PHASE CHANGES AND SEPARATIONS

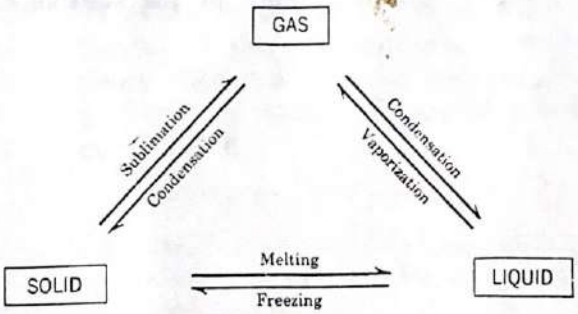
2

ANALYTICAL USES OF PHASE CHANGES

2–1 INTRODUCTION

Our study of chemical analysis begins with one of the earliest observations—substances melt and boil at particular temperatures, and in so doing change in form from a solid to a liquid, or from a liquid to a gas, or the reverse. The transitions between these states of matter, or *phases*, provide information which helps to identify the substance and determine its purity. Furthermore, since the mechanical separation of two phases is relatively straightforward, a study of the distribution of a component between two phases provides the basis for all separation techniques.

The phase changes represented below may occur with either a single pure compound or element, or a mixture of two or more substances.



2–2 PHASE CHANGES FOR PURE COMPOUNDS

Solid–Liquid Equilibrium. When a solid sample is heated its temperature rises as shown in Figure 2–1. At a characteristic temperature, the solid begins to melt and there is a discontinuity in the heating curve. If the heating is continued, the solid continues to melt at a constant temperature, known as the *melting point*, T_m.

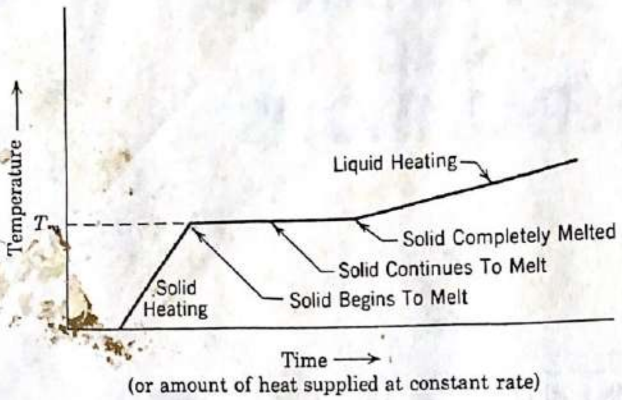


Figure 2–1 Heating curve for a typical pure solid substance.

The additional heat is absorbed as *latent heat of fusion*, ΔH_f, which is the energy required to disrupt the crystal lattice. When the solid is completely melted, the temperature of the liquid begins to rise again, but usually not at the same rate as for the solid because the heat capacity of the liquid differs from that of the solid. We have assumed that during the phase transition the system is well-mixed, so that an equilibrium is maintained.

$$\boxed{\text{SOLID}} \underset{-\Delta H_f}{\overset{+\Delta H_f}{\rightleftharpoons}} \boxed{\text{LIQUID}}$$

If we reverse the process just described and cool a pure liquid, we obtain a cooling curve that is not quite a mirror image of the heating curve, Figure 2–2. The temperature may fall below the equilibrium freezing (melting) point before the first crystals appear, a phenomenon known as *supercooling*. The extent of supercooling varies with the nature of the substance, the rate of cooling,

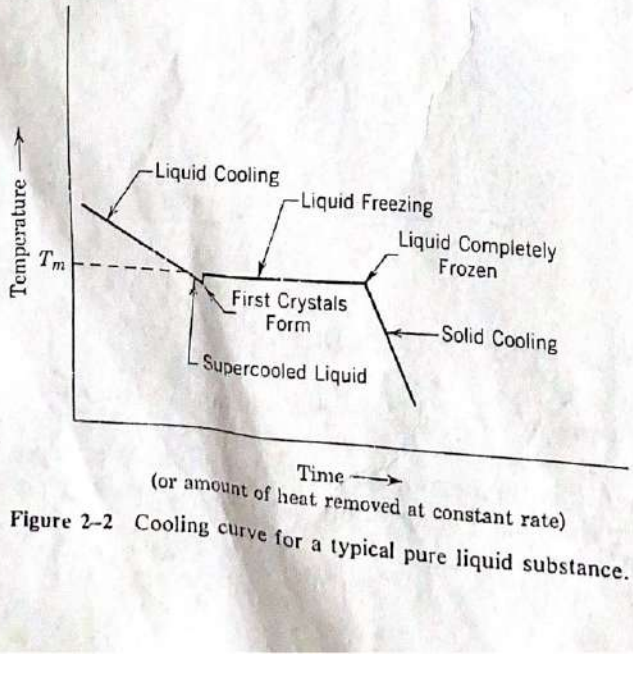


Figure 2–2 Cooling curve for a typical pure liquid substance.

