CHAPTER I

THEORY OF GENERAL TECHNIQUE

THEORY OF DISTILLATION

I,1. Vapour pressure. If a liquid is admitted into a closed vacuous space, it will evaporate or give off vapour until the latter attains a definite pressure, which depends only upon the temperature. The vapour is then said to be **saturated.** Experiment shows that at a given temperature the vapour pressure of a liquid substance in contact with its own liquid is a constant quantity and is independent of the absolute amount of liquid and of vapour present in the system. The vapour pressure is usually

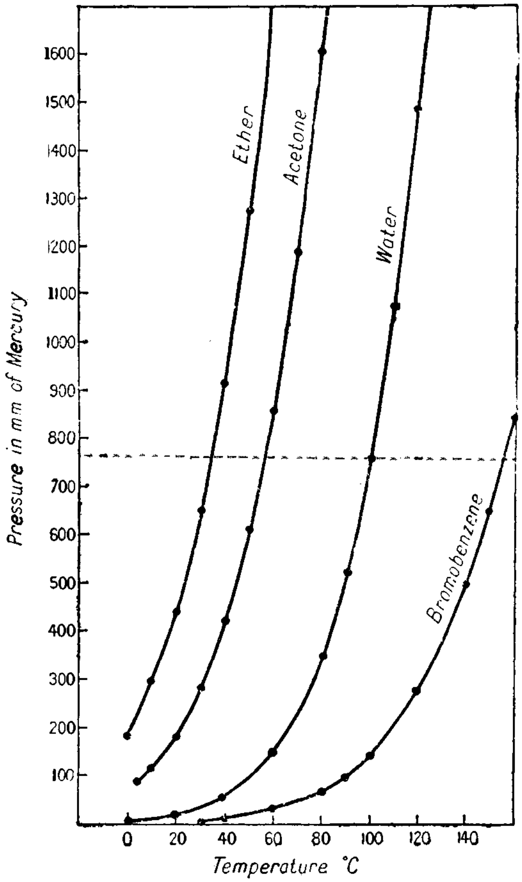

Fig. *I*, *1*, 1.

expressed in terms of the height of a mercury column which will produce an equivalent pressure.

The vapour pressure of a liquid increases with rising temperature. A few typical vapour pressure curves are collected in Fig. *I*, *1*, 1. When the vapour pressure becomes equal to the *total* pressure exerted on the surface of a liquid, the liquid boils, *i.e.*, the liquid is vaporised by bubbles formed *within* the liquid. When the vapour pressure of the liquid is the same as the external pressure to which the liquid is subjected, the temperature does not, as a rule, rise further. If the supply of heat is increased, the rate at which bubbles are formed is increased and the heat of vaporisation is absorbed. **The boiling point of a liquid** may be defined as the temperature at which the vapour pressure of the liquid is equal to the external pressure exerted at any point upon the liquid surface. This external pressure may be exerted by atmospheric air, by other gases, by vapour and air, etc. The boiling point at a pressure of 760 mm. of mercury, or one standard atmosphere, may be termed the **normal boiling point.**

If the pressure on the surface is reduced, say by connecting the vessel containing the liquid with a pump, the boiling point is lowered; the exact value may be obtained by reference to a vapour pressure curve (see, for example, Fig. *I*, *1*, 1). It is therefore necessary to specify the pressure in recording a boiling point: unless this is done, 760 mm. is understood. Advantage is taken of the lower boiling point under diminished pressure in the distillation of substances which decompose upon heating to the boiling point under atmospheric pressure; thus, ethyl acetoacetate, which boils with decomposition at 180° under 760 mm. pressure, boils without decomposition at 78° under 18 mm. pressure (usually written as 78°/18 mm.).

I,2. Calculation of the boiling point at selected pressures. One sometimes requires the boiling point of a liquid at a pressure which is not recorded in the literature. This can best be calculated from the vapour pressure - temperature curve. For most practical purposes this may be assumed to have the form:

$$\log p = A + \frac{B}{T},$$

where p is the vapour pressure, T is the temperature on the absolute scale, and A and B are constants. If $\log p$ is plotted as ordinates against $\frac{1}{T}$ as abscissae, a straight line is obtained. Two values of p with the corresponding values of T suffice. Values of p corresponding to any absolute temperature or *vice versa* can be obtained from the graph. A few typical $\log p - \frac{1}{T}$ diagrams, using the data from which Fig. *I*, *1*, 1 was constructed, are shown in Fig. *I*, *2*, 1; it will be seen that they approximate to straight lines.

For distillations conducted at atmospheric pressure, the barometric pressures are rarely exactly 760 mm. and deviations may be as high as 20 mm. To correct the observed boiling point to normal pressure (760 mm.), the following approximate expression may be used:

$$\Delta t = 0{\cdot}0012\ (760 - p)\ (t + 273),$$

where Δt is the correction in degrees Centigrade to be applied to the observed boiling point t, and p is the barometric pressure. For water, alcohols, acids and other associated liquids, it is better to use the expression :

$$\Delta t = 0{\cdot}0010\,(760 - p)\,(t + 273).$$

I,3. Superheating and bumping. If a liquid is heated in a flask by means of a Bunsen burner and wire gauze placed below it, the formation of bubbles of vapour at the lower surface of the liquid in contact with the heated glass is facilitated by the presence of air dissolved in the liquid or adhering as a film to the glass and by roughness on the surface of the glass. If a minute bubble of air is formed (this will be at atmospheric pressure), it will serve as a nucleus for a larger bubble of vapour. At the boiling point the liquid (at 760 mm. vapour pressure itself) will deliver vapour in relatively large quantity to the air bubble. With the heat supply at hand, the total pressure inside the bubble soon rises above that of the atmosphere and is sufficient to overcome the pressure due to the column of liquid; a vapour bubble is then expelled. Hence, if a source of minute air bubbles or other nuclei is available in the liquid, boiling will proceed quietly. If, however, the liquid is largely free from air and if the walls of the flask are clean and very smooth, bubbles are formed with greater difficulty and the temperature of the liquid may rise appreciably above the boiling point; it is then said to be **superheated.** When a

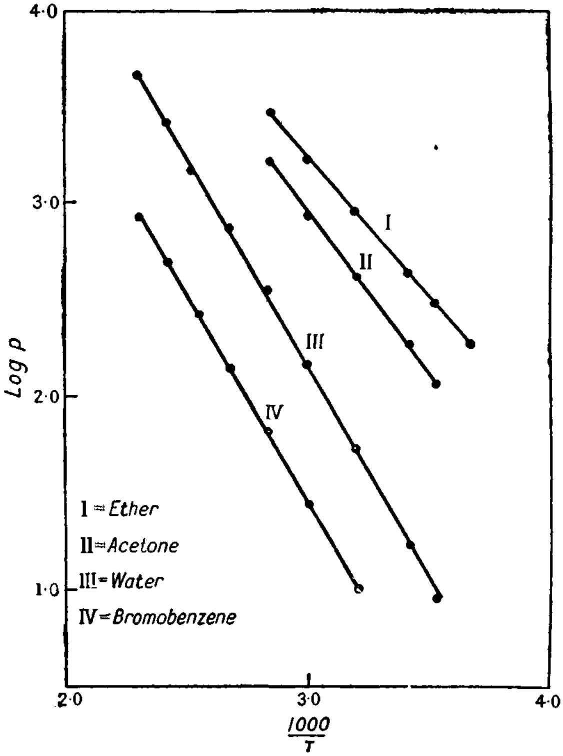

Fig. *I*, *2*, 1.

bubble does eventually form, the vapour pressure corresponding to the temperature of the liquid far exceeds the sum of the pressures of the atmosphere and of the column of liquid, hence vapour is evolved, the bubble increases in size rapidly and at the same time the temperature of the liquid falls slightly. These experimental conditions lead to irregular ebullition and the liquid is said to **bump**.

Various methods are available for preventing, or at least considerably reducing, bumping in a liquid. An obvious method is to surround the flask containing the liquid by a bath charged with a suitable fluid, the temperature of which is not allowed to rise more than 20° above the boiling point of the liquid. Bubbles of vapour may now rise from points around the edge of the liquid and not only from the bottom of the flask. Furthermore, the danger of superheating is considerably reduced.

The procedure most frequently employed to prevent bumping of a liquid during distillation under atmospheric pressure is to add a few fragments of unglazed porous porcelain (often termed " porous pot," " boiling stones " or " boiling chips "—the term " porous pot " will be used frequently in this book).* These emit small quantities of air and promote regular ebullition. It must be emphasised that the " porous pot " is added to the cold liquid before distillation is commenced. Under no circumstances should " porous pot " be dropped into a liquid which has already been heated to boiling: the sudden evolution of vapour may result in spray and sometimes of a large proportion of the liquid being ejected from the mouth of the flask. If the distillation has been interrupted, it is recommended that two or three small fragments of fresh " porous pot " be added before the heating is resumed ; the " porous pot " initially added, from which the air has been partially removed by heating, will probably be largely ineffective owing to their absorption of the liquid on cooling.

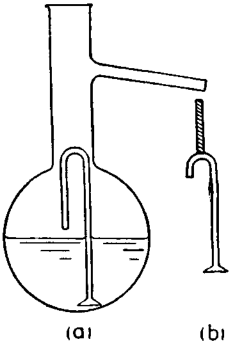

Fig. *1*, *3*, 1.

A useful device to prevent bumping of liquids during distillation consists of a glass tube, 2–3 mm. in diameter, bent in a U-form with one arm somewhat shorter than the other ; it should be long enough to extend from the bottom of the flask for a short distance into the neck in order that it should remain in an upright position (Fig. *I*, *3*, 1, *a*). If for any reason a shorter U-tube is desired, a glass rod may be sealed on as in Fig. *I*, *3*, 1, *b*. The short arm of the U-tube should be just above the level of the liquid in the flask, whilst the long arm should rest on the bottom of the flask just above the source of heat. With a large flask it is advantageous to employ two or three U-tubes, the short arm of one should be just above the fluid level at the start of the distillation ; the short arms of the other U-tubes should be of different lengths and below the initial level of the liquid.

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* The action of this and other anti-bumping devices (*e.g.*, minute carborundum chips) is dependent upon the fact that the transformation of a superheated liquid into the vapour will take place immediately if a vapour phase (*e.g.*, any inert gas) is introduced. The effect may be compared with that produced by the introduction of a small quantity of a solid phase into a supercooled liquid, *e.g.*, of ice into supercooled water.

Other aids for promoting regular boiling include the addition of the following :—fragments of pumice stone or of carborundum ; small strips of **Teflon** (a tetrafluoroethylene polymer) tape, *ca.* ¾″ wide, or of shredded Teflon (the strip may be washed with an organic solvent, dried and re-used) ; small pieces of platinum wire (use is made of the well-known property of platinum in absorbing large quantities of gases) ; sufficient glass wool to fill the flask and to rise 4–5 mm. above the surface of the liquid ; long capillary tubes sealed at a point about 0·5 mm. from the end (the short capillary end is immersed in the liquid, thus filling the small cavity with air, which is evolved in fine bubbles when the liquid is heated).

The boiling point of a pure liquid, if properly determined, has a definite and constant value at constant pressure, say, that of the atmosphere. The boiling point of an impure liquid will depend to a large extent on the physical nature of the impurities. If all the impurities are non-volatile, the liquid will have a constant boiling point and the impurities will remain behind when the liquid has been distilled. If, however, the impurities are themselves volatile, the boiling point may rise gradually as the liquid distils or it may remain constant at a particular stage of the distillation due to the formation of a constant boiling point mixture of two or more substances. The separation of liquids by distillation forms the subject of the next Section.

I,4. Fractional distillation. The aim of distillation is the separation of a volatile liquid from a non-volatile substance or, more usually, the separation of two or more liquids of different boiling point. The latter is usually termed **fractional distillation.** The theoretical treatment of fractional distillation requires a knowledge of the relation between the boiling points, or vapour pressures, of mixtures of the substances and their composition ; if these curves are known, it is possible to predict whether the separation is difficult or easy or, indeed, whether it will be possible.

At the outset it will be profitable to deal with an **ideal solution** possessing the following properties : (i) there is no heat effect when the components are mixed ; (ii) there is no change in volume when the solution is formed from its components ; (iii) the vapour pressure of each component is equal to the vapour pressure of the pure substances multiplied by its mol fraction * in the solution. The last-named property is merely an expression of Raoult's law, *viz.*, the vapour pressure of a substance is proportional to the number of mols of the substance present in unit volume of the solution, applied to liquid-liquid systems. Thus we may write :

$$p_A = Kx_A \qquad (1),$$

where p_A is the vapour pressure of the substance and x_A is its mol fraction in the solution. If $x_A = 1$, *i.e.*, we are dealing with the pure substance A, then $p_A = K = p_A'$, the vapour pressure of the pure substance at the given temperature. Substituting this value in equation (1), we have :

$$p_A = p_A' \, x_A \qquad (2),$$

i.e., the vapour pressure of a component of a solution at a given temperature is equal to the vapour pressure of the pure substance multiplied by its mol fraction in the solution. This is another form of **Raoult's law.**

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* The mol fraction of any constituent in a mixture is defined as the number of mols, or gram molecules, of that constituent divided by the total number of mols, or gram molecules, in the mixture.

Let us consider a mixture forming an ideal solution, that is, an ideal liquid pair. Applying Raoult's law to the two volatile components A and B, we have :

$$p_A = p_A' \, x_A \qquad \text{and} \qquad p_B = p_B' \, x_B \qquad (3).$$

The total pressure p will be :

$$p = p_A + p_B = p_A' \, x_A + p_B' \, x_B.$$

The vapour pressures are proportional to the mol fractions in the vapour phase, hence the composition of this phase will be given by :

$$x_A^{\bullet} = \frac{p_A}{p_A + p_B} \qquad \text{and} \qquad x_B^{\bullet} = \frac{p_B}{p_A + p_B}$$

The relative concentrations of either constituent, say B, in the vapour and liquid phases will be :

$$\frac{x_B^{\bullet}}{x_B} = \frac{p_B}{p_A + p_B} \cdot \frac{p_B'}{p_B}$$
$$= \frac{1}{x_B + \frac{p_A'}{p_B'} \cdot x_A} \qquad (4).$$

If $p_A' = p_B'$, $x_B^{\bullet}/x_B$ is unity, since in the liquid phase $x_A + x_B = 1$. If $p_B' > p_A'$, the concentration of B will be greater in the vapour phase, and if $p_B' < p_A'$, it will be less.

This may, perhaps, be made clear with the aid of an example. Let us assume that the two components A and B have vapour pressures of 60 and 100 mm. of mercury respectively, and that the mol fraction of A is 0·25 and of B is 0·75. Then for the solution :

$$p_A = 0{\cdot}25 \times 60 = 15 \text{ mm. (Hg)} \qquad \text{and} \qquad p_B = 0{\cdot}75 \times 100 = 75 \text{ mm. (Hg)}.$$

The total pressure will be :

$$p = p_A + p_B = 90 \text{ mm. (Hg)}.$$

The composition of the vapour phase will be :

$$x_A^{\bullet} = 15/90 = 0{\cdot}167 \qquad \text{and} \qquad x_B^{\bullet} = 75/90 = 0{\cdot}833.$$

Thus a solution containing mol fractions of 0·25 and 0·75 of A and B respectively is in equilibrium with a vapour containing 16·7 and 83·3 mol per cent. of A and B respectively. The component B with the higher vapour pressure is relatively more concentrated in the vapour phase than in the liquid phase.

