine in the University of Halle, recently established by Frederick III., Elector of Brandenburg, and drew up the statutes of the Faculty. Honours were showered upon him, and he was for a time court physician at Berlin, but retired from that post and died at Halle.

Hoffmann's *Opera Omnia Physico-medica* have been published in various editions, consisting of eleven to thirty-five volumes. He was mainly a medical writer, but three of his books apply to chemistry: *Observationes Physico-chymicarum Selectionum* (1722); *De Acido Vitrioli Vinoso* (1732); and *Dissertationes Physico-medico-chemicae* (1735). He accepted a good deal of Stahl's phlogiston theories, considering sulphur to be composed of sulphuric acid and phlogiston, but he did not admit that there was phlogiston in metals. He deemed it more probable that in place of the calx of the metal being formed by the loss of a constituent, it was formed by the union of the metal with something which he designated *sulphur acid*. By calcining an ore containing sulphur, the metal remains as a calx, because it has taken up the sulphur acid which had been contained in the sulphur, the phlogiston of which had been separated out by the calcination. Every calcination, he thought, is similar, and the reduction of a metal is the withdrawal of its sulphur acid.

His empirical discoveries are more important than his philosophy. He discriminated in 1722 between chalk, bitter earth, and alum, which up till that time had been thought identical, and showed that lime is a distinct earth. He made use of physical properties for the identification of substances. Mineral waters he investigated for the purpose of discovering their constituents, but without much success, and classified them as alkaline, ferruginous, bitter, salt, and so forth. Seidlitz water was discovered by him. He observed the poisonous action of vapours containing carbon, and described improved methods for the preparation of nitric and sulphuric acids.

One of the greatest practical chemists of his age, Hermann Boerhaave (1668—1738) was born at Voorhout, a village near Leyden. He was the son of the parish clergyman, and like Becher was left at an early age without fortune to shift for himself. His first intention was to follow his father and enter the Church, but an erroneous charge made against him, that he was inclined to the doctrines of Spinoza, injured his prospects, and caused him to turn his attention to medicine. He took his degree in 1693, and was one of the most distinguished physicians of his day, as well as an enthusiastic chemist. While practising his profession he purchased books and erected a laboratory. He had been a pupil of Dr. Archibald Pitcairn, Professor of Medicine in the University of Leyden and afterwards in the University of Edinburgh, who was a strong opponent of the iatrochemists. The opposition of the master passed to the pupil, and a series of practical experiments, devised to demonstrate Dr. Pitcairn's ideas, created for Boerhaave such a reputation that he was invited to the Hague by a friend of William of Orange. This honour he declined, but accepted the Chair of Medicine at Leyden, to which were afterwards added those of Botany and Chemistry. He was also elected dean and rector more than once. Under him the University of Leyden rose to the highest rank in Europe.

His principal work is *Elementa Chæmiæ, quæ anniversario labore docuit, in publicis privatisque scholis, Hermannus Boerhaave*, published at Paris in 1724 in two volumes. It is said to have been originally printed from notes of his lectures, and to have been afterwards revised by him. He also issued a *New Method of Chemistry* in 1741. The *Elementa* is a complete collection of the chemical facts and processes then known, written in plain language, and stripped of mysticism. According to his definition, chemistry is "the art which teaches the manner of performing certain physical operations whereby bodies cognisable to the senses, or capable of being rendered cognisable, and of being contained in vessels, are so changed by means of proper instruments, as to produce certain

determinate effects and at the same time to discover the causes thereof ; for the service of various arts."

Boerhaave combated the opinions of the iatrochemists with great earnestness, experimental skill, and success. He also objected to part of the phlogiston hypothesis, on the ground that he could not perceive in the different combustible bodies the same single combustible principle, and that the metals are not composed of their calces with a combustible property added.

He may be said to have been the founder of that branch of chemistry which deals with the chemical analysis of substances occurring in animals and plants, now known as the Chemistry of the Carbon Compounds. The old, vague alchemical ideas respecting vital fluids had been gradually dissipated by the labours of Vesalius, Harvey, Malpighi, Grew, and others, and Boerhaave set himself to decompose the organic structure of plants and animals in order to discover the materials contained in them. By a thorough examination of the fresh leaves of rosemary and the bark of cinnamon trees, he discovered the constituents of the moist and dry portions. Then by examining the earth in which the plants grew, he found that he could extract therefrom many of the substances which he had observed in the ashes of the plant. From the whole he inferred that plants take these salts out of the earth, and that animals derive them from plants. He traced out the process—how rain dissolves the salts in the earth ; how the water containing these salts in solution is sucked up by the roots of plants and carried to their leaves ; and how the salts are there altered under the influence of sunshine and air, so as to become food for the plants. Those constituents of plants which did not come from the soil, he concluded must be taken from the air. A similar discovery was made almost simultaneously in England by Dr. Hales (1677—1761), who measured the quantity of water taken in by the roots, and proved that plants breathe through the little *stomata* or mouths observed first by Grew.

By a like series of experiments on the fluids of animals—

milk, blood, bile, chyle, and lymph—he showed that animal bodies are made up of altered vegetable matter, just as plants are built up of altered mineral matter.

Boerhaave contradicted by experiments the view set forth by Boyle and others, that during calcination a ponderable fire-stuff is taken up, and that this addition explained the increase in weight observed in metals after calcination. We shall again have to refer to this curious phenomenon.

The term “salt,” prior to his time, was used by even such men as Stahl with great looseness of application. They applied it to acids and alkalis, as well as to the products of the union of acids and bases; but the experiments of Boerhaave gave greater precision to the conceptions of chemists regarding these compounds, and prepared the way for the definition formulated in 1745 by Rouelle. He also laid down a more rational theory of affinity. The term “affinitas” had been adopted by Albertus Magnus on the supposition that chemical affinity was due to *similar* substances interacting the one on the other. Boerhaave, on the contrary, maintained that it is *unlike* substances which display the greatest tendency to combine with one another.

The importance of the work of Boerhaave lies in the good use he made of known facts, rather than in his own discoveries. He tested many of the supposed discoveries of the old alchemists, and did not reject them until he had proved them to be erroneous. For example, he demonstrated by heating mercury for fifteen years in an open vessel that the fixation of quicksilver is impossible. He distilled the same metal five hundred times without change, thus disproving the alchemistic statement that a more volatile body may be obtained from mercury. He also showed that, contrary to the opinion of his time, lead and other metals contain no mercury.

Hence, although Boerhaave did not add much to our positive knowledge, yet his labours must be considered as to a certain extent epoch-making. This result is due to the perseverance he displayed in doing tedious work, and to the thoroughness,

care, and truly scientific method which he employed. He was in almost every respect a different man from Stahl. Possessed of great erudition, a clear thinker, and a patient and accurate experimenter, he did not allow himself to be carried away by one idea. He was what is termed an "all-round man." A distinguished physician, a skilled anatomist, an able chemist and a deep mathematician, he did not permit medicine, anatomy, chemistry, or physics to exclude one another, but was ready to apply any of these sciences to the elucidation of phenomena. He was, in fact, a great teacher, who had made himself familiar with what had been done by others, and was able by his wide scientific knowledge to criticise the opinions of his predecessors, to point out where they had probably erred, and to deduce what was the nett outcome of their labours.



## CHAPTER XXI

### THE PHLOGISTONISTS

(From 1650 A.D. till 1775 A.D.)

#### 2. JOHANN JUNCKER TO PIERRE JOSEPH MACQUER

THE Phlogiston theory was further extended by Johann Juncker (1683—1759). He was born at Lehnendorff, near Giessen, and the year of his birth is variously stated as 1679, 1680, or 1683, the last being probably the correct date. He became Professor of Medicine in the University of Halle. In 1730 he published a work, of which the title-page gives a fair abstract of the contents. It is "*Conspectus Chemiæ Theoretico-practicæ in forma tabularum representatus, in quibus physica præsertim subterranea [i.e., inorganic chemistry] et eviporum naturalium, habitus inter se, proprietates, vires et usus . . . e dogmatibus Becheri et Stahli potissimum explicantur.*"

Juncker applied himself to answer the objection raised by the anti-phlogistonists that when metals are calcined there is an increase of weight, instead of a loss. In his explanations he confused the absolute weight with the specific gravity, and in this way missed the point which ultimately, as we shall see, overturned the phlogiston theory. He was affected by the doctrines of the old school, and held many fashionable fallacies, such as the opinion that mercury could be obtained from various metals.

Ambrose Godfrey Hanckwitz (1660—1740), although born at Hamburg, was brought over to London by the Honourable Robert Boyle as his assistant. He discovered independently the method of making phosphorus, but Boyle appropriated

the discovery. In 1729 he was elected a Fellow of the Royal Society, and along with Sigismund August Frobenius conducted experiments before the Society in 1731 on *Phosphorus urinae* and *Spiritus vini aethereus* (ether). Hanckwitz believed neither in the philosopher's stone nor in any other branch of alchemy. His two elder sons, Boyle and Ambrose Godfrey, inherited his fondness for literary composition. The name Hanckwitz was dropped soon after the family came to England and that of Godfrey adopted. Boyle Godfrey wrote "Observations," and Ambrose a "Compleat Course of Chemistry" in four folio volumes, but the latter is best remembered as the originator of Godfrey's Cordial.

René Antoine Ferchault de Réaumur (1683—1757) was born and educated at La Rochelle, and went to Paris in 1703. He is distinguished for his practical discoveries in connection with iron. He improved the method of obtaining wrought iron, and showed how to convert the metal into steel. His chief metallurgical book is "Art de convertir le Fer forgé en Acier" (1722). He made experiments on the manufacture of porcelain, showing that it is necessary to use two earths, one infusible and the other melting at a high temperature, and tabulated the specific gravities of various mixtures of alcohol and water. He also devised the thermometer scale which bears his name, and wrote much upon natural history.

An energetic and successful chemist, Caspar Neumann (1683—1738) was a native of Zulichau, in Silesia, and was regularly trained as a pharmacist. He travelled with the king as Royal Apothecary, and at his majesty's expense journeyed throughout Germany, Holland, and England, learning all that was then known about drugs and medicines. On his return he was appointed Court Apothecary at Berlin, and Professor of Practical Chemistry in the Medico-chirurgical College. In 1724 he was created Supreme Superior of Prussian Apothecaries, and received numerous honours, including the rank of Hofrath.

Neumann's *Systematic Lectures* were published after his

death, and were translated into English in 1760. His generalisations on important subjects are generally incorrect, but he made a few discoveries—*e.g.*, that amber is not identical with dried albumen, and that a volatile oil may be prepared from ants. Various papers by him are included in the Transactions of the Royal Society of London, but his reputation is mainly that of a skilled and erudite teacher.

The tradition of Becher and Stahl was now taken up by one of their most distinguished pupils. Johann Heinrich Pott (1692—1777) was born at Halberstadt, where his father was a Prussian councillor and canonicus. Like Boerhaave, he was at first intended for the Church, but adopted medicine. He graduated at Halle and afterwards went to Berlin, where he was, almost on arrival, admitted a member of the Academy of Sciences. On the foundation of the Medico-chirurgical College he was appointed Professor of Theoretical Chemistry, and on the death of Neumann teacher of Practical Chemistry and Director of the Royal Pharmaceutical Establishment. He died at Berlin.

Pott's principal books are: *Lithogognosis ou Examen Chymique des Pierres et des Terres en general* (Paris, 1753), and *Wissenschaften Chymischen Untersuchungen* (Potsdam, 1746). He also wrote a memoir on "*The Sulphur of the Metals.*"

His chief practical work was in connection with borax, one of the many substances known to the Greeks and Romans under the name of *chrysocolla*, and one of two known to the Arabs as "*baurach*," the other being nitre. This Arabic name is the origin of the word "*borax*," which was applied to the product brought from Thibet and Nepal. He published his dissertation on this substance in 1741. Homberg's sal sedativum (boric acid) (p. 242), he considered a neutral salt compounded of molecules of copper-vitriol and borax. He believed that phlogiston was a variety of sulphur. His theoretical generalisations are of no great value, but his empirical work was important. He recognised the true properties of succinic acid, proved in 1740 that pyrolusite contains no

iron, and observed that silicic acid dissolved in alkali cannot always be re-precipitated by acids, although he gave a wrong explanation of the fact.

Pott's researches into the action of various bodies upon minerals at high temperatures were of great moment. For the purpose of these experiments, he designed suitable furnaces and vessels, but failed to make the discoveries he would otherwise have made, in consequence of his using exclusively the dry method. In this way he investigated the black oxide of manganese ( $MnO_2$ ) and talc (without finding either manganese or magnesium), common salt, and other substances. He thought there were four kinds of earth: the alkaline or chalky, the silicious, clay, and gypsum. These researches were undertaken with the object of finding a method for the manufacture of Dresden china, and on the instructions of the King of Prussia. On the whole, the results Pott achieved were not commensurate with his untiring efforts.

In France the views of Stahl were known and adopted soon after 1700, but the older names were retained in place of Stahl's names, and the teaching of the master was expressed as if it were the necessary result of earlier opinions. One of the great names in this French School was Guillaume Homberg (1652—1715). He had a varied career, which will be found fully recounted in the eloquent *Éloge* of M. de Fontenelle (*Œuvres*, 1767, Vol. V., p. 407). It is therefore unnecessary to repeat the tale here, especially as it has no bearing on the history of chemistry. Briefly, it may be said that he was born at Batavia, in the island of Java, his father being a gentleman of Quedlimburg, whose affairs having been ruined by the Swedish war, he was forced to emigrate in search of fortune. The son returned to Europe with his father, resided some years at Amsterdam, and, after studying law at Jena and Leipsic, began practice as an avocat at Magdeburg. Although he was diligent in the practice of his profession, he perceived that the knowledge of arbitrary human laws was not the only mundane knowledge, and was irresistibly led to the study of the greater

laws of Nature. After experimenting with the air-pump for some time, he went to Italy and there made phosphorus with the famous Bologna stone. He next visited France and England, in the latter country working under Boyle. He then returned to Holland. During these latter years he had been applying himself to medical studies, and graduated at Wittenberg as Doctor of Medicine. At this time he bought the secret of Kunckel's phosphorus. A wandering life ensued, during which he passed from place to place as he got advantageous offers, and finally those of M. Colbert were so tempting that he settled in Paris, and for the rest of his life his principal residence was in France. Thirty-one papers by him are preserved in the memoirs of the French Academy.

We find Homberg in 1703 writing of the "sulphur of common sulphur," an old alchemical expression, and calling the combustible principle "sulphur," although he knew that it differed from common sulphur, giving to the word "sulphur," after the fashion of the French School, the same meaning as Stahl assigned to the word "phlogiston." Again in 1710 he speaks of the combustible property in animal and vegetable substances as "sulphur" of different kinds. In experimenting with animal substances he made "pyrophorus" by roasting a mixture of fæces and alum. He retained the old Aristotelian conception of the constitution of matter, and believed in the possibility of transmuting metals. Although he made many discoveries, the value to science of his services is lessened by the fact that he did not possess the capacity of correctly interpreting the facts discovered. He observed the phosphorescence of molten calcium chloride; was the first to prepare boric acid in 1702 by the action of sulphuric acid on borax, calling the product *Sal sedativum*; noted the inflammability of oil when mixed with nitric and sulphuric acids; fixed the melting point of an alloy of tin, lead, and bismuth; and described a method of estimating the amount of acid in a solution by means of alkali. In addition, he made many observations on technical subjects,



such as the separation of metals from their ores, and the preparation of Indian Ink.

Another French chemist, Stephen Francis Geoffroy (1672—1731), the son of an apothecary, was born at Paris. He became a celebrated physician, and was made a Fellow of the Royal Society of London, as well as a member of the French Academy. He was Professor of Medicine at the Jardin des Plantes from 1712 till his death. His best work was the exhibition in tabular form of the order of chemical composition. These *Tables des Rapports*, or tables of affinity, exercised a prolonged influence upon that part of the science, and rendered him famous. In 1718 he used the expression "sulphurous principle" or "oily principle," with the same signification as the "terra pinguis" of Becher. His *Treatise of the Fossil Vegetable and Animal Substances that are made use of in Physic* was translated into English in 1736 by Dr. George Douglas.

Andreas Sigismund Marggraf (1709—1782), whose name is spelt in various ways, was born at Berlin, where he was trained under Neumann. After spending some years at the schools of Frankfort-on-Main and Strasburg, he studied medicine at Halle under Hoffmann and Juncker, and mineralogy and metallurgy at Freiberg under Henekel. Much of his time was occupied in travelling, partly among the Hartz Mountains. Returning to Berlin, he was successively head of the chemical laboratory of Berlin Academy and director of its physics class. He died at Berlin.

Marggraf was the last and most eminent adherent of the doctrine of phlogiston in Germany. He is more particularly remembered as the discoverer of beetroot sugar, a discovery destined to have far-reaching economical effects, but his other discoveries were numerous and valuable. He raised the importance of qualitative analysis by the wet method, and greatly improved it. Alumina, magnesia, and lime were clearly discriminated by his efforts, and he gave the names of the most common minerals which contain these earths. Caustic soda was prepared by him in a purer condition than was

previously known, and he distinguished between it and other alkalis. The precipitation of various metals by alkalis was described by him, and he observed that excess often dissolves the precipitate so formed. He improved the process for extracting phosphorus from urine, and made valuable observations on phosphoric acid; prepared metallic silver from the chloride of the metal by dissolving it in nitric acid and adding mercury, thus producing an amalgam; and invented various mixtures of metals suitable for commercial purposes. He just missed several greater discoveries, as, for example, when he investigated the black oxide of manganese without isolating the metal, and fluor spar without discovering fluorine. He introduced the microscope as an aid in distinguishing bodies.

The last of the Phlogistonists properly so called was a French chemist, Pierre Joseph Macquer (1718—1784). He is said to have been of Scottish origin, his family having removed from Scotland to France on account of their Roman Catholic religion and Jacobite principles. Paris was his native city, and he studied medicine and science, graduating in 1742; but the practice of medicine was almost from the first deserted by him for the study of chemistry. He became a teacher at the Jardin des Plantes. His death was due to ossification of the aorta and heart.

Macquer was a worker of great originality. He was one of the first Frenchmen who gave full recognition to the views of Stahl, but he seems to have been conscious of the defects of the Phlogiston hypothesis, and some of his work has a bearing on the later development of chemistry. It is probable that he would have upset the theory had he conducted his investigations respecting it in the same way as he investigated other subjects; but he failed, owing to the fact that, despite his using the method in other researches, he never in his work on the theory of combustion attempted to make use of *quantitative methods*.

His empirical discoveries were of greater value than his theoretical conceptions. He investigated the solubility of

oils and salts in alcohol, showing that sulphates are much less soluble than nitrates and chlorides, and that in general alcohol dissolves those salts most readily in which the acids are less firmly combined, a foreshadowing of more modern views. His researches formed the basis upon which many analytical separations rest. In technical work he experimented on making flint glass useful for optical purposes. His studies in relation to arsenic were of high importance. In 1746 he demonstrated its metallic character, and subsequently prepared arsenic acid and potassium arseniate. He observed that Prussian blue when heated loses colour, a phenomenon which he ascribed to the loss of phlogiston. Amongst his other work may be mentioned his examination of alumina, the sulphates of calcium, ammonium and magnesium, zinc, the oxidation of tin and silver, the volatilisation of gold, the preparation of platinum, the solubility of india-rubber, and the composition of milk. In 1771 he witnessed the combustion of a diamond, an experiment previously performed by Averami and Targioni in 1694. These philosophers, on the suggestion of Duke Cosmo III. of Tuscany, completely consumed a diamond in the focus of a convex lens. It remained for Lavoisier and Davy to demonstrate that the product of this combustion was carbon dioxide ( $\text{CO}_2$ ), and to infer from this that the precious stone is pure carbon.

The principal chemical writings of Macquer are : (1) *Elémens de Chimie* (1741) ; (2) *L'Art de la Teinture en Soie* (1763) ; (3) *Dictionnaire de Chymie* (1766). The last, his most important work, was translated into English by Kerr in 1777.

The Phlogiston theory held possession of most minds for more than a century after Stahl enunciated it. Priestley, the discoverer of oxygen ; Black, the re-discoverer of fixed air (carbon dioxide or carbonic acid gas), previously observed by Van Helmont ; Cavendish, who may be almost called the discoverer of hydrogen ; Scheele, the discoverer alike of oxygen and of chlorine ; in short, all the great pioneers who cleared the foundations of modern chemistry towards the end of the

eighteenth century, were Phlogistonists. They all began by accepting the hypothesis, and many of them died in the belief of it. We might have added the discoveries of these men to those we have considered in this and the preceding chapter, had they been no more than Phlogistonists. But they were much more. They introduced to the study of chemistry the accuracy and precision obtained by the expert use of the balance and the pneumatic trough, and they will be more fittingly discussed in the chapters which deal with the fifth and last section of the subject, the Quantitative Period.

We have already remarked on the importance which chemists have always assigned to the phenomena of combustion. The difficulties with which the older workers had to contend are well set out in the following passage extracted from Mr. Pattison Muir's "Chemistry" :—

“The alchemists thought of combustions, as they thought of many other changes, as processes wherein the qualities of certain things were destroyed in order that what they called the essence or soul of the things might become apparent. Qualities or properties were regarded by the alchemists as external wrappings that might be removed without alteration of the essential substance which they enfolded. As such qualities as colour, taste, and smell, are increased and sometimes decreased by mixing coloured, tasting, or smelling things, so the alchemists supposed that all the properties of a substance may be either increased or decreased by adding other substances to it. They had not discovered, it was impossible with their appliances to discover, that the mass of the product of adding one substance to another is the sum of the masses of the things that have been used. They did not trouble about that property of substances which we call mass, and know to be of extraordinary importance.”

Combustion, therefore, according to the alchemists, was a process whereby the external qualities of substances were destroyed and the internal soul was revealed. It was very hard for later chemists, trained in these views, to get rid of the mental bias produced by such doctrines. Consequently, we find in all attempts to explain the phenomena of combustion

an effort to show that something was removed. We have noted what Becher and Stahl thought upon this point, and we discover the same latent idea running through the theories of their successors.

When in 1766 the Honourable Henry Cavendish had proved the compound character of water, and had obtained an inflammable air from iron, zinc, and tin, when immersed in water acidulated by hydrochloric or sulphuric acid, he believed that this was the inflammable principle of these metals, which flew off when they were dissolved. He recorded his opinion that this "inflammable air" (hydrogen) was very rich in phlogiston, or even was pure phlogiston, just as Stahl had written of *soot* nearly fifty years earlier. Subsequently, he changed his view, and considered "inflammable air" as a compound of phlogiston and water. And yet the untenable character of the phlogiston theory had been demonstrated by the experiments of more than one chemist even before Becher had suggested it. We shall have more to say on this subject when we discuss the Anti-phlogistonists, but it will be expedient to close this chapter with some general reflections on the weakness of the theory.

Phlogiston was essentially a principle of combustion, but incidentally it was also a principle of composition. No man could explain why a body burns without first explaining how it is composed. The Phlogistonists, therefore, were compelled to devise a theoretical system which would account for the formation of all substances, inorganic and organic, and which would be logically consistent with their theory of phlogiston, just as the alchemists and iatrochemists before them had been forced to support their special doctrines by imaginary principles. In this the Phlogistonists were not more successful than their predecessors. In all three cases the fundamental idea was wrong, and in consequence the system built upon it was wrong also.

The great French chemist Lavoisier, whose labours finally overturned the phlogiston hypothesis, thus described its



defects : "Chemists have turned phlogiston into a vague principle which consequently adapts itself to all the explanations for which it may be required. Sometimes this principle has weight and sometimes it has not ; sometimes it is free fire and sometimes it is fire combined with the earthy element ; sometimes it passes through the pores of vessels, sometimes these are impervious to it : it explains both causticity and non-causticity, transparency and opacity, colours and their absence. It is a veritable Proteus, changing in form at each instant." A hypothesis of this sort was too flexible to be a secure foundation for a scientific doctrine.

Of the many objections to the phlogiston hypothesis we shall select two : its failure to account for the influence of atmospheric air on combustion, and its failure to explain the increase of weight in metals during calcination.

The older philosophers had observed by experiment that a lamp will not burn in a closed vessel, but the fact was familiar to every housewife. Neither candle, lamp, nor fire will burn without air. This obvious circumstance, and its important consequences, were practically ignored by the phlogiston theory. The decomposition of a body into its constituents might take place, and the combustible substance might escape, without any relation being established between the burning body and the atmospheric air. Stahl did, indeed, attempt to explain the fact by the assertion that phlogiston assumes a rapid, whirling motion, and that this cannot happen in a closed place ; but he adduced no proof in support of his statement. A hypothesis which passed over, without adequate explanation, a physical fact so obvious as the intimate relation between atmospheric air and combustion, was open to the criticism that some serious fallacy must lie at its root.

The second objection is even more forcible. It had long been known that many combustible bodies, among others, the metals, gain weight when burned. This circumstance is totally inconsistent with the suggestion that combustion means the loss of something. If the phlogiston escaped in

the act of combustion, we should expect the calcined material to be *lighter* than the original mass, not heavier. But it *is* heavier. As a matter of fact, it is now known that the calcined product is equal in weight to the weight of the combustible body burned and the weight of the oxygen consumed during the process of combustion. The Phlogistonists did not ignore this fact, but tried to explain it. They asserted that phlogiston is a principle of levity or lightness, which tends to cause a substance with which it is combined to recede from the earth in place of being attracted towards it by the ordinary action of gravity. Therefore, when the phlogiston escaped during the process of combustion, the principle of levity was expelled, and the ordinary laws of gravity came into play. The body would not be really heavier than it was previous to combustion, but its true weight would for the first time be perceptible. Thus, a body after combustion is not actually heavier, but only *seems to be heavier*. The explanation, although ingenious, was not merely improbable, but was incapable of proof. It was never regarded as satisfactory, and when the facts connected with combustion were better appreciated, and the results tested by more accurate measurements, the phlogiston hypothesis was entirely discredited.

Chemistry advanced during the Phlogiston Period, but its gain had little to do with phlogiston. That hypothesis was erroneous, and in due course passed away. The real advance was in a more correct appreciation of the objects of chemical science. The Alchemists sought to make gold; the Iatrochemists sought to make medicines; the Phlogistonists sought to arrive at the truth. That was the great lesson of the Period. It had, indeed, been hinted before the beginning of that period by one of the greatest pioneers of chemistry, the Honourable Robert Boyle, whom we shall have to discuss among the Anti-phlogistonists. The seed sown by Boyle developed during the operations of the phlogistonists and their opponents, and brought forth fruit long after his death. The close alliance with medicine which was effected by the teaching

of Paracelsus was at first of the greatest possible benefit to chemistry, but in the hands of the iatrochemists it tended to become a curb, checking further development. Under the auspices of the Phlogistonists this yoke was made lighter, and the relationship between medicine and chemistry was reduced to its proper dimensions, mutual assistance.

Chemists now began to apply the doctrine set forth by Francis Bacon in his *Novum Organum*: "True experience begins with an ordered, not chaotic, knowledge of facts, deduces axioms from these, and from the axioms again designs new experiments. Equipped with such axioms, chemistry might enrol itself amongst the exact sciences." The Phlogistonists were wrong in their theory, but not in their practice. They obtained by their experiments an ordered knowledge of facts, deduced axioms from these facts, and from these axioms designed new experiments. Chemistry was, in fact, at length in the way of becoming an exact science.

## CHAPTER XXII

### THE ANTI-PHLOGISTONISTS

*(From 1650 A.D. till 1775 A.D.)*

#### I. ROBERT BOYLE AND ROBERT HOOKE

IN the two preceding chapters we have been considering an ingenious and interesting, but wholly erroneous, theory of combustion. We shall now endeavour to trace the steps by which chemists reached a correct conception of this subject. In doing so it will be necessary to go back upon ground which we have already passed over, and also to anticipate some facts, which belong to a later period; but it is better to do this than to run the risk of giving an incomplete impression of an important matter.

Before entering upon a discussion of the work of the Anti-phlogistonists, it is requisite that we should draw attention to one of the most important influences which helped to bring about the great advance in scientific knowledge which is so distinguishing a feature of this period. The learned societies formed in every civilized country were of the utmost benefit to science. The Paris Académie des Sciences, the Academy of Berlin, the Royal Society of England, and many others, were centres of investigation and research. They gathered together the leading students of science in each nation, directed their labours into one common channel, prevented needless overlapping of work, and by using the resources at their disposal, rendered possible numerous expensive experiments, which would have overtaxed the means of individual workers. Many errors were doubtless encouraged by them, for no human institution is perfect, but on the whole they have been faithful to their trust. The Royal Society of England, after some pre-

liminary unincorporate proceedings, was regularly constituted by Royal Charter in 1662, under the auspices of Charles II., and forms at least one really good thing which can be laid to the credit of that monarch's reign. It is a great glory to the Society that at its outset it numbered among its members such men as Sir Isaac Newton, the Honourable Robert Boyle, and Robert Hooke.

We have already alluded to the conventional aspect in which the alchemists regarded combustion, but there were not wanting signs that the ordinary explanation of the phenomena was not found to be entirely satisfactory. It had been casually observed in the fourteenth and fifteenth centuries that metals when burnt to form their *calces* (or, as we would say, their *oxides*) increase in weight. Cardanus in his book *De Rerum Subtilitate* (1553) recognised as a fact the increase in weight on transforming lead into its calx, and explained this by its assumption of caloric or fire-matter. — Others, still later, among whom were Kunckel and Juncker, explained the phenomenon by supposing that particles of air were absorbed by the metal: but as these men confounded specific gravity with absolute weight, their reasoning is far from clear. Between 1630 and 1640 Van Helmont observed that air is diminished when bodies are burned in it, while Le Febure in his *Traité de Chemie* (1660) said that antimony fixes the matter of light and becomes heavier.

Otto Tachenius in his *Hippocrates Chemicus* (1666) determined the fact that lead when burnt to form red lead, increases its weight by one-tenth, and returns to its former weight on its reduction to the metallic state. He explained this by assuming that an acid, which exists in the flame, is absorbed by the lead calx. In this view he was followed by the French Academician Ducloux in 1667. A few years later Becher in his *Physica Subterranea* acknowledged that lead, tin, and antimony, while losing particles by being burned to their calces, nevertheless became heavier. For this he accounted by the weight of the fire-matter.



Such was the state of opinion among chemists of the first rank, when a philosopher appeared, who was before his age by more than a century—the Honourable Robert Boyle. Abundance of material exists for a biography of Boyle, and many such have been written. Among the best are the essays by Dr. George Wilson in the "*Religio Chemici*" (1861), and by Sir T. E. Thorpe in his "*Essays in Historical Chemistry.*" Although the former deals mainly with the work of Boyle as a physicist, it furnishes an admirable picture of the man and his times.

The Honourable Robert Boyle (1627—1691) was the seventh son and fourteenth child of the Earl of Cork, and brother of the famous Earl of Orrery. He was born at Lismore Castle, near Youghal in Munster, and was educated first at home and then at Eton under Sir Henry Wotton. When eleven years old he spoke both Latin and French, and travelled with one of his brothers



FIG. 86.—The Honble. Robert Boyle.

on the Continent, passing through France, Geneva, and Italy. The death of his father recalled him to England, and he succeeded to estates crippled by the Rebellion in 1642. His most valuable succession was the Manor of Stalbridge in Dorsetshire.

In 1644 Boyle went to Oxford, where in conjunction with Dr. Willis and others he formed what was called the *Invisible College*, an assembly of learned men, who applied themselves to the study of the new philosophy. This body was the foundation of the Royal Society of England, of which Boyle was elected president in 1680. He was much attracted by the invention

by Otto von Guericke of a rudimentary air-pump, and after many experiments produced in 1659 an improved form of the instrument, which he called his "great pneumatical engine," and which was known throughout the Continent as *Machina Boyleana*. In the construction of this and other forms of air-pump he was greatly assisted by Robert Hooke; but the ingenious experiments by which he made various important discoveries were entirely original. Many of these are lucidly explained in the *New Experiments* (1660). He occupied himself with experimental work in London until his death at the age of sixty-four, just a week after that of his sister Lady Ranelagh.

A few words may be said regarding the strong religious feeling which played such an active part in forming the character of this great man. On this point the words of Dr. Wilson cannot be improved: "Boyle was something more than a philosopher. He was a Christian philosopher. Foolish as this world is, it contains many philosophers; wicked as it is, it contains many Christians; but not many Christian philosophers. Boyle was one of the few who, from time to time, are granted to us by a kind Providence to make us wiser and better." If he would have taken Orders, he was offered the Provostship of Eton, but he declined the honour, for the very characteristic reason that he thought his writings on religious subjects would have greater weight as coming from a layman.

Boyle introduced into England the air-pump and the thermometer, and improved both. The latter instrument was in 1701 made accurate by Sir Isaac Newton, who fixed the points at which water boils and freezes, and divided the interval into equal degrees. Boyle was greatest as a physicist. As a chemist he laid down no doctrines of his own; his work was destructive rather than constructive; and he was most distinguished as a critic and corrector of the false chemistry of his time. His works are very numerous. The best edition is that of Thomas Birch (1744).

It has been remarked (although erroneously) that Boyle was born in the year which witnessed the death of Francis Bacon,

the Father of Inductive Philosophy, and it is his chief merit that he was the first to carry out thoroughly the principles laid down in that philosopher's *Novum Organum*. The acquisition of knowledge of facts was to Boyle an end sufficient in itself ; he objected to the devising of hypotheses. And yet he was so far the child of his age that he believed in the purely hypothetical doctrine of the transmutation of metals, conducted experiments to establish that doctrine, and even obtained the repeal in 1689 of the statute of Henry IV. against multiplying gold and silver to which we formerly alluded (*supra*, p. 147). So difficult is it to free the mind from the trammels of a generally accepted philosophy.

In the region of physics Boyle made three very important discoveries : (1) that the volume of a gas varies inversely as the pressure (still called *Boyle's Law*) ; (2) that air plays an important part in the transmission of sound ; and (3) that water expands in the act of freezing.

In chemistry he did valuable work in relation to combustion, respiration, and analysis—a term which he was the first to apply to the process of separating compound bodies into their ingredients ; he discovered methyl alcohol ; and prepared in 1664 cupric chloride ( $\text{CuCl}_2$ ) by the action of mercuric chloride ( $\text{HgCl}_2$ ) on copper. But, as we have said, he was greatest as a critic and corrector of the false chemistry of his day.

Boyle published his famous book, *The Sceptical Chymist*, in 1661. It has frequently been reprinted, and an edition has recently been issued in Everyman's Library with an admirable introduction by Mr. Pattison Muir. The work was based upon Boyle's experimental investigation of physical phenomena, and advocates the inductive method of scientific inquiry by experiment, observation, and measurement. In it he raised doubts as to there being a determinate number of elements, rejected the Aristotelian doctrine of four elements and the Paracelsian theory of three principles, and questioned the elements recognised by contemporary chemists, thus over-

turning the opinions of the iatrochemists, and introducing a new era in the history of our science. He showed that the root error was the conception that the manifoldness of Nature is a unity—a doctrine which conduced to the readiness of the ancient philosophers to construct and re-construct the order of the universe according to their own imagination. He declared that these men used experiments rather to illustrate than to demonstrate their theories.

He demanded a clearer definition of what was expressed by the term "element." He himself defined an element, as we do now, as a body which cannot be further subdivided or separated, but which can be obtained from a compound body, and from which the compound may be again constituted. The first elements of bodies, he said, are atoms of different shapes and sizes, and the union of these atoms produces the bodies which are commonly called elements. *Decomposition* takes place when a third body exerts a greater attraction on the particles of one element than the particles of the other element with which it is combined. In a later book, *The Imperfections of the Chemical Doctrine of Qualities*, he pointed out the hypothetical and insufficient character of the received notions.

His views were controverted by able writers, although a chemical academy at Paris confirmed his experiments. The iatrochemists sought to maintain the "acid and alkali" theory of disease by distilling blood with bole (clay), whereby they obtained an acid distillate. So far was science behind Boyle, that this was accepted as proof that blood contained an acid.

Boyle had a large share in the development of that true theory of combustion which we are now considering. He did not indeed detect the meaning of the observed fact that calces weigh more than the metals from which they are formed. He knew the fact, but owing to the prejudice caused by his early training, he did not recognise the nature of calces.

In 1673 he published a pamphlet containing *Experimenta Nova*, "by which it is shown," he said, "that it is possible to



render the parts of fire stable and ponderable." He observed that by heating a weighed portion of tin till it became a calx, it increased in weight, and he deduced from this that heat was ponderable matter which had united with the tin. This view was quite inconsistent with the subsequent phlogiston hypothesis of Stahl. Boyle says that the calx of tin is tin *plus* heat; Stahl says that it is tin *minus* phlogiston. It is, of course, neither; but is tin *plus* oxygen. The Phlogistonists failed to see that if phlogiston was a principle of *levity*, or the opposite of gravity—that is to say, if its gravity was a *minus quantity*—it could not attract, because gravity is an attraction of bodies for each other. Therefore, as phlogiston so constituted must *repel* all other substances, it could not become fixed in combustible bodies.

Boyle in 1675, in a paper "*On the Mechanical Origin and Production of Fixedness*," when discussing the formation of oxide of mercury, a substance which was called "*precipitatum per se*," says: "I have not been without suspicions, that in philosophical strictness this precipitate may not be made *per se*, but that some penetrating igneous particles, especially saline, may not have associated themselves with the mercurial corpuscles." This *precipitatum per se*, as we shall afterwards observe, played a very important part a hundred years later in the hands of Priestley, who, by heating it, obtained mercury and the gas which he called "dephlogisticated air" and we call "oxygen," and showed that this dephlogisticated air was the substance with which metals combined when they were burned and converted into calces. Priestley demonstrated that metals obtained this substance from the air.

We shall take leave of the Honourable Robert Boyle by quoting the eloquent summary of Mr. Pattison Muir:—

"Although the details of many, perhaps most, of Boyle's arguments against the four elements of the Peripatetics, and the three principles of the vulgar Spagyrist, have not any very great interest for modern physicists and chemists, nevertheless the acuteness of Boyle's reasoning must impress every



intelligent reader, the soundness of his philosophy must come home to scientific students of Nature, the wide and generous views he takes of natural phenomena and of the scope of natural science must encourage all who seek clear and imaginative knowledge, and his constant striving after lucidity both of thought and expression, his justness of phrasing, and his humorous fairness to his opponents, must delight every admirer of literary power."

Meanwhile, Lemery in his *Cours de Chimie* (1675) discussed the theory put forward by some chemists of his day, that lead becomes heavier when burnt, because, although it loses the sulphurous particles and so should be lighter, yet by long heating it absorbs the acid of wood, and thereby gains weight. He remarked that this cannot be so, because lead becomes heavier when heated by burning charcoal, in place of wood, and charcoal contains only one fixed salt, which remains in its ashes, and does not rise at all. This theory being untenable, he attributed the increase of weight to the corpuscles of fire insinuating themselves into the pores of the heated lead as it loses phlogiston and becomes a calx. He thought that these corpuscles remained, and increased the weight of the metal, and that when the metal is revived from its calx by fusion, the parts approach each other and squeeze out the small igneous bodies, and thus the lead becomes less heavy than its calx. In 1709 he developed this theory in a paper read before the Paris Académie des Sciences with reference to lead, tin, antimony, and mercury.

Most chemists adopted Lemery's view. Thus, Kunckel in his *Chymischen Anmerkungen* (1677) answers his own question, whence comes the increase of weight on calcination, by saying "the *particulæ igniæ* have insinuated themselves into it." And again, Homberg in 1700, in a paper read before the Paris Académie, said :—

"We have examples in which the matter of fire introduces itself into certain bodies, remains, and increases their weight ; as, for instance, the regulus of antimony. We cannot say

that the increase in weight is due to a volatile salt, or an oil of carbon, which has introduced itself into the interstices of the regulus, because the carbon fire has not touched it. One is therefore obliged to admit an introduction of the particles of fire, which remain in the body, and render it heavier than it was before it was calcined."

Although these were the views prevailing at the beginning of the eighteenth century, there were not wanting other suggestions. Van Helmont had in 1640 expressed himself in another sense—that burning is not the separation of a special fire-matter, but a glowing condition of volatile bodies. (*Flamma est fumus accensus ; fumus est corpus Gas.*) It will be recollected that Van Helmont was the inventor of the term "gas" as applied to various gaseous bodies, such as "*gas silvestre*" and "*gas pingue*" (*supra*, p. 200).

So also Sir Isaac Newton in 1701 : "Is not fire a body heated so hot as to emit light copiously ? What else is a burning coal than red-hot wood ? Is not flame a vapour, fume, or exhalation heated red-hot ; that is, so hot as to fume ?" Metals do not flame, because they lack a copious fume.

Boerhaave in his *Elementa Chemiæ* (1732), while attributing the increased weight of metals on calcination to a ponderable fire-material, recognised the incorrectness of the view, in so far as he weighed a mass of metal when cold, and again when red-hot, and found no difference in the weight. He does not allude to Stahl's theory, although he must have known it, since it was well known to, and accepted by, most chemists of his time. He gives many instances of heat arising from the mixing of liquids, but offers no explanation, and in writing of Homberg's *pyrophorus* shows that he had no notion of the reason why air is necessary to maintain combustion.

In some almost forgotten essays of an old French chemist, we find several remarkable statements on the subject of combustion. Jean Rey (*circa* 1575—1645) was born at Bergerac in the Department of Dordogne. He was a physician, but occupied himself specially with physical and chemical studies, and

wrote the essays referred to, which at the time were little known.

Rey discussed an experiment of an apothecary named Brun, in which two pounds six ounces of the finest English tin, by six hours' calcination, gained seven ounces in weight, while a similar quantity of lead gained one ounce in the pound less than this. He answered the question, why lead and tin thus increased in weight on calcination, by saying that the increase in weight came from the air, which had been condensed and rendered adhesive by the long-continued heat of the furnace, which air mixed with the calx and attached itself to its minutest particles. He did not know that the calx was simply a compound of the metal with air. He proved, however, that the increase in weight was not due to the vessels, the carbon vapour, a volatile salt of carbon, a volatile mercurial salt, or absorption of moisture. "The condensed air," he says, "becomes attached to the calx, and adheres, little by little, even to the smallest of its particles. Thus its weight increases from the beginning to the end. But when all of it is saturated, it cannot take up more. Do not continue your calcination in hope of this, or you will lose your labour" (*Alembic Club Reprints*, No. 11, p. 52). He also discussed why ashes and other calces (not metallic) do not increase in weight.

These passages are extracted from Rey's "*Essays sur la Recherche de la cause pour laquelle l'Estain et la Plomb augmentent de poids quand on les calcine*" (1630), which were republished by Gobet in 1777, and translated as No. 11 of the *Alembic Club Reprints*. They show how a man may hover on the brink of a great discovery, and yet fail to make it. Rey was within a short distance of the true theory of combustion, but just missed it.

In treating of Boyle we have already mentioned Robert Hooke (1635—1703), who assisted him so much in the construction of his pneumatic engine. Hooke belonged to the same Oxford school of chemists as Boyle and Mayow. He was born at Freshwater, in the Isle of Wight, being the son of the parish

clergyman. He was educated at Westminster School and Christ Church, Oxford. He assisted Boyle in his researches in 1655, and was in 1663 elected a Fellow of the Royal Society, of which he became secretary in 1667. He was in 1665 appointed Professor of Geometry at Gresham College, and received many honours, yet he died in London a disappointed man. In person he was haggard and crooked, and in temper irritable, but he was a truly religious man, like his friend. He originated much, but perfected little. He invented the wheel barometer, investigated the nature of sound and the function of the air in respiration and combustion, and originated the idea of using a pendulum as a measure of gravity. His books are: *Micrographia* (1664) and *Lectiones Cutlerianae* (1674—1679).

In his *Micrographia* he recorded an outline of a theory of combustion which was more nearly correct than many that succeeded it. His experiments showed the similarity of the actions produced by air and by saltpetre, and he inferred that combustion is effected by that constituent of the air which is fixed in the saltpetre, or is at least similar to that in saltpetre. In thus forecasting the action of oxygen he came very near the truth.

In his Cutlerian Lecture to the Royal Society in 1679 he related experiments on the use of air in respiration, and in maintaining fire. He said that "air is a menstruum that dissolves all sulphurous bodies by burning, and without air no such dissolution will follow, though the heat applied be never so great, which was tried particularly by charcoal enclosed in an iron case with a screw stopper, which, though violently heated, yet the coke was not burnt nor wasted when taken out."

Hooke was the first to recognise that flame is a mixture of gases undergoing chemical "dissolution," that is, union; and that a combustible body will not burn in the absence of air. "That transient shining body which we call flame is nothing but a mixture of air and volatile sulphurous parts of combustible bodies, which are acting upon each other as they ascend"; an action so violent, he says, that "it imparts such a motion

or pulse to the diaphanous parts of the air as was necessary to produce light."

In this manner, step by step, chemists were by means of experimental research drawing nearer to the truth. We shall in the next chapter relate how the final steps were taken, and the true theory of combustion was discovered.

*[Faint handwritten notes, possibly bleed-through from the reverse side of the page, including words like "Hoffmann", "Bunsen", and "Lavoisier".]*



## CHAPTER XXIII

### THE ANTI-PHLOGISTONISTS

(From 1650 A.D. till 1775 A.D.)

#### 2. JOHN MAYOW AND STEPHEN HALES

THE inquiry respecting a true theory of combustion was continued by John Mayow (1643—1679), a native of London, who was educated at Wadham College, Oxford, and was elected a Fellow of All Souls in 1660.

He graduated in law, but made medicine his profession. Removing to Bath, he had a large practice as a physician there. In 1678 he was elected a Fellow of the Royal Society. His published works are : two tracts, one on respiration (1668) ; five medico-physical tracts, one *De Sale Nitro et Spiritu nitro-aereo* (1669) ; and *Opera Omnia Medico-physica* (1681).



FIG. 87.—John Mayow.

Mayow recognised the fact that air is necessary to combustion, but advanced before other observers by asserting that fire is supported, not by the air as a whole, but by a more active and subtle part of it. Having also perceived the action of nitre in supporting fire, he identified the active and subtle part of the air with one of the constituents of the acid portion of nitre. He therefore named it *Spiritus Igneo-aereus* or *Nitro-aereus*. Nitre or saltpetre was composed of a *spiritus acidus* united to fixed alkali.

According to Mayow, when combustion takes place, certain *particulæ nitro-aerææ*, which are either pre-existent in the body burnt or are supplied by the air, combine with the calcined body. He showed that antimony, when heated with a burning-glass, undergoes an increase of weight, which can only be attributed to these particles. Similar particles are consumed in respiration. If a lighted candle and a small animal are placed in a closed vessel, the candle first goes out, and then the animal dies; whereas, if there is no lighted candle, the animal lives twice as long. He supposed that the lungs separate this constituent from the air, and pass it into the blood. Animal heat is due, he said, to the union of these nitro-aereal particles, inhaled from the atmosphere, with combustible particles in the blood, and it is also produced by a similar combination in muscle during violent exercise. The increase of weight in calcined bodies was due to a like union of the metal with the *spiritus nitro-aereus*. Undoubtedly, this was the gas which was later discovered by Priestley, and named "Oxygen" by Lavoisier.

Mayow was one of the first to describe experiments made with gases collected over water, and by showing that air is diminished in bulk by combustion and the breathing of an animal, clearly discovered that it is composed of *spiritus nitro-aereus* (oxygen) and an inert gas. He defined fire thus: "*Ignis nihil aliud est quam particularum nitro-aeriarum sulphurearumque, mutuo se commoventium, fermentatio maxima impetuose.*" But neither his nor Hooke's discoveries and views made any impression at the time. Contemporary chemists seem to have failed to appreciate their importance.

Mayow was also the first to determine the density of a gas, but did not discriminate between air and other gases. He thought that saltpetre could be made by the union of nitric acid derived from the air with an alkali, and that sulphur united with the *spiritus nitro-aereus* to form sulphurous acid, which again combined with the metals to form vitriols, blue, green, and so forth.

This view of Mayow was to some extent shared by Dr. Willis, who, in 1671, explained animal heat and the process of respiration, by likening these to a flame fed by a special sulphurous body and a nitrous body, which is existent everywhere in the air.

Another distinguished English philosopher, Stephen Hales (1677—1761), was born at Bekesbourne, in Kent. His father was a baronet. He was educated at Corpus Christi College, Cambridge, of which he was elected a Fellow in 1703. Entering the Church, he became perpetual curate of Teddlington, with other benefices attached. In 1717 he was admitted a Fellow of the Royal Society, whose Copley medal was awarded to him in 1739. He was elected Foreign Associate of the French Academy in 1753.

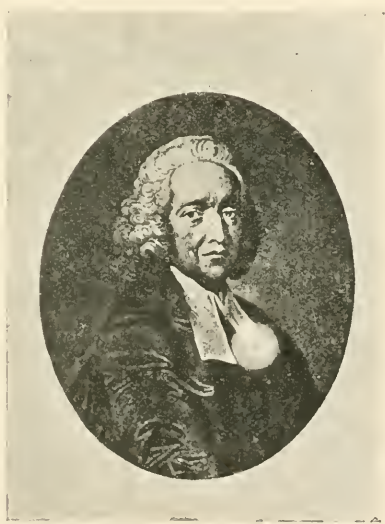


FIG. 88.—Stephen Hales.

Hales' chief books are his *Statical Essays*. The *Vegetable Staticks* (1727) deals with the loss of water in plants by evaporation and other phenomena of plant life. In the course of his experiments he collected gases over water, and thus practically invented the pneumatic trough. His *Haemostaticks* (1733) deals with the phenomena of the blood. He is also remarkable as the inventor of a system of ventilation by means of which air was introduced into confined places. In 1726 he obtained an inflammable gas from coal, and in the following year gaseous ammonia by heating sal ammoniac with lime. He examined gases principally with respect to their inflammability and power of supporting combustion. He believed that air which had been

breathed or used for supporting combustion could be used again for the same purpose, if freed from the impure substances produced in these operations. He did not recognise different sorts of air, but thought that it was a true element, and that the various gases he examined were all atmospheric air, and owed their different properties to impurities which they contained.

In 1727 in his *Vegetable Staticks* he attributed the increase of weight in lead calcined to form red lead to the addition of some substance. He also tells what fire does, without saying how it acts. He writes: "The action and reaction of the aerial and sulphurous particles is in many fermenting mixtures so great as to excite a burning heat, and in others a sudden flame, and it is, we see, by the like action and reaction of the same principles in fuel and the ambient air that common culinary fires are produced and maintained." Nevertheless he and others who held similar views were approaching much nearer to the truth than their rivals of the Phlogiston school.

While chemists and physicists were thus striving to solve the two mysteries of combustion—its relation to air, and its relation to the increased weight of calces—the observations of the Phlogistonists were for some time characterised by a great absence of exactitude, and their views varied as to the nature of combustion and the composition of calces.

Even Bergman as late as 1782, in his treatise *De Diversa Phlogisti Quantitate in Metallis*, spent much time in an endeavour to determine how much phlogiston each metal contained. He thought that when a metal is precipitated from a neutral solution by another metal, and the solution remains neutral, since a metal is calx plus phlogiston, the phlogiston of the precipitating metal leaves it, because it exists in the solution as calx, and goes to the metal which is precipitated out. Therefore, inferred Bergman, since the solution remains neutral, the proportions of phlogiston in each metal are inversely proportional to the quantities of metals interchanged.

He found that 100 parts by weight of silver precipitated out 135 parts of mercury, therefore the quantity of phlogiston in

mercury was  $\frac{100}{135} = 74$  hundredths of the same amount of phlogiston in the same weight of silver. We would say: "The quantity of oxygen with which equal weights of metal combine," because the term "phlogiston" is equivalent to "absence of oxygen," or "capacity for combining with oxygen." Bergman in tabular form referred his quantities to 100 parts by weight of copper, thus:—

Copper 2·12 to 2·34	Mercury, ·54 to ·58
Zinc, 1·33	Bismuth, ·42.
Tin, ·83	Lead, ·31 to ·34
Silver, ·73	

But an era was approaching, had even now arrived, when the importance of precise determinations of volume and weight was felt by every experimenter. A considerable advance had been made in this respect upon the apparatus of the old alchemists, Mayow in 1670 had employed a form of pneumatic trough in collecting gases, while Stephen Hales, sixty years later, had invented a pneumatic method for the same purpose, very similar to that now in use. Hales distilled various substances and measured the amount of gas given off by them, but the importance of his experiments was lessened by two circumstances—that he did not distinguish gases from air, and that he still deemed air to be a true element, varying in purity in his different products.

It is now necessary for us, with the object of completing our inquiry into the development of the true theory of combustion, to anticipate a part of what we shall have to describe in the chapters devoted to the Quantitative Period. In doing so we shall merely narrate the discoveries, without entering at this stage into the biographies of the discoverers. These will be given in their proper place.

While, therefore, Bergman was yet engaged in determining the quantity of phlogiston contained in each metal, a discovery was made which overturned the entire phlogiston hypothesis. In 1772 Priestley in England, and Scheele in Sweden, discovered oxygen, collected it by means of the pneumatic trough, and



experimented with it. Priestley demonstrated that the red calx of mercury, the so-called *precipitatum per se*, was formed by the union of a gas constituting one-fifth of the bulk of the atmosphere. In 1774 he prepared this gas in the pure state by heating the red calx of mercury to a higher temperature by means of the sun's rays concentrated by a burning-glass.

Priestley thus proved that metals are *simple* and calces *compound* bodies. He named the gas, which would not burn, but which removed the combustible property from combustibles, and which was so far from phlogiston that it was purer than common air—"dephlogisticated air." The name shows that he was even yet a phlogistonist, and in fact he remained so to the end of his life, although his own experiments had destroyed the theory.

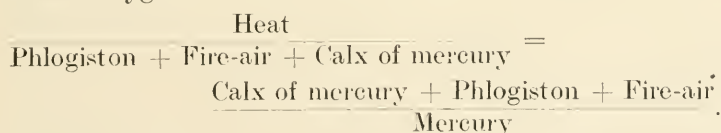
Lavoisier, following up Priestley's discovery, called the gas "oxygen," a singularly unfortunate name. Chemists could wish that he had chosen rather the name "hydrogen" for this gas, or that old John Mayow's discovery had been accepted in his day, and that the excellent descriptive term "spiritus nitro-aereus" had enforced its claim to adoption in respect of priority. Lavoisier showed by twelve years of steady experimenting that a combustible, in the ordinary sense of the term, is a body which can combine with oxygen, and that combustion is *practically combination with that gas*.

Scheele, the other simultaneous discoverer of oxygen, was, like Priestley, a strong supporter of the phlogiston theory, although he also disproved it by an investigation into the nature of fire and air. To find the relation of air to combustion, he heated in a confined volume of air various bodies supposed to contain phlogiston. In this way he found that a solution of potassium sulphide absorbed part of the volume of air, and that the residual air was incapable of supporting the combustion of a taper. Similarly, when moist iron filings were used, or the precipitate by caustic potash on green vitriol (sulphate of iron) he got a like result.

From these observations he argued that if the effect of combustion between phlogiston and air is to cause contraction, the

remaining air ought to be heavier. On weighing it he found it to be *slightly lighter*. Hence, he inferred that part of the air must have disappeared, and that common air must consist of two gases, one of which has the property of uniting with phlogiston.

In order to find out what had become of the air which had disappeared, he heated many metals, phosphorus, and other substances in air, and found that they behaved in the same way as the iron and the sulphide. His inference was that the compound formed by the union of phlogiston with one of the constituents of air is the heat, or the fire, which escapes through the glass. He fancied he had proved the decomposition of the substance heat into *phlogiston and fire-air*! He decomposed heat chemically, he thought, by heating manganese dioxide with sulphuric acid, and again by heating the red calx of mercury. The calx combined with the phlogiston of the heat, and the other constituent of heat was fire-air, which he collected. This was oxygen.



Another less known man, Bayen, in 1774 showed that calx of mercury loses weight when heated, and evolves a gas which weighs exactly what the calx has lost, and he drew the correct inference that the phlogiston theory was false. He proved that the calx can be reduced to metallic mercury without addition of phlogiston.

The extension of this truth systematically to a number of cases, and the investigation of the combination of the gas with every other combustible substance, was the work of Lavoisier. Therefore, he it was who, without being the discoverer of oxygen, was the author of the new and true theory of combustion, and who gave the *coup de grâce* to the phlogiston theory.

The triumph of the anti-phlogistic theory of Lavoisier, amongst contemporary chemists, was due to the Honourable Henry Cavendish's experiments, by which he discovered the

true composition of water, till then considered as an element. Cavendish was engaged in investigating the gas given off from dilute acid and zinc, tin, iron, and other metals. He determined the specific gravity of these gases, and used materials for drying them, at the same time noting the alterations of volume due to temperature and pressure. He thus found that from a given weight of each of these metals, the same volume of inflammable air (hydrogen) was always given off, whatever acid or strength of acid was employed; but that equal weights of different metals gave different volumes of gas. Finding that with nitric acid an *incombustible air* was obtained, and that with strong sulphuric acid sulphurous air was obtained, he concluded that when metals are dissolved in hydrochloric, or weak sulphuric acid, the phlogiston from the metals was set free, whereas when they were heated with nitric, or strong sulphuric acid, the phlogiston flew off in combination with an acid. At a later period, however, he changed his opinion that inflammable air was phlogiston, and thought that it was a compound of phlogiston and water.

In 1783 Cavendish made a series of experiments which were described in the *Philosophical Transactions* for 1784, pp. 119—133, and the papers form No. 3 of the *Alembic Club Reprints*. He exploded in a glass globe (his well-known "eudiometer"), by means of electricity, a mixture of "inflammable air" (hydrogen) and common air. The results of six explosions are noted. He says:—

"From the fourth experiment it appears that 423 measures of inflammable air are nearly sufficient to completely phlogistificate 1,000 of common air; and that the bulk of the air remaining after the explosion is then very little more than four-fifths of the common air employed; so that, as common air cannot be reduced to a much less bulk than that by any method of phlogistication, we may safely conclude that when they are mixed in this proportion and exploded, almost all the inflammable air, and about one-fifth of the common air, lose their elasticity, and are condensed into the dew which lines the glass."

He proceeds to describe the means which he adopted the better to examine the nature of this dew, and sums up the result in the following words :—

“By the experiments with the globe it appeared, that when inflammable and common air are exploded in a proper proportion, almost all the inflammable air, and near one-fifth of the common air, lose their elasticity, and are condensed into dew. And by this experiment it appears, that this dew is plain water, and consequently that all the inflammable air, and about one-fifth of the common air, are turned into pure water.”

