

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

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

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

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

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

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

- 6.2 What is the boiling point of water 2 miles above sea level? Assume the atmosphere follows the barometric formula (equation 1.54) with $M = 0.0289 \text{ kg mol}^{-1}$ and $T = 300 \text{ K}$. Assume the enthalpy of vaporization of water is 44.0 kJ mol^{-1} independent of temperature.

SOLUTION

$$h = (2 \text{ miles})(5280 \text{ ft/mile})(12 \text{ in/ft})(2.54 \text{ cm/in})(0.01 \text{ m/cm}) = 3219 \text{ m}$$

$$\begin{aligned} P &= P_0 \exp(-gMh/RT) \\ &= (1.01325 \text{ bar}) \exp \left[- \frac{(9.8 \text{ m s}^{-2})(0.0289 \text{ kg mol}^{-1})(3219 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} \right] = 0.703 \text{ bar} \end{aligned}$$

$$\ln \left(\frac{P_2}{P_1} \right) = \Delta_{\text{vap}}H(T_2 - T_1)/RT_2T_1$$

$$\ln \left(\frac{1.01325}{0.703} \right) = \frac{(44\,000)(373 - T_1)}{(8.314)(373)T_1}$$

$$\frac{373 - T_1}{T_1} = 2.576 \times 10^{-2}$$

$$T_1 = 364 \text{ K} = 90.6 \text{ }^\circ\text{C}$$

- 6.3 The barometric equation 1.44 and the Clausius-Clapeyron equation 6.8 can be used to estimate the boiling point of a liquid at a higher altitude. Use these equations to derive a single equation to make this calculation. Use this equation to solve problem 6.2.

SOLUTION

The two equations are

$$\ln(P_0/P) = gMh/RT_{\text{atm}}$$

$$\ln(P_0/P) = \Delta_{\text{vap}}H(T_0 - T)/RTT_0$$

where P_0 is the atmospheric pressure at sea level and P is the atmospheric pressure at a higher altitude. T_0 is the boiling point at sea level, and T is the boiling point at the higher altitude. Setting the right-hand sides of these equations equal to each other yields

$$\frac{1}{T} = \frac{1}{T_0} + \frac{gMh}{T_{\text{atm}}\Delta_{\text{vap}}H}$$

Substituting the values from problem 6.2 yields

$$\frac{1}{T} = \frac{1}{373.15} + \frac{(9.8 \text{ m s}^{-2})(0.0289 \text{ kg mol}^{-1})(3.219 \times 10^3 \text{ m})}{(298.15 \text{ K})(44,000 \text{ J mol}^{-1})}$$

$$T = 363.58 \text{ K} = 90.43 \text{ }^\circ\text{C}$$

- 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, $-38.87 \text{ }^\circ\text{C}$, 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 $-19.9 \text{ }^\circ\text{C}$.

SOLUTION

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

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

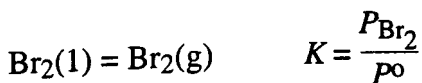
$$(a) \quad \Delta T = (6.22 \times 10^{-8} \text{ K Pa}^{-1})(9 \times 100,000 \text{ Pa}) = 0.056 \text{ K}$$

$$t = -38.87 + 0.06 = -38.81 \text{ }^\circ\text{C}$$

$$(b) \quad \Delta T = (6.22 \times 10^{-8} \text{ K Pa}^{-1})(3539 \times 100,000 \text{ Pa}) = 22.0 \text{ K}$$

$$t = -38.87 + 22.0 = -16.9 \text{ }^\circ\text{C}$$

- 6.5 From the $\Delta_f G^\circ$ of $\text{Br}_2(\text{g})$ at $25 \text{ }^\circ\text{C}$, calculate the vapor pressure of $\text{Br}_2(\text{l})$. The pure liquid at 1 bar and $25 \text{ }^\circ\text{C}$ is taken as the standard state.

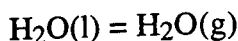
SOLUTION

$$\Delta G^\circ = -RT \ln \left(\frac{P_{\text{Br}_2}}{P^\circ} \right)$$

$$\frac{P_{\text{Br}_2}}{P^\circ} = \exp \left[- \frac{3110 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} \right]$$

$$P_{\text{Br}_2} = 0.285 \text{ bar}$$

- 6.6 Calculate ΔG° for the vaporization of water at 0°C using data in Appendix C.2 and assuming that ΔH° for the vaporization is independent of temperature. Use ΔG° to calculate the vapor pressure of water at 0°C .

SOLUTION

$$\Delta G^\circ(298.15 \text{ K}) = -228.572 + 237.129 = 8.577 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(298.15 \text{ K}) = -241.818 + 285.830 = 44.012 \text{ kJ mol}^{-1}$$

Using the equation in problem 4.10(a)

$$\Delta G_2 = \frac{\Delta G_1 T_2}{T_1} + \Delta H \left(1 - \frac{T_2}{T_1} \right)$$

$$\Delta G(0^\circ\text{C}) = 8.577 \left(\frac{273.15}{298.15} \right) + 44.012 \left(1 - \frac{273.15}{298.15} \right)$$

$$= 7.858 + 3.690 = 11.548 \text{ kJ mol}^{-1}$$

$$= -RT \ln \left(\frac{P}{P^\circ} \right)$$

$$P = P^\circ \exp \left(\frac{-11.548}{8.3145 \times 10^{-3} \times 273.15} \right)$$

$$= 6.190 \times 10^{-3} \text{ bar}$$

- 6.7 The change in Gibbs energy for the conversion of aragonite to calcite at 25°C is -1046 J mol^{-1} . The density of aragonite is 2.93 g cm^{-3} at 15°C and the density of calcite is 2.71 g cm^{-3} . At what pressure at 25°C would these two forms of CaCO_3 be in equilibrium?

SOLUTION

$$\Delta \bar{V} = \frac{100.09 \text{ g mol}^{-1}}{2.71 \text{ g cm}^{-3}} - \frac{100.09 \text{ g mol}^{-1}}{2.93 \text{ g cm}^{-3}}$$

$$= 2.77 \text{ cm}^3 \text{ mol}^{-1} = 2.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$\left(\frac{\partial \Delta G}{\partial P} \right)_T = \Delta \bar{V} \int_1^2 \quad ; \quad d\Delta G = \int_1^P \Delta \bar{V} dP$$

$$\Delta G_2 - \Delta G_1 = \Delta \bar{V}(P - 1)$$

$$0 + 1046 \text{ J mol}^{-1} = (2.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})(P - 1)$$

$$P = 3780 \text{ bar}$$

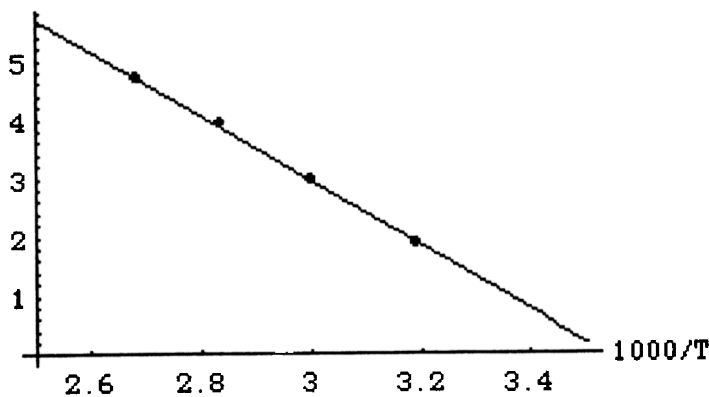
*6.8 *n*-Propyl alcohol has the following vapor pressures:

$t/^\circ\text{C}$	40	60	80	100
P/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:

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



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

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

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

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

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

6.9 For uranium hexafluoride the vapor pressures (in Pa) for the solid and liquid are given by

$$\ln P_s = 29.411 - 5893.5/T$$

$$\ln P_l = 22.254 - 3479.9/T$$

Calculate the temperature and pressure of the triple point.

