

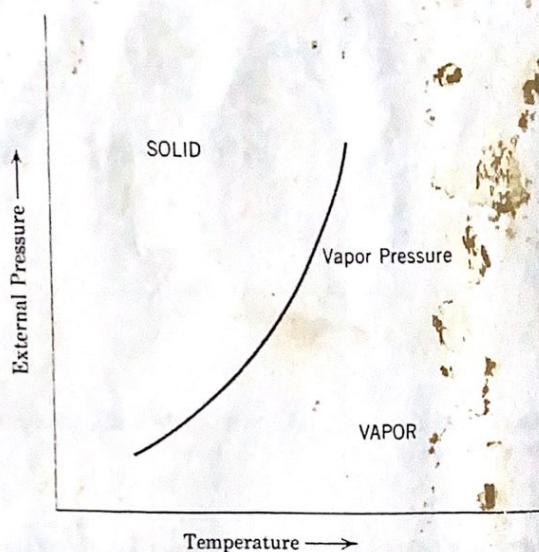


Figure 2-7 Vapor pressure curve for a typical pure solid substance.

function of temperature. The dashed portion of this line (curve *D*) gives the vapor pressure of the supercooled liquid, if it exists. Curve *C* shows the melting point as a function of pressure. It is very nearly a vertical line with a negative slope because water expands slightly on freezing.

For a given temperature and pressure, the phase diagram indicates which phase(s) will exist at equilibrium. If a particular combination of pressure and temperature lies on a curve, two phases will co-exist in equilibrium. There is one unique combination where the curves intersect, the *triple point*, at which all three phases can co-exist.

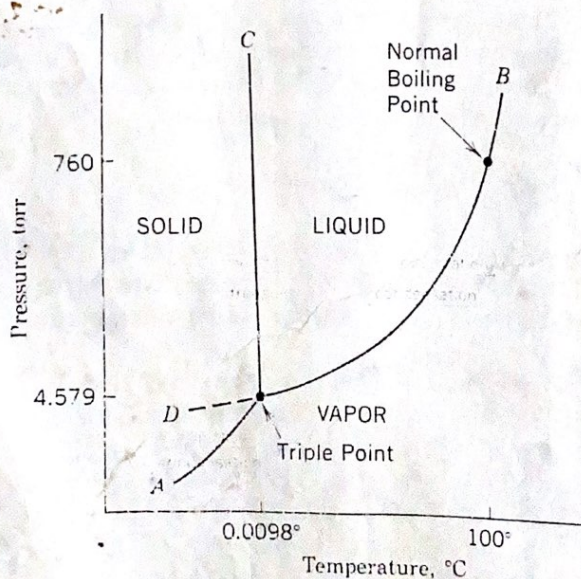


Figure 2-8 Phase diagram for water (not to scale).

2-3 PHASE CHANGES FOR MIXTURES

Solid-Liquid Equilibrium. The melting point of a pure substance is described as "sharp," that is, the entire transition from solid to liquid occurs at a single temperature. (In practice, a melting temperature range of 0.5 to 1.0° is considered to be "sharp.") If the substance is not pure (a mixture), the melting occurs over a range of temperatures as shown in Figure 2-9. Compare this figure with Figure 2-1. In general, the melting point of an impure substance is lower than that of the pure substance and the melting range is greater.

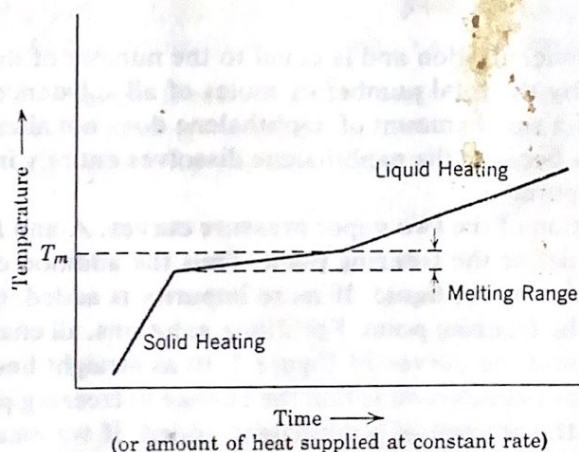


Figure 2-9 Heating curve for a solid mixture.