If the compositions of the vapour phase for various mixtures of the same two components are calculated and plotted against the vapour pressures, a diagram having the general features shown in Fig. *I*, *4*, 1 is obtained. The abscissae represent the composition of both the liquid and the vapour phases, and the ordinates the total vapour pressure of the liquid. The curve labelled *vapour* gives the composition of the vapour in equilibrium with the solution having the vapour pressure corresponding to the ordinate. Thus the liquid with composition l_1 and vapour pressure p represented by the point m is in equilibrium with vapour of composition l_1'. Since the mixture is an ideal solution of the two liquids, the vapour pressures are additive and the liquid vapour pressure - composition curve *AmB* is a straight line. The composition of the vapour in equilibrium with the various mixtures is given by *Am′B*, falling below the liquid vapour pressure-composition line. Figure *I*, *4*, 1 is therefore the vapour pressure diagram for an ideal liquid pair. The diagram shows clearly that the vapour in equilibrium with the ideal solution of two liquids is richer in the more volatile component than is the solution ; it follows, therefore, that the two components could be separated by fractional distillation.

Only a limited number of examples are known of mixtures which obey Raoult's law over the whole range of concentration and give straight line plots of the vapour pressure (ordinates) against the composition of the liquid expressed in mol fractions (abscissae). These include :— *n*-hexane and *n*-heptane at 30° ; ethyl bromide and ethyl iodide at 30° ; *n*-butyl chloride and *n*-butyl bromide at 50° ; and ethylene dibromide and propylene dibromide at 85°. In most cases, however, liquid pairs deviate from Raoult's law. The deviations may be either positive or negative, *i.e.*, the vapour pressure may be either greater or less than that calculated. If both components exhibit positive deviations (*e.g.*, carbon disulphide and acetone at 35°), the total vapour pressure curve will be greater than that calculated and the curve passes through a maximum. If the two components show negative deviations (*e.g.*, acetone and chloroform at 35°), the total vapour pressure curve will be less than that calculated and the curve will pass through a minimum. It can be shown that when the vapour pressure is a maximum or a minimum, the composition of the vapour is the same as that of the liquid with which it is in equilibrium.

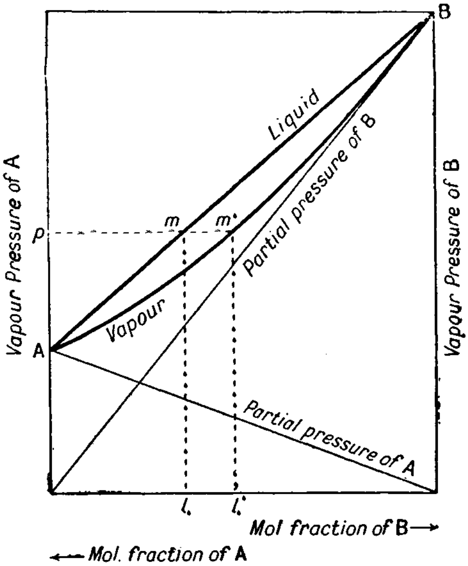

Fig. *I*, *4*, 1.

The normal boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the pressure of the atmosphere. Hence for the study of fractional distillation it is better to construct a diagram in which the boiling points are ordinates and the compositions are abscissae at constant (*i.e.*, atmospheric) pressure. In the vapour pressure-composition curves the vapour pressure is plotted against the composition at constant temperature, whereas in the boiling point-composition curves the boiling point is plotted against the composition at constant pressure. The two curves are similar in type except that they are inverted (see Figs. *I*, *4*, 2 and *I*, *4*, 3 below). In the boiling point-composition diagram two curves are obtained, one giving the composition of the liquid and the other that of the vapour with which it is in equilibrium at the boiling point. The vapour phase is relatively richer in the component which results in a lowering of the boiling point when added to the mixture, or, alternatively, the liquid phase is richer in the component which raises the boiling point. Three classes of curves will be considered: those in which (1) the boiling point rises steadily with change of composition from the more volatile to the less volatile component, (2) the boiling point reaches a minimum, and (3) the boiling point reaches a maximum.

(1) **The boiling point increases regularly.** The boiling-point-composition diagram for such a system is shown in Fig. *I*, *4*, 2 (the complementary vapour pressure-composition diagram is depicted in Fig. *I*, *4*, 3 for purposes of comparison only). Let us consider the behaviour of such a liquid pair upon distillation. If a solution of composition L_1 is heated, the vapour pressure will rise until at the point l_1 it is equal to the pressure of the atmosphere, and boiling commences at temperature t_1. The composition of the vapour first distilling is V_1; it is richer in A, the lower boiling point component, than was the original solution. As the boiling proceeds, the residue becomes increasingly richer in B, the higher boiling point component; consequently the boiling point will rise, say, to t_2 and the composition of the residue will gradually change to L_2, whilst that of the distillate (vapour) will change from V_1 to V_2. Thus from a solution of initial concentration L_1, a distillate is obtained of composition approximating to $(V_1 + V_2)/2$ and a residue of composition L_2. The distillation has thus effected a partial separation of A and B, and it is clear that by repeated distillation an almost complete separation of the two components can be made. For this purpose, each fraction collected between suitable temperature limits is redistilled; with each fractionation the separation of the two components is improved. It is evident that the greater the slope of the boiling point curve, the greater is the difference in composition between the liquid and the vapour; hence the greater the difference in the boiling points of the two liquids forming the mixture, the more easily can they be separated by distillation.

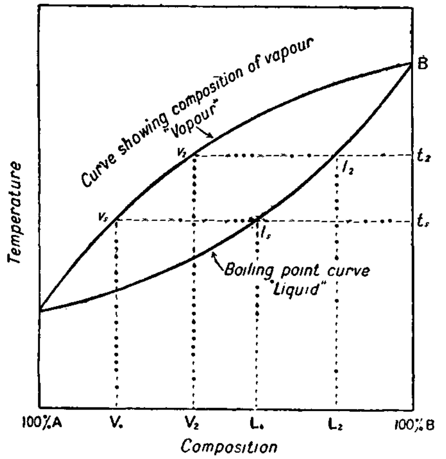

Fig. *I*, *4*, 2.

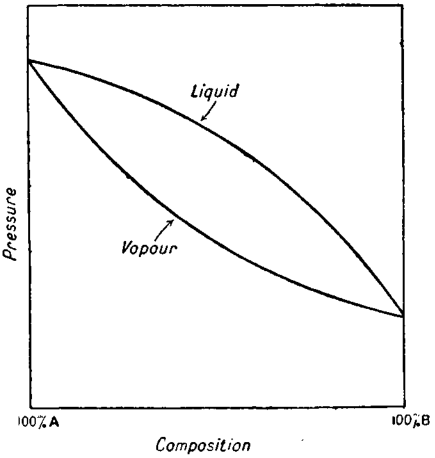

Fig. *I*, *4*, 3.

In practice, it is usual to employ a **fractionating column** to reduce the number of distillations necessary for reasonably complete separation of the two liquids. A fractionating column is designed to provide a continuous series of partial condensations of the vapour and partial vaporisations of the condensate and its effect is, indeed, similar to a number of separate distillations. The effect of partial condensation will be evident from Fig. *I*, *4*, 2. If the temperature of the vapour is lowered, it will partly condense giving a liquid richer in B and leaving the vapour richer in A. The vapour passing up the column will accordingly contain more of A than did the vapour which left the boiling liquid. Similarly the liquid returning to the flask will contain relatively more of the less volatile component B.

A fractionating column consists essentially of a long vertical tube through which the vapour passes upward and is partially condensed; the condensate flows down the column and is returned eventually to the flask. Inside the column the returning liquid is brought into intimate contact with the ascending vapour and a heat interchange occurs whereby the vapour is enriched with the more volatile component A at the expense of the liquid in an attempt to reach equilibrium. The conditions necessary for a good separation are :—(i) there should be a comparatively large amount of liquid continually returning through the column ; (ii) thorough mixing of liquid and vapour ; and (iii) a large active surface of contact between liquid and vapour. Excessive cooling should be avoided ; this difficulty is particularly apparent with liquids of high boiling point and may be overcome by suitably insulating or lagging the outer surface of the column or, if possible, by surrounding it with a vacuum jacket or an electrically heated jacket. Various types of laboratory fractionating columns are described in Sections **II,15–II,18**.

(2) **Minimum boiling point.** Typical boiling point-composition curves for systems of this kind are shown in Fig. *I*, *4*, 4. If a solution of composition L_1 is heated, the vapour pressure will rise until at the point l_1 it is equal to the pressure of the atmosphere and boiling commences at t_1. The composition of the vapour first distilling is V_1. As the boiling proceeds the temperature rises from t_1 to t_2, and during this period distillates with compositions ranging from V_1 to V_2 will be obtained. If the distillate be redistilled, the vapour approaches the composition of the minimum boiling point system, as can be seen from the figure. Hence fractional distillation will result in a distillate of composition L_{Mi}, although the final residue will approach A. Similarly, a solution of composition L_1' when distilled commences to boil at l_1', *i.e.*, at a temperature t_1' the vapour (and therefore the distillate) will have the composition V_1'. As the distillation continues the composition of the vapour changes to V_2' and the liquid to L_2'. Fractional distillation will, in this case, yield a solution of composition L_{Mi}, and the residue will approach B. The liquid mixture can then be separated only into the component present in excess (either A or B) and the mixture of minimum boiling point. The liquid represented by L_{Mi} will distil over completely without change of composition since at the boiling point the vapour has the *same* composition as the liquid. Such systems which distil unchanged are called **azeotropic mixtures** (Greek : *to boil unchanged*). The composition and boiling point of such constant boiling point mixtures vary with the pressure and consequently they are not chemical compounds.

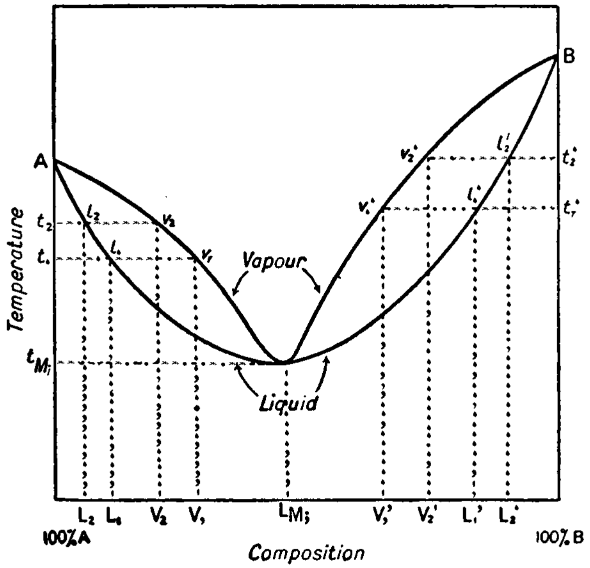

Fig. *I*, *4*, 4.

Examples of azeotropic mixtures of minimum boiling point are collected in Table *I*, *4*, A.

TABLE I, 4, A. AZEOTROPIC MIXTURES OF MINIMUM BOILING POINT

COMPONENT A	COMPONENT B	B.P. OF AZEOTROPIC MIXTURE	% OF A (BY WT.) IN MIXTURE
Water, 100·0°	Ethyl alcohol, 78·3°	78·15°	4·4
Water, 100·0°	*iso*Propyl alcohol, 82·4°	80·4°	12·1
Water, 100·0°	*n*-Propyl alcohol, 97·2°	87·7°	28·3
Water, 100·0°	*tert.*-Butyl alcohol, 82·6°	79·9°	11·8
Water, 100·0°	Pyridine, 115·5°	92·6°	43·0
Methyl alcohol, 64·7°	Methyl iodide, 44·5°	39·0°	7·2
Ethyl alcohol, 78·3°	Ethyl iodide, 72·3°	63·0°	13
Methyl alcohol, 64·7°	Methyl acetate, 57·0°	54·0°	19
Ethyl alcohol, 78·3°	Ethyl acetate, 77·2°	71·8°	31
Water, 100·0°	Butyric acid, 163·5°	99·4°	18·4
Water, 100·0°	Propionic acid, 140·7°	100·0°	17·7
Benzene, 80·2°	*cyclo*Hexane, 80·8°	77·5°	55
Ethyl alcohol, 78·3°	Benzene, 80·2°	68·2°	32·4
Ethyl alcohol, 78·3°	Toluene, 110·6°	76·7°	68
Methyl alcohol, 64·7°	Chloroform, 61·2°	53·5°	12·5
Ethyl alcohol, 78·3°	Chloroform, 61·2°	59·4°	7·0
Ethyl alcohol, 78·3°	Methyl ethyl ketone, 79·6°	74·8°	40
Methyl alcohol, 64·7°	Methylal, 42·2°	41·8°	18·2
Acetic acid, 118·5°	Toluene, 110·6°	105·4°	28

(3) **Maximum boiling point.** A typical boiling point - composition diagram is shown in Fig. *I*, *4*, 5. By reasoning analogous to that given

under (2), it is evident that fractional distillation of a liquid mixture of composition L_1 will yield ultimately a specimen of almost pure A and a residue of composition L_{Ma}, which will eventually distil unchanged. Similarly, a liquid mixture of composition L_1' will give ultimately pure B and a residue L_{Ma}, which will itself distil unchanged. Thus distillation will afford ultimately the component present in excess of the constant boiling point mixture and the constant boiling point mixture itself.

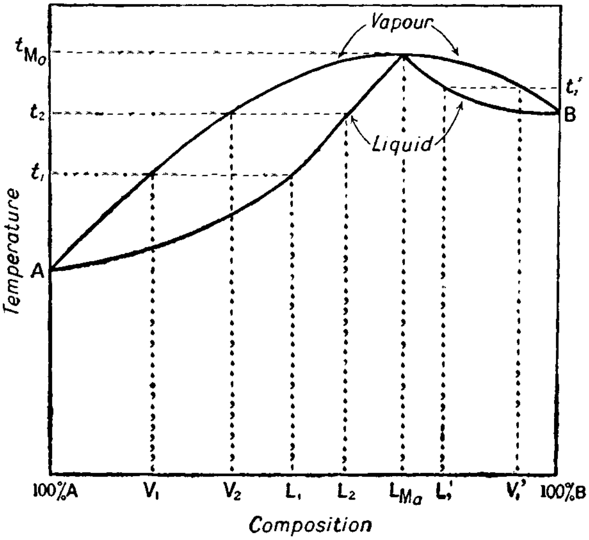

Fig. *I*, *4*, 5.

Examples of azeotropic mixtures of maximum boiling point are tabulated below; these are not as numerous as those of minimum boiling point.

TABLE I, 4, B. AZEOTROPIC MIXTURES OF MAXIMUM BOILING POINT

COMPONENT A	COMPONENT B	B.P. OF AZEOTROPIC MIXTURE	% OF B (BY WT.) IN MIXTURE
Water, 100·0°	Formic acid, 100·8°	107·1°	77·5
Water, 100·0°	Hydrofluoric acid, 19·4°	120·0°	37
Water, 100·0°	Hydrochloric acid, − 84·0°	108·6°	20·22
Water, 100·0°	Hydrobromic acid, − 73°	126°	47·6
Water, 100·0°	Hydriodic acid, − 35°	127°	57·0
Water, 100·0°	Nitric acid, 86·0°	120·5°	68
Water, 100·0°	Sulphuric acid, m.p. 10·5°	338°	98·3
Water, 100·0°	Perchloric acid, 110·0°	203°	71·6
Acetone, 56·4°	Chloroform, 61·2°	64·7°	80
Acetic acid, 118·5°	Pyridine, 115·5°	139·7°	65
Chloroform, 61·2°	Methyl acetate, 57·0°	64·8°	23
Phenol, 181·5°	Aniline, 184·4°	186·2°	58

I,5. The breaking up of azeotropic mixtures. The behaviour of constant boiling point mixtures simulates that of a pure compound, because the composition of the liquid phase is identical with that of the vapour phase. The composition, however, depends upon the pressure at which the distillation is conducted and also rarely corresponds to stoichiometric proportions. The methods adopted in practice will of necessity depend upon the nature of the components of the binary azeotropic mixture, and include :—

(1) Distillation with a third substance which alters the vapour pressure ratios in the azeotrope. This method is of particular value in industry for the production of absolute ethyl alcohol from the azeotropic mixture containing 95·6 per cent. of alcohol or from aqueous alcohol. Upon the addition of benzene and distillation through a suitable fractionating apparatus, a ternary azeotropic mixture of water, alcohol and benzene of minimum boiling point, 64·85°, and containing 7·4 per cent. of water, 18·5 per cent. of alcohol and 74·1 per cent. of benzene passes over first, followed by a second azeotropic mixture of benzene and alcohol (b.p. 68·25°, containing 32·4 per cent. of benzene), and finally absolute ethyl alcohol. By carrying out the fractional distillation under pressure, the water content of the ternary mixture is increased.