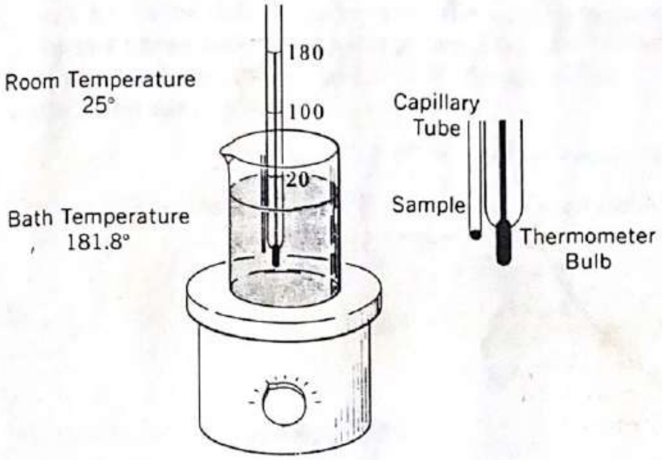


Figure 2–3 Simple apparatus for determining the melting point. Close-up of position of sample.

mechanical actions such as stirring and vibration, and with the presence of impurities which can act as nuclei in the formation of the crystals.

The melting point of a *pure* solid is always sharp (except for liquid crystals) and serves to identify it. If the substance is not pure, it will melt over a range of temperature, as we will discuss in a later section. The change in volume on melting or freezing is relatively small; therefore the effect of pressure is almost always negligible.

Melting points are often determined in the very simple apparatus shown in Figure 2–3. The sample, contained in a thin-walled capillary, and the thermometer should be in close proximity and heated at a rate not exceeding 1° per minute as the melting point is approached (final 10°). More sophisticated apparatus is available for increased accuracy, speed, and convenience.

There are several sources of error in this determination, some of which are easily corrected. Adequate heat transfer must be provided by using a well-stirred bath, a thin-walled capillary, and a very slow heating rate in the region of the melting point. The thermometer should not be trusted unless it has been properly calibrated. Calibration in an ice slush bath and in boiling water at a known pressure is usually adequate. If the bath temperature is well above room temperature, a thermometer correction may be necessary to allow for the variation in the density of mercury along the exposed column. For mercury thermometers, the correction, ΔT, is

$$\Delta T = 0.000154 l(t - n) \qquad (2\text{–}1)$$

where 0.000154 is the coefficient of linear expansion of mercury in a glass tube, l the length of the exposed column in degrees, t the observed temperature, and n the average temperature of the exposed stem.

Example / Problem 2–1. The thermometer in Figure 2–3 reads 180° and is immersed to the 20° mark. The correction is:

$$\Delta T = 0.000154 \times (180 - 20) \times \left(180 - \frac{180 + 25}{2}\right)$$
$$= 1.9^\circ$$

The corrected reading is therefore 181.9°C.

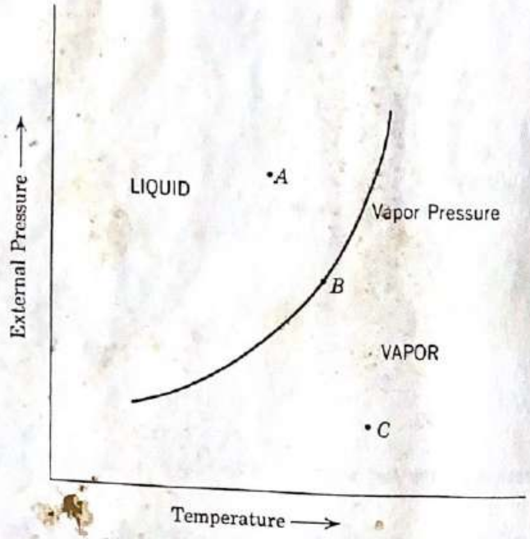


Figure 2–4 Vapor pressure curve for a typical pure liquid substance.