Freezing Point of Mixtures. Odd as it may seem, we will approach freezing points through vapor pressure curves. Let us consider an isolated system consisting of solid and liquid camphor at its melting point, 179°C . The vapor pressure curves for this system of *pure* camphor are the solid lines A and B in Figure 2-10. A small amount of naphthalene added to the system will dissolve in

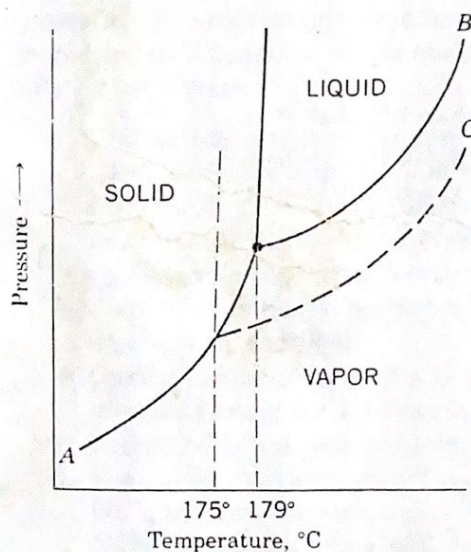


Figure 2-10 Phase diagram for pure camphor and for camphor with a small amount of naphthalene added (curve C).

the liquid camphor. The concentration of camphor molecules at the liquid surface is now less than before adding the naphthalene. As a consequence, the rate of vaporization of liquid camphor is decreased proportionately and its vapor pressure is decreased. The dashed line, C, in Figure 2-10 gives the vapor pressure of liquid camphor containing a small amount of naphthalene. The actual displacement of curve C from curve B was first investigated by F. M. Raoult in 1887, and is given by *Raoult's law* which states that the vapor pressure, P_c , of a solvent (in this case, camphor) in a solution is equal to the vapor pressure of the pure solvent P_c° multiplied by the mole fraction, X_c , of the solvent in the solution:

$$P_c = X_c P_c^\circ \quad (2-6)$$

Mole fraction is a measure of concentration and is equal to the number of moles of the given substance divided by the total number of moles of all substances in the same phase. The addition of a small amount of naphthalene does not alter the vapor pressure of solid camphor because the naphthalene dissolves entirely in the liquid phase, leaving the solid pure.

As in Figure 2-8, the intersection of the two vapor pressure curves, A and B, or A and C, in Figure 2-10, must define the freezing point. Thus the addition of an impurity lowers the freezing point of the liquid. If more impurity is added, there will be a still greater change in the freezing point. For *dilute* solutions, all changes will be small and we can represent the curves of Figure 2-10 as straight lines as shown in Figure 2-11. The obvious conclusion is that the change in freezing point, ΔT_f , is directly proportional to the amount of naphthalene added. If we measure concentration as molality (moles of solute per 1000 g of solvent), the proportionality constant is called the *molal freezing point depression constant*, K_f . For dilute solutions a simple equation describes this behavior:

$$\Delta T_f = K_f m \quad (2-7)$$

where m is the molality of the solute. The value of K_f depends only on the nature of solvent and not of the solute. Values of K_f for a few solvents are given in Table 2-3. If a known weight of a solute is dissolved in a known amount of solvent, a determination of the freezing point depression will yield the molality of the

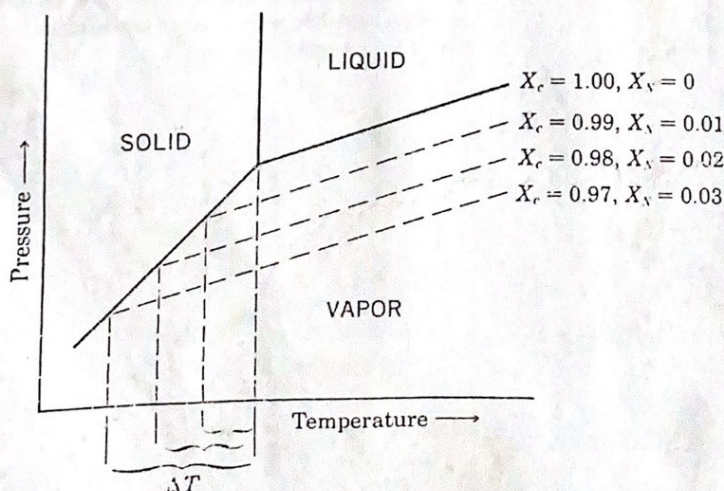


Figure 2-11 Expanded portion of phase diagram for camphor with several amounts of naphthalene added.