(2) Chemical methods may be employed if the reagent attacks only one of the components. Thus quicklime may be employed for the removal of water in the preparation of absolute ethyl alcohol. Also aromatic and unsaturated hydrocarbons may be removed from mixtures with saturated hydrocarbons by sulphonation.

(3) Preferential adsorption of one of the components may be used for the same purpose. Charcoal or silica gel may be employed to adsorb one of the constituents of an azeotrope in preference to the other. If the adsorbate is readily recoverable, the process will have practical applications.

(4) Fractional extraction may sometimes find application, since the components distribute themselves in a different proportion in the solvent (compare Section **II,44**).

(5) Fractional crystallisation is occasionally employed. The mixture is dissolved in a suitable solvent, the whole frozen, and then allowed to melt slowly in a centrifuge in order that the successive fractions may be removed as they are formed. The various melts are then fractionally distilled. If necessary, the fractional crystallisation may be repeated.

I,6. Steam Distillation. Distillation of a Pair of Immiscible Liquids. Steam distillation is a method for the isolation and purification of substances. It is applicable to liquids which are usually regarded as completely immiscible or to liquids which are miscible to only a very limited extent. In the following discussion it will be assumed that the liquids are completely immiscible. The saturated vapours of such completely immiscible liquids follow **Dalton's law of partial pressures** (1801), which may be stated : when two or more gases or vapours which do not react chemically with one another are mixed at constant temperature each gas exerts the same pressure as if it alone were present and that the sum of these pressures is equal to the total pressure exerted by the system. This may be expressed :

$$P = p_1 + p_2 + \quad . \quad . \quad . \quad + p_n$$

where P is the total pressure and p_1, p_2, etc., are the partial pressures of the components.

If a mixture of two immiscible liquids be distilled, the boiling point will be the temperature at which the sum of the vapour pressures is equal to that of the atmosphere. This temperature will be lower than the boiling point of the more volatile component. Since one of the liquids is water, steam distillation at atmospheric pressure will result in the separation of the higher boiling component at a temperature below 100°—a considerable advantage if the compound decomposes at or near its own individual boiling point ; the process would also be useful for separation from non-volatile or from undesirable (*e.g.*, tarry) substances. When a mixture of immiscible liquids is distilled, the boiling point of the mixture remains constant until one of the components has been almost completely removed (since the total vapour pressure is independent of the relative amounts of the two liquids) : the boiling point then rises to that of the liquid remaining in the flask. The vapour passing over from such a mixture contains all the components in proportion by volume to the relative vapour pressure of each.

The composition of the vapour can easily be calculated as follows :— Assuming that the gas laws are applicable, it follows that the number of molecules of each component in the vapour will be proportional to its partial pressure, *i.e.*, to the vapour pressure of the pure liquid at that temperature. If p_A and p_B are the vapour pressures of the two liquids A and B at the boiling point of the mixture, then the total pressure P is given by :

$$P = p_A + p_B \qquad (1),$$

and the composition of the vapour by :

$$n_A/n_B = p_A/p_B \qquad (2),$$

where n_A and n_B are the number of mols of the two substances in a given volume of the vapour phase. But $n_A = w_A/M_A$ and $n_B = w_B/M_B$, where w is the weight of substance in a given volume of the vapour, and M is the molecular weight. Hence :

$$\frac{w_A}{w_B} = \frac{M_A n_A}{M_B n_B} = \frac{M_A p_A}{M_B p_B} \qquad (3).$$

The relative weights of the two components of the vapour phase will be identical with the relative weights in the distillate, *i.e.*, the weights of the two liquids collecting in the receiver are directly proportional to their vapour pressures and their molecular weights.

Equation (3) indicates the great value of steam distillation, since the smaller the product $M_A p_A$, the larger is the value of w_B. Water has a small molecular weight and a comparatively moderate vapour pressure, so that its value of $M_A p_A$ is low. This permits substances of high molecular weight and of low vapour pressure to be separated economically on the technical scale. The following figures are given by S. Young (1922).

SUBSTANCE	MOLECULAR WT. M_B	B.P.	p_B AT 100°	PER CENT. IN DISTILLATE
Carvone .	150	230°	9 mm.	9·7
Geraniol .	154	230°	5 mm.	5·6
Anethole .	148	235°	8 mm.	7·1
Eugenol .	164	250°	2 mm.	1·7
α-Santalol .	228	301°	<1 mm.	0·5

As an example of steam distillation, let us consider bromobenzene which has a normal boiling point of 155°. The vapour pressures of water and bromobenzene at different temperatures are given in the following table.

TEMPERATURE	VAPOUR PRESSURE		
	WATER (p_A)	BROMOBENZENE (p_B)	MIXTURE ($P = p_A + p_B$)
30°	32 mm.	6 mm.	38 mm.
40°	55 mm.	10 mm.	65 mm.
50°	92 mm.	17 mm.	109 mm.
60°	149 mm.	28 mm.	177 mm.
70°	233 mm.	44 mm.	277 mm.
80°	355 mm.	66 mm.	421 mm.
90°	525 mm.	98 mm.	623 mm.
95°	634 mm.	118 mm.	752 mm.
100°	760 mm.	141 mm.	901 mm.

If we plot these as in Fig. *I*, *6*, 1 we find that the vapour pressure of the mixture attains 760 mm. at a temperature of 95·3°; this is therefore the boiling point of the mixture. At this temperature $p_A = 641$ mm. and $p_B = 119$ mm. The molecular weights of the two liquids are 18 and 157 respectively. Substituting these values in equation (3), we have:

$$\frac{w_A}{w_B} = \frac{641 \times 18}{119 \times 157} = \frac{6 \cdot 2}{10 \cdot 0}$$

Thus for every 6·2 grams of water collected in the receiver 10·0 grams of bromobenzene are obtained (or the distillate contains 62 per cent. by weight of bromobenzene) in spite of the fact that bromobenzene has only 119/641 of the vapour pressure of water at the boiling point of the mixture.

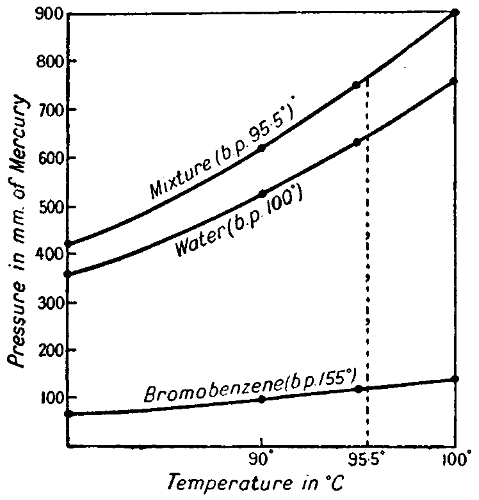

Fig. *I*, *6*, 1.

Similarly it is found that for chlorobenzene the boiling point of the mixture (T_{Mixture}) is 90·3°, $p_A = 530$, $p_B = 230$, $M_B = 112{\cdot}5$, and the distillate contains 71 per cent. of chlorobenzene by weight; for iodobenzene, the boiling point of the mixture is 98·2°, $p_A = 712$, $p_B = 48$, $M_B = 204$, giving a distillate containing 43 per cent. by weight of iodobenzene. For aniline T_{Mixture} is 98·5°, $p_A = 717$, $p_B = 43$, $M_B = 93$, and the calculated value is 23 per cent. of aniline by weight: the proportion found experimentally is somewhat lower because aniline is appreciably soluble in water and the vapour pressure is slightly reduced.

I,7. Distillation with superheated steam. Consideration of equation (3) (Section **I,6**) indicates that the proportion of the higher boiling point component in the steam distillate can be raised by increasing the vapour pressure of this component relative to water. This may be done with superheated (or high pressure) steam.

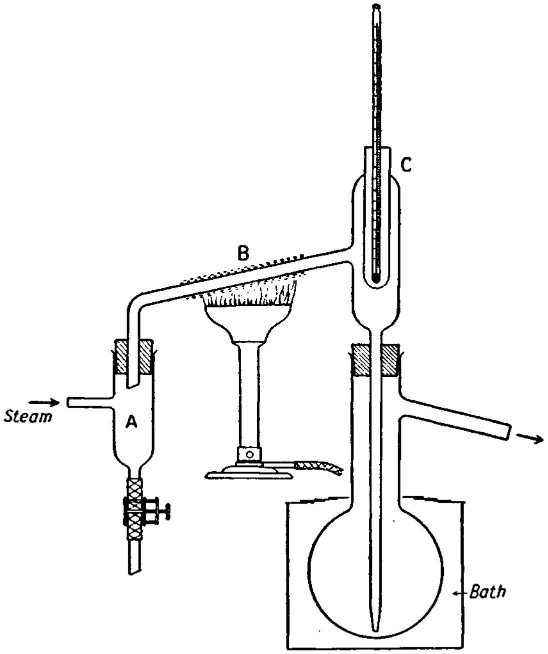

Fig. *I*, *7*, 1.

The effect of superheated steam may be illustrated by reference to benzaldehyde, which boils at 178° at 760 mm. It distils with steam at 97·9° ($p_A = 703{\cdot}5$ mm. and $p_B = 56{\cdot}5$ mm.) and the distillate contains 32·1 per cent. of benzaldehyde by weight. If one employs steam superheated to 133°, the vapour pressure of benzaldehyde (extrapolated from the boiling point - pressure curve) is 220 mm.: hence $p_A = 540$ (water), $p_B = 220$ (benzaldehyde), and

$$\frac{w_A}{w_B} = \frac{540 \times 18}{220 \times 106} = \frac{41{\cdot}7}{100}$$

i.e., the distillate contains 70·6 per cent. of benzaldehyde by weight. This compares with 31·4 per cent. with steam at 100° and one atmosphere.

The use of superheated steam has the advantage that less condensation takes place thus obviating the use of supplementary heat in the vessel containing the substance; beyond this no advantage over steam used under ordinary pressure will result so long as condensed water is present. If all condensation of the steam is prevented (*e.g.*, by surrounding the flask by a bath of liquid at the same temperature as the superheated steam), the higher temperature of the superheated steam will result in an increase in the proportion of the higher boiling point component in the distillate.

In practice superheated steam is generally employed for substances with a low vapour pressure ($<$ 5–1 mm.) at 100°. Thus in the recovery of the products of nitration or aromatic compounds, the *ortho* derivative (*e.g.*, *o*-nitrophenol) can be removed by ordinary steam distillation ; the temperature may then be raised, and the *para* compound distilled. The upper limit of temperature will of course be controlled by the stability of the compound.

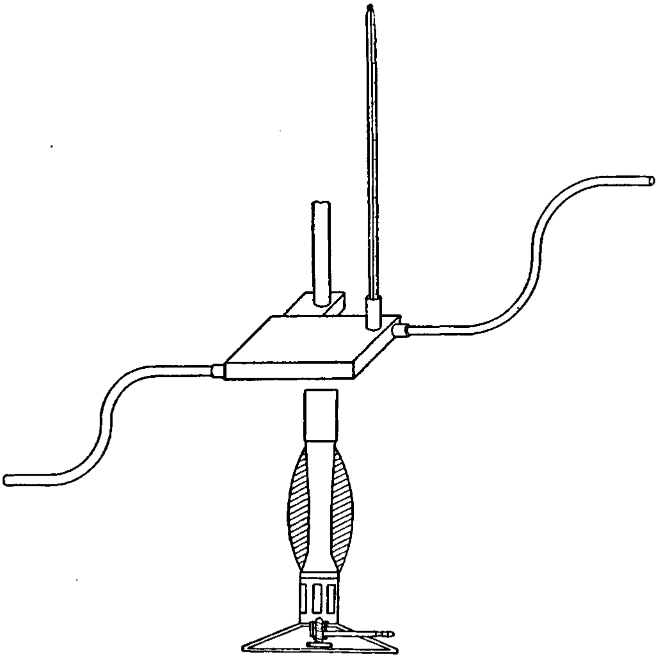

Fig. *I*, 7, 2.

A convenient apparatus for distillation in superheated steam (due to A. A. Morton) is shown in Fig. *I*, 7, 1. The Pyrex tube *B*, of 10 mm. diameter or larger, is wrapped with a few layers of wire gauze and heated with a wing-topped burner, the gauze being supported by a clamp to prevent sagging of the tube at the high temperature ; *C* is a thermometer and *A* is a trap for condensed water. The flask is heated in an oil bath to approximately the same temperature as the superheated steam. It will be observed that the superheater is close to the steam inlet tube, thus reducing the cooling of the steam, before it enters the flask, to a minimum. A commercial apparatus, constructed of metal (the Fisher superheater), is shown in Fig. *I*, 7, 2.

SOLUTIONS OF LIQUIDS IN LIQUIDS

I,8. Partially miscible liquids. Critical solution temperature. Some liquids are practically immiscible (*e.g.*, water and mercury), whilst others (*e.g.*, water and ethyl alcohol or acetone) mix with one another in all proportions. Many examples are known, however, in which the liquids are partially miscible with one another. If, for example, water be added to ether or if ether be added to water and the mixture shaken, solution will take place up to a certain point ; beyond this point further addition of water on the one hand, or of ether on the other, will result in the formation of two liquid layers, one consisting of a saturated solution of water in ether and the other a saturated solution of ether in water. Two such mutually saturated solutions in equilibrium at a particular temperature are called **conjugate solutions.** It must be mentioned that there is no essential theoretical difference between liquids of partial and complete miscibility for, as will be shown below, the one may pass into the other with change of experimental conditions, such as temperature and, less frequently, of pressure.

Three types of liquid/liquid systems are commonly encountered. The first type (*e.g.*, phenol and water) is characterised by increasing mutual solubility with rise of temperature. Thus when phenol is added to water at the ordinary temperature, a homogeneous liquid is produced. When the concentration of the phenol in the solution has risen to about 8 per cent., the addition of more phenol results in the formation of a second liquid phase, which may be regarded as a solution of water in phenol. If now the temperature is raised, the second liquid phase will disappear and more phenol must be added to produce a separation of the liquid into two layers. By increasing the amount of phenol in this way and observing the temperature at which the two layers disappear, the so-called solubility curve of phenol in water may be determined. In a similar manner the solubility curve of water in liquid phenol may be obtained, and it is found that the solubility also increases with rise of temperature. It is clear that since, with rise of temperature, the concentration of water in the phenol layer and also of phenol in the water layer increases, the compositions of the two conjugate solutions become more and more nearly the same, and at a certain temperature the two solutions become identical in composition. The temperature at which the two layers become identical in composition and are, in fact, one layer is known as the **critical solution temperature** (D. O. Masson, 1891) or the **consolute temperature** (W. D. Bancroft, 1894) of the system. Above this temperature the two liquids are miscible in all proportions. Some experimental results for the mutual solubility of phenol in water are plotted in Fig. *I*, *8*, 1 ; these lead to a critical solution temperature of 65·9° and a critical concentration of 34·0 per cent. of phenol. Fig. *I*, *8*, 1 enables one to predict the effect of bringing together phenol and water in any given quantities at any temperature. If the resulting mixture is represented by a point in the area enclosed by the solubility curve, separation into two layers will take place, whereas if the total composition of the mixture and the temperature is expressed by a point lying outside the solubility curve a clear homogeneous solution will result.