Liquid–Gas Equilibrium. All molecules in a liquid are in constant motion, thus generating an internal pressure and a tendency to escape from the liquid. The *vapor pressure* of a liquid is a measure of this escaping tendency and is the pressure that would be observed in the vapor phase if the pure liquid were placed in an evacuated chamber and allowed to come to equilibrium. If the chamber also contains another gas, the total pressure includes the vapor pressure of the liquid, and we speak of the *partial pressure* of each component. The vapor pressure of the liquid is a property of the liquid and does not depend on the composition of the vapor phase in contact with it. However, it does depend on the composition of the liquid phase (see below). Because vapor pressure is the result of molecular motions, we would expect it to increase with an increase in temperature. Figure 2–4 shows how the vapor pressure of a typical liquid changes with temperature. If the vapor pressure is equal to or greater than the external pressure, the liquid will boil as fast as the *latent heat of vaporization*, ΔH_v, can be supplied until the liquid is completely evaporated, or until an equilibrium is established between the liquid and the vapor.

$$\boxed{\text{LIQUID}} \underset{-\Delta H_v}{\overset{+\Delta H_v}{\rightleftharpoons}} \boxed{\text{GAS}}$$

The temperature at which the vapor pressure is one atmosphere (760 torr) is the *normal boiling point*; however, the boiling point at any pressure is given by the curve in Figure 2–4. This curve also separates two regions: any combination of external pressure and temperature to the left of the line (e.g., point A) is in a region in which the liquid phase is the stable form. Point C is in a region where the gas phase is the stable form. Point B and other points on the line give the only conditions for which the two phases can co-exist in equilibrium.

For pure liquids, the vapor pressure–temperature curve is expressed by the *Clapeyron equation*, developed by Emile Clapeyron in 1834.

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta V} \tag{2–2}$$

where ΔV is the difference between the volume occupied by a mole of substance in the gas phase and in the liquid phase. The liquid volume is very small compared to the gas volume, therefore $\Delta V \approx V$, the gas volume. If we also assume that the vapor is an ideal gas, then

$$V = RT/P \ (R = 1.987 \text{ cal mole}^{-1} \text{ deg}^{-1})$$

Thus, we can substitute RT/P for ΔV in Equation 2–2

$$\frac{dP}{dT} = \frac{\Delta H_v}{RT^2} \times P$$

or

$$\frac{dP}{P} = \frac{\Delta H_v}{RT^2} dT$$

Integration of this equation yields

$$\log P = \frac{-\Delta H_v}{2.3RT} + \text{const} \qquad (2\text{–}3)$$

or

$$\log \frac{P_2}{P_1} = -\frac{\Delta H_v}{2.3R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (2\text{–}4)$$

Over a considerable range of temperature, ΔH_v is constant and can be determined from the slope of a plot of the data (e.g., Table 2–1) according to Equation 2–3, as shown in Figure 2–5. Once we have a value for ΔH_v, Equation 2–4 is useful for computing the vapor pressure, P_2, at temperature T_2 from the known value, P_1, at another temperature T_1.

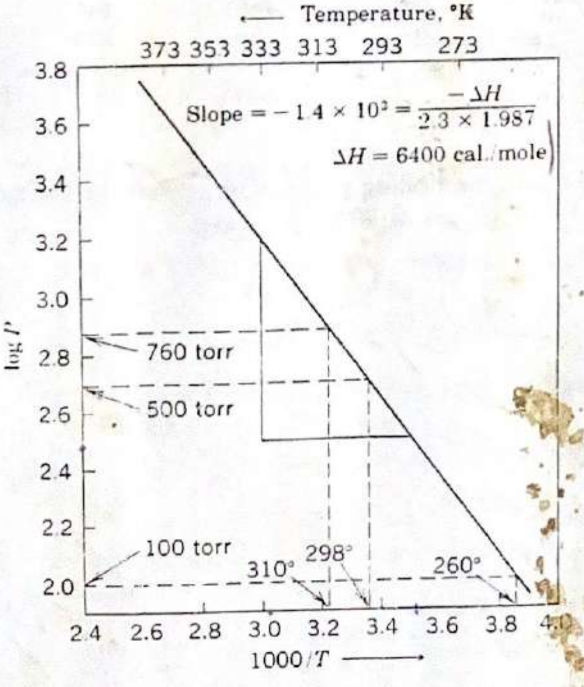
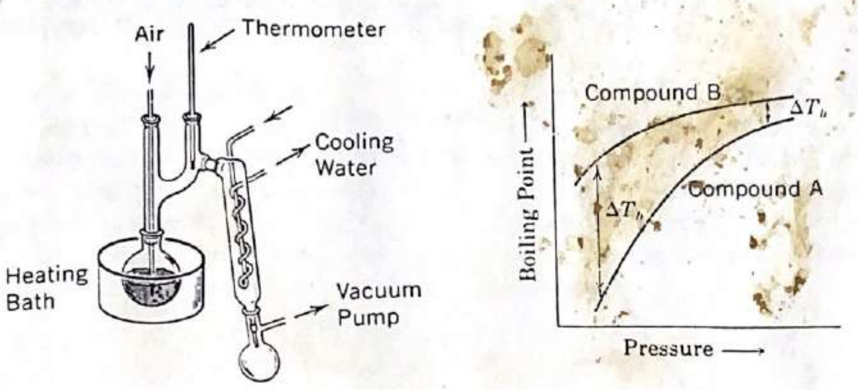


Figure 2–5 Vapor pressure–temperature plot for *n*-pentane according to Equation 2–3.