Table 2-3 Molal Freezing Point Constants

Solvent	Freezing Point, °C	K_f , deg/mole
Acetic acid	17	-3.9
Benzene	5.4	-5.12
Camphor	179	-38.0
Ethylene dibromide	10.1	-11.8
Naphthalene	80	-6.8
Water	0	-1.86

solution, from which the molecular weight of the solute can be computed. Although simple in principle, exact determination requires great care.

Example/Problem 2-4. Determine the molecular weight of an unknown from the following data: 4.35 g of the unknown was dissolved in 200 g of liquid camphor, giving a solution with a freezing point of 173.5°C.

$$\Delta T_f = 179.0^\circ - 173.5^\circ = 5.5^\circ$$

$$\Delta T_f = K_f m$$

$$5.5 = 38.0 \times m$$

$$m = 5.5/38.0 = 0.145 \text{ mole/1000 g solvent}$$

$$0.145/5 = 0.029 \text{ mole/200 g solvent}$$

$$\text{Molecular wt.} = \frac{4.35 \text{ g}}{0.029 \text{ mole}} = 150$$

In treating freezing points of mixtures, we generally assume that the liquid phase is homogeneous; that is, the two liquids are miscible. But the two solid substances may or may not form a homogeneous phase. A solid phase whose composition is the same throughout is, for the present discussion, called a *solid solution*. Some mixtures of solids are able to form homogeneous solid solutions while others remain as mixtures of two pure solid phases.

Mixtures with No Solid Solutions. If we start with pure naphthalene, m.p. 80°C, and add camphor, the argument is the same as for adding naphthalene to pure camphor. The two effects are combined in Figure 2-12, in which the melting point is plotted as a function of the mole % composition of the liquid phase. How can we use this graph?

1. The melting points of the pure compounds are given on the respective axes at 100% camphor and 100% naphthalene, points A and B.
2. Curve AE gives the initial freezing points of camphor containing various amounts of naphthalene, for example, a liquid mixture containing 20% naphthalene begins to freeze at 117°C, point C.
3. Curve BE gives the initial freezing points of naphthalene containing various amounts of camphor.
4. Curves AE and BE intersect at point E which gives the composition of the mixture having the lowest possible freezing point, called the *eutectic point* (from the Greek words meaning "easily melted").
5. If a liquid mixture containing 20% naphthalene (point D) is cooled (curve DC), crystals of pure camphor will appear when the temperature reaches 117°C. Further cooling will cause additional pure camphor to solidify. The

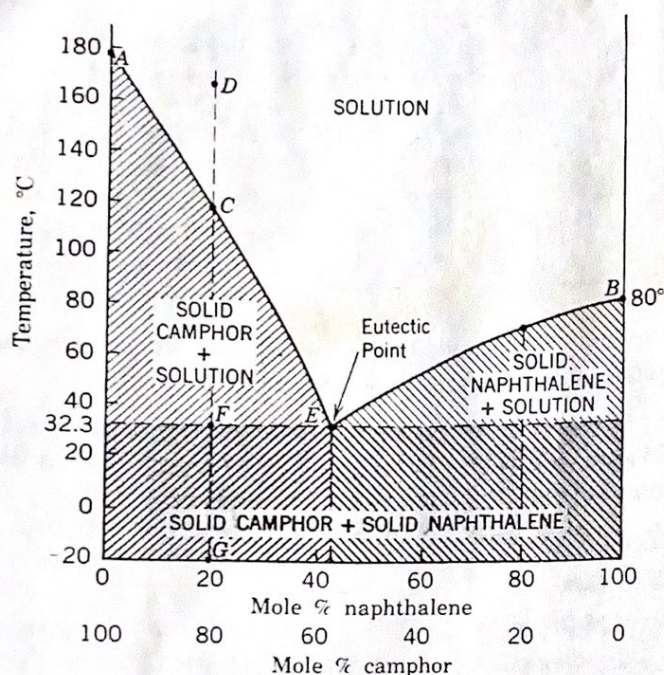


Figure 2-12 Melting point-composition diagram for the camphor-naphthalene system.

liquid phase thus becomes enriched in naphthalene and its freezing point decreases along curve CE . When point E is reached, the remaining liquid (now at the eutectic composition) freezes. When all the liquid has frozen, the composition of the solid must, of course, be the same as the composition of the original liquid mixture, 20% naphthalene. Further cooling follows line FG .