SOLUTION

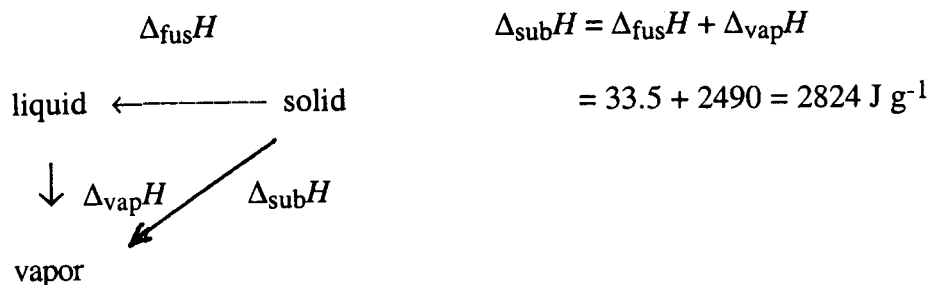
$$29.411 - \frac{5893.5}{T} = 22.254 - \frac{3479.9}{T}$$

$$T = 337.2 \text{ K} = 64.0 \text{ }^\circ\text{C}$$

$$P = e^{29.411 - 5893.5/337.2} = 152.2 \text{ kPa}$$

6.10

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

SOLUTION

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

$$P_2 = P_1 \exp \left[\frac{\Delta_{\text{sub}}H (T_2 - T_1)}{RT_1T_2} \right]$$

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

$$= 166 \text{ Pa}$$

- 6.11 The sublimation pressures of solid Cl_2 are 352 Pa at $-112 \text{ }^\circ\text{C}$ and 35 Pa at $-126.5 \text{ }^\circ\text{C}$. The vapor pressures of liquid Cl_2 are 1590 Pa at $-100 \text{ }^\circ\text{C}$ and 7830 Pa at $-80 \text{ }^\circ\text{C}$. Calculate (a) $\Delta_{\text{sub}}H$, (b) $\Delta_{\text{vap}}H$, (c) $\Delta_{\text{fus}}H$, and (d) the triple point.

SOLUTION

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

$$= \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(161.15 \text{ K})(146.65 \text{ K})}{14.5 \text{ K}} \ln \frac{352}{35}$$

$$= 31.4 \text{ kJ mol}^{-1}$$

$$(b) \quad \Delta_{\text{vap}}H = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(173.15 \text{ K})(193.15 \text{ K})}{20 \text{ K}} \ln \frac{7830}{1590}$$

$$= 22.2 \text{ kJ mol}^{-1}$$

$$(c) \quad \Delta_{\text{fus}}H = \Delta_{\text{sub}}H - \Delta_{\text{vap}}H = 31.4 - 22.2 = 9.2 \text{ kJ mol}^{-1}$$

(d) For the solid

$$\frac{3777}{T}$$

For the liquid

$$\ln P = \ln 1590 + \frac{9200}{8.314} \left(\frac{1}{173.15} - \frac{1}{T} \right) = 13.762 - \frac{1107}{T}$$

At the triple point

$$29.300 - \frac{3777}{T} = 13.762 - \frac{1107}{T} \quad T = \frac{2670}{15.538} = 172 \text{ K}$$

$$T = 172 \text{ K} - 273.15 \text{ K} = -101.2 \text{ }^\circ\text{C}$$

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

SOLUTIONCalculate 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 .

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

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

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

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

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

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

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

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

- 6.13 The surface tension of toluene at $20 \text{ }^\circ\text{C}$ is 0.0284 N m^{-1} , and its density at this temperature is 0.866 g cm^{-3} . What is the radius of the largest capillary that will permit the liquid to rise 2 cm ?

SOLUTION

$$\begin{aligned} \gamma &= \frac{1}{2}h\rho gr \\ r &= \frac{2\gamma}{\rho gh} = \frac{2(0.0284 \text{ N m}^{-1})}{(0.866 \times 10^3 \text{ kg m}^{-3})(9.80 \text{ m s}^{-2})(0.02 \text{ m})} \\ &= 3.35 \times 10^{-2} \text{ cm} \end{aligned}$$

- 6.14 Mercury does not wet a glass surface. Calculate the capillary depression if the diameter of the capillary is (a) 0.1 mm , and (b) 2 mm . The density of mercury is 13.5 g cm^{-3} . The surface tension of mercury at $25 \text{ }^\circ\text{C}$ is 0.520 N m^{-1} .

SOLUTION

$$\begin{aligned} \text{(a)} \quad h &= \frac{2\gamma}{\rho r} \\ &= \frac{(2)(0.520 \text{ N m}^{-1})}{(9.8 \text{ m s}^{-2})(13.5 \times 10^3 \text{ kg m}^{-3})(0.05 \times 10^{-3} \text{ m})} = 15.7 \text{ cm} \\ \text{(b)} \quad h &= (15.7 \text{ cm})(0.05 \text{ mm})/(1 \text{ mm}) = 7.86 \text{ mm} \end{aligned}$$

- 6.15 If the surface tension of a soap solution is 0.05 N m^{-1} , what is the difference in pressure across the film for (a) a soap bubble of 2 mm in diameter and (b) a bubble 2 cm in diameter.

SOLUTION

$$\begin{aligned} \text{(a)} \quad \Delta P &= \frac{2\gamma}{R} = \frac{4(0.05 \text{ N m}^{-1})}{0.001 \text{ m}} = 200 \text{ Pa} \\ \text{(b)} \quad \Delta P &= \frac{4(0.050 \text{ N m}^{-1})}{0.01 \text{ m}} = 20 \text{ Pa} \end{aligned}$$

- *6.16 From tables giving $\Delta_f G^\circ$, $\Delta_f H^\circ$, and \bar{C}_P° for $\text{H}_2\text{O}(1)$ and $\text{H}_2\text{O}(g)$ at 298 K , calculate (a) the vapor pressure of $\text{H}_2\text{O}(1)$ at $25 \text{ }^\circ\text{C}$ and (b) the boiling point at 1 atm .

SOLUTION

$$\begin{aligned} \text{(a)} \quad \text{H}_2\text{O}(1) &= \text{H}_2\text{O}(g) \\ \Delta G^\circ &= -228.572 - (-237.129) = 8.557 \text{ kJ mol}^{-1} \\ \Delta G^\circ &= -RT \ln\left(\frac{P}{p^\circ}\right) \end{aligned}$$

$$\frac{P}{P^0} = \exp \left[\frac{8557 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} \right] = 3.168 \times 10^{-2}$$

$$P = (3.168 \times 10^{-2})(10^5 \text{ Pa}) = 3.17 \times 10^3 \text{ Pa}$$

(b) $\Delta H^0(298.15 \text{ K}) = -214.818 - (-285.830) = 44.012 \text{ kJ mol}^{-1}$

In the absence of data on the dependence of \bar{C}_P on T we will calculate $\Delta H^0(T)$ from

$$\begin{aligned} \Delta H^0(T) &= 44\,012 + \int_{298.15}^T (33.577 - 75.291) dT \\ &= 44\,012 - 41.714(T - 298.15) \end{aligned}$$

$$\left[\frac{\partial \left(\frac{\Delta G^0}{T} \right)}{\partial T} \right]_P = - \frac{\Delta H^0(T)}{T^2}$$

$$\begin{aligned} \frac{\Delta G^0}{T} &= - \int \left[\frac{-44\,012}{T^2} - \frac{41.714}{T} + \frac{(41.714)(298.15)}{T^2} \right] dT \\ &= \frac{44\,012}{T} + 41.714 \ln T + \frac{(41.714)(298.15)}{T} + I \end{aligned}$$

where I is an integration constant to be evaluated from $\Delta G^0(298.15 \text{ K})$.

$$\frac{8590}{298.15} = \frac{44.012}{298.15} + 41.714 \ln 298.15 + \frac{(41.714)(298.15)}{(298.15)} + I$$

$$I = -398.191$$

At the boiling point $\Delta G^0 = 0$ and so we need to solve the following equation

by successive approximations.

$$0 = \frac{44012}{T} + 41.714 \ln T + \frac{(41.714)(298.15)}{T} - 398.191$$

$$\text{Trying } T = 373 \text{ K} \quad \text{RHS} = 0.163$$

$$\text{Trying } T = 374 \text{ K} \quad \text{RHS} = -0.130$$

Thus, the standard boiling point calculated in this way is close to 373.5 K.