From these interesting experiments, which are fully set out in the two papers entitled “Experiments on Air.” it is evident that Cavendish, as he thought, phlogisticated common air with inflammable air and obtained water, or, as we should say, combined the oxygen of the air with hydrogen and formed water. He certainly gave the data, which proved the composition of water, although he does not seem to have drawn the full conclusion from these data, nor to have expressed it in a definite way. It should be observed that in 1783 James Watt offered the opinion that water is composed of dephlogisticated air and inflammable air, that is, of oxygen and hydrogen, but he furnished no experimental proof. The controversy between Watt and Cavendish has been published in a folio book entitled *Correspondence between James Watt and the Honourable Henry Cavendish on the Composition of Water.*

On June 24th, 1783, Cavendish’s experiment was repeated by Lavoisier and Laplace. Lavoisier clearly recognised the meaning of the experiment, stated the inference, and definitely declared the fact—that the result of the explosion of a mixture of inflammable and common air is to produce water.

The effect of the elucidation of the true nature of combustion, and of the relation of calces to metals, has been far-reaching. In the first place it has given us a clear idea of what an element is. In the next place, it has led to the recognition of upwards of seventy elementary, simple, undecomposable bodies, which

cannot be transformed the one into the other, although they may be combined in an infinite variety of ways. The interrelation of radium and helium is as yet too exceptional and too little understood to form an exception to this principle, although it may lead to other discoveries which may tend to modify the views of chemists in regard to the elements (pp. 533 and 535). In the present state of chemical knowledge, we must include the metals amongst these untransformable elements, in contradiction of the doctrines of the old alchemists. Indeed, the alchemical philosophy suffered severely at the hands of the Anti-phlogistonists. Of their four elements, air, water, earth, and fire, it was shown that the first is a mixture of several gases, the second a compound of two, the third a mixture of many simple and compound bodies, while the fourth is not a substance but a condition, into which many substances, perhaps all, may pass, when they not only melt with fervent heat, but are gasified, and in that condition combine with each other, evolving more heat.

The nature of combustion having been thus settled, the nature of flame continued for another century to engage the attention of chemists. The true character of flame being known, the details of the series of changes taking place within and around every kind of flame next taxed the ingenuity of experimenters.

Sir Humphry Davy, experimenting on the nature and condition of flame, prior to his invention of the miner's safety-lamp, showed that the light of common flames depends almost entirely upon the deposition of solid particles of charcoal, in a state of glowing white heat, within the flame. These ignited solid particles afterwards undergo combustion, no doubt, but in order to render them white hot, and even to separate them from the other constituents of gasified combustibles, an intense heat is first necessary. Whence comes it? Davy showed that a flame of gaseous matter (and all substances are gasified before they form a flame) consists in ordinary circumstances of three parts:—



1. An internal, cold, conical, central portion of unconsumed gas.
2. A shell of burning gas, in which the more combustible constituents (those which when mixed with air take fire at the least elevated temperature) are burnt, chiefly hydrogen, thus evolving an intense heat; but the supply of air at this shell being limited, if there is much carbon it is separated in fine particles, which at the high temperature glow and emit light.
3. An outer shell, where these hot particles, meeting with a plentiful supply of air, burn, emitting heat but no light.

Several interesting questions arise out of these facts. What are the intermediate products in different circumstances? How do other combustible substances besides hydrogen and carbon burn? What are the ultimate products of the combustion of each? These and other similar questions have not yet received a complete answer.

When sufficient air is admitted into admixture with the combustible gas before reaching the flame, as by the blowpipe or the Bunsen burner, the flame consists of two parts only—the interior part is not a shell of half-burning material; not only hydrogen but some other substances are burned; the carbon is half burned to carbon monoxide, and the blue colour of its heated vapour is seen. The outer flame consists of the hot products of its complete combustion.

The most recent device for facilitating researches of this kind is that invented by Professor Smithells. Faraday employed a small glass tube as a syphon for drawing off the half-burnt products of combustion from the interior of a flame, but the apparatus of Professor Smithells enables more accurate results to be obtained.

While the nature of phenomena, and the details of the properties and changes of substances, are being made better known and more familiar to us every day, it is only in a very limited sense that we can be said to understand them. We have come to know how bodies act, and therefore we cease to wonder at the results of that action. But we do not yet possess

any more knowledge as to *why these things are so*, than we did at the time when the Book of Job was written.

We shall conclude this discussion of the theory of combustion by quoting the words of Thomas Carlyle, a philosopher and a thinker, who took a more comprehensive glance around him than the successful investigator is by the nature of his pursuits able at most times to secure. His remarks apply with equal force to all natural phenomena as well as to fire. He says :—

“The power of *Fire* or *Flame*, for instance, which we designate by some trivial chemical name, thereby hiding from ourselves the essential character of wonder which dwells in it as in all things, is with these old Northmen ‘Loki,’ a most swift, subtle demon, of the brood of the Jotuns. The savages of the Ladrones Islands too (say some of the Spanish voyagers) thought fire, which they had never seen before, was a devil or god, that bit you sharply when you touched it, and that lived upon dry wood. From us too no chemistry, if it had not stupidity to help it, would hide that flame is a wonder.”

## CHAPTER XXIV

### THE QUANTITATIVE PERIOD

(From 1775 A.D. till 1900 A.D.)

#### 1. THE PHILOGISTONISTS : DR. WILLIAM CULLEN TO THE HONOURABLE HENRY CAVENDISH

THE history of chemistry is conveniently divided into five periods. As has been already explained, these periods cannot be sharply defined as extending between definite points of time. On the contrary, they frequently merge into and overlap one another, the ideas prevalent in one period being accepted far into another. But the periodical divisions are of great use in the methodical arrangement of historical facts, and it is consequently impossible to dispense with them.

For the sake of clearness we shall here recapitulate these five periods, adding their approximate dates, subject to the qualification that these dates are to be regarded merely as convenient points, intended to indicate the time occupied by each period, and not as exact statements of chronological facts :—

1. *The Prehistoric Period*, from prehistoric times till 1500 B.C.
2. *The Alchemical Period*, from 1500 B.C. till 1650 A.D.
3. *The Iatrochemical Period*, from 1500 A.D. till 1700 A.D.
4. *The Phlogiston Period*, from 1650 A.D. till 1775 A.D.
5. *The Quantitative Period*, from 1775 A.D. till 1900 A.D.

The last period, indeed, may be said to extend down to the present time, but it will be more convenient for our purpose to hold it as closing with the end of the nineteenth century.

It is a matter of some difficulty to decide what is the best method of arranging the historical facts of the Quantitative Period, so as to illustrate and explain the wide ramifications of modern chemistry. Hitherto we have followed the development

of the science along a narrow and well-defined track, but we shall find that after the close of the eighteenth century the objects of chemistry became more numerous, varied, and important. The science was intimately connected with manufactures, commerce, and all the varied departments of human work and enterprise. To-day, no technical art or craft is independent of it. To do justice to this broad aspect of the subject is no easy task, but the logical course seems to be to devote certain chapters to a general consideration of the period and of the life and work of the great chemists, who advanced the development of their science, down to the latter half of the last century, and then in separate chapters to discuss the history of the more important branches of chemical philosophy.

The importance of the theory of phlogiston, and its influence on the development of the science of chemistry, arise from the fact that, although, as we believe, wrong, it was nevertheless the first successful attempt to give a rational explanation of a number of different phenomena, and to correlate a number of isolated facts and observations, and assign to them a common cause. It gave an intelligible account of the very important chemical process of combustion, and led to the discovery of hydrogen, oxygen, and many other elements and compounds.

The theory of phlogiston seems less mistaken to our modern ideas, if we recollect that a substance without weight, or with negative weight, is a contradiction in terms, and accordingly that what the phlogistonists termed a *substance* ought to be considered a *property*. If in this way we define phlogiston as "the property of combustibility," and read the phlogistic writers with that definition in our minds, we shall find that their ideas were not so far removed from our own, and that their knowledge was very considerable, even from our point of view. The phlogistic theory of combustion failed through the absence of quantitative determinations by means of the balance, and so soon as the balance was applied to the investigation of chemical processes, the phlogiston hypothesis had to make way for another and more correct explanation. The fifth and last

historical era may, therefore, be appropriately called the Quantitative Period.

It is a striking illustration of the overlapping of periods, to which we have already referred, that the first seven leaders of the Quantitative Period were in the main phlogistonists. Cullen, Black, Cavendish, Priestley, Bergman, Scheele, and Kirwan were, during the greater part of their lives, and in some cases till their death, believers in the phlogiston hypothesis. But they also, by insisting on the necessity of accurate estimation of weight and measure, laid the foundation of quantitative determinations, and are, therefore, more fittingly considered here than amongst the mere phlogistonists.

The first of these men, William Cullen (1710—1790), was celebrated rather as a physician than as a chemist, and owes his place in the history of the science mainly to his having been the teacher of Joseph Black. Dr. Cullen was born in Hamilton, where and in Glasgow he received his education. After making a voyage as surgeon in a vessel trading between London and the West Indies, he practised for some time at Shotts, in Lanarkshire. He then took a further medical course in Edinburgh University, and began the practice of his profession with great success at Hamilton. He also delivered lectures on scientific subjects in Glasgow. Contemporary reports assure us that as a lecturer Dr. Cullen was unrivalled—clear, precise, and interesting. After being for a time Professor of Chemistry in Glasgow University, he went in the same capacity to Edinburgh, where he filled the chair for ten years, when he was appointed Professor of the Institutes of Medicine. His fame is that of a great teacher, and the details of his life will be found in the biography by Dr. John Thomson, published in 1832. His writings, although of great value, are exclusively medical.

One of the most noteworthy names in Great Britain, towards the latter part of the eighteenth century, was that of Joseph Black (1728—1799). He was born at Bordeaux, where his father was engaged in the wine trade, and was educated at Belfast and Glasgow. In the latter city he studied chemistry under



Dr. Cullen, to whom he became practically an assistant, and whom he succeeded at Glasgow and afterwards in Edinburgh, where he died. His *Lectures on the Elements of Chemistry* were published in 1803. The characteristics of his work were carefulness in manipulation and caution in statement.

An investigation into the means of dissolving urinary calculi led Black to study the action of quick lime in rendering alkalis caustic. At that time the causticity of these substances was

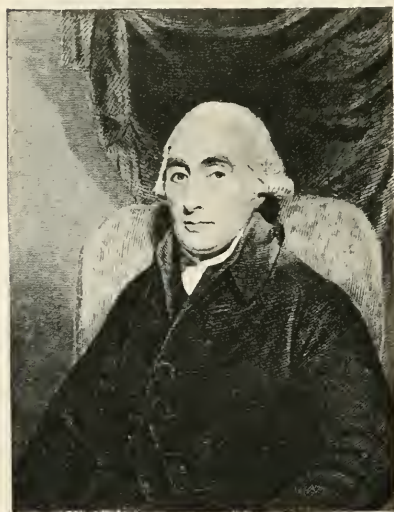


FIG. 89.—Dr. Joseph Black.

held to be dependent on phlogiston. He showed in 1754 that causticisation meant not the gain, but the loss of something. This he found to be a gas which he called "fixed air," and which was in 1781 named by Lavoisier "carbonic acid gas" (carbon dioxide). In this manner was re-discovered the *gas silvestre* of Van Helmont, which was described by that philosopher more than a hundred years before (p. 200), but which had entirely escaped the memory of chemists. Black's

great thesis, "*De Humore Acido a Cibis orto et Magnesia Alba*" (1754), shook the phlogiston theory.

By the experiments upon which this thesis was based, he demonstrated that magnesia alba when heated lost weight; that this loss was due to the escape of "fixed air"; and that its weight was regained when the calcined mass was made to re-absorb fixed air.

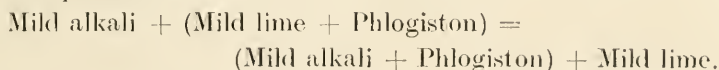
Before Black's time carbonates, such as magnesia alba (magnesium carbonate), were considered to be simple substances. When limestone was burned, chemists supposed

that it took up "fire-stuff" and became caustic, and this "fire-stuff" passed on to potash and soda, when they were causticised by lime. His experiments on magnesia alba, quick lime, and other alkaline substances proved that "fixed air" is given off when limestone is burned, and that the same loss is incurred when it is dissolved in muriatic acid (hydrochloric acid). Moreover, mild alkalis, instead of taking up an *acidum pingue*, or fire-stuff, when they become caustic by the addition of quick lime, give up something to the lime, which then becomes of its original weight, and capable of once more evolving fixed air. Therefore, it has received fixed air from the mild alkali. It now effervesces when treated with an acid, which quick lime will not do.

As the point is historically of great moment, we shall enter a little more fully into the argument. Prior to Black, the action by which potassium carbonate in combination with slaked lime (calcium hydroxide) produces caustic potash (potassium hydroxide) and carbonate of lime, and which we express by the following equation:—



was expressed thus:—



The bracketed terms, "mild lime *plus* phlogiston" and "mild alkali *plus* phlogiston," in this equation stand respectively for *caustic lime* and *caustic alkali*. Now, Black found that by heating magnesia alba in a crucible, weight was lost, due in part to the loss of a little water, but chiefly to the loss of an "air." The product after ignition became caustic, and on treatment with mild alkali gave the same weight as the original magnesia, and acquired the property of effervescing with acids, which it had lost by the ignition. He, therefore, concluded that the effervescence was due to fixed air, and that caustic alkali in combination with fixed air became mild alkali. A similar treatment of limestone produced similar results,

Black then neutralised some limestone with acid, and also a like amount of caustic lime obtained from the same quantity of limestone, and found that the amount of acid required to neutralise the substances was in both cases identical.

Some confusion existed at that time between magnesia and limestone, but Black distinguished the one from the other by observing that when both were treated with oil of vitriol (sulphuric acid) fixed air was in each case given off, but the lime product formed a sediment in water, which the magnesia product did not. Further, he noted the great heat produced when water is added to quick lime, and attributed this to a strong affinity subsisting between the two. He inferred that an alkali, destitute of fixed air, became acrid and caustic, not because it had taken up phlogiston or an *acidum pingue*, but because of its powerful affinity. In the course of these experiments he was the first to distinguish, in 1756, ammonia from ammonium carbonate.

Black's success in research work was largely due to his constant appeal to the balance, and from this aspect of his system it has been said that he laid the foundation of quantitative analysis. He also made many discoveries in physics. One of the most important of these was his doctrine of "latent heat," which he discovered in 1760 while he was a lecturer at Glasgow. When ice melts it takes up a quantity of heat without undergoing any change in temperature. Black argued that this absorbed heat must have combined with the particles of the ice, and become latent in its substance. He determined the latent heat of water as  $140^{\circ}$  Fahrenheit, and that of steam as  $810^{\circ}$ ; James Watt (1736—1819) with greater care found the latter to be  $950^{\circ}$ . Watt, who was a personal friend of Black, made use of these discoveries in his work on the steam-engine.

Black further observed that different bodies in equal masses require different degrees of heat to raise them to the same temperature, and hence derived his theory of "specific heat." He found that equal additions and abstractions of heat

produced equal variations in bulk in the liquid of his thermometers.

Altogether, Black was a very advanced experimenter, and there is no doubt that Lavoisier learned much from his correspondence ; but the latter does not appear to have recognised fully his correspondent's important services.

Black's work was not followed up by himself, owing to his weak health. It was taken up by the Honourable Henry Cavendish (1731—1810). This distinguished man was born at Nice, and was descended from the Devonshire family. He was educated at Hackney and at Peterhouse, Cambridge, but left the University without taking a degree. He led a most retired life, devoted to scientific pursuits, chiefly in chemistry, but also in electricity, meteorology, and other departments of science. His quiet manner of life afforded no opportunity for spending his fortune, which accumulated till at his death it reached the enormous total of £1,300,000. Many strange tales are told of his eccentric habits. He ordered his dinner by leaving a written note upon the hall table, and his women servants were instructed to keep out of his sight on pain of instant dismissal. Yet notwithstanding his eccentricity, he was an accurate observer, and in 1760 was elected a Fellow of the Royal Society.

The scientific work of Cavendish is remarkable for its width of range, and its extreme accuracy. Eighteen papers by him were published in the *Philosophical Transactions*, of which ten were on chemical subjects.

In 1766 Cavendish published his *Experiments on Fictitious Air*. In this paper he showed that an *inflammable air* (hydrogen) was evolved when sulphuric or hydrochloric acid, diluted with water, was poured upon iron, zinc, or tin. He concluded that this was the unaltered phlogiston of the metals. He was mistaken in his conclusion, but determined with fair accuracy the properties of the gas. Following up Black's experiment, he obtained "fixed air" from marble acidulated with hydrochloric acid, examined its properties, and measured

the quantity of it contained in different alkaline carbonates, in marble, and in the products of fermentation and decay. He demonstrated, as Van Helmont had done a century before, that the gas from these different sources was the same.

It will be convenient to remember, when discussing the work of the chemists of this period, that the four most important gases were known to them under the following names :—

- |                          |                       |
|--------------------------|-----------------------|
| 1. Oxygen . . . .        | Dephlogisticated air. |
| 2. Hydrogen . . . .      | Inflammable air.      |
| 3. Nitrogen . . . .      | Phlogisticated air.   |
| 4. Carbon dioxide. . . . | Fixed air.            |

This will obviate constant repetitions of the modern names.

Other papers by Cavendish were : one in 1767 on the salts found in water, particularly mineral waters, and on the solubility in water of bicarbonate of lime and magnesia ; another on eudiometric experiments to determine the quantity of dephlogisticated air in the atmosphere ; one to determine the freezing point of mercury (which he fixed at  $-38.66^{\circ}$  Fahrenheit) ; and one on freezing, in which he considered heat to be a rapid internal motion of the particles of a hot body.

But the most valuable work of Cavendish was contained in the two papers "*Experiments on Air*" (1784-5), which we considered in the preceding chapter. The object of these experiments was to determine the phlogistication of air ; that is to say, the change in air when metals are calcined in contact with it, and when sulphur, phosphorus, or similar substances, are burned in it.

The following are his principal conclusions :—

1. That *fixed air* is only produced when some animal or vegetable substance is present.
2. That *inflammable air*, when mixed with common air and exploded, produces water, the relation of the volumes of the two gases being as 1 to 2.
3. That *nitrous gas* gives nitric acid.
4. That when electric sparks are passed through a mixture of dephlogisticated air and phlogisticated air, the gases combine and produce *nitric acid*.



In his experiments with fixed air Cavendish introduced a novel feature. He dried the gas by passing it over or through ignited pearl ashes. Having done so, he was able to fix the specific gravity of the gas and of inflammable air. He also investigated their degree of absorption by liquids.

Having in one experiment fired a mixture of inflammable air and an excess of dephlogisticated air, mixed with common air, he found nitric acid in the water produced. From this he assumed that an inert gas must be present. He called this gas "phlogisticated air." He then proceeded to inquire whether the whole of the phlogisticated air in a given quantity of common air could be reduced to nitric acid. He found that only  $\frac{1}{120}$ th resisted change. It has lately been suggested that this small irreducible residue was probably argon and other analogous gases which were not identified until more than a century later (p. 525).

Cavendish bestowed much attention upon heat, and might have anticipated Black's doctrines of latent and specific heat. In his own day, the part of his work which created the greatest sensation was his attempt to measure the density of the earth. These and other matters not connected with the history of chemistry will be found in the *Life of Cavendish* by Dr. George Wilson (1851). How much more Cavendish knew but did not disclose, and how much of his research was frustrated by his eccentric mode of life, will never be ascertained.

## CHAPTER XXV

### THE QUANTITATIVE PERIOD

(From 1775 A.D. till 1900 A.D.)

#### 2. THE PHILOGISTONISTS : JOSEPH PRIESTLEY TO RICHARD KIRWAN

WHILE Cavendish was a member of a noble family, his celebrated contemporary, Joseph Priestley (1733—1804), sprang from a very ordinary stock. He was born at Fieldhead,

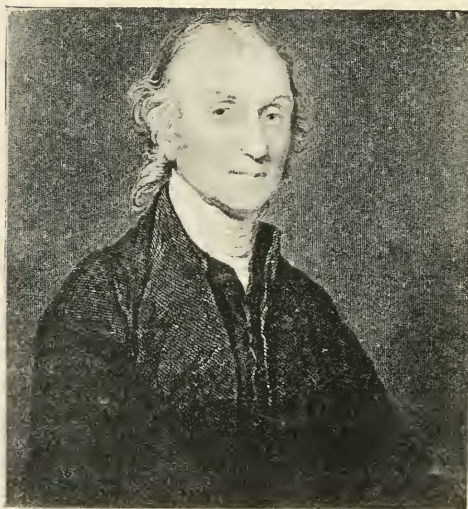


FIG. 90.—Joseph Priestley.

near Leeds, in Yorkshire, and was educated locally. He was, in the first instance, designed for the Nonconformist ministry, and was trained with that view: but he later adopted heterodox opinions. Until the age of twenty, he suffered from delicate health, and was in consequence mainly self-educated. He supported himself by teaching in a school

at Nantwich, where he obtained an appointment as minister at the meeting house. After successively serving as minister in Warrington and Leeds, he went to Birmingham, where he was aided in his researches by annuities from various gentlemen.

He had already by his writings made such a name for himself that he was in 1766 elected a Fellow of the Royal Society, and in 1772 Foreign Associate of the French Academy. Unfortunately, he engaged in religious controversy, and being suspected of sympathy with the French Republicans, the mob in 1791 burned his chapel, wrecked his house, and destroyed his library and apparatus. He then removed to London, and after a short residence there, went to join his son in America, where he died.

Dr. Thomson, in summing up the character of Priestley, says that as an electrician he was respectable, as an optician a compiler, and as a chemist a discoverer. He was a voluminous writer, and his works in Rutt's edition occupy twenty-five volumes. Many of them are on religious subjects.

Priestley's first work was in pneumatic chemistry. He devised a form of pneumatic apparatus, which is still in use, and which is superior to that of Cavendish. His first paper in 1772 was on a method of impregnating water with carbonic acid gas (carbon dioxide); his second, in the same year, gained him the Copley medal of the Royal Society. His most famous discovery, however, was that of "dephlogisticated air" (oxygen) on August 1st, 1774. About the same time he discovered "nitrous gas" (nitrogen dioxide). Soon after this he travelled on the Continent, and prepared dephlogisticated air in the house of Lavoisier, showing him the method of its preparation. It must be borne in mind, however, that Scheele independently discovered oxygen about the same date as Priestley, although he did not publish his discovery until three years later.

Priestley's system of experimenting was somewhat peculiar. It may be described as a series of blind experiments—heating a substance, or treating it with various reagents, and noting the results. In this fashion, by heating spirit of salt (hydrochloric acid) he obtained in 1772 what he termed "marine acid gas" (gaseous hydrochloric acid); but he would have lost it if he had not chanced to be using a mercurial pneumatic trough.

Similar treatment of oil of vitriol (sulphuric acid) produced nothing, so far as he could see, until he accidentally permitted some mercury to drop into the liquid, when he got "vitriolic acid gas" (sulphur dioxide). Heating fluor spar with oil of vitriol produced "fluor acid gas" (hydrofluoric acid), in circumstances in which Scheele had failed, simply because he was using a glass vessel. He obtained "alkaline air" (gaseous ammonia) by heating spirit of hartshorn, but he would have failed to collect it if he had not happened to be again using a mercurial trough. He also prepared alkaline air as Hales had done, by heating sal ammoniac with lime. Passing electric sparks through this alkaline air, he decomposed it into nitrogen and hydrogen. By the addition of marine acid gas to alkaline air he produced sal ammoniac (ammonium chloride). Oxygen he produced by heating the red oxide of mercury by means of a burning-glass. He also experimented with inflammable air (hydrogen), and by means of it reduced ferrous oxide ( $\text{FeO}$ ) to metallic iron. It was he who first formed nitric acid by passing electric sparks through moist air, thus leading Cavendish to the discovery of the composition of nitric acid.

Many of these discoveries were to some extent fortuitous, and it might be thought that Priestley had gained little merit through them. But it must not be forgotten that hundreds of chemists at that date were performing the same experiments without adding anything to our stock of knowledge. Priestley did not indeed, like Scheele, draw up a carefully conceived series of experiments, or proceed so methodically in his researches, but he possessed an inductive mind in no way inferior to that of the great Swedish chemist, and he was able to perceive the results of his operations, to correlate these results, and to grasp their bearing on the philosophy of the science. In this respect he was endowed with rare and valuable gifts.

The greatest of Priestley's additions to chemical knowledge was his establishing the relation between oxygen and the processes of combustion and respiration. Having satisfied himself as to the analogy subsisting between both processes, he

concluded that dephlogisticated air (oxygen) was the essential factor in each. He elaborated this theory in his important paper, published in the *Philosophical Transactions* for 1772. "On Different Kinds of Air," and in his "Experiments and Observations on Different Kinds of Air" (1775), part of which will be found in the *Alembic Club Reprints*, No. 7. In speaking of the effect of dephlogisticated air on supporting combustion, he anticipated the oxyhydrogen blowpipe when he says: "Nothing would be easier than to augment the force of fire to a prodigious degree, by blowing it with dephlogisticated air instead of common air." There can be no doubt, however, that the experiments of Priestley furnished Lavoisier with the weapon with which he destroyed the phlogiston hypothesis.

The following is a list of the principal chemical writings of Priestley:—

1. History and Present State of Electricity (1767).
2. Experiments and Observations on Different Kinds of Air (1774–86).
3. Experiments on the Generation of Air from Water (1793).
4. Experiments and Observations relating to the Analysis of Atmospheric Air (1800).
5. Considerations on the Doctrine of Phlogiston established and that of the Composition of Water refuted (1800).

With reference to the last of these works, it has to be observed that Priestley was a firm believer in phlogiston, and adopted the views of Cavendish and of Scheele, that hydrogen is pure phlogiston. Water he deemed a compound of dephlogisticated air and phlogiston. According to him all combustibles, including the metals, contained inflammable air (hydrogen). Calces are metals deprived of phlogiston, and when calx of iron (the black oxide) is heated in inflammable air phlogiston is absorbed and the metal produced. But all these results vanish when the products are *accurately weighed*. By more accurate estimation of quantities, both Scheele and Lavoisier showed that the loss of weight of air, when a body is burned in it, is due to the oxygen abstracted from it and condensed in the burning body.



In the latter part of the seventeenth century, and in the course of the eighteenth, Sweden produced many men of the first scientific rank—such as Heine, Brandt, Scheffer, Wallerius, and Cronstadt. One of the most distinguished Swedes was Torbern Olof Bergman (1735—1784). He was born at Katrineberg, in West Gothland, where his father was a tax-collector, and he was educated at the University of Upsala. There he exhibited a predilection for mathematics, which along with physics he studied to please himself, while he studied law and divinity to please his relatives, who were opposed to his scientific studies. He came under the influence of Linnaeus, then in the height of his fame. The subjects of his first papers were natural history and the manufacture of alum. He succeeded Wallerius in the Chair of Chemistry at Upsala in 1761, and among his pupils were Gahn of Fohln, Gadolin, and Elhuzart. He was the friend of the more famous Scheele. His death took place at Madevi, on Lake Wetter. His principal tracts (106 in all) were published as *Opuscula Physica et Chemica* (six volumes, 1779-90). One of the most important is that on *Elective Attraction* (1775).

Bergman greatly improved the methods of chemical analysis. He mainly conduced to this end by working out tables of what he termed "Elective Affinities." Newton, in a series of observations hitherto neglected by chemists, had demonstrated how the affinities of substances produced compounds when the substances were mixed together. Bergman, acting upon this suggestion, used these affinities for analysing solutions and discovering what substances were contained in them.

Boyle had previously pointed out that blue litmus reddens in the presence of an acid. This fact Bergman applied in his examination of Black's "fixed air" (carbon dioxide). From the fact that this substance united itself to lime he suspected it was an acid. Accordingly, he prepared fixed air and tested it with blue litmus. The litmus turned red, and his suspicion was converted into a certainty. He named the gas "aerial acid" or acid air. By weighing it, he found it was heavier than

atmospheric air, and by passing it through water demonstrated that it was soluble. He failed to discover, however, that it was a compound body.

Bergman made many other contributions to science. In 1774 along with Scheele he discovered a new element, manganese, in the mineral pyrolusite; he analysed mineral waters and imitated them artificially; investigated tartar emetic and magnesiä; and studied crystals, silica, liquor silicius, iron ore, and iron generally.

A still greater chemist was Karl Wilhelm Scheele (1742—1786). Born at Stralsund, in Swedish Pomerania, he was at his own request apprenticed to an apothecary in Gothenburg, with whom he remained eight years. During that period he made himself acquainted with all existing chemical writings and proficient in practical manipulation. After some changes of employment he went to Upsala in 1773 and assisted in an apothecary's house. There he made the acquaintance of Bergman, and established a lasting friendship with him. At this time he discovered hydrofluoric acid and, along with Bergman, made a thorough investigation of manganese. By the treatment of the ore of this metal with hydrochloric acid, he discovered "dephlogisticated muriatic (or marine) acid gas," that is, *chlorine*.

Next year (1774) he purchased an apothecary's business in Köping, on Lake Malar, and continued his researches on air and fire, but as these researches were founded upon the phlogiston theory, they did not lead him to correct conclusions. His work on the action of iron when exposed to air led him to the discovery of oxygen. He isolated this gas from black oxide of manganese and sulphuric acid, and afterwards from red oxide of mercury, which he thought a simple body that combined with phlogiston when heated. This discovery he made independently of Priestley, but the latter was the first to announce what he had found.

In 1777 he published his only book "*Fire and Air*," in which he says that the atmosphere contains two gases, one of which

supports, and the other prevents, combustion. The former, which he called "fire air" (oxygen), he prepared not only from the black oxide of manganese and red oxide of mercury, but also from nitric acid and saltpetre. He deemed heat to consist of "fire air" and phlogiston.

Scheele's papers were published in England, under the title of *Chemical Essays*, in 1786. He died at Köping.

This great chemist has never been surpassed as an experimental investigator. There was no blind experimenting in his case, as in Priestley's. His discoveries were the result of carefully planned series of experiments, and he left nothing in doubt where experiment could decide it. In this respect he is a model to all who are engaged in chemical research. The extent and variety of his labours will be gathered from the following chronological table :

- 1770. Isolated pure tartaric acid from cream of tartar by the process still followed.
- 1771. Proved that fluor spar consists of lime and an acid which he called "fluor acid" (hydrofluoric acid); discovered silicon fluoride; also isolated oxygen, as already mentioned.
- 1774. Chlorine, baryta, barium sulphate, manganates and permanganates; also acetaldehyde.
- 1775. Benzoic acid from gum benzoin; arseniuretted hydrogen, one of the most deadly of gases, and copper arsenite (Scheele's green).
- 1776. Uric acid in urinary calculi.
- 1777. Sulphuretted hydrogen, and the action of light upon the salts of silver.
- 1778. Molybdic acid; proved that molybdenite differed from plumbago by converting the latter into carbon dioxide by means of nitric acid; and improved manufacture of calomel.
- 1779. Showed that plumbago is essentially carbon, and discovered glycerol while heating olive oil with litharge.
- 1780. Lactic acid from sour milk, and proportion of oxygen in the atmosphere.
- 1781. Tungsten and tungstic acid from the mineral now called scheelite.
- 1782. Ether and mucic acid.

1783. Prussic acid (hydrocyanic acid) from Prussian blue, although he was unaware of its deadly properties; and isolation of glycerol (Scheele's sweet principle), which he found existed in all oils and fatty matter.

1784-86. Citric, malic, oxalic, and gallic acids.

Scheele prepared sulphuretted hydrogen by heating sulphur in inflammable air, but owing to his peculiar ideas about heat he regarded the gas as a compound of sulphur, phlogiston, and heat. His preconceived ideas as to phlogiston hampered him greatly; nevertheless his record of work is most honourable, and testifies what can be done, even by a man in comparatively poor circumstances, by patient and careful experiment and laboratory work.

The last phlogistonist of note in Great Britain was Richard Kirwan (1733-1812). The incidents of his life were few and not remarkable. He was born at Cloughballymore, Co. Galway. After some time spent as a novice among the Jesuits, he became a member of the Irish Bar, and then practised for a time in London. Law soon gave place to science. His earliest experiments were upon specific gravity and chemical affinity. In 1780 he was elected a member of the Royal Society, which awarded its Copley medal to him two years later. He returned to Ireland in 1790, where he became president of the Royal Irish Academy. He died at Dublin.

Kirwan wrote a number of papers. The most important were *Experiments and Observations* (1785), and *Essays on Phlogiston and the Constitution of Acids* (1787). His best work was done in the improvement of chemical analysis. His *Elements of Mineralogy* was the first systematic treatise on the subject in English, and was long regarded as the standard text-book.

Black, Cavendish, Priestley, and Scheele form a group of names which is highly distinguished among chemists. The phlogistonism of these men, indeed, prevented their fully appreciating the import of their discoveries; but these were so numerous and so valuable that they furnished Lavoisier and other anti-phlogistonists with data, by means of which they were enabled to shape the beginnings of the modern science of chemistry.

The re-discovery by Black of carbon dioxide and of its relation to the phenomena of causticity, proving that there are different sorts of air or gas, and that the gaseous elements have an intimate connection with processes which had hitherto been attributed to the agency of an imaginary phlogistic property, was the first step in a course of steady advance in accurate knowledge. To this succeeded the practical discovery of hydrogen by Cavendish, who, although he did not quite understand the nature of the gas, prepared it and experimented with it. Of all his experiments the most important was that which demonstrated that when oxygen and hydrogen are mixed and exploded, water is produced. With these were conjoined the great discoveries of Priestley and Scheele—the isolation of oxygen, the demonstration of the compound character of air, and the discovery of nitrogen, chlorine, and a number of bodies, both simple and compound.

From this time oxygen began to be conventionally spoken of as “the supporter of combustion,” and substances which burn in it were called “combustibles.” Yet this manner of speaking is purely conventional, and is due to the abundance of oxygen in the atmosphere. Combustion is merely a special case, in which the heat of combination is exceptionally augmented. After the discovery of chlorine, bromine, and iodine, and when bodies were found to burn in the vapours of these substances, as well as in oxygen, the term “supporter of combustion” was extended to every substance capable of forming vapour in which others could burn; but as the same substance may act at one time as a “supporter,” and at another time as a “combustible,” the distinction has gradually become obsolete.

The effect of these discoveries was immediate and far-reaching. The obstructions which had for so long impeded the course of chemical philosophy were to a large extent removed, and the door was laid wide open for unlimited research. In the next chapter we shall see what use the great Lavoisier made of the materials thus provided to his hands, and of the opportunity thus afforded to him.



## CHAPTER XXVI

### THE QUANTITATIVE PERIOD

(From 1775 A.D. till 1900 A.D.)

#### 3. THE ANTI-PHLOGISTONISTS : ANTOINE LAURENT LAVOISIER

M. AD. WURTZ opens the introduction to his treatise on the History of Chemical Theory with the declaration, "Chemistry is a French Science." Although the fervid patriotism of this author has led him to express himself more emphatically than was necessary, there is greater reason for his assertion than is often found in support of such patriotic claims. Before the great French chemists who laboured towards the end of the eighteenth century, there was no science of chemistry, but a mere collection of chemical facts loosely strung together upon a false theory of combustion.

This false doctrine of phlogiston looked upon combustion as a decomposition of the combustible body into a calx, which was left, and phlogiston, which escaped. The later chemists of the Phlogiston Period began to get approximately quantitative observations, which were gradually seen to be inconsistent with this hypothesis. Scheele was inclined to the opinion that combustion consists not only in a *decomposition*, but also in a *formation of a compound*. In France the way began to be cleared for a new theory of chemistry as early as 1775, but in England, Sweden, and Germany the phlogiston theory held its place longer. The consequence was that from 1780 till 1790 both the phlogiston and anti-phlogiston theories had a following.

That man wrought a complete revolution in chemistry, who proved, amongst other things, that when metals are burned and their weight increases, a portion of air equal to their increase in weight is absorbed, and that burning, rusting, and calcination

are not processes of decomposition. He thereby established a theory entirely opposed to the older one to which we have alluded, and introduced into the methods of chemical investigation the same precision, and into chemical generalisations and principles the same accuracy and deductive reasoning, as are found in other branches of science. The history of the life and work of such a man reveals so much of the foundations of modern chemistry, that it will be desirable to pay more pro-

longed attention to his biography than to that of any of his predecessors. His name was Antoine Laurent Lavoisier (1743—1794).



FIG. 91.—Antoine Laurent Lavoisier.

This eminent chemist was born at Paris. His father was opulent, and gave him a good education, intending him for the legal profession. Naturally endowed with a taste for science, he gained in 1764, at the age of twenty-one, a gold medal offered by the French Government

or the best method of lighting the streets of cities. He was a pupil of the great chemist Rouelle, and in 1768 was admitted a member of the Academy of Sciences. Having become acquainted with the discoveries of Black, Cavendish, and Priestley, he thenceforward devoted himself to scientific chemistry.

In 1774 Lavoisier published his *Opuscules Physiques et Chimiques*. In the first part of these essays he gave an historical account of all that had been done in reference to air and gases from Paracelsus to his own time; in the second part,

he gave the results of his own experiments on gases. He confirmed Black's account of fixed air, and proved its production when metallic calces are reduced to the metallic state by means of charcoal. Then he showed that when metals are calcined to produce calces, their weight increases, while the air not only loses in weight what the metal gains, but also loses its power to support combustion. Phosphorus and sulphur gave similar results when burned. The result of experiments which he made in 1772 caused him to abandon the theories of the phlogiston school.

In these essays there is no indication that he knew air to be a mixture of gases, although he must have inferred the existence of oxygen from his experiments. But Priestley came to Paris about the end of 1774, and as we said before, explained to Lavoisier the method of preparing dephlogisticated air from the red calx (or oxide) of mercury. This supplied the clue to the meaning of the experiments and to the nature of combustion. Lavoisier prosecuted experiments with oxygen for twelve years in a very precise way, and disproved the phlogiston theory, demonstrating the behaviour of the gas towards divers kinds of substances. Berthollet in 1785 declared his adherence to the views of Lavoisier, and was soon followed by De Morveau and Foureroy, while in 1792 the new doctrines received recognition at Berlin.

But public affairs were taking a shape which in the end proved fatal to Lavoisier. He had been in 1768 appointed adjoint chemist to the French Academy, and unfortunately for him, also adjoint to M. Baudon, one of the farmers-general of the Revenue. He now began to take a great interest in public matters. Agriculture and philanthropic schemes received his attention, and in 1775 he so improved French gunpowder that it was superior to British gunpowder during the American War. Five years later he made valuable reports upon agriculture and the cultivation of various crops.

Then came the French Revolution. Farmers-general of

Revenue and their assistants became obnoxious to the Revolutionary tribunals. Lavoisier was denounced under the administration of the infamous Robespierre, and perished on the guillotine. His appeal on the ground of his scientific services was dismissed with the characteristic remark: "La République n'a pas besoin de savants." Lagrange has said that the head of Lavoisier fell in a moment, but more than a hundred years have not sufficed to produce another equal to it.

We shall now consider the writings of Lavoisier. He published between 1772 and 1788 about sixty papers in the Transactions of the Academy of Sciences; *Opuscules Chimiques et Physiques* (1774); *Traité Élémentaire de Chimie* (1789); and after his death his widow published his *Mémoires de Chimie* (1805). A complete edition of his *Œuvres* was issued by the French Government between 1862 and 1893.

Lavoisier began with a paper on gypsum in 1768, which is remarkable for its ignoring the similar work of Marggraf, of which a French translation had appeared only six years previously. His first important research was "On the Nature of Water." In this essay he furnished an historical sketch of the progress of the investigation into the composition of water from Van Helmont to Marggraf and Rey, and then proceeded to explain his own work. In proving that water is not converted into earth by repeated heating or distillation (as was then believed), he used the balance with great effect. He weighed the glass vessel and the water separately, and noted the combined weight. Then, closing the vessel, he found that the total weight remained constant however long the water was boiled, but that the glass vessel lost weight to an extent exactly equal to the weight of the earth produced in the water. From this he concluded that the earth previously supposed to have come from the water was in reality dissolved out of the glass vessel in which the experiment had been performed.

In 1771 he put forth a project to establish a steam-engine to supply Paris with water—a scheme projected in ignorance of

Watt's great improvements. Next year he published a paper on the use of spirits of wine in the analysis of mineral waters, and another of great moment on the results of his calcination of the diamond. Here he began his researches into combustion. He confirmed the combustibility of the diamond by means of a burning-glass and also with charcoal. He settled the following points: (1) that the bulk of the air was not altered by combustion over mercury; (2) that over water the bulk of the air was diminished; and (3) that the air in which the diamond had been burned rendered lime water turbid, thus indicating the presence of fixed air (carbon dioxide). The practical outcome of the whole is the knowledge that the diamond consists of pure carbon.

Another series of experiments was made with sulphur and phosphorus. He found that when these substances were burned, no loss, but an increase, of weight occurred, and in these and similar cases he concluded that part of the air was fixed in the substance calcined. He confirmed this view by heating litharge (lead monoxide) with charcoal, and thus reducing it to metallic lead. By accurate weighing he ascertained that air (that is, gas) was liberated, and that the weight of the lead produced was less than that of the original litharge.

In the same year (1771) he wrote on the conversion of ice into water, and it is apparent from the paper that he was aware of Black's doctrine of latent heat. He also discussed the white lead ore of Sulloven.

From 1774 onwards Lavoisier published numerous papers. He analysed water taken from some Italian alum pits, and examined the ash used by saltpetre-makers in Paris. He investigated the air given off during breathing, combustion, and fermentation, and enunciated the same views as Black, but without any acknowledgment or even mention of Black's name. He again followed the Edinburgh chemist in a paper published in 1777 on the combination of fire-matter with evaporated fluids, and the formation of elastic aeriform fluids.



also without acknowledgment. The extreme cold of 1776 is the subject of another essay.

From certain papers read by him on the calcination of lead and tin, we might infer that he had perceived the facts which prove that air contains more than one gas, but he did not definitely draw that conclusion. When he read in 1775 his immortal paper, "*On the Nature of the Principle which combines with Metals during Calcination, and which augments their Weight,*" he did not recognise oxygen; but by the time that this paper was published in 1778, he had become acquainted with Priestley's discovery of dephlogisticated air, and modified his opinion accordingly. He spoke of the principle as "vital air" or "pure air," that is, air eminently adapted for supporting respiration and combustion. This air he demonstrated to be necessary for the calcination of metals—being consumed during the process, and "non-vital air" being left behind. This vital air might be prepared from *precipitatum per se* (red oxide of mercury), and in 1777 he named it "oxygen," *i.e.* the acidifying principle—an unfortunate title, as we mentioned before. In subsequent papers he elaborated the idea, showing that oxygen is the only air capable of supporting combustion. In 1778 he put forward the theory that oxygen is the universal acidifying principle, a theory which is now greatly modified.

The next few essays deal with miscellaneous matters: *On certain Fluids which may be obtained in an Aeriform State at a degree of heat not much higher than the mean temperature of the earth, namely—ether, alcohol, and water* (1780); *On Heat*, in which Laplace and he placed on a sound basis the theory of the heat of oxidation and combustion, described the ice calorimeter, and gave by its means the specific heats of a number of substances; *On the Prisons*; *On a Process for separating Gold and Silver*; *On Electricity evolved when bodies are evaporated or sublimed* (1781); *On the Value of Fuels*—coal, coke, charcoal, and wood; *On a Mode of Illuminating Theatres* (1781); *On a Method of Augmenting the Action of Fire and Heat, e.g., by a jet of oxygen* (1782); and *On Elastic Fluids from Fermentation*

(1782). In working on fermentation he came to the conclusion that, starting with a certain weight of sugar, there were obtained quantities of alcohol and carbonic acid gas, which were together equal in weight to the amount of sugar used. This was true, as regards about 95 per cent. of the sugar, approximately 5 per cent. being spent in developing the growth of the ferment, and by being converted into succinic acid, glycerine, and other products.

There was published in 1783 a paper, read some years before, *Reflections on Phlogiston*. In it Lavoisier denied that there was any principle of combustibility, upset the phlogiston theory, and demonstrated that such substances as sulphur, carbon, phosphorus, and the metals burned by entering into combination with oxygen. This led the way to the complete overthrow of the phlogiston theory, which was finally disposed of when Cavendish in 1783 discovered the composition of water. Cavendish observed the facts, although he did not draw the deduction; Watt drew conclusions from the facts, although he did not quite make out the composition of water; Lavoisier and Laplace in 1783 recognised the compound nature of water, and determined quantitatively its constituents. They not only repeated Cavendish's experiment by exploding hydrogen on a large scale, but also decomposed steam by red-hot iron wire in a porcelain tube. Lavoisier further evolved hydrogen from dilute sulphuric acid by zinc, and explained what took place. He was thus led to some general conclusions on the action of metals in acids, which we shall mention presently.

In 1781 he discussed the formation of Black's fixed air, which he termed "carbonic acid." He determined its composition as carbon 0.75, and oxygen 1.93.

One of his most valuable papers was published in 1785, read three years before: *General Considerations on the Solution of Metals in Acids*. He showed that when a metal is dissolved in an acid, the oxygen of the acid first converts it into an oxide, and then the remainder of the acid forms it into a salt, or compound with itself.

In all Lavoisier's later papers oxygen plays a conspicuous part, and phlogiston is altogether omitted. From this date the Anti-phlogistic or Lavoisierian views prevailed, and there is probably no other instance of an established scientific doctrine being so speedily and conclusively overthrown. Nevertheless, Priestley wrote against the new doctrines, and it was not until 1785 that Berthollet declared himself converted. With him all the great French chemists became anti-phlogistonists.

We shall now try to sum up the principal services which this epoch-making man rendered to chemistry. First of all he overthrew the phlogiston hypothesis and established the foundations of modern chemistry. His success in this respect was mainly due to his having made the balance the *ultima ratio* of the laboratory. The following seven propositions were deduced from the experiments of Lavoisier :—

1. That however long water is heated it cannot be converted into earth.

2. That when metals, sulphur, phosphorus, carbon, and similar substances, are burned in air, they increase in weight to an extent exactly equal to the volume of oxygen which they derive from the atmosphere ; and, on the other hand, when calces are reduced by means of charcoal, the resulting metal weighs less than the calx to an extent exactly equal to the volume of oxygen which has combined with the carbon and escaped in the form of carbon dioxide.

3. That the diamond is pure carbon, and is converted by combustion into a gas, which he named carbonic acid (carbon dioxide).

4. That sulphuric acid differs from sulphurous gas by containing a larger proportion of oxygen ; and likewise nitric acid from the nitrous gas discovered by Scheele.

5. That metallic salts are formed (firstly) by the disengagement of oxygen from the acid; which unites with the metal, forming an oxide, and (secondly) by the union of the acid with the oxide thus produced.

6. That by burning alcohol, oil, wax, or similar organic substances in a known volume of oxygen, the quantity of carbon, hydrogen or oxygen present in the organic body burned, can be calculated from the weight of water and carbon dioxide produced during combustion.

7. That there are three states of aggregation of matter—solid, liquid, and gaseous—depending upon the amount of fire-matter with which the ponderable substances are interpenetrated and combined. Lavoisier anticipated that gases could be reduced to liquids and solids by the influence of cold and pressure. He also clearly enunciated the first scientific proof of the indestructibility of matter.

The opinion of Lavoisier on these subjects has been modified by the results of modern research; but on the whole these propositions still form portions of chemical philosophy, and are accepted by modern chemists.

Lavoisier was associated with De Morveau and others in the reformation of chemical nomenclature and the classification of chemical elements. The old nomenclature which had arisen in the time of the iatrochemists was cumbersome and meaningless, and was superseded in 1787 by the new system. This was chiefly the work of Lavoisier and De Morveau, the former inventing most of the new names of substances, and the latter the method of naming salts. This reformation was one of the greatest benefits which the French chemists conferred on the science. It not only simplified the description of experiments and processes, but by inducing a systematic manner of regarding compounds, disclosed blanks which logically required to be filled, and thus directly conduced to the discovery of the new compounds which were needed to fill up these vacant spaces in the system.

Of all the men whom we have as yet mentioned in this history, Paracelsus alone can be ranked with Lavoisier as a fundamental reformer of the science. Geber, if we were really certain of his existence, might have claimed a place beside Paracelsus, but as we formerly explained, he is altogether a

mythical and doubtful personage. And if we set Paracelsus by the side of Lavoisier, it can only be in the capacity of a reformer. Between the two men there is no comparison. Both were distinguished by natural genius, both were great men, but Lavoisier was incomparably the greater.



## CHAPTER XXVII

### THE QUANTITATIVE PERIOD

(From 1775 A.D. till 1900 A.D.)

#### 4. THE ANTI-PHLOGISTONISTS: GUYTON DE MORVEAU TO LOUIS NICOLAS VAUQUELIN

ALTHOUGH Lavoisier was the leader of the reformation of chemistry, in the latter portion of the eighteenth century, the work of his followers was of great importance. His views were adopted by the principal chemists of France and Germany, and rapidly spread over the continent of Europe. The great English chemists held back for a time, but in the end they too became adherents of the new doctrines, and carried these to a higher development.

Amongst those who first adopted the theories of Lavoisier was Louis Bernard Guyton, Baron de Morveau (1737—1816). He belonged to a noble Burgundian family, and was born at Dijon, where his father was Professor of Civil Law in the University. De Morveau studied law and entered the Dijon parliament as *avocat-général*. His thoughts, however, were early turned to chemistry, and we find him in 1770 delivering a course of lectures on chemical subjects. Next year he published at Dijon his *Elémens de Chimie*, and some years later became editor of the chemical section of the *Encyclopédie Méthodique*. In the first part of this work he supported the doctrine of phlogiston; in the second, he declared his adherence to the principles of Lavoisier. Along with Maret and Durande he also published *Elémens de Chimie Théoretique et Pratique* (1776-7).

His most important essay was one on *Chemical Nomenclature*, which appeared in the *Journal de Physique* for May, 1782.

This was ultimately developed by De Morveau, in collaboration with Lavoisier, Berthollet, and Fourcroy, into *Méthode d'une Nomenclature Chimique*. (1787), a work which led to the complete reform of this branch of the science. A brief account of the leading points of the new system will be given at the end of this chapter.

De Morveau was a man of vast practical genius. He was a physiologist, an agriculturist, and an aeronaut, as well as a lawyer and a chemist. He distinguished between the uses of soda and potash in agricultural chemistry, pointing out that while plants near the sea contain much soda, as we get further inland the plants contain less and less soda and more potash. He set up a saltpetre manufactory, and in 1783 established the first chemical works in France devoted to making carbonate of soda. On April 25th, 1784, he ascended from Dijon in a balloon of his own construction, an experience which caused him to be selected ten years later to superintend the construction of balloons for military purposes. He studied the preparation of ether, the properties of mercury and ammonia, and the spontaneous combustion of oats when saturated with oil, and he was the first to advocate the disinfecting power of chlorine and hydrochloric acid gas, which he had used successfully at Dijon in 1773.

Like other public men of the time, De Morveau was involved in the Revolution, by no means to his credit. Being elected a member of the Constitutional Assembly, he went to Paris, and on June 16th, 1793, voted with the regieide majority of the Deputies. But after the storm passed over, he did good service as one of the committee that established the new *École Centrale et Polytechnique*. In 1799 Napoleon appointed him one of the administrators of the Mint, and later created him a baron of the Empire. He retired into private life and died at Paris.

One of the first great chemists outside France who adhered to the doctrines of Lavoisier was Martin Heinrich Klaproth (1743—1817). He was born at Wernigerode, where he was apprenticed to an apothecary. After serving various masters,

he obtained a post in Berlin, where for many years he worked in the laboratory of Valentine Rose. He was recognised as the leading chemist of his time in Germany. His thesis as apothecary in 1780 was "On Phosphorus and Distilled Water." Two hundred varieties of minerals were analysed by him, and he discovered the metals uranium, zirconium, and tellurium, and some of the compounds of tellurium, strontium, cerium, and chromium. The metal titanium was named by him. He was an exact and conscientious worker and greatly improved the methods of chemical analysis. His principal books are: *Beitrag zur Chemischen Kenntniss der Mineralkörper* (1795—1810) and *Chemisches Wörterbuch* (1807—10), and besides these he wrote papers, mostly on mineral analysis, to the number of two hundred. On the foundation of the University of Berlin in 1810, he was appointed Professor of Chemistry, and died in that position. Klaproth's most valuable contribution to the science was his long and careful research into the composition of rare minerals.

Claude Louis Berthollet (1748—1822) was born at Talloire, near Annecy, in Savoy, and educated at Chambéry and Turin. Coming to Paris in 1772 a total stranger, he became private physician to the Duke of Orleans, the father of Philip Égalité. In 1780 he was admitted a member of the Academy of Sciences, and five years later declared his adherence to the theories of Lavoisier. He succeeded Macquer, not indeed in his chair at the Jardin du Roi, but as superintendent of dyeing processes, which caused him



FIG. 92.—Claude Louis Berthollet.

to write an important work; *Elémens de l'Art de la Teinture* (1791).

Although Berthollet in the main was a Lavoisierian, he differed from his master, in so far as he did not consider oxygen the acidifying principle, because there are substances with acid properties which do not contain oxygen, as, for example, sulphuretted hydrogen. In this he was right, and Lavoisier was wrong.

After the French Revolution France was hemmed in by the Austrian and Prussian armies by land, and the British fleet by sea. She was therefore unable to import as usual saltpetre for gunpowder, and iron for arms. In this extremity Berthollet and other chemists were called upon to help the Republic. Accordingly, Berthollet showed the French people how to extract and make saltpetre, and how to purify it and to make gunpowder; also how to obtain iron and convert it into steel. His discovery of chlorate of potash suggested to him the attempt to manufacture gunpowder with it, but the liability of the chlorate to explode when rubbed with sulphur rendered it too dangerous for use on a large scale.

Berthollet had a distinguished public career. In 1792, as one of the Commissioners, he introduced improvements into the Mint; in 1794 he was Commissioner of Agriculture and Arts, and Professor at the Polytechnic and the Normal Schools. Napoleon Bonaparte studied under him, and when preparing for his famous expedition into Egypt induced Berthollet to form one of the body of scientific men who accompanied him. Berthollet remained to the end an intimate friend and scientific adviser of the great Emperor, and received from him many honours, including the rank of Count. He died at the age of 74 at Arcueil, where he had gathered around him a chemical coterie engaged in research work.

The earlier papers of Berthollet were spoiled by his adherence to the phlogiston theory, which he then defended. He made a careful study of ammonia, repeating the experiments of Priestley with the electric spark, and proving that by elec-

trolysis the volume of volatile alkali is doubled. Chlorine he held to be oxymuriatic acid, and he was the first to propose its use as a bleaching agent in place of the old mode by sun and air. Watt saw the process in Paris and introduced it to his father-in-law Macgregor, a bleacher in Glasgow. The objectionable odour of the free gas led the Glasgow and Lancashire bleachers to seek a substitute, which they found in chloride of lime (*vide infra*, Chapter XLVIII.).

In the course of his experiments Berthollet discovered chlorate of potash, which he called a salt of hyperoxymuriatic acid. At a later date (1810), it was shown by Gay-Lussac and Thénard that chlorine contains no oxygen; Davy proved that it was an element; and Gay-Lussac finally isolated chloric acid ( $\text{HClO}_3$ ).

Prussic acid and the prussiates received attention from Berthollet. From the fact that prussic acid ( $\text{HCN}$ ) and sulphuretted hydrogen ( $\text{H}_2\text{S}$ ), although they contain no oxygen, possess acid properties, he was confirmed in his opinion that oxygen is not, as Lavoisier said, the "acid-maker." He was the first to manufacture crystallised prussiate of potash, chloride of cyanogen, and fulminating silver.

Finally, mention must be made of his *Essai de Statique Chimique* (1803), the first attempt to grapple with the problems of chemical physics. This work entitles him to be ranked as one of the founders of the doctrine of chemical affinity. He denied the definite composition of compound bodies, and held that chemical affinity is influenced by the relative masses of the substances acting in a chemical reaction, a theory to which we shall have to refer in Chapter XLVI.

We now come to a man who was equally remarkable as a politician and as a chemist—Antoine François, Comte de Fourcroy (1755–1809), who was born at Paris. His ancestors had been distinguished at the Bar, but the family had fallen into extreme poverty, his father being an apothecary in the household of the Duke of Orleans. With the greatest difficulty he studied medicine, and obtained a degree. In 1784



he was appointed, under the patronage of Buffon, successor to Macquer in the Chair of Chemistry at the Jardin du Roi. The appointment gave satisfaction. Fourcroy remained at the Jardin du Roi for twenty-five years, and his lectures attracted crowds to his lecture room.

The Revolution disturbed him as well as others. He became a member of the National Convention and of the Committee of Public Safety during the Reign of Terror. In this capacity he was associated with the trial and condemnation of Lavoisier, and a dark shadow rests on his memory in consequence. If he did not secretly participate in the crime, he was culpably indifferent to the fate of that great man. After the death of Robespierre and collapse of the Terror, Fourcroy was influential in raising new schools and other educational institutions in place of those which had been destroyed by the National Convention. He was created a Count of the Empire, and died at Paris.

Fourcroy was a voluminous writer. He wrote a *System of Chemistry*, which is diffuse, and a *Philosophy of Chemistry*, which is clear and concise; also 59 memoirs in his own name and 58 jointly with Vauquelin, his assistant. He was one of the earliest converts to the views of Lavoisier, but was a teacher and organiser rather than an original investigator. He discovered adipocere, and investigated the biliary substance resembling spermaceti, which he thought to be adipocere, but which is now called cholesterin. Other subjects of his study were the double salts of magnesium and ammonium, the sulphate and other salts of mercury, urine (in regard to which he was forestalled by Wollaston), and pure baryta (which he obtained by roasting the nitrate).

The last member of this distinguished group was Louis Nicolas Vauquelin (1763—1829). He was of peasant parentage, and born at Saint André de Hebertot, in Normandy. As laboratory boy to an apothecary in Rouen, he attracted by his quickness and honesty the attention of Fourcroy, to whom he became assistant. He was afterwards appointed Inspector of the Mint and Professor of Chemistry at Paris, giving a course of

lectures at the Museum of Natural History. Besides the papers already mentioned, in which he collaborated with Foureroy, he published 376 in his own name. In 1802 Napoleon made him a member of the Legion of Honour, and he returned to his birth-place, where he died.

Vauquelin was a great lecturer, and a patient and diligent laboratory worker. For our present purpose it will suffice to name some of the principal branches of research in which he was engaged. He discovered chromium in red lead ore from Siberia (1797); also beryllium or glucinum in beryl (1798); benzoic acid (1798); investigated the hyposulphites (1799); urea (1799); malic acid (1800-17); published a method for separating the platinum metals (1813-14); studied lithium (1814), cyanogen and cyanic acid (1818); and investigated allantoin with a few of its compounds, and quinic, camphoric and other organic acids. He also ascertained the composition of carbon disulphide. In some of this work he was associated with Foureroy, Klaproth, and others. For several years he edited the *Annales de Chimie et de Physique*, in which and in similar publications most of his papers are to be found. His work greatly resembled that of Klaproth, and he may be said to have excelled especially in analysis and in the improvement of analytical methods.

