

# 6

## Phase Equilibrium

- 6.1 The boiling point of hexane at 1 atm is 68.7 °C. What is the boiling point at 1 bar?  
Given: The vapor pressure of hexane at 49.6 °C is 53.32 k Pa.

### SOLUTION

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}}H(T_2 - T_1)}{RT_1T_2}$$

$$\Delta_{\text{vap}}H = \frac{RT_1T_2}{(T_2 - T_1)} \ln \left( \frac{P_2}{P_1} \right)$$

$$= \frac{(8.3145)(322.8)(341.9)}{19.1} \ln \left( \frac{101.325 \text{ k Pa}}{53.32 \text{ k Pa}} \right) = 30,850 \text{ J mol}^{-1}$$

$$\ln \left( \frac{101.325}{100} \right) = \frac{30850}{8.3145} \left( \frac{1}{T_1} - \frac{1}{341.9} \right)$$

$$T_1 = \frac{1}{\frac{30850}{8.3145} \ln \left( \frac{101.325}{100} \right) + \frac{1}{341.9}} = 341.5 \text{ K}$$

Thus the boiling point is reduced 0.4 °C to 68.3 °C.

- 6.4 Liquid mercury has a density of 13.690 g cm<sup>-3</sup>, and solid mercury has a density of 14.193 g cm<sup>-3</sup>, both being measured at the melting point, -38.87 °C, at 1 bar pressure. The heat of fusion is 9.75 J g<sup>-1</sup>. Calculate the melting points of mercury under a pressure of (a) 10 bar and (b) 3540 bar. The observed melting point under 3540 bar is -19.9 °C.

### SOLUTION

$$\frac{\Delta T}{\Delta P} = \frac{T(V_1 - V_2)}{\Delta_{\text{fus}}H} = \left[ \frac{(234.3 \text{ K}) \left( \frac{1}{13.690} - \frac{1}{14.193} \right) \text{ cm}^3 \text{ g}^{-1}}{9.75 \text{ J g}^{-1}} \right] (10^{-2} \text{ m cm}^{-1})^3$$

$$= 6.22 \times 10^{-8} \text{ K Pa}^{-1}$$

(a)  $\Delta T = (6.22 \times 10^{-8} \text{ K Pa}^{-1})(9 \times 100,000 \text{ Pa}) = 0.056 \text{ K}$   
 $t = -38.87 + 0.06 = -38.81 \text{ °C}$

(b)  $\Delta T = (6.22 \times 10^{-8} \text{ K Pa}^{-1})(3539 \times 100,000 \text{ Pa}) = 22.0 \text{ K}$   
 $t = -38.87 + 22.0 = -16.9 \text{ °C}$

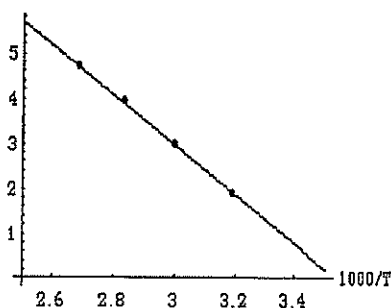
\*6.8 *n*-Propyl alcohol has the following vapor pressures:

$t/^{\circ}\text{C}$	40	60	80	100
$P/\text{kPa}$	6.69	19.6	50.1	112.3

Plot these data so as to obtain a nearly straight line, and calculate (a) the enthalpy of vaporization, (b) the boiling point at 1 bar, and (c) the boiling point at 1 atm.

SOLUTION:

$\ln(P/\text{kPa})$



$$(a) \quad \text{slope} = -2.34 \times 10^3 \text{ K} = \frac{\Delta_{\text{vap}}H}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}$$

$$\Delta_{\text{vap}}H = 44.8 \text{ kJ mol}^{-1}$$

$$(b) \quad \ln \frac{112.3}{100} = \frac{44800}{8.3145} \left( \frac{1}{T} - \frac{1}{373.15} \right)$$

$$T = \frac{1}{\frac{8.3145}{44800} \ln \frac{112.3}{100} + \frac{1}{373.15}} = 370.18 \text{ K} = 97.03^{\circ}\text{C}$$

$$(c) \quad T = \frac{1}{\frac{8.3145}{44800} \ln \frac{112.3}{101.325} + \frac{1}{373.15}} = 370.51 \text{ K} = 97.36^{\circ}\text{C}$$

6.10 The heats of vaporization and of fusion of water are  $2490 \text{ J g}^{-1}$  and  $33.5 \text{ J g}^{-1}$  at  $0^{\circ}\text{C}$ . The vapor pressure of water at  $0^{\circ}\text{C}$  is 611 Pa. Calculate the sublimation pressure of ice at  $-15^{\circ}\text{C}$ , assuming that the enthalpy changes are independent of temperature.