- 6.17 What is the maximum number of phases that can be in equilibrium in one-, two-, and three-component systems?

SOLUTION

$$F = C - p + 2$$

$$0 = 1 - p + 2, p = 3$$

$$0 = 2 - p + 2, p = 4$$

$$0 = 3 - p + 2, p = 5$$

- 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/m^3 .

SOLUTION

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

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

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

$$P/23.756 = \exp 0.07289$$

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

- 6.19 A binary liquid mixture of A and B is in equilibrium with its vapor at constant temperature and pressure. Prove that $\mu_A(g) = \mu_A(l)$ and $\mu_B(g) = \mu_B(l)$ by starting with

$$G = G(g) + G(l)$$

and the fact that $dG = 0$ when infinitesimal amounts of A and B are simultaneously transferred from the liquid to the vapor.

SOLUTION

$$dG = dG(l) + dG(g) = 0 \quad (1)$$

since the transfer is made at equilibrium.

$$dG(l) = \mu_A(l) dn_A(l) + \mu_B(l) dn_B(l) \quad (2)$$

$$dG(g) = \mu_A(g) dn_A(g) + \mu_B(g) dn_B(g) \quad (3)$$

since $dn_A(l) = -dn_A(g)$ and $dn_B(l) = -dn_B(g)$, substituting equation 2 and 3 into equation 1 yields

$$dG = [\mu_A(g) - \mu_A(l)] dn_A(g) + [\mu_B(g) - \mu_B(l)] dn_B(g) = 0 \quad (4)$$

Since $dn_A(g)$ and $dn_B(g)$ are independently variable, both terms in equation 4 have to be zero for dG to be zero. This yields the desired expression for components A and B.

- 6.20 Ethanol and methanol form very nearly ideal solutions. At 20°C , the vapor pressure of ethanol is 5.93 kPa , and that of methanol is 11.83 kPa . (a) Calculate the mole fractions of methanol and ethanol in a solution obtained by mixing 100 g of each. (b) Calculate the partial pressures and the total vapor pressure of the solution. (c) Calculate the mole fraction of methanol in the vapor.

SOLUTION

$$(a) \quad x_{\text{CH}_3\text{OH}} = \frac{100/32}{100/46 + 100/32} = 0.590$$

$$x_{\text{C}_2\text{H}_5\text{OH}} = \frac{100/46}{100/46 + 100/32} = 0.410$$

$$\begin{aligned}
 (b) \quad P_{\text{CH}_3\text{OH}} &= x_{\text{CH}_3\text{OH}} P^*_{\text{CH}_3\text{OH}} \\
 &= (0.590)(11,830 \text{ Pa}) = 6980 \text{ Pa} \\
 P_{\text{C}_2\text{H}_5\text{OH}} &= x_{\text{C}_2\text{H}_5\text{OH}} P^*_{\text{C}_2\text{H}_5\text{OH}} \\
 &= (0.410)(5930 \text{ Pa}) = 2430 \text{ Pa} \\
 P_{\text{total}} &= 2430 \text{ Pa} + 6980 \text{ Pa} = 9410 \text{ Pa}
 \end{aligned}$$

$$(c) \quad y_{\text{CH}_3\text{OH, vapor}} = \frac{6980 \text{ Pa}}{9410 \text{ Pa}} = 0.742$$

- 6.21 One mole of benzene (component 1) is mixed with two moles of toluene (component 2). At 60 °C the vapor pressures of benzene and toluene are 51.3 and 18.5 kPa, respectively. (a) As the pressure is reduced, at what pressure will boiling begin? (b) What will be the composition of the first bubble of vapor?

SOLUTION

$$\begin{aligned}
 (a) \quad P &= P_2^* + (P_1^* - P_2^*)x_1 \\
 &= 18.5 \text{ kPa} + (51.3 \text{ kPa} - 18.5 \text{ kPa})(0.333) \\
 &= 29.4 \text{ kPa}
 \end{aligned}$$

$$\begin{aligned}
 (b) \quad y_1 &= \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*)x_1} \\
 &= \frac{(0.333)(51.3 \text{ kPa})}{18.5 \text{ kPa} + 32.8 \text{ kPa} (0.333)} \\
 &= 0.581
 \end{aligned}$$

- 6.22 The vapor pressures of benzene and toluene have the following values in the temperature range between their boiling points at 1 bar:

$t / ^\circ\text{C}$	79.4	88	94	100	110.0
$P_{\text{C}_6\text{H}_6}^* / \text{bar}$	1.000	1.285	1.526	1.801	
$P_{\text{C}_7\text{H}_8}^* / \text{bar}$		0.508	0.616	0.742	1.000

- (a) Calculate the compositions of the vapor and liquid phases at each temperature and plot the boiling point diagram. (b) If a solution containing 0.5 mole fraction benzene and 0.5 mole fraction toluene is heated, at what temperature will the first bubble of vapor appear and what will be its composition?

SOLUTION

(a) At 88 °C $x_B(1.285) + (1 - x_B) 0.508 = 1$
 $x_B = 0.633$

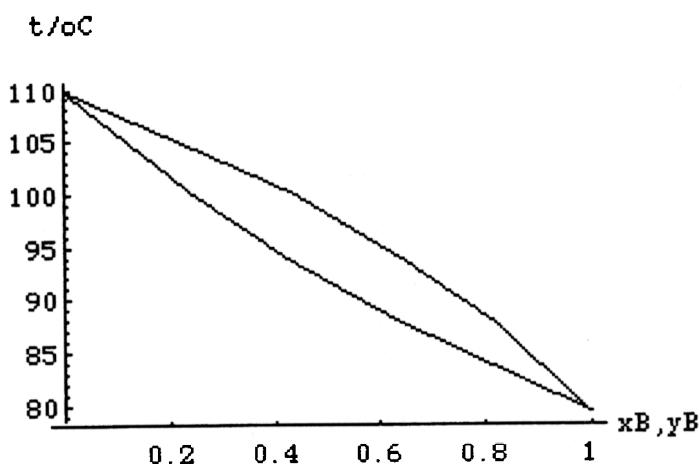
$$y_B = (0.633)(1.285)/1 = 0.814$$

At 94 °C $x_B(1.526) + (1 - x_B) 0.616 = 1$
 $x_B = 0.422$

$$y_B = (0.4222)(1.526)/1 = 0.644$$

At 100 °C $x_B(1.801) + (1 - x_B) 0.742 = 1$
 $x_B = 0.244$

$$y_B = (0.244)(1.801)/1 = 0.439$$



The liquid curve is below the vapor curve. These curves were plotted by using *Mathematica*™ to fit them with quadratic equations.

- (b) The fit of the liquid data with $t = a + bx_B + cx_B^2$ yields $t = 109.9 - 42.72x_B + 12.29x_B^2$. At $x_B = 0.5$, $t = 91.6$ °C. Fit of the vapor data yields $t = 109.9 - 15.13y_B - 15.13y_B^2$. Setting the temperature in this equation equal to the bubble point temperature 91.6 °C yields $y_B = 0.72$, by use of the quadratic formula. This is the composition at which the first bubble of vapor will appear.

6.23 At 1.013 bar pressure propane boils at -42.1 °C and *n*-butane boils at -0.5 °C; the following vapor-pressure data are available.

$t/^\circ\text{C}$	-31.2	-16.3
$P/\text{kPa}(\text{propane})$	160.0	298.6
$P/\text{kPa}(n\text{-butane})$	26.7	53.3

Assuming that these substances form ideal binary solutions with each other, (a) calculate the mole fractions of propane at which the solution will boil at 1.013 bar pressure at -31.2 and -16.3 °C. (b) Calculate the mole fractions of propane in the equilibrium vapor at these temperatures. (c) Plot the temperature-mole fraction diagram at 1.013 bar, using these data, and label the regions.