Other pairs of liquids which exhibit an upper consolute temperature are methyl alcohol - *cyclo*hexane (C.S.T. 49·1° ; critical composition 29 per cent. by weight of methyl alcohol) ; *iso*pentane - phenol (63·5° ; 51 per cent. of *iso*pentane) ; and carbon disulphide - methyl alcohol (40·5° ; 80 per cent. of carbon disulphide).

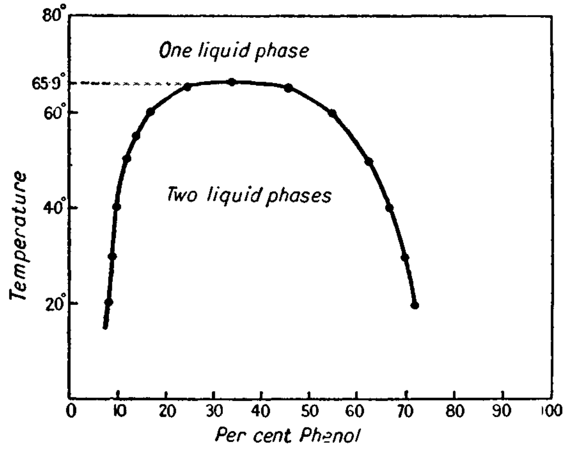

Fig. *I*, *8*, 1.

The second type of system is characterised by decreasing mutual solubility with rise of temperature. As the temperature is lowered the mutual solubilities increase and *below* a certain critical temperature the two liquids become miscible in all proportions. A typical example is triethylamine and water. The behaviour of this system with respect to

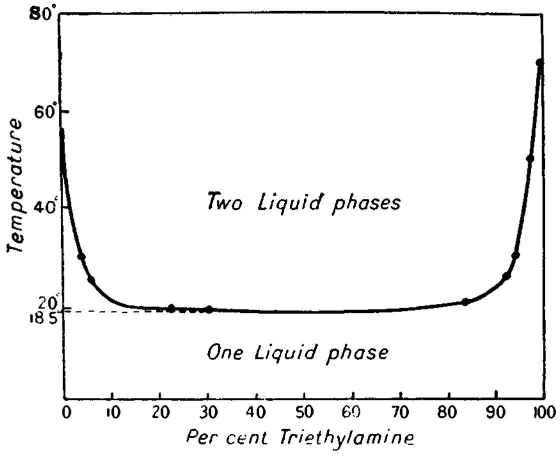

Fig. *I*, *8*, 2.

concentration and temperature is shown in Fig. *I*, *8*, 2 ; the critical solution temperature is 18·5°. Other pairs of liquids which exhibit a lower critical solution temperature are : diethylamine - water (C.S.T. 43° ; 13 per cent. by weight of diethylamine) ; β-collidine - water (6° ; 4 per cent.) ; 1-methylpiperidine - water (48° ; 5 per cent.).

The third type of system gives a closed solubility curve and therefore possesses both an upper and lower critical solution temperature. The first case of this type to be established was that of nicotine and water; the solubility curve is illustrated in Fig. *I*, *8*, 3. The lower and upper consolute temperatures are 60·8° and 208° respectively; below the former and above the latter the two liquids are completely miscible.

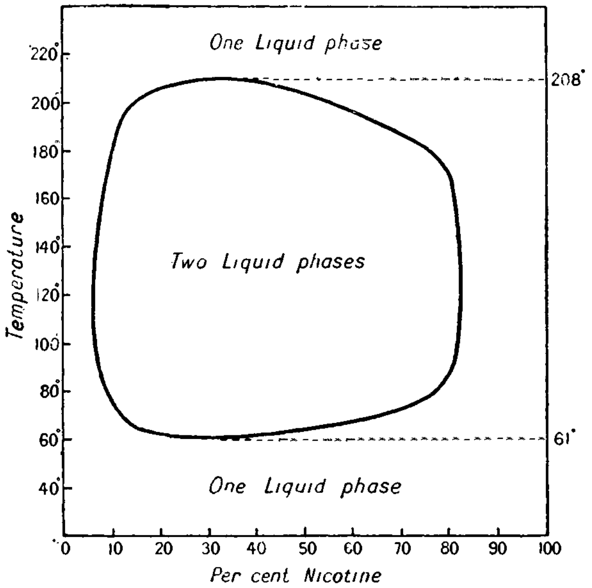

Fig. *I*. *8*, 3.

It should be noted that the modern view is that all partially miscible liquids should have both a lower and upper critical solution temperature so that all such systems really belong to one class. A closed solubility curve is not obtained in all cases because the physical conditions under normal pressure prevent this. Thus with liquids possessing a lower C.S.T., the critical temperature (the critical point for the liquid - vapour system for each component, *i.e.*, the maximum temperature at which liquefaction is possible) may be reached before the consolute temperature. Similarly for liquids with an upper C.S.T., one or both of the liquids may freeze before the lower C.S.T. is attained.

Many pairs of partially miscible liquids possess neither a lower nor an upper C.S.T. for reasons outlined in the previous paragraph. Thus consider the two liquid phases from the two components water and diethyl ether. Upon cooling the system at constant pressure, a point will be reached when a third phase, ice, will form, thus rendering the production of a lower C.S.T. impossible. Likewise, if the temperature of the two layers is raised, the critical point for the ether-rich layer will be reached while the two liquid phases have different compositions. Above the critical point the ether-rich layer will be converted into vapour, and hence the system will be converted into a water-rich liquid and an ether-rich vapour; the upper C.S.T. cannot therefore be attained.

A few systems with both lower and upper critical solution temperatures are tabulated below.

System (A,B)	Lower C.S.T.	Upper C.S.T.
Water : 2-methylpiperidine	79°	227°
Water : 3-methylpiperidine	56°	236°
Water : 4-methylpiperidine	85°	189°
Water : β-picoline	49°	153°
Water : αα-lutidine	45°	164°
Glycerol : *m*-toluidine	7°	120°

I,9. Influence of added substances upon the critical solution temperature. For a given pressure the C.S.T. is a perfectly defined point. It is, however, affected to a very marked extent by the addition of quite a small quantity of a foreign substance (impurity), which dissolves either in one or both of the partially miscible liquids. The determination of the consolute temperature may therefore be used for testing the purity of liquids. The upper consolute temperature is generally employed for this purpose.

If the third substance dissolves in only one of the liquids, it is found that their mutual solubilities are decreased and the C.S.T. is generally raised. For example, a concentration of 0·15 mol of potassium chloride per litre of water raises the C.S.T. of the water - phenol system by about 12° ; a similar concentration of naphthalene in the phenol produces a rise of about 30°.

If the third substance dissolves in both liquids (and the solubility in each of the liquids is of the same order), the mutual solubility of the liquids will be increased and an upper C.S.T. will be lowered, as is the case when succinic acid or sodium oleate is added to the phenol - water system. A 0·083 molar solution of sodium oleate lowers the C.S.T. by 56·7° : this large effect has been applied industrially in the preparation of the disinfectant sold under the name of "*Lysol.*" Mixtures of tar acids (phenol + cresols) do not mix completely with water at the ordinary temperature, but the addition of a small amount of soap (= sodium oleate) lowers the miscibility temperature so that "Lysol" exists as a clear liquid at the ordinary temperature.

An important application of the critical solution temperature is to the **determination of the water content in such substances as methyl and ethyl alcohols.** Here the system is usually the alcohol and a hydrocarbon, such as *n*-hexane or di*cyclo*hexyl ; the water is, of course, insoluble in the hydrocarbon. Thus, the methyl alcohol - *cyclo*hexane system has a C.S.T. of 45·5° and even 0·01 per cent. of water produces a rise of 0·15° in the C.S.T. The experimental details are given below.

For methyl alcohol, two volumes of synthetic *n*-hexane, b.p. 68·6–69·0° (uncorr.), and one volume of the alcohol to be tested are mixed and the homogeneous mixture is cooled in ice until the appearance of a cloudiness. A thermometer is placed in the solution, which is allowed to warm gradually to the temperature at which the second phase disappears. The temperature at which the solution just becomes homogeneous is taken as the critical solution temperature. The same result is obtained by observing the temperature at which the second phase appears. The water content may then be deduced with the aid of the following table, and checked, if desired, by a determination of the density (Section **XI,2**).

PURITY OF CH_3OH (%)	C.S.T.	$d_{4°}^{20°}$
100·0	36·55°	0·79578
99·80	37·90	0·79634
99·65	38·95	0·79676
99·50	40·05	0·79718
99·35	41·00	0·79760
99·05	43·00	0·79845
98·69	45·00	0·79947
98·41	46·25	0·80026
98·01	48·05	0·80140
97·48	50·15	0·80292
97·13	51·10	0·80390

For ethyl alcohol, two volumes of di*cyclo*hexyl * are mixed with one volume of the alcohol, a thermometer is introduced, and the mixture heated until it becomes clear. The solution is then slowly cooled, with constant stirring, and the temperature is determined at which the opalescent solution suddenly becomes turbid so that the immersed portion of the mercury thread of the thermometer is no longer clearly visible. This is the C.S.T. The water content may then be evaluated by reference to the following table.

PURITY OF C_2H_5OH (%)	C.S.T.	$d_{4°}^{20°}$
100·0	23·4°	0·78934
99·9	25·4	0·78966
99·8	27·3	0·78997
99·7	29·2	0·79028
99·6	31·0	0·79059
99·5	32·8	0·79089
99·0	41·0	0·79243
98·5	48·0	0·79346

THEORY OF MELTING AND FREEZING

I,10. Melting point and vapour pressure. The melting point of a crystalline solid is the temperature at which the solid begins to change into liquid under a pressure of one atmosphere. For pure substances, the change from the solid to the liquid state is quite sharp (within 0·5°), hence the temperature is valuable for purposes of identification. Moreover, the melting point is considerably influenced by the presence of other

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* This may be prepared by the catalytic reduction of pure diphenyl (see Section **III,150**).

substances, and it is therefore an important criterion of purity. If the liquid is cooled, solidification will occur at the same temperature,* and for a pure substance the melting point and freezing point are identical. The **freezing point** is usually defined as the temperature at which both liquid and solid can exist in contact with each other under a total pressure of one atmosphere.

The reason for the constancy and sharpness of the melting point of a pure crystalline solid can be appreciated upon reference to Fig. *I*, *10*, 1, in which (*a*) is the vapour pressure curve of the solid and (*b*) that of the liquid form of the substance. Let us imagine a vessel, maintained at constant temperature, *completely* filled with a mixture of the above liquid and solid. The molecules of the solid can only pass into the liquid and the molecules of the liquid only into the solid. We may visualise two competitive processes taking place : (i) the solid attempting to " evaporate " but it can only pass into the liquid, and (ii) the liquid attempting to " distil " but it can only pass into the solid. If process (i) is faster, the solid will melt, whereas if process (ii) proceeds with greater speed the substance would completely solidify. To decide which process is likely to occur at a particular temperature, curve (*a*) must be superimposed upon curve (*b*) thus giving curve (*c*). The rate of rise of vapour pressure with temperature is greater for the solid than for the liquid, consequently the two curves will intersect. At the intersection (and only at this temperature), both solid and liquid can coexist ; this is therefore the freezing point or melting point since these two constants are identical for a pure substance. Provided the pressure is atmospheric, the temperature *M* is an absolute constant. If the temperature is less than *M*, the liquid will pass more rapidly into solid than the solid into liquid and hence the substance will remain solid, whilst for temperatures greater than *M* the solid, having the greater vapour pressure, will pass more rapidly into the liquid phase. It is only at the temperature *M*, at which the vapour pressures of the liquid and the solid are equal in magnitude, that the rates of transformation are identical and both liquid and solid can coexist, provided the temperature is maintained constant. As soon as the

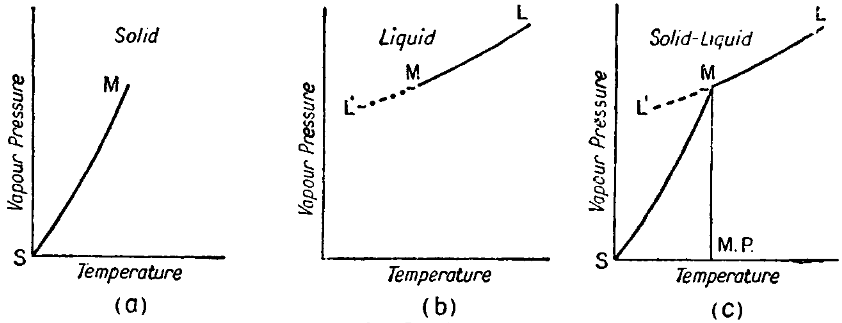

Fig. *I*, *10*, 1.

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* A liquid can sometimes be supercooled, *i.e.*, the temperature can be reduced below the freezing point without solid separating, but as soon as solid does appear the temperature immediately rises to the true freezing point.

temperature is raised even a fraction of a degree above *M*, the solid will be completely converted into the liquid phase, assuming of course that sufficient time is allowed for the transformation to take place. This is why the rate of rise of temperature in the vicinity of the melting point must be small (say, 1–2° per minute) for an accurate determination of this constant.

It is a well-known fact that substances like water and acetic acid can be cooled below the freezing point: in this condition they are said to be **supercooled** (compare supersaturated solution). Such supercooled substances have vapour pressures which change in a normal manner with temperature: the vapour pressure curve is represented by the dotted line *ML′*—a continuation of *ML*. The curve *ML′* lies above the vapour pressure curve of the solid and it is apparent that the vapour pressure of the supersaturated liquid is greater than that of the solid. The supercooled liquid is in a condition of metastability. As soon as crystallisation sets in, the temperature rises to the true freezing or melting point. It will be observed that no dotted continuation of the vapour pressure curve of the solid is shown; this would mean a suspended transformation in the change from the solid to the liquid state. Such a change has not been observed nor is it theoretically possible.

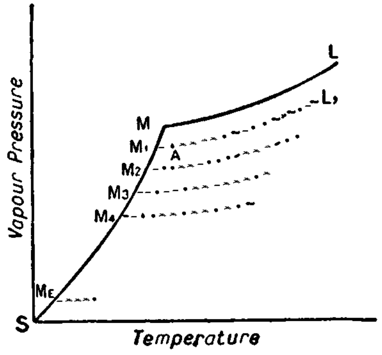

Fig. *I*, *11*, 1.

I,11. Effect of impurities upon the melting point. Let us take a specific example and examine the effect of the addition of a small quantity of naphthalene to an equilibrium mixture of pure solid and liquid α-naphthol at the temperature of the true melting point (95·5°) at atmospheric pressure. The naphthalene will dissolve in the liquid α-naphthol and, according to Raoult's law, the vapour pressure of the latter will be reduced. Hence α-naphthol will pass preferentially into the liquid phase and, if the external temperature is maintained at 95·5°, the ultimate result will be the complete melting of the solid α-naphthol; since melting requires heat and no heat is imparted to the system, the temperature will fall. The effect can easily be interpreted by reference to Fig. *I*, *11*, 1. The initial state of the system is represented by *M*. Upon the addition of a small amount of the second substance, the vapour pressure of the *liquid* first falls to *A*. Now a solid phase with vapour pressure *M* cannot coexist with a liquid phase with lower vapour pressure *A*. The solid represented by *M* will therefore melt and tend to pass into the condition expressed by *A*. However, in melting heat is absorbed, and the temperature will consequently fall. Thus the vapour pressures of the solid *M* and the liquid *A* will fall along their respective vapour pressure curves, which will intersect at M_1. At M_1 equilibrium results and no further change will take place; here solid α-naphthol and the solution of naphthalene in α-naphthol may coexist indefinitely—this, it will be observed, is below the melting point of the pure substance (α-naphthol). Further addition of naphthalene will result in the depression of the melting point of α-naphthol to points represented by M_2, M_3, etc.; the curve through these points indicates the temperatures at which solid α-naphthol can coexist with solutions of increasing naphthalene content. It is natural to enquire as to how far the melting point may be depressed by additions of the second substance. The limiting temperature M_E is known as the eutectic point; it is the temperature below which not even the impure liquid can exist. Further cooling merely results in both components solidifying completely.

