

Topic 5A - Vapor Pressure

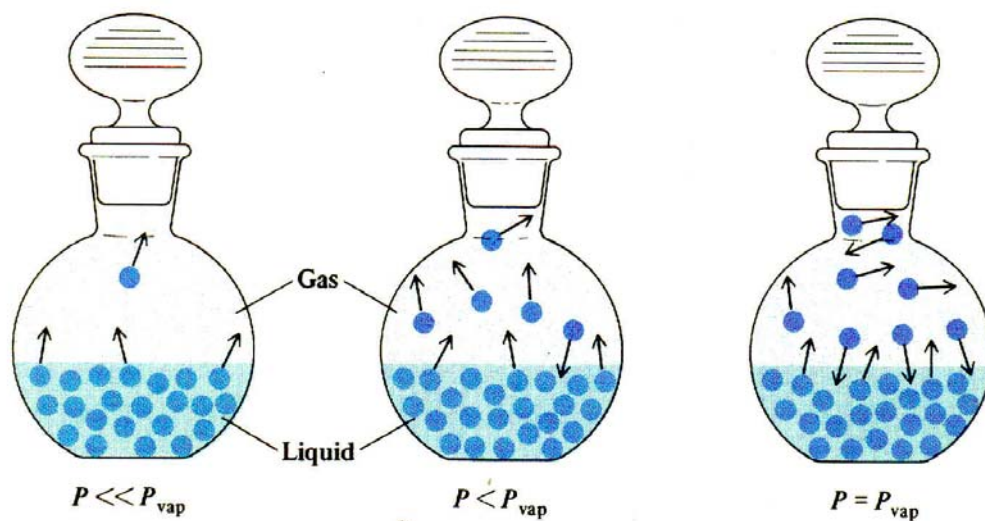
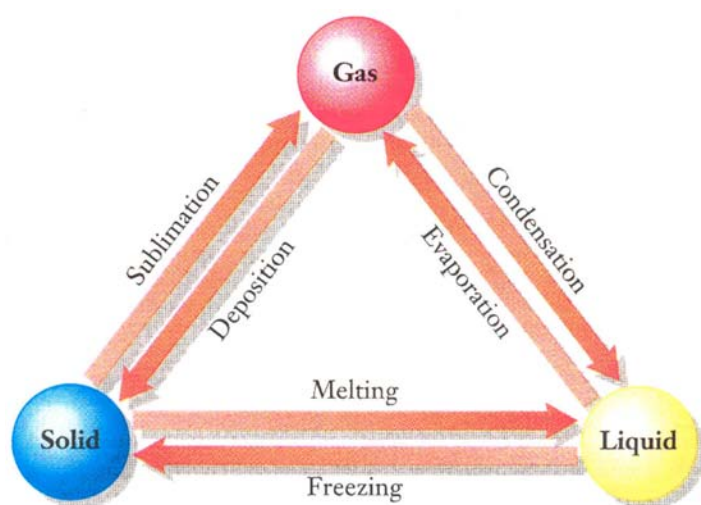
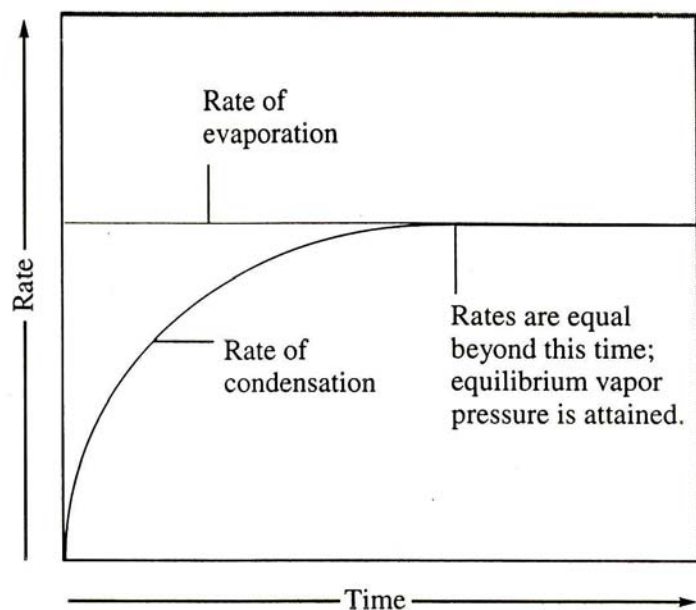


Figure 4-2

The approach to equilibrium in evaporation and condensation. Initially the pressure above the liquid is very low, and many more molecules leave the liquid surface than return to it. As time passes, more molecules fill the gas phase until the equilibrium vapor pressure P_{vap} is approached; the rates of evaporation and condensation then become equal.

**Figure 16.46**

The rates of condensation and evaporation over time for a liquid sealed in a closed container. The rate of evaporation remains constant, while the rate of condensation increases as the number of molecules in the vapor phase increases, until the two rates become equal. At this point the equilibrium vapor pressure is attained.