SOLUTION

(a) At -31.2 °C, $P_P = x_P/60.0$ kPa, $P_B = (1 - x_P) 26.7$ kPa

$$P = 101.3 \text{ kPa} = x_P 160.0 + (1 - x_P) 26.7$$

$$= 26.7 + 133.3 x_P$$

$$x_P = 0.560$$

At -16.3 °C, $P_P = x_P 298.6$ kPa, $P_B = (1 - x_P) 53.3$ kPa

$$P = 101.3 \text{ kPa} = x_P 298.6 + (1 - x_P) 53.3$$

$$= 53.3 + 245.3 x_P$$

$$x_P = 0.196$$

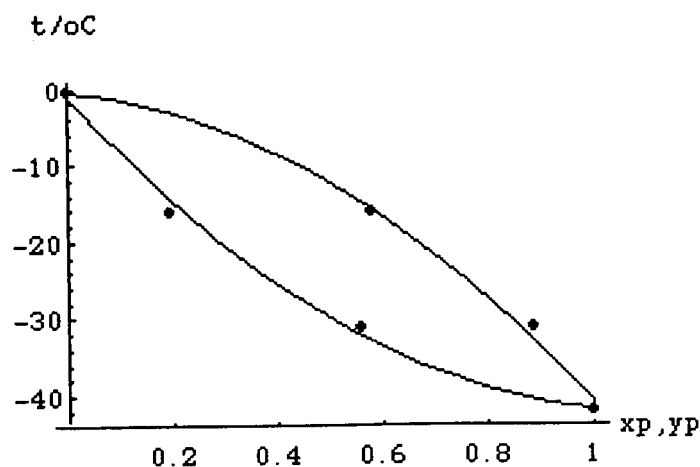
(b) At -31.2 °C,

$$y_P = \frac{(0.560)(160.0)}{(0.560)(160.0) + (0.440)(26.7)} = 0.884$$

At -16.3 °C

$$y_P = \frac{(0.196)(298.6)}{(0.196)(298.6) + (0.804)(53.3)} = 0.577$$

(c)



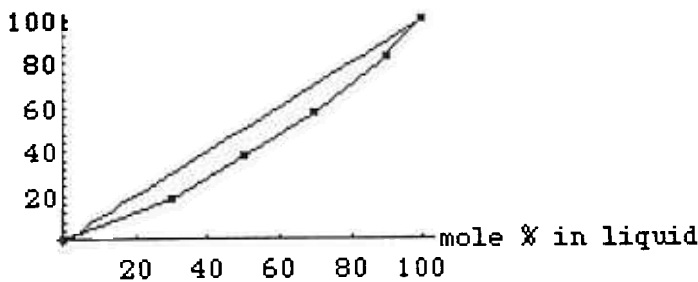
- 6.24 The following table gives mole % acetic acid in aqueous solutions and in the equilibrium vapor at the boiling point of the solution at 1.013 bar.

B.P., °C	118.1	113.8	107.5	104.4	102.1	100.0
Mole % of acetic acid						
In liquid	100	90.0	70.0	50.0	30.0	0
In vapor	100	83.3	57.5	37.4	18.5	0

Calculate the minimum number of theoretical plates for the column required to produce an initial distillate of 28 mole % acetic acid from a solution of 80 mole % acetic acid.

SOLUTION

mole % in vapor



Since there are four steps, three theoretical plates are required in the column. The distilling pot counts as one plate.

- 6.25 If two liquids (1 and 2) are completely immiscible, the mixture will boil when the sum of the two partial pressures exceeds the applied pressure: $P = P_1^* + P_2^*$. In the vapor phase the ratio of the mole fractions of the two components is equal to the ratio of their vapor pressures.

$$\frac{P_1^*}{P_2^*} = \frac{x_1}{x_2} = \frac{m_1 M_2}{m_2 M_1}$$

where m_1 and m_2 are the masses of components 1 and 2 in the vapor phase, and M_1 and M_2 are their molar masses. The boiling point of the immiscible liquid system naphthalene-water is 98 °C under a pressure of 97.7 kPa. The vapor pressure of

water at 98 °C is 94.3 kPa. Calculate the weight percent of naphthalene in the distillate.

SOLUTION

$$\frac{m_1}{m_2} = \frac{P_1^* M_1}{P_2^* M_2} = \frac{(97.7 - 94.3)(128)}{(94.3)(18)} = 0.256$$

$$\text{Weight percent naphthalene} = \frac{0.256}{1.256} = 0.204 \text{ or } 20.4\%$$

6.26 A regular binary solution is defined as one for which

$$\mu_1 = \mu_1^0 + RT \ln x_1 + wx_2^2$$

$$\mu_2 = \mu_2^0 + RT \ln x_2 + wx_1^2$$

Derive $\Delta_{\text{mix}}G$, $\Delta_{\text{mix}}S$, $\Delta_{\text{mix}}H$, and $\Delta_{\text{mix}}V$ for the mixing of x_1 moles of component 1 with x_2 moles of component 2. Assume that the coefficient w is independent of temperature.

SOLUTION

$$G = \sum_i n_i \mu_i = x_1 \mu_1^0 + x_1 RT \ln x_1 + wx_1 x_2^2 + x_2 \mu_2^0 + x_2 RT \ln x_2 + wx_2 x_1^2$$

$$G^0 = \sum_i n_i \mu_i^0 = x_1 \mu_1^0 + x_2 \mu_2^0$$

$$\Delta_{\text{mix}}G = RT(x_1 \ln x_1 + x_2 \ln x_2) + wx_1 x_2$$

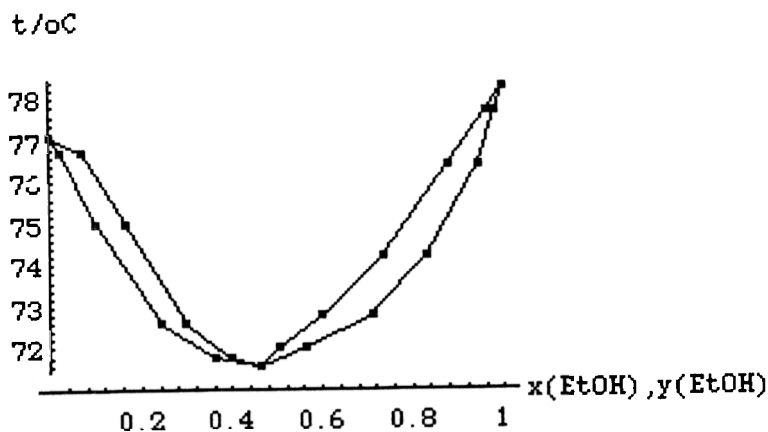
$$\Delta_{\text{mix}}S = -(\partial \Delta_{\text{mix}}G / \partial T)_P = -R(x_1 \ln x_1 + x_2 \ln x_2)$$

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T \Delta_{\text{mix}}S = wx_1 x_2$$

$$\Delta_{\text{mix}}V = (\partial \Delta_{\text{mix}}G / \partial P)_T = 0$$

6.27 From the data given in the following table construct a complete temperature-composition diagram for the system ethanol-ethyl acetate for 1.013 bar. A solution containing 0.8 mole fraction of ethanol, EtOH, is distilled completely at 1.013 bar. (a) What is the composition of the first vapor to come off? (b) That of the last drop of liquid to evaporate? (c) What would be the values of these quantities if the distillation were carried out in a cylinder provided with a piston so that none of the vapor escapes?

x_{EtOH}	y_{EtOH}	B.P., °C	x_{EtOH}	y_{EtOH}	B.P., °C
0	0	77.15	0.563	0.507	72.0
0.025	0.070	76.7	0.710	0.600	72.8
0.100	0.164	75.0	0.833	0.735	74.2
0.240	0.295	72.6	0.942	0.880	76.4
0.360	0.398	71.8	0.982	0.965	77.7
0.462	0.462	71.6	1.000	1.000	78.3

SOLUTION

The composition of the liquid is given by the lower curve, and the composition of the vapor is given by the upper curve.