We shall now refer to two of the greatest benefits for which chemistry is indebted to this group of chemists. These were the first rational classification of elementary bodies, and the reform of chemical nomenclature.

When chemists recognised only the four elementary principles of Aristotle, and believed in the unity of matter and that "one is all," there was little use of a formal classification of substances. But the discoveries of the eighteenth century had changed the opinions of chemists in this respect, and it had become apparent that there were a considerable number of elementary bodies, which defied decomposition and which readily entered into union with one another, producing a vast number of chemical compounds. It became essential that the

mass of facts relating to these elements should be arranged in a regular system, and the first step towards attaining this end was to classify the elements themselves.

Accordingly, Lavoisier in his *Traité Élémentaire de Chimie* (1789) proposed the following general classification of chemical elements :—

1. *Simple Substances*.—Light, caloric, oxygen, hydrogen, and nitrogen.
2. *Oxidisable and Acidifiable Substances*.—Sulphur, phosphorus, carbon and the muriatic, fluoric, and boracic radicles, which at that time had not been isolated.
3. *Metallic Substances Producing Oxides*.—Antimony, silver, arsenic, bismuth, cobalt, copper, tin, iron, manganese, mercury, molybdenum, nickel, gold, platinum, lead, tungsten, and zinc.
4. *Simple Earthy Substances*.—Lime, baryta, magnesia, alumina, and silica.
5. *Alkaline Substances* (which were not considered elements).—Potash, soda, and ammonia.

This table is interesting for many reasons. It shows the extent to which the elementary bodies were known to Lavoisier in 1789, and, although differing materially from the classification adopted in modern systems, it indicates how soon the natural relations of substances began to be perceived. It is curious as a first attempt, but not many years elapsed before it had to be altered and extended.

The new nomenclature was obviously modelled upon the system which Linnaeus had recently put forward as a substitute for the clumsy method of naming plants and animals previously in use among naturalists. The two systems agree in devising names composed of two factors—the *generic* and the *specific*. Chemical nomenclature was based principally upon the combinations of oxygen with other elements. Thus :—

1. The product of the union of a simple substance, generally non-metallie, with oxygen was called an *acid*.
2. The product of the union of a metallic substance with oxygen was called an *oxide*.

3. The product of the union of an acid with an oxide was called a *salt*.
4. The product of the union of a metallic substance with chlorine, sulphur or phosphorus, was called respectively a *chloride*, a *sulphide*, or a *phosphide* (although the chlorides were unknown in the Lavoisierian system).

The simplest compounds of oxygen are acids and oxides. These were each indicated by a name, of which the generic part was the term "acid" or "oxide," and the specific part was an adjective derived from the other element in the compound. Thus, one of the products of the union of sulphur with oxygen was called *sulphuric acid*; one of the products of the union of lead with oxygen was called *lead oxide* or *plumbic oxide*. The same principle supplied names for chlorides (when they were discovered), sulphides, and phosphides.

But some substances combine with oxygen to produce more than one acid or oxide. These were distinguished by an alteration of the termination of the specific name or by the addition of a Greek prefix. Sulphur, for example, combines with oxygen to produce acids of various degrees of oxidation, which were indicated by the terms *sulphuric*, *sulphurous*, or *hyposulphurous acid*; lead forms more than one oxide, indicated by the terms *lead protoxide* and *lead dioxide*.

In the case of salts, names were adopted, of which the generic part was derived from the acid, and the specific from the metallic base. Thus, the product of the union of lead oxide with sulphuric acid was called *lead sulphate* or *plumbic sulphate*. To indicate the salts of variously oxidated acids, the termination was varied. The salts of sulphuric acid were *sulphates*, those of sulphurous acid, *sulphites*; the salts of nitric acid were *nitrates*; those of nitrous acid, *nitrites*; and so forth. Many alterations have been made upon the form of this nomenclature since the time of Lavoisier and his colleagues, but its general principles have not been materially changed.

As the result of the labours of this small group of chemists, who gathered together the research of contemporary and





## CHAPTER XXVIII

### THE QUANTITATIVE PERIOD

(From 1775 A.D. till 1900 A.D.)

#### 5. THE ATOMIC THEORY : CARL FRIEDERICH WENZEL TO JOHN DALTON

WE have now to consider a development of quantitative research which had a profound influence on chemistry, both theoretical and practical. The conception of an Atomic Theory, based upon equivalent weights, and the determination of the fundamental laws of chemical combination, not only added precision to chemical philosophy, but facilitated the labours of the student of chemical principles, the laboratory worker, and the manufacturer.

Several tentative efforts in this direction had already been made. Bergman in 1775 and Kirwan in 1780 endeavoured to fix the composition of certain salts, but did not succeed so well as to be able to propound a doctrine of definite composition. Cavendish was the first to prove that acids and bases combine in accordance with a fixed law, and to him we owe the introduction of the term "equivalent." He made no attempt, however, to determine the laws of chemical combination, and the next advance was made by Wenzel and Richter.

Carl Friederich Wenzel (1740-1793) was chiefly distinguished as a metallurgist. He was born at Dresden, where his father was a bookbinder. He was destined by his parents to follow his father's trade, but being unwilling to do so, left home and took lessons in surgery and chemistry. Thus equipped, he engaged himself as a ship's surgeon, in which capacity he made a voyage to Greenland. After this experience he returned to Saxony in 1766, and ultimately studied at Leipsic, specially

applying himself to metallurgy and assaying. In 1780 he was appointed chemist to the Freiberg foundries, and a few years later chemist to the Meissen Porcelain Works. He died at Freiberg.

Wenzel's chief works are : *Introduction to the Higher Chemistry* (1773), in which he appears as the last defender of alchemy ; and *Lectures on the Theory of the Chemical Affinity of Bodies* (1777), which contains analyses of numerous salts, showing the proportion of acid and base in each.

In the course of this work he was struck by the phenomenon that many saline solutions, when mixed together in certain proportions, completely decompose each other, so that two new salts are produced, but that if there be an excess of one of the salts, that excess remains in the solution without affecting the result. If the salts are neutral before being mixed, their neutrality is not generally affected by the decomposition, and consequently the elements in the respective salts have such affinities that the bases in each just saturate the acid in the other. Wenzel was so far before his time that this important observation did not impress his contemporaries, nor were his really accurate series of analyses recognised as such ; in fact they had less authority than others of far inferior precision.

It has been assumed by some authors from these observations of Wenzel that he had discovered the law of neutralisation. This assumption arose from an error on the part of Berzelius, who ascribed to him some of the work of Richter. It was pointed out, however, by Germain Henri Hess, in 1841, that the published works of Wenzel do not indicate that he realised the existence of a law of invariable and reciprocal proportion in the combination of acids and bases.

The next step in advance was the publication in 1792 of Richter's *Elements of Stoichiometry* (Chemical Mathematics). Jeremias Benjamin Richter (1762—1807) was born at Hirschberg, in Silesia. He became a mining secretary and assayer, and afterwards assessor of the Prussian Mines and chemist to the Royal Porcelain Factories at Berlin, where he died.

Richter carried out some of the earliest determinations of the quantities by weight in which acids and bases mutually saturate one another. In the book we have mentioned, *Stoichiometry of the Chemical Elements* (1792-4), he stated the quantities of acid and base necessary for saturation in a great number of instances, and showed that the proportions by weight of the various bases that will saturate the same weight of a given acid (say, 1,000 parts of sulphuric acid) will also saturate a different but constant weight of another acid. From the facts thus ascertained he deduced the important Law of Neutralisation.

The following table will illustrate the result of Richter's investigations :—

ACIDS.		BASES.	
Fluoric . . . .	427	Alumina . . . .	525
Carbonic . . . .	577	Magnesia . . . .	615
Sebacic . . . .	706	Ammonia . . . .	672
Muriatic . . . .	712	Lime . . . .	793
Oxalic . . . .	755	Soda . . . .	859
Phosphoric . . . .	979	Strontia . . . .	1329
Formic . . . .	988	Potash . . . .	1605
Sulphuric . . . .	1000	Barytes . . . .	2202
Succinic . . . .	1209		
Nitric . . . .	1405		
Acetic . . . .	1480		
Citric . . . .	1683		
Tartaric . . . .	1694		

These figures represent the mutual combining proportions of acid and base. If we take the quantity of any acid named in the table, we shall find that that quantity will be exactly saturated by the weight of each base given in the table. Although the importance of the figures was not recognised during Richter's lifetime, they really laid the foundation of the Law of Reciprocal Proportions. Their importance was overlooked, partly because the attention of chemists was at that time absorbed in the controversy between phlogistonists and anti-phlogistonists.

Richter also stated that "when different metals are separately dissolved in the same quantity of sulphuric, or of any acid, each takes up the same quantity of oxygen." He further attempted to prove that the quantity of different bases required to saturate a given acid forms an arithmetical progression, and the quantity of different acids required to saturate a given base a geometrical progression, but the figures do not warrant such a conclusion.

While Richter has the credit of laying the foundation of the Law of Reciprocal Proportions, the honour of establishing the Law of Definite Proportions rests with Josèphe Louis Proust (1755—1826). Proust was born at Angers, the son of an apothecary. Going to Paris, he was appointed apothecary-in-chief to the Salpêtrière, and lecturer on chemistry in a private establishment. At the request of Charles IV. he went to Spain—first to Segovia, then to Salamanca, and finally to Madrid, where he was Director of the Royal Laboratory. When the French took Madrid, they destroyed his magnificent laboratories and collections, reducing him to poverty, yet he refused an invitation of Napoleon to conduct a manufactory of grape sugar, a substance he had himself discovered in 1799. Returning to France, he was made a member of the Academy in 1816, received a pension from Louis XVIII., and retired to his native town, where he died.

Proust's most important writings are : *Indagaciones sobre el Estanada de Cobre la Vajilla de Estano y el Vidriado* (1803) and *Mémoire sur le Sucre de Raisins* (1808). In practical work he studied the sugars of sweet vegetable juices from 1799 to 1809, distinguishing three kinds, and as we have said, discovering grape sugar, which he demonstrated to be identical with that obtained from honey ; studied urea in 1803 ; fermentation in 1806 ; gum in 1818 ; and urine in 1820. In 1799 he showed that carbonate of copper always has the same composition, whether it is found in a natural condition, or is prepared artificially ; that the two oxides of tin and the two sulphides of iron always contain the same relative weights of their

components; and that no indeterminate compounds exist. He was, therefore, the first to prove that the elements combine in a small number of fixed proportions.

As the result of these observations he had a controversy with Berthollet on this point. It was formerly mentioned that the latter chemist considered chemical combination as due to mechanical laws, and was therefore obliged to admit that mass, as well as other physical conditions, must produce an alteration in chemical compounds. Proust, however, gained the day by demonstrating that when a metal combines with oxygen in more than one proportion the combination does not take place by gradual increment of one element, but *per saltum*, by sudden increments. Consequently, the weight of the one element which combines with the same quantity of the other is a different but *fixed* quantity. Further, compounds always contain definite quantities of their constituent elements.

Proust, therefore, established the law of definite proportions, but while he succeeded in this respect, his analyses were not correct enough to bring out the law of multiple proportions. This law was established by John Dalton, who explained it by his Atomic Theory.

The conception of an atomic theory based upon equivalent weights is inseparably associated with the name of John Dalton (1766—1844). This philosopher was born at Eaglesfield, near Cockermouth, in Cumberland. His father was a weaver in humble circumstances, a member of the Society of Friends, who struggled to give his son a fair education. Dalton at the early age of twelve tried to earn a living by teaching, but without success, and after an interlude of farm labour, went to assist a cousin who kept a school at Kendal. There he made the acquaintance in 1781 of a man who was to exercise the greatest influence upon his life's work—Mr. John Gough—a blind philosopher. With Mr. Gough he lived, read, and studied mathematics, until in 1793 he removed to Manchester, which was his home for the remainder of his life.

At Manchester Dalton first taught mathematics and natural



philosophy at the new college in Moseley Street, which was afterwards transferred to York, and is now incorporated with Manchester College, Oxford. When the college was removed, Dalton became a teacher of mathematics and chemistry, and as his reputation increased, gave lectures on chemistry at the Royal Institution, London, and in other large cities. According to contemporary accounts he was an ineffective lecturer, although a very able man. Honours came to him by degrees. He was chosen as a Corresponding Member of the French

Academy of Sciences; was admitted in 1822 to the Royal Society of London, whose gold medal was awarded to him in 1826; was appointed one of the Foreign Associates of the French Academy in 1830; while in 1831 Oxford, and in 1834 Edinburgh, conferred upon him the Degree of Doctor of Laws. A Royal pension was granted to him in 1833 of £150 a year, afterwards raised to £300. He had become a member of the Manchester Literary and Philosophical Society in 1794, and was elected to be its secretary in 1800, and



FIG. 93.—John Dalton.

its president in 1817. Many of his most important papers were first communicated to it, no less than 116 essays by him on scientific subjects being published in its *Memoirs*.

Dalton first distinguished himself by meteorological observations, particularly on the aurora borealis. For fifty-seven years from 1787 he kept a meteorological diary, in which he recorded more than 200,000 observations. His first important publication was an essay on this subject in 1793. He suffered from a peculiar form of colour blindness, which is sometimes called Daltonism, and in 1794 he described his symptoms in an

essay to the Society. Another important subject of discussion was volumetric analysis, which occupied his attention in 1814.

But the foundation of his reputation was laid in 1802 by the publication of six papers in the *Memoirs*, of which the following may be especially distinguished :—“ Experimental Essays on the Constitution of Mixed Gases ; ” “ On the Force of Steam or Vapour from Water and other Liquids at different Temperatures both in a Torricellian Vacuum and in Air ; ” “ On Evaporation ; ” and “ On the Expansion of Gases by Heat.”

In these papers he drew some important conclusions. He inferred that when two elastic fluids or gases, called A and B, are mixed, the particles of A do not repel the particles of B, as they repel one another ; hence the pressure on any one particle arises solely from particles of its own kind. This inference has neither been confirmed nor refuted, but if true would account for the diffusion of gases.

He demonstrated that water evaporates, forming an elastic fluid like air, at all temperatures, and that the elasticity of its vapour increases with the temperature, being equal to a half-inch of mercury at 30° Fahrenheit, and to thirty inches at 212°.

In another essay he proved that all elastic fluids expand alike for equal measurements of heat, an observation which was afterwards confirmed and put forward as a law bearing the names of Dulong and Petit. In the same essay he made a curious anticipation of the result of later research by saying that in his opinion all elastic fluids might be reduced into liquids by means of low temperature and strong pressure exerted upon the unmixed gases.

Dalton's greatest work, however, was in relation to the constitution of chemical substances. His views on this subject were first communicated by him to Dr. Thomson, and included by the latter in the third edition of his *System of Chemistry* (1807). They were afterwards set forth in the first part of the first volume of Dalton's *New System of Chemical Philosophy*, which was published in 1808, although the second part was not

issued until 1810, and the first part of the second volume in 1827.

We shall defer to the end of next chapter (p. 330) what we have to say about Dalton's atomic theory, and confine ourselves at present to a general explanation of its character and an account of the manner of its conception. More than once we have had to refer to atomic theories, which were common enough among the ancient philosophers, but in no previous theory of atoms were bodies differentiated by the *weights of their atoms*. Dalton supposed that the ultimate particles of all simple bodies are atoms incapable of further division. These atoms (at least, when they are viewed along with their atmospheres of heat) are spheres, each possessed of a weight peculiar to its own substance, which can be denoted by figures. Therefore, it is of great importance and advantage to ascertain the relative weights of the ultimate particles of each body, both simple and compound. Dalton accordingly ascertained by analysis the simple equivalent of each element, and his figures in his opinion represented—(1) the equivalent, (2) the atomic weight, and (3) the combining proportion, of each element.

With regard to the history of this conception, Thomson states that Dalton was led to the atomic theory by his examination of the composition of the two hydrocarbons, marsh gas and olefiant gas. A desire for clearness caused him to adopt a system of graphic representation of the atoms of the elements of these substances. The ordinary accounts hitherto given in histories respecting the way in which Dalton was led to the law of multiple proportions, and so to the atomic theory, are somewhat like this:—"He noticed that nitric oxide would combine with two different amounts of oxygen to form two more highly oxygenated compounds, but that between these two no definite compound could be obtained. . . . Dalton observed that marsh gas contains just double as much hydrogen as olefiant gas." It was these facts, as we learn from Thomson, in his *History of Chemistry*, that

formed the foundation of Dalton's theory, and it was supposed that he conceived the idea of atoms in order to account for them.

For upwards of eighty years this was believed to be a correct account of the matter, for, during all that time, Dalton's own laboratory notes were lying unheeded and undiscovered in the rooms of the Manchester Literary and Philosophical Society, where his experimental work was carried on. These papers came to light in 1895, or about that date, and from notes in his own handwriting it appears that the genesis of the idea was in inverse order.

Dalton was a great admirer of the Newtonian doctrine of the atomic constitution of matter, and was thus conducted to a realistic conception of the constitution of gases. From this physical standpoint he approached the atomic theory, and conceived the idea that atoms of different substances have different characteristic weights. This led him on to the idea that chemical combination takes place between varying numbers of atoms of definite weight, and he confirmed this idea by the result of analysis. It was, therefore, the theory of atoms which led him to the facts of combination in multiple proportion, not those facts which led him to the atomic theory to account for them, as we had been induced to assume. (*Vide* "A New View of the Origin of the Daltonian Atomic Theory," by Roscoe and Harden, 1896.)

This happy idea has been of the greatest use in giving clearness to chemical discussions, although the forms of the symbols employed by Dalton have been superseded by those soon afterwards introduced by Berzelius. Dalton's figures expressing the weights of the atoms were not quite correct. He corrected them later, and very accurate determinations were obtained by the careful analyses of Berzelius, who, though at first an opponent, became an enthusiastic supporter of the atomic theory.

Some difference of opinion prevailed among the supporters of the theory as to the best standard to be adopted. While

Dalton represented the weight of an atom of hydrogen by 1, because it is the lightest of all known bodies, Wollaston, who at once adopted the new ideas, represented the atomic weight of oxygen by 1, because it unites with a greater number of substances than any other elementary body. So he thought; but this reason ultimately disappeared, and the *hydrogen* = 1 *unit* has become the favourite. Berzelius reckoned oxygen equal to 100, and hydrogen to 12.5.

Thomson's *System of Chemistry* was translated into French by Berthollet, although in his introduction he opposed Dalton's views, chiefly because they would have overturned his own theory of chemical statics, to which we have more than once referred.

Meantime, other chemists were at work on similar lines. In 1809 Gay-Lussac published a paper in which he showed that gaseous bodies unite with each other in equal volumes, or very simple multiples, intending by this observation to confirm the atomic theory. Proust soon after proved that there is a close connection between the atomic weight of a gas and its specific gravity, a connection which was not quite so obvious then as it is now, when the law of Avogadro and Ampère is recognised. Thomson demonstrated that the specific gravity of a gas, even of a compound gas, is equal to its atomic weight multiplied by 1.1111 (the then specific gravity of oxygen), or by half of this (.5555), or by one-fourth of this (.2777), according to the condensation when the elements unite. Berzelius, attracted by the reciprocity foreshadowed by Richter, had set himself to analyse certain salts with extreme accuracy, in order that from them he might calculate the composition of the rest. While so engaged, Dalton's views became known, and those of Gay-Lussac, which stimulated Berzelius to extend his analyses. These were not published till 1811. He found that in a compound formed by the union of two metallic oxides, the metal which attaches itself to the positive pole, when decomposed by a galvanic battery combines with 2, 3, 4, or 5 times as much



oxygen as the metal which attaches itself to the negative pole. Finally, accepting the Daltonian atomic theory, he analysed very many minerals, and showed that most of them were compounds in definite atomic proportions. Thus was the theory confirmed on every hand.

It is one of the most curious facts in the history of chemistry that this original and instructive hypothesis, and the law of multiple proportions with which it was connected, were revealed to a mathematician and not to a professional chemist. Many distinguished chemists were at that time studying the composition of chemical compounds, with magnificent laboratories and extensive libraries at their command. Yet the secret was hidden from them and shown to John Dalton, a man who in chemistry was by comparison only an amateur, who possessed little apparatus, and that of the roughest and most common description, and whose library, as he said himself, he could carry on his back.

## CHAPTER XXIX

### THE QUANTITATIVE PERIOD

(From 1775 A.D. till 1900 A.D.)

#### 6. THE ATOMIC THEORY: JOSEPH LOUIS GAY-LUSSAC TO PIERRE LOUIS DULONG

ALTHOUGH the realisation of the laws of chemical combination and the conception of the atomic theory were due to Dalton, many of the practical applications and confirmations of these were the work of French chemists, particularly Gay-Lussac, Thénard, and Dulong. We shall therefore consider the biographies of these men before we discuss the laws and theory.

Joseph Louis Gay-Lussac (1778—1850) was born at St. Leonard, in Haute Vienne. His father was Procureur du Roi and a judge, whose original name was Gay, but who took that of Lussac from a small estate which belonged to him. Gay-Lussac was educated at the *École Polytechnique des Ponts et Chaussées* at Paris, from which he passed to be assistant to Berthollet. His career was one of steady promotion. In 1802 he became demonstrator to Foureroy; in 1808 Professor of Physics at the Sorbonne; in 1809 Professor of Chemistry at the *École Polytechnique*; and in 1832, after resigning his chair at the Sorbonne, Professor of Chemistry at the *Jardin des Plantes*. He also took an interest in public affairs, being elected deputy for Haute Vienne in 1831, and created a Peer of France in 1839. He died in Paris.

Gay-Lussac was one of the most brilliant of the French chemists, and spent his whole life in research. His principal subjects of investigation may be thus summarised:—

1. The combining volumes of gases;
2. The relation between the volume of a gas and its temperature.

3. Iodine and its compounds.
4. Cyanogen and its compounds. He called this gas "the first compound radicle," and it formed the basis of the Radicle Theory, of which we shall afterwards speak.

But, in addition to these subjects, he was engaged in the study of almost every department of chemistry, and of many departments of physics.

His early researches were mostly physical. He confirmed the observations of an earlier observer, M. Charles, on the behaviour of gases in combination and under heat. He found that gases are dilated in the same proportion by heat from  $0^{\circ}$  to  $100^{\circ}$  Centigrade. From his researches laws have been deduced, which are known sometimes as Gay-Lussac's Laws, and sometimes as Charles's Laws—(1) there is a simple ratio between the volumes of gases which combine; and (2) the volume of the resulting compound bears a simple ratio to the volumes of the original gaseous constituents.

He then turned his attention to the investigation of the air at different altitudes, and to the study of terrestrial magnetism. For this purpose he made two perilous balloon ascents—one on August 24th, 1804, when he reached an altitude of 13,000 feet, and another on September 16th following, when he reached an altitude of 23,000 feet. On these occasions he made numerous observations of the temperature and humidity of the air, and found that there is no difference in its composition at different heights.

In 1805 he accompanied Humboldt on a scientific journey through Switzerland, Italy, and Germany. In the same year he read a paper, published towards the end of 1808 in the *Mémoires de la Société d'Arceuil* (Vol. II., p. 207), in which he proved that oxygen and hydrogen, when they combine, do so in the proportion of one volume of oxygen to two volumes of hydrogen—a discovery which had an important bearing on the development of the atomic theory. Dalton assumed that one part by weight of hydrogen combined with eight of oxygen to form water; modern chemists, in view of the

discoveries of Gay-Lussac and others, are of opinion that water consists of two parts by weight of hydrogen to sixteen of oxygen, or more precisely 2 to 15.88.

Gay-Lussac was elected a member of the French Academy in 1806, and two years later prepared metallic potassium by the action of red-hot iron filings upon fused potash. In this operation he was assisted by Thénard, and in 1809 the two chemists by means of potassium reduced boron from boracic acid, thus finding what Lavoisier had termed the "boracic radicle."

In 1809 he established the proposition that when gases combine they do so in the most simple proportions, as 1 to 1, 1 to 2, 1 to 3, and that the volume of the compound thus formed bears a simple ratio to the volume of its constituents. From these and his previous observations, the laws to which we have already alluded were ultimately deduced.

In 1810 he prepared an important paper on fermentation, in which he drew several practical conclusions, which have been of great value to those engaged in the distillation of spirits.

Thénard and he collaborated in the study of chlorine, and read a memoir on the subject to the Institute. The paper dealt with muriatic acid and oxymuriatic acid, and they demonstrated that all anomalies could be explained by holding either that water was a constituent of the former (hydrochloric acid), or that chlorine was a simple gas. They decided for the former view, holding that chlorine is a compound, although they failed to get oxygen out of it by carbon. It is obvious that they were reluctant to oppose Lavoisier's opinion that oxygen is always essential to an acid. Davy, unhampered by prejudice, declared that hydrochloric acid is an acid without oxygen, and that chlorine is an element, a view which Gay-Lussac and Thénard ultimately adopted. In 1814 they prepared by a new process chloric acid and other compounds of the gas.

Between 1810 and 1811 they made analyses of organic

compounds by burning them with potassium chlorate ( $\text{KClO}_3$ ) in a tube, and collecting the products over mercury. They had previously tried cupric oxide ( $\text{CuO}$ ) and described their method. In this way they analysed fifteen substances. But in 1815 Gay-Lussac analysed cyanogen by means of cupric oxide, and in consequence abandoned potassium chlorate ever after. The cupric oxide method was afterwards perfected by Liebig in Gay-Lussac's laboratory, and the great German chemist then invented the modern process of organic analysis by combustion in a furnace.

The work of Gay-Lussac between 1811 and 1815 in relation to cyanogen was of great importance. He obtained the gas in a liquid state, and described it as a compound radicle. He proved that prussic acid is a compound of this radicle and hydrogen alone, while prussiates (now called "cyanides") are compounds of the radicle with metals, the yellow prussiate of potash containing the radicle ferrocyanogen. This demonstration completed the overthrow of Lavoisier's theory that oxygen is the only "acid-maker." The isolation of cyanogen bridged the gap between inorganic and organic substances.

Gay-Lussac's *Memoir on Iodine* appeared in 1814. This substance had been discovered three years previously by Bernard Courtois. Davy, in respect of its analogy to chlorine, had declared it to be an elementary body. Gay-Lussac, doubting this conclusion, made a careful investigation of iodine, and described its peculiar properties and those of its compounds. This substance was shortly afterwards recognised as an element.

After 1815 Gay-Lussac, being now an important man, was much engaged in solving technical and practical problems. He improved the system of manufacturing sulphuric acid in 1818, and of oxalic acid in 1829, in the former case devising what are still called the "Gay-Lussac towers." He introduced the very useful mode of determining the composition of chemical compounds, which is known as volumetric analysis. This he applied to the estimation of the amount of real alkali



in samples of potash and soda, by the volume of standard acid required to neutralise a given amount of the sample; of chlorine in bleaching powder, by a standard solution of arsenious acid; and of silver, in assaying, by a standard solution of sodium chloride (common salt). He invented a centesimal alcoholometer in 1824, which was much commended, while Liebig and he investigated fulminic acid in 1823-4.

Gay-Lussac, as an investigator, was bold and energetic, yet patient and accurate: as a man, he was cold, reserved, and, perhaps, a little vain of his great ability. He wrote 148 papers, the titles of which will be found in the Royal Society's Catalogue, and many of which appeared in the *Annales de Chimie et Physique*, which he edited for several years. Towards the end of his life he sometimes expressed his regret that he had to leave this world, where the many discoveries, which were being made, only pointed to still greater discoveries to come.

The principal colleague of Gay-Lussac was Louis Jacques Thénard (1777-1857), who was born of peasant parentage, at Louptière, in Aube. He studied pharmacy at Paris under Berthollet, Foureroy, and Vauquelin. In 1797 he became Demonstrator, and later Professor, at the *École Polytechnique*. He was elected a member of the French Academy, and Professor of Chemistry in the College of France and the Science Faculty of the University of Paris. Charles X. created him a Baron in 1825, and in 1832 a Peer of France. He died at Paris.

Thénard was above all things a teacher, and had a great influence upon scientific education in France. His *Traité de Chimie Élémentaire Théorique et Pratique* (1813-6) was the standard authority for a quarter of a century. In research work his name is inseparably associated with that of Gay-Lussac.

These two chemists reduced potassium to the metallic state by means of red-hot iron filings: found the peroxides of potassium and sodium; investigated fermentation and ethers in 1807; discovered sebacic acid in fatty substances in 1802; and peroxide of hydrogen in 1818, calling it "oxygenated

water." They studied bile in 1807, and Thénard afterwards produced the blue cobaltic pigment for colouring porcelain, which bears his name. Most of his papers appeared in scientific periodicals and transactions; and Gay-Lussac and he published in 1811 their *Recherches Physico-chimiques*, in which they narrated their researches in relation to sodium and potassium, boron, fluorine, fluo-boric gas, hydrofluoric acid, oxymuriatic acid, light, and vegetable and animal analysis.

But some of their most valuable joint work was directed towards laying the foundation of organic chemistry and organic analysis. In the latter department, they carried out Lavoisier's idea of heating the organic substances with a body which gives off its oxygen readily. For this purpose they chose potassium chlorate, a weighed quantity of which was mixed with an accurately known weight of the organic substance. The mixture was then moistened and rolled into pills, which were dried at 100° Centigrade. The combustion apparatus consisted of a perpendicular hard glass tube, provided with an exit tube, the bottom of the tube being heated by means of a furnace or lamp. Into this tube the balls of organic substance mixed with potassium chlorate were dropped, until all the air was displaced. A weighed quantity of the same mixture was introduced, and the gases evolved by heat were collected over mercury and analysed. The method of analysis adopted was in the case of oxygen, by adding hydrogen and exploding the mixture; and in the case of carbon dioxide, by absorbing it with potassium hydroxide (KOH). They analysed, as we have mentioned already, fifteen substances free from nitrogen, and four containing nitrogen, with fairly accurate results. They were careful when nitrogen was present to avoid employing an excess of oxygen.

Pierre Louis Dulong (1785—1838) was born at Rouen, and educated at the *École Polytechnique* at Paris, in which city he was for a time a doctor in one of the poor districts. He then became successively assistant to Berthollet; teacher of chemistry in various schools; in 1820 Professor of Chemistry,

and in 1830 Director, of the École Polytechnique. He was elected perpetual secretary of the Academy of Sciences in 1832, and died at Paris.

Dulong was a bold experimenter. A series of dangerous experiments in 1811—in the course of which two violent explosions occurred, causing him the loss of an eye, and severe injury to his hand—led to the discovery of nitrogen chloride. He investigated the compounds of oxygen with phosphorus and nitrogen, and was one of the first to hold the hydrogen theory of acids. He was associated in much important research with Alexis Therese Petit (1791—1823). They compared the mercury and air thermometers, and conducted a series of experiments for the determination of specific heat, and its relation to atomic weight. These inquiries led to the announcement of what are known as the Laws of Dulong and Petit, that atoms of simple substances have equal capacities for heat, and that the specific heat and atomic weight of simple substances are in inverse proportion.

Dulong in 1816 studied oxalic acid and organic acids in general, showing that water is an essential constituent of them ; later discovered hypophosphorus acid ; discussed in 1820 the density of fluids ; in 1830 the elastic force of steam at high temperature ; and in 1835 the basicity of acids.

Having now considered the men who were most intimately associated with the discovery of the Laws of Chemical Combination and the Atomic Theory, we shall indicate, so far as is necessary for our present purpose, what were those laws and theory as they were understood by their first exponents. Since we are only concerned with the laws in their historical aspect, we are at liberty to state them somewhat more broadly than we should do in a treatise on Chemical Philosophy. An excellent account of the whole subject will be found in the essay on John Dalton in Dr. Wilson's *Religio Chemici* (1862), to which we refer the student who seeks greater detail. To avoid confusion we shall substitute modern equivalents (freed of decimals) for the crude and often erroneous figures of Dalton, merely

premising that these figures do not represent absolute weights, but only relative or combining weights.

The Laws of Chemical Combination are usually considered as four in number, but for the sake of logical completeness, we shall add the general law of Definite Composition.

*Law of Definite Composition.*—A chemical compound invariably consists of the same components. Thus—

*Water* invariably consists of hydrogen and oxygen.

*Litharge* invariably consists of lead and oxygen.

*Cinnabar* invariably consists of mercury and sulphur.

Without this law, systematic chemistry would be impossible. If chemical compounds varied as indefinitely as the compounds of the paint-maker, for instance, no definite laws of combination could be conceived.

(1) *Law of Constant or Definite Proportions.*—The elements which form a chemical compound are united in it in an invariable ratio, which is characteristic of it. Thus—

*Water* ( $\text{H}_2\text{O}$ ) is invariably composed of 2 parts of hydrogen and 16 parts of oxygen.

*Litharge* ( $\text{PbO}$ ) is invariably composed of 207 parts of lead and 16 parts of oxygen.

*Cinnabar* ( $\text{HgS}$ ) is invariably composed of 200 parts of mercury and 32 parts of sulphur.

(2) *Law of Multiple Proportions.*—When one element combines with another to form more than one distinct compound, the higher proportions are invariably multiples of the lowest. Thus—

*Nitrogen* combines with *oxygen* to form five distinct compounds, in the following proportions:—

Nitrogen 14—oxygen 16—Nitric oxide ( $\text{NO}$ ).

Nitrogen 28—oxygen 16—Nitrous oxide ( $\text{N}_2\text{O}$ ).

Nitrogen 28—oxygen 48—Nitrogen trioxide ( $\text{N}_2\text{O}_3$ ).

Nitrogen 14—oxygen 32—Nitrogen peroxide ( $\text{NO}_2$ ).

Nitrogen 28—oxygen 80—Nitrogen pentoxide ( $\text{N}_2\text{O}_5$ ).

We never find in the compound, for instance, 18 or 25 parts of nitrogen; but if the proportion passes 14, it must be a multiple

of that number ; nor 20, 27, 35, or other odd proportions of oxygen : but if the proportion passes 16, it must be a multiple of that number.

(3) *Law of Reciprocal Proportions or Equivalents.*—When two or more elements combine with a third in certain proportions, they combine in the same proportions with each other, or in multiples of the same proportions. Thus—

32 parts of sulphur combine with 207 parts of lead to form galena (PbS).

16 parts of oxygen combine with 207 parts of lead to form litharge (PbO).

And 32 parts of sulphur combine with  $16 \times 2$  (32) parts of oxygen to form sulphur dioxide (SO<sub>2</sub>).

(4) *The Law of Compound Proportions.*—The combining proportion or equivalent of a compound body is equal to the sum of the combining proportions or equivalents of its several component elements. Thus—

Carbon dioxide (CO<sub>2</sub>) consists of 12 parts of carbon and 32 parts of oxygen : therefore its equivalent is 44.

Marble (CaCO<sub>3</sub>) consists of 40 parts of calcium, 16 parts of oxygen, and 44 parts of carbon dioxide ; therefore its equivalent is 100. Or, we may express it in another way, as consisting of 40 parts of calcium, 12 parts of carbon, and 48 parts of oxygen ; but the sum is still 100, which is the equivalent of marble.

The atomic theory partly explains these laws, and is partly explained by them. It proceeds upon the assumption that matter, although it may be conceived as infinitely divisible, is only finitely divided. There comes a point at which it can be no further subdivided, and it then consists of ultimate atoms, imperishable and indivisible. In shape these ultimate atoms of matter are probably spherical, in size they are equal, though extremely minute, and their relative weight corresponds with the combining proportion or equivalent of the body which they ultimately compose. Thus, the relative weight of the ultimate atoms of hydrogen is 1, of oxygen 16, of nitrogen 14, of sulphur



32. of lead 207. of mercury 200. and so forth. Oxygen having an equivalent of 16, the atom of oxygen is 16 times heavier than the atom of hydrogen, which has 1 for its equivalent ; sulphur (32) is twice the weight of oxygen.

This was the great and original conception of Dalton, which differentiated his hypothesis from all the atomic theories which had preceded it. Of course it is founded upon an impossible assumption. Matter, however minutely divided, must conceivably be capable of further division. Our reason cannot conceive anything which, if it existed at all, could not be split in half. But this does not affect the value of the theory as a convenient working hypothesis, and so chemists suppose that the proportions in which bodies combine with each other, depend on the weights of the ultimate atoms of which they are respectively composed, and are identical with them.

Amongst other clear conceptions which we owe to the atomic theory is the distinction between an element, a compound, and a mixture. An *element* is a substance composed of similar simple ultimate atoms ; a *compound* is a substance composed of similar compound atoms or molecules ; a *mixture* is a substance composed of different compound atoms or molecules. Thus, lead is an element ; litharge a compound ; and lead-colour paint, a mixture.

The Laws of Chemical Combination are founded upon the conception that all the simple atoms in an elementary body are alike, and that a compound atom or molecule can only be altered by the addition or subtraction of one or more complete atoms, hence the proportional relation which always subsists between the elements in their several combinations.

It is possible that the Daltonian Atomic Theory may share the fate of other hypotheses which have preceded it. As research extends, it may have to be abandoned, and may give place to some other doctrine, which will be more consistent with later discoveries. But that time has not yet arrived. The Theory and the Laws of Chemical Combination have been, and are still being, modified in parts, but no modern discovery has

discredited the possibility of atoms, although it seems probable that they are neither so imperishable, nor so indivisible, as Dalton conceived. The laws, therefore, are still received by chemists as being founded upon fact, and the atomic theory is still accepted as a useful working hypothesis.

*Handwritten notes:*  
 Lavoisier & Laplace  
 Dalton's Atomic Theory  
 Gay Lussac's Law  
 Avogadro's Hypothesis

## CHAPTER XXX

### THE RISE OF ELECTRO-CHEMISTRY

(From 1790 A.D. till 1820 A.D.)

#### 1. SIR HUMPHRY DAVY AND JONS JAKOB BERZELIUS

AT the period at which we have now arrived, the discovery of voltaic electricity by Galvani and Volta, and the controversy between these two pioneers of electric science in 1790, began to influence chemical research. Nicholson, the editor of *Nicholson's Philosophical Magazine*, and Carlisle in 1800 repeated Volta's experiments with the voltaic pile, performed electrolysis of water, distinguished the positive and negative poles, and established the connection between electricity and chemistry.

Nicholson and Carlisle observed that by conducting the electric current from the voltaic pile through water, the latter was decomposed into its constituents. They further found that at the end of one wire hydrogen was evolved, while at the end of the other oxygen appeared, provided the metal of which the wire was made was not oxidisable. When the current was passed through tincture of litmus, they also noticed that the latter was coloured red in the neighbourhood of the positive pole, as if by an acid.

Between 1803 and 1807 Berzelius and Hisinger in Sweden reported the following conclusions at which they had arrived, as the results of experimental work :—That neutral salts are decomposed by the electric current ; that, in general, chemical compounds are decomposed by the current, and their constituents collect at the poles ; and that combustible substances, alkalis, and earths migrate to the negative pole ; while oxygen, acids, and oxidised compounds migrate to the positive pole.

Gay-Lussac also worked on electro-decomposition, but the

first to investigate completely electro-chemical decompositions, and to explain the laws which regulate them, was Sir Humphry Davy (1778—1829). This great chemist, perhaps of all British chemists the one whose name sounds most familiar to the general public, was born at Penzance, in Cornwall. An interesting narrative of his parentage and early years will be found in *A History and Account of Penzance*, prepared for the use of visitors to the ancient town, which contains a race of men who



FIG. 94.—Sir Humphry Davy.

are chiefly devoted to mining, and who are descended from those who in early times came into contact with the Romans, and with traders from Europe and Africa, seeking tin from the famed Cassiterides.

From this little book we learn that there was an outbreak of fever in Penzance. In a certain house both parents were struck down by the deadly disease without hope of recovery. The doctor in attendance was so touched

by the distress of the mother, that he promised to do his best for her three daughters. When the end came, the worthy physician took the little girls to his own home, and adopted them as his daughters. The second of these married a wood-carver named Robert Davy, and the philosopher was their first-born.

There was not much of the apparent philosopher about young Davy. He is described as a rather uncouth little fellow, very fond of play and not very fond of work, but even then a keen angler. The only indication of the future chemist was his

predilection for making "thunder powder" and fireworks. In 1793 he was placed under a renowned teacher, Dr. Cardew, at Truro, who, writing at a later date, said: "I could not discern the faculties by which he was afterwards so much distinguished; I discovered indeed his taste for poetry, which I did not omit to encourage." We are not surprised. The scientific acumen of Humphry Davy was not likely to find an outlet in Latin prose or Greek iambs.

On the death of his father, Davy was apprenticed to Mr. Borlase, a surgeon and apothecary in Penzance, in whose house he began to show his interest in chemistry, particularly gases, with the result that his master used to declare that some day he would blow them all up into the air. But Davy had now realised his responsibility for his career, and set resolutely to work upon a systematic and remarkably wide course of self-instruction.

While in the service of Mr. Borlase, Davy made the acquaintance of two visitors to Penzance, Gregory Watt, a son of the great engineer, and Davies Gilbert. The latter recommended him to Dr. Beddoes, Professor of Chemistry at Oxford. The doctor had established at Bristol a Medical Pneumatic Institution for investigating the medicinal properties of various gases, and in 1798 he made Davy superintendent of this establishment. There the latter set to work upon original research, and amongst other things discovered that nitrous oxide was perfectly respirable, but produced absolute intoxication. In 1800 he published the result of his investigation under the title "Researches, Chemical and Philosophical, chiefly concerning Nitrous Oxide or Dephlogisticated Nitrous Gas, and its Respiration." This treatise was the beginning of the use of nitrous oxide as an anæsthetic and intoxicant, and at once gave Davy a high reputation. Shortly before this Count Rumford had established the Royal Institution of London, and the first Professor of Chemistry, Dr. Garnet, having resigned, Davy was appointed in 1801 lecturer, and next year professor in his room.

From this time Davy's career was a succession of triumphs.



As a lecturer he was extremely popular, his audience at the Royal Institution sometimes numbering a thousand. In 1802, at the request of the Board of Agriculture, he delivered a course of lectures, which he continued for ten years, and then published as *Elements of Agricultural Chemistry* (1813).

Davy was elected a member of the Royal Society in 1803, and delivered under its auspices his celebrated Bakerian Lectures. In the first of these, in 1806, "On some Chemical Agencies of Electricity," described by Berzelius as one of the most remarkable memoirs in the history of chemical theory, he demonstrated that hydrogen, alkaline substances, metals, and some metallic oxides are attracted by negatively electrified, and repelled by positively electrified, metallic surfaces; while, on the contrary, oxygen and acid substances are attracted by positively electrified, and repelled by negatively electrified, metallic surfaces.

His great discovery, the production of metallic potassium and sodium by electrolysis, of which we shall have more to say, was made in 1807. Next year in his third Bakerian Lecture he dealt with this subject, and disproved the idea of Gay-Lussac that potassium is not a simple substance, but a compound of potash and hydrogen. At the same time he described the preparation of boron, which he then thought a metal.

The study of chlorine next occupied his attention, and formed the subject of his fifth Bakerian Lecture in 1810. Discussing the nature of what was called oxymuriatic acid, he demonstrated that it was not a compound, but a simple substance, for which he proposed the name "chlorine," by which it has since been known.

Trinity College, Dublin, in 1811 conferred upon him the degree of Doctor of Laws, the only honorary degree he received. He was knighted by the Prince Regent in 1812, and created a baronet in 1818. In 1812 his *Elements of Chemical Philosophy* was published, and next year he travelled on the Continent. During this journey, while in Paris, he examined iodine, and declared it to be an element, as we formerly mentioned.

The numerous accidents in mines caused by explosions of fire-damp led him to study the principles of the ignition of explosive gases. After an investigation on the spot, he invented the safety-lamp, which bears his name, and with characteristic generosity declined to patent his idea, but left it free for the benefit of all miners.

But the end of a strenuous life was approaching. He had two or three attacks of paralysis, and died at Geneva at the comparatively early age of fifty-one.

Davy commenced his researches with the newly discovered Voltaic electricity, especially its chemical effects. His most celebrated paper on this subject was published in the *Philosophical Transactions* for 1807, after his first Bakerian Lecture. It had previously been observed that when two platinum wires from a battery are plunged into water, an acid appears round the positive, and an alkali round the negative wire, but both acid and alkali had been variously explained. Davy proved that in all cases these are derived from the decomposition of some salt dissolved in the water. On this observation he founded the Electro-chemical Theory of Affinity. He asserted that all substances which have chemical affinity for each other are in different states of electricity, one positive, the other negative; and that the degree of affinity is proportional to the intensity of these opposite states. When a compound is placed in contact with the poles of a galvanic battery, the positive pole attracts the electro-negative and repels the electro-positive, while the negative pole acts in the opposite way. He noticed that when copper and sulphur are mixed, they exhibit an electric potential, which increases with increasing temperature until finally they combine, and all traces of electricity disappear. Hence, he inferred that the same forces which, acting on masses at a distance, produce electric phenomena, when acting on atoms at small distances, produce chemical combination, the positive electricity of the one atom attracting and holding the negative of the other. In electrolysis the positive charge is on one and the negative

on the other, but these two charges have to be discharged through the electrode before the elements are set free. This is the reverse of what takes place in combination. Davy in this view differed from the electro-chemical theory of Berzelius.

Davy held that if the battery is strong enough any compound may be decomposed, and that chemical affinity is merely a form of electric attraction. He vigorously put his theory into practice, and by means of a powerful battery of 500 cells decomposed in 1807 potash and soda, and in 1808 lime, magnesia, strontia, baryta, and lithia, yielding the metals potassium, sodium, calcium, magnesium, strontium, barium, and lithium.

The method he adopted was to pass a current from the Voltaic pile through a solution of caustic potash or soda, which was then believed to be an element, and thus obtain metallic potassium or sodium, as the case might be, at the negative pole. He inferred that these caustic alkalis are hydrates, and guessed that the alkaline earths have a similar constitution. Gay-Lussac and Thénard, as already mentioned, prepared potassium by heating potassium hydroxide (caustic potash) with red-hot iron filings. On passing gaseous ammonia ( $\text{NH}_3$ ) over the metal thus obtained, they evolved hydrogen, and consequently refused to believe the simple nature of potassium, declaring it to be a compound of potash and hydrogen. Davy met this by maintaining that *potassamide* (the substance they obtained) is a potassium-substitution compound of ammonia.

Another far-reaching result of Davy's research was the proof of the elemental nature of chlorine. Berthollet's conclusion that chlorine is oxymuriatic acid was universally accepted until Gay-Lussac and Thénard in 1809 endeavoured to decompose the gas and failed. They concluded that it contained water, because it yielded water when passed over litharge. Their researches read to the Institute in 1809 led Davy to investigate muriatic acid (hydrochloric acid) gas,

which in 1808 he had shown to be decomposed by potassium, with evolution of hydrogen. In 1810 he proved that chlorine is an element, and that muriatic acid gas is a compound of chlorine and hydrogen. He thus overturned the oxygen-acid theory, and demonstrated that muriates are compounds of metals with chlorine. He pointed to the fact that some acids, such as sulphuretted hydrogen, contain no oxygen, and argued that muriatic acid gas was one of these, chlorine in it taking the place of oxygen. He used the following arguments to show that there is no oxygen in muriatic acid gas :—

- (a) He sparked it and got no trace of oxygen.
- (b) He heated carbon in it and got neither carbon monoxide (CO) nor carbon dioxide (CO<sub>2</sub>).
- (c) He heated tin in it and got no stannic oxide (SnO<sub>2</sub>).
- (d) He got no oxides with phosphorus, only chlorides.
- (e) Chlorine is very different in character from the known oxides of chlorine.
- (f) He explained the bleaching action of chlorine by its liberating oxygen from water.

The conclusions of Davy were at first doubted, but when iodine and bromine were also discovered, Gay-Lussac and his followers adopted Davy's views. The latter worked out fluorine, and proved that hydrofluoric acid (HF) contains no oxygen. Berzelius also opposed Davy until the discovery of iodine, but embraced the latter's opinion in 1820. A controversy in Nicholson's *Magazine* on these questions, between Dr. John Murray and Dr. John Davy, a brother of Sir Humphry, resulted in the discovery of phosgene or chlorocarbonic gas (COCl<sub>2</sub>), otherwise termed carbon oxychloride.

Sir Humphry Davy was a man of sanguine but somewhat irritable temperament. He was fond of fishing and shooting, and went a good deal into society, numbering among his personal friends Sir Walter Scott and most of the distinguished men of his time. He was an enthusiastic and energetic experimenter, an admirable lecturer, and an expert manipulator. He was highly imaginative, and Coleridge said of

him that if he "had not been the first chemist, he would have been the first poet of his day," a remark which, allowing for the characteristic exaggeration of its author, perhaps contains the germ of a truth.

One of the greatest contemporaries of Davy and Dalton was the Swedish chemist Jons Jakob Berzelius (1779—1848). He was born at Vafversunda Sargard, near Linköping, in East Gothland, and studied medicine at the University of Upsala, especially chemistry under Afzelius. His first chemical research was an analysis of mineral waters in 1799. Graduating as Doctor of Medicine in 1802, his thesis was "On the Action of Galvanism on Organic Bodies," in which he made use of the discovery in 1800 by Volta of the battery known by his name. Next year, in an essay "On the Division of Salts through Galvanism," he propounded a theory of electrochemistry. After being teacher of chemistry at the Carlberg Military School and assistant professor of botany and chemistry in the medical school at Stockholm, he was appointed professor at that establishment. In 1808 he was admitted a member of Stockholm Academy of Sciences, of which in 1818 he became perpetual secretary. He was ennobled in 1818, and created a baron in 1835. An unfortunate explosion during an experiment in 1842 caused him serious injury, but he continued his work, and died at Stockholm six years later.

The writings of Berzelius were numerous and important. The principal publications are: *Animal Chemistry* (including his own new analysis of blood) (1806–8); over 250 papers in various periodicals; *Treatise on Chemistry* (1808); *Treatise on the Blowpipe*; *New System of Mineralogy*; *Theory of Chemical Proportions and the Chemical Action of Electricity* (1814–18); *Lehrbuch der Chemie*; and *Jahresbericht*, or Annual Reports on the Progress of Physics and Chemistry (1821–48).

Berzelius spent ten years in ascertaining with unprecedented care and accuracy the atomic or molecular weights of over two thousand simple and compound bodies. The results



were published in 1818, and revised in 1826. In making these calculations he regarded oxygen as the pivot round which chemistry revolves, and therefore took it as the basis of reference for atomic weights. The greater part of his figures bear comparison with the most accurate determinations of more modern date. In 1815 he applied the Atomic Theory to the mineral kingdom, and made a new arrangement of minerals, founded on their being definite chemical compounds.

As the outcome of his study of voltaic electricity, he proposed a theory based upon the supposition that the atoms of elements are electrically polarised, the positive charge predominating in some, and the negative in others. He also put forward a dualistic hypothesis that chemical compounds are composed of two *electrically different* components. In extending this hypothesis to organic chemistry, he regarded organic compounds as containing a group or groups of atoms forming compound radicles, in place of simple substances or elements. Although his views never commanded full assent from other chemists, he is entitled to be deemed one of the founders of the Radicle Theory.

One of his most useful services to chemistry was the invention of a system of symbols and notation, which with modification is still used in stating chemical formulæ. He indicated each simple substance or element by the initial letter (or, where more than one had the same initial, by two letters) of its Latin or Greek name. In the case of compound bodies he added a small subscript figure to show the number of atoms of each element present in the compound when these atoms exceeded unity. Thus—

*Oxygen* was represented by the letter O.

*Hydrogen* was represented by the letter H.

*Mercury* was represented by the letters Hg (*Hydrargyrum*).

*Lead* was represented by the letters Pb (*Plumbum*).

*Water*, a compound of two atoms of hydrogen and one of oxygen, was represented by  $H_2O$ .

*Litharge*, a compound of one atom each of lead and oxygen, was represented by PbO.

The valuable work of Berzelius in practical research may be summarised thus : He analysed many rare minerals ; in 1818 discovered selenium, selenic acid, and its compounds ; in 1822 studied the mineral waters of Carlsbad ; in 1823 made experiments on uranium, fluoric acid, and pure silicon ; in 1824 zirconium and tantalum ; in 1826 thio acids and those salts in which sulphur was held to replace oxygen ; in 1828 examined palladium, rhodium, osmium, iridium ; in 1833 tellurium and thio derivatives ; and in 1834 meteoric stones.

Davy and Berzelius were chemists of the first rank in all branches of the science, but we have especially associated them with electro-chemistry, in which they were the leading pioneers. In the next chapter we shall consider several men whose work was closely connected with that of Davy and Berzelius, but who were not so intimately associated with electro-chemical research. It will, however, be more convenient to treat them as forming members of the same historical group.

## CHAPTER XXXI

### THE RISE OF ELECTRO-CHEMISTRY

(From 1790 A.D. till 1820 A.D.)

#### 2. WILLIAM HYDE WOLLASTON TO HEINRICH ROSE

THE group of chemists whom we are to consider in this chapter have much in common with Davy and Berzelius. The work of all chiefly related to the study of minerals, the improvement of methods of chemical analysis, and the discovery of new elements by the application to new minerals of the improved methods that they had devised. It is only possible for us to consider a few of the leaders in this research work. In France, Germany, and Sweden many chemists were diligently pursuing it, and in particular there were a number of eminent men, educated by Berzelius in his laboratory, who like him did much to advance analytical chemistry.



FIG. 95.—William Hyde Wollaston.

One of the ablest of British chemists, and one who has never received his due measure of appreciation, was William Hyde Wollaston (1766—1828). He was born at East Dereham, in Norfolk, the second of the seventeen children of the Rector of Chislehurst. He was educated at Charterhouse and Caius

College, Cambridge, of which he was elected a Fellow. In 1793 he graduated Doctor of Medicine, and practised first in Bury St. Edmunds and then in London. He was uniformly unsuccessful, and a disappointment he met in an attempt to obtain a physicianship at St. George's Hospital caused him to abandon medicine and devote himself to original research.

Wollaston was a man of the highest ability, great versatility, and original genius, but eccentric and reserved. He lived alone and in rigid seclusion. His experiments were performed in private, and their results grudgingly disclosed. He absolutely forbade visitors to his laboratory. It is told of him that on one occasion an acquaintance succeeded in entering the private chamber in spite of its owner's precautions. Wollaston treated him with perfect courtesy, but directed his attention to a furnace, saying, "Make a profound bow to it, for as this is the first time, it will also be the last time, of your seeing it."

In spite of his secretive and reserved habits, the repute of his skill and knowledge spread abroad. In 1793 he had been elected a member of the Royal Society, in 1801 he became its secretary, and if he had not voluntarily made way for Sir Humphry Davy, he would have occupied the President's chair. The Bakerian Lecture for 1828 was delivered by him on "A Method of rendering Platina Malleable." He died in London on December 22nd, 1828, of a peculiar form of brain disease the fatal termination of which he long foresaw and met with calm fortitude. Wishing to leave an account of several discoveries, which he was reluctant should perish with him, and being unable to write, he spent many of his few remaining hours in dictating to an amanuensis those papers which appeared in the *Philosophical Transactions* for 1829. An admirable account of his life will be found in Dr. Wilson's *Religio Chemici* (1862).

The work of Wollaston was in many fields—chemistry, optics, acoustics, mineralogy, astronomy, physiology, botany, and other branches of science, but from among his discoveries

two may be especially selected as entitling him to the gratitude of all students of science—his method of rendering platinum malleable and his reflecting goniometer.

The peculiar qualities of platinum had long been known and appreciated. It was impervious to the action of almost every known substance save *aqua regia*; it neither rusted nor corroded, and it was infusible in the most powerful furnace. Such a material was needed at the stage to which chemical analysis had now attained—in fact, further progress was almost impossible without it. Vessels of glass, porcelain, or silver were sufficient so long as it was not necessary to deal with substances which attacked the material of which the vessels were composed, but it was now necessary to deal with such substances. Blowpipe analysis and heat tests formed an important portion of analytical processes, but the great heat fused ordinary materials like wax. Platinum met all these difficulties, but unfortunately it was only found in granules, mixed with impurities, so that it could neither be welded nor fused.

Wollaston solved this problem. Dissolving the metal in *aqua regia*, purifying it in solution, precipitating it with sal ammoniac, and dissipating the chlorine and ammonia by heat, he obtained platinum in the form of a fine black powder. After various processes this powder was welded into an ingot, which could be rolled into foil, drawn into wire, or otherwise wrought into any shape which was required.

To Wollaston this discovery brought fortune. He kept the process secret until the close of his life, and is said to have acquired £30,000 by means of it; but to laboratory workers it was an inestimable benefit. Platinum crucibles, wire and foil are essentials of the modern laboratory, which could not have been procured without the invention of Wollaston. He was himself an expert blowpipe manipulator, and used to carry his whole laboratory on a tea-tray.

Wollaston's reflecting goniometer, produced in 1809, in its own way wrought a revolution in the methods of mineralogy



and crystallography. As is generally known, the classification of crystals is based upon the measurement of their angles. For this purpose goniometers were used, but prior to the time of Wollaston these were applied directly to the facets of the crystals. Consequently, it was only possible to measure large crystals, and even these very inaccurately. Wollaston attained his object by measuring, not the angle formed by the meeting of the facets, but the angle formed by the meeting of rays of light *reflected from those facets*. The student with this instrument could measure with absolute accuracy the angles of the most minute, as easily as those of the largest, crystals. We shall have to return to this subject in the next chapter.

Another of Wollaston's optical inventions, the *camera lucida*, has been of much assistance to microscopists and others engaged in research work who have to make accurate drawings of very small objects.

But as we have said, his energies covered a wide field. Confining our attention to his labours in chemical philosophy, we find that he made a thorough examination of urinary calculi, in which he traced the formation of "mulberry" calculus (chiefly calcium oxalate), triple phosphate, cystic oxide, and chalk stones in joints: he was the first to demonstrate the identity of galvanism and electricity; and he discovered palladium (1804), rhodium (1805), columbium or niobium (1809), and titanium (1809), although Richard Chenevix laid claim to the prior discovery of palladium. It is now admitted that the honour rests with Wollaston, although his own secretive habits caused misunderstanding which might have been avoided. There is also some question as to his discovery of niobium or columbium.

There can be no doubt that the oblivion which has overtaken much of Wollaston's work was due to his secretive and retiring disposition. He was also hampered by too excessive caution in regard to generalisations, a commendable quality in moderation, but one which in his case probably lost the world valuable philosophical doctrines. His very versatility of interest was a

snare to him, and so it comes to pass that with abilities equal to those of Black, Cavendish or Davy, Dr. Wollaston has not attained in the history of chemistry a position equal to that held by any of these distinguished men. Behind his stiff manners he had a kind heart, for he sent a cheque for £10,000 to a professional brother who had been overwhelmed by financial misfortune; but he never forgot his early disappointment, and would not ask any favour either for himself or for another.