A somewhat different method of plotting the results will help the reader to appreciate the significance of the eutectic temperature. In Fig. *I, 11,* 2 melting points are plotted against composition.* The curve *AC* portrays the decreasing melting point of α-naphthol as naphthalene is added up to a mol fraction of 0·605. The curve *BC* represents the melting points of naphthalene with α-naphthol regarded as the "foreign ingredient" up to a mol fraction of 0·395 of α-naphthol. The curves intersect at *C* giving a eutectic temperature of 61·0°.

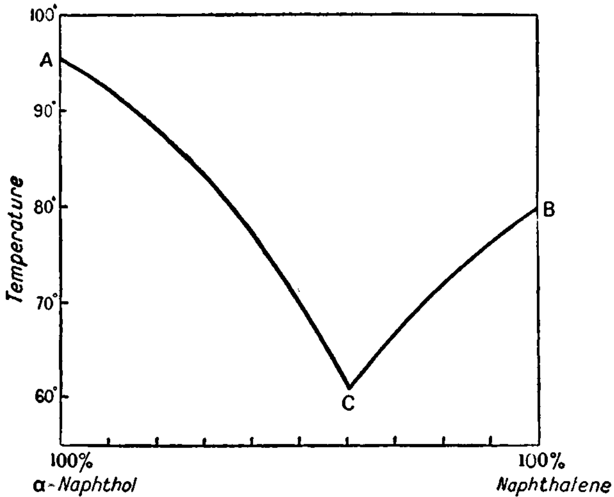

Fig. *I, 11,* 2.

I,12. System in which the solid phases consist of the pure components and the components are completely miscible in the liquid phase. We may now conveniently consider the general case of a system in which the two components *A* and *B* are completely miscible in the liquid state and the solid phases consist of the pure components. The equilibrium diagram is shown in Fig. *I, 12,* 1. Here the points *A* and *B* are the melting points of the pure components *A* and *B* respectively. If the freezing points of a series of liquid mixtures, varying in composition from pure *A* to pure *B*, are determined, the two curves represented by *AC* and *BC* will be obtained. The curve *AC* expresses the compositions of solutions which are in equilibrium, at different temperatures, with the solid component *A*, and, likewise, the curve *BC* denotes the compositions

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* Frequently composition is expressed in mol fractions or in mol fractions × 100, *i.e.*, molecular composition × 100 (compare footnote to Section I,IV).

of solutions in equilibrium with the solid *B*. At the point of intersection of the two curves *C*, both solid components can exist in equilibrium with a liquid solution of definite composition corresponding with the point *C*. This point is called the **eutectic point** (Greek : *easy melting*), and represents the temperature and composition at which the system liquid - solid *A* - solid *B* can exist in equilibrium ; in short, it gives the temperature and composition of the system when both components crystallise out simultaneously. This solid mixture is known as the **eutectic mixture.** It has a fixed composition and melts and freezes, like a pure substance, at a definite temperature. This temperature is the **eutectic temperature** and is always the lowest freezing point of the whole series of mixtures of *A* and *B*. The eutectic mixture is not, however, a definite chemical compound because (i) separate crystals of the two components can be seen under the microscope and (ii) it rarely corresponds to the exact composition of a simple chemical compound; it is, in fact, an intimate mechanical mixture or **conglomerate** of the two solid components. If a liquid solution having a composition represented by a point lying to the left of the eutectic point *C* be cooled, the solid component *A* will crystallise out (it is assumed that supersaturation is excluded) when the temperature reaches the point on the curve *AC* corresponding with the initial composition of the solution. If the cooling be continued, more and more of the component *A* will separate and the composition of the solution will change in the direction of *C*. When the composition corresponding to the point *C* is reached, solid *B*, also, can crystallise out. If withdrawal of heat from the system be continued, both solid *A* *and* solid *B* will separate while the temperature remains constant. Since, according to the phase rule (compare Section **I,20**), the composition of the solution at the point *C* must remain constant, it follows that the components *A* and *B* must crystallise from the eutectic solution in constant proportions. In a similar manner, if a liquid having a composition represented by a point to the right of *C* be cooled, the solid *B* will separate and the composition of the solution will change in the direction of *C*. At *C*, solid *A* will also crystallise out, and the temperature and composition of the solution will remain constant whilst the solid components crystallise out as a eutectic mixture. If a liquid mixture of composition denoted by the eutectic point *C* be cooled, no solid will separate until the eutectic temperature *D* is reached and then the eutectic mixture will crystallise out.

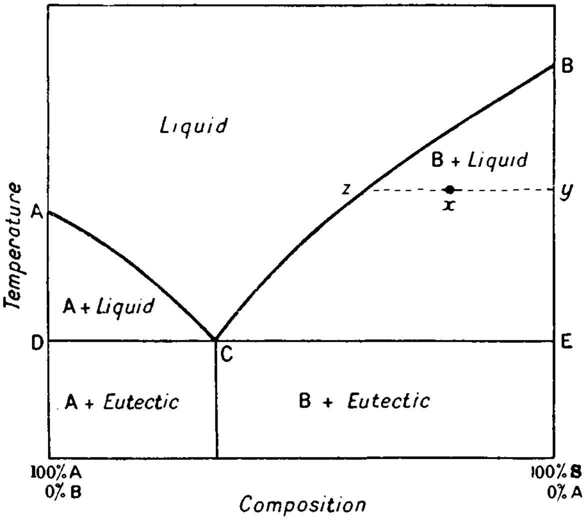


Fig. *I*, *12*, 1.

It is convenient, when dealing with mixtures, to call the temperature at which the solid commences to crystallise from the liquid, the **freezing point of the mixture**, and to term the temperature at which the solid mixture begins to liquefy the **melting point of the mixture**. The complete equilibrium diagram usually includes two curves, which are called liquidus and solidus respectively. The **liquidus** (or liquidus curve) is the temperature - composition curve of the liquid phase and is therefore the freezing point curve ; it represents " the beginning of freezing." The **solidus** (or solidus curve) is the temperature - composition curve of the solid mixture and is therefore the melting point curve ; it corresponds to the " beginning of melting " on heating or to the " end of freezing " on cooling the system. In Fig. *I*, *12*, 1 the liquidus curve is *ACB*, whilst the solidus curve is *ADCEB*. These curves divide the figure into regions which contain the phases indicated in the diagram, and the composition of the system represented by any point can be easily ascertained. Thus the point x (Fig. *I*, *12*, 1) is a mixture of solid B ($\equiv y$) and liquid of composition z : the proportion of liquid to solid is given by the ratio of the distance xy/xz.

I,13. Construction of equilibrium diagrams. It is interesting to consider how a complete equilibrium diagram (including solidus and liquidus curves) may be constructed. For simplicity, only the system considered in the previous Section will be studied. The procedure is known as the **cooling curve method**. When a pure substance is allowed to cool slowly and the temperature observed at definite intervals of time, a cooling curve may be constructed, *e.g.*, *ab* in Fig. *I*, *13*, 1, i. When the freezing point is reached, if supercooling is absent, solid will commence to separate out and the temperature will remain constant until all the liquid has solidified (*bc* in Fig. *I*, *13*, 1, i). With further cooling of the solid phase, the temperature will fall steadily as indicated by *cd*. If, however, a solution is allowed to cool slowly and the cooling curve similarly determined, a continuous curve *ef* (Fig. *I*, *13*, 1, ii) is obtained as long a the solution is entirely liquid. When a solid phase commences to form, the heat of fusion will be liberated so that at the point *f* the rate of cooling will be checked. Since the composition of the solution changes with the separation of the solid phase, the temperature will not remain constant but will gradually fall until the eutectic is reached (*fg*). At the eutectic

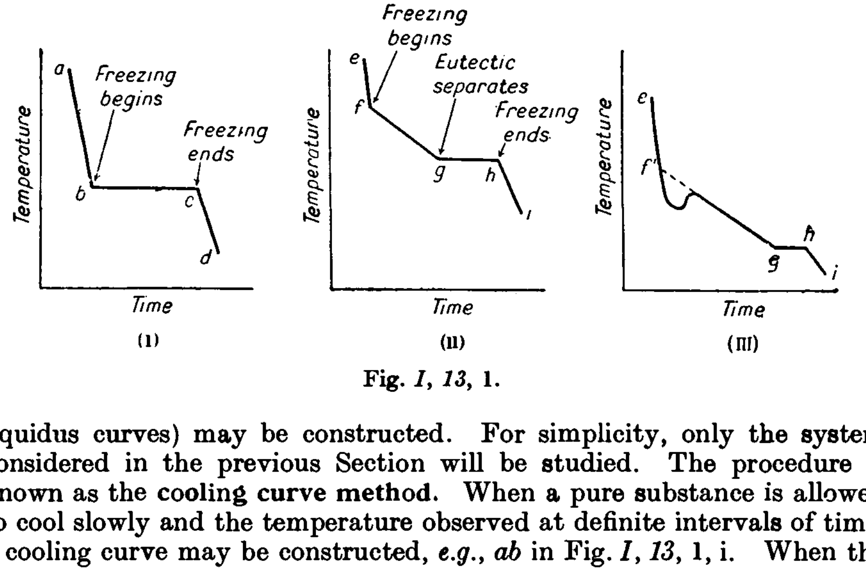
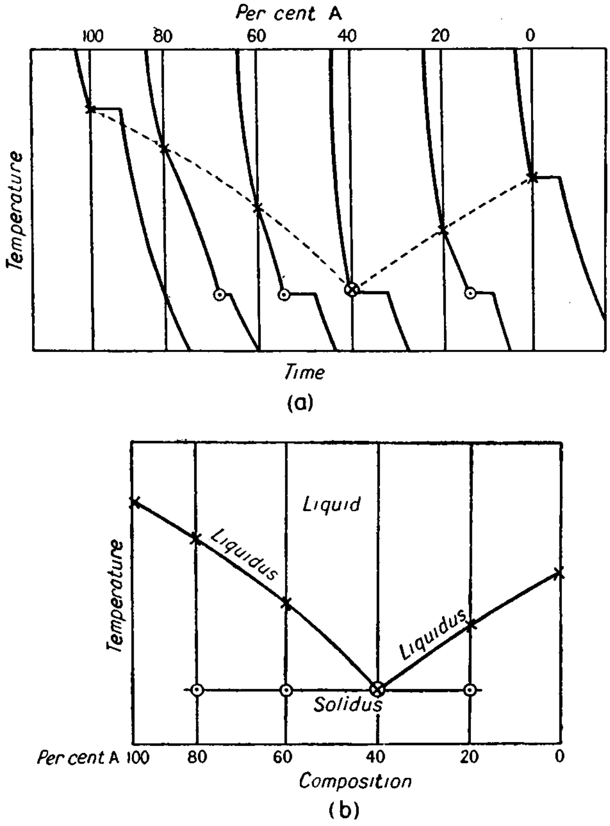


Fig. *I*, *13*, 1.

point both components crystallise out as a eutectic mixture and the temperature remains constant until complete solidification has occurred (line *gh*). After complete solidification of the mixture the fall in temperature of the system becomes uniform (line *hi*) until the room temperature is reached. It is clear from what has already been said that the cooling curve of the eutectic mixture will be similar to (i)—that of a pure substance. The points *b*, *f* and *g* at which a " break " occurs in the cooling curve are called " *arrests* " or " *arrest points* " of the cooling curve.

The separation of the solid phase does not occur readily with some liquid mixtures and supercooling is observed. Instead of an arrest in the cooling curve at *f′*, the cooling continues along a continuation of *ef′* and then rises suddenly to meet the line *f′g* which it subsequently follows (Fig. *I*, *13*, 1, iii). The correct freezing point may be obtained by extrapolation of the two parts of the curve (as shown by the dotted line). To avoid supercooling, a few small crystals of the substance which should separate may be added (the process is called "**seeding**"); these act as nuclei for crystallisation.



(a)

(b)

Fig. *I*, *13*, 2.

By constructing cooling curves for several mixtures of different composition, the total weight of the mixture being kept the same in each case, a series of cooling curves may be obtained which may be employed for the construction of the equilibrium diagram. Thus in Fig. *I*, *13*, 2, *a*, the cooling curves obtained with various mixtures of the two components *A* and *B* are shown. The first and last curves refer to pure *A* and pure *B* respectively, whilst the other curves are for mixtures of 80 per cent. *A* and 20 per cent. *B*, 60 per cent. *A* and 40 per cent. *B*, 40 per cent. *A* and 60 per cent. *B*, and 20 per cent. *A* and 80 per cent. *B*. By joining the first arrest points (represented by crosses) the liquidus curve is obtained, whilst the solidus curve is obtained by drawing a line through the second arrest points (denoted by circles; see Fig. *I*, *13*, 2, *b*). In practice, it is only necessary to plot the arrest temperatures against the composition, but it is believed that Fig. *I*, *13*, 2 brings out clearly the connexion between cooling curves and the equilibrium diagram for the system under discussion, and is therefore of considerable interest.

Another procedure, known as the **thaw-melt method**, is available for the construction of equilibrium diagrams; it involves heating, instead of cooling, mixtures of known composition. This has certain advantages over the cooling curve method, particularly in those cases where supercooling is serious and also where the quantity of material is limited. Let us consider, for example, a system of composition represented by the line *ad* (Fig. *I*, *13*, 3), where *d* denotes the system completely solidified and *a* the same system completely liquefied, *i.e.*, above its melting point. If the temperature of the solid expressed by *d* is slowly raised, no change will occur until the point *c*, the eutectic temperature, is reached ; liquid of composition *C* will then commence to form. As the temperature is raised from *c* to *b*, the quantity of liquid increases and its composition changes from *C* to *b* ; at *b* the last trace of solid is about to disappear and above *b* the system is completely liquid. This forms the basis of the thaw-melt procedure. A mixture of known composition—made by melting (to ensure thorough mixing), cooling and then powdering—is placed in a wide capillary tube (of about 2 mm. diameter) and the powder well pressed down with a thin glass rod or platinum wire so that the material

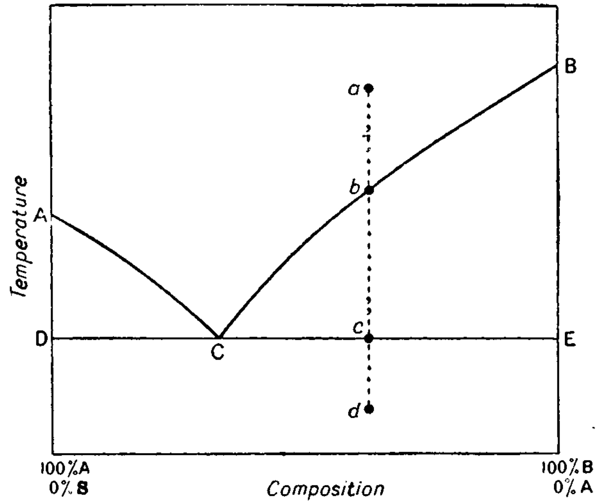


Fig. *I*, *13*, 3.

occupies 3–5 mm. at the bottom of the tube. The tube is then placed in a well-stirred bath of a suitable liquid and the temperature slowly raised. The temperature at which the first minute drops of liquid appear (*i.e.*, at *c*), the so-called **thaw point**, is the eutectic temperature for the given mixture. The mixture is heated further and the temperature at which the last trace of solid just disappears (*i.e.*, at which the fused mass becomes perfectly clear) is taken as the melting point (*b*). The thaw points and melting points of other mixtures, as well as of the pure components, are determined in the same way. Thaw points and melting points are then plotted against composition. The curve obtained by joining the thaw points is the *solidus* and that obtained by joining the melting points is the *liquidus*. Only a pure substance, or a mixture having the composition of the eutectic, melts sharply at a definite temperature. The thaw-melt procedure demonstrates very clearly why an impure substance may melt over a considerable range of temperature. The system (Section **I,12**), just studied in considerable detail, in which the components are completely miscible in the liquid state and the solid phases consist of the pure components, is very common with many pairs of organic and inorganic substances. Examples are given in the following table.