- The liquid with 0.8 mole fraction ethanol will start to boil at 73.7 °C. The vapor in equilibrium with it is 0.69 mole fraction in ethanol.
- As the boiling continues, more and more of the EtAc will be removed. As the mole fraction of EtOH increases, the boiling point will also increase. Finally, the very last vapors will be pure EtOH.
- The first vapor to come off will be the same as in part (a). However, when all of the mixture is in the vapor state, the mole fraction of the vapor state will be 0.800, simply because that is the total mole fraction of EtOH in the entire mixture. Thus, to find the composition of the last drop to evaporate into the cylinder, simply note that liquid ($y_{\text{EtOH}} = 0.9$) is in equilibrium with vapor which has 0.800 EtOH in it.

6.28 The Henry law constants for oxygen and nitrogen in water at 0 °C are 2.54×10^4 bar and 5.45×10^4 bar, respectively. Calculate the lowering of the freezing point of water by dissolved air with 80% N_2 and 20% O_2 by volume at 1 bar pressure.

SOLUTION

$$x_{N_2} = \frac{P_{N_2}}{K_{N_2}} = \frac{0.8 \text{ bar}}{5.45 \times 10^4 \text{ bar}} = 1.47 \times 10^{-5}$$

$$x_{O_2} = \frac{P_{O_2}}{K_{O_2}} = \frac{0.2 \text{ bar}}{2.54 \times 10^4 \text{ bar}} = 7.87 \times 10^{-6}$$

The mole fraction of dissolved air is $2.26 \times 10^{-5} = \frac{m}{m + \frac{1000}{18.02}}$

$$m_{\text{air}} = 1.25 \times 10^{-3} \text{ mol/1000 g solvent}$$

$$\Delta T_{\text{fp}} = K_{\text{fp}} m = -(1.86)(1.25 \times 10^{-3}) = -0.00233 \text{ K}$$

6.29

Use the Gibbs-Duhem equation to show that if one component of a binary liquid solution follows Raoult's law, the other component will too.

SOLUTION

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

$$\text{If } \mu_1 = \mu_1^{\circ} + RT \ln x_1$$

$$d\mu_1 = \frac{RT}{x_1} dx_1$$

Using the first equation

$$d\mu_2 = -\frac{x_1}{x_2} d\mu_1 = -\frac{RT}{x_2} dx_1$$

$$\text{Since } x_1 + x_2 = 1, \quad dx_2 = -dx_1$$

$$d\mu_2 = \frac{RT}{x_2} dx_2 = RT d \ln x_2$$

$$\mu_2 = \text{const} + RT \ln x_2$$

$$\text{If } x_2 = 1, \quad \text{const} = \mu_2^{\circ}$$

$$\mu_2 = \mu_2^{\circ} + RT \ln x_2$$

6.30 The following data on ethanol-chloroform solutions at 35 °C were obtained by G. Scatchard and C. L. Raymond [*J. Am. Chem. Soc.* **60**, 1278 (1938)]:

$x_{\text{EtOH,liq}}$	0	0.2	0.4	0.6	0.8	1.0
$y_{\text{EtOH,vap}}$	0.0000	0.1382	0.1864	0.2554	0.4246	1.0000
Total P/kPa	39.345	40.559	38.690	34.387	25.357	13.703

Calculate the activity coefficients of ethanol and chloroform based on the deviations from Raoult's law.

SOLUTION

$$x_{\text{EtOH}} = 0.2 \quad \gamma_{\text{EtOH}} = \frac{y_{\text{EtOH}} P}{x_{\text{EtOH}} P_{\text{EtOH}}^*} = \frac{(0.1382)(40.559)}{(0.2)(13.703)} = 2.04$$

$$x_{\text{EtOH}} = 0.4 \quad = \frac{(0.1864)(38.690)}{(0.4)(13.703)} = 1.316$$

$$x_{\text{EtOH}} = 0.6 \quad = \frac{(0.2554)(34.387)}{(0.6)(13.703)} = 1.065$$

$$x_{\text{EtOH}} = 0.8 \quad = \frac{(0.4246)(25.357)}{(0.8)(13.703)} = 0.982$$

$$x_{\text{EtOH}} = 1.0 \quad = \frac{(1.000)(13.703)}{(1.000)(13.703)} = 1.000$$

$$x_{\text{CHCl}_3} = 1 \quad \gamma_{\text{CHCl}_3} = \frac{y_{\text{CHCl}_3} P}{x_{\text{CHCl}_3} P_{\text{CHCl}_3}^*} = \frac{(1)(39.345)}{(1)(39.345)} = 1$$

$$x_{\text{CHCl}_3} = 0.8 \quad = \frac{(0.8618)(40.559)}{(0.8)(39.345)} = 1.111$$

$$x_{\text{CHCl}_3} = 0.6 \quad = \frac{(0.8136)(38.690)}{(0.6)(39.345)} = 1.333$$

$$x_{\text{CHCl}_3} = 0.4 \quad = \frac{(0.7446)(34.387)}{(0.4)(39.345)} = 1.627$$

$$x_{\text{CHCl}_3} = 0.2 \quad = \frac{(0.5754)(25.357)}{(0.2)(39.345)} = 1.854$$

- 6.31 Show that the equations for the bubble-point line and dew-point line for nonideal solutions are given by

$$x_1 = \frac{P - \gamma_2 P_2^*}{\gamma_1 P_1^* - \gamma_2 P_2^*}$$

$$y_1 = \frac{P \gamma_1 P_1^* - \gamma_1 \gamma_2 P_1^* P_2^*}{P \gamma_1 P_1^* - P \gamma_2 P_2^*}$$

SOLUTION

$$P = P_1 + P_2 = x_1 \gamma_1 P_1^* + (1 - x_1) \gamma_2 P_2^*$$

$$= \gamma_2 P_2^* + x_1 (\gamma_1 P_1^* - \gamma_2 P_2^*)$$

$$x_1 = \frac{P - \gamma_2 P_2^*}{\gamma_1 P_1^* - \gamma_2 P_2^*}$$

$$y_1 = \frac{P_1}{P_1 + P_2} = \frac{x_1 \gamma_1 P_1^*}{\gamma_2 P_2^* + x_1 (\gamma_1 P_1^* - \gamma_2 P_2^*)}$$

Substituting the expression for x_1 yields the desired expression for y_1 .

6.32 A regular binary solution is defined as one for which

$$\mu_1 = \mu_1^{\circ} + RT \ln x_1 + wx_2^2$$

$$\mu_2 = \mu_2^{\circ} + RT \ln x_2 + wx_1^2$$

Derive the expressions for the activity coefficients of γ_1 and γ_2 in terms of w .

SOLUTION

$$\mu_1 = \mu_1^{\circ} + RT \ln \gamma_1 x_1$$

$$\mu_1 = \mu_1^{\circ} + RT \ln x_1 + wx_2^2$$

$$= \mu_1^{\circ} + RT \ln x_1 + RT \ln e^{wx_2^2/RT}$$

$$= \mu_1^{\circ} + RT \ln (e^{wx_2^2/RT}) x_1$$

Therefore,

$$\gamma_1 = e^{wx_2^2/RT}$$

$$\gamma_2 = e^{wx_1^2/RT}$$

6.33 The expressions for the activity coefficients of the components of a regular binary solution were derived in the preceding problem. Derive the expression for γ_1 in terms of the experimentally measured total pressure P , the vapor pressures of the two components, and the composition of the solution for the case that the deviations from ideality are small.