We now come to a Swedish chemist of considerable ability, whose work was mostly merged in that of others, John Gottlieb Gahn (1745—1818). He was born at the ironworks in Helsingland, and was descended from a Scottish family. He was educated at the University of Upsala. The discovery of the rhombohedron in six-sided crystal of Iceland spar and of the composition of bone-ash were due to him; but he made many discoveries, for which others received the credit. He paid particular attention to minerals, mining, and practical metallurgy, in which he was engaged as a manufacturer. The metal manganese was in 1774 first isolated by him. His most important scientific work was the development of the use of the blowpipe, the results of which are embodied in the writings of Berzelius.

Smithson Tennant (1761—1815) was born at Selby, in Wensleydale. He studied medicine at Edinburgh University, where he commenced chemistry under Dr. Black. His training in chemistry and botany was completed at Christ's College, Cambridge. In 1784 he travelled in Denmark and Sweden, where he made the acquaintance of Scheele, and afterwards passed through Holland and France, learning what he could in these countries. He graduated as Doctor of Medicine in 1790, and next year confirmed Lavoisier's opinions by the analysis of carbon dioxide. He passed phosphorus through red-hot calcium carbonate, procuring a deposit of charcoal, and discovering calcium phosphide ( $\text{Ca}_3\text{P}_2$ ). In 1796 he proved that the diamond is pure carbon by heating it in a gold tube

with potassium nitrate (saltpetre), and his work, along with the proof furnished by Mackenzie that equal parts of graphite, diamond and charcoal yield equal amounts of carbon dioxide on combustion, was of special importance in establishing the similar chemical character of the three substances. He was appointed Professor of Chemistry at Cambridge in 1813, and was accidentally killed near Boulogne two years later by the fall of a bridge over which he was riding. His most important discoveries were the metals iridium and osmium in the residues from the solution of platinum ores (1804), and the composition of magnesian limestone or dolomite.

A group of German and Swedish chemists close this division of our subject. Wilhelm August Lampadius (1772—1844) was born at Hehlen, in Brunswick, and studied pharmacy at Göttingen. In 1794 he obtained the post of Assistant Professor and next year that of Professor of Chemistry and Mining at the School of Mines at Freiberg. He discovered carbon disulphide in 1796. Most of his writings were meteorological, although he wrote a large number of works in German on chemical subjects. Of these the most important are: *Systematische Chemische Darstellung d. einfachen Naturkörper* (1806); *Grundriss d. Elektrochemie* (1817); and *Handbuch d. Chemischen Analyse d. Mineralkörper* (1801-18).

Of Nils Nordeuskiöld we need only say that he was Superintendent of Mines in Finland, and in 1820 published analyses of fourteen new varieties of Lapland minerals, and in 1827 a tabular view of mineral species, arranged chemically.

There were a number of distinguished chemists named Gmelin. One of these, Christian Gottlieb Gmelin (1792—1860), was Professor of Chemistry and Pharmacy in the University of Tübingen. He invented in 1828 a process for the manufacture of ultramarine, and devoted much time to the analysis of minerals, amongst others helvine and tourmaline. Leopold Gmelin (1788—1853) was even better known. He was educated at Göttingen, Tübingen and Vienna, and became Professor of Chemistry and Medicine at Heidelberg, where he died. In

1822 he discovered the red prussiate of potash (potassium ferri-cyanide), and he is particularly remembered by his *Handbuch der Chemie* (1817-19), one of the most complete treatises on chemistry ever written, which was translated into English by H. Watts for the Cavendish Society.

The German family of Rose numbered many well-known chemists. A distinguished member of it, Heinrich Rose (1795-1864), is remarkable for his career, as well as for his chemical attainments. He was born at Berlin and educated at Danzig, where he nearly lost his life from typhus fever during the siege of 1807. This untoward experience did not cool his zeal for soldiering, for he served in the Prussian army during the Waterloo campaign. When peace was established, he returned to Berlin, and studied chemistry under Klaproth. In 1819 he went to Stockholm, then a famous chemical school, and continued his studies

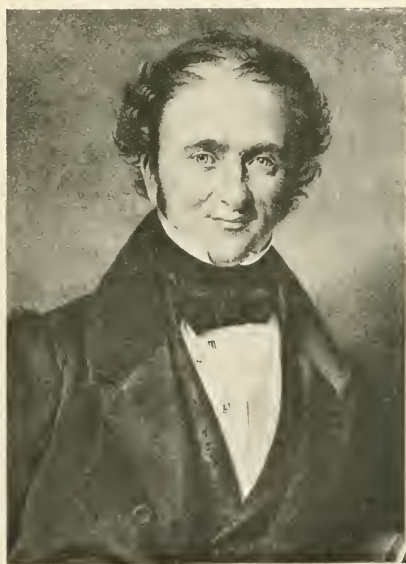


FIG. 96.—Heinrich Rose.

under Berzelius. Graduating at Kiel in 1821, he devoted himself to research, and became Professor of Chemistry in Berlin University in 1835. He discovered antimony pentachloride, and was the first to study the mass-action of water in chemical reactions. His chief work was connected with inorganic chemistry, and he published the result in an excellent book, *Ausführliches Handbuch der Analytischen Chemie* (1829).

The years which witnessed the rise of electro-chemistry also

witnessed an extraordinary advance in chemical knowledge. The ten years before and twenty years after the beginning of the nineteenth century formed one of the most fruitful periods in the history of chemistry. Never were a greater number of distinguished chemists at work in different countries at the same time seeking to discover the mysteries of the science, and never were their labours more liberally rewarded. The isolation of potassium, sodium, calcium, magnesium, strontium, barium, selenium, iridium, osmium, palladium and other rare metals; the recognition of the elemental character of chlorine, iodine, fluorine, and bromine; the adoption of platinum apparatus; the improvement of blowpipe manipulation; and the introduction of more accurate methods of analysis—had all tended to effect an entire change in the state of chemical knowledge.

Chemists were now taking an enlarged view of the number and variety of chemical elements and their possible compounds. Not only oxides and sulphides, but phosphides, chlorides, iodides, fluorides and bromides had to be studied. Much had still to be learned regarding salts; the oxygen-acid theory had been overturned, but the hydrogen-acid theory was yet in its infancy. Although inorganic chemistry had been developed to a great extent, the vast field of organic chemistry and the carbon compounds was almost untouched; it was for a later group of chemists to open up that immense subject of research. But a firm base of operations had been secured, from which further advance was rendered easier and more certain.



## CHAPTER XXXII

THE CHEMISTRY OF THE EARLY NINETEENTH CENTURY

(From 1820 A.D. till 1850 A.D.)

### I. MICHAEL FARADAY TO CHRISTIAN FRIEDRICH SCHÖNBEIN

THE electro-chemical views which were put forward and developed by Davy, Berzelius, Gay-Lussac, and Thénard received their full development at the hands of Faraday, to whose work we owe our knowledge of the principal facts and laws of electrical science. Besides being an electrician *par excellence*, Faraday was a distinguished chemist, and published many purely chemical researches, but his chief influence on chemistry has arisen from his physical and electrical researches.

Michael Faraday (1791—1867) was born at Newington, in Surrey. He was the son of a Yorkshire blacksmith, who had migrated to London.

Faraday was apprenticed to a bookbinder, but early inclined to scientific pursuits. In 1812 one of his master's customers, who was aware of his scientific taste, took him to hear four lectures by Sir Humphry Davy at the Royal Institution. Of these lectures he wrote out full notes, and sent them to Sir Humphry, receiving a kind and favourable reply. Next year he became assistant to Sir Humphry in the



FIG. 97.—Michael Faraday.

laboratory of the Royal Institution, an establishment with which he was to be connected for fifty-four years. When Davy travelled on the Continent between 1813 and 1815 his assistant accompanied him. In 1825 Faraday was appointed Director of the Laboratory, and in 1833 Fullerial Professor of Chemistry, at the Royal Institution, and died at Hampton Court.

Naturally, at the outset of his career, his chemical work followed the old lines of Davy. He discovered two new chlorides of carbon in 1820; experimented on the diffusion and liquefaction of gases; studied the alloys of steel; examined the relations between vapours and gases, and in 1825 the isomeric and polymeric hydrocarbons; and in 1830 devised a new glass for optical purposes. In particular, he tried to popularise the general methods of chemistry, as distinguished from its results, and wrote an excellent book on chemical manipulation.

But Faraday's electrical researches soon overshadowed his chemical work. Beginning with the decomposition of magnesium sulphate (Epsom salts) by means of a voltaic pile composed of seven halfpence, seven small discs of zinc, and six pieces of paper, he proceeded from experiment to experiment, and from one discovery to another, until he had laid the foundations of the whole science of electricity as it is known at the present day, elucidated its principal laws, and discovered and explained electro-magnetism, induced currents, diamagnetism, and the effects of magnetism on polarised light.

The bulk of this work lies outside the scope of our history, the only portion of Faraday's electrical researches which bears on chemistry being his work in relation to electrolysis. He found in 1832 that no decomposition is possible without conduction, although there may be conduction without decomposition. Three years later he showed that decomposition is the result of the attractive force of the poles on the elements in the compound, and next year (1836) proved that the amount of decomposition depends on the quantity, not on the intensity,

of the electricity, and on the chemically equivalent weights of the constituents. From these observations he deduced what is called Faraday's Law (*Experimental Researches*, 505); "For a constant quantity of electricity, whatever the decomposing conductor may be, whether water, saline solutions, acids, fused bodies or the like, the amount of electro-chemical action is also a constant quantity." This law, which implies that the same quantity of electricity will produce the same amount of chemical effect, is the basis of all electro-chemical work. On this principle he invented the voltameter, in which the gas produced per minute is an absolute measure of the mean strength of the current during the time.

Dulong and Petit in 1819 found an inverse ratio between the combining weights and the specific heats of the chemical elements, and other relations subsisting between the physical and chemical properties of these bodies were traced. Faraday, on the other hand, discovered that substances might have the same empirical composition—that is to say, the same elements in the same proportions—and yet have different properties. This phenomenon is expressed by the term *Metamerism*. We are reminded of the discovery of Mitscherlich that substances may be composed of different elements, and yet have similar properties—a phenomenon called *Isomorphism*. These two phenomena modified the old ideas of atomic composition, and will be referred to later.

From the letters and recorded conversation of Faraday we learn that he always sought for whatever could awaken a healthy interest, and avoided anything that could arouse ill-feeling. In conducting discussions, he simply stated the facts from his point of view, without saying anything which might produce rancour. He was a modest and earnest student, willing to be corrected, and entirely free from self-assertion or false pride.

His principal works were: *Chemical Manipulation* (1827); *Experimental Researches in Electricity* (1844); *Experimental Researches in Chemistry and Physics* (1859); *Lectures on the*

*Chemical History of a Candle* (1861); and *On the Various Forces in Nature* (undated).

The attitude of Faraday towards his scientific studies may be gathered from the closing words of his *Experimental Researches in Chemistry and Physics*: "I have never seen anything incompatible between those things of man which can be known by the spirit of man which is within him, and those higher things concerning his future which he cannot know by that spirit."

It is as a student of crystals and crystallisation, particularly among minerals, that Ernst Eilhard Mitscherlich (1794—1863) was most distinguished. He was born at Neuend, in Oldenburg, where his father was pastor. He was educated at Jever and Heidelberg, where he studied Oriental languages and philosophy, being intended for a diplomatic career. He then went to Paris, but being disappointed in his expectations, returned to Göttingen and Berlin, where he studied chemistry, and various branches of natural science. His studies in crystallography secured for him the friendship of Berzelius, whom he accompanied to Stockholm. Returning in 1821 to Berlin, he was first appointed Extraordinary, and then Ordinary, Professor of Chemistry in the University. He died at Schönberg, near Berlin.

Apart from his work in relation to crystals, the researches of Mitscherlich may be briefly summed. In 1827 he discovered selenic acid, and found that its salts are isomorphous with sulphates; examined the combination of sodium and iodine; between 1830 and 1832 investigated the oxygen compounds of manganese, manganic and permanganic acid, and improved the apparatus used for mineral and organic analysis; between 1833 and 1835 studied the decomposition products of benzoic acid and benzoic aldehyde, thus adding a whole series of compounds to science; and, in 1834, the constitution and formation of ethers. His papers appeared in the *Abhandlungen* of Berlin Academy and other scientific periodicals, while his *Lehrbuch de Chemie* was published in 1829-30.

Mitscherlich's discovery of isomorphism and dimorphism, and the relationship between chemical constitution and crystalline form, as well as the bearing of isomorphism on the determination of atomic weights, was the most important work of his life. Such success did he attain in this work, that in 1823 he was able to produce inorganic bodies, such as minerals, by artificial processes.

Crystallography first assumed importance in 1801 when Haiiy published his system of classifying minerals, and indicated as a principle that a difference in crystalline form implies a difference in chemical composition. He assumed as the result of his researches that the same chemical elements, when combined in the same proportions, invariably exhibit the same crystalline form, which form is a property of the compound. But evident exceptions were soon made known. Leblanc had previously found cupric sulphate ( $\text{CuSO}_4$ ) and ferrous sulphate ( $\text{FeSO}_4$ ) crystallising together in the same form, while Vanquelin had observed the alums also crystallising together. In red silver ore, antimony and arsenic replace each other. Gay-Lussac in 1816 grew ammonia alum on a crystal of potash alum, and in 1819 Bendant observed the crystallisation in similar form of zinc, cupric, and ferrous sulphates.

Various attempts were made to solve this problem. Fuchs in 1815 guessed the truth, when he said of gehlenite that the oxide of iron is not an essential component of that mineral, but merely a vicarious constituent replacing so much lime. Berzelius attributed general properties to oxides which contain equal proportions of oxygen.

Mitscherlich in 1819 removed much of the obscurity which surrounded the subject. He demonstrated that compounds of several elements, if they have a similar constitution chemically, have the same crystalline form, as determined by the measurement of their angles. He instanced the phosphates and arseniates of sodium, potassium, and ammonium. These have the same water of crystallisation and the same crystalline



form, and when two of the salts are mixed in varying proportions they crystallise as one crystal.

As the result of these observations Mitscherlich concluded that analogous elements or groups can replace one another in compounds without alteration of crystalline form. Such analogous substances he termed *Isomorphous*. It has to be observed, however, that the angles of the crystals of isomorphs are not absolutely, but only nearly, identical.

There are other substances which crystallise in forms belonging to two distinct crystallographic systems, but which have nevertheless one constant chemical composition. For example, calcite and aragonite crystallise, the former in hexagonal and the latter in rhombic crystals, but both consist of calcium carbonate. Such substances he termed *Dimorphous*.

It occasionally happens that isomorphism subsists between the two forms severally of two dimorphous substances. Arsenious oxide ( $\text{As}_2\text{O}_3$ ) normally crystallises as regular octahedra, but sometimes in rhombic crystals like the ordinary form of antimonious oxide ( $\text{Sb}_2\text{O}_3$ ), and yet senarmonite, a form of the latter substance, crystallises in octahedra. Such substances are termed *Isodimorphous*.

Lastly, there are substances which crystallise in forms belonging to three distinct crystallographic systems, but which have one constant chemical composition. Thus, the mineral rutile crystallises in quadratic four- or eight-sided prisms, anatase in quadratic octahedrons, but with a different relation of axes, and brookite in flat rhombic prisms, yet all three are titanite oxide ( $\text{TiO}_2$ ). Such substances are termed *Trimorphous*.

These principles, the fruit of the research of Mitscherlich, have laid the foundations of the modern science of crystals. It is unnecessary to point out how greatly they have affected the study of mineralogy, where the crystalline form predominates, and serves as a definite factor in systems of classification. But they have also materially affected the science

of chemistry by defining more accurately the relation between chemical composition and crystalline form, and indicating relations between groups of substances which would never have been recognised apart from the study of their respective modes of crystallisation.

Two widely different discoveries distinguish Christian Friedrich Schönbein (1799—1868)—ozone and gun-cotton—the life-giving principle of the atmosphere and the death-dealing explosive. Schönbein was born at Metzingen, in Swabia, and at fourteen was apprenticed in the chemical works at Böblingen, where he stayed seven years. In his leisure hours he studied science, and while employed in Dingler's manufactory near Erlangen continued to prosecute his studies. In 1821 he entered the University of Tübingen, where he studied under Gmelin, and then returned to complete his education at Erlangen. Becoming a teacher of chemistry, he taught first at Kielbau, and then at Epsom, near London. After this he went to Paris, where he attended lectures by Gay-Lussac, Ampère, Thénard, and Depretz. In 1829 he was appointed Professor of Chemistry in the University of Basle, and died in that city. It is recorded of him that he was a clear lecturer and a good teacher.

About 1836 he was occupied with the study of Isomerism, especially the kind called Allotropy, and in 1839 discovered allotropic oxygen or ozone. He constructed a very large galvanic battery for the purpose of investigating the nature of this substance, and was led incidentally to study peroxide of hydrogen. He described three forms of oxygen—ordinary oxygen, ozone, and antozone. In the latter supposition he was wrong; but it was not until his labours had been followed up by Andrews, and the speculations of Odling had been confirmed by Soret, that the true nature of ozone was satisfactorily proved. It was then shown to be an allotropic form of oxygen, in which the molecules consist of three atoms.

Schönbein's other great discovery, gun-cotton, was made in 1846. This was one of the first and most important of that

large group of explosives termed "nitro-compounds," which are produced by the chemical action of nitric acid, either alone or combined with sulphuric acid, upon a carbonaceous substance. Its applications in the arts of peace and war are very numerous, and it is in some respects one of the least dangerous of the high explosives.

Schönbein was a voluminous writer, his papers on physico-chemical researches numbering 364. He is an excellent specimen of the practical German chemist—as a teacher lucid, painstaking, and thorough; as an investigator, patient, careful, and accurate.

## CHAPTER XXXIII

### THE CHEMISTRY OF THE EARLY NINETEENTH CENTURY

(From 1820 A.D. till 1850 A.D.)

#### 2. JEAN BAPTISTE ANDRÉ DUMAS

We propose to devote this chapter to the consideration of one of the greatest French chemists of the first half of the nineteenth century, Jean Baptiste André Dumas (1800—1884). He was a contemporary of the famous German chemists Mitscherlich, Liebig, and Wöhler, all of whom he survived.

Dumas was born on July 14th, 1800, at Alais, in the Department du Gard, and died on April 11th, 1884. He attended school at Alais, and in 1815 was apprenticed to a local pharmaceutical chemist, and thus, like Liebig, began his career as a practical pharmacist. In 1816 he went to Geneva as assistant to M. le Roger, in whose employment he had a laboratory at his disposal, and was able to attend the lectures of De Candolle on botany, of Pietet on physics, and of Gaspard de la Rive on chemistry. In the same year he delivered lectures to a society of pharmaceutical students.

At Geneva Dumas did his first piece of original research in the shape of experiments on the water of crystallisation of salts. He presented the results to De la Rive, who was greatly pleased with them, and informed him of the work previously done by Berzelius on the subject. At this period he made the acquaintance of Prevost, and the two became fast friends and fellow-workers, publishing conjointly many physiological researches, on the composition of blood, uric acid, and other subjects. The researches on blood were published when Dumas was only twenty years old. In 1823 Von Humboldt paid him a visit, while he was staying at Geneva, and to his

accounts of Paris, Dumas listened with keen interest. Paris was then the seat of learning. Laplace, Berthollet, Gay-Lussac, Thénard, Arago, and Cuvier were there. It was impossible for Dumas to resist the attraction, and so he went to Paris, where he studied under Gay-Lussac.

Dumas was in 1823 appointed Repetiteur de Chimie in Thénard's laboratory at the École Polytechnique, and subsequently succeeded Roliquet as Lecturer on Chemistry at the Athenæum. Along with two other young investigators, Andouin and Broignart, he founded the *Annales des Sciences Naturelles*. In 1826 he married the sister of his friend Broignart, and from this time devoted all his energies to chemical science, and made some important investigations. He encountered in Liebig a formidable rival to his views. The well-known struggle between these two ardent workers was long and often bitter, but resulted in a mutual appreciation of each other's labours, a mutual respect, and finally a true friendship.

In 1826 Dumas published a paper in the *Annales de Chimie et de Physique* on "Some Points in the Atomic Theory," in which he pointed out the important bearing to chemists of Avogadro's and Ampère's hypothesis (*vide* p. 418, *infra*). It is in this paper that he brought forward his first work on vapour densities. The results of numerous experiments are given: amongst others, the determination of the vapour densities of the chlorides of phosphorus, arsenic, bismuth, tin, and silicon, as well as of the fluorides of some of these elements. From these experiments he deduced the atomic weight of the several bodies, erring only in the cases of silicon and tin. The composition of silica he regarded as silicon oxide ( $\text{SiO}$ ), the combining weight of oxygen being taken as 8, while it was just at this time that Berzelius put forth his ideas on the constitution of the same body, regarding it as a trioxide, and building up on this supposition the constitution of the numerous silicates. It is now deemed to be silicon dioxide ( $\text{SiO}_2$ ).

The views of the younger chemist gained ground slowly



but surely. His influence was augmented by the publication in 1826 of his celebrated "*Traité de Chimie appliquée aux Arts*," in which he again maintained the importance of Avogadro's and Ampère's hypothesis, and pointed out with great clearness the necessity of distinguishing atoms and molecules.

Dumas now continued experimental work in conjunction with his assistant Boullay. Their investigation of the ethers of acetic, benzoic, oxalic, and nitrous acids, which they deemed to be combinations of ethylene with the hydrates of the acids, comparing them with ammonium compounds, was followed by the discovery in wood-spirit of a homologue of alcohol. Sugar they also regarded as a body of this class. In seeking to obtain by the action of phosgene gas on alcohol a substance which treated with water would yield carbon dioxide ( $\text{CO}_2$ ), and by means of which they could procure sugar *in statu nascendi* from alcohol and carbon dioxide, they were led to the discovery of the chlor-carbonic-acid ether of the urethanes.

Then followed Dumas's great work on the chlorine substitution products, from which, in the face of all existing ideas on the nature of the chemical elements, and of the determined and jealous opposition of Berzelius, and, for a time, of Liebig, he developed his grand and lasting theory of substitution. This theory had a great effect upon the progress of organic chemistry, particularly of metalepsy—the variation of a series of compounds embraced under a single type.

The idea of compound radicles, which had been stated by Berzelius and in the main supported by Liebig, was accepted by Dumas. In 1834 the latter found that chlorine has the power of uniting with hydrogen derived from organic bodies, and of replacing it atom for atom. Laurent and Gerhardt assisted in the elaboration of the new doctrine. Berzelius, however, had developed the dualistic doctrine that bodies are formed of two proximate elements, either simple bodies, or compounds of a low order, and he opposed the idea of the substitution of hydrogen by chlorine on the ground that, hydrogen and chlorine are of opposite electro-chemical

character, and therefore cannot perform the same function. Dumas expressed in 1837 the view that organic substances are to be considered as consisting of compound radicles, which play the part of simple bodies, while inorganic substances are formed of indecomposable bodies.

As the result of his investigation of substitution compounds, he further declared that the number and arrangement of the elements in a compound determine its properties, rather than the nature of the elements themselves. He thus by means of the doctrine which he had explained, accounted for the chlorine-substitution compounds discovered by Laurent and other French chemists, as well as the chlor-turpentine, chlor-acetic acids, etc., discovered by himself. Laurent had at first stated that in these bodies the chlorine replaces the hydrogen, a doctrine originally repudiated and then accepted by Dumas; but the latter in 1839 improved upon the nucleus theory of Laurent by his own theory of types, which he thus stated—“(1) the elements of a compound body can be replaced either by other elements, or by compound bodies capable of playing the part of simple bodies; and (2) when such a substitution takes place in equivalent proportions, the body which is formed retains its chemical type, and the element which has entered into the compound plays the same part as the element which has been withdrawn.”

Among Dumas's many researches which guided him to the formation of his substitution theory may be mentioned the preparation of tetrachlor-cinnamic aldehyde, of dichlorethylene (from ethylene), and of tetrachlor ether. The discovery by Liebig in 1832 of chloroform, through the action of chlorine on alcohol, gave substantial support to Dumas's theory, and he himself then prepared tetrachlor-methane (carbon tetrachloride). Following upon this he prepared from acetic acid the trichlor derivative, thus recognising clearly the analogous relation between ethyl aldehyde and acetic acid on the one hand, and chloral and trichloroacetic acid on the other.

A few years later Dumas was working on the fatty acids,

when he realised that these formed a homologous series, the adjacent members of which differed by one atom of carbon and two of hydrogen ( $\text{CH}_2$ ). To this succeeded a study of the sulphonic acids of indigo blue and indigo white, to which he gave the formulæ since adopted by all chemists; also of nitro-salicylic acid and picric acid, both of which he declared to be nitro-substitution products.

In organic analysis Dumas effected several improvements, and his volumetric method for the determination of nitrogen in organic bodies was a great step in advance, and to this day is the process most generally used.

Dumas found in many analyses of organic bodies based upon the accepted atomic weights that the carbon and hydrogen which were evolved weighed more than the original substance. He therefore undertook his classical revision of the atomic weight of carbon, assigning to it as the result of his experiments 12 instead of 12.24 as given by Berzelius. This was followed by the determination, in conjunction with Stas, of the exact composition of water, and, in conjunction with Boussingault, of the composition of air. The former remains a model of chemical investigation.

The direct cause of Dumas taking up the subject of atomic weight determinations was the advancement of Prout's hypothesis. With the object of testing this hypothesis, he re-determined the atomic weights of no less than thirty elements, involving, it is said, nearly two hundred separate experiments. In this way he determined the atomic weights of lithium, sodium, potassium, oxygen, sulphur, selenium, tellurium, magnesium, calcium, strontium, barium, carbon, silicon, iron, molybdenum, tungsten, aluminium, manganese, cobalt, nickel, antimony, and bismuth.

Although he found that Prout's theory did not always hold true, yet he was led by these studies to observe groups of three elements, of which the atomic weight of one is the mean atomic weight of the other two. These groups were thereafter known as "Dumas's Triads," and were the fore-

runners of Newland's octaves, which were almost equivalent to Mendeléeff's periodic classification in its first form. We shall have to return to these subjects when we are considering the history of chemical doctrines.

For many years Dumas had thrown his whole energy into purely chemical investigation, but in the latter part of his life we again find him pursuing inquiries in those fields in which in his youth he had achieved so much. Among his later researches in physiological chemistry is included work on the nature and similarity of the neutral nitrogenous substances found in the animal and vegetable body—albumen, casein, and legumin—on the milk of various animals, and on his old subject, the nature and composition of blood. He considered blood corpuscles as belonging to the group of proteids. He also investigated the formation of fat in the animal body, and came to the conclusion that fat, as such, was supplied to the animal by the vegetable world. In this opinion he was strongly opposed by his former rival Liebig, who on this occasion was right. On the subject of fermentation he again found himself in opposition to Liebig, but he clearly disproved by experiment the conclusions of the latter on the nature of fermentative changes.

Numerous subjects in general chemistry were studied by Dumas. He investigated the nature of isomerism, the determination of specific heat, the formulæ for the cacodyl compounds (which proved to be correct), the combinations of phosphorus and hydrogen, the chlorides of sulphur, the various forms of fulminating gold, the composition of different sorts of manufactured glass, and the preparation of calcium by the action of sodium on calcium iodide ( $\text{CaI}_2$ ). In addition to the researches already mentioned, he worked together with Pelletier on the composition of the alkaloids, on analyses of cerosin, naphthalene, mustard oils, orcein and orcin, on the abnormal vapour density of acetic acid, on the products of the dry distillation of resin, on the constitution of the more important organic acids (tartaric and citric), on compounds

of the camphor group, and on ethereal oils. His last scientific communication was published in 1878, on the occlusion of oxygen by metallic silver.

As an author Dumas had a clear and lucid style. His great work, "*Traité de Chimie appliquée aux Arts*"—the first of the twelve volumes of which appeared in 1828, the last twenty years later—is characterised by the systematic arrangement of its contents, and by the way in which theoretical considerations are brought to bear on technical processes.

In 1838 he published his "*Leçons sur la Philosophie Chimique*," a series of eleven lectures delivered two years previously at the College of France. An essay which he wrote in collaboration with Boussingault, entitled "*Essai de Statique Chimique des Êtres Organisés*," in which the reciprocal action of plant and animal life was demonstrated more clearly than ever before, was the result of long-continued investigations, and is justly celebrated.

Other work of this class may be briefly noted. Dumas along with others collected and published the complete works of Lavoisier. Many *Éloges historiques* fell to be delivered by him: amongst others, the *Éloges* on Pelouse, Saint Hilaire, the anatomist, De la Rive, the physicist (son of the Geneva chemist, under whose guidance Dumas first entered the field of science), his friend Boussingault, and Victor Regnault. In 1869 he gave the Faraday Lecture before the London Chemical Society, and in 1883 published a most interesting biography of Count Rumford in the *Journal des Savants*.

Dumas succeeded Guizot as a member of the Académie and was a member of numerous commissions of that body, including those on the alarming decrease of the silk trade in 1857, and on the ravages of the phylloxera of the vine in 1873. From 1840 till his death he was one of the joint editors of the *Annales de Chimie et de Physique*.

Like other great French chemists, he was diligent in the discharge of his political duties. From 1848 till the political crisis of 1870, his wide knowledge and untiring energy were



devoted to the service of his country. He became successively member of the Senate, vice-president of the Board of Education, and finally, in 1868, master of the Mint. In 1863 he received the Grand Cross of the Legion of Honour. While occupying his various posts, he was often connected with science in its more practical aspects, and under his direction the gas and water supplies of Paris were reformed and vastly improved.

After the crisis of 1870 we find him busy with science. But now he regarded it from its practical side more than he had previously done, and his communications to the Académie of a truly scientific nature were not numerous. Still, to the end, his interest in the study of science for its own sake, and his earnest encouragement to the younger workers in its cause, never flagged. When, at the age of almost eighty-four years, he passed peacefully away at Cannes, full of activity, and in the complete possession of all his faculties, his country mourned a statesman—chemistry, one of its greatest pillars during the century—and those who could pride themselves on his friendship, one of the best and kindest of men.

## CHAPTER XXXIV

### THE RISE OF ORGANIC CHEMISTRY

(From 1820 A.D. till 1850 A.D.)

#### I. BARON JUSTUS VON LIEBIG

WE now come to one of the greatest of the German chemists, Justus von Liebig (1803—1873). In some aspects he may be regarded as the greatest chemist of the nineteenth century, and he is generally recognised as the real founder of organic chemistry, or, as it is now termed, the chemistry of the carbon compounds. Before his time organic chemistry, as it is known to us, did not exist. It is true that Thénard, Gay-Lussac, Berzelius, Prout and others had in the early part of the century laid the foundations of organic analysis, but inorganic chemistry monopolised the attention and energy of the ablest men, and it was left for Liebig and his followers to place the organic division of the science upon a sound and logical basis.



FIG. 98.—Baron Justus von Liebig.

Liebig was born at Darmstadt. His father carried on a colour warehouse in connection with his business of drysalter, and frequently occupied himself in making the colours in which he dealt, so that the future chemist at an early age was introduced to some of the most beautiful and interesting processes of the science. Besides assisting at experiments in his father's

laboratory. Liebig read an enormous number of chemical works, having free access to the Court Library, through the kindness of the librarian Hess. In an interesting *Autobiographical Sketch* which Liebig left, he has recorded an opinion as to the effect of such unregulated reading.

“ I am quite sure,” he says, “ that this manner of reading was of no particular use so far as acquisition of exact knowledge is concerned, but it developed in me the faculty, which is peculiar to chemists more than to other natural philosophers, of *thinking in terms of phenomena*; it is not very easy to give a clear idea of phenomena to anyone who cannot recall in his imagination a mental picture of what he sees and hears, like the poet and artist, for example. Most closely akin is the peculiar power of the musician, who, while composing, thinks in tones which are as much connected by laws as the logically arranged conceptions in a conclusion, or series of conclusions. There is in the chemist a form of thought by which all ideas become visible to the mind as the strains of an imagined piece of music. This form of thought is developed in Faraday in the highest degree, whence it arises that to one who is not acquainted with this method of thinking, his scientific works seem barren and dry, and merely a series of researches strung together, while his oral discourse, when he teaches or explains, is intellectual, elegant, and of wonderful clearness.”

At the age of fifteen he was apprenticed to an apothecary at Appenheim. The engagement did not suit him. The dry practical details of pharmacy were not congenial to him, and he left the shop after ten months. While employed by the apothecary he continued his chemical experiments, and his reading of chemical treatises, in both of which exercises he considered quantity rather than quality, repeating the same experiment again and again, and perusing every book that came in his way.

In this fashion he became deeply read in chemical literature of the old school, and expert in research, although he confesses

that he was backward in respect of learning which had to be acquired by rote, such as languages, whether dead or living. In 1819 he went to the University of Bonn, and soon after to that of Erlangen, where he studied chemistry under Kastner, and took the degree of Ph.D. He gives an amusing account of the lectures of Kastner, particularly of his description of the relations of phenomena. The Professor would say, for instance: "The influence of the moon upon the rain is clear, for as soon as the moon is visible, the thunderstorm ceases," or "the influence of the sun's rays on water is shown by the rise of the water in the shafts of mines, some of which cannot be worked in the height of summer." Liebig remarks: "That we see the moon when the thunderstorm is dispelled, and that the water rises in the mine when the brooks which drive the pumps dry up in summer, was, of course, too blunt an explanation for a clever lecture."

In 1822 Ludwig I. of Hesse-Darmstadt sent him to Paris, where he made the acquaintance of Runge, Mitscherlich, and Rose, and attended the lectures of Gay-Lussac, Thénard, and Dulong. As regards these lectures, he makes a very shrewd comparison with the German system. He says that what impressed him most in the French lectures was their intrinsic truth, and the careful avoidance of all pretence in the explanations. This formed a most complete contrast to the German lectures, in which the whole scientific teaching had lost its solid construction, through the preponderance of the deductive method. He was the means of effecting a great change for the better in this respect.

A paper read by Liebig upon fulminating silver had the good fortune to attract the notice of Von Humboldt, who introduced him to Gay-Lussac, with whom he worked upon the fulminates and fulminic acid in his private laboratory. Liebig declares: "I can well say that the foundation of all my later work, and of my whole course, was laid in his laboratory at the Arsenal."

Von Humboldt did not restrict his exertions to this introduction. He got Liebig appointed Extraordinary Professor of

Chemistry at Giessen in 1824, at the age of twenty-one, and at the same time secured recognition of his Erlangen degree. Two years later he became Ordinary Professor.

Then succeeded many years of strenuous work. Professor and students worked together. He says himself: "We worked from break of day till nightfall. Dissipations and amusements were not to be had at Giessen. The only complaint, which was continually repeated, was that of the attendant (Aubel), who could not get the workers out of the laboratory in the evening, when he wanted to clean it." The fruits of this work are apparent in the history of organic chemistry.

He was created Baron von Liebig in 1845, and in 1852 accepted the offer of the Chemical Chair at the University of Munich, which he held till his death.

The following list contains the principal works of Liebig:—

1. Analysis of Organic Bodies, 1837.
2. Chemistry in its Relation to Agriculture and Physiology, 1840.
3. Animal Chemistry, 1842.
4. Handbook of Organic Chemistry with regard to Pharmacy, 1843.
5. Chemical Letters, 1844.
6. Chemical Researches, 1847.
7. Foundations of Agricultural Chemistry, 1855.
8. Theory and Practice of Husbandry, 1856.
9. Nature-science Letters on Modern Husbandry, 1859.

In addition to these he wrote 318 papers on chemical and scientific subjects, besides many in which he collaborated with others. He acted as editor of the *Annals of Pharmacy* from 1832 till 1840, and when it was changed to the *Annals of Chemistry and Pharmacy*, edited it jointly with Wöhler. He was also associated with two other periodical publications—*Handwörterbuch der reinen und angewandten Chemie* (1837) and *Jahresbericht der Chemie* (1847—1850).

The practical work of Liebig covers the whole range of the science. His influence on the history of chemistry may be classified under five heads—(1) The opening of Giessen Labora-



tory to students ; (2) improvements in apparatus and methods of investigation ; (3) the discovery of new facts ; (4) the development of theory ; and (5) the application of chemistry to physiology and agriculture.

1. *The Effect of the Opening of Giessen Chemical Laboratory.*—Up till this time no means of studying practical chemistry had been afforded at the universities. Even the laboratories provided for professors and their assistants were utterly inadequate. Liebig worked at first in rooms which we would consider barely fit for the domestic animals of a well-ordered farm. He induced the Darmstadt Government to build and equip a chemical laboratory, in which any student of the university might receive a thorough practical training. To this laboratory students resorted from all the States of Germany and from other parts of the world, in spite of the prohibitions of the ruling powers in some of the former. Ultimately, through the influence and example of Liebig, other universities vied with each other in providing similar facilities. His pupils were legion, and included such distinguished chemists as Hoffmann, Kopp, Regnault, Fresenius, Playfair, Gerhardt, Würtz, and Frankland, who spread his doctrines throughout the continent of Europe.

2. *Improvements in Apparatus and in the Methods of Chemical Investigation.*—Liebig's first great work in this respect was the introduction of an easy and accurate method of determining the empirical composition of organic substances. For this purpose he invented the apparatus which has since been known as Liebig's Combustion Furnace. To this he added his potash bulbs, and other convenient accessories. This apparatus is the first thing with which the student becomes acquainted when he begins the practical study of organic chemistry, and its introduction may be said to have constituted Liebig the founder of this division of the science. No one has made more use of the combustion furnace than he did himself.

Among other new forms of apparatus and modes of investigation due to the inventive genius of Liebig were his condenser ;

the mercuric nitrate method of estimating urea; a method of determining the equivalents of alkaloids by chloroplatinate; the separation of nickel from cobalt; a method of depositing a film of silver on smooth surfaces, as, for example, in silvering astronomical reflectors; analysis of air by an alkaline pyrogallate; and a test for hydrocyanic acid.

3. *The Discovery of New Facts.*—After the elaboration of his combustion furnace and other apparatus, between 1822 and 1830, he discovered and analysed hippuric acid (1829); investigated malic acid, quinic acid, roccellie acid, camphor, and camphoric acid (1830); lactic acid (1832); meconic acid and its products; asparagin and aspartic acid (1833); uric acid (1834); discovered, along with Pelouze, oenanthic acid; investigated mandelic and formic acids; between 1831 and 1835 discovered various derivatives of alcohol; sulphocyanogen (1834); and mellone, melam, sulphocyanides and other derivatives of cyanogen (1834—1841).

Besides Liebig's numerous additions to organic chemistry may be mentioned his analysis of mineral waters and of natural alkaloids; the discovery of aldehyde, chloral, and chloroform; the investigation of uric acid, along with Wöhler, with the resulting addition to science of fifteen new bodies; and the analysis of murexide.

4. *The Development of Theory.*—Liebig defined organic chemistry as the chemistry of compound radicles. The term "radicle" was first mentioned in 1787 by Guyton de Morveau; but the idea of radicles, as we now conceive them, arose in the time of Lavoisier, who applied the term to that part of a compound which united with oxygen. Berzelius adopted the idea, and said in 1817 that the difference between inorganic and organic compounds lies in the circumstance that in inorganic compounds all the oxidised substances have a *simple* radicle, while all organic substances have *compound* radicles. Gay-Lussac had already, in 1815, discovered cyanogen, and demonstrated that it is the radicle of the prussiates, while Ampère and Berzelius had worked out the constitution of the

ammonium salts on the theory that ammonium ( $\text{NH}_4$ ) is a radicle.

Starting with a knowledge of these views of his seniors, Liebig first worked on organic compounds containing the radicle cyanogen ( $\text{CN}$ ). Then, in 1832, working with Wöhler, he showed that benzoyl ( $\text{C}_7\text{H}_5\text{O}$ ) is the radicle of a series of bodies. This demonstration was followed by the long controversy on the constitution of alcohol and ether. Gay-Lussac had in 1815 suggested that these substances were compounds of olefiant gas. Dumas and Boullay in 1828 developed this suggestion, and termed olefiant gas ( $\text{C}_2\text{H}_4$ ) the radicle of all the ethers, as ammonium ( $\text{NH}_4$ ) is the radicle of all the ammonium compounds. Thus, sugar would be ( $\text{C}_2\text{H}_4\text{CO}_2\text{H}_2\text{O}$ ), and might be called the bicarbonate of this radicle, just as the principal ingredient of smelling salts is called the bicarbonate of ammonium ( $\text{NH}_3\text{CO}_2\text{H}_2\text{O}$ ). Berzelius, after opposing, accepted this etherin theory.

Liebig in 1833 argued that just as sal ammoniac is regarded as  $\text{NH}_4\text{Cl}$ , not  $\text{NH}_3\text{HCl}$ , so muriatic ether should be regarded as  $\text{C}_2\text{H}_5\text{Cl}$ , not  $\text{C}_2\text{H}_4\text{HCl}$ , because, he said, contrary to the opinion of Dumas, alcohol contains combined water, which ether does not. Thus, alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) contains oxidised hydrogen, as water is oxidised hydrogen, while, on the other hand, ether is ( $\text{C}_2\text{H}_5$ )<sub>2</sub>O. Regnault explained this constitution on the basis of the radicle aldehydene ( $\text{C}_2\text{H}_5$ ), and Liebig compared this with  $\text{NH}_2$ . In short, Liebig borrowed his radicle theory from Berzelius, but carried it out from a more practical point of view, further, and more consistently.

Laurent and Gerhardt maintained a radicle theory founded on the idea, conceived by the former, that there is a nucleus in all compounds round which other atoms cling. Chemists recoiled from the theory of radicles thus expounded. The result was a long controversy, in which Liebig took part, and many new substances were discovered in the course of researches undertaken to support the theory.

Liebig's radicle of the alcohol and ether group ( $\text{C}_2\text{H}_5$ ) was

accepted by all chemists after the researches of Williamson on etherification, which depended on the use of sulphovinic acid, a substance discovered by Liebig. His radicles are also made use of in the unitary notation of Laurent and Gerhardt, adopted by Odling and later writers, and now almost universally accepted.

Another branch of chemical theory which was enriched by the labours of Liebig was the question of the basicity of acids. He was struck very forcibly by Graham's researches on phosphoric acids and their varying polybasicity. In 1837 he joined Dumas in his views regarding the polybasicity of acids, and next year wrote on the constitution of organic acids. He declared that basicity does not depend on the oxygen, but on the number of replaceable hydrogen atoms. His own words are: "Acids are particular compounds of hydrogen, in which the latter can be replaced by metals." This was really following up Davy's opinion as to the function of hydrogen as the acid-maker.

He adopted in 1839 certain ideas as to fermentation which are not those now accepted. He tried to explain fermentation on chemical principles, in opposition to physiological theory, considering such ferments as amygdaline as the cause, and the fungoid growths as merely incidents.

5. *Application of Chemistry to Physiology and Agriculture.*—Before Liebig's time, apart from the speculations of Boerhaave, nothing was known of the manner in which plants are nourished. The green parts were known to decompose carbon dioxide ( $\text{CO}_2$ ) under the influence of light and to evolve oxygen, while carbon was retained in the form of vegetable tissues and products. Ashes of plants had indeed been analysed, but the real importance of their mineral constituents was not suspected. In 1840 Liebig showed that the plant owes its carbonic acid and water, ammonia, and nitric acid (its sources of nitrogen) to the atmosphere: while the soil supplies its potash, soda, lime, magnesia, iron, sulphuric acid, phosphoric acid, and silica. The atmosphere is inexhaustible,

but the soil contains only a limited amount of soluble salts, and when these are exhausted, it becomes barren. Liebig showed that the right proportion of mineral constituents must be restored to the soil, and in an easily soluble form, and since the air does not supply ammonia fast enough, some ammonia must be added, particularly for less leafy plants.

In like manner he demonstrated that animals require not only sufficient food, but the right proportions of different kinds of food, both organic and mineral. Food he classified as heat-forming and flesh-forming. In a secondary inquiry as to the classification of carbohydrates, he proved that these are converted into fat in the animal body. He satisfied himself that the only source of heat in the animal body is the oxidation of the tissues, and in support of this view he argued with great force.

We cannot conclude this summary of the fruits of an arduous life more fittingly than by repeating the words with which Baron von Liebig closes the little *Autobiographical Sketch*, from which we have already quoted. "Now, when the paths of research are beaten roads, it is a much easier matter; but all the wonderful discoveries which recent times have brought forth were then our own dreams, whose realisation we surely and without doubt anticipated."

NOTE BY THE EDITOR.—It ought to be mentioned that the quotations from the *Autobiographical Sketch* are taken from the translation of it made by Dr. Campbell Brown.



## CHAPTER XXXV

### THE RISE OF ORGANIC CHEMISTRY

(From 1820 A.D. till 1850 A.D.)

#### 2. FRIEDRICH WÖHLER AND JEAN SERVAIS STAS

LIEBIG'S great collaborateur, and one of the founders of organic chemistry, was Friedrich Wöhler (1800—1882). A very touching and generous reference to Wöhler is made by Liebig in his *Autobiographical Sketch*, in a passage which displays a side of his character that all his pupils knew well—his unselfishness and kindness of heart. “I had the great good fortune, from the commencement of my career at Giessen, to gain a friend of similar tastes and similar aims, with whom, after so many years, I am still knit in the bonds of warmest affection. While in me the predominating inclination was to seek out the points of resemblance in the behaviour of bodies or their compounds, he possessed an unparalleled faculty of perceiving their differences. A keenness of observation was combined in him with an artistic dexterity, and an ingeniousness in discovering new means and methods of research or analysis such as few men possess. The achievement of our joint work upon uric acid and oil of bitter almonds has frequently been praised; it was his work. I cannot sufficiently highly estimate the advantage which the association with Wöhler brought to me in the attainment of my own as well as our mutual aims, for by that association were united the peculiarities of two schools—the good that was in each became effective by co-operation. Without envy and without jealousy, hand in hand, we pursued our way; when the one needed help, the other was ready. Some idea of this relationship will be obtained if I mention that many of our smaller pieces

of work which bear our joint names were done by one alone ; they were charming little gifts which one presented to the other."

Wöhler was born at Eschersheim, near Frankfort-on-Maine. From the local gymnasium he went to the University of Marburg, in his twentieth year, to study medicine. He there improvised a laboratory in his rooms, in which he began his great work on the cyanogen group, preparing mercuric sulphocyanide, iodide of cyanogen, and other carbon-nitrogen compounds. Next year (1821), under the influence of Gmelin, he deserted medicine for chemistry, and went to the laboratory of that distinguished chemist at Heidelberg, although he pursued his medical studies so far as to take his degree in 1823. At Heidelberg he continued his researches on cyanic acid.

He then proceeded to Stockholm, where he worked in Berzelius's laboratory on cyanogen compounds. At the same time Liebig and Gay-Lussac were working at Paris on fulminic acid, and the two acids, cyanic and fulminic, were found to have the same ultimate composition. This discovery led to a lifelong intimacy and collaboration between Liebig and Wöhler, and caused Berzelius to coin the word Isomerism to describe the peculiar relation between the two substances. Wöhler just missed discovering vanadium, having isolated an unknown oxide, which was afterwards identified by Sefstrom in the same laboratory. With Berzelius, Wöhler chiefly worked on mineral analysis, and in the course of his research prepared oxychloride of tungsten and sodium tungstate or tungsten sodium-bronze ( $\text{Na}_2\text{W}_3\text{O}_9$ ).

Wöhler was appointed teacher in the Polytechnic School at Berlin about 1825, and remained there for seven years. While there he isolated aluminium by a method afterwards carried out by Deville on a manufacturing scale, and also glucinum and yttrium. But his most remarkable work at this time was the synthesis of urea in 1828. This was the first example of the synthesis of a truly organic compound. By this experiment, which depended on the molecular trans-

formation of ammonium cyanate, of purely inorganic origin, into urea, an eminently characteristic animal product, he broke down the idea that organic compounds are the result of a vital action, which is independent of ordinary chemical laws, and which often brings about changes in defiance of them. A new era began from this discovery—an era which has already been marked by the synthetical production of innumerable carbon compounds, resembling in character, and often identical with, those produced in the organs of plants and animals. Wöhler also worked on urine, and on the physiological secretion through it of matter from the body. In 1830 he published, in collaboration with Liebig, papers on mellitic and cyanic acids.

In 1831 Wöhler was called to Cassel, where he planned the new laboratories of the Gewerbe School. Next year Liebig and he published their great work on bitter almond oil, in which the radicle benzoyl was established, and they demonstrated the doctrine of radicles, which were capable of being transferred unchanged from one compound to another, in a manner analogous to inorganic elements.

Wöhler in 1836 succeeded Stronmeyer at the University of Göttingen, being succeeded at Cassel by Bunsen. Next year he isolated hydrocyanic acid (HCN) from amygdalin, and worked out the decomposition of amygdalin with water. In the products Liebig found sugar, thus constituting amygdalin the prototype of the class of glucosides.

In 1838 Liebig and Wöhler made their famous investigation of uric acid. This substance had been discovered by Scheele, and found by Prout to be the chief constituent of serpents' excrement.

They discovered fifteen new bodies derived from it. Liebig in his *Autobiographical Sketch* narrates the following incident of this period :—

“ During our joint research on uric acid, Wöhler one day sent me a crystalline body, which he had obtained by the action of peroxide of lead upon this acid. I immediately

thereupon wrote to him with great joy, and without having analysed the body, that it was allantoin. Seven years before I had had this body in my hands; since that time I had not seen it again."

It is a wonderful instance of what Liebig called "sight or eye memory," that his identification of allantoin was ultimately found to be correct.

In the latter portion of his life Wöhler principally worked on inorganic bodies. He discovered the gaseous hydride of silicon ( $\text{SiH}_4$ ), isolated glucinum, yttrium, and other metals, and investigated silicon, bismuth, chromium, cerium, uranium, and the platinum metals—titanium, tantalum, thorium, and tungsten. He died at Göttingen.

The chief works of Wöhler are: *The Foundations of Inorganic and Organic Chemistry* (1831 and 1832); and *Practical Exercises in Chemical Analysis* (1854). In addition, he wrote 270 papers enumerated in the catalogue of scientific papers of the Royal Society, besides 40 or 50 jointly with Liebig and others, and many more which were issued since the date of the catalogue.

Although the researches of the Belgian chemist Stas were only partially directed towards organic chemistry, it will be convenient to consider his work at this point, since it had an important influence on chemical philosophy.

Jean Servais Stas (1813—1891) was born at Louvain. In 1835, without having access to a properly equipped laboratory, he made an investigation, in conjunction with De Koninck, of phloridzin, which led to his securing a place in Dumas's laboratory at Paris. There he continued his work on phloridzin, and although he failed to establish correctly its formula, he demonstrated that upon treatment with acids it split up into phloretin and glucose. This research attracted the notice of Berzelius.

Dumas and Stas soon afterwards worked together upon the action of a mixture of potash and lime on various alcohols, ethers, and esters of the fatty series, producing salts of

formic, acetic, and valerianic acids from the corresponding alcohols, and establishing the identity with natural products of some of the bodies thus obtained.

In the same year they began together their determination of the atomic weight of carbon, a research which formed the starting point of the long train of work in this department, which is identified with the name of Stas.

On the completion of this work Stas left Paris, and in 1840 was appointed Professor of Chemistry at the *École Royale Militaire* at Brussels, a post which he held for many years, until an affection of the larynx compelled him to resign it. He then for a time held office in connection with the Mint, but soon retired into private life, and died at Brussels.



FIG. 99.—Jean Servais Stas.

Besides his work on the atomic weights, Stas communicated to the French Academy in 1842 the results of analyses of air made at Brussels, and published next year a report on the action of sulphuric acid on acetic acid.

In 1847 he published a paper in the *Annales de Chimie et de Physique* on acetal, and in 1850 sent to the Academy a note on substances discovered in the amniotic and allantoic fluids of various animals.

In connection with the case of Count Hippolyte de Bocarme, in which a murder was alleged to have been committed by means of nicotine poisoning, Stas devised a method for the detection of individual vegetable alkaloids. This process was modified by Friedrich Julius Otto (1809—1870), and is now known as the Stas-Otto Process, although it has had to be somewhat modified, since the discovery of the ptomaines. He also took part in many inquiries of a technical nature,



such as the potato disease, saponification of fats with acid or with lime, international weights and measures, the metals of the platinum group, and the construction of ordnance.

The great work of Stas was the determination of atomic weights, and as he was led to undertake this inquiry mainly by a predilection in favour of what is known as "Prout's Hypothesis," we must explain what that was. William Prout (1785—1850) was born at Horton, in Gloucestershire, and spent his life as a practising physician in London. He was an active worker in physiological chemistry, and among other things discovered in 1823 that the acid contents of the stomach contain hydrochloric acid. Having found by calculation that the atomic weights of many elements are exact multiples of that of hydrogen, he suggested that in that gas is realised the *prōtē hylē* of the Greeks, and that from it the other elements are formed by some process of condensation or grouping. That was Prout's Hypothesis, and it has been the inspiring cause of numerous calculations of atomic weights made to test its validity. It was, in fact, a rerudescence of the old alchemical doctrine of the Unity of Matter.

Starting with confidence in the exactitude of the principle suggested by Prout, Stas set himself to answer the following questions :—

1. Is the weight of an atom of a given element always absolutely constant ?
2. Are the atomic weights of all other elements integer multiples of the atomic weight of hydrogen ? or, in a more general form, assuming that the atomic weights of the various elements are severally fixed and immutable, are they represented by numbers which are commensurable ?
3. Assuming that Prout's hypothesis is true, are all elements built up of the same kind of matter in different states of complexity ?
4. Do experiments with bodies raised to a very high temperature justify the belief that not only admittedly compound bodies, but also the elements themselves, may thus be dissociated into simpler forms of matter ?

Never have experiments been conducted with greater care, caution, and exactitude than those of Stas. It is said that the greatest variation between his many individual determinations of the atomic weight of the same element was from  $\cdot 005$  to  $\cdot 01$ . He used simple and well-defined reactions, observing carefully the limits within which they approached completeness. To guard against "constant" errors, he determined the atomic weight of each element by several independent processes. The vessels which he used were composed of materials little acted upon by the substances examined or employed. All substances used were scrupulously purified, and, where possible, obtained from various sources; for example, potassium chloride (KCl) was prepared from the nitrate, chlorate, platino-chloride, and tartrate.

Some illustrations may be given of his care in purifying materials. He purified iodine either (1) by dissolving it to saturation in an aqueous solution of potassium iodide, precipitating it with an excess of water, rather less than was sufficient to throw down the full amount possible, washing, distilling with steam, and drying under a bell-glass beside calcium nitrate (the only salt which was found not to affect the purity of iodine); or (2) by acting with solution of ammonia on the iodine to be treated, thus forming nitrogen iodide, or diiodamine, as he considered it, decomposing the violently explosive body by heating with excess of water to  $60^{\circ}$  or  $65^{\circ}$  Centigrade, and distilling and drying as before. By this latter method he treated some 10 kilogrammes of iodine in lots of 500 grains at a time.

Out of several processes adopted for the preparation of pure silver, he preferred the precipitation of a dilute ammoniacal solution of argentic nitrate ( $\text{AgNO}_3$ ) by a solution of ammonia cuprous sulphite, exhaustion of the metal with ammonia, and careful washing. The metal was fused in a crucible of pure lime by the oxyhydrogen flame, and heated to its boiling point, till the sodium line could no longer be perceived in the spectrum of the vapour, or it was actually distilled in vessels of lime.

When required in the form of sheets, the metal was rolled between two plates of silver, so as to avoid taking up iron from the rollers.

Pure water he obtained by distilling three times, passing the steam for the first time through a red-hot copper tube containing oxidised copper turnings; or by distilling from potassium permanganate ( $\text{KMnO}_4$ ), then from a little acid sodium or potassium sulphate; and finally condensing in a long tube of platinum.

Many other precautions were taken to eliminate the possibility of error. All weighings were reduced to equivalent values *in vacuo*; apparatus was carefully calibrated; argentic chloride and substances affected by light were precipitated in a dark room; evaporations were conducted in closed vessels to keep out dust; and large quantities of material were used—for example, from 77 to 405 grains of silver were converted into nitrate.

As the result of all this careful research, Stas arrived at the following conclusions:—

1. He determined the exact atomic weights of oxygen, silver, nitrogen, sulphur, chlorine, bromine, iodine, potassium, sodium, lithium, lead, and carbon.
2. He proved, in the case of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) at least, that changes of temperature or pressure, within wide limits, have no perceptible influence on the proportions in which its constituents are combined, and hence atomic weights determined by different methods have constant values.
3. He satisfied himself that Prout's hypothesis does not hold.
4. He concluded from various experiments at high temperatures that no facts are known to justify a belief in the dissociability of atoms of chemical elements, in their interconvertibility, or in their production by aggregation from hydrogen, or any simpler form of matter. They must, in fact, be regarded as "*individualités à part*," and the unity of matter is unsupported by proof.

The long and arduous researches of Stas thus determined a number of important facts, and in consequence take their place

as part of the history of chemistry. On the whole, they supported the atomic theory of Dalton, proved the constant character of atomic weights, and for the time put an end to speculations as to hydrogen being the original constituent of the other elements, and as to the unity of matter.

## CHAPTER XXXVI

### THE CHEMISTRY OF THE LATER NINETEENTH CENTURY

(From 1830 A.D. till 1900 A.D.)

#### 1. ROBERT WILHELM BUNSEN AND VICTOR MEYER

THE interval which has elapsed since the latter part of the nineteenth century is too short to render historical the work of some of the chemists who laboured during the period. That work will ultimately take its place in the history of chemistry, but at present we stand too near to it, and we are unable to view it in its proper proportions. Other chemists of the time have rendered historical services, which will be discussed in the chapters on the Chemistry of the Carbon Compounds. From these various causes it happens that we need only consider in this and the subsequent chapter three chemists — Bunsen, Meyer, and Mendeléeff.



FIG. 100.—Robert Wilhelm Bunsen.

Robert Wilhelm Bunsen, Baron von Bunsen (1811—1899), was born at Göttingen, where his father was librarian and Professor of Modern Philology at the University. In 1828 he entered that university, and studied chemistry under Strommeyer, graduating in 1830 with a thesis on "Hygrometrical Solutions." The winter of 1832–3 he passed in Paris, where he met Regnault,



Pelouze, and other French chemists. After visiting Berlin and Vienna, he settled as a privatdocent in his native place, lecturing at the university for a half year after the death of Strommeyer. In 1836 he succeeded Wöhler as teacher of chemistry in the Polytechnic School at Cassel; in 1839 he was appointed Professor of Chemistry in Marburg; in 1851, at Breslau; and in 1852, at Heidelberg, in succession to Leopold Gmelin. He did fifty-six years' work as a teacher of chemistry, and in that capacity was almost unrivalled. Retiring in 1889, he died at Heidelberg ten years later.