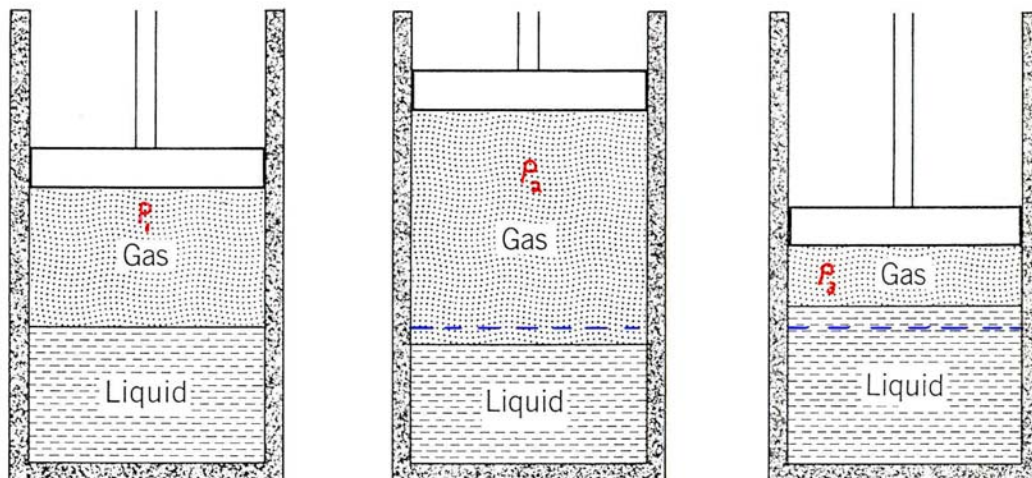


Fig. 5.18. The constancy of the vapor pressure of a liquid at constant temperature. (a) Original position of the piston, when the system is at equilibrium. (b) Equilibrium restored after piston is moved up. (c) Equilibrium restored after piston is moved down (see text).

$$\text{At Const. } T, P_1 = P_2 = P_3$$

Thermodynamics of Vaporization

Liquid-Vapor Equilibrium

When the liquid and vapor phases of a pure substance are in equilibrium with each other, $G_m(g) = G_m(l)$. Thus,

$$\Delta G_{\text{vap}} = G_m(g) - G_m(l) = 0$$

It can be shown on the basis of thermodynamic arguments that

$$G_m(g) = G_m^\circ(g) + RT \ln P$$

Since liquids are essentially unaffected by pressure, $G_m^\circ(l) = G_m(l)$. Thus,

$$\begin{aligned}\Delta G_{\text{vap}} &= [G_m^\circ(g) + RT \ln P] - G_m^\circ(l) \\ &= [G_m^\circ(g) - G_m^\circ(l)] + RT \ln P \\ &= \Delta G_{\text{vap}}^\circ + RT \ln P = 0\end{aligned}$$

Hence,

$$\ln P_{\text{v.p.}} = - \frac{\Delta G_{\text{vap}}^\circ}{RT}$$

$$G_m = G_m^\circ + RT \ln P$$

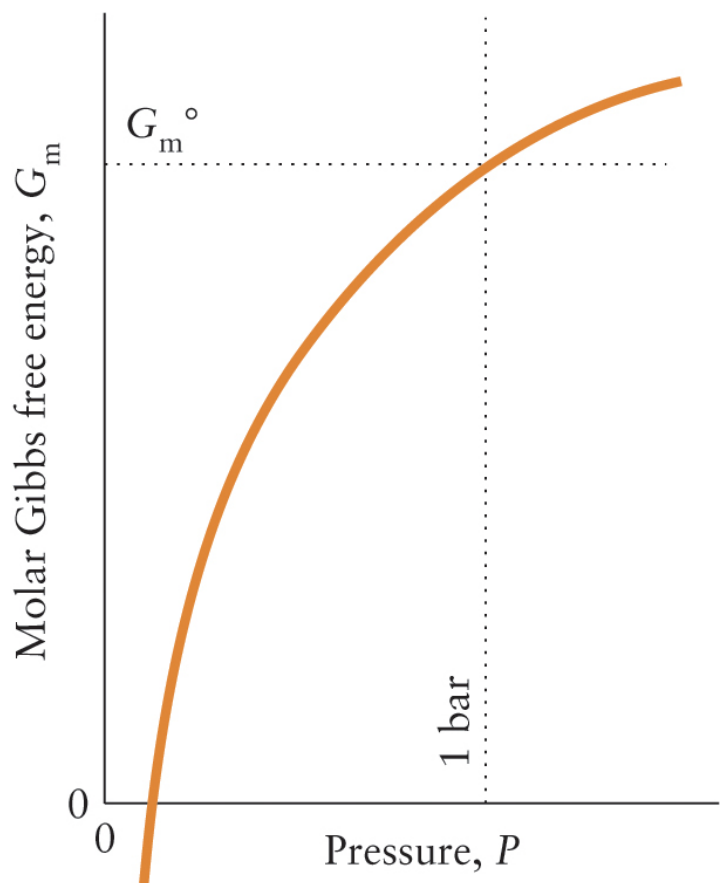


FIGURE 10.4 The variation of the molar Gibbs free energy of an ideal gas with pressure. The Gibbs free energy has its standard value when the pressure of the gas is 1 bar. The value of the Gibbs free energy approaches minus infinity as the pressure falls to zero.