SOLUTION

$$\gamma_1 = \exp(wx_2^2/RT)$$

$$\gamma_2 = \exp(wx_1^2/RT)$$

$$P = P_1 + P_2 = \gamma_1 x_1 P_1^* + \gamma_2 x_2 P_2^*$$

$$= x_1 P_1^* \exp\left(\frac{wx_2^2}{RT}\right) + x_2 P_2^* \exp\left(\frac{wx_1^2}{RT}\right)$$

If the exponentials are not far from unity, the exponentials may be expanded to obtain

$$P = x_1 P_1^* \left(1 + \frac{wx_2^2}{RT}\right) + x_2 P_2^* \left(1 + \frac{wx_1^2}{RT}\right)$$

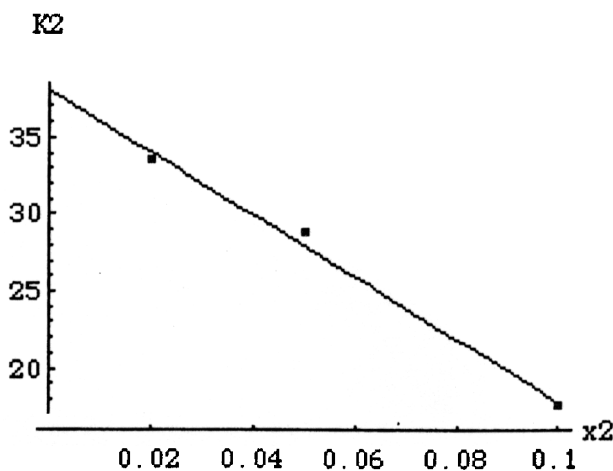
Thus from a measurement of the total pressure of a mixture of the two components, the activity coefficients of the components can be calculated over the entire concentration range using the first two equations given above. This is a particular example of the general situation that γ_1 and γ_2 can be calculated from the total pressure as a function of x_1 .

- 6.34 Using the data in Problem 6.75, calculate the activity coefficients of water (1) and *n*-propanol (2) at 0.20, 0.40, 0.60, and 0.80 mole fraction of *n*-propanol, based on deviations from Henry's law and considering water to be the solvent.

SOLUTION

The data at the lowest mole fractions of *n*-propanol are used to calculate the Henry law constant for *n*-propanol in water.

x_2	$K_2 = P_2/x_2$
0.02	33.5
0.05	28.8
0.10	17.6



The intercept indicates that $K_2 = 37$ kPa.

At

$$x_2 = 0.2 \quad \gamma_2' = \frac{P_2}{x_2 K_2} = \frac{1.81}{0.2(37)} = 0.24$$

$$x_2 = 0.4 \quad = \frac{1.89}{0.4(37)} = 0.13$$

$$x_2 = 0.6 \quad = \frac{2.07}{0.6(37)} = 0.093$$

$$x_2 = 0.8 \quad = \frac{2.37}{0.8(37)} = 0.080$$

$$x_2 = 0.2 \quad \gamma_1 = \frac{P_1}{x_1 P_1^*} = \frac{2.91}{(0.8)(3.17)} = 1.15$$

$$x_2 = 0.4 \quad = \frac{2.89}{(0.6)(3.17)} = 1.52$$

$$x_2 = 0.6 \quad = \frac{2.65}{(0.4)(3.17)} = 2.09$$

$$x_2 = 0.8 \quad = \frac{1.79}{(0.2)(3.17)} = 2.82$$

- 6.35 If 68.4 g of sucrose ($M = 342 \text{ g mol}^{-1}$) is dissolved in 1000 g of water: (a) What is the vapor pressure at 20°C ? (b) What is the freezing point? The vapor pressure of water at 20°C is 2.3149 kPa.

SOLUTION

$$(a) \quad x_2 = \frac{\frac{68.4}{342}}{\frac{68.4}{342} + \frac{1000}{18}} = 3.59 \times 10^{-3}$$

$$\frac{P_1^* - P_1}{P_1^*} = x_2 \quad \frac{2.3149 - P_1}{2.3149} = 3.59 \times 10^{-3}$$

$$P_1 = 2.3149(1 - 3.59 \times 10^{-3}) = 2.3066 \text{ kPa}$$

$$(b) \quad \Delta T_f = K_f m = 1.86(0.2) = -0.372$$

$$T_f = -0.372^\circ\text{C}$$

- 6.36 The protein human plasma albumin has a molar mass of $69,000 \text{ g mol}^{-1}$. Calculate the osmotic pressure of a solution of this protein containing 2 g per 100 cm^3 at 25°C in (a) pascals and (b) millimeters of water. The experiment is carried out using a salt solution for solvent and a membrane permeable to salt as well as water.

SOLUTION

$$\pi = \frac{cRT}{M} = \frac{(20 \times 10^{-3} \text{ kg L}^{-1})(10^3 \text{ L m}^{-3})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{69 \text{ kg mol}^{-1}}$$

$$= 719 \text{ Pa}$$

$$h = \frac{\pi}{dg} = \frac{719 \text{ Pa}}{(1 \text{ g cm}^{-3})(10^{-3} \text{ kg g}^{-1})(10^2 \text{ cm m}^{-1})(9.8 \text{ m s}^{-2})}$$

$$= 7.34 \times 10^{-2} \text{ m} = 73.4 \text{ mm of water}$$

- *6.37 The following osmotic pressures were measured for solutions of a sample of polyisobutylene in benzene at 25°C .

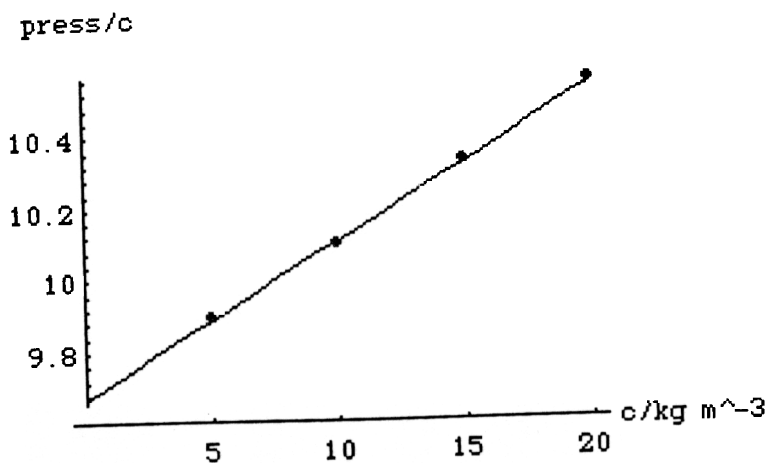
$c/\text{kg m}^{-3}$	5	10	15	20
π/Pa	49.5	101	155	211

Calculate the number average molar mass from the value of π/c extrapolated to zero concentration of the polymer.

SOLUTION

$c/\text{kg m}^{-3}$	5	10	15	20
$(\pi/c)/(\text{Pa}/\text{kg m}^{-3})$	9.90	10.1	10.3	10.6

$$\frac{\pi}{c} = \frac{RT}{M} + Bc$$



$$M = \frac{RT}{9.7 \text{ Pa/kg m}^{-3}} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{9.7 \text{ Pa m}^3 \text{ kg}^{-1}} = 255 \text{ kg mol}^{-1}$$

- 6.38 Calculate the osmotic pressure of a 1 mol L⁻¹ sucrose solution in water from the fact that at 30 °C the vapor pressure of the solution is 4.1606 kPa. The vapor pressure of water at 30 °C is 4.2429 kPa. The density of pure water at this temperature (0.99564 g cm⁻³) may be used to estimate \bar{V}_1 for a dilute solution. To do this problem, Raoult's law is introduced into equation 6.89.