6. Heating a mixture of solids containing 20% naphthalene would follow the reverse course from (5) above. At a temperature of 32.3°C, eutectic proportions (58% camphor-42% naphthalene) of the solid will melt until no solid naphthalene remains. The temperature remains fixed at 32.3°C during the melting of the eutectic. Then the remaining camphor melts, gradually decreasing the concentration of naphthalene in the liquid melt and thus raising the melting temperature along EC . The heating curve for this process is given in Figure 2-13.
7. A eutectic mixture has a sharp melting point and a sharp freezing point. Thus a sharp melting point doesn't necessarily prove a pure compound. However, the addition of a small amount of either pure compound to a eutectic mixture will raise its melting point, whereas the addition of a small amount of either pure compound to the other pure compound will lower its melting point.

Identification by Melting Point. The sharp melting point of a pure compound serves as a means of identification. However the usual "pure" organic compound seldom has a melting range of less than 0.3 to 0.5°. Thus, several compounds may have essentially the same melting points and could be confused. Pure samples of the suspected compounds permit a more positive identification. Portions of the unknown are mixed with each of the known compounds and the melting point of each mixture is taken. The "mixed" melting point of all such mixtures will be lowered except when the two compounds are identical.

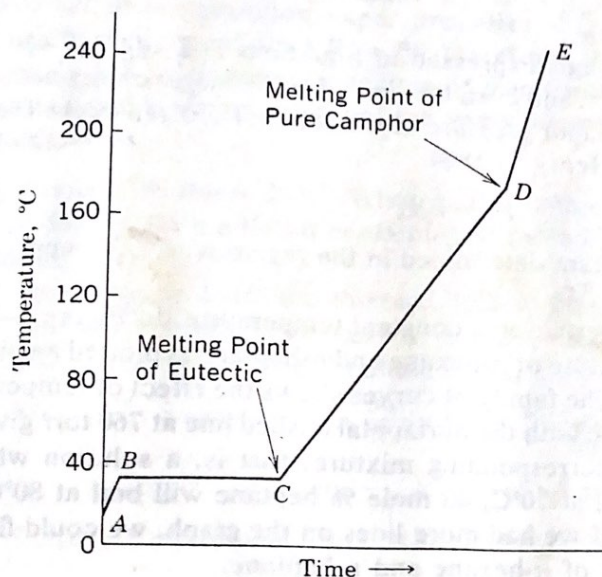


Figure 2-13 Heating curve for a solid sample with an average composition of 20 mole % naphthalene-80 mole % camphor.

Liquid-Vapor Equilibrium for Binary Mixtures. Let us consider a mixture of *n*-hexane (*A*) and *n*-heptane (*B*). The molecules of *A* will exert a certain vapor pressure, P_A , which will be less than if the liquid were pure *A*, having a vapor pressure of P_A° . Likewise, molecules of *B* exert a vapor pressure of P_B which is less than P_B° . As given by Raoult's law (Equation 2-6):

$$P_A = X_A P_A^\circ \quad (2-8)$$

$$P_B = X_B P_B^\circ \quad (2-9)$$

$$P = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ \quad (2-10)$$

where X_A and X_B are the mole fractions of *A* and *B* in the liquid solution and P is the total pressure in the vapor phase above the liquid. This law is valid only for an ideal solution, or to put it the other way around, an *ideal solution* is one that obeys Raoult's law. Ideal behavior is most likely to be observed if the two components are chemically similar. For example, our mixture of two paraffins, *n*-hexane and *n*-heptane, has ideal behavior as shown in Figure 2-14.

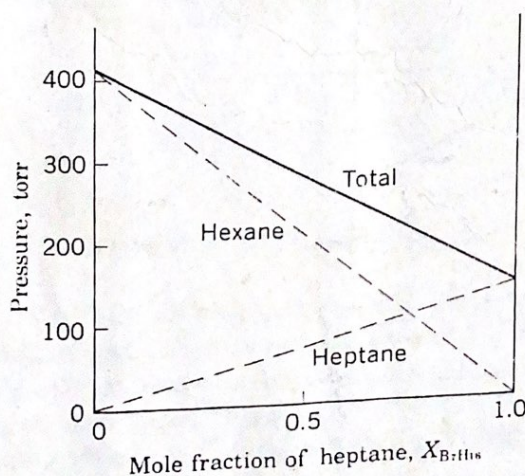


Figure 2-14 Vapor pressure-composition curves for the hexane-heptane system at 50°C.