SOLUTION

$\Delta_{\text{fus}}H$

$$\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H$$

liquid  $\leftarrow$  solid

$$= 33.5 + 2490 = 2824 \text{ J g}^{-1}$$

$\downarrow \Delta_{\text{vap}}H$   
vapor

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{sub}}H (T_2 - T_1)}{RT_1 T_2}$$

$$P_2 = P_1 \exp \left[ \frac{\Delta_{\text{sub}}H (T_2 - T_1)}{RT_1 T_2} \right]$$

$$= (611 \text{ Pa}) \exp \left[ \frac{(2824 \times 18 \text{ J mol}^{-1})(-15 \text{ K})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})(258.15 \text{ K})} \right]$$

$$= 166 \text{ Pa}$$

- 6.12 The vapor pressure of solid benzene,  $C_6H_6$ , is 299 Pa at  $-30^\circ C$  and 3270 Pa at  $0^\circ C$ , and the vapor pressure of liquid  $C_6H_6$  is 6170 Pa at  $10^\circ C$  and 15,800 Pa at  $30^\circ C$ . From these data, calculate (a) the triple point of  $C_6H_6$ , and (b) the enthalpy of fusion of  $C_6H_6$ .

SOLUTION

Calculate the enthalpy of sublimation of  $C_6H_6$ .

$$\Delta_{\text{sub}}H = \frac{(8.314)(253.15)(223.15)}{30} \ln \frac{3270}{299}$$

$$= 44,030 \text{ J mol}^{-1}$$

Express sublimation pressures as a function of  $T$ .

$$\ln P_{\text{sub}} = -\frac{\Delta_{\text{sub}}H}{RT} + \frac{\Delta_{\text{sub}}S}{R}$$

$$\text{At } 273.15 \text{ K, } \ln 3270 = -\frac{44\,030}{RT} + \frac{\Delta_{\text{sub}}S}{R}$$

$$\ln P_{\text{sub}} = -\frac{44\,030}{RT} + 27.481$$

Calculate the enthalpy of vaporization of  $C_6H_6$

$$\Delta_{\text{vap}}H = \frac{(8.314)(283.15)(303.15)}{20} \ln \frac{15800}{6170}$$

$$= 33,550 \text{ J mol}^{-1}$$

Express vapor pressures as a function of  $T$ .

$$\ln P_{\text{vap}} = -\frac{\Delta_{\text{vap}}H}{RT} + \frac{\Delta_{\text{vap}}S}{R}$$

$$\text{At } 303.15 \text{ K, } \ln 15,800 = -\frac{33\,550}{8.314(303.15)} + \frac{\Delta_{\text{vap}}S}{R}$$

$$\ln P_{\text{vap}} = -\frac{33\,550}{8.314 T} + 22.979$$

(a) At the triple point,  $\ln P_{\text{sub}} = \ln P_{\text{vap}}$

$$-\frac{44\,030}{RT} + 27.481 = -\frac{33\,550}{RT} + 22.979$$

$$T = 279.99 \text{ K} = 6.85^\circ C$$

$$P = \exp\left(-\frac{44\,030}{8.314 \times 279.99} + 27.481\right) = 5249 \text{ Pa}$$

(b)  $\Delta_{\text{fus}}H = \Delta_{\text{sub}}H - \Delta_{\text{vap}}H = 44.03 - 33.55 = 10.48 \text{ kJ mol}^{-1}$

- 6.18 The vapor pressure of water at  $25^\circ C$  is 23.756 mm Hg. What is the vapor pressure of water when it is in a container with an air pressure of 100 bar, assuming the dissolved gases do not affect the vapor pressure. The density of water is  $0.99707 \text{ g/m}^3$ .

SOLUTION

$$RT \ln (P/P_0) = \bar{V}_L(P - P_0)$$

$$(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln (P/23.756)$$

$$= (18.015 \text{ g mol}^{-1}/0.99707 \text{ g m}^{-3})(10^{-2} \text{ m/cm})^3(99 \times 10^5 \text{ Pa})$$

$$P/23.756 = \exp 0.07289$$

$$P = 25.552 \text{ mm Hg} = 3406 \text{ Pa}$$