Bunsen's earliest work was on the use of freshly precipitated hydrated ferric oxide ( $\text{Fe}(\text{OH})_3$ ) as an antidote in arsenical poisoning; on allophane procured from a lignite bed; and on a new series of double cyanides. His first great work was on the cacodyl compounds. In the course of his experiments he lost the sight of an eye, and nearly died of arsenical poisoning; but his research won for him much praise from Berzelius, particularly his study of Cadet's fuming liquid, which the Swedish chemist characterised as the foundation-stone of the theory of compound radicles. In fact, cacodyl was the first iso'ated radicle of its kind. Although Bunsen confirmed the suggestion of Berzelius that cacodyl or arsen-dimethyl is  $\text{As}_2\text{C}_4\text{H}_{12}$ , he made no attempt to define its constitution. Kolbe first suggested that it may be  $(\text{As}(\text{CH}_3)_2)_2$ , and experiments of Frankland and others have rendered this constitution probable; but Baeeyer proved it, and produced in 1853 arsenomonomethyl and a series of compounds. Cacodyl also gave Frankland his first example illustrating chemical valency.

At various periods between 1838 and 1845 Bunsen studied the gases given off by blast furnaces, visiting England in the course of his inquiry. Along with Lyon Playfair, he calculated the waste of heat at the ironworks of the latter country, and found it equal to 80 per cent. This investigation led to his book, "*Methods of Gas-Measuring*," which was translated into English by Roscoe in 1857.

In 1841 he invented the carbon-zinc electric cell, which bears

his name. With forty-four of these cells he produced electric light, and by electrolysis isolated a number of metals, including calcium, magnesium, strontium, lanthanum, cerium, and didymium. Hence he thought he might isolate organic radicles by the same process; but in this hope he was disappointed, although his pupil Kolbe, along with Frankland, and afterwards Mangman, accomplished this by the electrolysis of acetic and valeric acids. Of his electrolytic experiments the most important was the isolation for the first time in 1852 of magnesium in a metallic state.

In 1844 Bunsen produced his grease-spot photometer, which he contrived for the purpose of measuring the light of the electric arc produced by his battery, and from 1855 till 1863 worked with Roscoe on actinometry or photo-chemical measurements and investigations.

Bunsen conferred an immense benefit upon chemistry by the research which Kirchhoff and he conducted in 1859 in relation to spectrum analysis. Kirchhoff found out the cause of the Fraunhofer lines in the solar spectrum, and by means of the spectroscope Bunsen and he not only analysed the solar atmosphere, but detected metals in minute quantities of terrestrial substances—*e.g.*, lithium in 20 grammes of sea-water. By means of this system they discovered in 1859 caesium and rubidium (17 grammes of caesium chloride being obtained from forty tons of Durkheim mineral water), and others have found thallium (1861), indium (1863), gallium (1875), scandium (1879), and germanium (1886). It may be remarked that in Bunsen's *Memoir* the first of these metals is spelt "coesium."

About 1850 Bunsen was occupied in the study of geological problems, particularly mineral and volcanic phenomena, and in 1868 described his separation of the platinum metals, and his filter-pump. Other important inventions were the burner called after him (1859), the ice calorimeter (1870), and the vapour calorimeter (1887). The bunsen burner has been of the utmost value both to chemists and technical operators, and has assumed an infinite variety of forms. Flame reactions are rendered

possible by it, and it is a convenient substitute for the blow-pipe in chemical analysis. Incidentally, Bunsen heated erbia in the burner flame, and obtained the brilliant glow that is now utilised in the incandescent gas-mantle. The last of his works which we need mention is his series of analyses of mineral waters, which he undertook for the information of the public authorities, and his examination, in collaboration with Schischkoff, of the composition of gases and residues after the explosion of gunpowder, by which they laid a foundation for the theory of its combustion.



Fig. 101.—Victor Meyer.

Bunsen did not engage in controversies regarding theory, nor did he discuss theory in his lectures. He devoted himself with infinite pains and patience to the acquisition of accurate facts, and while others were engaged in theoretical controversies he was busy in accumulating experimental data, and in teaching how these can best be obtained, in order to settle all

pending questions. He used to say: "One fact properly proved is worth all the theories that can be invented."

Another earnest worker and theoretical writer was Victor Meyer (1848—1897). He was born at Berlin, and studied at Heidelberg under Bunsen, Kopp, Kirchhoff, and Helmholtz. In 1868 he entered the laboratory of Baeyer at Berlin, where he made original researches as to the chemical composition of camphor. He then became a teacher at the Stuttgart Polytechnic, and next year went to Zürich, where in 1882 he was appointed Professor of Chemistry. Between 1871 and 1884 he devised his method for determining vapour densities, and investigated the dissociation of the halogens. In 1882 he made a study of the benzene derivatives, and discovered

thiophene. He was called to the University of Göttingen on the death of Wöhler in 1885, whence he was transferred to succeed his old master Bunsen at Heidelberg, where he died. Stereochemical questions occupied him between 1885 and 1889, and in 1891 he was awarded the Davy medal of the Royal Society of England.

Meyer published along with Jacobson a "*Text-book of Organic Chemistry*," which was not finished; also, either alone or in conjunction with his pupils, upwards of 300 memoirs and papers, some of the more important of which may be noted. His first paper, in 1869, was on the action of trimethylamine on monochlorhydrin, and was followed by others on the preparation of diethylthiodicarbonate,  $S(\text{COOC}_2\text{H}_5)_2$ , from ethylchloroformate,  $\text{ClCOOC}_2\text{H}_5$ , and sodium sulphide,  $\text{Na}_2\text{S}$ , and on the constitution of the disubstituted benzenes. The following is a summary of his other researches:—

1. New method of introducing  $\text{COOH}$  by the action of  $\text{HCOONa}$  on the potassium salt of an aromatic sulpho-acid.
2. The orientation of the phthalic acids, from naphthalin.
3. Sulphanilic acid.
4. Camphor and camphoric acid (now of merely historic interest).
5. Di- and tri-bromobenzene, in work on which he gained further evidence in support of his view that in the case of the chlorine, bromine, iodine, and nitroxyl ( $\text{NO}_2$ ) derivatives of aromatic amines, obtained by the direct substitution of an element, it is always the hydrogen contiguous to the  $\text{NH}_2$  group that is replaced.
6. The chemical nature of chloral hydrate.
7. The nitro-compounds of the fatty series, the characteristics of primary, secondary, and tertiary compounds, and the discovery of the nitrolic acids.
8. Action of nitrous acid on hydroxylamine.
9. Discovery of the oximes.
10. The constitution of the ammonium salts.
11. Method of determining vapour densities.
12. Dissociation of the halogens, supposed decomposition of chlorine, and pyrochemical problems.

13. Discovery of thiophene.
14. Benzil and its derivatives, aldoximes, etc. (stereo-chemical work).
15. Investigation of the conditions determining the combustion of gaseous mixtures.
16. Decomposition of hydriodic acid (HI) by heat.
17. Determination of the fusing-points of salts melting at relatively high temperatures.
18. Discovery of iodoso, iodo, and iodonium compounds.
19. A study of the conditions determining the formation and hydrolysis of the ethereal salts of aromatic acids.

Meyer and Bodenstein made an elaborate examination of the phenomena of chemical equilibrium at different pressures and temperatures. It is a matter of general knowledge that the term "equilibrium" in its literal signification is applied to the condition of a pair of scales, when the weight in each pan is exactly the same. It is employed in physics, when forces neutralise one another, so that no motion occurs. In chemistry, forces as a rule do not exhibit their action by motion, and consequently two substances in a chemical reaction are said to be in equilibrium, when no variation of their properties occurs.

The two chemists sealed up in glass bulbs, under various pressures, mixtures of hydrogen and iodine, and also hydriodic acid. These bulbs were constructed of a special glass called borosilicate, containing no free alkali to absorb the hydriodic acid, and they were capillary, so that only minute portions of the gases were under the influence of heat when the bulbs were sealed. As each bulb was filled with the required quantities of mixed hydrogen and iodine, or of hydriodic acid, under the various pressures, the end was fused and sealed off. The bulbs were then heated to various temperatures (200° to 500° Centigrade) in baths kept during any one experiment at a constant temperature by means of a thermostat.

It usually took a day or two to establish equilibrium. The bulbs were then taken out of the bath in which they had been heated, and the end of each was broken over potassium



hydroxide. The hydriodic acid and iodine were thus absorbed and hydrogen was left. The amount could be determined by weighing. The composition of the original gas being known, the chemical action could be readily calculated.

To determine the equilibrium at any one point, two bulbs were filled, one with equal molecules of hydrogen and iodine, and one with hydriodic acid. After heating for a few days, the contents of both bulbs were found to be identical, and hence equilibrium was attained. The points of equilibrium (the percentage of hydriodic acid formed) were plotted for various temperatures, and so a curve of equilibrium was attained. For the reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$  we have the following equation :—

$$\frac{C^2/\text{HI}}{C/\text{H} C/\text{I}} = K.$$

In this equation  $C/\text{HI}$  represents the *Concentration of hydriodic acid*;  $C/\text{H}$ , the *Concentration of hydrogen*;  $C/\text{I}$ , the *Concentration of iodine*; and  $K$ , the *Equilibrium-constant*.  $K$  is the constant for any one temperature and pressure.

Now, if the pressure is altered from  $x$  to  $y$ .m.n., then the concentration of hydriodic acid is equal to  $C/\text{HI} \times y/x$ ; that of hydrogen to  $C/\text{H} \times y/x$ ; that of iodine to  $C/\text{I} \times y/x$ ; while the equilibrium-constant is represented by  $K_1$ . Therefore, for equilibrium we have the equation :—

$$\frac{(C/\text{HI} \times y/x)^2}{(C/\text{H} \times y/x)(C/\text{I} \times y/x)} = K_1,$$

which gives  $\frac{C^2/\text{HI}}{C/\text{H} C/\text{I}} = K_1$ ; but  $\frac{C^2/\text{HI}}{C/\text{H} C/\text{I}}$  was  $= K$ ; and consequently  $K = K_1$ . Hence, we infer that the position of equilibrium is *unaltered by pressure*; yet although this is proved by these equations, it is not borne out by experiment. The case of hydriodic acid may be generalised and from the generalisation the rule enunciated that if definite states are not altered by given processes, a change in these states has, conversely, no influence on the process.

We have now arrived at a stage in the history of the science when chemists became more particularly engaged in the attempt to solve problems of chemical philosophy. Henceforward we shall be more directly concerned with theoretical questions, and we are reminded of the chemical history of early times. The affinities and reactions of the elements and their compounds had by the middle of the nineteenth century been found to be so complicated, and the number and variety of these elements and compounds had become so great, that it was necessary to formulate theories to explain the one, and systems of classification to arrange the other. But the modern chemist differs from his ancient brother in this respect, among others, that he rests his doctrines upon the results of experiment; he does not either ignore experiment, or use it merely to illustrate his preconceived opinions. And so, although he may be mistaken in his theories, the facts which he has ascertained by practical laboratory work remain as permanent additions to knowledge.

## CHAPTER XXXVII

### THE CHEMISTRY OF THE LATER NINETEENTH CENTURY

(From 1830 A.D. till 1900 A.D.)

#### 2. DMITRI IVANOVICH MENDELÉEFF

THE subject of this chapter, Dmitri Ivanovich Mendeléeff (1834—1907), was born at Tobolsk, in Siberia, the youngest of a family of seventeen. He was educated at the local gymnasium and at the University of St. Petersburg, where he graduated in chemistry in 1856. For a time he acted as a privatdozent in various Russian cities, until in 1860 he removed to Heidelberg, where he set up a private laboratory. Three years later he was appointed Professor of Chemistry at the Technological Institute of St. Petersburg, and in 1866 succeeded to the Chair of Chemistry in the university. He resigned this post in 1890, and three years afterwards became Director of the Bureau of Weights and Measures, an office which he held until his death.

He was well known to English chemists. In 1882 he was awarded the Davy medal of the Royal Society of England for his researches on the periodic classification of the chemical elements, and ten years later was elected one of the Society's foreign members. He was the Faraday Lecturer of the Chemical Society of London in 1889, when he delivered an important address on his Periodic Law, while in 1905 he received in person the crowning honour at the disposal of the Royal Society, in the shape of the Copley medal. On his death the Tsar sent a personal message of condolence to his widow, in which he said "Russia has lost one of her best sons."

Mendeléeff was a great chemist, but the outstanding event of his life was his enunciation of the Periodic Law. The relations of the atomic weights of the elements had been observed and

commented upon by others, but he was the first to state these observed facts, not merely as a convenient basis for a classification of the elements, but as a fundamental law of Nature, which could be utilised for the prediction of new facts and the correction of old errors. The more one studies the facts of chemical science in the light of this law, the more fully does one become convinced that a great truth underlies it, which we may one day be able to understand, and which will account for the law. Nothing equal to it in importance has been added to chemical philosophy since Dalton's Atomic Theory and Dumas's Law of Substitution.

It was after Mendeléeff was appointed to the Chair of Chemistry at St. Petersburg, and while he was engaged in writing his *Principles of Chemistry* (1869-70), that the periodic generalisation occurred to him, and in March, 1869, he submitted his ideas on the subject to the Russian Chemical Society. Before we discuss those ideas, a few words of preliminary explanation are necessary.

Aristotle, as we formerly saw, recognised four elements or fundamental properties :—

1. Fire, the property of dryness and heat.
2. Air (or steam), the property of wetness and heat, or of gaseousness.
3. Water, the property of wetness and cold.
4. Earth, the property of dryness and cold, or of solidity.

A very simple and natural classification sufficed for the arrangement of the Aristotelian elements. After the fall of alchemy, in the hands of the iatrochemists, phlogistonists, and anti-phlogistonists, the number of simple substances and compounds rapidly increased, and it became essential that a scheme for their classification should be devised. Many were invented, of which the best was that of Lavoisier (*supra*, p. 310).

The first great division of the chemical elements which had any pretence to be natural, divided them into metallic and non-metallic substances. This classification rested upon the obvious difference in appearance and in general physical

characters which subsisted between the two classes. When, therefore, it became difficult to determine the composition of an element, such as arsenic or tellurium, whose physical characters were not decided, it was necessary to make the criterion the possession of chemical properties resembling those of either decidedly metallic or decidedly non-metallic substances. As the cause of these properties was unknown, the system rested upon an unstable basis.

The electro-chemical character has also been used as a means of classification, metals being electro-positive, and non-metals electro-negative, when their compounds are submitted to electrolysis; but this method is open to the same objection as that founded upon chemical properties.

The metallic and non-metallic elements were for a number of years classified according to their respective atomicity, or, better, their quantivalence—that is to say, according to the number of atoms of hydrogen, or its equivalent, which each atom of the element can replace, or with which it can combine.

Curious relations, triads, and octaves were discovered to exist among the atomic weights of substances possessing similar physical characters and chemical properties. Chlorine, iodine, and bromine formed such a triad. Adding the atomic weights of chlorine and iodine, 35 and 125, the sum is 160. The mean or half, therefore, is 80, which is the atomic weight of bromine. These three substances are strictly analogous in their modes of combination, their salts are isomorphous, and with the increase in their atomic weight there is a uniform modification of their properties—chlorine is a green gas, bromine a very volatile red liquid, and iodine a slate-coloured solid, volatilised only by heat. Chlorine is the most active chemically, and can expel the others, bromine is next, and iodine is least active. Chloride of silver is easily soluble in ammonia, the bromide soluble with difficulty, and the iodide quite insoluble.

Similar triads appear in the case of other groups. Sodium (23) is the mean of lithium (7) and potassium (39); while



strontium (88) is the mean of calcium (40) and barium (136). J. A. R. Newlands in 1864, writing of the relations between atomic weights, said: "The eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note of an octave in music." For example—

An octave starting with hydrogen ends with oxygen.

An octave starting with fluorine ends with sulphur.

Other chemists have made attempts to formulate a scheme which would explain these facts upon a scientific basis, but their efforts were not convincing, and the marked relations subsisting between the atomic weights and chemical properties of the elements were regarded rather as of the nature of coincidences.

The genius of Mendeléeff placed the whole matter on a new footing by the statement of the following generalisation, which is termed the *Periodic Law*:—"The properties of simple bodies, the constitution of their compounds, as well as the properties of these compounds, are periodic functions of the atomic weights."

The fundamental facts, on which this law rests, are arithmetical, and can be appreciated by anyone whose attention is drawn to them. Hydrogen is placed in a line apart by itself, because its atomic weight is taken as unity, and its relations to other elements are exceptional. The remaining elements, with their atomic weights (freed of decimals), are arranged in lines of seven across the page from left to right, thus:—

Series 1.—Hydrogen.				
Series 2.—Lithium.	Glucinum.	Boron.	Carbon.	Nitrogen.
7	9	11	12	14
Oxygen.	Fluorine.			
16	19			
Series 3.—Sodium.	Magnesium.	Aluminium.	Silicon.	
23	24	27	28	
Phosphorus.	Sulphur.	Chlorine.		
31	32	35		

and so on. The whole elements, as known at the time of Mendeléeff, fall into twelve horizontal lines or series.

If we read the names and figures vertically, we find that these form seven columns or groups, to which it is now the practice to add a *zero column* or *group* to contain the inert gases helium, neon, argon, krypton, xenon, and the emanation niton, and an *eighth column* or *group* to contain three clusters of elements which stand in a peculiar relation to each other. Although the chemical properties of the elements do not invariably coincide with those appropriate to the group in which they are placed, a circumstance which may be partly due to errors in calculation, we find that, on the whole, related elements present a remarkable uniformity in physical characters and chemical properties, and in their mode of combining with oxygen and hydrogen. These facts will be more apparent if we arrange the elements in tabular form as they follow one another vertically from top to bottom of the columns:—

*1st Group.*—Elements which combine with oxygen in the proportion of two atoms of the element to one of oxygen ( $R_2O$ ), but which do not combine with hydrogen:

Lithium, sodium, potassium, copper, rubidium, silver, caesium, and gold.

*2nd Group.*—Elements which combine with oxygen in the proportion of one atom of each, or two atoms of each ( $RO$  or  $R_2O_2$ ), but which do not combine with hydrogen:

Glucinum, magnesium, calcium, zinc, strontium, cadmium, barium, mercury, and radium.

*3rd Group.*—Elements which combine with oxygen in the proportion of two atoms of the element to three of oxygen ( $R_2O_3$ ), but which do not combine with hydrogen:

Boron, aluminium, scandium, gallium, yttrium, indium, lanthanum, and thallium.

*4th Group.*—Elements which combine with oxygen in the proportion of one atom of the element to two of oxygen, or two to four ( $RO_2$  or  $R_2O_4$ ), and with hydrogen in the proportion of one atom of the element to four of hydrogen ( $RH_4$ ):

Carbon, silicon, titanium, germanium, zirconium, tin, cerium, lead, and thorium.

*5th Group.*—Elements which combine with oxygen in the proportion of two atoms of the element to five of oxygen

( $R_2O_5$ ), and with hydrogen in the proportion of one atom of the element to three of hydrogen ( $RH_3$ ):

Nitrogen, phosphorus, vanadium, arsenic, columbium, antimony, tantalum, and bismuth.

*6th Group.*—Elements which combine with oxygen in the proportion of one atom of the element to three of oxygen, or two to six ( $RO_3$  or  $R_2O_6$ ), and with hydrogen in the proportion of one atom of the element to two of hydrogen ( $RH_2$ ):

Oxygen, sulphur, chromium, selenium, molybdenum, tellurium, tungsten, and uranium.

*7th Group.*—Elements which combine with oxygen in the proportion of two atoms of the element to seven of oxygen ( $R_2O_7$ ), and with hydrogen in the proportion of one atom of the element to one of hydrogen ( $RH$ ):

Fluorine, chlorine, manganese, bromine, and iodine.

*8th, or extra Group.*—Iron, cobalt, and nickel; ruthenium, rhodium, and palladium; osmium, iridium, and platinum.

As the result of a careful study of the facts concerning these relations of the atomic weights of the chemical elements, Mendeléeff in his Faraday Lecture (*Journal of the Chemical Society*, 1889, 55,635) thus summarised the conclusions at which he had arrived:—

1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.
2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (*e.g.*, platinum, iridium, osmium), or which increase regularly (*e.g.*, potassium, rubidium, caesium).
3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights corresponds to their so-called *valencies*, as well as, to some extent, to their distinctive chemical properties, as is apparent, among other series, in that of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.
4. The elements which are the most widely diffused have small atomic weights.
5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.

6. We must expect the discovery of many yet unknown elements, for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.
7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.
8. Certain characteristic properties of the elements can be foretold from their atomic weights.

It is indeed apparent that there is not only a remarkable arithmetical sequence in the atomic weights of the elements, but also an equally remarkable relationship subsisting between their properties. If we take the elements forming the first group, we observe a regular increase in their atomic weights.

	At. Weight.	Increase.
Lithium . . . . .	7	—
Sodium . . . . .	23	= 7 + 16
Potassium. . . . .	39	= 23 + 16
Copper . . . . .	64	= 39 + 25
Rubidium. . . . .	85	= 64 + 21
Silver . . . . .	108	= 85 + 23
Caesium . . . . .	133	= 108 + 25
Gold . . . . .	197	= 133 + 22 + 21 + 21

We see at once that the atomic weights of lithium, sodium, and potassium exceed each other by 16; those of copper, rubidium, silver, caesium, and gold by amounts varying from 21 to 25. Three periods of 21 or 22 separate gold from caesium, but this is probably due to the fact that we do not yet know the elements which possess the atomic weights required to fill the gaps.

It has been ascertained that almost all the properties of the elements are closely connected with the atomic weights, as periodic functions of them. Melting-points and other physical properties, valency, and solubility of salts correspond with considerable regularity. Every chemist knows that the elements of the first group, for example, lithium, sodium, potassium, rubidium, and caesium, form one family, and copper,

silver, and gold form another, which possess many characters and properties in common. The same fact will be observed in the other groups.

Looking first at physical properties, we shall compare the *specific gravities* of the third and sixth horizontal series :—

	At. Wt.	Sp. Gr.		At. Wt.	Sp. Gr.
Sodium	. 23	.98	Silver.	. 108	10.6
Magnesium	. 24	1.7	Cadmium	. 112	8.6
Aluminium	. 27	2.7	Indium	. 115	7.4
Silicon	. 28	2.4	Tin	. 119	7.3
Phosphorus	. 31	1.8	Antimony	. 120	6.7
Sulphur.	. 32	2.0	Tellurium	. 127	6.2
Chlorine	. 35	1.3	Iodine	. 127	5.0

The specific gravity rises with the atomic weight. But the connection of gravity with atomic weight is most conspicuous when we compare the *ratio between atomic weights and densities*, instead of the densities themselves; that is to say, if we compare the *atomic volume*, the volume occupied by the atomic weight, instead of the weight of the unit volume. This atomic volume cannot be measured absolutely, but only relatively, by taking the volume of the quantities of the different elements which are proportional to the atomic weights. For example, taking the density of water as a unit, and the space occupied by the unit weight as the unit of volume, then—

$$\text{Atomic volume} = \frac{\text{Atomic weight}}{\text{Specific gravity}}$$

Lithium has atomic weight 7 and sp. gr. .59; then, 7 divided by .59 gives 11.9 as the atomic volume of that element.

On considering the atomic volumes of the elements we discover certain definite relations. We see—

(1) That similar elements have frequently atomic volumes almost identical, as—

	At. Vol.
Chlorine, bromine and iodine	. 26 approximately.
Manganese, iron, chromium, and nickel	7 "
Ruthenium, rhodium, palladium, osmium, iridium, and platinum	. 9 "
Gold and silver	. 10 "



(2) That in the phosphorus and sulphur families of elements the atomic volume increases with the atomic weight, as—

	At. Wt.	At. Vol.		At. Wt.	At. Vol.
Phosphorus .	31	13·5	Sulphur .	32	15·7
Arsenic .	75	13·4	Selenium .	79	17·1
Antimony .	120	17·9	Tellurium .	127	20·2
Bismuth .	208	21·1			

When we look at the relation between atomic volume and atomic weight from a common standpoint, the former seems to be a function of the latter, for there is a periodicity in the changes which the atomic volume undergoes with increasing atomic weight. The atomic volume periodically increases and decreases in sympathy with the atomic weight. The maxima occur with the alkali metals, and the minima occur with those elements whose atomic weights lie midway between two alkali metals. These relations are more readily appreciated in a curve regularly plotted than in a table laid down on a flat surface. In such a curve similar elements occupy corresponding positions. The maxima are occupied by light metals, and the minima by heavy metals. Perhaps the most remarkable coincidence is that elements with similar atomic volumes have different properties, according as they are in an ascending or in a descending curve; that is, according as the element has a larger or a smaller atomic volume than the element having the next higher atomic weight. As an illustration, the properties of the following elements with nearly similar atomic volumes may be compared:—

Phosphorus	13·5	with	Magnesium	13·8.
Chlorine	25·6	with	Calcium	25·4.
Nickel	6·7	with	Iridium	8·6.
Molybdenum	11·1	with	Cadmium	12·9.

It is also noteworthy that only metals at the maxima and minima, or next to these positions, have malleability, and that similar relations exist between the fusibility and volatility of metals and their atomic weights and atomic volumes.

The utility of the Periodic Law is not limited to purposes

of classification. It indicates the existence of elements in unoccupied positions between certain of the known elements, having intermediate atomic weights, and properties which differ to a certain extent from those of the known elements. Guided by this law, Mendeléeff was able to foretell the existence of several elements required to fill gaps in the scheme. He prophesied in 1871 (1) that a metal must exist, intermediate in properties between aluminium and thallium, between cadmium and tin, and between zinc and lead, which forms an oxide of the form  $R_2O_3$ , which is a more distinct base than alumina ( $Al_2O_3$ ), and which has an atomic weight not far from 115; (2) a metal, to which he assigned the name *Ek-aluminium*, occupying the place immediately below aluminium, having atomic weight about 68, bearing the same relation to that metal that zinc does to magnesium, forming an oxide,  $R_2O_3$ , being a stronger base than alumina, forming a salt resembling alum, and having a specific gravity about 6; and (3) an element to which he assigned the name *Eka-boron*, next to boron, with atomic weight about 44, which should have only one stable oxide,  $R_2O_3$ , should be a stronger base than alumina but weaker than magnesia, a weaker base than yttria, but greatly resembling it and difficult to separate from it, the oxide of which should be insoluble in alkalis, and the salts colourless and giving gelatinous precipitates with potash, sodium carbonate, and sodium hyposulphite. The subsequent discoveries of the atomic weight of indium (115); of the metal gallium in 1875 with atomic weight 69 and specific gravity 5.9, and of the metal scandium in 1879 with atomic weight 45, fulfilled these predictions, the characters of the new metals agreeing closely with those foretold by Mendeléeff. Another gap was filled by the discovery in 1886 of germanium, with atomic weight 72.5, Mendeléeff having predicted an atomic weight of about 72, for an element to which he assigned the name *Eka-silicon*.

The Periodic Law further suggests the correction of some of the atomic weights already determined, and aids in the determination of the atomic weights of elements hitherto undeter-

mined. The atomic weight of glucinum had been determined at 14.1, but that weight belonged to nitrogen, an element having very different properties. The properties of glucinum are more like those of magnesium than aluminium, and Mendeléeff suggested that its atomic weight must be 9.4. Accordingly, the whole subject was investigated by different experimenters, and it has been found that the atomic weight of glucinum is really 9.4. In like manner the atomic weights and properties of cerium, lanthanum, didymium, yttrium, and others have been investigated and corrected in consequence of the Periodic Law having indicated that the old atomic weights must be wrong.

The Periodic Law stimulates us to enlarge our knowledge of the forms and properties of chemical compounds by indicating a great variety of hitherto unsuspected resemblances between elements occupying neighbouring positions on the spiral table, or double spiral arrangement, with which the name of Sir William Crookes is associated. It must be admitted that the differences between the consecutive members of the several series are not exactly uniform, or, in other words, the atomic weights of very many of the elements are not exactly what we should expect them to be. We might explain away these discrepancies by supposing that the atomic weights have not been quite correctly determined; but without taking refuge in any such special pleading, it is enough to accept such variations as facts, and to hold with Mendeléeff that if there is a slight irregularity in the increments of the atomic weights, the reciprocal relations between the properties of the elements ought to be modified in a correspondingly slight degree.

In 1902 Mendeléeff was led to attempt to form a chemical conception of the aether. He suggested the hypothesis that there are two elements of a smaller atomic weight than hydrogen, which form the first two members of the zero group, and that the lighter of these is a chemically inert, exceedingly mobile, all-pervading and all-penetrating gas, which constitutes the aether.

He also addressed himself to the study of solutions. These he regarded as homogeneous liquid systems of unstable dissociating compounds of the solvent with the substance dissolved. He admitted that this was only one of several possible hypotheses. The laws of the expansion of gases engaged his attention, and he partly forestalled the "critical temperature" of Andrews by his conception of the "absolute boiling point," which he defined as that temperature at which a liquid cannot exist as a liquid, but forms a gas that cannot pass into the liquid state under any pressure whatever, and at which the cohesion and the latent heat of evaporation are both nothing.

In addition to his *Principles of Chemistry*, Mendeléeff wrote a book on *Naphtha Production in America and the Caucasus* (1877). For the purpose of ascertaining the facts, he made a journey to Pennsylvania. He also examined the nitro-compounds with the object of preparing a smokeless powder for the Russian Government. But it is as a distinguished student of chemical philosophy, with a marvellous gift of generalising principles from ascertained facts, and expressing these as clear and logical propositions, that the name of Dmitri Mendeléeff will take its permanent place in the history of chemistry.

## CHAPTER XXXVIII

### THE CHEMISTRY OF THE CARBON COMPOUNDS

(From 1830 A.D. till 1900 A.D.)

#### I. AUGUSTE LAURENT

WE have already said that Liebig founded organic chemistry. By his researches he made known to us a great variety of compounds and series of compounds, and furnished science with a ready and precise method of determining their ultimate composition by means of his combustion furnace. Wöhler removed organic chemistry from the position of a supposed distinct science, with special laws of its own, and made it a branch of chemistry, subject to the same laws and following the same general principles. Henceforth organic chemistry was regarded as the chemistry of the carbon compounds.

It has been necessary for us to say a good deal about this branch of the science when considering the work of the chemists, mentioned in preceding chapters, particularly in Chapters XXXIV. and XXXV., since all the great chemists of the nineteenth century devoted much attention to organic substances. In collecting into this and the following chapters a more particular account of the development of the chemistry of the carbon compounds, we shall avoid as far as possible recapitulating what has already been said, although some repetition will be unavoidable if we are to obtain a clear view of this complex subject. In its later development the constantly increasing number of individual substances has been reduced to order, and as we proceed we shall see how its laws have gradually emerged from obscurity under the investigations of philosophers, and how these laws have influenced the development of chemical theory in general,



Lavoisier stated that in the mineral, or inorganic kingdom, all the oxidisable radicles (the portions of a compound which combine with oxygen) are simple; while in the organic kingdom the radicles are compound, consisting of at least two substances. These substances were, in the vegetable kingdom, always at least carbon and hydrogen, and in the animal kingdom, often nitrogen and phosphorus in addition.

The majority of organic bodies gave analytical results showing that they were very complex, and perhaps not combined in accordance with atomistic laws. Berzelius analysed many of them with great care in 1811, and showed that, although complicated, their composition could be stated in conformity with the atomic formulæ. The differences he expressed very much as Lavoisier had done.

In 1817 Leopold Gmelin in his *Handbook of Theoretical Chemistry* said that, though distinct, the differences between inorganic and organic compounds could be more easily perceived than stated. He considered the binary character peculiar to the mineral kingdom, and that it was characteristic of organic compounds that they could not be produced synthetically from their elements.

Then followed in 1815 Gay-Lussac's view of the composition of alcohol and ether ( $C_2H_4$  and water), which was extended by Dumas to many other alcohol-derivatives; for example, sulphovinic acid and several ethers.

In 1827 Berzelius said that "the elements present in living bodies obey laws totally different from those which rule inanimate nature." This opinion, which closely followed that of Stahl (*supra*, p. 232), was at that period generally accepted. New organic bodies might be produced from other organic bodies, as alcohol from sugar, but no such body could be produced by synthesis. This idea was exploded by Wöhler in 1828, although he did not shake the belief in a mysterious vital force, so long as the synthesis of urea was an isolated instance.

A new era in chemistry, as Berzelius said, was created in 1832 by the publication of Liebig and Wöhler's researches on

the radicle of benzoic acid (*Annalen der Chemie und Pharmacie*, Vol. III., p. 249). They demonstrated that that radicle, which they termed benzoyl ( $C_7H_5O$ ), might be regarded as a compound element entering into a host of combinations. The idea of a radicle containing oxygen was then quite a new suggestion.

In 1837 Dumas was converted by Liebig to his views, and they jointly published a paper, in which they asserted that numerous organic compounds are formed from a small number of simple substances, which first combine to form radicles, some of which resemble chlorine and oxygen, and others resemble metals. These radicles are the elements of organic chemistry, and they cannot be decomposed into their simple elements without annihilating their organic nature. The dualistic theory of the constitution of chemical compounds thus included organic bodies, but the electro-chemical theory also held its place.

The next great advance took place about 1834, when Dumas evolved his Law of Substitution from a number of discoveries—Gay-Lussac's chloride of cyanogen (1815), Faraday's series (1821) from ethylene dichloride ( $C_2H_4Cl_2$ ) to carbon sesquichloride ( $C_2Cl_6$ ), Liebig and Wöhler's chloride of benzoyl, the formation of chloral, and his own substitution compounds of turpentine.

This law and the facts upon which it was based interfered with the electro-chemical view of Berzelius, and led Laurent in 1836 to propose his Nucleus Theory. According to this theory, every organic compound contains a group of atoms called "kernel" or "nucleus" (Fr. *noyau*; Ger. *Kern*). Primary nuclei are hydrocarbons, of which the hydrogen may be replaced by chlorine, or another element, without altering the shape of the nucleus. There are also secondary nuclei, of which the compounds are substitution products of the corresponding compounds of the primary nuclei. Laurent's views are noticeable, inasmuch as he doubled the old formulæ, as indeed we do now. The nucleus theory was the basis of classification in Leopold Gmelin's large *Handbook of Chemistry* already mentioned, but was not much further recognised.

The Substitution Theory led Dumas himself to his Theory of Types. According to it, all bodies which are derived from each other by simple substitution belong to the same type: for example, acetic acid and its chlor-derivatives; chloroform, bromoform, and iodoform; aldehyde and chloral. He further recognised with Regnault mechanical types—that is to say, bodies containing the same number of equivalents but having different properties, as alcohol and acetic acid.

A fierce contest now ensued between Berzelius, with his electro-chemical dualistic theories, and Dumas, with his substitutions, which ended in the victory of the Substitution Theory and the Type Theory in improved form. These prevailed because they were in the main founded upon ascertained facts; while Berzelius had to meet these facts by endless modification and complication of formulæ, in order to make the new bodies, discovered in great numbers at this period, appear to conform to his theoretical views. For instance, he had to say that acetic acid is a compound of methyl and oxalic acid— $C_2H_3 + C_2O_3 + HO$ .

Liebig argued against the views of Berzelius because they were founded upon supposition, rejected Laurent's nucleus theory as being unscientific and useless, and said that Dumas went too far with his Substitution Theory, especially in saying that even carbon could be replaced by other elements or groups.

The continually increasing number of new substitution compounds firmly established the Law of Substitution in the form in which we now have it. Great support was rendered to it by Melsens in 1842, when he showed that the original compound can be reproduced by inverse substitution; for example, that by the action of potassium amalgam on trichloroacetic acid one again obtains acetic acid.

Hoffmann in 1845 discovered the chlorinated anilines, whereupon Liebig enunciated the doctrine that the nature of a compound depends not on the nature of the elements composing it, but on their position in the compound. This admission of

chlorine into radicles subsequently led to the recognition that oxygen might exist in a radicle.

At first it was not conceived that it might be possible to isolate radicles, any more than the nuclei of Laurent; both were deemed hypothetical bodies. But this idea of radicles was gradually modified, until their isolability was held to be possible, and became an object of research. Then followed Bunsen's work on the cacodyl compounds, which resulted in his isolation of cacodyl ( $C_2H_6As$ )<sub>2</sub>, a radicle that enters into numerous combinations, in which it plays the part of a metal.

For a time the hydrocarbons, which Kolbe and Frankland obtained, were believed from their mode of formation to be free alcohol radicles, such as ethyl. Although it is now known that these are identical with marsh gas and other series of hydrocarbons, there can be no doubt that their isolation, and the investigations which followed, greatly advanced the radicle theory, and organic chemistry in general.

It is now necessary that we should speak of the men who took the lead in the process of development that we have sketched. Of Liebig, Wöhler and Dumas, we have already said all that is necessary, but amongst those who next to Liebig played the most important part in developing and modifying the radicle theory, there are no more eminent names than two which we have not yet considered, Laurent and Gerhardt.

Auguste Laurent (1807—1853) was born at La Folie, near Langres. In 1826 he entered the *École des Mines*, and three years later gained the diploma of *Ingénieur*. He was appointed *Repetiteur* at the *École Centrale des Arts et Manufactures* in 1831, under Dumas, who taught him organic analysis. Afterwards he was Professor of Chemistry at Bordeaux and Warden of the Mint at Paris.

Laurent was intimately associated with Gerhardt in the development of chemistry, and particularly in grafting the theory of radicles upon that of types. By his skill in analysis and experiment, and his power of classification, he supplied the

facts and evidence, while Gerhardt's talents lay rather in generalisation.

His work began with the extraction of naphthalene from coal tar, the determination of its composition, and the formation of chlorine substitution compounds from it. He also made important researches into the constitution and properties of phenol or carbolic acid.

Naphthalene formed an excellent subject for study, as it is very susceptible of substitution. Laurent at first considered its chlorine-substitution compound as the chloride of a new radicle containing less hydrogen than the hydrocarbon: but two years later he announced the substitution of chlorine, bromine, nitroxyl ( $\text{NO}_2$ ), and other substances, accompanied by the formation of hydrochloric, hydrobromic or nitric acid. This constituted the germ of his Nucleus Theory, of which we have already spoken, and which he announced in 1836-7. It was also the germ of the more important and successful theory of substitution, which was developed into a law by Dumas, subject to modification by Laurent.

In developing his ideas of nuclei, which were used as a basis of classification in Gmelin's large *Handbook of Chemistry*, as well as in his own *Chemical Method*, and in his theory of types, he introduced to science the words "anhydride," "amide," "imide," "amidic acid," and others. His Theory of Nuclei was originally mentioned in his Inaugural Dissertation at the *Faculté des Sciences* at Paris in 1837, but it must not be forgotten that these doctrines are also associated with the name of Gerhardt, who has a share in the honour of their conception and introduction.

The Nucleus Theory amounted to this:—The molecules of organic bodies, he said, are either nuclei, or compounds of nuclei, with other substances placed outside them. These nuclei are groups of carbon atoms united with other elements, and are either (1) fundamental nuclei, consisting of carbon and hydrogen only, or (2) derivative nuclei, derived from the fundamental nuclei by substitution. The bodies substituted



are generally chlorine, bromine, iodine, oxygen, or nitrogen, but compound bodies, acting as radicles, may be in like manner substituted for hydrogen, and enter into the nucleus; for example:—

Nitrogen tetroxide	.	$N_2O_4 = (N_2O_5 - O)$ .
Amidogen	.	$NH_2 = (NH_3 - H)$ .
Imidogen	.	$NH = (NH_3 - H_2)$ .
Arsidogen	.	$AsH_2$ .
Cyanogen	.	$CN$ .

All of these can replace hydrogen, and other elements may group themselves round a nucleus; thus,  $C_2H_4$ ,  $C_2H_4Br_2$ ,  $C_2H_4O$ ,  $C_2H_4O_2$ , are all nuclei developed from  $C_2H_4$ . He compared his nuclei to prisms with carbon atoms at the angles, and hydrogen at the edge, and so on. In constructing his nuclei and comparing them to prisms, he abandoned the dualistic system, and viewed the compound as a single unitary whole like a crystal. Although the Nucleus Theory has not survived, it laid the foundation of the theory of types which we still use.

Bodies formed by additions to nuclei have different properties—neutral, acid, and so forth. The addition of four atoms of oxygen ( $O = 8$ ) made a *monobasic* acid, the addition of six atoms of oxygen, a *tribasic* acid. This idea of a connection subsisting between oxygen and basicity had a germ of truth in it. Laurent further observed that these atoms always pass into a compound in pairs, never as single atoms.

Laurent's statement of the Substitution Theory is as follows:—

1. Whenever chlorine, bromine, oxygen, or nitric acid exerts a dehydrogenating action on a hydrocarbon, the hydrogen removed is replaced by an equivalent of chlorine, bromine, oxygen, or nitroxy ( $NO_2$ ).
2. At the same time there is formed hydrochloric acid and water, or nitrous acid, which are sometimes disengaged, sometimes remain combined, in all the new radicles produced.

Referring to Dumas's theory of substitution, where he argued

from the action of chlorine on alcohol, and stated as a rule that if water be present, its hydrogen is first removed without substitution, and that the remaining hydrogen is substituted by another element—Laurent maintained that whenever substitution takes place, the chemical and physical properties of the new substance resemble those of the original body; but that substitution does not always take place. Many substitution-compounds were produced by the researches of Laurent, Regnault, and others, and the production of trichloroacetic acid converted Dumas to Laurent's views. These views, however, and the researches upon which they were founded, are so intimately associated with the work of Gerhardt, that it is impossible to understand them without reference to the labours of the latter chemist, whom we are to consider in the next chapter.

## CHAPTER XXXIX

### THE CHEMISTRY OF THE CARBON COMPOUNDS

(From 1830 A.D. till 1900 A.D.)

#### 2. CHARLES FRÉDÉRIC GERHARDT

THE famous collaborateur of Laurent, Charles Frédéric Gerhardt (1816—1856), was born at Strassburg, and educated there and at Karlsruhe and Leipsig. He had a very remarkable career. At first, in 1834, he entered his father's white lead factory at Leipsig, but disliking the business, quarrelled with his father and enlisted as a soldier. The military life appealed to him as little as the manufacturing life. Finding it intolerable he was bought off by a friend, and went to Giessen, where he studied chemistry under Liebig. Again changing his mind he re-entered his father's factory in 1837, but next year quarrelled again, and left it, this time finally. With an introduction to Dumas, he went to Paris in 1838, and there worked on essential oils, along with Auguste Cahours, in Chevreul's laboratory. Cahours and he published the result of their researches in a joint paper.

In 1841 he was appointed to the Chair of Chemistry at Montpellier, and in the following year published a memoir, *Researches on the Classification of Organic Substances*, in which he foreshadowed the opinion that led to his doubling the atomic weights of carbon and oxygen. This paper caused a dispute with Liebig, and the friends were at variance till 1850, when they were reconciled, no doubt through the wise reasonableness of the great German chemist. Meanwhile, between 1848 and 1855, Gerhardt resided in Paris, where he published a series of controversial papers, in which he developed the idea of types of structure and reactions. But he made a mistake

in advocating Laurent's Nucleus Theory, which, as we said in the last chapter, grouped some of the atoms in a compound round a nucleus, as it were a central prism, of what Gerhardt called "residues," which resembled Liebig's radicles, except in so far as they were not transférable to other compounds. This defect gives a clue to the failure of the Nucleus System. Residues, according to Gerhardt, were "atomic complexes which remain over from the interaction of two compounds, as the result of the stronger affinity of particular elements for one another, and which combine together because they are incapable of existing separately." He also suggested that there might be different residues in the same compound, according to its mode of formation or decomposition.

In 1851 Gerhardt resigned his chair at Montpellier, having some years before established at Paris an *École de Chimie Pratique*, of which he had great hopes, but which proved commercially a failure. Finally, in 1855, he was appointed Professor of Chemistry at Strassburg, in the *École Polytechnique*, and at the Faculty of Sciences, and died suddenly in that city.

Gerhardt wrote only two books of importance: *Précis de Chimie Organique* (1844-5) and *Traité de Chimie Organique* (1853-6). In his research he was much indebted to the analytical and experimental skill of Laurent. His work on the preparation of acid anhydrides in 1852 was important, but he was rather an introducer of new ideas, which vitalised and organised old facts, than an investigator of new compounds. In collaboration with Laurent he reformed the methods of stating chemical formulæ, by insisting upon the distinction between atoms, molecules, and equivalents. His unitary system, directly opposed to the dualistic doctrine of Berzelius, combined Dumas's substitution theory with the older radicle theory, and greatly extended our notion of types and structures. His theory of homologous and heterologous series marked an epoch in the history of chemistry.

After Graham had studied the different modifications of

phosphoric acid and established its polybasicity, and Liebig had examined organic acids and their salts and published his theory of polybasic acids (*Ann. Pharm.*, Vol. XXVI., p. 113), Laurent and Gerhardt further developed the latter theory. Gerhardt defined as polybasic an acid which forms double salts with any bases, or which contains more than one atom of hydrogen that can be replaced by metals. The best way of determining this fact he found to be the ascertaining whether the acid can form more than one compound ether, or, as we now say, "ester," the hydrogen replaceable by metals being replaceable by alcohol radicles. Laurent added that a monobasic acid can form but one amide, a dibasic two, a tribasic three, and so on. They wrote the formula of each salt and ether in such a way as to show that it was of the same type as the acid itself; thus— $H_2S_2O_8$ ,  $K_2S_2O_8$ ,  $KHS_2O_8$ ,  $(C_4H_5)_2S_2O_8$ ,  $(C_4H_5)HS_2O_8$ . Their constant endeavour was to interpret similar chemical reactions in a uniform way.

Actuated by a desire to avoid assumptions, Gerhardt established the Unitary Theory of Notation, which soon superseded the then generally accepted binary method of representing salts and other compounds. For example, sodium sulphate was then considered to be composed of sodium monoxide ( $Na_2O$ ) and sulphuric acid ( $SO_3$ ). Gerhardt showed it to be  $Na_2SO_4$ , consequently sulphuric acid must be  $H_2SO_4$ , and not, as was then supposed, a compound of  $SO_3$  and  $H_2O$ . This had the further result of breaking down the distinction between hydracids, such as hydrochloric acid, which contain no oxygen, and the oxygenated acids, which are really hydrogen compounds like the so-called hydracids. It may be remarked, however, that Gerhardt's Type Theory maintained a distinction between the two groups of acids, for hydrochloric acid, sodium chloride, and similar compounds were formed on a simpler type than the oxygen acids and their salts, which were built on the "water type."

In formulating his acids and their derivatives on the same plan or type, Gerhardt was the first to attempt to ascertain



the molecular weight by the study of chemical analogies. Laurent demonstrated that a molecule of chlorine must consist of two atoms, because when chlorine acts on organic bodies, two, four or six atoms enter into action, never one, three or five. By studying the reactions of cyanogen chloride and similar compounds, he proved that as a molecule of cyanogen chloride can be divided into two parts, precisely the same arguments prove the same thing to be true of a molecule of chlorine, the changes of  $\text{ClCl}$  being the same as those of  $\text{CyCl}$ ,  $\text{C}_6\text{H}_5\text{OCl}$ , and other chlorides. These views led to a clearer conception and definition of the terms "equivalent," "atom," and "molecule."

To explain the law of gases, an Italian physicist, Amedeo Avogadro, had advanced in 1811 the hypothesis that equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules in unit and volume. This hypothesis has become an accepted law, known as *Avogadro's Rule*. It is confirmed by the fact that all gases expand alike for equal increments of heat, but it may have to be changed on the discovery of further facts.

Gerhardt followed up the discoveries of Laurent and himself by arguments derived from this hypothesis of Avogadro. He was led to double the old atomic weights of some of the elements, such as oxygen, sulphur, and carbon, defining the atomic weight as the smallest quantity of an element that exists in a molecule of one of its compounds. He first proposed doubling the atomic weight of oxygen, sulphur, and carbon in 1843, but the proposal met with no acceptance, or even recognition, yet after his death it was adopted, and was extended by Cannizzaro to all atomic elements. The rule as stated by Cannizzaro is this:—

"The atom of every element is expressed by that quantity of it which invariably enters as a whole into equal volumes of the simple substance and its compounds."

By adopting unitary formulæ in place of the dualistic formulæ then in use, Laurent and Gerhardt brought out analogies, got

rid of false hypothetical theories of constitution, and made way for the introduction of a notation founded on the formulation of radicles. They used symbols to represent groups, which were sometimes those of the radicle theory and sometimes those of the nucleus theory.

An amalgamation of the Radicle and Type Theories followed. The radicles were placed in substitution for hydrogen. Laurent and Gerhardt objected to the Radicle Theory, on the ground that it is impossible from a limited number of decompositions or reactions to infer the constitution of a body, or ascertain its proximate constituents. But the exclusive use of the empirical formulæ of the unitary notation does not always show the relations of bodies to each other so clearly as the notation of the Radicle Theory. Hence, they came to use synoptical formulæ, in which groups of atoms, which remain together in a series of changes (as Dumas had shown that nitroxyl can do in replacing hydrogen), were written together apart from the rest, or expressed by a sign—as "Bz" for benzoyl and "Et" for ether. Those formulæ were not intended to express the constitution of the body, nor did Gerhardt admit that such groups formed a chemical entity. As much as this had been said by Liebig in 1835, when he declared that a radicle is not an unalterable quantity. Gerhardt termed the group which can be assumed to be a radicle, "le restant"—the *rest* or *residue*.

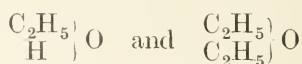
In 1840 Gerhardt developed his doctrine of residues by explaining how a simple element in a compound is replaced by a compound group. He held, for instance, that when nitric acid acts upon a body so as to substitute nitroxyl ( $\text{NO}_2$ ) for hydrogen, something is taken from each; namely, the hydrogen from the organic compound, and one atom each of hydrogen and oxygen from the nitric acid—and the residues from each unite to form a *unitary whole*, and not an articulated or conjugated binary compound.

The older theory of radicles has been replaced by our present conception of a radicle, which resembles the idea of a residue.

These radicles introduced into the new form of the theory of types caused the fusion of the two theories that now prevails.

Thus, when Wurtz discovered the compound ammonias in 1845, they were deemed to be formed by the union of the two residues  $C_2H_5$  and  $NH_2$ , because Liebig had predicted that by combining an alcohol radicle with amidogen ( $NH_2$ ) a body would be produced having the properties of ammonia. Berzelius, in his endeavour to prevent the acceptance of the Substitution Theory, had adopted an expression first used by Gerhardt in another sense—the term “copula.” Hoffmann at the outset looked upon “ethyliaque” of Wurtz as a conjugated ammonia containing olefiant gas as a copula ( $C_2H_4NH_3$ ), and began his researches on ethylamine with this idea in his mind: but he soon proved that it is a substitution-product of ammonia, containing  $C_2H_5$  in place of hydrogen, and so he called the substance “ethylamine.” He replaced one, two, and three atoms of hydrogen in the same manner by the residue or radicle, “Et,” thus producing compounds which were still in character and constitution ammonias, and which all belonged to the ammonia type.

Similarly, Williamson in his researches on the constitution of ether, proved in 1850 that alcohols and ethers can be referred to the water type—



He also showed that acetic acid might be regarded as constructed on the type of water, in which one atom of hydrogen was replaced by  $C_2H_3O$ ; thus— $\left. \begin{array}{l} C_2H_3O \\ H \end{array} \right\} O$ . He predicted a class of bodies in which the other atom of hydrogen in water was replaced by  $C_2H_3O$ , related to the acids in the same way as ether is related to alcohol. Gerhardt verified this prediction by discovering the anhydrides in 1852.

Gerhardt, as well as chemists generally, now sought types for organic compounds amongst the simple inorganic compounds. He proposed four types as follows:—

<i>Hydrogen Type.</i>	<i>Hydrochloric Acid Type.</i>	<i>Water Type.</i>	<i>Ammonia Type.</i>
$\begin{array}{l} \text{H} \\ \text{H} \end{array}$	$\begin{array}{l} \text{H} \\ \text{Cl} \end{array}$	$\begin{array}{l} \text{H} \\ \text{H} \end{array} \text{O}$	$\begin{array}{l} \text{H} \\ \text{H} \cdot \text{N} \\ \text{H} \end{array}$

For example—

*Ethyl hydride.*

$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{H} \end{array}$	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{Cl} \end{array}$	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \text{O}$	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{H} \\ \text{H} \end{array} \left. \vphantom{\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{H} \\ \text{H} \end{array}} \right\} \text{N}$
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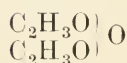
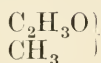
*Ethyl.*

$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array}$	$\begin{array}{l} \text{C}_2\text{H}_5\text{O} \\ \text{Cl} \end{array}$	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \text{O}$	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{H} \end{array} \left. \vphantom{\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{H} \end{array}} \right\} \text{N}$
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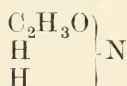
*Aldehyde.*

$\begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array}$	$\begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{Cl} \end{array}$	$\begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \text{O}$	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \left. \vphantom{\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array}} \right\} \text{N}$
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*Acetone.*

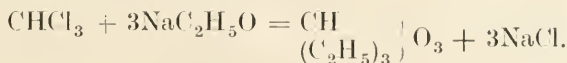


*Acetamide.*



Williamson in the same paper (*Journal Chem. Socy.*, Vol. IV., p. 237) demonstrated that sulphuric acid might be considered as derived from two molecules of water, the radicle of the acid replacing one hydrogen atom in each of the two molecules. He extended this to other dibasic acids.

In 1854 Williamson by heating chloroform with sodium ethylate formed tribasic formic ether :—



He showed that this might be formed on the type of three condensed molecules of water; while chloroform might be regarded as formed on the type of three condensed molecules of hydrochloric acid. Williamson, Odling, and Gerhardt's ideas of polyvalent types were published in Gerhardt's *Traité de Chimie Organique* in 1856.

Odling applied the same principle to a large number of compounds, and Gerhardt in 1856 adopted the theory of

condensed types. Berthollet's researches on glycerine interpreted by Wurtz, and the discovery of glycol by Wurtz himself, afforded powerful support to this doctrine. Kekulé afterwards

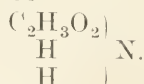
added another type—marsh gas  $(\text{CH}_4) = \begin{matrix} \text{H} \\ | \\ \text{H} \\ | \\ \text{H} \\ | \\ \text{H} \end{matrix} \cdot \text{C}$ .

To mixed types are referred such bodies as Gerhardt had in 1838 called congested or copulated compounds (*Sel copulé*), an idea which Berzelius ridiculed, although he used the term "copula" soon after in a somewhat different sense. Even acetic acid may be regarded as of a mixed type.



Chloroacetic acid, formed by chlorinating acetic acid, yields with ammonia *amidacetic acid*  $(\text{C}_2\text{H}_2\text{O} \frac{\text{NH}_2}{\text{OH}})$ , containing the dyad radicle  $\text{C}_2\text{H}_2\text{O}$ . It is monobasic; but it presents analogies with the compound ammonias, and may be considered as formed on various types; thus—

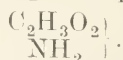
(1) On the *Ammonia Type*—



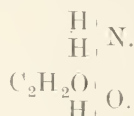
(2) On the *Water Type*, being derived from acetic acid, inasmuch as it is formed from chloroacetic acid by the substitution of chlorine by  $\text{NH}_2$ —



(3) On the *III Type*, being a compound of a monad radicle—



(4) On the mixed type of *Ammonia and Water*—





Which of these four formulæ is to be preferred depends on which of the several relations it is desired to make prominent.

The nett result of Gerhardt's research, therefore, was that he banished the old idea of rigid radicles, replaced it by the conception of residues, which can be resolved into simpler residues, and introduced these into the Theory of Types. Radicles in this sense were thereafter recognised in mineral chemistry, and thus both the theory of radicles and that of types were extended to inorganic chemistry.

In 1842 Schiel noticed that the alcohol radicles form a very simple graduated series of bodies, whose properties and composition alike show regular gradations. These are tabulated here, the radicle  $\text{CH}_2$  being represented by "R":—

RH	Methyl
$\text{R}_2\text{H}$	Ethyl
$\text{R}_3\text{H}$	Propyl
$\text{R}_4\text{H}$	Butyl
$\text{R}_5\text{H}$	Amyl
$\text{R}_{16}\text{H}$	Cetyl
$\text{R}_{24}\text{H}$	Ceretyl

He surmised the existence of other series. Then Dumas observed that fatty acids form a regular series, whose boiling points rise with each increment of  $\text{CH}_2$ .

Founding upon these observations, Gerhardt in 1844–45 in his *Précis de Chimie Organique*, arranged a number of organic compounds in series, the members of which differed by increments of  $\text{CH}_2$ . He termed these *Homologous Series*; while series formed from homologues by analogous changes, and by simple and simpler reactions, he termed *Heterologous Series*.

Gerhardt discovered few new substances, the most important being acetic and benzoic anhydrides in 1852. He was a man of peculiar temper, apt to express himself offensively in controversy, and to quarrel with those who differed from him. His reputation rests upon his powers of bold yet accurate generalisation.

## CHAPTER XL

### THE CHEMISTRY OF THE CARBON COMPOUNDS

(From 1830 A.D. till 1900 A.D.)

#### 3. CHARLES ADOLPH WURTZ TO HENRI ETIENNE SAINTE-CLAIRE DEVILLE

WE have already spoken more than once of the work of Charles Adolph Wurtz (1817—1884). He was born at Wolfisheim, near Strassburg, where his father was a Lutheran pastor. As in the case of several distinguished chemists whom we have mentioned, his father wished him to enter the Church, but the son was averse to doing so, and as an alternative studied medicine. In 1839 he was appointed *Chef des Travaux Chimiques* at the Faculty of Medicine, and in 1843 graduated as Doctor of Medicine at Strassburg. He spent a year with Liebig at Giessen, and then went to Paris, where he became an assistant in the laboratory of Dumas. From 1850 till 1852 he was Professor of Chemistry at the Agricultural Institute at Versailles. In 1853 he was appointed Professor of Organic and Mineral Chemistry and Toxicology at the *École de Médecine* at Paris, an office which he retained till his death, and after 1875 he was also Professor of Organic Chemistry at the Sorbonne. He was an honorary member of almost every scientific society in Europe; he was one of the founders and the first secretary of the Paris Chemical Society; and in 1867 he entered the *Académie des Sciences*, of which in 1881 he became president.

After Liebig and Dumas, Wurtz is most conspicuous as one of the founders of organic chemistry. He was an active member of the French Academy of Sciences, and the author of a large number of papers. He was also a member of the

Royal Society of England, and in 1878 received its Faraday medal. His principal book is *Dictionnaire de Chimie pure et appliquée* (1869—1878), the introductory discourse to which (published separately as *Histoire des Doctrines Chimiques*), opens with the celebrated phrase: "La Chimie est une science française." His other chief works are *Chimie Médical* (1874), *La Théorie Atomique* (1875), and *Traité de Chimie Biologique* (1880—85).