A	*B*	EUTECTIC
α-Naphthol, m.p. 95·5°	Naphthalene, m.p. 80°	M.p. 61°
Camphor, m.p. 179°	Naphthalene, m.p. 80°	M.p. 32·3°
Diphenylmethane, m.p. 27°	Naphthalene, m.p. 80°	M.p. 14°
Benzoic acid, m.p. 122°	Cinnamic acid, m.p. 133°	M.p. 82°
o-Nitrophenol, m.p. 44°	*p*-Toluidine, m.p. 43°	M.p. 15·5°
Antimony, m.p. 630°	Lead, m.p. 327°	M.p. 246°
Bismuth, m.p. 271°	Cadmium, m.p. 321°	M.p. 146°
Gold, m.p. 1063°	Thallium, m.p. 303°	M.p. 131°

I,14. System in which the two components form a compound possessing a congruent melting point. This system, which occurs less frequently than that of Section **I,12**, is of considerable interest. The equilibrium diagram depicted in Fig. *I, 14*, 1 (for benzophenone and diphenylamine) is an illustration of a system in which the two components form a compound possessing a **congruent melting point**, *i.e.*, capable of existing as a solid compound in equilibrium with a liquid of the same composition. Point *A* is the melting point of benzophenone (47·7°) and *B* that of diphenylamine (52·8°). When diphenylamine is added to benzophenone, the freezing point is lowered along the curve *AC*. At *C* (31·9°) there is the first eutectic point where benzophenone and the addition compound $\{(C_6H_5)_2CO.(C_6H_5)_2NH)\} \equiv D$ separate together as a eutectic mixture. Further addition of diphenylamine raises the freezing point to a maximum at *D* (40·2°). At *D*, the composition of the liquid and solid phases are identical, and this maximum temperature is therefore the congruent melting point of the addition compound. In a similar manner the freezing point of diphenylamine (*B*) is lowered by the addition of benzophenone as indicated by the curve *BE*. The point *E* is the second eutectic point, where a eutectic mixture of diphenylamine and the addition compound separates. Further addition of benzophenone results in the freezing point rising along *ED* to a maximum at *D*, the melting point of the addition compound.

The liquidus consists of the curves *AC*, *CDE* and *EB*; the solidus comprises the horizontal lines *FCG* and *HEJ* as well as the vertical lines *FA*, *JB* and *GD*. The areas have the significance indicated in the figure. The details of the phase diagram can be best understood and the behaviour of various systems on cooling or heating readily predicted by regarding it as composed of two diagrams of the simple eutectic type (Fig. *I*, *12*, 1) placed side by side with the dividing line at *DK*. To the left of the dividing line the figure gives the equilibria of the two component system *A* and compound *D*, whereas to the right of the line the components may be regarded as *D* and *B*.

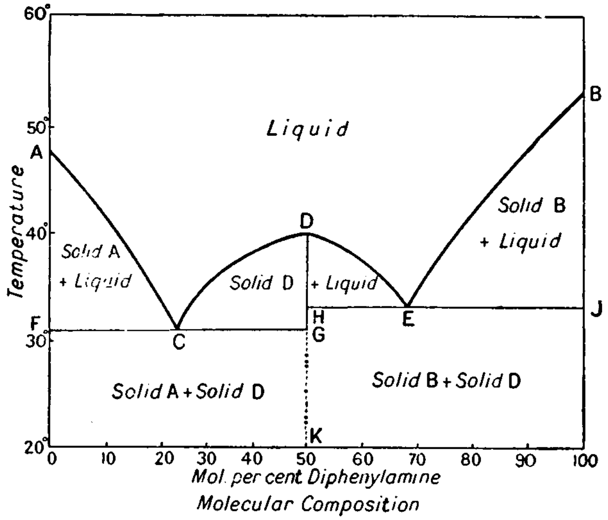


Fig. *I*. *14*, 1.

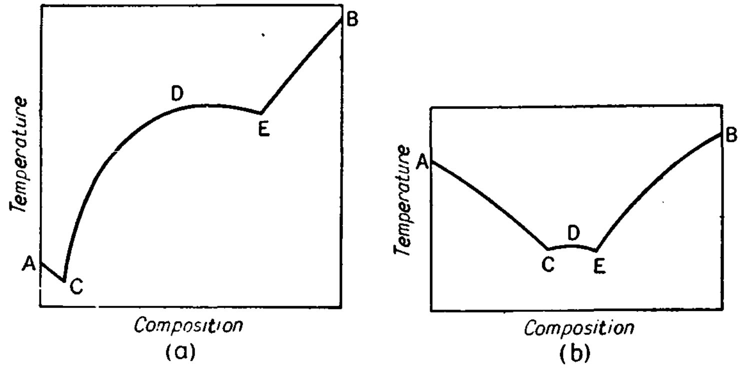


Fig. *I*, *14*, 2.

It is clear from the figure that the presence of a stable compound is characterised by (i) a maximum point on the liquidus, (ii) a meeting point of the solidus and liquidus, and (iii) the existence of a eutectic point on either side of the maximum. The melting point of the compound may be above, below or between those of the two components. If the compound is not completely stable but tends to decompose (dissociate) into its components in the liquid state, the melting point will be lowered by the products of decomposition. The shape of the middle branch of the curve will therefore give a rough indication of the stability of the compound. The greater the stability of the compound the sharper is the maximum and, usually, the larger is the central branch *CDE* of the curve as in Fig. *I*, *14*, 2, *a* (*e.g.*, phenol and picric acid). A flat maximum and a small *CDE* curve indicate considerable decomposition of the addition compound into its components as in Fig. *I*, *14*, 2, *b* (*e.g.*, naphthalene and *m*-dinitrobenzene). Other examples of this system are collected in the following table.

SUBSTANCE *A*	SUBSTANCE *B*	COMPOUND *D*	EUTECTICS
Phenol, m.p. 40·4°	α-Naphthylamine, m.p. 48·3°	*AB*, m.p. 28·8°	16·0° (66·5 % *A*), 24·0° (32 % *A*)
Phenol, m.p. 40·4°	*p*-Toluidine, m.p. 43°	*AB*, m.p. 28·5°	8·0° (76 % *A*), 19·9° (31 % *A*)
Phenol, m.p. 40·4°	Picric acid, m.p. 122·5°	*AB*, m.p. 83·1°	36° (94 % *A*), 80·6° (42 % *A*)
α-Naphthol, m.p. 93·9°	*p*-Toluidine, m.p. 43°	*AB*, m.p. 53·7°	50·2° (60 % *A*), 30·3° (19 % *A*)

I,15. System in which the two components form a compound with an incongruent melting point. In this system the compound formed

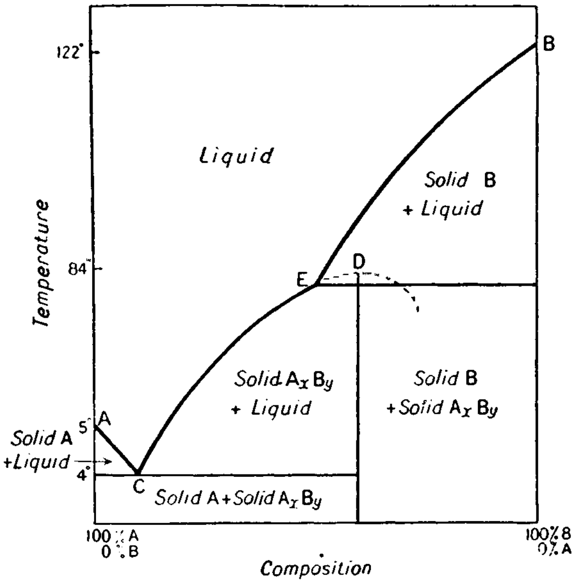


Fig. *I*, *15*, 1.

is so unstable that it decomposes *completely* at a temperature below its melting point, so that the solid cannot be in equilibrium with a liquid of the same composition as itself—in other words, it has no true melting point. Such a system is exemplified by benzene and picric acid: the equilibrium diagram is shown in Fig. *I, 15*, 1 (for clarity, the illustration is not drawn to scale). The point *A* is the melting point of benzene, *B* that of picric acid, and *C* that of the eutectic composed of solid benzene and the addition compound (represented by the symbol A_xB_y). The curve *CE* is the equilibrium curve for the compound A_xB_y—in the example under consideration $x = 1$ and $y = 1$—with the submerged maximum at *D*. The point *D* is not realised in practice because the compound decomposes completely at *E* into solid picric acid and liquid benzene. The point *E* is spoken of as the **incongruent melting point** of the compound (since the composition of the liquid is not the same as that of the original compound) or as the *transition point*. The curve *EB* represents the equilibrium between solid *B* and the liquid. This system is rarely encountered among compounds, but other examples are acetamide - salicylic acid and dimethylpyrone - acetic acid; it is, however, comparatively common in alloy systems (*e.g.*, gold - antimony, $AuSb_2$).

I,16. System in which the two components form a continuous series of solid solutions. In all the preceding examples the individual components (*A* or *B* or A_xB_y) form separate crystals when solidifying from the melt. There are, however, a number of examples of the separation of a homogeneous **solid solution** of *A* and *B* (or *A* and A_xB_y, *etc.*).

Before studying the equilibrium diagrams of these systems, the significance of the term solid solution must be made clear. A solid may dissolve completely in another solid to form a solid solution in a manner analogous to the dissolution of one liquid in another to yield a liquid solution. The solid thus obtained is perfectly homogeneous and has been called *mixed crystals* or *isomorphous mixtures*; these two terms may suggest heterogeneity and it is therefore better to employ the expression solid solution, proposed by van't Hoff in 1890. The phenomenon is different from the process of ordinary solution in a liquid since a liquid has no space lattice of its own. The formation of a solid solution involves the structural dissolution of one solid by another crystalline solid: this process entails, particularly for inorganic compounds, the spatial marshalling of the one in the other with respect to a definite space lattice, and the resulting solid solution therefore behaves as a single entity. The physical properties of solid solutions are continuous functions of their percentage composition. The conditions which must generally be satisfied in the case of pairs of non-polar organic compounds are: (*a*) their chemical constitution must be analogous, (*b*) their molecular volumes must be approximately equal, and (*c*) their crystal structures must be similar.

The general case of two compounds forming a continuous series of solid solutions may now be considered. The components are completely miscible in the solid state and also in the liquid state. Three different types of curves are known. The most important is that in which the freezing points (or melting points) of all mixtures lie between the freezing points (or melting points) of the pure components. The equilibrium diagram is shown in Fig. *I, 16*, 1. The liquidus curve portrays the composition of the liquid phase in equilibrium with solid, the composition of which is given by the solidus curve. The composition of the solid phase changes continuously with that of the liquid from which it separates. It is found experimentally, and can also be deduced theoretically, that at any temperature the concentration of that component by the addition

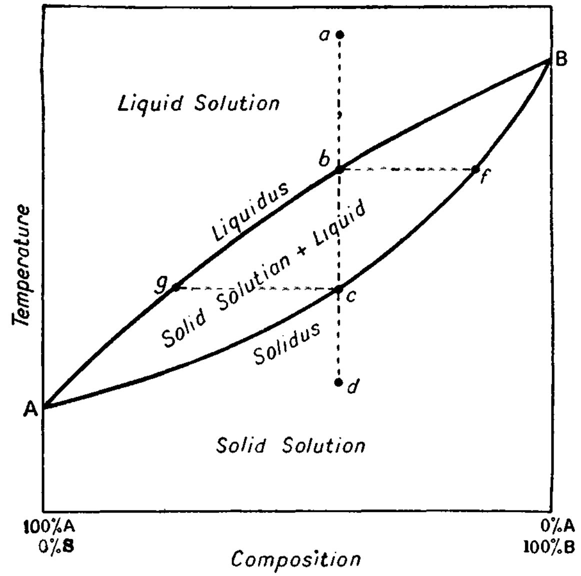


Fig. *I*, *16*, 1.

of which the freezing point is depressed is greater in the liquid than in the solid phase. It is evident from the figure that upon cooling a fused mixture of two substances capable of forming solid solutions, the temperature of solidification (freezing point) will not remain constant during the separation of the solid, nor will the temperature of liquefaction (melting point) of the solid solution be constant. Thus, for example, if a liquid solution of composition *a* is allowed to cool very slowly (so as to ensure equilibrium conditions as far as possible), a solid of composition *f* will separate at *b*. As the temperature continues to fall, more and more solid will be deposited and, since the solid phase is relatively richer in *B*, the liquid will become richer in *A*. The composition of the liquid will therefore pass along *bg*; the composition of the solid will at the same time follow the curve *fc*. At the point *c*, the last traces of liquid of composition *g* are just disappearing and solidification is complete. The cooling curve will have the shape shown in Fig. *I*. *16*, 2; solid commences to separate at *b* and solidification is complete at *c*. There is no complete arrest, only a change in the rate of cooling during the separation of the solid.

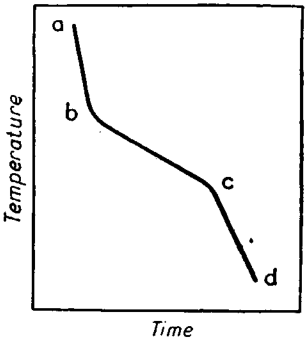


Fig. *I*, *16*, 2.

If a mixture of composition *d* is slowly heated (as in the thaw-melt method), it will commence to melt at the temperature *c* (*i.e.*, the first drops of liquid will appear) with the production of liquid of composition *g*. Thereafter, as the temperature of the mass rises, more of the solid will melt and the composition of the solid and liquid will change as represented by the curves *cf* and *gb* respectively. Finally, when the temperature has reached *b*, complete liquefaction will have occurred. The process of melting or freezing thus extends over the temperature interval *bc*. Examples of this system are β-naphthol, m.p. 122° - naphthalene, m.p. 80°, and α-monochlorocinnamic aldehyde, m.p. 31·2° - α-monobromocinnamic aldehyde, m.p. 69·6°.

Two other types of equilibrium curves are occasionally encountered with the system of two components forming a continuous series of solid solutions. These are shown in Figs. *I*, *16*, 3 and *I*, *16*, 4. In the former the freezing or melting curve passes through a minimum (examples: *p*-chloroiodobenzene, m.p. 57° - *p*-dichlorobenzene, m.p. 53°; naphthalene, m.p. 80° - β-naphthylamine, m.p. 112°), and in the latter it passes through a maximum (example: *d*- and *l*-carvoxime, m.p. 72°).

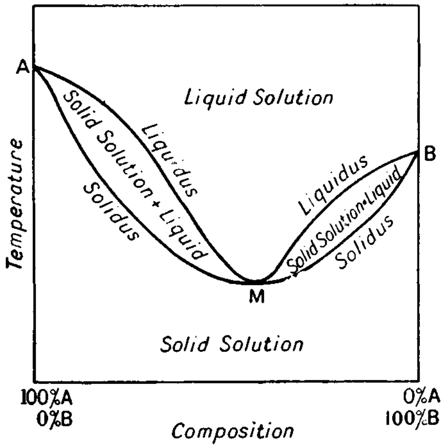


Fig. *I*, *16*, 3.

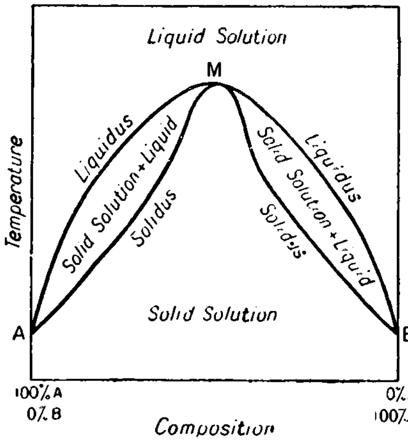


Fig. *I*, *16*, 4.