SOLUTION

$$\bar{V}_1 \pi = -RT \ln x_1$$

Substituting Raoult's law $P_1 = x_1 P_1^0$

$$\pi = - \frac{RT}{\bar{V}_1} \ln \frac{P_1}{P_1^0}$$

$$\bar{V}_1 = \frac{18.02 \text{ g mol}^{-1}}{0.99564 \text{ g cm}^{-3}} = 18.10 \text{ cm}^3 \text{ mol}^{-1} = 0.01810 \text{ L mol}^{-1}$$

$$\pi = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})}{0.0180 \text{ L mol}^{-1}} \ln \frac{4.2429 \text{ kPa}}{4.1606 \text{ kPa}} = 27.3 \text{ bar}$$

- 6.39 Calculate the solubility of *p*-dibromobenzene in benzene at 20 °C and 40 °C assuming ideal solutions are formed. The enthalpy of fusion of *p*-dibromobenzene is 13.22 kJ mol⁻¹ at its melting point (86.9 °C).

SOLUTION

At 20 °C

$$\begin{aligned} \ln x_2 &= - \frac{\Delta_{\text{fus}} H_2 (T - T_{2f})}{RTT_{2f}} \\ &= \frac{(13\,220 \text{ J mol}^{-1})(-66.9 \text{ K})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(360.1 \text{ K})(293.2 \text{ K})} \end{aligned}$$

$$x_2 = 0.365$$

At 40 °C

$$\ln x_2 = \frac{(13\,220 \text{ J mol}^{-1})(-46.9 \text{ K})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(360.1 \text{ K})(313.2 \text{ K})}$$

$$x_2 = 0.516$$

- 6.40 Calculate the solubility of naphthalene at 25 °C in any solvent in which it forms an ideal solution. The melting point of naphthalene is 80 °C, and the enthalpy of fusion is 19.19 kJ mol⁻¹. The measured solubility of naphthalene in benzene is $x_1 = 0.296$.

SOLUTION

$$-\ln x_1 = \Delta_{\text{fus}}H_1(T_{0,1} - T)/RTT_{0,1}$$

$$\ln x_1 = \frac{-(19\,190 \text{ J mol}^{-1})(353 \text{ K} - 298 \text{ K})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(353 \text{ K})(298 \text{ K})}$$

$$x_1 = 0.297$$

- 6.41 The addition of a nonvolatile solute to a solvent increases the boiling point above that of the pure solvent. The elevation of the boiling point is given by

$$\Delta T_b = \frac{R(T_{bA})^2 M_A m_B}{\Delta_{\text{vap}}H_A^\circ} = K_b m_B$$

where T_{bA} is the boiling point of the pure solvent and M_A is its molar mass. The derivation of this equation parallels that of equation 6.82 very closely, and so it is not given. What is the elevation of the boiling point when 0.1 mol of nonvolatile solute is added to 1 kg of water? The enthalpy of vaporization of water at the boiling point is 40.6 kJ mol⁻¹.

SOLUTION

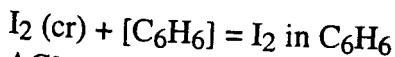
$$K_b = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(393.1 \text{ K})^2(0.018\,01 \text{ kg mol}^{-1})}{40\,600 \text{ J mol}^{-1}}$$

$$= 0.513 \text{ K kg mol}^{-1}$$

$$\Delta T_b = (0.513 \text{ K kg mol}^{-1})(0.1 \text{ mol kg}^{-1}) = 0.0513 \text{ K}$$

- 6.42 The NBS Tables of Chemical Thermodynamic Properties list $\Delta_f G^\circ$ for I₂ in C₆H₆: x as 7.1 kJ mol. The x indicates that the standard state for I₂ in C₆H₆ is on the mole fraction scale. What is the solubility of I₂ in C₆H₆ at 298 K on the mole fraction scale? A chemical handbook lists the solubility as 16.46 g I₂ in 100 cm³ of C₆H₆. Are these solubilities consistent?

SOLUTION



$$\Delta G^\circ = -RT \ln x$$

$$7.1 = -(8.314 \times 10^{-3})(298) \ln x$$

$x = 0.0569$ where x is the equilibrium mole fraction of I_2

The mole fraction calculated from the chemical handbook is

$$\frac{\frac{16.46}{253.8}}{\frac{16.46}{253.8} + \frac{(100)(0.8787)}{78.12}} = 0.0545$$

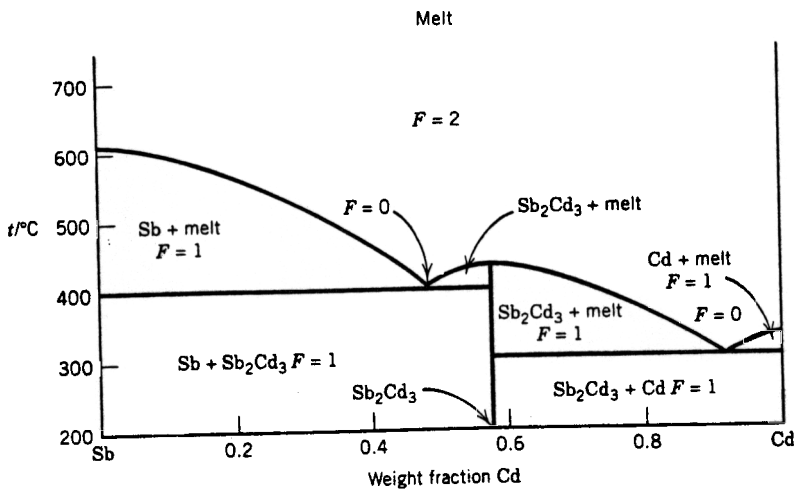
so the values are consistent.

6.43 The following cooling curves have been found for the system antimony-cadmium.

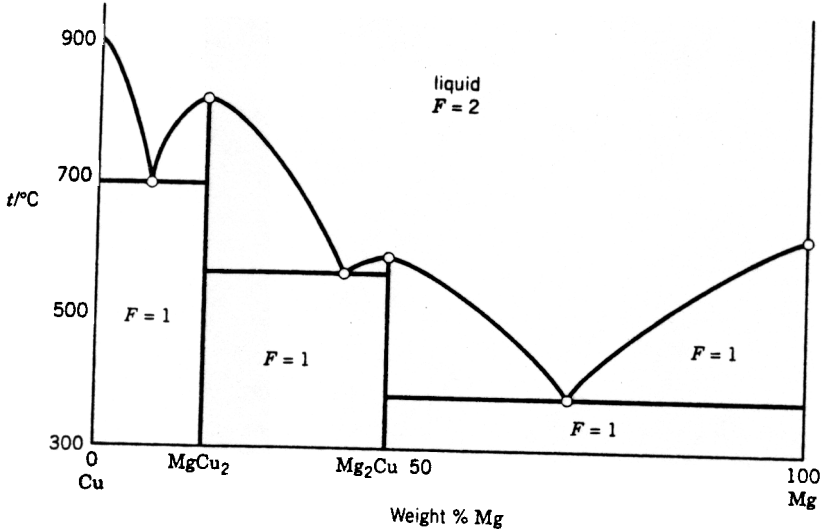
Cd Wt. %	0	20	37.5	47.5	50	58	70	93	100
First break in curve, °C		550	461		419	--	400	--	
Constant temperature, °C	630	410	410	410	410	439	295	295	321

Construct a phase diagram, assuming that no breaks other than these actually occur in any cooling curve. Label the diagram completely and give the formula of any compound formed. How many degrees of freedom are there for each area and at each eutectic point?

SOLUTION



6.44 The phase diagram for magnesium-copper at constant pressure shows that two compounds are formed: MgCu_2 that melts at 800°C , and Mg_2Cu that melts at 580°C . Copper melts at 1085°C , and Mg at 648°C . The three eutectics are at 9.4% by weight Mg (680°C), 34% by weight Mg (560°C), and 65% by weight Mg (380°C). Construct the phase diagram. How many degrees of freedom are there for each area and at each eutectic point?

SOLUTION

$F = 2 - p + 1$ In the liquid region $F = 2$; in the two-phase regions $F = 1$; and at the eutectic point $F = 0$.