Wurtz's first paper was published in 1842 on hypophosphorous acid and the constitution of the hypophosphites. He discovered copper hydride, and noticed its decomposition with hydrochloric acid, a reaction which played some part in supporting the belief that a molecule of hydrogen contains two atoms. In 1845 he discovered sulphophosphorous acid and potassium oxychloride, and three years later cyanic and cyanuric ethers, thus opening out a new field of research in organic chemistry, and discovering a method of forming primary amines from cyanic ethers.

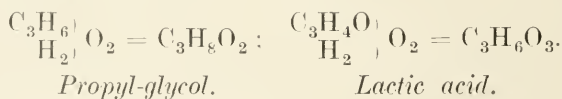
In 1849 he discovered methylamine, the simplest organic derivative of ammonia, and also the compound ammonias, which he regarded as conjugated compounds of olefines and ammonia ( $C_2H_4$ ,  $NH_3$ ), until Hoffmann reproduced them by another process, and thus disclosed their true nature. His study of the compound ureas followed in 1851.

Wurtz then interpreted Berthollet's glycerine and its derivative on the "condensed type" theory, and discovered in 1856 the first diatomic alcohol, named glycol. This he formed by combining olefiant gas with bromine and replacing the bromine by the radicle "hydroxyl" (HO). By the action of hydrochloric acid on glycol he produced ethene chlorhydrate, which by oxidation yields chloracetic acid, and by ammonia chloracetamide.

A controversy ensued between Frankland and Kolbe, on the one hand, who maintained that the radicles isolated from the alcohols remained free, and Laurent, Gerhardt and Hoffmann, on the other, who asserted that they com-

lined with themselves, as, for example,  $C_2H_5C_2H_5$ . Wurtz entered into this discussion, and produced evidence in favour of the latter view by treating a mixture of iodides of two different alcohol radicles with sodium, and so forming a mixed radicle.

But a more important branch of his research was his work on lactic acid, by which he contributed to the development of the doctrine of the atomicity, as distinguished from the basicity, of an acid. Lactic acid was first isolated from sour milk by Scheele; Berzelius obtained it from other sources; Liebig and Mitscherlich determined its composition; and Strecker produced it synthetically. Wurtz formed it by the oxidation of propyl-glycol. As this formation is analogous to the oxidation of alcohol to produce acetic acid, he explained the constitution of lactic acid; thus—

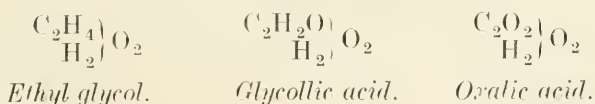


Kolbe, using equivalent formulæ, regarded propyl-glycol as the hydrate of oxypropylene,  $C_3H_5 \left( \begin{array}{c} \text{H}_5 \\ \text{H} \end{array} \right) C_2O_2 \cdot 2HO$ , which is in atomic formula  $C_2H_5 \left( \begin{array}{c} \text{H}_5 \\ \text{H} \end{array} \right) COH_2O$ , and lactic acid is oxypropionic acid,  $HO_2C_3 \left( \begin{array}{c} \text{H}_4 \\ \text{HO}_2 \end{array} \right) C_2O_2$ , or in atomic formula,  $C_2 \left( \begin{array}{c} \text{H}_4 \\ \text{OH} \end{array} \right) COOH$ . He gave as his reasons that he considered lactyl dichloride to be chloride of chloropropionic acid, and the ethyl compound as chloropropionic ether. He showed that by replacing the chlorine in the ether by hydrogen, propionate of ethyl is produced. But two atoms of hydrogen in lactic acid can be replaced by metals under certain conditions, and Wurtz showed that lactic acid forms not only a monomethyl ether, but also a dimethyl ether, a property which had been regarded by Gerhardt as characteristic of a dibasic acid.

Following up his master's work, Kolbe's pupil Lanteman replaced the hydroxyl (HO)—that is, one atom each of hydrogen and oxygen—in lactic acid by hydrogen through the action of

hydriodic acid (HI). In this manner he produced propionic acid. Then Kolbe by the action of ammonia on chloropropionic acid formed alanine or amidopropionic acid, while Strecker combined aldehyde with hydrocyanic acid, and converted the resulting nitrile into lactic acid by means of hydrochloric acid. It may be said that Kolbe's facts were so far right, but he erred in not acknowledging propyl-glycol as an alcohol of a dyad radicle.

Wurtz, continuing his research, pointed out that the exchange of hydrogen for a metal does not depend only on the number of atoms of hydrogen which there are outside the radicle, but also on the nature of the radicle itself. He further demonstrated that the exchange of hydrogen increases with the increase of oxygen in the radicle. For example—

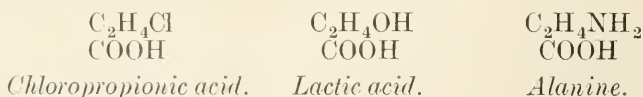


Each of these three substances—ethyl glycol, glycollic acid, and oxalic acid—contains two atoms of hydrogen outside the radicle; yet while glycol is neutral, glycollic is a *monobasic* and oxalic a *dibasic* acid. Now, lactic acid is analogous to glycollic acid, but Wurtz regarded it as a dibasic acid, although a weak one, on account of the difficulty in replacing the second atom of hydrogen by a metal. He did, however, draw a distinction between the basicity and the atomicity of an acid, that is, the valency of its radicle.

The true explanation was given by Kekulé in the first part of his *Lehrbuch der Organischen Chemie*. He showed that the two typical or extra-radicle atoms of hydrogen differ in the same way as the extra-radicle atom of alcohol differs from that of acetic acid. One of them is readily exchanged for metals, in the same manner as the corresponding atom of acids, while the other does not exchange so readily, but is easily replaced by an acid radicle, such as the radicle of alcohols. Lactic acid is therefore at once an acid and an alcohol.



As the determination of the constitution of lactic acid has an important historical interest, we shall illustrate the subject by a little further explanation of the acid and its relations. Its character is well expressed by our modern formula, not then developed— $\text{CH}_2 \begin{matrix} \text{CH}_2\text{OH} \\ \text{COOH} \end{matrix}$  or  $\text{CH}(\text{CH}_3)\text{OH} \begin{matrix} \\ \text{COOH} \end{matrix}$ . It is derived from propionic acid ( $\text{C}_2\text{H}_5\text{COOH}$ ) by replacing one atom of hydrogen in its ethyl by hydroxyl (OH). It is readily converted into lactyl dichloride ( $\text{C}_2\text{H}_4\text{ClCOCl}$ ), which is identical with chloropropionyl chloride, and this, like other acid chlorides, forms with water hydrochloric acid and chloropropionic acid ( $\text{C}_2\text{H}_4\text{ClCOOH}$ ). The other remaining chlorine atom is combined with carbon in the same way as the chlorine of ethyl chloride ( $\text{C}_2\text{H}_5\text{Cl}$ ), and further reacts with potassium hydroxide and with ammonia in analogous ways—that is to say, it yields lactic or oxypropionic acid, and alanine or amidopropionic acid; thus—



The further elucidation of the constitution of this remarkable substance is of recent date. By oxidation it yields carbon dioxide ( $\text{CO}_2$ ) and acetic acid, which contains methyl ( $\text{CH}_3$ ); there must therefore be methyl in lactic acid, and its formula may be written thus—



This view is confirmed by Strecker's formation of alanine, and by the production of lactic acid from aldehyde or oxide of ethidene by hydrocyanic acid and then hydrochloric acid acting on the product. Theory would indicate the existence of another lactic acid with the formula  $\text{CH}_2 \begin{matrix} \text{CH}_2\text{OH} \\ \text{COOH} \end{matrix}$ , and this has been actually formed under the name of *Ethylenelactic acid* ( $\text{C}_2\text{H}_2(\text{OH})\text{CH}_2\text{COOH}$ ).

We have discussed this portion of the work of Wurtz at

some length on account of its historical importance, but he did other research of much value. In 1867 he produced neurine by synthesis, and in 1872 discovered aldol, which possesses the double character of an alcohol and an aldehyde, hence its name. He also conducted an investigation into vapour densities, discovered phosphorus oxychloride, and worked upon the saturation capacity of the nitrogen atom. Of great importance also was the discovery of phenol, which was first observed by Wurtz and Kekulé by fusing benzene-sulphonic acid with potash.

The next chemist whom we have to mention is Antoine Jerome Balard (1802—1876). He was born at Montpellier. He became an apothecary, and also did duty locally as a teacher of chemistry. One day, in 1824, when botanising near a salt marsh, he observed a deposit of sodium sulphate which during a cold night had crystallised from the mother liquor derived from common salt. The idea of utilising these mother liquors occurred to him, and in the course of his experiments he discovered bromine in 1825. His name was then associated with that of Scheele, the discoverer of chlorine, and of Courtois, the discoverer of iodine, which was investigated by Davy and Gay-Lussac. The repute thus attained secured for him the position of Professor of Chemistry at the Faculty of Sciences at Paris, in succession to Thénard, and in 1851 the Chair of Chemistry at the College of France. He died at Paris.

In addition to the discovery of bromine, Balard discovered hypochlorous acid and studied the bleaching compounds of chlorine. In organic chemistry he did valuable work. He discovered oxamic acid, and investigated amylic alcohol, the decomposition of ammonium oxalate, the cyanides, and the difference between nitric and sulphuric ethers.

France also contributes our next subject, in the person of Henri Victor Regnault (1810—1878). He was born at Aix-la-Chapelle, and in his earlier years was very poor. Having obtained a situation in a drapery establishment at Paris, he devoted all his spare time and means to the

study of chemistry. At length he was able to enter the *École Polytechnique* in 1830, and two years later the *École des Mines*, and was rewarded by the appointment of Professor of Chemistry at Lyons. In 1840 he exchanged this for the Chair of Chemistry at the *École Polytechnique* at Paris, and was elected a member of the *Académie des Sciences*, next year succeeding Dulong as Professor of Physics at the College of France. In 1847 he published a *Treatise on Chemistry*, in four volumes, which has been translated into many languages. In 1854 he became director of the Royal Porcelain Factory at Sèvres. The results of his latest work were destroyed during the Franco-Prussian war, in which also his son was killed. The double blow was too much for him, and he was able to do no more research. He died at Paris, having, besides his book, published eighty papers.

Regnault, in common with many men of his date, was a physicist as well as a chemist. In 1835 he examined the haloid and other derivatives of the carbohydrates, the alkaloids, and the organic acids, and devised a new classification of the metals. This was based upon the facility with which each metal or its sulphide is oxidised by steam at high temperature, but the system had no permanent value. He also compared the composition of atmospheric air brought from different parts of the globe. Later, he made a careful re-determination of the specific heat of all the simple bodies which he could procure, and of a large number of their compounds. The expansion of gases received much attention from him. He maintained that no two gases have precisely the same rate of expansion, and that Boyle's law is consequently only approximately true. The gases which diverge most widely from the law are those which are most readily liquefied.

We have again to consider a French chemist, who was also a physicist. Henri Etienne Sainte-Claire Deville (1818—1881) was born at St. Thomas, in the West Indies, and studied chemistry at Paris under Dumas. In 1851 he succeeded Balard in the Chair of Chemistry at the *École Normale* at Paris. Two

years previously he had discovered nitrogen pentoxide ( $N_2O_5$ ). He manufactured aluminium on a large scale, a secondary result of which was the reduction of the cost of sodium from £40 to 5s. per pound. The platinum group of metals he studied along with Debray, his successor in the chair. From this he naturally passed to the artificial production of crystalline minerals, and other work which requires extreme heat. He also studied gas and vapour densities at high temperatures, and in the course of this research discovered the phenomenon of dissociation.

The term "dissociation" in physico-chemistry is applied to those balanced or reversible chemical reactions which occur when one at least of the acting bodies is a gas. For example, if we heat nitrogen peroxide ( $N_2O_4$ ), it becomes decomposed, the molecules of  $N_2O_4$  having split up, or *dissociated*, into two molecules of  $NO_2$ . When we allow it to cool, it re-forms as  $N_2O_4$ . In this phenomenon the two preponderating influences are *temperature* and *mass-action*. Rise of temperature accelerates the forward action of decomposition more than the reverse action of combination. Each temperature corresponds to a particular percentage of decomposed molecules, the amount of which can be ascertained by measurement of the gas density. In the other relation, that of the active mass of the substances present, we find that pressure is the main factor. In the dissociation, for instance, of calcium carbonate into calcium monoxide and carbon dioxide, pressure when increased increases the concentration of carbon dioxide alone, and thus reduces decomposition.

With Deville we leave France, and pass once more to the chemists of England and Germany.

## CHAPTER XLI

### THE CHEMISTRY OF THE CARBON COMPOUNDS

(From 1830 A.D. till 1900 A.D.)

#### 4. THOMAS GRAHAM TO FRIEDRICH AUGUST KEKULÉ

DURING the eighteenth century and in the early part of the nineteenth English chemists occupied a prominent place in the history of chemistry. In the latter part of the nineteenth century, such names occur more seldom. This circumstance does not arise from any want of attention devoted to chemistry in Great Britain, where indeed the science was being assiduously cultivated. It is due in a great measure to the dominating influence of Liebig and Dumas, which tended to establish in Germany and France the centre of chemical investigation and research. We are now however, to consider the work of an English chemist of the first rank, Thomas Graham (1805—1869). As a matter of fact, Graham was a Scotsman, having been born at Glasgow, in which city his father was a merchant. He studied chemistry at the University of Glasgow under Dr. T. Thomson, and at the University of Edinburgh under Dr. Hope.

At the outset of his career Graham was a teacher in Glasgow, in 1829 delivering lectures at the Mechanics Institution. In 1830 he was appointed Professor of Chemistry at the Andersonian Institution at Glasgow, a post which he held for seven years, when he succeeded Turner at University College, London. There he was a most successful teacher, succeeding not by eloquence, but by philosophical method. His *Elements of Chemistry*, published in 1833, was a standard work. He became master of the Mint in 1855, and died in London. His scientific attainments were honourably recognised. In



1836 he was elected a Fellow of the Royal Society of England, and in 1847 a corresponding member of the Institute of France, while in 1855 the University of Oxford conferred upon him the degree of D.C.L.

Graham's work was remarkable for originality of plan and simplicity of method, and his contributions to the progress of chemical science were many. The earliest of these was his epoch-making research in 1833 into the properties and combinations of phosphoric acid. It was known that solutions of that acid varied in properties, and these varieties were called isomeric forms. Graham showed that they contained different proportions of the elements of water, and were really different compounds. Perceiving that hydrogen in acids can be replaced by metals, he came to the conclusion that phosphoric acid exists in three distinct forms, whose basicity is different, and therefore that the acid is polybasic. This led to the theory of polybasicity, according to which a polybasic acid is held to be so constituted that one or more equivalents of hydrogen contained in it are replaceable by certain metals. At the same period he investigated phosphuretted hydrogen, and experimented upon the slow oxidation of phosphorus, finding that this is arrested by olefines and turpentine.

He determined the water of crystallisation of many salts, and the alcohol in alcoholic compounds of salts, and made some attempts to explain the conversion of alcohol into ether by sulphuric acid, an investigation that had been commenced by Liebig, and was afterwards successfully settled by Williamson.

The subject, however, which occupied most of Graham's attention was diffusion of gases and of liquids. Observations upon the diffusion of gases had been made by Priestley, and also by Döbereiner in 1825, but it was Graham who defined the law that the velocity of diffusion of gases is inversely proportional to the square roots of their densities, and who gave the explanation of it.

Graham conducted his experiments on the diffusion of gases in a wide straight tube, closed above by a disc of plaster or

graphite. This tube he filled with the gas over a mercurial trough, the mercury being kept constantly at the same level within and without the tube. After a measured time the volume and composition of the gas in the tube was determined. In this way he found that the velocity of diffusion is inversely proportional to the square root of the density of the gas.

The explanation depends upon the mechanical theory of gases. The molecules of a gas never move in straight lines till they come in contact with each other or the walls of the vessel. If these walls have sufficiently large intermolecular spaces to permit of the passage of a molecule of gas; some molecules will pass through, while others will rebound, and molecules from the external atmosphere will in like manner penetrate inwards. If the density of the gases on the two sides of the partition is equal, the number of molecules passing in equals the number passing out: but if the gases are of different densities, molecules of the lighter gas pass through more readily, because they strike on a given area more frequently than those of a heavier gas, and consequently the opportunities of passing through are also more frequent.

The reason why the molecules of a lighter gas must be believed to strike more frequently will be evident when it is remembered that according to the dynamical theory of gases, pressure is the result of the continuous showering down of the molecules on the sides of the vessel, and since the molecules of different gases have different weights, the lighter molecules must move with greater velocity than the heavier, in order to produce the same amount of pressure.

Graham allowed hydrogen and oxygen separately to escape through a very fine hole in a plate of platinum. He found that the hydrogen atoms moved out four times as fast as the oxygen atoms. He also observed that heat increases the velocity of the atomic motions, at the same time that it increases the force with which a given weight of gas resists the pressure upon it.

The power which some gases have of passing a membrane,

or a sheet of indiarubber, or sheets of metal which are destitute of pores, is an entirely different phenomenon, since the lighter gases in these instances do not penetrate most rapidly. Metals which transmit some gases speedily do not transmit others at all. The gas is absorbed by one surface of the film or plate, transmitted to the other surface by liquid diffusion, and volatilised into the air or vacuum. This phenomenon is related rather to liquid diffusion than to gaseous, and to occlusion. In each case a selective power on the part of the metal is manifested.

Graham's study of the condensation of gases by solids led to many remarkable results, amongst which may be mentioned his formation of alloys of hydrogenium, through the absorption of hydrogen by palladium and other metals, and his recognition of that hypothetical substance as a metal, and determination of its properties.

On the subject of liquid diffusion Graham also did some important work. He observed that if a coloured solution of sugar be placed at the bottom of a glass of water, graduated into equal divisions, the colour gradually extends upwards through the water in the upper portion of the glass, although the sugar solution is heavier than the water. This spontaneous mixture he called diffusion, and by removing the liquid occupying the different divisions of the vessel, and ascertaining the extent to which diffusion had taken place after stated intervals, he was able to define the laws by which the process was regulated. These may be stated as follows :—

1. Different quantities of a salt, dissolved in the same quantity of water, give proportionate amounts of diffusion.
2. The rate of diffusion increases in proportion as the temperature rises.
3. The rate of diffusion diminishes gradually as time elapses.
4. In mixtures each constituent diffuses independently.
5. Bodies are divisible as regards diffusibility into two classes :—

(1) *Crystalloids*, or crystalline bodies, which are

readily diffusible, as common salt ; and (2) *Colloids*, or gelatinous bodies, which are much less diffusible, as gum arabic.

6. Equal rates of diffusion are often shown by members of isomorphous groups.

These studies of the spontaneous movements of liquids led to practical results. Graham found that by interposing a septum of colloid material between a mixed solution and water, the crystalloid bodies diffuse through the septum, while the colloid bodies do not. This process of separation is termed *dialysis*. By means of it, Graham discovered soluble forms of the colloid bodies hydrogen silicate ( $H_4SiO_4$ ), ferric hydroxide ( $FeH_3O_3$ ), tungstic and molybdic acids, alumina, and others, which had been previously known only in the pectous state.

Graham considered the difference between crystalloids and colloids to depend on differences of molecular structure. He regarded the unit of a colloid as formed by the coalescence of a large number of molecules, hence their instability, and at the same time their inertness. Ice is a crystalloid, but when found in contact with water at zero it possesses colloid properties.

Another English chemist of this period was Henry Deacon (1822—1877). He was born in London, where he had the advantage of being taught chemistry by Faraday at the Royal Institution. He was trained as an engineer, but did some important work for chemistry. He patented a process for the formation of chlorine by passing hydrochloric acid gas and steam over cupric chloride ( $CuCl_2$ ), diffused upon bricks or coke.

Deacon made a study of chemical forces, and held that the theory of the parallelogram of forces is equally applicable to these as to mechanical forces. As a body moving to a point in a south-easterly direction need not first move due south and then due east, but may proceed uniformly south-east, so a substance formed by the reaction of two chemical forces may be the direct resultant of the two forces, and need not be supposed to be formed only by the decomposition of some necessary

intermediate body. The application of this doctrine to the chemistry of the carbon compounds had important results.

It is now needful that we should return to German chemists. Geheimrath Gustav Robert Kirchhoff (1824—1887) was born at Königsberg, in Prussia, and was educated at the local university, where he graduated in 1847 as Ph.D. After being a privatdocent at Berlin University, he was appointed in 1850 Extraordinary Professor of Physics at Breslau, and in 1854 Professor of Physics at Heidelberg. In 1874 he was transferred to Berlin, where he died. For some years prior to his death he was unable to lecture, owing to the effects of an accident which he had sustained at Heidelberg many years previously.

Kirchhoff dealt mainly with physical and electrical problems. His *Gesammelten Abhandlungen* was published in 1882; *Lectures on Dynamics* in 1876; and *Untersuchungen über das Sonnenspectrum* in 1862. This last was his chief book, and had an important influence on chemistry. It was based on his work with Bunsen between 1859 and 1860 on spectrum analysis. This process provided a new and perfect means of detecting small quantities of elements, whether known or hitherto unknown, available not only for the detection of minute quantities in our own world, but also for distant worlds. Its only requisite is a ray of light from a heated body. Kirchhoff did not invent this invaluable process, but he was the first to describe it fully, and to give an account of its theory.

Friedrich August Kekulé (1829—1896) was born at Darmstadt, and while studying architecture at Giessen came under the influence of Liebig. He then visited Paris, Switzerland, and England, finally studying chemistry at Heidelberg. In 1858 he was appointed Professor of Chemistry at Ghent, and in 1865 was transferred to Bonn, where he died. He published many papers in the *Annalen der Chemie*, of which he was editor, and also an excellent *Lehrbuch der Organischen Chemie* (1861—1887).

Kekulé is intimately associated with the doctrine of the *linkage of atoms*, to which we shall have occasion to refer later.



The subject need therefore be only mentioned here. After Frankland had enunciated the theory of atomicity, Kekulé declared carbon to be tetravalent, and then set forth his doctrine of the linkage of atoms. He said that in a substance containing several carbon atoms it must be assumed that some of the affinities of each carbon atom are bound by the affinities of the atoms of other elements in the substance, and some by an equal number of the affinities of the other carbon atoms.

But he engaged in other research of great moment. His theory of the constitution of benzene founded on the linkage of



FIG. 102.—Friedrich August Kekulé.

atoms has been called "the most brilliant piece of prediction to be found in the whole range of organic chemistry." It has led to the elucidation of the constitution of the aromatic compounds, and to new methods which amongst other things have conduced to the development of the coal-tar colours, and to the preparation of artificial and synthetic medicines.

We have now reached a period at which we find all the principal doctrines propounded, upon which the modern development of organic chemistry has been based. At this point, therefore, we shall close our account of the history of the chemistry of the carbon compounds. Much excellent work in this department of the science was done during the latter half of the nineteenth century, especially in the synthesis, or building up from their constituents, of organic compounds, and in the production of substances useful in the arts and medicine. But this work is not yet historical; we stand too near to it to see it aright, and to assign to it a true position in the science, and

consequently to extend further this portion of our subject would serve no good purpose.

We shall now proceed to consider the application of chemistry to physiology and to agriculture ; to discuss some of the more important philosophical doctrines ; and to furnish an outline of the history of the chemical elements. Having done this, our task will be at an end.

## CHAPTER XLII

### PHYSIOLOGICAL CHEMISTRY

THE development of the chemistry of animal and vegetable physiology proceeded along four main lines—respiration, circulation, digestion, and fermentation. Other functions of animals and vegetables were studied, but it was in connection with these four that the most important discoveries were made. It will, therefore, be convenient in tracing the history of that development to follow in general the same divisions of the subject. A few words, however, must be said by way of introduction, although we have already mentioned some of the facts. Animal physiology was in particular the field of study of the Iatrochemists. François de la Boë, otherwise Franciscus Sylvius (1614—1672), was led by the work of Glauber to study salts, and was the first to prove the presence of volatile alkali (ammonia) in plants. He looked at the phenomena of life from a purely chemical point of view. Like Van Helmont, he explained many of the operations of the living body as due to a kind of fermentation, but his idea of fermentation was quite different from that of Van Helmont. The latter, who founded his opinions upon vinous fermentation, attributed the change to a subtle and peculiar agency, wholly different in kind from ordinary chemical action. Sylvius, on the other hand, connected the escape of bubbles of gas with an essential change, analogous to the spontaneous effervescence, which occurs when an acid is poured over an earth or over chalk. He actually used the word "effervescence" occasionally in place of the word "fermentation." Van Helmont knew the acid gastric juice of the stomach and the alkaline bile, but Sylvius also recognised the importance of the salivary secretion in digestion, and the pancreatic juice, whose action was investigated by some of his pupils. Sylvius even attributed

much of the change which takes place in the stomach to the saliva swallowed along with the food, rather than to any ferment secreted by the stomach itself. Saliva, he thought, caused the first stage of fermentation, while the second was due to the interaction of the bile and the pancreatic juice.

We see, then, that Sylvius and his pupils identified physiological fermentation with chemical effervescence. They also recognised that the inspired air enters the blood. Sylvius did not know how the air did so, but thought that a change was brought about by there being dispersed in the air nitrous and sub-acid particles, which are able to condense the rarefied and boiling blood, and so restrain its ebullition. Although he could not explain the various chemical changes, he believed in them, and discarded the idea of subtle influences and occult agencies, such as the *Archæus* of Paracelsus.

Not long after the death of Sylvius, Becher put forward his views respecting the essential principle of fire. He was succeeded by Stahl, who asserted that much of the action in the animal body is due not to physical chemical laws, but to a sensitive soul, that makes itself felt in even the simplest changes of the body. This soul works directly on chemical processes, without the intervention of *Archæus*. It is not a mortal thing associated with an immortal mind, but is itself an immortal principle, coming to the body at birth, and at death returning whence it came. He wrote a treatise "On the Real Difference between a Chemical Compound and a Living Body," in which he argued that the soul builds up the body, and makes use of it for its own ends. He admitted fermentation as a property of non-living things, and regarded putrefaction as a sort of fermentation possible in dead things. His teaching laid down as general principles that we should learn as much as possible of the chemical and physical processes going on in the living body, as well as in non-living bodies, but we are not to conclude that the changes which we see taking place in a non-living body will also take place in a living body. He said that although the events of the body may be rough-

hewn by chemical and physiological forces, the phenomena are modified by the soul. This doctrine of the "sensitive soul" is the same as the "vital principle" of somewhat later times.

Considering now the processes of respiration and circulation, we find that before Boyle's period, the old Galenical doctrine of respiration asserted that the air introduced by breathing served to maintain and at the same time to temper or cool the innate heat of the heart. That fire, placed in the heart at the beginning, continued there during life, and was the one source of the warmth of the body. The pumping action of the chest introduced into the blood the air which was necessary for the generation in the left side of the heart of the vital spirits, and these were then distributed by the arteries. The same pumping action got rid of the fuliginous vapours, the products of the innate fire burning in the heart. Both the pure air and the foul vapours were supposed to pass by the pulmonary vein, the one moving in one way and the other in another.

Harvey disposed of this absurd idea of two currents passing in opposite directions along the same vein. Borelli cleared up the mechanical problem and rejected the whole chemical aspects of breathing. He showed that air does not enter the pulmonary vein, but he yet maintained that it does somehow find its way from the lungs into the blood, assumed the existence of minute pores, and insisted that air inhaled by breathing is the chief cause of the life of animals, and is far more essential than the working of the heart. He quoted Boyle's experiment of removing air, when animals immediately die; but if the air be instantly renewed they may be brought to life again. This exposition of Borelli was published in 1681.

In 1660 Boyle showed by means of the air-pump, in the course of his investigation of the spring of the air, that in a vacuum a burning candle ceased to burn and a mouse died. Robert Hooke proved that the essential business of respiration is carried on in the lungs, and that the movements of the chest are only useful in causing external expansion and collapse of the lungs. He demonstrated that an animal can be kept alive by the bellows



without any pumping of the lungs. The essential feature, in short, was a supply of fresh air to effect a continuous change in the blood. At the same time Richard Lower, assistant to Willis, prolonged life by the transfusion of aerated blood, and stated his belief that the change of colour in blood, from venous to arterial, took place in the lungs, and was simply due to the exposure of the blood to the action of the air. Hooke's experiment gave practical confirmation to Lower's supposition.

Neither Lower nor Hooke had any conception that a part only of the air was taken. At that period air was considered a single substance. It remained for John Mayow, a Cornishman, like Lower himself, to show in 1688 that not the whole air, but only one-fifth part of it, the *spiritus nitro-aereus*, of which we have already spoken, was useful in respiration. He showed also that this part of the air is essential to combustion, and is identical with the "*spiritus acidus*" portion of nitre, not being contained in the "*sal alkali*" portion. Mayow thus sums up the conditions necessary for combustion, which in some respects are analogous to those essential to respiration :—

“ Concerning fire, it must be noted that for the ignition of this it is necessary that ‘igneo-aereal’ particles should either pre-exist in the thing to be burnt, or should be supplied from the air. Gunpowder is very easily burned by itself, by reason of the igneous-aereous particles in it; vegetables are very easily burned, partly by reason of the igneous-aereous particles existing in them, and partly by help of those brought to them by the air. Purified sulphureous matter, on the contrary, can be burned only by the help of igneous-aereous particles brought to it by the air.”

Mayow noted that antimony burnt by a burning-glass increases considerably in weight, and said :

“ Now we can hardly conceive that the increase of weight to the antimonium arises from anything else than from the igneous-aereous particles inserted into it during the calcination ”; and further on, “ Indeed, I have found by observation that an animal shut up in a flask together with a candle will continue to breathe for not much more than half the time it otherwise would, that is, without the candle.”

He means, of course, a *lighted* candle.

When a small animal is made to breathe in a closed vessel standing over water, the water rises.

“I have found,” says Mayow, “by experimenting with various animals, that air is, by the breathing of animals, reduced in volume by one-fourteenth, when it dies for want of air, just in the same way that it is diminished by the burning of a flame. We may infer that animals deprive the air of particles of the same kind.”

The chemical meaning of Mayow's discoveries was soon forgotten because his chemical exposition was premature. His physical exposition of the elastic force of the particles of air continued to be spoken of, and in his tract on respiration he explains that air enters the lungs during breathing, because the pressure or elastic force of the atmosphere drives in air to fill up the increased space afforded by the dilated thorax.

Mayow's teaching is almost fit for a text-book of the present day. He says :

“It is evident that something necessary for sustaining life passes from the air into the blood. Hence, air which has been already breathed, is exhausted of these particles of an elastic nature. . . . The union of the nitro-aereal particles taken in by breathing and the salino-sulphureous particles of the blood, gives rise to the heat of the blood. The greater heat which accompanies violent exercise is due to the increased effervescence caused by the greater supply of nitro-aereal particles during the increased respiration. . . . About respiration, it is to be noted that this serves a further purpose, namely, that together with the air driven out of the lungs, the vapour of the blood agitated by the fermentation is blown away also.”

He was here on the track of carbon dioxide ( $\text{CO}_2$ ), but failed to arrive at the conception of something being expelled from the blood into the pulmonary vesicles. For a hundred years the chemical work of Mayow passed from the knowledge of the world, to reappear with a new dress in the last years of the eighteenth century.

Regarding digestion, Boerhaave in his *Institutiones Medicæ*

(1706) recognised that this process is in part a solution of some of the constituents of the food by means of various juices. Saliva, the gastric fluid, bile, the pancreatic and intestinal juices, all take part in an operation of ordinary solution, rather than of fermentation.

Réaumur, of thermometer fame, experimented on the digestion of food by birds and dogs. He proved that the gastric juice dissolved various constituents of food, and that it did so, not by inducing putrefaction, but by some process which was antagonistic to putrefaction.

Spallanzani, Professor of Natural History in the University of Pavia and afterwards at Padua, took up Réaumur's method, namely, acting upon food by gastric juice drawn by means of a sponge from various sorts of animals, and also by passing spheres or tubes containing food into the stomachs of different animals, which he opened after the lapse of a given time. He also made animals swallow bits of meat attached to threads or wires, which he could after a time withdraw. On himself he experimented by swallowing linen bags containing food, and examining the contents after they had been voided *per anum*. He even ventured to swallow perforated tubes of wood containing food. In these ways he confirmed and extended Réaumur's results, and found that trituration is merely a preparation for solution, and does not in itself constitute the digestive process. He was led by numerous experiments to the conclusion that while gastric juice is a solvent of all kinds of food, the juice of any particular animal is specially active on the natural food of that animal.

Spallanzani obtained from his colleague Scopoli, Professor of Chemistry at Pavia, the earliest analysis of gastric juice. This was Scopoli's report:—

“ The fluid contains, firstly, pure water: secondly, a saponaceous and gelatinous animal substance: thirdly, sal ammoniac: and fourthly, an earthy matter, like that which exists in all animal fluids. It precipitates silver from nitrous acid, and forms *luna cornea*. These phenomena might

induce us to suppose that common salt exists in the gastric juice: but the salt contained in this fluid is not common salt, but sal ammoniac.

He failed to find that gastric juice is acid, but asked himself whether, since it curdled milk, it might not contain some acid in a latent form.

Contemporaneously with Spallanzani, John Hunter was investigating digestion from 1772 till 1786. He attributed the action of the gastric juice to a vital principle, and was of opinion that digestion was not due to fermentation, but to a superior power—neither fermentation, nor chemical solution, but a species of generation—two substances making a third, the chyle. He attached importance to the acidity of gastric juice.

Stephen Hales returned to the problems of respiration. He observed that breathing through diaphragms of cloth dipped in alkaline solution made the air last longer for the purposes of life. Joseph Black, after discovering “fixed air” (carbon dioxide), proved that (1) it was given off in fermentation; (2) it was the product of burning charcoal; and (3) (what immediately concerns our present subject) it was present in *expired air*. He convinced himself that the change produced on wholesome air by breathing consisted in the conversion of part of it into fixed air. Animals made to breathe fixed air died. This opinion was published in 1757.

Priestley, after his discovery of oxygen in 1774, demonstrated that blood exposed to it, or, as he said, to “dephlogisticated air,” gave up its phlogiston, and became bright arterial dephlogisticated blood. Arterial blood exposed to phlogisticated air (nitrogen) became phlogisticated, dark, and viscous. But even Priestley did not understand that fixed air was produced by the lungs.

In this matter, as in regard to combustion, the real facts of the case were seen by Lavoisier, who gave in 1777 a correct explanation of the phenomena. In 1775 he had clearly expounded respiration as a combustion, producing heat by the

burning of the constituents of the body with oxygen, and converting them into carbon dioxide and water. He made the mistake of supposing that this combustion takes place in the bronchii. "There transudes into the bronchii," he said, "a humour which is secreted from the blood, and which is presumably composed of carbon and hydrogen." This view was accepted for a time, but Spallanzani explained that it is the tissues and the body as a whole which consume oxygen and produce carbon dioxide. He thus overthrew Lavoisier's theory of hydrocarbonous secretion.

We shall now return to the question of fermentation. After many conflicting views had been expressed, the whole subject was elaborately discussed by Dumas. During the first seventy years of his life the following explanations of fermentation had been proposed :—

1. The physiological explanation, which ascribes fermentation to the life processes of the cell.
2. The theory that the decomposition of sugar, for instance, depends upon the fluid in the cell passing out into the sugar solution.
3. Berzelius's explanation, catalytic or contact action.
4. Liebig's theory, which ascribes fermentation to chemical changes under the influence of putrefactive ferments.

The researches of Dumas showed, contrary to the theory of Liebig—

- (i) That chemical actions which are brought about in sugar solutions are not in a position to change sugar into alcohol and carbon dioxide. The actions which fermentation shows take place neither through aqueous, oily, nor metallic fluids, nor even through their membranes. In superposed layers of fluids, the action never extends from one layer to another.
- (ii) That the view of Berzelius was, in face of the facts, quite untenable—that if certain salts are present, ferments, and a mixture of water and sugar can remain together inactive, without fermentation taking place.

According to Dumas, fermentation in its simplest form, sugar and yeast, is proportional to the quantity of the former.



It is not a process of oxidation, but a reduction process. This is shown by the fact that sulphur in fermenting liquids becomes sulphuretted hydrogen ( $H_2S$ ). Neutral gases are without effect. The action of acids, bases, and salts either accelerates, delays, disturbs, or suspends the fermentation, according to circumstances, but acceleration is rare. Very dilute acids in quantity are without effect, while fermentation is delayed by dilute alkalis, even in small quantities, and is suspended by larger quantities. Alkaline carbonates, however, unless in large quantities, do not delay the process; carbonates of alkaline earths and most other salts, even in large quantities, have no effect; but a few salts, such as potassium silicate and borax, coagulate the yeast and stop fermentation. It thus appears that chemical action, although unable to start fermentation, can nevertheless modify it. Dumas also investigated ferments of a second class, such as diastase, synaptase, and the myrosins, which are destroyed during their action.



FIG. 103.—Louis Pasteur.

Little has been done to advance our real knowledge of fermentation beyond the research of Dumas. Liebig worked earnestly, and gave us in 1848 some additional information. He followed Stahl in regarding fermentation and putrefaction as analogous processes; but his explanations did not gain lasting acceptance. It remained for the investigators of microbes, starting with Leuwenhoek in 1680, continuing through Schwann and Carignard Latour in 1838, Bastian, Tyndall, Frankland, Pasteur, and a long list of names still familiar in our ears, to give further insight into the subject of ferments. Even now, however, the same sort of doubt

and controversy remains. The question is still an open one, whether it is the action of the growth of the living-cell, or a chemical substance incidental to cell growth, which is the true ferment, or whether both kinds—the living physiological and the dead chemical agent—have each its own separate and independent position, and are both true causes of fermentation.

We recognise, as Dumas did, that no chemical substance ferments except in presence of water, and unless it is kept by means of the water in contact with some specific ferment. Alcohol in quantity will stop fermentation, and even small quantities of certain substances—sulphurous acid, carbon disulphide, phenol, corrosive sublimate, and others—have the same effect, more or less completely. Perfectly pure grape sugar will not ferment, unless started by at least temporary contact with air, and Mitscherlich showed that while the liquid contents of a yeast cell will convert cane sugar into glucose, the cell does not ferment the glucose into alcohol and carbon dioxide.

Such is the history of the development of opinion in regard to those processes of animal and vegetable physiology. The history of the investigation of the composition and chemical attributes of animal and vegetable substances forms a part of the chemistry of the carbon compounds.

## CHAPTER XLIII

### AGRICULTURAL CHEMISTRY

THE rise of agricultural chemistry was necessarily contemporaneous with the rise of scientific agriculture. As there was really no science of agriculture until the latter part of the eighteenth century, it follows that the division of chemistry applicable to the cultivation of the soil has had a short history.

The cultivation of the soil has been one of the great industrial arts from the earliest times. Men have always had to till the ground, if they wished to reap crops, but the old system of tillage was a rough one handed down from generation to generation, often erroneous and always wasteful. In Great Britain it cannot be said that the scientific side of agriculture received adequate consideration until after the Union of the Crowns in 1603. It is true that Tusser, who may be termed the father of modern agriculture, and who was the author of the *Hundred Points of Husbandry*, lived in the preceding reign of Elizabeth, but the admirable advice which he gave to farmers received little attention in his own day. It was only after increasing wealth and increasing population created a demand for more and better food that farmers endeavoured to meet the demand by the scientific cultivation of their holdings.

Towards the middle of the eighteenth century an improved system of agriculture spread over the land. Regular rotation of crops was introduced, turnips were sown in drills or rows, instead of broadcast, better implements were constructed, and a more judicious manner of breeding stock was adopted. To carry out these new methods, farmers began to see that a systematic training was needed. In 1790 a chair of agriculture and rural economy was established in the University of Edinburgh, and twelve years later the Board of Agriculture,

as we have already seen, invited Sir Humphry Davy to deliver a course of lectures on agricultural chemistry. Although a few chemists prior to Sir Humphry had devoted attention to the aspect of the science which had reference to agriculture, the recognition of a distinct branch of chemistry, dealing with plants and soils, may be said to date from this period.

Sir Humphry lectured between 1802 and 1812, and the lectures were published later, with alterations and additions rendered necessary by advances that had been made in chemical science. In these lectures he recognised the importance of agricultural chemistry.

“All varieties of substances found in plants,” he says, “are produced from the sap, and the sap of plants is derived from water, or from the fluids of the soil altered by, or combined with, principles derived from the atmosphere. Soils in all cases consist of a mixture of different finely-divided earthy matters, with animal or vegetable substances in a state of decomposition, and certain saline ingredients. The earthy matters are the true basis of the soil; the other parts, whether naturally or artificially introduced, operate in the same manner as manures. Four earths jointly abound in soils; the aluminous, the silicious, the calcareous, and the magnesian. These earths, as I have discovered, consist of highly inflammable metals united to pure air or oxygen; and they are not, so far as we know, decomposed or altered in vegetation. The great use of the soil is to afford support to the plant, to enable it to fix its roots, and to derive nourishment by its tubes, slowly and gradually from the soluble and dissolved substances mixed with the earths. That a particular mixture of the earths is connected with fertility cannot be doubted, and almost all sterile soils are capable of being improved by a modification of their earthy constituents.”

Sir Humphry described the simplest method known of analysing soils to ascertain the constituents and chemical ingredients which appear to be connected with fertility. In the previous century it was supposed that minute earthy particles supplied the whole nourishment of the vegetable world, and that manures acted in no other way than in ameliorating the texture of the soil. Their agency was thought to be

mechanical. But after the time of Cavendish, it was shown by Saussure and Hassenfratz's experiments that animal and vegetable matters deposited in soil are absorbed by plants, and that neither water, nor air, nor earth supplies the whole of the food of plants, although they all operate in the process of vegetation. Water acts as a solvent, vegetables decompose the carbonic acid gas of the atmosphere in the sunshine, and saline manures furnish a part of the true food of plants. The use of gypsum, particularly in the growth of clover, was recognised; slaked lime had been used by the Romans for manuring the ground in which fruit trees were grown; and marl had been employed by the British and the Gauls from the earliest times as a "top-dressing." Davy says that—

"chalks and marls or powdered limestones are useful earthy ingredients of fertile soil, and their efficacy is proportionate to the deficiency of calcareous matter; but quartz or calcined magnesia are prejudicial to vegetation."

The advantage of "fallowing" was understood by Davy, and he remarks that two opinions were current respecting the nature of heat. By one school it was considered to be a peculiar subtle fluid, of which the particles repel each other, but have a strong attraction for the particles of other matter. By another school it was considered as a vibration of the particles of matter, which differs in velocity, producing different degrees of temperature.

Soils, as we have said, are mainly useful for giving support. The portion which is absorbed by plants must always be in a fine state of subdivision, but the proportion of these absorbed particles should be very small. In all cases the ashes of plants contain some of the earths of the soil in which they grow. A black soil, containing much vegetable matter, is most heated by the sun and air. On analysis, plants are found to consist principally of charcoal (carbon) and aeriform matter. They give out by distillation volatile compounds, the elements of which, according to Davy, are pure air (oxygen), inflammable air (hydrogen), coaly matter (carbon), and azote (nitrogen).



These elements they gain, either by their leaves from the air, or by their roots from the soil. All manures from organic substances contain the principles of vegetable matter, which during putrefaction are rendered either soluble in water, or aeriform, and so capable of being assimilated by the organs of plants. Neither carbon, nor hydrogen, nor nitrogen alone will suffice, but all of them together, in various states and various combinations.

“It has generally been supposed,” says Davy, “that gypsum, alkalis, and saline substances act as condiments or stimulants in the animal economy, and that they render the common food nutritious. It seems much more probable that they supply a part of the true food of plants, and supply that kind of matter to the vegetable fibre which is analogous to the bony matter in animal structure.”

Davy's experiments favoured the opinion that soluble matters pass unaltered into the roots of plants, and in consequence that water is essential to vegetable growth; the action of the roots is not selective, poisons being absorbed as well as useful substances. The great object in the application of manure, therefore, should be to make it afford as much soluble matter as possible to the roots of the plants.

At the period when Sir Humphry Davy was lecturing on agricultural chemistry, it was popularly believed, although not universally accepted, that plants under the influence of sunlight absorb carbonic acid gas (carbon dioxide), decompose it, and exhale oxygen, while the reverse process takes place in the dark. It is now known that this is only a very rough, and not invariably correct, generalisation. Thirty years later, in Liebig's time, great importance was attached to humus, as the principal food of plants, absorbed from the soil by the roots. Experiments and calculations, however, have shown: (1) that the largest conceivable proportion of humus absorbed could not introduce more than a very small proportion of the carbon actually produced in vegetation; and (2) that humus in the form in which it exists in the soil is not absorbed, and

does not yield the smallest degree of nourishment to plants. The mistake arose through the crude observation that dark soils rich in humus are always very fertile.

Saussure's investigations established the belief that the carbonaceous material of plants is derived from carbonic acid gas, although it was not known in what way the change took place. The rotation of carbon and other elements between plants and animals was clearly established before 1845. The carbonic acid gas is mainly derived from the air, but a small quantity in solution is constantly absorbed by the roots. During the night carbonic acid gas is accumulated in all parts of plant structure, and decomposition begins when the rays of the sun strike the growing plants. It has to be observed, however, that humus exposed to the air by tilling and loosening supplies an atmosphere of carbonic acid gas.

Next to Davy, no one has done more for agricultural chemistry than Baron von Liebig. His most important influence on agriculture was his recognition of the necessity of a sufficient, though small, supply of mineral matter as part of the essential food of plants, and his observation that most soils contain very small proportions of these soluble mineral constituents, which are soon expended by continual cropping and removal of the crop, while, on the other hand, carbonic acid gas is furnished spontaneously by Nature. He made analyses of the ashes of plants, and introduced the practice of applying to the land manures containing potash salts, lime, and phosphates.

Liebig believed that ammonia, or nitrogenous matter yielding ammonia, was mainly a stimulus, increasing the growth of leaves, and in that way increasing the plant's power of dealing with carbonic acid gas. He proved by experiment the presence of ammonia in rain water, but he and his followers applied ammoniacal salts as manures in conjunction with mineral salts.

The action of light was not well understood in Liebig's time. The conversion of starch into sugar was recognised as

a hydrolytic action, but the chemists of that period had no conception of the way in which carbonic acid is transformed either into starch, or sugar, or any other vegetable matter. The synthesis of sugar by Fischer, and the formation of formaldehyde from carbonic acid, have rendered it easy in modern times to conceive that carbonic acid gas may be reduced to formaldehyde, and then polymerised to formose, from which all other plant constituents may conceivably be produced. The only thing remaining to be determined at the present day is by what agency light falling upon the green parts of plants reduces carbonic acid to formaldehyde. Such conjectures are very easily formed, but very difficult to verify by experiment.

From Liebig's time onwards the supplying of artificial manures has been an important industry, and has resulted in greatly increasing the yield of food crops by most soils. Opinion has varied from time to time as to the source of plant nitrogen. The investigations of Liebig naturally led to the belief that it is mainly derived from ammonia or nitrates, through the roots of the plants. The recognition of microbes in the nodules of roots, especially of clover and other leguminous plants, proved that ammonia salts and other nitrogenous matter is converted by these roots into nitrates, and taken up by the sap of the plant in that soluble form. On the other hand, however, it has more recently been established, without leaving much room for doubt, that leaves have the power, in some plants at any rate, of absorbing nitrogen from the air.

It is thus apparent in the brief history of agricultural chemistry, as in the longer history of the science in general, that there has been much diversity of opinion in regard to matters of principle. But if there has been much diversity of opinion as to theory, there has been still more as to practice. While the judicious application of suitable chemical manures in appropriate quantities has a beneficial influence upon crops, it is quite possible to overdo such application. The commercial zeal of rival manufacturers has in many cases forced the use of chemical manures without sufficient regard to measure

or propriety, with the result that serious injury has been done to the soil. The right understanding of the relation between soils and manures is a matter of study. With the extension of technical classes and laboratories, excessive use of chemical applications will be restrained, and mistakes will be avoided. Agricultural chemistry will then be esteemed one of the most important technical branches of the science.

## CHAPTER XLIV

### THE DOCTRINES OF ATOMICITY AND VALENCY

HAVING now considered the history of chemistry, both in the direct line of research and discovery, and also in the principal divisions of the science, we shall proceed to give some account of the development of the leading doctrines of modern chemical philosophy. These have already been mentioned more than once, but have not yet been explained. For this purpose we have selected :

1. The doctrines of atomicity and valency.
2. The doctrine of isomerism.
3. The doctrines of chemical affinity and kinetics.
4. The doctrine of bases, acids, and salts.

It must be kept in mind that it is not our purpose to discuss these subjects at length, as part of the philosophy of chemistry, but merely to trace their development as branches of chemical knowledge. Consequently, we shall not enter into the details of the several doctrines further than is necessary to render intelligible an account of their development, and we shall use the privilege which we have exercised in similar instances, of stating philosophical theories with greater breadth and freedom than we should do in a purely philosophical treatise.

Speaking broadly, therefore, we understand by the *Atomicity* of a chemical element its power of combining with other elements in equivalent proportions ; by its *Valency* or *quantivalence*, the difference between that element and other elements in their respective powers of combining with hydrogen as a standard. Thus :

1. Hydrogen, chlorine, bromine, iodine, and fluorine combine with hydrogen *atom for atom*, and are termed *Monovalent elements* or *Monads*.



2. Oxygen, sulphur, selenium, and tellurium combine with hydrogen in the proportion of one atom of the element to two of hydrogen, and are termed *Divalent elements* or *Dyads*.
3. Nitrogen, phosphorus, and arsenic combine with hydrogen in the proportion of one atom of the metal to three of hydrogen, and are termed *Trivalent elements* or *Triads*.
4. Carbon and silicon combine with hydrogen in the proportion of one atom of the element to four of hydrogen, and are termed *Tetravalent elements* or *Tetrads*.

As few compounds of metals with hydrogen are known, their valency is judged by the standard of chlorine. Thus, potassium combines with chlorine atom for atom; calcium takes two atoms of chlorine to one; antimony takes three atoms of chlorine to one; and tin takes four atoms of chlorine to one. Even in the case of compound radicles, such as hydroxyl (HO), sulphuryl (SO<sub>2</sub>), and others, we find their combining power monovalent, divalent, or trivalent, like that of the simple elements. Such being the general conception of the doctrine, we shall now inquire how it attained its present shape.

Every student of elementary chemistry knows that some elements combine with each other in only one proportion, while others combine with each other, and with other elements, in more than one proportion. A replacement of more than one atom of hydrogen by a single radicle having been originally observed in the case of polybasic acids, such radicles were at first called polybasic. When it was perceived that these radicles were not confined to the class of acids, the term was deemed inaccurate, and was changed to polyatomic, polyhydrogenic, or polyvalent. For example, ethylene, or olefiant gas, is divalent in its alcohol (glycol) and other compounds. To prevent confusion it must not be forgotten that the term "polyatomic" was originally used in another sense by Berzelius in 1827—namely, to denote the character of the atoms of fluorine, chlorine, and other substances, many atoms of which could combine with a single atom of another element. When

the new term was introduced, the doctrine of polyatomicity, or as it is better expressed multivalence, was extended from acids to elements.

As early as 1852 Frankland called attention to the symmetry in the compounds of certain groups of elements; for example, the compounds of nitrogen, phosphorus, antimony, and arsenic, which show a tendency to combine with three or five atoms of other elements, and therefore a tendency on the part of these elements to have their affinity or combining power always satisfied by the same number of atoms. This statement of Frankland is the basis of what came to be called the doctrine of atomicity.

According to this doctrine the elements were at first classed as mono-, di-, tri-, and tetr-atomic, but as the phrase "a diatomic atom" is absurd, the terms mono-, di-, tri-, and tetra-valent are preferable. In Latin, these are uni-, bi-, ter-, and quadri-valent, or in German ein-werthig, zwei-werthig, etc. Odling suggested the terms monad, dyad, triad, tetrad, pentad, hexad, and so on, and grouped the monads, triads, and pentads as perissads or uneven elements, and the dyads, tetrads, and hexads as artiads or even elements.

The recognition of quantivalence aided the growth of the Type Theory, but that hypothesis led to the idea that the atoms of each element possessed a constant atom-fixing power. This idea is not supported by facts, although Kekulé endeavoured to maintain that the atomicity of an element is constant.

The simplest hypothesis which we can propose to account for the facts of quantivalence is that "every atom of an element has the inherent power of holding in combination a certain number of other atoms." It is necessary, however, to distinguish carefully between affinity and valency. Affinity is the force with which one atom attracts another or others; valency, which has no apparent connection with the strength of affinity, means the number of atoms which are held in combination, not the strength with which these are held.

But the hypothesis just stated is not sufficient to express

all the facts. For instance, phosphorus, which combines with three atoms of hydrogen, and is, therefore, trivalent, in combining with chlorine takes either three atoms (which correspond with three atoms of hydrogen) or five atoms. In its combination with oxygen we have phosphorus oxide ( $P_4O_6$ ) and phosphoric oxide ( $P_4O_{10}$ ). Nitrogen, again, which combines with three atoms of hydrogen, also combines with oxygen in various proportions as under :

Nitrous oxide ( $N_2O$ ) . . . . .	Monad.
Nitric oxide (NO) . . . . .	Dyad.
Nitrogen trioxide ( $N_2O_3$ ) . . . . .	Triad.
Nitrogen tetroxide ( $N_2O_4$ ) or ( $NO_2$ ) . . . . .	Tetrad.
Nitrogen pentoxide ( $N_2O_5$ ) . . . . .	Pentad.

Similar proportions occur in its combination with chlorine and other elements. Some elements, therefore, seem to be both triads and pentads, and others both dyads and tetrads.

An attempt was made to explain these facts by the assumption that there are two kinds of compounds, atomic and molecular. In atomic compounds we have the true chemical compounds, in the usual sense ; while in the molecular compounds the real molecules formed in the ordinary way by the affinity of their elements, whose valency is satisfied by their union, have an attracting and combining power of their own, by virtue of which they combine with each other to form molecular compounds. We find illustrations of this in the combination of the molecules of water of crystallisation with a molecule of a salt ; or the combination of phosphorus trichloride ( $PCl_3$ ) with the molecule ( $Cl_2$ ) to form phosphorus pentachloride ( $PCl_5$ ) ; or in the combination of ammonia ( $NH_3$ ) with the molecule HCl to form ammonium chloride ( $NH_4Cl$ ).

There is some little foundation for this assumption, because phosphorus trichloride is more stable than phosphorus pentachloride, which dissociates by heat into the combining molecules, and ammonium chloride is also an unstable compound, dissociating by heat into ammonia and hydrochloric

acid gas, while crystallised salts lose the water of crystallisation on being heated.

In determining the valency of atoms, atomic compounds only can be used. Hence, phosphorus, nitrogen, and the rest would have to be considered triads, sulphur a dyad, and so on. But phosphorus oxychloride ( $\text{POCl}_3$ ) is just as stable as phosphorus trichloride ( $\text{PCl}_3$ ), and is as much a true atomic compound, and it has been proved by the substitution of methyl ( $\text{CH}_3$ ) and other radicles for the hydrogen in ammonium chloride that all the positions of hydrogen are of equal value. Therefore, phosphorus pentachloride and ammonium chloride are true atomic compounds, and nitrogen and phosphorus are both trivalent and pentavalent.

If we assume that an element can be monovalent, trivalent, and pentavalent, we must look upon it in the highest compound as saturated, while in the others the element is unsaturated. An explanation has been suggested in the supposition that in the unsaturated compounds one affinity-unit, or so-called "bond," is taken up by another affinity-unit or "bond" of the same atom. This double-linkage idea is a useful provisional explanation of some facts—namely, those in which the valency of an element varies by twos—1, 3, 5, or 2, 4, 6.

Another explanation which meets certain cases is that of which we have a supposed example in ferric chloride ( $\text{Fe}_2\text{Cl}_6$ , *i.e.*,  $\text{Cl}_3\equiv\text{Fe}-\text{Fe}\equiv\text{Cl}_3$ ), where two atoms tetravalent, or of higher atomicity, are linked together, so that the double atom is hexavalent—three affinity-units for each atom.

From the view that valency is fixed for each element, we are forced by the consideration of facts, and some chemists have gone to the opposite extreme, thinking that valency is of almost unlimited variation, while there is a prevailing tendency on the part of each element to act with some particular valency. Thus, the triad compounds of nitrogen are, as a rule, more stable than the pentad, and the same remark applies to the other elements. But we find that the preferential valency of a given element is not the same throughout all its

compounds. The triad compounds, for instance, of nitrogen with hydrogen, and of phosphorus with chlorine, are more stable than any other, yet the pentad compounds of the same elements with oxygen are the most stable of their oxygen compounds. Chlorine is preferentially monad with hydrogen, but heptad in potassium perchlorate ( $\text{KClO}_4$ ).

Wurtz employed the term "valency" to signify the power of holding other atoms, which an atom exhibits in any given compound, not the absolute atom-holding power of the atoms of an element. He very justly called attention to the fact, which has been too much overlooked, that the force with which one atom attracts another depends upon the properties not of one, but of both. Phosphorus is, therefore, trivalent to hydrogen, but pentavalent to chlorine, and the cause of the difference lies in the atoms of hydrogen and chlorine, as well as in those of phosphorus.

On the whole, we come to the conclusion that the valency of the elements is a most important property controlling the action of chemical attraction, but that it varies partly with temperature and partly with the nature of the several elements with which the particular element we are considering may be combined. We must never forget that chemical atomic attraction is *reciprocal*. This admitted variation in the valency of the elements is a difficulty in the way of classification in respect of valency, and in this view Mendeléeff's classification according to the Periodic Law is a more distinctly natural one.

There have been put forward three groups of views on valency :

1. Those which regard "an affinity" as an action of some kind proceeding from a definite quantity of matter.
2. Those which regard "an affinity" as a part of an atom, or at least as something connected with a part of an atom.
3. Those which regard the affinities of an atom as definite forms of a motion of the atom.

1. Under the first head comes Erlenmeyer, who stated the rule that "in all chemical combinations a constant quantity



of one element always attracts a constant quantity of another." These constant quantities are the "affinivalencies" of the element; thus the affinivalency of oxygen is 8, of nitrogen 4.7, of carbon 3, and so on. But if three parts of carbon attract one of hydrogen in methane ( $\text{CH}_4$ ), the atom of carbon cannot be homogeneous. There is, however, reason to believe that the atom of carbon is homogeneous, and therefore the whole atom (12) attracts all the four atoms of hydrogen. Hofmann likewise uses language incorrect to some extent in the same way, while L. Meyer fails to distinguish between equivalent and atomic weights. It must not be forgotten, when considering this subject, that *equivalent* weights are relative weights of divisible masses, and are relatively often smaller figures than the atomic weights, while *atomic* weights are relative weights of indivisible masses, of mutually reacting bodies.