I,17. Mixed melting points. In the majority of cases the presence of a " foreign substance " will lower the melting point of a pure organic compound. This fact is utilised in the so-called **mixed melting point** test for the identification of organic compounds. Let us suppose that an unknown compound *X* is supplied which is suspected to be *o*-chlorobenzoic acid since its melting point is 140°. This is tested for by intimately mixing together approximately equal weights of *X* and an authentic specimen of *o*-chlorobenzoic acid (*A*) and determining the melting point of the mixture. If the melting point is still 140°, then *X* is *o*-chlorobenzoic acid, but if the melting point is depressed by several degrees *A* and *X* cannot be identical. It is recommended that at least three mixtures containing, say, 10 per cent. *X* + 90 per cent. *A*, 50 per cent. *X* + 50 per cent. *A*, and 90 per cent. *X* + 10 per cent *A* be prepared, and the melting points be determined. Alternatively, if time permits, the complete melting point curve (*i.e.*, the temperature at which the **mixture**

liquefies completely) may be determined by the thaw point method (Section **I,13**)—this will supply more information than mere evidence of non-identity, should this be desired.

Cases may arise in which the melting point of certain mixtures are higher than the individual components, *e.g.*, if an addition compound of higher melting point is formed (compare Fig. *I*, *14*, 1) or if the two compounds are completely soluble in the solid state forming solid solutions (compare Figs. *I*, *16*, 1 and *I*, *16*, 4). Furthermore, for certain optical isomers, *e.g.*, *d*- and *l*-camphoroximes and for *d* and *l*-borneol, there is no depression in the melting point, the freezing or melting points of all mixtures being the same as the pure components. It will be seen, therefore, that the mixed melting point test, although of great practical value, is not infallible and should accordingly be used with reasonable regard to these possibilities.

I,18. System in which the solid phases consist of the pure components and the components are only partially miscible in the liquid state. In concluding the discussion on the theory of melting and freezing, the system in which the two components are only partially miscible in the liquid state and the solid phases consist of the pure components will be considered. In all the previous cases the components were completely miscible in the liquid state, but examples are known (*e.g.*, succinonitrile and water) where, over a limited range of concentration, the liquids are partially miscible and two liquid phases are formed. The equilibrium diagram of a such a system is presented in Fig. *I*, *18*, 1 (for the sake of clarity, this has not been drawn to scale; the salient features have been exaggerated). Point *A* is the melting point of succinonitrile and *B* that of ice. If succinonitrile (*A*) is added to ice at *B*, the freezing point will fall along *BC*, ice (solid *B*) separating; ultimately the temperature of the eutectic *C* (— 1·2°) will be reached. If the temperature is now raised slightly so that the eutectic mixture just melts and the addition of *A* is continued, the concentration of *A* in the solution will increase (curve *CD*) and the solid phase in equilibrium with the solutions denoted by *CD* will be *A* (succinonitrile). At the point *D* (18·5°), solid *A* melts and two liquid phases make their appearance. This is the well-known phenomenon of **melting under the solvent** or the separation of an " oil " during the recrystallisation of a pure substance from a solvent. The compositions of the two liquid phases are represented by the points *D* and *E* and there will be, in addition to the vapour, three phases present, *viz.*, *A* (the solid succinonitrile), solution of liquid *A* in *B* (water) and of *B* in liquid *A*. The temperature t_Q is therefore a quadruple point (*i.e.*, four phases coexist). The addition of more *A* will result in a change of the relative amounts of the two layers—increased amount of *B* in liquid *A*, decreased amount and eventual disappearance of liquid *A* in *B*—the temperature remaining constant (*DE*). At *E* only one liquid phase is present; with further addition of *A*, the equilibrium temperature rises as expressed by *EA*.

If the system represented by the point *D* be heated, the solid *A* will disappear and two partially miscible liquids will remain. The curve *ETD* is the ordinary solubility curve for two partially miscible liquids (compare Section **I,8**, Fig. *I*, *8*, 1). As the temperature rises, the mutual solubility of the two components increases until at the critical solution, temperature *T* (55·5°) they become miscible in all proportions. At all temperatures above the curve *BCDTEA* there is only one liquid phase; at temperatures between *D* and *T*, mixtures of total composition denoted by points inside the area *DTE* will separate into two liquid phases.

The equilibrium diagram expresses in shorthand form the behaviour of all mixtures upon heating or cooling. Thus, let us examine the effect of cooling a homogeneous liquid mixture of composition expressed by the point *a*. Two layers (conjugate solutions) commence to form at *b*, the compositions of which are given by *b* and *b′*; with further cooling, the compositions follow the curves *bE* and *b′D* respectively. When the composition of the system as a whole is expressed by the point *c*, the compositions of the liquid layers are at *E* and *D*: solid *A* then commences to separate, the relative amount of the liquid layer richer in *B* (*i.e.*, *D*) increases and eventually the layer *E* disappears. The temperature remains constant up to the point of the disappearance of the two layers. Thenceforth the temperature falls gradually from *c* to *d*, and the composition follows *DC*, solid *A* separating. At *C*, the eutectic point, the other solid *B* deposits and the temperature again remains constant until the liquid has disappeared. The solid mixture of *A* and *B* then cools slowly along *de*. The behaviour of any other system to the left of the curve *AETD* will be obvious from what has already been said; systems to the right of *D* behave normally like those of which the components are completely miscible in the liquid state and the solid phases consist of pure components (Section **I,12**). For this reason the recrystallisation of a substance which tends to "melt under the solvent" should be confined to the area of composition to the right of the point *D*.

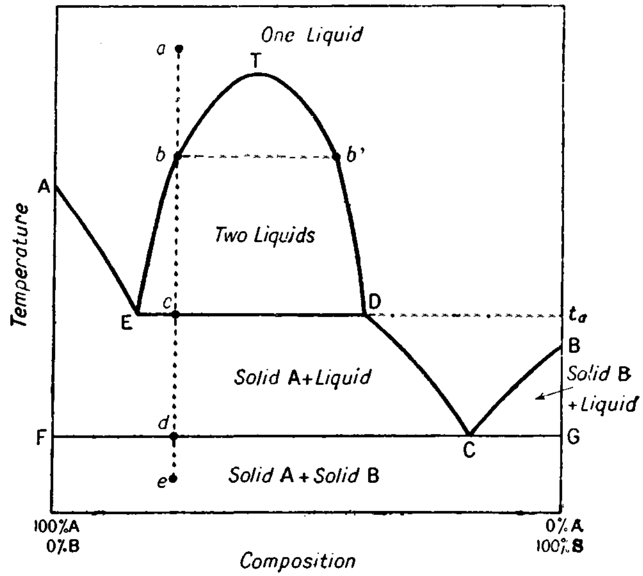


Fig. *I*, *18*, 1.

Examples of solid - liquid systems with two liquid layers are given below : the temperature t_Q is the temperature at which the two layers separate or the quadruple point.

COMPONENT *A*	COMPONENT *B*	t_Q
Water, m.p. 0°	Acetanilide, m.p. 114°	83°
Water, m.p. 0°	Succinonitrile, m.p. 54°	18·5°
Water, m.p. 0°	Benzoic acid, m.p. 121°	98°
Water, m.p. 0°	Phenol, m.p. 43°	1·7°
Benzene, m.p. 5°	Resorcinol, m.p. 110°	95·5°

I,19. THEORY OF SUBLIMATION

The processes of distillation and sublimation are closely related. There are three ways in which the vaporisation of a thermally stable substance may take place on heating :—

(i) If the substance is liquid under ordinary conditions, it may boil at a definite temperature depending upon the pressure.

(ii) If the substance is solid under ordinary conditions, it may first melt at a definite temperature and, upon rise of temperature, boil like an ordinary liquid.

(iii) If the substance is solid under ordinary conditions, it may volatilise without melting, at a definite temperature depending upon the pressure.

The condensation of the vapour of a stable substance may, likewise, take place in three ways :—

(i) There may be liquefaction only.

(ii) Liquefaction may take place first, followed by solidification.

(iii) The vapour may pass directly, without the intermediate formation of a liquid, into the solid state.

The term **distillation** is applied to vaporisation and subsequent condensation according to (i) ; it should also be applied to (ii) since it is really the liquid which is converted into vapour and is first formed by condensation. Strictly speaking, the term **sublimation** should be applied to changes according to (iii). However, in practice, a substance when heated may first melt and then boil, but on cooling it may pass directly from the vapour to the solid : the process is then also called sublimation. Indeed the mode of vaporisation, whether directly from solid to vapour or through the intermediate formation of a liquid, is of secondary importance ; it is the direct conversion of vapour to solid which is really the outstanding feature of sublimation in the laboratory.

To understand the conditions which control sublimation, it is necessary to study the solid - liquid - vapour equilibria. In Fig. *I, 19,* 1 (compare Fig. *I, 10,* 1) the curve *TW* is the vapour pressure curve of the liquid (*i.e.*, it represents the conditions of equilibrium, temperature and pressure, for a system of liquid and vapour), and *TS* is the vapour pressure curve of the solid (*i.e.*, the conditions under which the vapour and solid are in equilibrium). The two curves intersect at *T* : at this point, known as the **triple point,** solid, liquid and vapour coexist. The curve *TV* represents the temperatures and pressures at which the solid and liquid can be in equilibrium, that is, it indicates the influence of pressure upon the melting point. This curve meets the other curves at the triple point *T*.

The normal melting point of a substance is the temperature at which solid and liquid are in equilibrium at atmospheric pressure. At the triple point, the pressure is the equilibrium vapour pressure of the system (solid - liquid - vapour) and the temperature differs from the melting point. The difference is, however, quite small—usually only a fraction of a degree—since the line *TV* departs only slightly from the vertical within reasonable ranges of pressure.

It is clear that if the vapour at a pressure below the triple point is reduced sufficiently in temperature, it will condense directly to the solid form, or, sublimation will ensue. In order that a solid may pass directly into vapour without the intermediate formation of a liquid phase, the pressure of the vapour must not be allowed to exceed that of the triple point. This can easily be done if the vapour pressure at the triple point is fairly high and consequently the rate of vaporisation will be considerable; the conditions are then favourable for the purification of the solid by sublimation at atmospheric pressure. Thus, if camphor (triple point, 179°; equilibrium pressure, 370 mm.) is slowly heated below 179°, it will vaporise without melting and, if the vapour is deposited on a cooled surface, the pressure will be kept below 370 mm. so that vaporisation will continue until the solid has disappeared. Condensation takes place on the cold surface directly as the solid because the pressure is below that at the triple point.

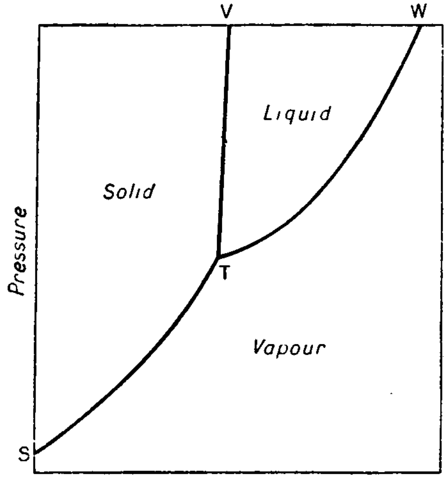


Fig. *I*, *19*, 1.

If the triple point pressure of a solid is below one atmosphere, it will melt if the heating is conducted rapidly so that the vapour pressure can exceed that at the triple point. If camphor is heated in a closed space, the vapour pressure increases and when the value of 360 mm. is reached, the solid will melt; further heating results in an increase in the vapour pressure and the camphor will boil when the vapour pressure is 760 mm.

For substances with a moderate triple point pressure (*e.g.*, benzoic acid, 6 mm., m.p. 122°; naphthalene, 7 mm., m.p. 80° *), the simple process described above for camphor will not give a satisfactory yield of a sublimed product. Thus, for example, if naphthalene is heated it will melt at *T* (80°), and will boil when the vapour pressure is 760 mm. (218°);

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* For most practical purposes the temperature and pressure at the triple point may be regarded as not differing appreciably from the melting point and the vapour pressure at the melting point respectively.

it will be necessary to maintain the compound at about this temperature if any substantial quantity is to be completely converted into vapour. Upon cooling the vapour, naphthalene will deposit as a liquid until the temperature T' (Fig. *I, 19,* 1) is reached (the vapour pressure is then 7 mm.) and thenceforth as a solid. To improve the yield of sublimate, the pressure in the system must be reduced ; this may be done by exhausting the apparatus with a pump. In the present and similar cases, a simpler procedure is to dilute the vapour with an inert gas (carbon dioxide or nitrogen). This dilution will reduce the partial pressure of the substance and also simultaneously cool the vapour ; the sublimed crystals are collected in a cooling chamber, where they deposit usually in a finely-divided form. True sublimation can occur only when the partial pressure of the vapour of the substance is lower than its triple point pressure. Substances with low vapour pressures at their melting points can only be satisfactorily sublimed under greatly diminished pressure.

Two cases of direct sublimation at atmospheric pressure are worthy of mention. Hexachloroethane has a triple point temperature of 186° and a triple point pressure of 780 mm. Complete sublimation can therefore be easily effected by merely heating to about 185° (the vapour pressure is 760 mm. at 185°). The melting point of this substance is most satisfactorily determined in a sealed capillary tube. The triple point temperature and pressure of carbon dioxide are — 56·4° and 5·11 atmospheres respectively. This means that liquid carbon dioxide can only be formed if the pressure exceeds 5·11 atmospheres. If liquid carbon dioxide, from a cylinder, is allowed to escape into the air (best into a cloth bag tied to the nozzle of the cylinder), it absorbs so much heat during the rapid evaporation that part of it is frozen into a snow-like solid. Commercially, the carbon dioxide " snow " is compressed hydraulically into slabs of *Dry Ice* or *Drikold.* The solid evaporates comparatively slowly, owing to its high latent heat (87·2 cal. per gram), its high density (1·56), and the fact that it is surrounded by an insulating layer of heavy vapour. The solid will pass directly into the gas since atmospheric pressure is well below the triple point pressure. Solid carbon dioxide (Dry Ice ; Drikold) has the following advantages over ice as a refrigerant :—

(1) As already stated, it passes directly into the vapour.

(2) It can produce a lower temperature (— 78°).

(3) It occupies less space.

(4) It forms excellent freezing mixtures with many organic liquids, *e.g.*, with alcohol, — 72° ; with ether, — 77° ; and with chloroform, — 77°.

(5) It has a higher latent heat and a greater density producing an over-all cooling effect which is about twice as efficient as ordinary ice.

I,20. THEORY OF THE ACTION OF DRYING AGENTS

Drying agents may be divided broadly into (*a*) those which combine with water reversibly and (*b*) those which react chemically with water by a non-reversible process giving rise to a new water-free compound. Sodium, calcium carbide and phosphorus pentoxide belong to the latter class and will be discussed in Section **II,39.**

To appreciate the action of a drying agent of class (*a*), let us imagine some anhydrous copper sulphate in an evacuated vessel provided with a pressure gauge, and water is allowed to enter slowly ; the temperature is assumed constant at 25°. The results may be best expressed by means of a vapour pressure-composition diagram (Fig. *I*, *20*, 1). The initial system is represented by the point *A* ; the pressure will rise along *AB* until the monohydrate $CuSO_4,H_2O$ commences to form at *B*.

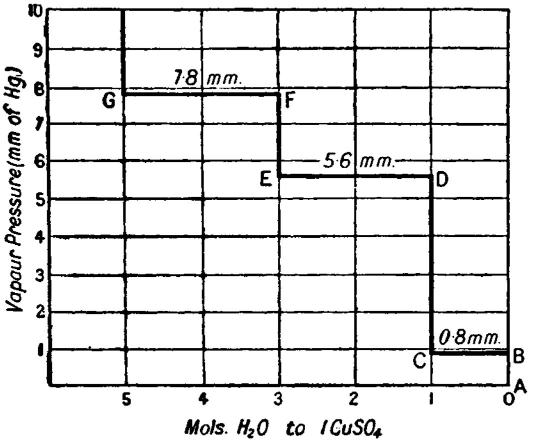

Fig. *I*, *20*, 1.