Vapor Pressure

At equilibrium,

$$\text{Rate}_{\text{evap}} = \text{Rate}_{\text{cond}}$$

The equilibrium vapor pressure, $P_{\text{v.p.}}$, is inversely proportional to the strength of intermolecular forces in the liquid.

Vapor pressure is given by

$$\ln P_{\text{v.p.}} = -\frac{\Delta G^{\circ}_{\text{vap}}}{RT} = -\frac{\Delta H^{\circ}_{\text{vap}}}{RT} + \frac{\Delta S^{\circ}_{\text{vap}}}{R}$$

$$P_{\text{v.p.}} = A e^{-\Delta H^{\circ}_{\text{vap}}/RT}$$

where

$$A = e^{\Delta S^{\circ}_{\text{vap}}/R} \approx \text{constant} = 39,520$$

since, according to Trouton's Rule:

$$\Delta S^{\circ}_{\text{vap}} \approx 10.5R = 88 \pm 5 \text{ J/mol-K}$$

the entropy of vaporization is similar for most liquids.

Dependence of $P_{\text{v.p.}}$ on Temperature

$$\ln P_2 - \ln P_1 = \left(-\frac{\Delta H^\circ_{\text{vap}}}{RT_2} + \frac{\Delta S^\circ_{\text{vap}}}{R} \right) - \left(-\frac{\Delta H^\circ_{\text{vap}}}{RT_1} + \frac{\Delta S^\circ_{\text{vap}}}{R} \right)$$

$$= \frac{\Delta H^\circ_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H^\circ_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

This is the so-called **Clausius-Clapeyron equation**. It assumes that both $\Delta H^\circ_{\text{vap}}$ and $\Delta S^\circ_{\text{vap}}$ are independent of temperature.

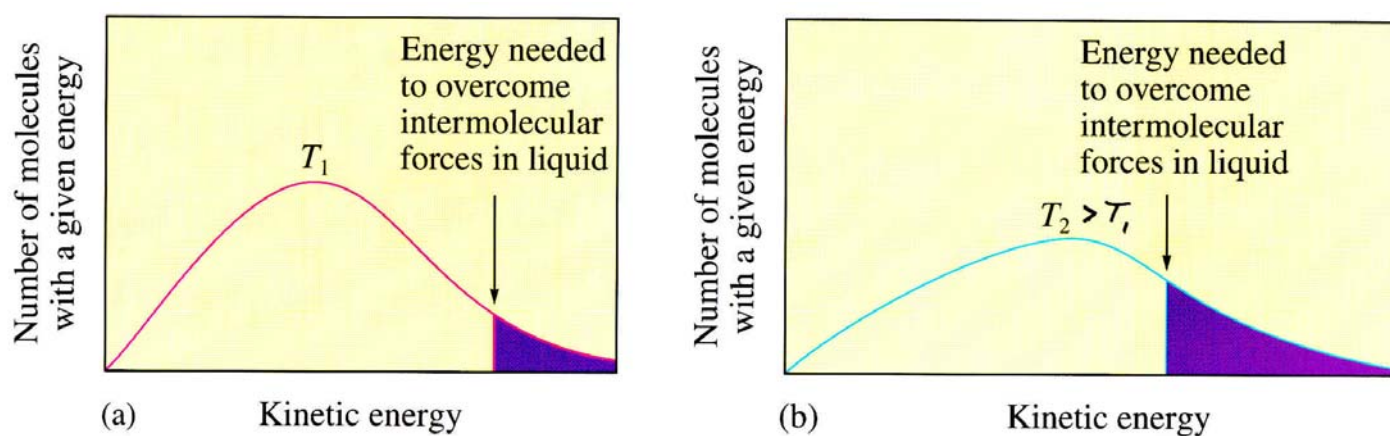


Figure 10.39

Diagrams showing the reason vapor pressure depends on temperature

FIGURE 10.3 The vapor pressures of liquids increase sharply with temperature, as shown here for diethyl ether (red), ethanol (blue), benzene (green), and water (orange). The normal boiling point is the temperature at which the vapor pressure is 1 atm (101.325 kPa). Notice that the curve for ethanol, which has a higher enthalpy of vaporization than benzene, rises more steeply than that of benzene, as predicted by the Clausius–Clapeyron equation; see below (Eq. 1). The diagram on the right shows the vapor pressure of water close to its normal boiling point in more detail.