(a) (b)

Figure 2–6 (a) Apparatus for distilling under reduced pressure. (b) The effect of pressure on the boiling points of two compounds to be separated.

their boiling points is larger. There is a practical limit to conducting distillations at reduced pressures, namely, the time required because of the reduced rate of evaporation. Typical times required to distil 1 g of substance at various pressures are given in Table 2–2.

Table 2–2 Time Required to Distil 1 g of Material

Pressure, Torr	*Time*
10	0.5 min
1	1 hr
10^{-1}	1 wk
10^{-2}	2 yr
10^{-3}	40 yr

Solid–Gas Equilibrium. The escaping tendency of a molecule in a solid is usually very low compared to a liquid. Nevertheless, a vapor pressure does exist (approx 10^{-26} torr for lead metal at room temperature) and it depends on temperature in the same manner as the Clapeyron equation.

$$\log P = \frac{-\Delta H_s}{2.3RT} + \text{constant} \tag{2–5}$$

where ΔH_s is the *latent heat of sublimation.* The vapor pressure of a typical solid as a function of temperature is shown in Figure 2–7. In general, the vapor pressure of a solid is less than that of its liquid phase, and the pressure–temperature curve is steeper.

Phase Diagram. It is convenient to summarize the three types of phase transitions in a single graph, called a *phase diagram.* As a familiar example, the phase diagram for water is given in Figure 2–8. Curve A, separating the regions in which the solid and vapor are stable, gives the vapor pressure of the solid as a function of temperature. If the pressure above the solid is less than this, the solid will sublime. If the pressure is greater, the vapor will condense. Similarly curve B between the liquid and vapor regions, depicts the vapor pressure of the liquid as a

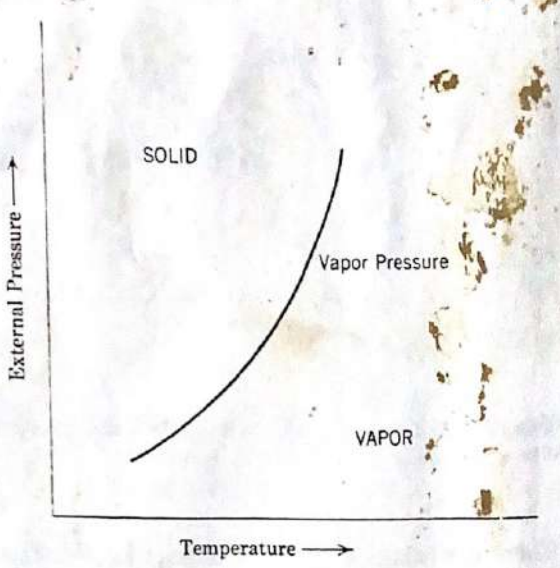


Figure 2-7 Vapor pressure curve for a typical pure solid substance.

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.

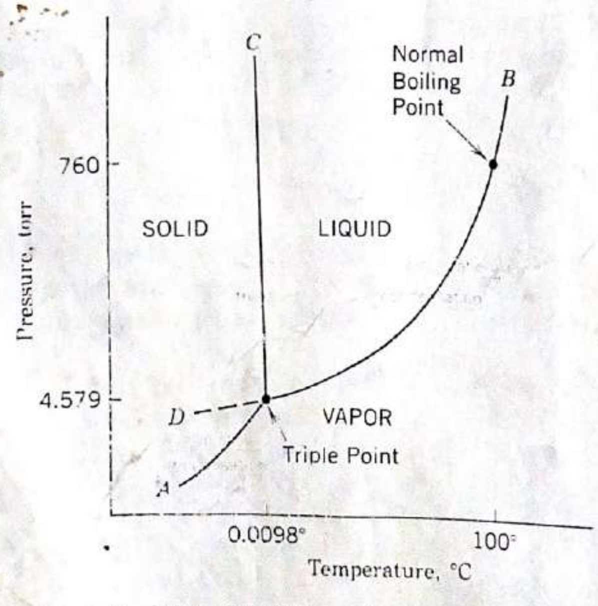


Figure 2-8 Phase diagram for water (not to scale).