At this point the system has three phases ($CuSO_4$; $CuSO_4,H_2O$; H_2O vapour) and the number of components is two (anhydrous salt ; water). Hence by the phase rule, $P + F = C + 2$, *i.e.*, $3 + F = 2 + 2$, or $F = 1$. The system is consequently univariant, in other words, only one variable, *e.g.*, temperature, need be fixed to define the system completely ; the pressure of water vapour in equilibrium with $CuSO_4$ and $CuSO_4,H_2O$ should be constant at constant temperature.

As more water vapour is absorbed by the system, the pressure remains constant along *BC* until the anhydrous salt is completely converted into the monohydrate. The conversion is complete at *C* : the pressure then rises along *CD* until the trihydrate is formed at *D*. Two solid phases ($CuSO_4,3H_2O$; $CuSO_4,H_2O$) are now present and the pressure remains constant until all the monohydrate is transformed into the trihydrate at *E*. The pressure again rises to *F*, and when it attains the value denoted by *F*, the pentahydrate commences to form and the system has a constant pressure until all the trihydrate has passed into the pentahydrate at *G*. The same curves are obtained if copper sulphate pentahydrate is dehydrated at constant temperature (25°) : here the powdered crystals of the pentahydrate are contained in a vessel and the water vapour is gradually removed by means of a pump. The pressure remains constant along *GF* whilst the pentahydrate is being converted into trihydrate ; at *F* only the trihydrate is present. A sharp drop in pressure to *E* then occurs and along *ED* the trihydrate passes at constant pressure into the monohydrate. This change is complete at *D*, the pressure falls again to *C*, at which point dissociation of the monohydrate to the anhydrous salt occurs. This transformation is complete at *B*, and, with the complete removal of the water, the pressure drops to almost zero at *A*.

It is evident from these results that three equilibria are to be considered, *viz.* :—

$$\begin{array}{llll}
CuSO_4 & + H_2O \rightleftharpoons CuSO_4,H_2O \,; & 0\cdot8 \text{ mm. at } 25^\circ & \text{(i)} \\
CuSO_4,H_2O & + 2H_2O \rightleftharpoons CuSO_4,3H_2O \,; & 5\cdot6 \text{ mm.} & \text{(ii)} \\
CuSO_4,3H_2O & + 2H_2O \rightleftharpoons CuSO_4,5H_2O \,; & 7\cdot8 \text{ mm.} & \text{(iii)}
\end{array}$$

Furthermore, it is the system, Hydrate I/Hydrate II (or Anhydrous Salt), that possesses a definite pressure at a particular temperature ; this is independent of the relative amounts, but is dependent upon the nature of the two components in equilibrium. It is incorrect, therefore, to speak of the " vapour pressure of a salt hydrate."

Similar results are obtained at other temperatures, *e.g.*, at 50°, the above three systems give equilibrium vapour pressures of 4·5, 30·9 and 45·4 mm. respectively. There is some evidence for the existence of a tetrahydrate $CuSO_4,4H_2O$, but this does not affect the general nature of the change described above. At temperatures higher than about 102°, the pentahydrate is unstable and $CuSO_4,3H_2O$ is the first stable hydrate.

We may now understand the nature of the change which occurs when an anhydrous salt, say copper sulphate, is shaken with a wet organic solvent, such as benzene, at about 25°. The water will first combine to form the monohydrate in accordance with equation (i), and, provided sufficient anhydrous copper sulphate is employed, the effective concentration of water in the solvent is reduced to a value equivalent to about 1 mm. of ordinary water vapour. The complete removal of water is impossible ; indeed, the equilibrium vapour pressures of the least hydrated system may be taken as a rough measure of the relative efficiencies of such drying agents. If the water present is more than sufficient to convert the anhydrous copper sulphate into the monohydrate, then reaction (i) will be followed by reaction (ii), *i.e.*, the trihydrate will be formed ; the water vapour then remaining will be equivalent to about 6 mm. of ordinary water vapour. Thus the monohydrate is far less effective than the anhydrous compound for the removal of water.

Magnesium sulphate is a useful drying agent as can be seen from the following table of equilibrium vapour pressures of the various possible systems at 25° ;

$$\begin{array}{lll}
MgSO_4 & + H_2O \rightleftharpoons MgSO_4,H_2O \,; & 1 \text{ mm.} \\
MgSO_4,H_2O & + H_2O \rightleftharpoons MgSO_4,2H_2O \,; & 2 \text{ mm.} \\
MgSO_4,2H_2O & + 2H_2O \rightleftharpoons MgSO_4,4H_2O \,; & 5 \text{ mm.} \\
MgSO_4,4H_2O & + H_2O \rightleftharpoons MgSO_4,5H_2O \,; & 9 \text{ mm.} \\
MgSO_4,5H_2O & + H_2O \rightleftharpoons MgSO_4,6H_2O \,; & 10 \text{ mm.} \\
MgSO_4,6H_2O & + H_2O \rightleftharpoons MgSO_4,7H_2O \,; & 11\cdot5 \text{ mm.}
\end{array}$$

Another valuable drying agent of general application is anhydrous calcium sulphate, marketed under the name of "*Drierite.*" It is rapid in its action, but has only a limited drying capacity because it forms the hydrate $2CaSO_4,H_2O$ and thus combines with only 6·6 per cent. of its weight of water. The vapour pressure of the system :

$$2CaSO_4 + H_2O \rightleftharpoons 2CaSO_4,H_2O$$

is only 0·004 mm. at about 25°. The residual water content is therefore very low, and the substance may be employed for drying alcohols, esters, ketones, acids, etc. If the water content of the organic substance is somewhat high, a preliminary drying with another desiccant such as anhydrous magnesium or sodium sulphate, which can absorb a higher proportion of water, is recommended.

A rough method for comparing the drying powers of the common desiccants consists in passing moist air over the drying agent maintained at a constant temperature and then determining the residual moisture with phosphorus pentoxide—the most efficient drying agent known. Some results, due largely to Bower (1934), are tabulated below.

RESIDUAL WATER VAPOUR PER LITRE OF AIR AT 30·5°

MATERIAL	RESIDUAL WATER (MG.)	MATERIAL	RESIDUAL WATER (MG.)
Na_2SO_4, anhydrous	12	$Mg(ClO_4)_2,3H_2O$	0·03
$CuSO_4$, anhydrous	2·8	Silica gel	0·03
$CaCl_2$, granular *	1·5	KOH, sticks	0·01
$CaCl_2$, technical anhydrous †	1·25	Al_2O_3	0·005
$ZnCl_2$, sticks	1·0	$CaSO_4$, anhydrous	0·003
$Ba(ClO_4)_2$, anhydrous	0·8	H_2SO_4	0·003
NaOH, sticks	0·8	CaO	0·002
$CaCl_2$, anhydrous (fused)	0·4	$Mg(ClO_4)_2$, anhydrous	0·002
H_2SO_4, 95 %	0·3	BaO	0·0007

* Approximate composition : $CaCl_2,H_2O$. † Approximate composition : $4CaCl_2,H_2O$.

As a rough approximation it may be assumed that one mg. of water contained in one litre of gas at 25–30° exerts a 1 mm. partial vapour pressure. Obviously, the lower the residual water content or the vapour pressure, the more intense is the ultimate drying capacity of the substance.

The vapour pressures of the various hydrate systems increase with temperature (compare the figures for the three copper sulphate - water systems of equations (i), (ii) and (iii) at 25° and 50° already given). It follows, therefore, that the efficiency of desiccants decreases with rise of temperature and, indeed, at high temperatures certain desiccating agents may actually undergo dehydration. Thus the vapour pressures of some calcium chloride - water systems exceed atmospheric pressure at high temperatures, as can be seen from the following table.

VAPOUR PRESSURE OF CALCIUM CHLORIDE SYSTEMS

TEMPERATURE	PRESSURE (MM.)	SOLID PHASES
−55°	0·0	Ice — $CaCl_2,6H_2O$
+29·2°	5·7	$CaCl_2,6H_2O$ — β $CaCl_2,4H_2O$
29·8°	6·8	$CaCl_2,6H_2O$ — α $CaCl_2,4H_2O$
38·4	7·9	β $CaCl_2,4H_2O$ — $CaCl_2,2H_2O$
175·5°	842·0	$CaCl_2,2H_2O$ — $CaCl_2,H_2O$

It follows that liquids of high boiling point should not be distilled from drying agent systems which have appreciable vapour pressures. An extreme case of this action is the dehydration of oxalic acid dihydrate by distillation over toluene or over carbon tetrachloride.

I,21. Deliquescence and efflorescence. A substance is said to **deliquesce** (Latin : *to become liquid*) when it forms a solution or liquid phase upon standing in the air. The essential condition is that the vapour pressure of the saturated solution of the highest hydrate at the ordinary temperature should be less than the partial pressure of the aqueous vapour in the atmosphere. Water will be absorbed by the substance, which gradually liquefies to a saturated solution ; water vapour will continue to be absorbed by the latter until an unsaturated solution, having the same vapour pressure as the partial pressure of water vapour in the air, is formed. In order that the vapour pressure of the saturated solution may be sufficiently low, the substance must be extremely soluble in water, and it is only such substances (*e.g.*, calcium chloride, zinc chloride and potassium hydroxide) that deliquesce.

In the British Isles the atmosphere is normally about two-thirds saturated and the partial vapour pressure of a well-ventilated laboratory is 12–14 mm. at about 20°. The vapour pressure of calcium chloride ($CaCl_2,6H_2O$ - $CaCl_2,4H_2O$) at room temperature is about 4 mm., that of the saturated solution about 7–8 mm., and 100 grams of water will dissolve 74·5 grams of the hydrate at 20° ; it is therefore deliquescent. Sodium and potassium hydroxides possess similar properties. Copper sulphate pentahydrate, on the other hand, is not deliquescent as the vapour of the saturated solution is about 16 mm. at 20° and that of the $CuSO_4,5H_2O$ - $CuSO_4,3H_2O$ system is considerably less than this (see Fig. *I, 20,* 1).

A salt hydrate is said to **effloresce** (Latin : *to blossom*) when it loses water and falls to a powder upon exposure to the atmosphere. Efflorescence will occur when the vapour pressure of the hydrate system is greater than that of water vapour in the atmosphere ; dehydration will then occur in the effort for equilibrium to be attained between the hydrate system and the surroundings. A good example is washing soda, $Na_2CO_3,10H_2O$, which gives off water vapour with the production of the monohydrate, Na_2CO_3,H_2O. Other examples are the systems containing $Na_2SO_4,10H_2O$ and $Na_2HPO_4,12H_2O$.

It must be emphasised that deliquescence and efflorescence are relative properties, since they depend upon the actual presence of water vapour in the atmosphere, which varies considerably with place and time.

A substance is said to be **hygroscopic** when it attracts moisture from the atmosphere. All deliquescent compounds are consequently hygroscopic, but there are many hygroscopic substances which absorb water vapour without deliquescing. Most dry substances, particularly if in a fine powder form, are slightly hygroscopic. Substances which are commonly regarded as hygroscopic include quicklime and cupric oxide. The term is also applied to liquids : thus concentrated sulphuric acid, absolute methyl and ethyl alcohols, and deuterium oxide (" heavy water ") have hygroscopic properties.

I,22. EXTRACTION WITH SOLVENTS

The process of **extraction** with solvents is generally employed either for the isolation of dissolved substances from solutions or from solid mixtures or for the removal of undesired soluble impurities from mixtures. The latter process is usually termed **washing**.

The theory of the process can best be illustrated by considering the operation, frequently carried out in the laboratory, of extracting an organic compound from its aqueous solution with an immiscible solvent. We are concerned here with the **distribution law or partition law** which, states that if to a system of two liquid layers, made up of two immiscible or slightly miscible components, is added a quantity of a third substance soluble in both layers, then the substance distributes itself between the two layers so that the ratio of the concentration in one solvent to the concentration in the second solvent remains constant at constant temperature. It is assumed that the molecular state of the substance is the same in both solvents.* If c_A and c_B are the concentrations in the layers A and B, then, at constant temperature :

$$c_A/c_B = \text{constant} = K.$$

The constant K is termed the **distribution or partition coefficient**. As a very rough approximation the distribution coefficient may be assumed equal to the ratio of the solubilities in the two solvents. Organic compounds are usually relatively more soluble in organic solvents than in water, hence they may be extracted from aqueous solutions. If electrolytes, *e.g.*, sodium chloride, are added to the aqueous solution, the solubility of the organic substance is lowered, *i.e.*, it will be **salted out**: this will assist the extraction of the organic compound.

The problem that arises in extraction is the following. Given a limited quantity of the solvent, should this be used in one operation or divided into several portions for repeated extractions in order to secure the best result ? A general solution may be derived as follows. Let the volume, v ml., of the aqueous solution containing w_0 grams of the dissolved substance be repeatedly extracted with fresh portions of s ml. of the organic solvent, which is immiscible with water. If w_1 grams is the weight of the solute remaining in the aqueous phase after the first extraction, then the concentrations are w_1/v g. per ml. in the aqueous phase and $(w_0 - w_1)/s$ g. per ml. in the organic solvent layer. The partition coefficient K is given by :

$$\frac{w_1/v}{(w_0 - w_1)/s} = K$$

or

$$w_1 = w_0 \frac{Kv}{Kv + s}$$

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* For a theoretical treatment involving association or dissociation in one solvent, see, for example, S. Glasstone, *Text Book of Physical Chemistry*, Second Edition 1947, p. 737 (Van Nostrand ; Macmillan).

Let w_2 grams remain in the aqueous layer after the second extraction, then:

$$\frac{w_2/v}{(w_1 - w_2)/s} = K$$

or

$$w_2 = w_1 \frac{Kv}{Kv + s}$$

$$= w_0\left(\frac{Kv}{Kv + s}\right)^2$$

Similarly if w_n grams remain in the aqueous layer after the nth extraction:

$$w_n = w_0\left(\frac{Kv}{Kv + s}\right)^n \qquad (1).$$

We desire to make w_n as small as possible for a given weight of solvent, *i.e.*, the product of n and s is constant, hence n should be large and s small; in other words, the best results are obtained by dividing the extraction solvent into several portions rather than by making a single extraction with the whole quantity. It must be emphasised that the expression deduced above applies strictly to a solvent which may be regarded as completely immiscible with water, such as benzene, chloroform or carbon tetrachloride; if the solvent is slightly miscible, *e.g.*, ether, the equation (1) is only approximate, but is nevertheless useful for indicating the qualitative nature of the results to be expected.

Let us consider a specific example, *viz.*, the extraction of a solution of 4·0 g. of *n*-butyric acid in 100 ml. of water at 15° with 100 ml. of benzene at 15°. The partition coefficient of the acid between benzene and water may be taken as 3 (or $\frac{1}{3}$ between water and benzene) at 15°. For a single extraction with benzene, we have:

$$w_n = 4\left(\frac{\frac{1}{3} \times 100}{\frac{100}{3} + 100}\right) = 1\cdot0 \text{ g.}$$

For three extractions with 33·3 ml. portions of fresh benzene:

$$w_n = 4\left(\frac{\frac{1}{3} \times 100}{\frac{100}{3} + 33\cdot3}\right)^3 = 0\cdot5 \text{ g.}$$

Hence one extraction with 100 ml. of benzene removes 3·0 g. (or 75 per cent.) of the *n*-butyric acid, whilst three extractions remove 3·5 g. (or 87·5 per cent.) of the total acid. This clearly shows the greater efficiency of extraction obtainable with several extractions when the total volume of solvent is the same. Moreover, the smaller the distribution coefficient between the organic solvent and the water, the larger the number of extractions that will be necessary.

The above considerations apply also to the removal of a soluble impurity by extraction (or washing) with an immiscible solvent. Several washings with portions of the solvent give better results than a single washing with the total volume of the solvent.