2. Erlenmeyer also speaks of mutual actions between atoms as occurring at certain points of these atoms, as if "an affinity" were an action proceeding from a definite quantity of matter. The attracting points must be regarded as qualitatively different from the rest of the atom, some parts being chemically active, others inactive. The shape of multivalent atoms must be such that several parts of one can touch the same number of points of another. Kekulé's graphic formulæ would illustrate this idea, although he did not mean to imply it. If this were true, our conception of an atom would have to be very much changed, unless the difference between one part and another were assumed to be an electrical difference.

Michaelis supposed that the attractive force is exerted in certain fixed directions only, for example, in the straight line



FIG. 104.—August Wilhelm von Hofmann.

joining the two atoms ; but a difficulty arises in attempting to explain what occurs when the atom is bound to less than its full number of other atoms. Van't Hoff's idea was that the affinities are arranged in a different form in space ; but unfortunately we can neither define an affinity, nor assign a geometrical figure to it.

3. Amongst those who regard the affinities as definite forms of motion of the atom, L. Meyer supposed that there is *one position* during its motion in which a monovalent atom, and *two positions* in which a divalent atom, can combine with another atom, and so on, the number of positions corresponding to the degree of valency ; thus, in water ( $H_2O$ ) the oxygen atom swings through *two*, and in ammonia ( $NH_3$ ) the nitrogen atom swings through *three* positions, in each of which it can take up one hydrogen atom. On this theory, the form of the molecule must be determined by the path of the atoms swinging in it, and this again by the valencies of the atoms. But physical and dynamical researches go to show that the forms of molecules depend more on the number of the constituent atoms than on their valencies.

Into the discussion of this question several absurd or erroneous assumptions have intruded. Thus, it has been falsely assumed that those affinities of an atom which are not satisfied by the affinities of another must be satisfied by other affinities of the atom itself, and that no molecule can contain an odd number of atoms of uneven valency. In contradiction to this assumption we have iodine (I), nitric oxide (NO), nitrogen peroxide ( $NO_2$ ), chlorine peroxide ( $ClO_2$ ), nitrogen chloride ( $NCl_3$ ), and others. Then, if by the valency of an atom we mean a "bond," we ultimately land in absurdities. The real meaning of the valency of an atom is the maximum number of other atoms between which and the given atom there is, so far as we know, direct action and reaction. There is no standard by which we can state the "value of a bond," and the whole controversy about equal and unequal bonds is a war of words, not things.

Elements of variable valency exercise the lower valency when combining with those elements for which they have the greater affinity, and the higher valency when uniting with those for which they have but small affinity. Thus, phosphorus is trivalent with hydrogen, but pentavalent with oxygen; sulphur, divalent with hydrogen, but hexavalent with oxygen. It would appear, therefore, that affinity is able to make up in quantity what it lacks in intensity, concentrating itself as it were upon a single point when the elements are most dissimilar, whilst with elements more nearly allied, affinity extends its action, and consequently loses its power.

Valency, however, is not constant. This was proved by Nilson and Pettersson in 1888, when they discovered that the three chlorides of indium ( $\text{InCl}$ ,  $\text{InCl}_2$ ,  $\text{InCl}_3$ ) can all exist in the gaseous state. The determination of the true density of ferric chloride ( $\text{Fe}_2\text{Cl}_6$ ) by Meyer dismissed the supposition that  $\text{FeCl}$  was a compound of tetrad iron.

Electro-chemical theories of valency have not found acceptance. The ability of electro-positive and electro-negative elements to form stable molecules with themselves, and with other elements of the same sign, is fatal to any electro-chemical explanation of the matter.

We find that molecules can combine with other molecules to form very stable compounds; for instance, double salts, and water of crystallisation. The idea of an indefinite residual valency, suggested by Abegg and others, is merely a contradiction of the doctrine of valency, not an extension or explanation of it.

Friend (*J. C. S.*, 1908, 94, p. 201) distinguished three kinds of valency: free-negative, free-positive, and residual or latent. If we accept this, not as a theory, but as a classification of facts, it may be useful.

Since no definite compound of hydrogen with one atom of the same element in two or more proportions is known, hydrides may be taken as the guide to the numerical value of the free-negative valencies of the elements. For example, ammonia

( $\text{NH}_3$ ) and methane ( $\text{CH}_4$ ) are stable and easily prepared, while ammonium ( $\text{NH}_4$ ) and methyl ( $\text{CH}_3$ ) cannot be isolated.

Since oxygen is divalent, and the oxygen compounds do not give a clear indication of the valency of elements, Friend suggested fluorine as the most suitable element for determining the maximal positive valency of the elements, having itself the advantage of being monovalent. Chlorine, fluorine, and oxygen are the only elements which possess free-negative but no free-positive valency. It has been thought that metals possess free-positive valency only. Most of the other elements are amphoteric—that is, possess both free-negative and free-positive valencies; but it is not correct to assert, as has been done, that the sum of the negative and positive valencies is always 8. We can only say that it is *often* 8.

Residual or latent valency is positive and negative valency, which can only be called out in pairs of equal and opposite sign. These latent valencies account for all diatomic and polyatomic molecules, either of the same element or of different elements of the same sign.

According to these ideas, therefore, the elements form four groups:

1. Those with free-positive valency only—hydrogen and the metals.
2. Those with free-negative valency only—fluorine, chlorine, and oxygen.
3. Those with free-positive and free-negative valencies—nitrogen and other amphoteric elements.
4. Those with no free valencies—the inert gasses.

Carbon is exceptional, and is largely a neutral element. Although its total free valency is 8, no compound is known in which more than four of its valencies are used at once. These valencies may, therefore, be all positive, or all negative, or partly positive and partly negative, in all proportions. It is never monovalent, and may not be truly divalent, but may be trivalent. The free valencies correspond to Werner's

“principal” valencies, and the latent valencies to his “auxiliary” valencies.

The most important service rendered historically to the theory of valency was the recognition that carbon is tetravalent. In 1854 Williamson and Kay prepared tri-ethyl-orthoformate (tribasic formic ether),  $\text{CH}(\text{OC}_2\text{H}_5)_3$ , and in this carbon is tetravalent. In 1857 they drew up a table of compounds of the marsh gas type, and in the same year Kolbe and Frankland observed the tetravalency of carbon. But Kekulé was the first to call attention to the fact, and to realise its importance.

Carbon stands in the middle of the first series of the periodic classification, and unites with every element, electro-positive and electro-negative alike. It even combines with itself in a unique way, dimyricyl ( $\text{CH}_3(\text{CH}_2)_{58}\text{CH}_3$ , having sixty atoms of carbon in single chain. The directions in which the valencies act is an important point, especially in the case of carbon. These directions cannot be towards the four corners of a square, because then there would be two isomeric bodies ( $\text{CH}_2\text{Cl}_2$ ), and no such bodies are known. Le Bel and Van't Hoff simultaneously, but independently, assumed that a carbon atom acts as if it were at the centre of a tetrahedron; but although their theories and conclusions are so much alike that their names are usually associated, there is really a great difference between them. Van't Hoff in 1874 regarded the valencies as acting in the direction of the angles of the tetrahedron. Auwers in 1890 pointed out many difficulties in this view. Thus, in ethylene there are two sets of forces each acting from two points, no two forces acting in the same straight line, but all inclined to each other. That would imply that the valencies have a definite direction in space, and would attribute to mere forces properties which they cannot possess.

Le Bel, on the other hand, assumed that each atom has a definite sphere of attraction. If two such spheres intersect, their atoms are drawn towards each other, bringing into play



a new repulsive force. When those two opposing forces exactly counteract each other, the atoms remain relatively at rest. Any three such atoms would naturally arrange themselves at the angles of an equilateral triangle, while a fourth would complete the tetrahedron. The atom of carbon being at the centre of the tetrahedron its spheres of repulsion would be bounded by the sides of the figure, and the direction of the valencies might be towards the middle of these sides, not the angles of the tetrahedron.

All theories and speculations regarding stereo-chemistry assume as true the tetra-valency of carbon, and from this discovery it may be said that the whole doctrine of valency has been evolved.

## CHAPTER XLV

### THE DOCTRINE OF ISOMERISM

BY Isomerism we mean the relation which subsists between two or more substances, which although differing in chemical and physical properties, are yet composed of the same elements in the same percentage. Such substances are termed "isomerides," and are said to be "isomeric." Thus, propyl iodide and isopropyl iodide differ in their chemical and physical properties, and yet both are composed of three atoms of carbon, seven atoms of hydrogen, and one atom of iodine. But it has to be observed in these and in other instances of isomerism, that although the percentage composition is the same, the grouping of the atoms differs. Thus, if we examine further the two compounds we have just named, we find the atoms in three groups as under :

1. Propyl iodide .  $\text{CH}_3, \text{CH}_2, \text{CH}_2\text{I}$
2. Isopropyl iodide .  $\text{CH}_3, \text{CHI}, \text{CH}_3$

The three linked carbon atoms are in the one case united to three of hydrogen, two of hydrogen, and two of hydrogen united to one of iodine ; and in the other case united to three of hydrogen, one of hydrogen united to one of iodine, and three of hydrogen.

The term "Isomerism" is restricted to those cases where the compounds having the same percentage composition contain the *same number of atoms in the molecule*. When the molecular weights differ, the term "Polymerism" is used, and the compounds are said to be polymeric. Thus, ethylene ( $\text{C}_2\text{H}_4$ ), propylene ( $\text{C}_3\text{H}_6$ ), butylene ( $\text{C}_4\text{H}_8$ ), and amylene ( $\text{C}_5\text{H}_{10}$ ) are all distinct compounds of carbon and hydrogen which have the same percentage composition, because there are in each just twice as many atoms of hydrogen as of carbon,

yet the molecular weights are quite different, being 28, 42, 56, and 70 respectively.

There is yet a third class of related compounds, to the relation of which the term "metamerism" is applied. In these the percentage composition and the molecular weight are identical, but they are made up of different radicles united by a single atom of oxygen, nitrogen, sulphur, or similar element. Thus, propylamine, methyl-ethyl-amine, and tri-methyl-amine are each composed of three atoms of carbon, nine of hydrogen, and one of nitrogen, but contain different radicles as under :

- |                       |       |                                   |                               |                 |
|-----------------------|-------|-----------------------------------|-------------------------------|-----------------|
| 1. Propyl-amine       | . . . | N C <sub>3</sub> H <sub>7</sub> : | H                             | H               |
| 2. Methyl-ethyl-amine | . . . | N CH <sub>3</sub> :               | C <sub>2</sub> H <sub>5</sub> | H               |
| 3. Tri-methyl-amine   | . . . | N CH <sub>3</sub> :               | CH <sub>3</sub>               | CH <sub>3</sub> |

Isomerism, polymerism, and metamerism occur most frequently amongst organic and mineral compounds.

Berthelot has indicated that theoretically we might imagine different isomeric compounds to be produced in one or other of three ways :

1. According to a difference in the mode of formation, whereby the compound might contain different residues, or according to the nature of the generating hydrocarbon ;
2. According to a difference in the part played in the compound by these residues ;
3. According to the order in which the substitution has been effected, in the case of substitution derivatives.

There are objections to all these theoretical views. A difference in the mode of formation is not sufficient evidence to determine isomerides, because compounds having a different origin may be identical ; they are only to be considered isomerides when they have different properties, although the same ultimate composition. Moreover, a difference in the order of substitution may produce no difference in the product, if the substituted elements or groups are the same.

Isomerism can only be explained on the assumption that each molecule has a definite structure, and that the same

atoms may be differently arranged in different molecules. We can as yet have but vague and roughly approximate ideas of the arrangement of atoms in a molecule. Our structural formulæ merely express reactions of formation and decomposition, and indicate in some imperfect measure variations in properties.

Variations in configuration and structure may be imagined to be due either to :

1. Variations in the *relative positions of the atoms* ; or
2. Variations in the *distances between the atoms*.

There is a strong presumption in favour of the first and against the second of these suggestions, in the fact that in all isomeric bodies known, we can set down a limited number of possible arrangements of the atoms, while on the second supposition an almost unlimited number of variations may be imagined, and every two-atom molecule ought to show isomerism. Now, we find, on the contrary, that the number of isomerides of any one empirical formula is never practically unlimited, and is always within, or not exceeding, the number of possible variations in the relative position of the atoms, while no two-atom molecule shows isomerism ; in fact, no well-established instance of isomerism is known in the case of a molecule containing less than three atoms. The key to isomerism is furnished by the doctrine of atomicity, which led to the recognition of the molecule as a structure, and indicated the possible arrangements of that structure.

The maximum number of theoretically possible isomerides of a given formula is a purely mathematical problem, but many atomic arrangements that are mathematically possible are physically impossible, because the stability of molecules does not depend solely on the valencies of the atoms. Caley calculated that among the paraffins in molecules containing 1, 4, 7, 10, 12, and 13 atoms of carbon, the possible isomerides are 1, 2, 9, 75, 357, and 799 respectively, according to the theory of valency.

What has to be done next, if possible, is to find the connection between molecular structure and configuration and the stability of compounds. We know that the following kinds of molecules cannot exhibit isomerism :—

1. Molecules containing only monovalent atoms ;
2. Molecules containing one multivalent atom united with monovalent atoms only ; or
3. Molecules containing two multivalent atoms united with monovalent atoms, if the latter are all the same, or all but one atom are the same element.

Any molecule containing more than two atoms and not belonging to the above classes may exhibit isomerism.

In the case of carbon atoms the following principles have been defined :—

1. A molecule containing two tetravalent carbon atoms, united with five monovalent atoms of one element and one of another cannot show isomerism ; but isomerism is possible if the carbon atoms are united with four of one kind and two of another.
2. Three carbon atoms combined with seven atoms of one kind and only one of another may show isomerism.
3. Molecules containing five carbon atoms can have these arranged in 4 different ways ; those containing six in 5 ; and those containing eight in 18.
4. Some of the carbon atoms may be doubly or trebly linked, and are then only equivalent to triad or dyad atoms.
5. When each carbon atom is tetravalent, two structural formulæ are possible ; when some are di- or tri-valent, six structural formulæ are possible.

In assigning a structural formula to a compound, the first step is to determine to which class it belongs. This is done by comparing its reactions with certain reagents, with the behaviour of known substances of various classes, which behave in a characteristic way with these reagents. By a study of many members of different classes it has been found that the structural formulæ of classes of carbon compounds can be



so far generalised that we can say that any one class invariably includes a special atomic group, characteristic of it, and which may be termed the *class group*. Thus, COOH for organic acids; HCO for aldehydes; CH<sub>2</sub>OH for primary alcohols; CHOH for secondary alcohols; and COH for tertiary alcohols.

The next step is to look at all the possible structural formulæ, and set aside those which do not contain the class group characteristic of that class to which it has been ascertained that the compound under examination belongs.

Lastly, we choose from among the remaining possible formulæ that which we find, by further investigation of the behaviour of the substance with reagents, whether by oxidation, substitution, or otherwise, most completely summarises those relations. As a general guide in such investigations, L. Meyer laid down the following rules for distinguishing isomerides:—

1. An undecomposed group of atoms obtained in the analysis of a compound is contained in that compound as a group of directly connected atoms; for example, the radicle methyl (CH<sub>3</sub>) from acetic acid.
2. A group of atoms passing from one compound to another, retains as a rule the same arrangement of its atoms; for example, C<sub>7</sub>H<sub>5</sub>O from benzoic acid, aldehyde, etc.
3. When an atom, or a group of atoms, replaces another of the same valency as itself, it takes the same position as the atom or group which it replaces; for example, C<sub>2</sub>H<sub>6</sub>O + K = C<sub>2</sub>H<sub>5</sub>KO + H distinguishes CH<sub>3</sub>CH<sub>2</sub>OH from CH<sub>3</sub>OCH<sub>3</sub>.

Le Bel and Van't Hoff, the great authorities on stereochemistry, the branch of the science which treats of the phenomena we are now considering, tried to explain isomerism, amongst other ways, by arranging symbols, not in a plane, but *in three dimensions*. As stated in the preceding chapter, Van't Hoff in 1874 assumed the carbon atom in a molecule to be in the centre of a tetrahedron, with its four affinities at the four angles of the figure. When the monads with which the atom combines are the same, no isomeride is possible; but when the *four monads are different*, two isomerides may be

shown. A carbon atom in the latter state is said to be *asymmetric*. This hypothesis indicates more isomerides than the previous theory of atomicity, in the case of compounds in which the carbon atoms are united by two affinities each, but not if united by three. Van't Hoff pointed out that on this supposition it is possible to explain the isomerism of hydrobenzoin and isohydrobenzoin; lactic and sarcolactic acids; fumaric and maleic acids; citraconic and mesaconic acids; crotonic and isocrotonic acids; chlorocrotonic and chlorisocrotonic acids; and oleic and elaidic acids.

One difficulty in the way of accepting Van't Hoff's theory is that it does not account for the very considerable difference in the properties of some of the above pairs, such as the hydrobenzoin, mannite and dulcitol, the glucoses, angelic and methylerotonic acid, etc. Another difficulty is that the theory would indicate isomerides which have not been found, and which could hardly have been missed, if they existed; for example, in derivatives of marsh gas containing four different bodies, in place of the several atoms of hydrogen.

On the whole, it is probable that the difference must be sought in the dynamics of the molecules, the action of one molecule on another, and the difference in the loss or gain of energy in the passage of one system into another in similar reactions of isomerides. We know nothing of intermolecular actions, and very little about the comparative energy in isomerides.

Besides the compounds which exhibit true isomerism, polymerism, or metamerism, there is another class of compound bodies which are often called *physical isomerides* or *stereoisomerides*. These have different physical properties, but respond to the same chemical reactions, behaving in exactly the same way towards reagents, and being, in fact, capable of representation only by identical formulæ. They contain one or more asymmetric carbon atoms, that is, as we have said, carbon atoms to which are linked four different atoms or groups of atoms. Thus lactic acid ( $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ )

contains one carbon atom (the second in the formula) linked to four groups— $\text{CH}_3$ , H, OH, and COOH. These groups can be arranged round the carbon atom in two ways, and represent two forms of lactic acid which differ physically, in respect that they rotate polarised light in opposite directions.

The section of hydrocarbons called terpenes includes a great number of bodies having the same empirical formula  $\text{C}_{10}\text{H}_{16}$ . They form two groups—one, the terpenes or turpentine oil group, boiling at  $155^\circ$  to  $160^\circ$ ; the other, the citrenes or orange oil group, boiling at  $174^\circ$  to  $176^\circ$ . Much of the difference is due to different molecular grouping of these bodies, and it is certainly in part due to different asymmetrical arrangements of the molecules in the mass, which produce variations in their power of rotating the plane of polarisation of a polarised ray. There are dextro- and lævo-rotary members of both sections. The solid camphene ( $\text{C}_{10}\text{H}_{16}$ ) is a true isomeride of the others, forming camphor by oxidation. Many of the members of the terpene group are dextro- and lævo-rotary, and these members differ by physical isomerism.

It has to be observed, however, that some so-called physical isomerides are only physical modifications. Thus, there are two di-nitro-chlor-benzenes formed by the nitration of chlor-benzene, one of which is converted into the other by bringing the two kinds of crystals into contact, and the process is reversed by suddenly cooling the fused mass. These differences are due to variations in the mutual action rather between groups of molecules than between the atoms constituting the molecules. They consist mainly in differences in crystalline form, solubility, fusibility, or similar physical properties.

Fincke's two benzophenones—rhombic, melting at  $48^\circ$ , and monoclinic, melting at  $26^\circ$ , and Fallen's two crystalline forms of di-brom-propionic acid, of different melting-points—are further instances of physical isomerism due to varying aggregations of the molecules. The aggregations differ in complexity, the less complex being more stable and of higher melting-point, and the more complex of less stability

and of lower melting-point, produced by heating the substance. Armstrong thought that these should be called "physical modifications," not "physical isomerides."

Lehmann divided physical isomerides into two classes :

1. Those which change from one form to another at a definite temperature, the direction of the change being dependent on very small differences of temperature ; and
2. Those which exhibit two forms, one more stable than the other, and in which change from one to the other does not occur at a definite temperature, and is not reversible by heat alone.

This classification cannot be carried out rigorously, and only indicates broad differences, which are not always seen in detail.

*Ammonium nitrate* is an example of the first class. The ortho-rhombic crystals formed at ordinary temperatures melt at  $158^{\circ}$  ; as the molten mass cools, crystals belonging to the regular system are formed : at  $125^{\circ}$  these change to rhombohedral forms ; at  $87^{\circ}$  to rhombic needles ; and at  $30^{\circ}$  or so the original ortho-rhombic crystals are re-formed. The inverse changes occur as the crystals are again slowly heated, and the mass now finally melts at  $198^{\circ}$ . So with sulphur, monoclinic crystals are formed as molten sulphur cools ; as the temperature falls they change to rhombic forms ; and by regulating the temperature the crystals pass from one form to another.

As an example of the second class di-brom-propionic acid is cited. It crystallises in rhombic form, melts at  $62^{\circ}$ , and if the molten mass is heated only a little higher, rhombic forms appear on cooling ; but if it is heated much above  $62^{\circ}$ , the form on cooling is altered to flat right-angled tables, which melt at  $51^{\circ}$ . If this last, *less stable*, form is slowly heated, the other form grows ; but before the change proceeds far, the whole melts at the melting-point of the less stable form. If, on the other hand, the *more stable* form is melted, heated strongly, and then brought into contact

with both forms, the two forms grow until the crystals touch, when the more stable form grows into the others, and completely changes them into the stable form.

From the whole facts of isomerism, the following conclusions have been drawn: That the properties of a molecule depend not only on

1. The valencies of the atoms composing it;
2. The distribution of atomic actions within it; and
3. The quantity of energy associated with this atomic configuration; but also on
4. Actions and reactions between groups of molecules, the parts of these molecular groups holding together during more or less wide variations in the physical conditions to which the compound may be subjected.

The fourth of these causes explains many differences amongst mineral compounds, solid and liquid, somewhat analogous to isomerism amongst carbon compounds. For example, calcium carbonate ( $\text{CaCO}_3$ ) crystallises as two minerals—*aragonite* in rhombic form, and *calcite* in hexagonal form. On comparing these two forms of the same chemical compound, we find that *aragonite* is harder, has a greater specific gravity, and is less easily acted upon by hydrochloric acid and other reagents. When powdered *aragonite* is heated to redness it is changed into *calcite*. Both can be produced at low temperatures, but above a certain point only *calcite* is formed. Here we have identity of chemical composition and probably of molecular weight, combined with difference of physical properties, and partly of chemical.

Again, *antimony iodide* ( $\text{SbI}_3$ ), crystallised in red hexagonal forms, when heated to  $114^\circ$ , changes to a mass of yellow ortho-rhombic crystals. Also, chloro-di-nitro-benzene, anthracene, and others show similar changes of form and melting-point, produced by heat, sunlight, or the like.

The doctrines of atomicity, valency, and isomerism, dealing with the relations of the atoms in the molecule, are deemed of such importance that they form in themselves a special branch



of chemical science, to which the name of Stereo-chemistry is applied. For historical purposes it is unnecessary to enter more fully into an extremely complicated, and as yet imperfectly understood, division of chemical philosophy. What we have said will suffice to show its importance, and to indicate how its study tended to accelerate the progress of the science.

## CHAPTER XLVI

### THE DOCTRINES OF CHEMICAL AFFINITY AND KINETICS

THE terms "Chemical Affinity," "Chemical Attraction," or "Elective Attraction" are severally used to express the specific attraction of particular atoms, or groups of atoms, of dissimilar nature towards each other, as the result of which chemical compounds are formed, differing in their nature from any of their constituents. We do not know what this affinity really is, and in many cases we are prevented from estimating with accuracy its relative value, in consequence of the action of other things, as, for example, the mass of the acting bodies. Chemical kinetics is the branch of applied mathematics or dynamics which treats of the motions of masses and forces, causing or changing motion in the atoms or molecules of chemical bodies.

In ancient times many fanciful modes of representing chemical changes were suggested. These generally assumed that like attracts like; that substances which combine to form a different substance contain some principle or essence common to both; and that such bodies are constituted of particles of various forms, round or angular, pointed or hooked, straight or spiral. Lucretius explained why wine passes rapidly, and oil slowly, through a sieve by the assumption that the particles of oil are either larger than those of wine, or are more hooked and interwoven together.

Another fancy of Lucretius exhibits to us in action a confusion between the literal and metaphorical use of such words as "keen" and "sharp," which had a profound influence upon mediæval thought. He says that the difference between substances which have a sweet or a bitter taste consists in the sweet things being sharp and jagged, and the bitter things round and smooth. Later alchemists

without hesitation adopted similar conceptions, and asserted that acids consisted of sharp, pointed particles. "One needs but taste an acid," says Lemery, "to be satisfied of it, for it pricks the tongue like anything keen and finely cut." The angular or needle-shaped form of crystals was cited as further proof of the pointed shape of acid particles, and the variety in the avidity with which different acids attacked different metals was alleged to be due to the greater or less degree of sharpness of the points and edges of such particles. Alkalis, on the other hand, were composed of particles so formed that the points of the acid particles readily struck into and divided them. Of all this theory only one idea had a foundation in truth, that any conception which we may form as to the shapes of the ultimate atoms of bodies, and their mode of combination, must be such as to explain the facts of crystallisation as well as the facts of chemical change. Mediæval theories on the doctrine of affinity did little to advance chemical philosophy.

Although the marked and surprising character of chemical changes has caused them to be attributed to a peculiar and special force called "chemical affinity" or combining power, the necessity for assuming the existence of such a distinct force has often been denied. This has been done on the following grounds:—

1. Because chemical combination is another form of gravitation or of electrical attraction; or
2. Because the power of attraction, or action at a distance through space, being denied, the phenomena of chemical attraction are explainable by the movement of material particles, just as the kinetic theory of gases explains pressure by the movement of particles.

Le Sage in 1758 tried to account for attraction, including chemical phenomena, by motions of ultimate particles.

In modern times attraction in the domain of molecular physics has received a kinetic explanation, and the theory of vortex atoms may extend a similar explanation to chemical affinity. According to the vortex theory, atoms are small but

finite systems of matter, which rotate about an endless curve as axis, and which, according to Helmholtz's calculations, have the peculiar property that their mass cannot be affected by external influences.

Until this, or some other explanation of affinity, has been worked out, we may use the term "affinity" to designate something, we know not what, which is the cause of chemical phenomena, which belongs to the quality of atoms, which we must always remember we do not understand, nor explain by giving it a name, and of which we speak as an attractive force merely for convenience, since we do not know whether there is any force of attraction acting through space from particle to particle. Keeping these things in mind, we shall now consider the development of the modern doctrines of chemical affinity and kinetics.

Boerhaave first used the term "affinity" to signify the force which holds together substances which are chemically dissimilar. Newton viewed these affinities as the result of attractive action exerted between minute particles at a minute or insensible distance.

It had previously been noticed both by alchemists and iatrochemists that sometimes one substance will turn out another from a combination, and take its place. This was attributed to the possession of a greater affinity. Geoffroy in 1718 drew up tables of affinity, in the sense of arranging together bodies supposed to be related to each other. The following is an example of such a table :

ACIDS.	SULPHURIC ACID.	NITRIC ACID.
Fixed alkali.	Oily principle.	Iron.
Volatile alkali.	Fixed alkali.	Copper.
Absorbent earth.	Volatile alkali.	Lead.
Metals.	Absorbent earth.	Mercury.
	Iron.	Silver.
	Copper.	
	Silver.	

Each substance was said to have a *greater affinity* than those

lower in the table, for the substance at the head of each column. The term "oily principle" meant phlogiston.

In Wenzel's *Lehre von die Verwandtschaft der Körper*, published in 1777, we find tables drawn up on the principle that "the affinity of a substance for a common solvent is inversely as the times required for solution." He made equal cylinders of different metals covered with varnish except on one surface, immersed these in the same solvent, at the same temperature, for equal periods. From the weights dissolved he calculated the time which would be required to dissolve the whole of each cylinder. He got contradictory results, and came to the conclusion that chemical changes are the result of various reactions which balance one another.

Bergman in 1775 constructed two tables of affinity for fifty-nine substances, one representing the affinities at low temperatures in the wet way, the other the affinities between solid substances at high temperatures. He regarded the quantity of acid needed to neutralise a given quantity of base as the *measure of affinity* of that acid for that base. He distinguished two affinities: the *affinity of aggregation*, between homogeneous substances, whose union only increases the mass; and the *affinity of composition*, between homogeneous substances mixed to form compounds. The union of two out of three substances to the exclusion of the third, was due to what he called "single elective attraction," and the exchange of constituents by two compounds, each consisting of only two proximate principles was "double attraction."

The only external condition which Bergman admitted as weakening or inverting the affinities of bodies, was the different intensity of heat, and he drew up the two tables which we have mentioned, to show the attractions thus influenced. He was surprised to observe that the series of metals was the same for all acids.

The views generally held by chemists about the end of the eighteenth century are given by Guyton de Morveau in the



*Encyclopédie Méthodique*. The laws of affinity were thus stated :

1. Bodies only act in the fluid state.
2. Affinity is manifested only between the smallest molecules of substances.
3. Excess of one or other of two substances modifies their affinities.
4. Affinity of composition, to be effective, must exceed affinity of aggregation.
5. The product of the action of affinity of composition is a distinct substance, with properties of its own, unlike those of its constituents.
6. There is a condition of temperature which makes the action of the affinities of substances slow or rapid, of no account or efficacious.

A great difficulty in the way of the study of the subject was caused by the circumstances that the composition of the same neutral salt was differently represented by chemists, and De Morveau concluded that no certain method of general application existed at his time for determining affinities. He considered, like Bergman, the order of affinities to be constant, but modified by temperature, by solubility or insolubility and by the presence of excess of the one or the other constituent of a salt.

Such was the state of chemical philosophy when Berthollet began to study and to publish his researches. As formerly mentioned, he was with Napoleon Bonaparte in Egypt, and the many savants who accompanied that expedition formed an "Institut du Caire." Before this body Berthollet read in 1799 a paper, which was amplified and continued, and published in 1801 in the 30th volume of the *Memoirs of the Institut National des Sciences et Arts at Paris*, with the title "*Recherches sur les Lois de l'Affinité, par le citoyen Berthollet*" (*Prairial An neuf*), pp. 1, 207, 229. In 1803 (*An onze*) he published his *Essai de Statique Chimique*, in which he amplified and illustrated his previous paper, and somewhat modified his views on the action of mass.

Berthollet came to the conclusion that affinity, or the tendency to combine, is a fundamental property of matter which gives rise also to gravitation. We know more about gravitation, because of the greater size and distance of the heavenly bodies, as compared with atoms and molecules, and because of the greater complication of the affinities of invisible molecules. Yet he considered the path of an atom, under the influence of given affinities, to be as clearly and certainly marked out as the path of a planet, the only difference arising from our ignorance of the former. It was, therefore, necessary to investigate the phenomena of chemical change step by step, with the view of ascertaining the principles on which chemical equilibrium depends, and the nature of chemical energy.

He promoted this object by investigating the influence of mass on chemical change, a subject which has recently attracted attention, although but little is really known even now. He explained chemical action as the result of attraction between *small particles*, as gravitation between *large masses*, of bodies. He fell into the fallacy of supposing that because action is proportional to the reacting mass, every resulting compound must contain so much the more of any of its constituents as there is more of that constituent present when the compound is formed. In opposition to this view stands the other idea, that the affinity of the most active chemical substances, acids and bases, is measured by their capacity of saturation. Contrary to both is the theory, just then beginning to be developed, that all chemical action is attributable to the interaction of constant weights.

Berthollet opposed Bergman's doctrine that substances can be arranged in the order of their affinities for a given substance, each one completely displacing the whole of the others whose affinities are weaker than its own. He wrote, "Chemical action is reciprocal, the result of a mutual tendency to combination." It is only for convenient expression that we assign all the action to one of the two substances, and it is not strictly

true that a liquid acts on a solid, rather than that the solid acts on the liquid.

Chemical actions proceed continuously, and are conditioned chiefly by the affinities and the quantities of the reacting substances, so that quantity is able to do duty for the force of affinity in producing an equal degree of saturation. "If I prove," he said, "that the quantity of a substance can take the place of the force of its affinity, it follows that the action of the substance is proportional to the quantity of it which is required to produce a determinate degree of saturation. I denote that quantity by the term 'mass.'" He did not use the term "mass" with the same signification as we do. His mass was *the product of the quantity and the affinity of a substance*. "Every substance which tends to enter into combination, acts in proportion to its affinity and its quantity" (*Essai*, p. 2).

He further recognised that the chemical action of a substance is modified by any circumstance which alters the affinities of its parts, such as condensation, expansion, secondary action, and the like, as well as quantity.

In measuring affinities he considered that each of the acids which compete for an alkaline base, acts in proportion to its mass, using the term in his sense. "In order to determine the masses, I compare," he says, "the capacities of saturation, whether of all the acids with one base, or of all the bases with one acid." Bergman had recognised the influence of extraneous forces besides mass, such as elasticity, crystallisation, precipitation, insolubility, and cohesion.

It must be remembered that in 1803 constancy of composition was not recognised as a law of chemical combination, and hence Berthollet made the mistake of believing that the quantity of a reagent affected the composition of a compound, and of regarding fixity of composition as the exception and not the rule amongst chemical compounds.

The views of Berthollet led him into a controversy, which has become famous, with his countryman, Proust, on the question whether the proportions in which two or more substances

combine chemically are constant or continually change with circumstances. It was Proust who criticised Berthollet's work, and established the fact that very many compounds contain their constituents in fixed and definite proportions, and in these only (*vide* Nicholson's *Magazine*, 1802, 1806, 1807 and 1810).

Then followed in 1808 Dalton's new system of chemical philosophy, which many thought to be quite inconsistent with Berthollet's views. Although that is not the case, yet Dalton's atomic theory stimulated accurate analysis, for example, the valuable work of Berzelius in that department. The facts thus determined disproved Berthollet's ideas of the variability of composition. Work on affinity now gave place to determination of the relations between the amounts of reacting substances, the properties of elements and compounds, and something, though little, was done towards elucidating the relations between the rates of chemical changes, and the affinities and quantities of interacting substances.

The development of Dalton's atomic hypothesis and its ultimate adoption as a theory, gave chemical doctrine a stability which was greatly conducive to progress. Berthollet viewed chemical action as a branch of mechanics, but the development of physics began to have an influence on the growth of a true conception of chemical affinity. As early as 1798 Count Rumford argued in the *Philosophical Transactions* that anything which an insulated body can continue to furnish without limitation, cannot possibly be a material substance, "and it appears to me," he says, "difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated, in the manner in which heat was excited and communicated in these experiments, except it be motion."

Rumford's idea was opposed to the Newtonian emanation theory of light. However, in due time the immaterial nature of what are now called the physical forces was recognised, and

the correlation of heat, light, and electricity with chemical energy, opened up the way for an intelligent investigation and discussion of the phenomena of chemical affinity.

Notwithstanding the mistake of Berthollet, he had a clear idea of a system held in equilibrium by the actions and reactions of its several constituents, and of the forces which maintained that equilibrium. He said in his *Essai* that the chemical qualities of different substances depend (1) on their tendencies to combine, whereby they mutually saturate each other; (2) on their relations to heat, which modify their combining powers, although he adds,—“by causing variations in the quantities of the substances coming within the spheres of mutual action, and also by opposing elasticity to condensation, the latter of which is one of the effects of combination”; (3) on the mutual actions of their small particles acting in the same direction as the affinity which has produced combination; and (4) on the relations to other substances which combine with them. The “tendency to combine” mentioned by Berthollet is what is technically termed “Chemical Affinity.”

Davy regarded chemical and electrical effects as due to the same cause—certain mutual relations between small particles of matter produce chemical effects, and certain mutual relations between large masses, electrical effects. He considered a fixed chemical system stable because of the balance of chemical and electrical forces.

In like manner Berzelius' idea of a chemical reaction was mainly equilibrium resulting from the actions of chemical and electrical forces. He thought that each elementary atom had definite quantities of positive and negative electricity, but was yet really unipolar by the predominance of one. The strivings of atoms to neutralise their opposite electricities measured the intensity of the unipolarity of each, and was what he called chemical affinity.

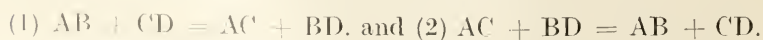
Berthollet started with the idea that affinity is a phase of the same fundamental property of matter as that on which gravity depends, but is complicated by acting at short distances.



He wished chemists to study fully each reaction step by step, with the view of elaborating a general theory of affinity or chemical statics. But the subject stands almost where he left it for the reason which we have already stated, that Dalton and others developed chemistry in another direction. It is only in recent years that the action of mass has begun to be again studied. We must now recognise as a fact that while the atomic weights of the constituents determine the proportions of the different elements which will replace each other in a double decomposition for instance, yet the extent to which the interchange in atomic proportions will be carried, and the rate or degree of speed at which it will take place, are influenced by the mass of one or other of the reacting bodies. In short, we must combine the study of chemical affinity with that of chemical kinetics.

No philosophical treatment of chemical affinity was attempted for sixty-five years from the time of Berthollet's *Essai*, but in 1867 was published *Études sur les Affinités Chimiques*, by C. M. Guldberg and P. Waage (Christiania). In this book the authors took into consideration the influence which tonic volume, temperature and strength of affinity exercise upon decompositions. They endeavoured to eliminate the effect of secondary forces and so arrive at relative measurements of chemical affinities. The subject is too abstruse for a general history of chemistry, but we shall give an outline of the doctrine put forward by these two chemists, and refer the reader who wishes a more detailed analysis of the book, to *A History of Chemical Theories and Laws*, by Mr. Pattison Muir (1907), p. 400. *et seq.*

Guldberg and Waage studied chiefly reversible double decompositions, such as those arising among four bodies which we shall call A, B, C, and D, namely.—



This cycle of changes presents analogies with dissociation, to which we formerly alluded (*supra*, p. 431). Neither of the

above changes is complete, but at the close of the reaction there will always be four bodies, AB, CD, AC, and BD. If we call these four bodies A, B, A', and B', we may perceive that the force which caused the formation of A' and B' is held in equilibrium by the force which caused the formation of A and B. This force increases in proportion to the *coefficient of affinity* in the reaction  $A + B = A' + B'$ , and is dependent on the quantities of A and B. It is also proportional to the *product of the active masses* of A and B.

Let us now represent these active masses by the letters  $p$  and  $q$  respectively, and the coefficient of affinity by the letter  $k$ . The force of formation will be equal to the product of  $k : p : q$ . Next let us represent the active masses of A' and B' by  $p'$  and  $q'$ , and the coefficient of affinity in the reaction  $A' + B' = A + B$  by  $k'$ . Then the force which tends to re-form A + B is equal to the product of  $k' : p' : q'$ . As the one force is held in equilibrium we thus get the *Equation of Equilibrium*,  $k : p : q = k' : p' : q'$ .

By experimentally determining the values of  $p$ ,  $q$ ,  $p'$ , and  $q'$ , the ratio  $k : k'$  can be calculated; and also the number of molecules transformed; and from the former we can determine the result of the reaction for any initial condition of the four substances A, B, C, and D.

The *active mass* is defined by Guldberg and Waage as the quantity of the substance in the unit-volume which undergoes change, all the substances being present in the ratio of their equivalent weights. The symbols  $p$  and  $q$ , therefore represent *certain numbers of the equivalents of the substances A and B*.

As an example of the kind of change which they selected for determining the value of the coefficient of affinity by this method of equilibrium, we may instance the action of alcohol and acetic acid producing ethylic acetate and water, in which the reverse reaction occurs, and ultimately the system, alcohol, acetic acid, ethylic acetate and water, remains in equilibrium.

The following principles were established by Guldberg and Waage :—

1. The affinity constants of acids are proportional to the square roots of the velocities of the reactions brought about by them.
2. The force of attractions between A and B, etc., and any other bodies that may be present, is proportional to the product of their active masses and what is termed the "coefficient of action."
3. If A and A' are solid bodies, while B and B' are liquids, the active masses of A and A' remain practically constant throughout the reaction, if A be made equal to A'.
4. The amount of any chemical change is proportional to the products of the active masses of the substances concerned and the coefficient of affinity of the reaction.

The value of the coefficient of affinity ( $k$ ) has been determined by Ostwald. He found that when A and A' are two acids and B and B' two of their neutral salts with the same base, the coefficient of affinity is the proportion in which the base is shared between the two acids, when the three substances react in equivalent quantities, for the amount of base combined with each acid is a measure of the affinity of the acid for that base, and therefore the affinity coefficients express the ratios of the affinities, that is, they express the relative affinities of the acids for the base. His general conclusion is that the relative affinities of the acids are expressed by constant numbers, whatever be the temperature and whatever the base.

Ostwald in his second paper (*Journal für Praktische Chemie*, 18. 328) besides extending his observations by the volumetric method to many acids, endeavours to estimate the amount of change by determining the refractive indices of solutions of acids, bases and salts. The results agree very well with those obtained by the volumetric method, which he thinks the more trustworthy. In applying the action of acids on insoluble salts as a method for determining the relative affinities, he found that the method was satisfactory, provided that the

acids were as dilute as possible. In measuring the velocity of some of the processes, he found that velocity depends on dilution, temperature, and the nature of the acid, which exerts what has been called a "predisposing affinity" on the reaction.

From all his researches Ostwald concluded that each acid and each base has a specific affinity constant, and that all the chemical reactions in which the acid or base plays a part are determined by the magnitude of this constant.

A few words may be added on the researches of Thomsen into the relations of acids and bases. He found :

- (a) When soda, nitric acid, and sulphuric acid react in equivalent quantities in dilute aqueous solution, two-thirds of the soda combines with the nitric, and one-third with the sulphuric acid.
- (b) The final division of the base is the same whether it was originally present as sulphate or nitrate.
- (c) The "striving" of the nitric acid to saturate itself with soda is twice as great as that of sulphuric acid. This striving he called the "avidity" of the acid, and the term has the same meaning as Ostwald's "affinity."

The following table shows the comparative avidity of the several acids named :

Nitric . . . . .	100	Oxalic . . . . .	24
Hydrochloric . . . . .	100	Orthophosphoric . . . . .	13
Hydrobromic . . . . .	89	Monochloroacetic . . . . .	9
Hydriodic . . . . .	79	Hydrofluoric . . . . .	5
Sulphuric . . . . .	49	Tartaric . . . . .	5
Selenic . . . . .	45	Citric . . . . .	5
Trichloroacetic . . . . .	36	Acetic . . . . .	3

It will be apparent from what has been said in this chapter that chemical affinity is a very complex subject and that we are yet very far from having a complete view of it and an accurate knowledge of its philosophy.

## CHAPTER XLVII

### THE DOCTRINES OF ACIDS, BASES, AND SALTS : ELECTRO-CHEMISTRY

THE subjects which we have been considering in the three preceding chapters lead us naturally to the present subject. Atomicity, valency, isomerism, and chemical attraction are all exhibited in those relations between acids and bases, which result in the production of what are termed "chemical salts." It is therefore fitting that we should close the examination of the development of chemical doctrines by considering the history of the various views which have been entertained respecting bases and acids, and the salts which are the products of their reactions.

The term "acid" was originally specific, and signified "vinegar," in Latin *acetum*. The word "*oxos*," related to "*oxys*" (from which "oxygen" is derived) was the Greek name of the same substance. It was noticed that calcareous earths, such as chalk, dissolve with effervescence in vinegar. Many other liquids also dissolve calcareous earth with effervescence, and these were classified as acids. That was the ancient generic meaning of the term "acid."

The properties of ashes were also known in very ancient times. Natron, the first source of soda, was then used for dissolving oils and sulphur, and for making glass. Wood ashes, the first source of potash, possessed similar properties. These substances change the green and red colours of plants, and so the Arabic term for ashes, "alkali," came to have a generic meaning including all similar substances.

In the seventeenth century much notice was taken of the behaviour of acids and alkalis towards each other. It was observed that the characteristic properties of each disappeared



when they were mixed, and the product no longer affected the colours of plants, and had neither detergent nor solvent powers. These bodies were called "salts," a term which had been in use for a thousand years to signify anything resembling sea-salt, and possessing the property of solidity and non-volatility.

Rouelle in 1744 introduced the term "base." In this he included alkalis, earths (substances like alkalis, but not effervescing with acids), metals, and certain oils. His idea was that a salt is formed by the combination of an acid with something, alkali, earth, metal or oil, and that that something is its base.

Then followed Black's important memoir published in 1755 on the nature of magnesia alba, quicklime, and the mild and caustic alkalis, which we discussed in Chapter XXIV. Black established the difference between mild and caustic alkalis and earths as due to the fact that fixed air (carbon dioxide) is present in the mild and absent from the caustic.

Lavoisier, in 1787, taking the view that acids are composed of oxygen and something else, called that something a base, a simple or compound acidifiable base. This view was for a long time adopted by Berzelius, during his controversy with Sir Humphry Davy regarding the composition of muriatic acid and the nature of chlorine. He regarded salts as made up of oxides of acidifiable bases, combined with oxygen compounds of metals or of radicles; but some time after 1815 he admitted Davy's opinion to be correct. This opinion which Davy established in 1816, held that hydrogen is the essential ingredient in all acids. But Davy maintained that all new facts went to show that acidity did not depend on any peculiar elementary substance, but upon peculiar arrangements of various substances.

Gay-Lussac still believed that salts are formed by the union of an acid and a base, and that they continue to contain both the acid and the base. He considered acids and salts to have the same constitution, because both are compounds of

anhydrous acids with bases, water being the base in the acids. After Davy had proved muriatic acid to consist of hydrogen and chlorine, Gay-Lussac's own work on hydriodic acid (HI) and hydrocyanic acid (HCN) negatived his notions (*Ann. Ch. and Phys.*, 1814, 91, 5). Thereafter, in 1814 and 1815 he distinguished "hydro" acids from ordinary acids, which contain oxygen.

In 1833 Graham proved the existence of three acid hydrates of phosphorus pentoxide (formula  $PO_5$ , if oxygen equal to 8). This led Liebig in 1838 to extend the theory of the polybasicity of acids to carbon compounds, and he thus made two corrections of the existing doctrine of salts. He found (1) that not all the hydrogen and oxygen in an acid is basic water, and (2) that the products obtained by the decomposition differ under different conditions, and that neither these products, nor the constituents from which the salt is formed exist in the salt. Were it otherwise, the different decompositions of the same carbon compound would lead to two different views of the composition of that compound. "The two views," he said, "are merely expedients employed by the mind to give an account of certain phenomena, and to bring these into relation with one another; and all views of the constitution of chemical compounds are to be thought of in no other way but this." . . . "If it can be certainly proved that sulphate of potash contains sulphuric acid ( $SO_3$ ) and potash (KO), there is an end of Davy's hypothesis; but no conclusive proof has been given, or can be given, of this assertion." . . . "What we certainly know is that base *plus* acid is equal to salt *plus* water. When lime and sulphuric acid react, sulphate of lime and water are formed; when lime and hydrochloric acid react, chloride of lime and water are produced. The hypothesis which asserts a difference of kind between the salts of oxyacids and the salts of hydracids says that water is in sulphuric acid before the reaction begins ( $SO_3 + HO + CaO = SO_3 CaO + HO$ ); but that in the reaction between hydrochloric acid and lime, the water is formed by

the union of the hydrogen of the acid with the oxygen of the base ( $\text{HCl} + \text{CaO} = \text{CaCl} + \text{HO}$ ). Davy's hypothesis says that the two reactions are strictly similar; that in both the metal of lime replaces the hydrogen of the acid, and this hydrogen combines with the oxygen of the lime to form water." It will be borne in mind that Liebig in these formulae is using the old notation, not the modern.

Liebig decided in favour of the view which brings the reactions of acids with bases under the same scheme: he declared all acids to be compounds of hydrogen, the hydrogen of which can be replaced by metals. The saturation capacity of an acid is dependent on the quantity of replaceable hydrogen in it, and in his day the radicle of an acid was the whole of it, except its replaceable hydrogen. This was indeed the Unitary Notation, but that was not adopted until some time after the death of Gerhardt.

In 1815, while Gay-Lussac was investigating hydro-cyanic acid, he isolated cyanogen, and spoke of it as a remarkable and then unique example of a body which, although a compound, plays the part of a simple body in its combination with hydrogen and with metals. In 1832 Liebig and Wöhler published researches on the radicle of benzoic acid prepared from oil of bitter almonds. From 1838 the radicles of the acids were deemed the parts which determined the reactions of acids and salts. These compound radicles were essential to the dualistic doctrine of Berzelius.

Davy tried in 1807 to connect positive and negative electricity with the chemical affinity of substances, and considered a charge of electrical energy to be the cause of "elective affinity." It will be remembered that Lavoisier had thought of an acid as the union of a simple or compound acidifiable base with the acidifying principle, oxygen. Liebig, on the other hand, following Davy, said that acids are compounds of certain radicles with hydrogen, and that salts are compounds of the same radicles with metals. We have now to consider a doctrine which differed from both.

Between 1820 and 1830, or about that period, Berzelius developed his doctrine of *electro-dualism*. In order to make the facts concerning the electrical properties of a substance fit into chemical classification, he adopted the hypothesis that the electricity of every atom is concentrated at two opposite poles, one of which is stronger than the other, consequently each atom, each element, each radicle, has on balance a unipolarity which determines its chemical character. The more intense its electric polarity, the stronger its affinity, because "affinity is the action of the electric polarity of particles." Any chemical reaction, he thought, strives towards electrical neutrality, and every compound is a dual structure of an electrically positive and an electrically negative simple body, or compound radicle.

Compound atoms of the first order are formed according to Berzelius by the union of elementary atoms; inorganic compounds by the union of two, and organic compounds by the union of three elements at least. Compounds of the second order are formed by the union of atoms of the first order; as potassium monoxide (KO), sulphuric acid (SO<sub>3</sub>) unite to form potassium sulphate (KO, SO<sub>3</sub>). (The *old notation* was used by Berzelius.) Compounds of the third order were formed by the union of atoms of the second order, as dry alum; while hydrated alum is a compound of the fourth order.

The restoration of electrical polarity to the constituents broke up the compound. All substances were regarded by him as either electro-positive or electro-negative. Of all substances oxygen is the most electro-positive, and it is also the only substance in the electro-chemical system whose electrical relations are unchangeable. Every other substance is electro-positive to some substances, and electro-negative to others, and no substance is as electro-positive as oxygen is electro-negative.

Berzelius prepared a list of elements arranged in electrical order, beginning with oxygen, and ending with the most

electro-positive elements—sodium and potassium. Oxides he divided into electro-negative or acids, and electro-positive or bases. “What we call chemical affinity,” he declared, “is nothing but the action of electric polarities of the particles, and electricity is the first cause of all chemical activity. Every chemical compound is wholly dependent on two opposing forces—positive and negative electricity. So alum, for example, is not to be thought of as immediately formed from its simple constituents, but as the product of the reactive positive and negative parts.”

The discovery of the facts on which the Substitution Theory of Dumas was based gave the *coup de grâce* to these dualistic views of Berzelius, which were not inferences from facts, and to the form of electro-chemical theory which was part of them.

Faraday in 1834 defined a number of terms which he introduced for the purpose of expressing the phenomena of electrolysis. When a body had been decomposed directly by the electric current, and its elements set free, these liberated elements were termed *electrolytes*. For convenience he substituted the word “*electrode*” for “pole”—that which is supposed to lie upwards towards the east being the *anode*, that downwards towards the west the *cathode*. The bodies which pass to those electrodes are termed *ions*, and are thus distinguished—those which go to the anode of the decomposing body are called *anions*, those which go to the cathode, *cations*. It is necessary to bear these terms in mind when considering what we are now to say.

In 1839 and 1840 Daniell, the celebrated electrician, observed that many salts separate into two parts when an electric current is passed through their aqueous solutions. In this electrolysis the cation is the metal, and the anion is what Liebig called the radicle of the salt. From 1853 till 1859 Hittorf extended Daniell's work and proved that acids, bases, and salts are electrolytes. During the discussion on ammonium, Daniell pointed out that the simplest explanation of the



electrolysis of ammonium salts is that the cation is ammonium ( $\text{NH}_4$ ), and the anion the negative element or radicle.

Daniell, starting from the fundamental principle that the "force which is measured by its definite action at any one point of a circuit cannot perform more than an equivalent proportion of work at any other point of the same circuit," measured the quantity of hydrogen and oxygen liberated at the cathode and anode during electrolysis of aqueous solutions of sulphuric acid, sodium sulphate, and potassium sulphate, and the quantities of the same gases liberated by passing the same current simultaneously through acidulated water. He came to the conclusion that water was not decomposed during any of these changes, but only the acid or salt. Measuring the hydrogen given off, the ammonia formed, and the metal of the cathode dissolved, during the electrolysis of ammonium salts, he inferred that these salts are compounds of negative ions with the positive radicle ammonium. In all these cases the substances liberated may be, and often are, the products of secondary actions.

In 1844 Daniell and Miller showed that although the quantities of anion and cation liberated at the electrodes are always the chemical equivalent of each other, yet the number of anions which travel to the anode in a given time is greater than the number of cations which travel to the cathode in the same time. They did not devise means for measuring the rate of travel or transfer, but this was done by Hittorf between 1853 and 1859. Hittorf determined the transport numbers of the ions of many salts, and established the principle that the electric current travels with the ions.

Clausius in 1857 reasoned thus:—If the ions of an electrolyte are bound into complete molecules in a solution, then electrical energy will be required in tearing the ions apart, and therefore a current will not pass till the electro-motive force is sufficient to overcome the mutual attractions of the ions. But as soon as the necessary electro-motive force is attained, a large number of molecules will be decomposed at

the same time, since all the molecules are under the influence of the same force and their relative positions are alike. "So long as the active driving force is less than a certain limiting value, no current will pass; but when the force exceeds this limit, a very strong current will suddenly be produced."

This conclusion of Clausius is the reverse of the facts which established Ohm's Law. The fact is that the smallest electromotive force produces a current, and the intensity of the current increases with the force. Clausius's inference was that "the ions of an electrolyte cannot be firmly held together so as to form complete molecules which are disposed in a definite and regular manner."

Hittorf adopted the conclusion of Clausius, and regarded a solution as molecules continually exchanging their ions. He considered the interchange between two electrolytes in contact as identical with those which occur between the same compounds.

Ultimately Arrhenius about 1887 asserted that the act of solution actually frees the ions. Hittorf had clearly distinguished between the rates of conductivity of electrolytes and the strength of the affinity between ions, while Arrhenius systematically pointed out the relations between substances in solution and gaseous substances, and identified the laws of osmotic pressure with gas laws. We further learn from Arrhenius that the reactions of electrolytes, that is, of acids, bases, and salts, are the reactions of the ions of the compounds when in solution, and that these are different from the reactions of the dry solids.

Electrical theory distinguishes between *quantity of electricity* and *intensity of electro-motive force*, and electric energy is the product of the quantity into the intensity. The modern electro-chemical theory figures corpuscles of electricity as resident in chemical atoms, and represents chemical interactions as atomic attractions which are electrical in their origin. So far it agrees with the views alike of Berzelius, Davy, and Faraday; but in certain respects it differs from all three.

Whether an atom interacts chemically or not depends on

its power of acquiring a charge of electricity; that is, it must be able to gain or lose one or more corpuscles, and these processes are conditioned by the number of corpuscles in the atom, their motion, and their configuration. Thus—

1. The valencies are represented as depending on the number of corpuscles which each atom must gain or lose in order to become stable.
2. The form of the compound is conditioned by the valencies of the atoms.
3. The formation or non-formation of the compound is conditioned by the readiness of the atoms, under the experimental conditions, to gain or lose the number of corpuscles which make it possible to form a system more stable than the original system of atoms.

So that atoms combine into molecules because they become charged positively or negatively, not because they carry positive or negative electric charges. The modern idea is that the formation of a complex element from a simpler one is a process of the same kind as the formation of a compound, only the elements are the stable stages in the aggregations, while the compounds are less stable collections of what we call elements.

Here we may take leave of the history of modern chemical philosophy. It is not a long story, so far as its main features are concerned. The most important doctrines recognised at the present day are not more than a century old, and some of them are much less. The real progress of the science dates from the time when quantitative methods were brought to the aid of laboratory work. No chemist, and no student of chemical history, can doubt that the development will be maintained. It is assuredly possible for us to know more than we do about chemical philosophy, and the lesson of past history seems to be that once a firm foundation has been laid, the rate of progress becomes more rapid. Some of the discoveries of recent years suggest that the truth of this lesson is likely to be verified in the course of the century upon which we have entered.

## CHAPTER XLVIII

### THE CHEMICAL ELEMENTS

#### (1) *The Non-metallic Elements*

THE last stage of our course is to take account of the history of the chemical elements. In preceding chapters it has been necessary to mention these elements repeatedly, and to note the discovery of the most important, but it is expedient that we should complete our work by gathering the whole into a connected narrative. For this purpose the most logical method will be to consider the elements as nearly as possible in the order of their modern classification.

It will be remembered that the word "element" was originally applied to the four elemental properties of Aristotle,—fire, air, water, and earth. The term, however, is now employed with a much wider signification to include every substance which has hitherto resisted efforts to decompose or split it up into two or more different bodies, and out of which nothing essentially different from the original substance has been obtained. We say "hitherto," because there is no possibility of predicting what discoveries lie in the future. Magnesia was assumed to be a simple body, but the advance of chemical science showed it to be a compound of magnesium and oxygen. There is every probability, therefore, that improved methods and increasing knowledge may lead to the decomposition and subdivision of some bodies which we at present deem to be simple or elementary.

1. *Oxygen* has been called the "pivot round which the science of chemistry turns," and although this saying is hardly true in the sense in which its author intended, the importance and scientific interest of the reactions of this gas make it one of the most important elements, as it is the most widely

diffused. We have already said so much about it that we need only repeat that it was discovered by Priestley in England in 1774, and independently by Scheele in Sweden in 1775, but the former was the first to announce his discovery. A little later, Lavoisier recognised the rôle it plays in respiration and combustion, and gave it the name of Oxygen, the "acid maker." The negative oxides make acid solutions, and were themselves formerly termed acids.

2. *Hydrogen* plays a rôle equally important with the last gas, and was observed even earlier. In the sixteenth century Paracelsus observed that an inflammable gas was given off when metals were acted on by dilute acids. In 1766 its properties were determined by Cavendish with fair accuracy, and in 1783 he proved that water is the product of exploding a mixture of the gas with atmospheric air. The name Hydrogen, the "water-producer," was conferred by Lavoisier.