6.45 The Gibbs-Duhem equation in the form

$$\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \sum (x_i dM_i) = 0$$

applies to any molar thermodynamic property M in a homogeneous phase. If this is applied to G^E , it may be shown that if the vapor is an ideal gas.

$$x_1 \frac{d \ln (y_1 P)}{dx_1} + x_2 \frac{d \ln (y_2 P)}{dx_1} = 0 \quad (\text{constant } T)$$

Show that this can be rearranged to the coexistence equation

$$\frac{dP}{dy_1} = \frac{P(y_1 - x_1)}{y_1(1 - y_1)}$$

Thus if P versus y_1 is measured, there is no need for measurements of x_1

SOLUTION

$$x_1 d \ln y_1 + x_1 d \ln P + x_2 d \ln y_2 + x_2 d \ln P = 0$$

$$d \ln P = -\frac{x_1}{y_1} dy_1 - \frac{x_2}{y_2} dy_2 = \left(-\frac{x_1}{y_1} + \frac{x_2}{y_2}\right) dy_1$$

$$= \frac{x_2 y_1 - x_1 y_2}{y_1 y_2} dy_1 = \frac{y_1 - x_1}{y_1(1 - y_1)} dy_1$$

- 6.46 For a solution of ethanol and water at 20 °C that has 0.2 mole fraction ethanol, the partial molar volume of water is 17.9 cm³ mol⁻¹ and the partial molar volume of ethanol is 55.0 cm³ mol⁻¹. What volumes of pure ethanol and water are required to make a liter of this solution? At 20 °C the density of ethanol is 0.789 g cm⁻³ and the density of water is 0.998 g cm⁻³.

SOLUTION

Component 1 is water and component 2 is ethanol.

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 = 4n_2 \bar{V}_1 + n_2 \bar{V}_2 = n_2(4\bar{V}_1 + \bar{V}_2)$$

$$1000 \text{ cm}^3 = n_2[(4)(17.9 \text{ cm}^3 \text{ mol}^{-1}) + 55.0 \text{ cm}^3 \text{ mol}^{-1}]$$

$$n_2 = 7.90 \text{ mol} = w_2/46.07 \text{ g mol}^{-1}$$

$$w_2 = 363.9 \text{ g of ethanol}$$

$$\text{Volume of pure ethanol} = 363.9 \text{ g}/0.789 \text{ g cm}^{-3} = 461 \text{ cm}^3$$

$$n_1 = 4n_2 = 31.50 = w_1/18.016 \text{ g mol}^{-1}$$

$$w_1 = 569.3 \text{ g of water}$$

$$\text{Volume of pure water} = 569.3 \text{ g}/0.998 \text{ g cm}^{-3} = 570 \text{ cm}^3$$

Thus there is a shrinkage of 31 cm³ when these amounts of ethanol and water are mixed at 20 °C.

- 6.47 When 1 mol of water is added to an infinitely large amount of an aqueous methanol solution having a mole fraction of methanol of 0.40, the volume of the solution is increased by 17.35 cm³ at 25 °C. When one mole of methanol is added to such a solution, the volume increases by 39.01 cm³. (a) Calculate the volume of solution containing 0.40 mol of methanol and 0.60 mol of water. (b) What is the volume of 0.6 mol of water plus the volume of 0.4 mol of methanol before they are mixed? The densities of water and methanol at 25 °C are 0.998 g cm⁻³ and 0.791 g cm⁻³, respectively.

SOLUTION

$$(a) \quad \bar{V} = 0.4(39.01 \text{ cm}^3 \text{ mol}^{-1}) + 0.6(17.35) = 26.01 \text{ cm}^3 \text{ mol}^{-1}$$

$$(b) \quad \bar{V} = 0.4\left(\frac{32.04}{.791}\right) + 0.6\left(\frac{18.02}{.998}\right) = 27.03 \text{ cm}^3 \text{ mol}^{-1}$$

- 6.48 Derive

$$\bar{C}_P = -T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_P$$

from equation 4.44,

$$H = G - T \left(\frac{\partial G}{\partial T} \right)_P$$

SOLUTION

For one mole of substance

$$\bar{H} = \mu - T \left(\frac{\partial \mu}{\partial T} \right)_P$$

$$\bar{C}_P = \left(\frac{\partial \bar{H}}{\partial T} \right)_P = \left(\frac{\partial \mu}{\partial T} \right)_P - T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_P - \left(\frac{\partial \mu}{\partial T} \right)_P = -T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_P$$

6.49 The freezing point is lowered to -5°C under the skates, and so the answer is yes.

6.50 $3.611 \times 10^3 \text{ Pa K}^{-1}$, 0.05%

6.51 $6.29 \times 10^{-3} \text{ bar}$

6.52 $2.66 \times 10^{-6} \text{ bar}$

6.53 4.9 K

6.54 53.0 kJ mol^{-1} , 28.4 kJ mol^{-1} , $158.6 \text{ J K}^{-1} \text{ mol}^{-1}$

6.55 383.38 K, -0.4°C

6.56 96°C

6.57 $27.57 \text{ kJ mol}^{-1}$

6.58 0.0773 Pa

6.59 (a) 0.123 14 bar, (b) 0.125 110 bar

6.61 (a) 38.1 kJ mol^{-1} , (b) 3.78 kPa

6.62 (a) $50.91 \text{ kJ mol}^{-1}$, (b) 50.14 Pa K^{-1} , 44.20 Pa K^{-1} , (c) $P_{\text{ice}} = 361 \text{ Pa}$,

$$P_{\text{liq}} = 390 \text{ Pa}$$

6.63 (a) -0.46°C , (b) -0.59°C

6.64 $-8.59 \text{ kJ mol}^{-1}$

6.65 4

6.66 (a) 1, (b) 2

6.67 166.5 Pa

- 6.68 (a) $y_{\text{EtBr}_2} = 0.802$, (b) $x_{\text{EtBr}_2} = 0.425$
- 6.69 (a) $y_{\text{CHCl}_3} = 0.635$, (b) 20.91 kPa
- 6.70 (a) $y_{\text{B}} = 0.722$, $P = 69.55$ kPa, (b) 0.536
- 6.71 (a) $x_{\text{ClB}} = 0.591$; (b) $y_{\text{ClB}} = 0.731$; (c) 1.081 bar
- 6.72 $x_{\text{B}} = 0.240$, $y_{\text{B}} = 0.434$
- 6.73 571 g of $\text{H}_2\text{O}(\text{g})$
- 6.74 $5.293 \text{ J K}^{-1} \text{ mol}^{-1}$, -1577 J mol^{-1}
- 6.75 $y_{n\text{-Pr}} = 0.406$
- 6.76 $x_{\text{C}_6\text{H}_6} = 0.55$; pure C_6H_6 can be obtained by distillation provided $x_{\text{C}_6\text{H}_6} > 0.55$
- 6.77 (a) $y_{\text{Pr}} = 0.37$, (b) $y_{\text{Pr}} = 0.59$
- 6.78 33.0% O_2 , 67.0% N_2
- 6.79 $\gamma = 1.67$, $\gamma_{\text{CS}_2} = 1.38$
- 6.80
- | | | | | | | |
|------------|------|------|------|------|------|------|
| x_1 | 0 | 0.2 | 0.4 | 0.6 | 0.8 | 1 |
| γ_1 | | 0.58 | 0.70 | 0.84 | 0.96 | 1.00 |
| γ_2 | 1.00 | 0.98 | 0.89 | 0.74 | 0.61 | |
- 6.81 -1311 J mol^{-1}
- 6.82 $11.17 \text{ kJ mol}^{-1}$
- 6.83 (a) $K = 19.9$ kPa (b) $\gamma'_{\text{CHCl}_3} = 1.13, 1.37, 1.65, 1.88, 1.96$
- 6.84 $\gamma_1 = 3.12, 1.63, 1.19, 1.02$
 $\gamma'_2 = 0.314, 0.417, 0.571, 0.772$
- 6.86 92.4 g mol^{-1}
- 6.88 122 kg mol^{-1}
- 6.89 $x_{\text{A}} = 0.108$. The solution is not ideal.
- 6.90 $x_{\text{Cd}} = 0.842$