

Exc.1

$$\Delta G_m = V_m \Delta p$$

$$V_m = \frac{891.51 \text{ g mol}^{-1}}{0.95 \text{ g cm}^{-3}} = 938 \text{ cm}^3 \text{ mol}^{-1} = 9.4 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

$$\Delta p = \rho gh = 9.81 \text{ m s}^{-2} \times 1.03 \times 10^3 \text{ kg m}^{-3} \times 2.0 \times 10^3 \text{ m} = 2.0 \times 10^7 \text{ Pa}$$

$$\Delta G_m = 9.4 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \times 2.0 \times 10^7 \text{ Pa} = +1.9 \times 10^4 \text{ J mol}^{-1} = \boxed{+19 \text{ kJ mol}^{-1}}$$

Exc.2

$$\Delta G_m = RT \ln \frac{p_f}{p_i} \quad [3.3]$$

$$\begin{aligned} \text{(a)} \quad \Delta G_m &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 293 \text{ K} \times \ln \left(\frac{2.0 \text{ bar}}{1.0 \text{ bar}} \right) \\ &= 1.7 \times 10^3 \text{ J mol}^{-1} = \boxed{+1.7 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta G_m &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 293 \text{ K} \times \ln \left(\frac{0.00027 \text{ bar}}{1.0 \text{ bar}} \right) \\ &= -2.0 \times 10^4 \text{ J mol}^{-1} = \boxed{-20 \text{ kJ mol}^{-1}} \end{aligned}$$

Exc.3

(a) The Clapeyron equation for the solid–liquid phase boundary is

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} H}{T_{\text{fus}} \Delta_{\text{fus}} V} \quad [3.5].$$

$$\begin{aligned} \Delta_{\text{fus}} V &= V_m(\text{l}) - V_m(\text{s}) = M \left(\frac{1}{\rho_l} - \frac{1}{\rho_s} \right) \\ &= 18.02 \text{ g mol}^{-1} \left(\frac{1}{0.99984 \text{ g cm}^{-3}} - \frac{1}{0.91671 \text{ g cm}^{-3}} \right) \\ &= -1.634 \text{ cm}^3 \text{ mol}^{-1} \\ &= -1.634 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

$$\frac{dp}{dT} = \frac{6.008 \times 10^3 \text{ J mol}^{-1}}{(273.15 \text{ K}) \times (-1.634 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}$$

$$= -1.346 \times 10^7 \text{ Pa K}^{-1} = \boxed{-134.6 \text{ bar K}^{-1}}$$

The slope is very steep with an unusual negative slope that is caused by the decrease in volume that occurs when ice melts. The melting process destroys some of the hydrogen-bond scaffolding that holds ice in a larger molar volume.

$$(b) \quad \frac{\Delta p}{\Delta T} = -134.6 \text{ bar K}^{-1}$$

For $\Delta T = -1 \text{ K}$, $\Delta p = 134.6 \text{ bar}$. Consequently, $p = p_1 + \Delta p = 1.0 \text{ bar} + 134.6 \text{ bar} = \boxed{135.6 \text{ bar}}$.

Exc.4

(a) To obtain the explicit expression for the vapor pressure at any temperature we rearrange the Clausius–Clapeyron equation into

$$d \ln p = \frac{\Delta_{\text{vap}} H}{RT^2} dT$$

and integrate both sides. If the vapor pressure is p at a temperature T and p' at a temperature T' , this integration takes the form

$$\int_{\ln p}^{\ln p'} d \ln p = \int_T^{T'} \frac{\Delta_{\text{vap}} H}{RT^2} dT$$

The integral on the left evaluates to $\ln p' - \ln p$, which simplifies to $\ln(p'/p)$. To evaluate the integral on the right we assume that the enthalpy of vaporization is constant over the temperature range involved, so together with R it can be taken outside of the integral sign. Then,

$$\ln \frac{p'}{p} = \frac{\Delta_{\text{vap}} H}{R} \int_T^{T'} \frac{1}{T^2} dT = \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

$$\text{or } \ln p' = \ln p + \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

(b) We use the result from part (a).

$$\ln \frac{p'}{p} = \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

with $T = 293 \text{ K}$, $p = 160 \text{ mPa}$, and $T' = 313 \text{ K}$; then solve for p' .

$$\ln \frac{p'}{p} = \frac{59.30 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{293 \text{ K}} - \frac{1}{313 \text{ K}} \right) = 1.56$$

$$\frac{p'}{p} = e^{1.56} = 4.74$$

$$p' = (4.74) \times (160 \text{ mPa}) = 758 \text{ mPa} = \boxed{0.758 \text{ Pa}}$$

Exc.5 (a) There is only one volume, so using the amount of nitrogen and partial pressure of nitrogen we can calculate the volume.

$$n_{\text{N}_2} = \frac{0.225 \text{ g}}{28.02 \text{ g mol}^{-1}} = 8.03 \times 10^{-3} \text{ mol}, \quad p_{\text{N}_2} = 15.2 \text{ kPa}, \quad T = 300 \text{ K}$$

$$V = \frac{n_{\text{N}_2} RT}{p_{\text{N}_2}} \text{ [Each component of the mixture satisfies the perfect gas law.]} \\ = \frac{(8.03 \times 10^{-3} \text{ mol}) \times (8.3145 \text{ dm}^3 \text{ kPa K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{15.2 \text{ kPa}} = \boxed{1.32 \text{ dm}^3}$$