3. *Nitrogen* seems to have been first detected in 1772 by Dr. Rutherford, of Edinburgh, who showed that after air had been breathed for some time by an animal, and the carbon dioxide had been removed by potassium hydroxide, there remained a gas which supported neither life nor combustion, and which he called "mephitic air." Scheele proved that this gas is a constituent of the atmosphere, and Lavoisier demonstrated that the air is composed mainly of two gases, one of which supports life and combustion, while the other does not. To the latter he gave the name "azote," meaning "that which does not support life," a name still used in France. The term Nitrogen, the "nitre-maker," was applied to the element by Chaptal, because it was found to be a constituent of that salt.

4. *Carbon* being one of the essential constituents of organic matter is one of the most widely diffused elements. In the forms of charcoal and of plumbago or graphite, it has been known from the earliest times, but the fact that in its crystalline form it constitutes the diamond was not fully established until the experiments of Lavoisier in 1775-6, already mentioned.



We have repeatedly alluded to its important compound, carbon dioxide or carbonic acid gas, which was first detected by Van Helmont, re-discovered by Black as "fixed air" in 1754, liquefied by Faraday, and solidified by Thilorier.

5. *Chlorine* has had such a powerful influence on the progress of chemical philosophy that it merits more detailed consideration. It was known in early times that *aqua regia* evolved a peculiar gas, which must have seriously incommoded the alchemists who eleven hundred years ago used that liquid for dissolving gold. It appears to have been observed by Van Helmont, Glauber, and Boyle, but those early chemists obtained the gas without knowing it, and without investigating it. Scheele was its real discoverer. In 1774 he produced it by the action of marine acid ( $\text{HCl}$ ) on pyrolusite ( $\text{MnO}_2$ ), investigated it, and drew the attention of chemists to his discovery. The gas, which resembled the fume of *aqua regia*, had a yellow hue, and so destroyed vegetable colours that they could not be restored by alkalis. Scheele thought that the gas was obtained by removing something rich in phlogiston from marine acid; he found that it combined with hydrogen and hydrocarbons; and he named it "dephlogisticated marine acid gas." In 1785 Pelletier, and in 1786 Karsten, showed that it could be condensed to a liquid by cold, and in 1810 it was solidified.

After Lavoisier's discovery of the properties of oxygen, and when his views on combustion were generally accepted, chlorine was deemed to be oxymuriatic acid, because it supported combustion, bleached substances, formed salts with bases, and was obtained by the use of a peroxide. It must, therefore, as chemists thought, contain oxygen.

Between 1808 and 1810 Berthollet showed that Scheele's gas, when it was dissolved in water and the solution was exposed to the sunlight, gave off oxygen and left muriatic acid ( $\text{HCl}$ ). This he held to be proof that it was oxygenated muriatic acid. It was Sir Humphry Davy who in 1810 demonstrated that it did not itself yield oxygen, and that it

bleached by uniting with the hydrogen of water and liberating the oxygen. He declared it to be an element, and named it Chlorine, the "green gas," from its colour (*Trans. Royal Socy.*, July 12th, 1810).

One of the most interesting passages in the history of chlorine is its use as a bleaching agent. Berthollet prepared it for technical bleaching purposes from common salt, sulphuric acid, and binoxide of manganese, a method which remained in use down to a recent date. He first used it in aqueous solution, but soon found it more advantageous to absorb the

gas in caustic potash solution. This industrial preparation of hypochlorite was carried on in 1789, and the solution was sold and known as Eau de Javelles. The works are still situated at the Quai de Javelles, in Paris.



FIG. 105. — Charles Tennant.

We have already told how James Watt became acquainted with this process, and brought it to Glasgow. In 1798 Charles Tennant, of the St. Rollex Works, at Darnley, near Glasgow, made a cheap and efficient bleaching liquid by using milk of lime in

place of the more costly caustic potash. Next year he made a further step by substituting dry calcium hydrate, and so preparing dry bleaching powder for the market. This not only gave an immense impulse to the bleaching industry, but also was the beginning of a large and important manufacture.

It was many years before the views of Davy triumphed over the oxy-muriatic theory. The great Berzelius himself argued stoutly against the evidence of experiment adduced by Sir Humphry. In the end, however, truth prevailed. Meantime, the technical process of manufacture was exposed to many

drawbacks. Berthollet's method was still in use, giving a residue of sulphate of soda, when the Le Blanc process of alkali manufacture yielded as a noxious vapour torrents of hydrochloric acid gas. The next advance was made by Mr. William Gossage, a man to whom we owe several hundreds of industrial patents, and in whose memory there is now a large laboratory at the University of Liverpool. He abated the nuisance emanating from the chimneys of alkali works by absorbing the gas by water in coke towers. Solution of hydrochloric acid now became abundant and cheap, a drug in the market, and the bleach manufacturer reverted to Scheele's process, and used manganese dioxide and solution of hydrochloric acid for the manufacture of chlorine on a large scale. That was how it came to pass that the alkali manufacture and bleach manufacture have been associated in the same works.

But in this way only half the chlorine was recovered, the other half and all the manganese being wasted and got rid of with difficulty. In 1845 an advance was attempted by Mr. Dunlop, grandson of Charles Tennant. He went back to the old reaction of the alchemists, and decomposed a mixture of common salt and nitre by means of sulphuric acid, but separated the nitrous gases from the chlorine by absorbing them in sulphuric acid, and so forming nitro-sulphuric acid, as in Gay-Lussac's towers. The remaining chlorine he washed with water, and got it pure. The nitro-sulphuric acid was utilised for sulphuric acid manufacture, but the extension of the process is limited by the comparatively small amount that can be utilised.

Another line of improvement consisted in the regeneration of manganese dioxide. This was first accomplished by Mr. Dunlop, who neutralised the excess of hydrochloric acid, and precipitated the iron by means of ground chalk. By filtration and pressure he got solution of manganous chloride ( $MnCl_2$ ) and calcium chloride ( $CaCl_2$ ). To this solution he added milk of lime and chalk under pressure, obtaining finely divided manganous carbonate ( $MnCO_3$ ), which being exposed

to hot air at 300° Centigrade yielded the higher oxide. The plan is right in principle but imperfect, and has not been generally adopted.

Walter Weldon's process was founded on Gossage's patent of 1837 for treating the manganese liquors with lime and agitating the mixture with air, which had not been commercially successful. Weldon used one-fourth excess of lime after removing the free acid and iron by chalk. He then forced



FIG. 106.—Walter Weldon.

in air under pressure. Calcium manganate is formed in a few hours, when the clear liquor, chiefly calcium chloride, is run off. The remaining so-called "Weldon mud," consisting of manganese dioxide with a little calcium manganate, is used in place of pyrolusite for the generation of chlorine. These processes have been improved and extended by the late Mr. Henry Deacon, senior, Dr. Mond, and others, but the details are too intricate to be described here.

6. *Bromine* was discovered by Balard in 1826 in the "bittern" or mother-liquor that remained after the common salt had crystallised out of concentrated sea-water. He gave it this name from a Greek word signifying "stench." The larger part of the bromine of commerce comes from the salt wells of the United States, particularly West Virginia, Michigan, and Ohio. In Europe the chief source of supply is the potassium chloride mines of Stassfurt, in Germany.

7. *Iodine* was discovered by Courtois of Paris in 1812 in the mother-liquors collected in the process of manufacturing the sodium salts from kelp or burnt sea-weeds. The name is derived from a Greek word meaning "violet," in allusion to

the colour of the vapour of iodine. Its elementary character was established by Gay-Lussac in 1815.

8. *Fluorine* occurs in the mineral called fluor-spar, which is found in Derbyshire, and from which its name was derived. It also exists in the mineral cryolite, which occurs in Greenland, and strange to say, minute quantities of it have been detected in the teeth and blood of animals. It was observed in its compounds in the beginning of the nineteenth century, but its isolation is very difficult, being an exceedingly active element. Moissan in 1886 succeeded in isolating it by the electrolysis of hydrofluoric acid in the presence of potassium fluoride.

9. *Sulphur* derives its name from the Latin word "sulphur." Its old name "brimstone," from the ancient English "brenston," means "burn-stone," and refers to its combustibility. This element has played so important a part in chemical science that a little space may be devoted to its history.

The original discovery of sulphur dates long prior to the historic period. A millennium before our era it was well known for religious and sanitary purposes. Its fine smelly smoke when burned fitted it for the former, and the smell combined with the genuine disinfecting power of its vapour rendered it effective for the latter. The early materia medica books of Dioscorides in Greek, and of Pliny in Latin, mention it, while Georg Agricola's book, "*De Re Metallica*," tells how to extract it. Geber gave directions for preparing "milk of sulphur" as a medicine, by heating sulphur with lime, lixiviating it, and treating the dissolved product with one-fourth part of good vinegar. Both Agricola and Libavius in the sixteenth century describe the preparation of "flowers of sulphur," while the Pseudo-Geber notes the solubility of the substance in caustic alkali, as well as in *aqua regia*, and Lully knew that strong nitric acid dissolves it. Solutions of sulphur in certain oils, or in turpentine, were called "sulphur-balsam." In 1793 Westrumb discovered that arsenic sometimes occurs in



sulphur as an impurity. The alchemists recognised this element as a fatty mineral substance, which could be melted and whose oil could be burned, but which was homogeneous and therefore of uniform substance. The "sulphur of the philosophers" was, of course, a different matter, and purely imaginary.

The compounds of sulphur with the known metals were familiar from an early date, as also its compound with oxygen, now called "sulphuric acid." It was soon perceived that a similar substance could be obtained from other materials. Vincent de Beauvais in the thirteenth century mentions the solvent power of the acid distilled from alum; Albertus Magnus mentions the "spirit of Roman vitriol"; Sala in 1613 denied that the oil of vitriol from copper and iron vitriols differed from the acid obtained from alum, and Kunckel distinguished vitriol spirit from oil of vitriol as merely containing more water. Boyle (1664) showed that the acid from sulphur and oil of vitriol are identical. He produced sulphur by heating sulphuric acid with oil of turpentine in a small glass flask, leaving it undetermined whether the sulphur was contained in the acid; but Stahl taught that the sulphur in this experiment was produced by the combination of sulphuric acid with phlogiston.

Nicolas Lemery (1675) remarks that iron vitriol gives a pure acid, while copper vitriol gives acid with a bad smell. His son, Louis Lemery, said, in a treatise referred to in the *Histoire de l'Académie des Sciences* for 1736, that "an acid combined with a metal gives a vitriol differing according to the metal, or with a pure white earth gives alum, or with a fat or oily substance gives common sulphur. The acid is always the same in these three mixtures; it is the vitriolic acid." They did not weigh products in those days!

In the eighteenth century sulphuric acid was made in England by burning sulphur with saltpetre. In 1758 this was done in glass globes. Dr. Roebuck in Birmingham, about 1746, made lead chambers, and Boerhaave in 1732 mentions the clearing of brown oil of vitriol by boiling it.

The phlogistic view was that sulphuric acid was a constituent of sulphur, which was composed of oil of vitriol and the principle of combustibility. Kirwan in 1782 assumed that the proportions were 41 parts by weight of phlogiston and 59 of sulphuric acid. Yet as early as 1669 Mayow in his tract "*De Salnitro et Spiritu Nitro-aereo*" had put forward the view that instead of being composed of sulphuric acid, as one of its constituents, sulphur was really a constituent of the acid. It was in 1779 that Lavoisier proved that the forgotten view of Mayow was correct, by combining sulphur with the oxygen of the air, forming a heavier substance, and showing that the same body was produced by heating oil of vitriol with mercury. The elementary nature of sulphur was established in 1809 by Gay-Lussac and Thénard.

Although sulphurous acid, being produced whenever sulphur is burned in air, was known naturally far earlier than sulphuric acid, its true nature was not recognised until much later. The fumigation of Homer's time was effected by this substance, and Pliny mentions its use for bleaching wool. George Starkey, a seventeenth century alchemist, in a tract published in the *Collectanea Chemica* (London: Elliot & Co., 1893) gives a most eulogistic account of its virtues, under the name of "the true oil which is made of sulphur vive set on fire, and commonly called oil of sulphur *per campanam*." According to Starkey it is a sovereign remedy for most of the ills that flesh is heir to.

Down to the end of the seventeenth century sulphurous and sulphuric acids were confounded together and not recognised as different substances. Stahl first, in his *Specimen Becherianum* (1702), pointed out a difference between them, writing of the one as *acidum volatile* and the other as *acidum fixum*. After mentioning that oil of vitriol is the stronger acid, he goes on to describe the preparation of potassium sulphite and ammonium sulphite. The former was long known as Stahl's *Sal Sulphuratum*. In his *Observationes Chymico-physico-medicae* (1697) he tells how water saturated with sulphurous acid solidifies in winter, and loses its smell without losing its

acid properties, but regains its characters when thawed. In the middle of the eighteenth century sulphurous acid was termed "sulphuric acid," while true sulphuric acid was called "vitriolic acid." Phlogistonists and anti-phlogistonists alike recognised sulphurous acid by whatever name they called it as intermediate between sulphur and sulphuric acid. The phlogistonists attributed the difference to the amount of phlogiston the two acids respectively contained, but Lavoisier in 1777 showed that the difference lies in the proportions of oxygen with which sulphur combines.

Thiosulphuric, otherwise hyposulphurous, acid seems to have been first dimly perceived by Stahl in 1718, and it formed the subject of researches by Berthollet, Fourcroy, Vauquelin, and others. Our knowledge of the true nature of so-called hyposulphuric acid (as thio-sulphuric acid) and the existence of a true hyposulphurous acid, or rather the salts of these, is due to the prolonged labours of Debus and his various critics.

In the preparation of "liver of sulphur," and from it "milk of sulphur," sulphuretted hydrogen must have been produced, and certainly must have been observed, yet strange to say there is no mention of it. One can only conclude that the phrase "sulphur gas" included all the odorous products of sulphur without distinction. However, Lemery in his *Cours de Chimie* (1675) noted the blackening of silver by the vapour produced in preparing milk of sulphur. Libavius (1595) noted a similar blackening of white lead surfaces, and Hofmann mentions clearly the very fœtid odour, like rotten eggs, on the addition of acid in preparing milk of sulphur. Meyer in 1764 discovered that the gas so given off is inflammable. Rouelle and Scheele both investigated this gas, the latter producing it from sulphide of iron as we do, while Bergman recognised the identity of the gas from liver of sulphur and that from sulphuretted water, and taught its reactions with metallic solutions. As formerly stated, it played an important part in the discussion as to whether oxygen is the sole acidifying principle.

10. *Selenium* was discovered by Berzelius in 1817 in the

deposit in the leaden chambers of a sulphuric acid manufactory at Gripsholm, in Sweden. He called it "selenium," from "selene," the Greek word for the moon, on account of its affinity with tellurium, discovered a short time before, which had been named from "tellus," the earth.

11. *Tellurium*, just mentioned, was first prepared by Klaproth in 1798, but more fully investigated by Berzelius in 1832.

12. *Silicon*, being one of the principal constituents of the crust of the earth, is an element as widely distributed as carbon. Its name is derived from "silex," flint, and it occurs only in Nature in the form of silica or silicon dioxide, which may be found almost pure in rock-crystal, flint, or sand. It was first isolated in 1810 by Berzelius, by fusing a mixture of iron, carbon, and quartz.

13. *Boron* in combination with sodium and oxygen is found in Nature as borax, a word derived from the Persian "baurach" and Arabic "buraq." In that form it has been known from ancient times, but the element itself was only isolated in 1808 by Gay-Lussac and Thénard.

14. *Phosphorus*, one of the most interesting of the elements, was totally unknown in ancient chemistry, being accidentally discovered in 1669 by Brandt, of Hamburg, while he was distilling a mixture of sand and evaporated urine. It was thoroughly investigated in 1771 by Scheele, who found that it existed in bone, and described a method of preparing it from bone-ash. Until 1772 it was deemed a compound of phlogiston with an acid, but Lavoisier then proved that the product of its combustion in the air was heavier than the quantity burned, and in 1789 showed that phosphoric acid was a compound of phosphorus with oxygen. The name signifies "light bearer," and was formerly applied to any substance which is luminous in the dark. This element was distinguished as *phosphorus mirabilis*, Brandt's, Boyle's, or English phosphorus. Matches were first made in 1805 of wood splinters dipped in sulphur, tipped with a mixture of sugar and potassium chlorate, and ignited by dipping them into sulphuric acid. Friction matches

made with antimony sulphide were introduced in 1832. Phosphorus was used for match-making about the middle of the nineteenth century.

15. *Arsenic* may be regarded as a link connecting the non-metallic with the metallic elements. Among the former group it has close analogies with nitrogen and phosphorus, and among the latter with antimony and bismuth. It occurs naturally in combination with sulphur as realgar and orpiment, which were both familiar to the alchemists, as already mentioned, by the names of "sandarach" and "arsenicon." Arsenious oxide was known to Geber, Albertus Magnus, and Basil Valentine, but its composition was first determined by Brandt in 1773. Arsenic itself was obtained by Schröder in 1694. Perhaps no substances have played such a terrible part in toxicology as the compounds of this deadly element.



## CHAPTER XLIX

### THE CHEMICAL ELEMENTS

#### (2) *The Metallic Elements and Inert Gases*

WE resume our history of the chemical elements with those bodies which are usually termed "metallic," according to a classification, which is convenient, but, as was explained when discussing the Periodic Law, not always capable of being strictly applied. To these we shall add the inert gases lately discovered, and deal with the radio-active elements in a concluding chapter.

1. *Lithium* is a very rare metal, which was found in the minerals petalite and spodumene in 1817 by Arfvedson, the pupil of Berzelius, and obtained in metallic form in 1855 by Bunsen and Matthiessen. It also occurs in lithium mica or lepidolite. The name is derived from the Greek "lithos," a stone, and was given to the metal because it was then supposed to be found in rocks only, and not in plant and animal bodies. Its salts impart a red colouration to flame, a fact first observed in 1818 by C. G. Gmelin. Stas definitely determined its atomic weight.

2. *Sodium*, as the source of sea-salt, is very widely distributed, and through its compounds was known from the earliest period. Sodium carbonate was called *nator* by the Hebrews, *nitron* by the Greeks, and *nitrum* by the Romans. In the fifteenth century, to distinguish saltpetre from the sodium compound, the former was called *nitrum*, the latter *natrum*. The English name comes from the Latin "solida," solid, through the Italian "soda," a term applied in the Middle Ages to all alkalis. The metal was first prepared by Davy in 1807 by electrolysis of the hydroxide.

3. *Potassium* has also been known in its compounds from a remote antiquity. A substance termed "potash" was obtained from wood-ashes by bleaching and evaporation, and from this was derived the name of the metal, which was first prepared by Davy in 1807 by electrolysis of the hydroxide.

4. *Rubidium*, although widely distributed, occurs only in minute quantities in sea and mineral waters, and in lepidolite and other minerals. It was discovered in 1861 by Bunsen and Kirchhoff, by means of the spectroscope, its spectrum containing two bright lines in the extreme red, hence its name from the Latin "ruber," red.

5. *Caesium*, like rubidium, was discovered by Bunsen and Kirchhoff in 1860 in the Durkheim mineral waters. The blowpipe analyst, Plattner, many years previously, when he was examining the mineral *pollux*, found a deficiency in the results of his analysis. This was due to his mistaking caesium sulphate for the mixed sulphates of soda and potassium. It was the first element discovered by means of the spectroscope, its spectrum containing two bright lines in the blue, from which circumstance its name is derived. It is found in sea and mineral waters, ashes of tobacco, tea, coffee, and certain woods, and in the rare mineral pollucite.

6. *Ammonium* is the name given to a hypothetical radicle, containing one atom of nitrogen and four of hydrogen, which forms the ammoniacal salts. It has never been isolated. Sal ammoniac (ammonium chloride) was known to Geber, and the name was originally given to a salt brought from the Libyan desert in the vicinity of the temple of Jupiter Ammon. Aqueous ammonia or spirit of hartshorn was prepared by distilling the hoofs and horns of animals.

7. *Calcium*, the metal which forms lime, was obtained in 1808 by Davy by electrolysis of the oxide, quicklime. Calcium, strontium and barium were isolated from their amalgams, which Seebeck was the first to prepare. The substance called "lime" was known and used by the ancients, but it was not till 1722 that Hoffman showed that it was a distinct earth.

8. *Strontium* takes its name from the village of Strontian in Argyllshire. In 1790 Crawford suggested the presence of a peculiar earth in the mineral strontianite, which was found in the Strontian district. In 1791 Hope, and in 1792 Klaproth, verified this suggestion, while Davy in 1808 prepared the metal by electrolysis.

9. *Barium* derives its name from the Greek "barus," heavy, on the suggestion of Guyton de Morveau. In 1602 a Bolognese shoemaker, V. Casciorolus, observed that heavy-spar became phosphorescent when ignited with a combustible. This attracted much attention to the "Bologna stone," as it was called, and indirectly led to the discovery of phosphorus. In 1774 Scheele discovered a new earth baryta, which Gahn proved to exist in heavy-spar. Davy obtained the metal in 1808 by electrolysis.

10. *Beryllium* or *Glucinum* is a rare metal obtained from beryl. In 1797 Vauquelin showed that that precious stone contained a peculiar earth, and the metal was isolated in 1827 by Wöhler, and prepared in a pure state by Humpidge in 1885. The name "glucinum" is derived from the Greek "glueus," sweet, from the fact that its compounds have a sweet taste.

11. *Magnesium*, like many other elements, was known by means of its salts long before it was isolated. Its sulphate was first obtained by a London physician, Nehemiah Grew, in 1695 by evaporating the water of the mineral spring at Epsom. The product was called Epsom Salts. About the same time magnesium carbonate was introduced as a medicine under the name of "magnesia alba," a name which became classical through the investigations of Dr. Black. In 1800 Davy prepared the oxide and the metal in a crude state, while in 1830 it was obtained in a purer state by Bussy. Bunsen got it by electrolysis. The name "magnesia" was also applied to the mineral pyrolusite (native manganese dioxide), because of its supposed magnetic properties, but the two metals gradually acquired their present names.

12. *Zinc*, as a constituent of the alloy brass, was known to

the ancients, but was not recognised as a distinct metal until the time of Paracelsus. The name is first used by Basil Valentine, and the metal in reasonable purity was prepared in 1720 by Henckel.

13. *Cadmium* takes its name from "cadmia," the original name for zinc, having been discovered in 1817 by Strohmeyer amongst the products of the zinc furnace.

14. *Mercury* was so fully described in the first part of this History, that we need add little here. Theophrastus about 300 B.C. speaks of liquid silver which may be obtained by mixing cinnabar (mercuric sulphide) with vinegar. It was named from the planet, and was one of the principal ingredients of alchemical compositions. It must be distinguished from the imaginary "mercury of the philosophers."

15, 16 and 17. *Copper, silver and gold*, may for the same reason be passed over. It may be remarked, however, respecting gold, that its brilliancy has ever seemed to men to be its most striking characteristic. The Hebrew *zahab*, Greek *chrysos*, and Sanskrit *hiranya*, all allude to glittering or shining, while the English name is probably derived through the Anglo-Saxon from a Sanskrit verb, "joal," to shine. It is, therefore, no wonder that it was from the first symbolised by the sun, with which it was supposed to be connected.

18. *Aluminium* was first prepared by Wöhler in 1827, but alumen or alum, the double sulphate of aluminium and potash, was known from the earliest times, although the substances so-called were not always accurately distinguished.

19. *Gallium* was in 1875 discovered by Lecocq de Boisbaudran by means of the spectroscope in a zincblende from the Pyrenees, and he named it after ancient Gaul. It is specially interesting as being identical with the hypothetical element, "ek-aluminium," the existence of which was predicted by Mendeléeff.

20. *Indium* was discovered in 1863 by Reich and Richter through a bright indigo-blue line in its spectrum, whence its name. It occurs in minute quantities in the zincblendes from

Freiberg, and the Hartz Mountains, and its presence in the sun's atmosphere has been ascertained by Lockyer.

21. *Thallium* was simultaneously discovered by Crookes and Lamy in 1861 in the leaden chamber deposit of sulphuric acid manufactories. The former named it from the bright-green line seen in its spectrum. Lamy established its chemical nature, while Crookes determined its atomic weight.

22. The *Gadolinite Earths* are a group of rare and obscure earths mostly found in Scandinavia, whose chemical characters have not been fully worked out, and which are, indeed, best known by their spectra. Their history is peculiar, and merits a little more space than we have given to the preceding metallic elements. For a full account the student is referred to Truchot's "Les Terres Rares."

In 1751 Cronstedt discovered cerite and in 1794 Gadolin detected rare earths in a mineral afterwards called gadolinite which had been found six years previously by Arrhenius near the town of Ytterby in Sweden. After the discovery of glucinum, Ekerberg, in 1799, separated glucina, and called the remaining mass of earths yttria. In 1804 ceria was discovered in cerite by Klaproth, Berzelius and Hissengen, the last of whom named it. Much confusion existed as to these substances until 1839 when Mosander made his celebrated research separating ceria into ceria and lanthana. Three years later Mosander found didymium in ceria, and thus obtained the latter nearly pure. Ultimately, about 1897, ceria was freed from yttria and thoria.

Lanthana went through a similar history. After a long series of experiments Schutzenberger, in 1895, separated didymium and lanthanum, and obtained a substance varying in atomic weight between 138 and 135. The lower figure was shown to be due to mixture with yttria.

The didymia separated in 1842 by Mosander from ceria was investigated as a single substance down till 1878, when Delafontaine announced the separation of decipium from it with a peculiar absorption spectrum. In 1879 Lecocq de Boisbaudran and J. L. Smith separated decipium and samarium



from the didymium of samarskite, with more feeble basic character and a peculiar absorption spectrum. Delafontaine continued his work on decipium, and in 1881 found that it was a mixture of samarium with atomic weight 151.5 and decipium with atomic weight 171. It appears, however, that Delafontaine's decipium is identical with Barignac's Y, which he separated from  $Y_2$ , and which has since received the name "gadolinium" with atomic weight 156, while decipium, if it exists, has a higher atomic weight. In 1883 Cleve freed didymium from samarium, while in 1885 Welsbach showed that the former is a mixture of neodidymium with red salts and praseodidymium with green salts.

Samarium was prepared in 1885 by Cleve, while Crookes, finding it as a constant impurity in yttria, fractionated and examined spectra of its phosphorescence, and arrived at the conclusion that two elements were indicated by the bands in these. More work followed until, in 1901, Demarcay distinguished another element and called it "europium." The old samarium is, therefore, a mixture of samarium and europium.

The yttria group had also a complicated history. In 1833 Berlin described compounds of the old compound yttria as those of a homogeneous element, but in 1842 Scherer, founding on the changeable colour of the oxide, suggested a doubt, which was confirmed by Mosander in 1843, who divided the earth into yttria, terbia and erbia. In 1860, as the result of experiments by Berlin, the name "erbia" was reserved for the substance with rose salts, and "terbia" for the substance with yellow oxide and colourless salts. After much research by various chemists, Lecocq, in 1886, determined the true nature of what was called "mosandrum," as a mixture of terbium, gadolinum, a little samarium and traces of didymium. This confusion arises from the necessities of the case. A certain number of salts are separated by their solubility in potassium sulphate, and if their oxides are treated as a single one, certain properties are assigned to an element. Then, by other methods,

it is found that these properties belong to an aggregation of oxides, each of which away from the rest has quite different properties.

The history of philippium recalls that of decipium, both started by Delafontaine, who, when he had placed yttria and terbia out of doubt, recognised an intermediate body which he called philippium. The old controversy began. One chemist said it was a compound body, another held that it was a simple one. At last, in 1882, Roscoe showed that philippium is a mixture of yttrium and terbium; Crookes confirmed this; but in 1897 Delafontaine reaffirmed the existence of philippium. Delafontaine has fallen into a very natural error. One is apt to suppose that one's opponent has not had a sufficiently good method of separation, and to think that when fractionation is carried so far that it no longer gives a different product, that product is a distinct element. It may be only a constant mixture. The fact is that fractional precipitation, fractional solution, fractional anything, is just like fractional distillation in this respect—there are substances which one cannot separate by fractional distillation because they distill together; so in other fractionations. One must combine and compare many methods of separation, and many methods of identification—chemical properties, colours of salts and oxides, spark spectra, absorption bands, cathodic phosphorescence, and so forth. And this is the great lesson to be learned from the study of these rare earths.

Thus, the old erbia, Mosander's rose earth, was a mixture, a very complex mixture. In 1878 Marignac, seeking for Delafontaine's philippium, separated from erbia a colourless oxide which he called ytterbium. In 1879 Nilson pushed the process further and discovered yet another earth which he called scandium. In 1879 Cleve, fractionating the remainder of erbia, separated three earths, named thulia, holmia and new erbia. Demareay in 1900 suggested the existence of two other intermediate earths.

The following elements have been detected by the investi-

gation of cerite, gadolinite, and similar minerals—yttrium, erbium and terbium (from Ytterby), neodidymium and praseodidymium, lanthanum (from “lanthanos,” concealed), gadolinum, ytterbium, samarium, europium, and scandium (named by Nilson in 1879 from Scandinavia). The last is remarkable as agreeing with the hypothetical element foretold by Mendeléeff under the name of “eka-boron.” The investigation of these bodies is so difficult for the reasons already mentioned, that it is impossible to say at present how many of them will ultimately be accepted as homogeneous elements.

23. *Germanium* was discovered in 1886 by Cl. Winckler of Freiberg, and the properties of the element are in striking agreement with a hypothetical body predicted by Mendeléeff in 1871, as existing between tin and mercury, and called by him “eka-silicon.” The impulse to look for a new metal was given to Winckler by a certain deficit in the analysis of Freiberg silver ore, which suggested the presence of some element hitherto unknown.

24. *Tin* was known from the earliest times and is a constituent of the implements used by primitive man in the Bronze Age. Pliny called it *plumbum-album*, a name now applied to basic carbonate of lead. The name “stannum” dates from the fourth century, and the word “tin” is Anglo-Saxon. The British Isles were called by Herodotus the Cassiterides, or Tin Islands.

25. *Lead* has also been known throughout the historic period. In the Biblical books, Job and Numbers, it was termed “biblicalex,” while Pliny called it *plumbum nigrum* to distinguish it from silver, *plumbum candidum*, and tin, *plumbum album*.

26. *Titanium* was first recognised as a distinct metal in 1791 by William MacGregor, and was further investigated in 1795 by Klaproth, who named it after the Titans. Rose obtained the pure oxide in 1821.

27. *Zirconium* was discovered by Klaproth in 1789 as a new earth, which he termed “zirconia,” from the mineral zircon,

in which it was obtained. It was first isolated by Berzelius, and obtained in crystalline form by Proust. The name is probably Persian, and signifies "gold-coloured."

28. *Cerium* was separated in 1803 by Klaproth from the Swedish mineral cerite, which yielded also several substances which we mentioned under the group of gadolinite earths. The earth was named ceria, from the planet Ceres which had just been discovered. The metal was first prepared by Mosander in 1826.

29. *Thorium* was discovered in 1828 by Berzelius as an earth found in the rare mineral thorite, from Norway. He named the earth thoria, after the Scandinavian god Thor. It is used along with ceria and other earths in making mantles for the Welsbach gas-light.

30. *Antimony*, in the form of grey antimony or sulphide, has been known from the earliest times as the mineral "stibnite." It was called *kohl* by the Hebrews and Arabs, *stimmi* by Dioscorides, *stibium* by Pliny, and *antimonium* by the translators of Geber. The method of preparing the metal was first described by its great panegyrist Basil Valentine.

31. *Bismuth* was one of the substances called marcasite, and was known by that name up till a comparatively recent date. It was mentioned by Paracelsus and Agricola, but first described by Basil Valentine. Bergman was the first chemist who accurately studied it. The name is from the German *wismuth* or *bismuth*.

32. *Vanadium* was originally noticed by Del Rio in 1801, who suggested the existence of a new metal in a lead ore from Mexico. In 1830 Wöhler showed that this ore was a lead vanadate. In the same year Sepstrom found the new metal in iron ore from Taberg, Sweden, and called it after Vanadis, the Scandinavian name of the goddess Freia. The element was carefully studied by Berzelius in 1831, and its properties were more accurately ascertained by Roseoe in 1867.

33. *Niobium* or *Columbium* was found in 1801 by Hatchett in a mineral called columbite from Connecticut, and was by

him named "columbium." In 1844 Rose detected in a mineral from Finland, along with Tantalum, an element which he named "niobium." The two elements proved to be the same. The name "niobium" is generally used in Europe, and "columbium" in America.

34. *Tantalum* was discovered in 1802 by Ekerberg in Sweden, in some yttrium minerals, and he called it tantalum, from Tantalus, because its investigation was troublesome. Some confusion exists between this element and Hatchett's columbium, which was found in the same minerals, associated with tantalum.

35. *Chromium* was discovered in a mineral named "crocoisite" described by Lehmann in 1762. Its existence was shown by Vauquelin and Klaproth in 1797, and its name is taken from the Greek *chroma*, colour, because many of its compounds are coloured. The metal was obtained by Deville in 1857.

36. *Molybdenum* was isolated in 1783 by Hjelm, and fully investigated by Scheele and Bergman. The name is derived from the Greek word for lead, and was in earlier times applied to any substance with a lead-like appearance such as galena, graphite, stibnite and molybdenite, the last of which is the chief source of the metal.

37. *Tungsten* or *Wolfram* is another element which was twice identified, and twice named. The word "tungsten" is from the Swedish, and means "heavy-stone." It was applied to the mineral Scheelite, in which Scheele in 1761 proved the existence of a peculiar acid, termed "tungstic." In 1783 the Spanish chemists Juan Jose and Fausto d'Elhujar obtained the same acid from the mineral wolfram, and also separated the element, which was called by the name of the mineral. Tungsten is of commercial importance, being used for the production of steel, and for fire-proofing fabrics.

38. *Uranium* was found by Klaproth in 1789 in the mineral pitchblende, and he named it from the planet Uranus, which Herschel had discovered a few years before. The body which



he obtained was only the oxide of uranium, and it was not until 1842 that the metal was really separated by Peligot.

39. *Manganese* in the form of the mineral pyrolusite or manganese dioxide has been known from a remote period. It was used by the Romans for decolourising glass. It was confused with magnetic iron ore and called "magnesia," referring probably to its supposed magnetic properties. In 1740 Pott proved that pyrolusite contained no iron, and in 1774 Scheele and Bergman showed that it contained a new element. The metal was first isolated by Gahn.

40. *Iron*, and the method of separation from its ores, have been known from prehistoric times. It was used by the Egyptians, Assyrians and Greeks, and is mentioned in the Bible repeatedly. The name is derived from the Scandinavian "iarn."

41. *Cobalt* takes its names from the German "kobold," an evil spirit. This name was originally given by the miners to certain bad ores from which they could not obtain the expected metal. These ores were used in the preparation of smalt. The metal was first prepared by Brandt in 1733, and was more carefully studied in 1780 by Bergman.

42. *Nickel* was obtained in an impure state by Cronstedt in 1751, and more fully investigated by Bergman. The name is taken from the word "kupfernickel," false copper, which was applied to the native nickel arsenide, which resembled copper ore, but yielded no copper.

43. *Ruthenium* is generally a constituent of platinum ores and osmiridium. It is also found as sulphide in the mineral laurite. In 1828 Osann announced that he had discovered three new metals in a Russian platinum ore, one of which he called "ruthenium," from Ruthenia, an old name for Russia. In 1845 Claus showed that Osann's ruthenium oxide consisted mainly of other oxides, but yet contained a small amount of a new metal, for which the name "ruthenium" was retained. Ruthenium and its oxygen compounds were also investigated by Debray.

44. *Rhodium* was discovered by Wollaston in 1803, as a

result of his previous discovery of palladium. It occurs in small quantities in platinum ores, and in some native golds. The name is from the Greek "rhodos," a rose, and refers to the rose-red colour of many rhodium salts.

45. *Palladium* was also discovered by Wollaston in 1803 and named from the planet Pallas, which had been detected by Olbers the previous year. Its remarkable property of combining with hydrogen was first observed by Graham, and has already been noticed (*supra*, p. 435).

46. *Osmium* was observed by Smithson Tennant in 1804, and named from the Greek "osme," smell, in allusion to the peculiar odour of the tetroxide. It was first detected in the residues left from the solution of platinum ores.

47. *Iridium* was also discovered by Tennant in 1804, and its name is derived from the Greek "iris," the rainbow, referring to the varying colours of its salts. The extreme hardness of this metal causes it to be used for tipping gold pens.

48. *Platinum* seems to have been mentioned in 1558 by Joseph Justus Scaliger (1540—1609) of Leyden, who describes it as infusible. It was brought to Europe from South America in 1735 by Ulloa, and after 1823 from the Ural mountains. It was described by Watson in 1748, and afterwards studied by many investigators. The Spaniards called it "platina del pinto," *platina* being the diminutive of *plata*, which means silver, and the Rio Pinto in South America being the place whence it was obtained. As formerly mentioned, Wollaston was the first to devise a process for making platinum workable.

We shall now in conclusion mention a group of gases, recently discovered, which may be termed inert from the circumstance that they form no compounds with other elements. A detailed account of some of these is given in "The Gases of the Atmosphere," by Sir William Ramsay (1896).

In the year 1868 Jansen observed a prominent yellow line in the spectrum of the sun's chromosphere. As this could not be referred to any terrestrial element then known, he supposed it to be produced by an element peculiar to the sun, and hence

called it *helium*. His observations were confirmed by Lockyer and Frankland, and in 1882 Palmieri observed the same line when investigating lava from Vesuvius. In 1895 Ramsay and Cleve obtained the gas itself from the mineral cleveite.

The presence of the other inert gases might have been anticipated. As early as 1785 Cavendish in his experiments with atmospheric air had noticed that a residue of about 0.6 per cent. remained after the nitrogen and oxygen had been removed (p. 283). In 1894 Rayleigh observed that nitrogen obtained from the atmosphere was 0.5 per cent. heavier than nitrogen prepared chemically. Thereupon, Ramsay and he procured large quantities of the atmospheric residue, and on investigation found in it a gas different from nitrogen, which they called *argon*, from the Greek "argos," lazy, in allusion to its inert action.

In 1898 Ramsay and Travers separated from the same atmospheric residue three other gases, *neon* (Greek, "neos," new), *krypton* (Greek, "kryptos," concealed), and *xenon* (Greek, "xenos," a guest, because it accompanies argon, neon, and krypton in the air).

There only remain to be mentioned the remarkable radioactive elements. These are so interesting from their chemical and physical properties, and open up so many problems and unsettled questions, that we shall set apart our final chapter for their special consideration.

## CHAPTER L

### THE CHEMICAL ELEMENTS

#### (3) *The Radio-active Elements*

THE discovery of Radium and other radio-active bodies, an event of the first importance in the History of Chemistry, was the ultimate result of a long course of research. Observations of various physical properties—such as the spectra of minerals and other mixtures of substances—had on eight or nine occasions since 1860 led to chemical investigations, which resulted in the discovery of new chemical elements, and the isolation of their compounds. Eighteen or more elements had been in this way added to the list.

The methods of chemical manipulation had been improved. The discovery of the Röntgen or X rays and of the cathode rays of Crookes' tubes, and more recently of the somewhat analogous Becquerel rays, which were found to proceed from uranium and its minerals, placed at our disposal new methods of investigation, as much more delicate and minute in their application as spectrum analysis is more delicate than the older methods of precipitation, borax beads, and other reactions. These new methods were, first, the effect produced upon a photographic plate through an opaque substance, and second, the extremely delicate electroscope.

By means of these improved methods in recent years a series of elements were discovered whose properties place them outside the old familiar definition of the term "element," as a body so simple that it cannot be resolved into simpler forms. These elements, *radium*, *polonium*, *actinium*, *thorium*  $\alpha$  and others, have all extremely high atomic weights, and are spontaneously but slowly breaking up into simpler forms

with evolution of much energy in the same way that nitroglycerine and other explosive compounds, under certain circumstances split up into their constituent elements with evolution of force. These explosives break up quickly, but the radio-active elements do not. In fact, we know no way of breaking them up speedily, and until they do spontaneously break up, they have all the functions of elements,—have a constant atomic weight, form definite salts, and pass from one salt to another like ordinary metals.

The Becquerel rays and other kindred phenomena, were found associated with ores of uranium and of thorium, both metals of high atomic weight. We shall only lightly touch on the historical side of the discovery of these rays, which have been investigated by Becquerel, the Curies, Debierne, Giessel, Marckwald, Rutherford, Ramsay, Soddy, Bielby, Strutt, Bragg, Mackenzie, Godlawski, and other distinguished chemists. Poincaré suggested in 1896 that, as the source of X rays was apparently the fluorescence of the glass tube, it was possible that X rays accompanied all fluorescence. Henri Becquerel, acting on this suggestion, examined phosphorescent zinc sulphide, and discovered that it emits rays capable of traversing black paper and afterwards affecting a sensitive photographic plate. He next found that uranium, salts of which fluoresce, similarly affected a photographic plate through black paper, and even through metals, without being exposed to light rays. Further research showed that non-fluorescent uranium salts (that is, salts which have not been exposed to light) have the same property. The rays thus discovered were named *Becquerel rays*.

Madame Curie, a Polish lady whose maiden name was Marie Sklodowska, and who was engaged at Paris in teaching chemistry and physics, found that pitchblende, chalcotite, carnotite, and other ores of uranium, are more radio-active than the metal itself or its salts. She imagined that the rays emitted by uranium might be due to some substance which accompanied that metal. With the aid of her husband, Pierre Curie, she



proceeded by chemical methods to endeavour to realise this idea, and by experiment either to verify or correct the hypothetical inference from the known facts that uranium and thorium compounds possessed properties to which the term *radio-activity* was applied. These properties were :—

1. Affecting a photographic plate through glass or aluminium ;
2. Producing a potential up to 100 volts, when placed as one plate of a condenser, 3 centimetres apart ;
3. Making air a conductor of electricity ;
4. Causing certain substances to become fluorescent ; and
5. Ionising gases, that is, rendering them conductors of electricity. This last was the favourite practical test.

Being supplied with £800 worth of pitchblende by societies and individuals in Paris who knew their aims, the Curies proceeded in 1898 to investigate the facts. Pitchblende is a black mineral found in Cornwall, Bohemia and elsewhere which consists of 80 per cent. or more of dark green uranium oxide ( $U_3O_8$ ), with small quantities of bismuth, copper, calcium and other substances. They roasted the ore with sodium carbonate in the usual way, and extracted the uranium by water and dilute sulphuric acid. The insoluble residue contained all the radio-active matter except the uranium. It mainly consisted of alumina, iron oxide, calcium and lead sulphates, with traces of many other metals. By boiling it with solution of sodium carbonate, most of the sulphates were decomposed. The sodium sulphate was then removed by washing with water. The residue was dissolved in hydrochloric acid and treated with sulphuretted hydrogen, which took down all the lead, copper, bismuth and other metals. The precipitated sulphides were separated. Associated with the bismuth sulphide was found a radio-active substance, insoluble in ammonia and ammonium sulphide. When concentrated this yielded a substance, the sulphide of which on being heated in an infusible glass tube at 700 degrees, sublimed as a black film on that part of the tube which is hotter than from 250 to 300 degrees. This black substance contained a body which was 400 times

more active than uranium, and was named by Madame Curie, *polonium*, after her native country.

Polonium was the first radio-active element discovered and partly isolated, but it is not on this body that the most recent investigations have been made. In the filtrate from sulphuretted hydrogen, from ammonium sulphide, and from ammonia, there remained barium precipitated as sulphate. This sulphate was boiled with concentrated sodium carbonate, and then converted into a chloride. By fractional crystallisation of this barium chloride, there was found in combination with it a substance which seemed to be more radio-active than polonium. The chloride of this substance, which the Curies named *radium*, was found in the less soluble portion accompanying barium chloride. This discovery was made in 1902.

Radium has not yet been isolated, but its salts have been studied. They closely resemble those of barium, the chlorides of both being soluble in water but insoluble in alcohol, and the sulphates very insoluble. Neither element is precipitated from solution by sulphuretted hydrogen, ammonia, or ammonium sulphide. Berthelot has found that in the dark radium slowly decomposes iodine pentoxide and nitric acid, and effects slow oxidation of oxalic acid, in these respects resembling light; but it does not, as light does, form insoluble sulphur from a solution of octohedral sulphur crystals in carbon disulphide. Again, it does not polymerise acetylene as the electric current does, but light does not. Its radio-activity colours glass, transforms oxygen into ozone, and phosphorus into the red form, and ionises not only gases but liquid dielectives such as carbon disulphide, petrol, liquid air, and even solid paraffin.

Coehn endeavoured to separate radium by electrolysis, using a small potential difference, and an amalgamated zinc rod, partly coated with paraffin to prevent oxidation. After electrolysis the rod exhibited strong activity towards an electroscope, and caused a phosphorescent screen to glow brightly. As the separation is not possible in aqueous solution, Coehn's experiments were carried out in methyl alcohol. The

radium forms an amalgam with the mercury, and remains as metallic radium, when the methyl alcohol is evaporated off in hydrogen in a closed vessel. As in the case of its compounds, the activity of radium rises after several days to a maximum.

In the preparation of barium amalgam according to the method of Guntz (*Comp. Ren.* 133, 872), it was shown that if barium-radium chloride were used, the first separations of metal were much more strongly radio-active than the original substance. It thus appears that concentration of radium by an electrolytic method is possible, and that this mode will probably replace the long and tedious one by fractional crystallisations.

In addition to radium and polonium, Debierne discovered a third element which he called *actinium*, resembling titanium, and giving the general reactions of the iron group and which may be the same as Crookes' *uranium x*. This last substance, and a substance named *thorium x*, have been found as the result of investigations of salts of uranium and thorium. These make five radio-active elements at least, but there are really more. All give some kind or kinds of similar active rays, but not all in the same degree, or in precisely the same variety.

Nearly all the remarkable properties of radium are due, not to itself, but to the results of its decomposition, of which we have already spoken. When a radium molecule splits up, it gives off a gas and three kinds of rays termed *alpha*, *beta* and *gamma*. It is possible that one man's *alpha* is another man's *beta* and *vice versa*, but there are certainly three kinds of radiation known to us.

The peculiarity of the so-called radio-active bodies generally is that they exhibit in a marked degree the following phenomena which it seems probable that many bodies exhibit in a slight degree :

1. They emit three kinds of rays, alpha, beta and gamma.
2. They emit an emanation or gas with peculiar properties ;  
and

3. They produce secondary effects, or induce radio-activity in other bodies.

These may be deemed their most marked peculiarities.

The *gamma rays* penetrate dark substances, solid bodies and even metals. They are propagated with a speed comparable to light ; but are neither refracted nor reflected by anything. They are not deflected by a magnetic or electric field, are rays only, and are comparable to, though not identical with the Röntgen rays, producing shadow photographs through opaque screens, and showing phosphorescence on a barium platino-cyanide screen.

The *beta* or *Becquerel rays* are also penetrating, passing through even solid bodies, but with less than 1-150th of the power of the gamma or Röntgen rays, and are not absorbed by gases. They are deviated by a magnet, affect a photographic plate through an opaque screen, only slightly ionise gases, are similar to the cathode rays of Crookes' tubes, and produce some phosphorescence on a platino-cyanide screen. They are believed by Rutherford to consist of negatively charged electrons, that is, particles 1-1000th smaller than atoms, projected at a speed exceeding 100,000 miles per second, and emitting rays of very short wave length, but not so short as Röntgen rays. When these rays strike upon glass, or certain bodies, they render them phosphorescent. Becquerel discovered these beta rays and not the alpha rays in uranium, because he investigated the salts by means of a photographic plate ; had he used an electroscope instead he would have discovered the far more important alpha rays.

The *alpha rays* are readily absorbed by metals and other bodies, although they pass through paper and porous material have only 1-100th part of the penetrating power of the beta rays, do not much affect a photographic plate through an opaque body, and are not deviated by a magnetic field, or only slightly by one very intense, and then in the opposite direction from the deviation of beta rays. They powerfully ionise a gas, causing air and gas to discharge an electroscope.

This is their most characteristic property. They render a zinc sulphide screen fluorescent, though not a barium platino-cyanide screen.

Rutherford's theory was that the alpha rays are projected bodies about double the size of hydrogen atoms, and 2,000 times the size of the beta particles, positively charged with electricity, that is, devoid of negative electrons, projected with immense rapidity. They travel at first about one-tenth of the velocity of light (about 12,500 miles per second). By their speed they ionise gas molecules by striking them, until their own speed is too much reduced by passing through a thickness of air or the like. A plate of mica, for example, stops them. They are probably helium atoms shot off with this immense velocity from the disintegrating radium atoms. With so much energy let loose, it is remarkable that very little appears in the form of heat. Radium compounds are always two or three degrees Centigrade warmer than the surrounding atmosphere, and could melt their own weight of ice in an hour, but one would expect more heat. Yet some people express surprise that radium is at all warm!

The theory of atomic disintegration is due to Rutherford and Soddy. The radium gives off an emanation or gas, and at the same time alpha rays. This is explained as being due to a sudden rapid disruption of some of the atoms, of the nature of an explosion. The gas, or emanation, also gives off rays, and is broken down into a second substance, sending off more alpha rays; this again splits into a third; the third into a fourth, now giving off alpha and beta rays; and the final emanation again gives off alpha rays and a final product the nature of which is not known. The emanation is self-luminous and ionises gases, and is condensable by liquid-air to a solid substance vaguely called *emanium*; but this extreme cold does not prevent either it or the radium from giving off rays, consisting of rapidly projected particles.

Ramsay enclosed some of this emanation, highly rarefied by means of the air-pump, in a tube hermetically sealed. This he



sparked electrically for the purpose of observing its spectrum. After some days, on observing it again, he saw faintly the spectrum line of helium. The helium line became more marked later, and then disappeared. Subsequent experiments proved that the emanation is not capable of a lasting existence, and if kept in a sealed tube for a month becomes almost entirely disintegrated, and the tube then contains helium. The fact is curious, and we shall refer to it later.

Radium, according to Rutherford, passes through a series of rapid changes by splitting of particles, and then finally gives rise to two slow-transformation products. The changes are shown by Rutherford diagrammatically, thus :

RADIUM, giving off emanation and alpha rays.

1. Radium emanation, giving off alpha rays.
2. Radium A, giving off alpha rays.
3. Radium B, giving off no rays.
4. Radium C, giving off alpha, beta and gamma rays.
5. Radium D, giving off no rays.
6. Radium E, giving off beta rays.
7. Radium F, giving off alpha rays, and probably identical with *polonium*.
8. Radium G, giving off no rays, and probably some well-known element, most probably *lead*.

Radio-activity, although most strongly manifested in the group of elements we are now considering, is not confined to these, but as we already mentioned is slightly exhibited by many bodies. J. J. Thomson (*Proc. Cambr. Phil. Socy.*, Vol. 12, p. 391), states that eighteen samples of water of different origin showed the presence in small quantities of a radio-active gas, which behaved like the emanation from radium. Sand, glass and other substances were shaken with inactive water, and the emanation removed by boiling, and tested in the usual manner. The emanation, as in the case of radium, falls in four days to half its value ; the induced radio-activity in forty minutes. From this it follows that traces of radium are widely distributed in the earth's crust. Salts and metals were also examined, but with negative results. Although the

emanation is not a common property of bodies, the giving off of ionising rays seems to be so.

The peculiar phenomena of radio-activity, and the peculiar attributes of radium, have led to much speculation and many guesses, some of them bad. The phenomena are undoubtedly governed by ordinary chemical and physical laws. It is now pretty generally agreed, alike by chemists and physicists, that the energy comes from within. Energy arises from chemical change, and radio-activity and the heat evolved by radium are the accompaniments of the chemical change producing such energy. The radio-activity of the emanation is due to its particles breaking up into something else. That is an ordinary chemical occurrence. Every student of elementary chemistry learns in his first lesson that evolution of heat, or energy in some form, is the invariable accompaniment of chemical union. It is one of the general characteristics: but that is only true of combinations taking place within the usual limits of temperature and pressure.

Thus, carbon and hydrogen unite with oxygen in an ordinary flame, and rays of heat and light dart from this flame with a speed of 185,000 miles per second. To separate these elements again and to decompose the products, energy is absorbed and heat is lost. This is the ordinary experience. But at other temperatures and pressures the reverse is the case, and, even within ordinary limits of temperature and pressure, there are substances which give out violent energy, instead of absorbing energy, when they are decomposed into simpler and more stable bodies. Examples of such substances are the explosives to which we formerly alluded, such as *gun-cotton* and *nitro-glycerine*. The general rule, as we have said, is that bodies are formed by chemical reactions or combinations, with the evolution of heat: but others, as ethylene or acetylene, are formed with absorption of heat. The former are classed as *exothermic*, the latter as *endothermic*.

We know the difference between endothermic and exothermic bodies. Nitroglycerine decomposes quickly. But there is

a substance in our brain which decomposes slowly and emits energy in a very remarkable form, the form which is the physical accompaniment of every thought we think, every memory we recall and every message we send along our nerves to command the contraction of a muscle. The source of the energy manifested by radium and other radio-active bodies, as well as the emanations, is plain and simple, and there is no special miracle about it ; it is part of the great miracle of the Universe.

Radium is an endothermic body, undergoing decomposition into a gas and something else. This source of the energy of the radio-activity of the emanation—the gas—is similar. It too, one of the products of the decomposition of radium, is itself decomposing further, with evolution of energy in the form of what is called radio-activity. All this is in accordance with the ordinary laws and with known facts.

Uranium and polonium, which do not give off emanations, but only rays, do not exhibit the power of exciting radio-activity in other bodies. Radium and thorium, which do exhibit this power, lose it by very strong heating, which drives off all their emanations ; but by keeping them, they regain their power of emitting emanations. The power, therefore, of exciting secondary or induced radio-activity, arises from something, which is the result of the decomposition of the gaseous emanations.

We have referred to the experiment in which emanation, sealed up in a tube, became entirely disintegrated, and the gas helium remained in its place. What else remained did not appear. On further keeping, the helium and emanation diminished to almost nothing, and something had been shot into the substance of the glass tube which rendered the glass purple. Some of this "something" might have been recovered from the glass by heating. Helium, it will be remembered, is got from uranium and thorium minerals ; something in uranium minerals decomposes into gas and something else ; while this gas decomposes into helium and something else.

It may be asked, are the other inert gases also dead atoms from the splitting up of something? Allusion has already been made to the fact that other bodies, besides the radio-active elements, exhibit slight radio-activity. Air from the ground of Munich, and from the Hartz Mountains, has been found to be charged with emanations, which are slightly radio-active, and ionised in the sense of being conductors of electricity. Again we may ask, is there much matter in the earth undergoing slow decomposition, and evolving helium, argon, and their relatives? Inert gas has been discovered in Bath waters, and recently these waters have been found to be radio-active, which is quite consistent with what has just been said.

There are yet other facts known, regarding the electric state of the radiations and emanations. These facts have led to speculations which are most interesting but which will be regarded by chemists with extreme caution. We have noted the theory of Rutherford that the alpha rays of radium are really minute particles, atoms charged with positive electricity and projected from the radium with great velocity, which is gradually checked as the atoms pass through other matter. These charged bodies ionise the gas, that is to say, split the molecules of the gas into their constituent ions by rapid collision with them.

This is mere speculation. The existence of ions is hardly accepted as an absolute fact, and the carrying of negative electricity by minute particles—"electrons" we suppose physicists would call them—is only an attempt to establish a working hypothesis that may be right but is probably only a step in the direction of the truth.

The beta rays undoubtedly carry a negative charge, and are repelled by negative electricity. The rays are believed to consist of negative electrons. In Crookes' tubes the particles striking on a platinum foil render it red hot.

In the case of the emanation, the vapour has been shown by experiment to project negatively charged particles, as the

result of throwing off positive atoms, and these projected particles ionise the gases in their path. This account of the matter explains the experimental fact that the amount of the induced, that is, secondary, activity is in direct proportion to the amount of radiation from the emanation or vapour.

The amount of energy set free by the decomposition or breaking up of the atoms of radium and its emanations is very great. Measured in foot pounds it is equal to the mechanical force required to elevate its own weight ten thousand feet per hour, while in the same time the heat alone produced by a radium salt is enough to melt its own weight of frozen water.

But this hardly justifies the statement in the newspapers that one gramme of radium contains enough energy to raise the whole British Fleet to the top of Ben Nevis! (Why, it may be asked, Ben Nevis?) Can we give some idea of the way in which we ought to look upon such statements, and upon the sensational articles about the "mystery of radium," "the miracle of radium"?

There was in ancient Egypt a very able Hebrew gentleman who was educated in the royal and priestly laboratories of the time. In these days the cathedral was built first, and the university was built within the cathedral precincts, and the priests and professors were of the royal race, so that Moses, if he had lived now might have been demonstrator to "His Royal Highness the Most Reverend Archbishop and Professor of Chemistry, the Duke of . . . ." And there were other learned men, magicians, magi (that is, philosophers), scientific men (all these terms meant "men who knew things"), these magicians, when Moses performed wonders before the Pharaoh, did likewise with their enchantments. *They had been demonstrators also, and knew the tricks!*

NOTE BY THE EDITOR.—The two preceding paragraphs contain, so far as is known, the last words penned by the late Dr. Campbell Brown in connection with his History Course. The Editor has preserved in them the original lecture form, partly for this reason, and partly for their



interest. Old students will recognise in them "the touch of a vanished hand," and others who did not personally know the Professor will obtain from them a characteristic impression of the man. Dr. Campbell Brown had no sympathy with mere sensationalism, and little patience with the exaggerated phrases of the newspaper paragraph-writer. Possessed of a deep knowledge of his subject, both in its historical and in its philosophical aspects, he did not believe in "miracles of science," or "mysteries of science." To him the world was a beautifully ordered system, which to a certain extent it was possible for the human understanding to comprehend. Such knowledge was to be sought in patient laboratory work, and the keys to it were *thoroughness* and *accuracy*. Great discoveries he could admire as much as others, but to him they were not subjects for extravagant declamation, but steps towards the comprehension of the truth, which ought to be made the foundation for other discoveries. They were admirable, not as miracles or mysteries, but as fruits of legitimate work. That is the import of the passage the Editor has just transcribed.

Had Dr. Campbell Brown lived to complete his work, he would probably have devoted a chapter to a consideration of the future course of chemical science. Such a forecast by a chemist of his eminence would have had great interest and value: but he is gone from us, and the prophet's mantle has not fallen upon the Editor, who will not presume to attempt a task, which would be very difficult for him to perform, and would be worth little when done. This much, however, may be said, as it is within the observation of any one who has carefully perused the preceding chapters. The development of chemistry has proceeded steadily forward, only during those periods in which its philosophy has been based upon experiment and observation. Correlation of facts, comparison of observations, hypothesis, invention, even imagination, are useful aids to practical labour, but they are no more than aids. As it has been, so it will be. Laboratory work and research are the only methods upon which we can safely rely for the discovery of facts, by the generalisation of which we may discover principles, and so maintain that course of steady development which has distinguished the latter portion of the History of Chemistry.

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