

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 kPa.

SOLUTION

$$\begin{aligned}\ln \frac{P_2}{P_1} &= \frac{\Delta_{\text{vap}}H(T_2 - T_1)}{RT_1T_2} \\ \Delta_{\text{vap}}H &= \frac{RT_1T_2}{(T_2 - T_1)} \ln \left(\frac{P_2}{P_1} \right) \\ &= \frac{(8.3145)(322.8)(341.9)}{19.1} \ln \left(\frac{101.325 \text{ kPa}}{53.32 \text{ kPa}} \right) = 30,850 \text{ J mol}^{-1} \\ \ln \left(\frac{101.325}{100} \right) &= \frac{30850}{8.3145} \left(\frac{1}{T_1} - \frac{1}{341.9} \right) \\ T_1 &= \frac{1}{\frac{30850}{8.3145} \ln \left(\frac{101.325}{100} \right) + \frac{1}{341.9}} = 341.5 \text{ K}\end{aligned}$$

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⁻³, and solid mercury has a density of 14.193 g cm⁻³, both being measured at the melting point, -38.87 °C, at 1 bar pressure. The heat of fusion is 9.75 J g⁻¹. 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

$$\begin{aligned}\frac{\Delta T}{\Delta P} &= \frac{T(V_l - V_s)}{\Delta_{\text{fus}}H} = \left[\frac{(234.3 \text{ K}) \left(\frac{1}{13.690} - \frac{1}{14.193} \right) \text{ cm}^3 \text{ g}^{-1}}{9.75 \text{ J g}^{-1}} \right] (10^{-2} \text{ m cm}^{-1})^3 \\ &= 6.22 \times 10^{-8} \text{ K Pa}^{-1} \\ (\text{a}) \quad \Delta T &= (6.22 \times 10^{-8} \text{ K Pa}^{-1})(9 \times 100,000 \text{ Pa}) = 0.056 \text{ K} \\ t &= -38.87 + 0.06 = -38.81 \text{ }^\circ\text{C} \\ (\text{b}) \quad \Delta T &= (6.22 \times 10^{-8} \text{ K Pa}^{-1})(3539 \times 100,000 \text{ Pa}) = 22.0 \text{ K} \\ t &= -38.87 + 22.0 = -16.9 \text{ }^\circ\text{C}\end{aligned}$$

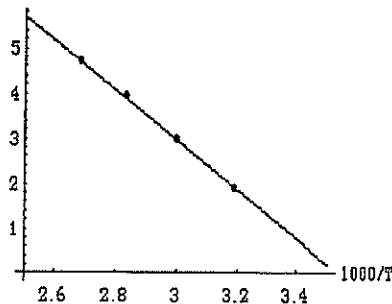
*6.8 *n*-Propyl alcohol has the following vapor pressures:

<i>t</i> /°C	40	60	80	100
<i>P</i> /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:

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



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

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

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

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

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

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

SOLUTION

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

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



$$\begin{aligned} \ln \frac{P_2}{P_1} &= \frac{\Delta_{\text{sub}}H(T_2 - T_1)}{RT_1T_2} \\ P_2 &= P_1 \exp \left[\frac{\Delta_{\text{sub}}H(T_2 - T_1)}{RT_1T_2} \right] \\ &= (611 \text{ Pa}) \exp \left[\frac{(2824 \times 18 \text{ J mol}^{-1})(-15 \text{ K})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})(258.15 \text{ K})} \right] \\ &= 166 \text{ Pa} \end{aligned}$$

- 6.12 The vapor pressure of solid benzene, C_6H_6 , is 299 Pa at -30 °C and 3270 Pa at 0 °C, and the vapor pressure of liquid C_6H_6 is 6170 Pa at 10 °C and 15,800 Pa at 30 °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, $\ln P_{\text{sub}} = \ln P_{\text{vap}}$

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

$$T = 279.99 \text{ K} = 6.85 \text{ °C}$$

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

(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 °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 g/m³.

SOLUTION

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

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

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

$$P/23.756 = \exp 0.07289$$

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