(b) $n_{\text{CH}_4} = \frac{0.320 \text{ g}}{16.04 \text{ g mol}^{-1}} = 2.00 \times 10^{-2} \text{ mol}$

$$n_{\text{Ar}} = \frac{0.175 \text{ g}}{39.95 \text{ g mol}^{-1}} = 4.38 \times 10^{-3} \text{ mol}$$

$$n = n_{\text{CH}_4} + n_{\text{Ar}} + n_{\text{N}_2} = (2.00 + 0.438 + 0.803) \times 10^{-2} \text{ mol} = 3.24 \times 10^{-2} \text{ mol}$$

Solving the perfect gas law for the total pressure p of n moles of gas, we find

$$p = \frac{nRT}{V} = \frac{(3.24 \times 10^{-2} \text{ mol}) \times (8.3145 \text{ dm}^3 \text{ kPa K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{1.32 \text{ dm}^3} = \boxed{61.2 \text{ kPa}}$$

Exc.6

$$x_{\text{sucrose}} = 0.124 = \frac{n_{\text{sucrose}}}{n_{\text{sucrose}} + n_{\text{H}_2\text{O}}} = \frac{m/M_{\text{sucrose}}}{m/M_{\text{sucrose}} + \frac{100 \text{ g}}{18.02 \text{ g mol}^{-1}}}$$

Solve the above equation for mass (m).

$$0.124 \left(\frac{m}{M_{\text{sucrose}}} + 5.55 \text{ mol} \right) = \frac{m}{M_{\text{sucrose}}}$$

$$0.124 \times 5.55 \text{ mol} = \frac{m}{M_{\text{sucrose}}} (1 - 0.124)$$

$$m = \frac{0.124 \times 5.55 \text{ mol} \times M_{\text{sucrose}}}{0.876} \quad \left[M_{\text{sucrose}} = \frac{342.30 \text{ g}}{\text{mol}} \right]$$

$$\text{mass} = \boxed{269 \text{ g sucrose}}$$

Exc.7

(a) $\Delta G_m = RT(x_A \ln x_A + x_B \ln x_B)$ [3.20], where A = N₂(g) and B = O₂(g)

$$\Delta G_m = 2.479 \text{ kJ mol}^{-1} \{0.78 \ln(0.78) + 0.22 \ln(0.22)\}$$

$$= \boxed{-1.31 \text{ kJ mol}^{-1}}$$

Because ΔG_m is negative, the mixing is **spontaneous**.

(b) $\Delta S_m = -R(x_A \ln x_A + x_B \ln x_B)$ [3.21b]

$$= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \{0.78 \ln(0.78) + 0.22 \ln(0.22)\}$$

$$= \boxed{+4.38 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Exc.8

$$K_{\text{CO}_2/\text{lipid}} = (8.6 \times 10^4 \text{ Torr}) \times (101.325 \text{ kPa}/760 \text{ Torr}) = 1.15 \times 10^4 \text{ kPa}$$

$$x_{\text{CO}_2} = p_{\text{CO}_2}/K_{\text{CO}_2/\text{lipid}} [3.13] = (55 \text{ kPa})/(1.15 \times 10^4 \text{ kPa}) = \boxed{4.8 \times 10^{-3}}$$

Check the provided alternative equation [3.13] for Henry's law in your textbook!

Exc.9

$$[J] = p_J \times K_H(J) [3.14] = x_J(\text{gas}) \times p \times K_H(J)$$

We assume that $p = p^\circ = 1.00 \text{ bar} = 100 \text{ kPa}$.

$$[\text{N}_2] = 0.78 \times (100 \text{ kPa}) \times 6.48 \times 10^{-3} \text{ kPa}^{-1} \text{ mol m}^{-3} [\text{Table 3.2}] = 0.51 \text{ mol m}^{-3} = 0.51 \text{ mmol dm}^{-3}$$

$$[\text{O}_2] = 0.21 \times (100 \text{ kPa}) \times 1.30 \times 10^{-2} \text{ kPa}^{-1} \text{ mol m}^{-3} [\text{Table 3.2}] = 0.27 \text{ mol m}^{-3} = 0.27 \text{ mmol dm}^{-3}$$

The magnitudes of molarity and molality concentrations are equal in very dilute solutions such as these. Consequently, $b_{\text{N}_2} = 0.51 \text{ mmol kg}^{-1}$ and $b_{\text{O}_2} = 0.27 \text{ mmol kg}^{-1}$.

Exc.10

Assume 150 cm^3 of water has a mass of 0.150 kg .

$$\Delta T_f = K_f b_B [3.22] = 1.86 \text{ K kg mol}^{-1} \times \frac{7.5 \text{ g}}{342.3 \text{ g mol}^{-1} \times 0.150 \text{ kg}} = 0.27 \text{ K}$$

The freezing point will be approximately $\boxed{-0.27^\circ\text{C}}$

Exc.11

$$\Pi V = n_B RT [3.23a]$$

$$\frac{n_B}{V} = M_B (\text{molarity}) \approx b \rho \quad [\rho = \text{density}]$$

with $\rho = 10^3 \text{ kg m}^{-3}$ for dilute aqueous solutions

Then,

$$b \approx \frac{n_B}{V \rho} = \frac{\Pi}{RT \rho}$$

$$\Delta T_f = K_f b_B \approx K_f \times \frac{\Pi}{RT \rho}$$

Therefore, with $K_f = 1.86 \text{ K kg mol}^{-1}$ (Table 3.4)

$$\Delta T_f = \frac{(1.86 \text{ K kg mol}^{-1}) \times (120 \times 10^3 \text{ Pa})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times (1.00 \times 10^3 \text{ kg m}^{-3})} = 0.089 \text{ K}$$

Therefore, the solution will freeze at about $\boxed{-0.09^\circ\text{C}}$.