Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

1. For the equilibrium, \( \text{N}_2\text{O}_4(g) \leftrightarrow 2 \text{NO}_2(g) \), the degree of dissociation, \( \alpha_e \), at 298 K is 0.201 at 1.00 bar total pressure. Calculate (a) \( \Delta_r G \), (2) \( K \), and (3) the standard Gibbs energy change, \( \Delta_r G^\circ \) at 298 K.

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)
\]

Amount at equilibrium

\[
\begin{array}{cc}
(1 - \alpha)n & 2\alpha n \\
\end{array}
\]

Mole fraction

\[
\begin{array}{cc}
\frac{1 - \alpha}{1 + \alpha} & \frac{2\alpha}{1 + \alpha} \\
\end{array}
\]

Partial pressure

\[
\begin{array}{cc}
\frac{(1 - \alpha)P}{1 + \alpha} & \frac{2\alpha P}{1 + \alpha} \\
\end{array}
\]

Assuming that the gases are perfect, \( \alpha_j = \frac{p_j}{p^\circ} \)

\[
K = \frac{(p_{\text{NO}_2}/p^\circ)^2}{(p_{\text{N}_2\text{O}_4}/p^\circ)} = \frac{4\alpha^2 p}{(1 - \alpha^2)p^\circ}
\]

For \( p = p^\circ \), \( K = \frac{4\alpha^2}{1 - \alpha^2} \)

(a) \( \Delta_r G = 0 \) at equilibrium

(b) \( \alpha = 0.201 \quad K = \frac{4(0.201)^2}{1 - 0.201^2} = 0.16841 \)

(c) \( \Delta_r G^\circ = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.16841) \)

\[= 4.41 \text{ kJ mol}^{-1} \]

6.3 (a) (copied for your convenience)
The standard Gibbs energy of the reaction \( \text{N}_2 (g) + 3\text{H}_2 (g) \rightarrow 2\text{NH}_3 (g) \) is \(-32.9 \text{ kJ mol}^{-1}\) at 298 K. What is the value of \( \Delta_r G \) when \( Q = (a) 0.10, (b) 1.0, (c) 10.0 \) and \( (d) 100.0 \)?

**Estimate** (by interpolation) the value of \( K \) from the values that you calculated above. What is the actual value of \( K \)?

Use tables to find \( \Delta_r G^\circ \)

Then \( \Delta_r G = \Delta_r G^\circ + RT \ln(Q) \). Find \( \Delta_r G \) for each \( Q \).

Make plot of \( \Delta_r G \) as a function of \( Q \). Since \( \Delta_r G = 0 \) when \( Q = K \), use this plot to **estimate** the value of \( Q \) when \( \Delta_r G = 0 \). This is \( K, \sim 6 \times 10^5 \).

3. At 2257 K and \( P = 1.0 \text{ Bar} \) total pressure, water is 1.77 % dissociated at equilibrium by way of the reaction \( 2\text{H}_2\text{O} (g) \leftrightarrow 2\text{H}_2 (g) + \text{O}_2 (g) \). Calculate \( K \).

Draw up an equilibrium table. Let \( \alpha = 0.0177 \) be the fraction dissociated at equilibrium.

\[
\begin{align*}
2 \text{H}_2\text{O}(g) & \rightleftharpoons 2 \text{H}_2(g) + \text{O}_2(g) \quad T = 2257 \text{ K}, \quad P = 1 \text{ bar} = p^*, \quad \alpha = 0.0177 \text{ at equilibrium} \\
\text{We draw up the following equilibrium table (Example 6.2).} \\
\begin{array}{cccc}
\text{Amount at} & \text{H}_2\text{O}(g) & \text{H}_2(g) & \text{O}_2(g) \\
\text{equilibrium} & (1-\alpha)n & \alpha n & \frac{1}{2} \alpha n \\
\text{Mole fraction} & \frac{1-\alpha}{1+\frac{1}{2} \alpha} & \frac{\alpha}{1+\frac{1}{2} \alpha} & \frac{\frac{1}{2} \alpha}{1+\frac{1}{2} \alpha} \\
\text{Partial pressure} & \frac{(1-\alpha)p}{1+\frac{1}{2} \alpha} & \frac{\alpha p}{1+\frac{1}{2} \alpha} & \frac{\frac{1}{2} \alpha p}{1+\frac{1}{2} \alpha}
\end{array}
\end{align*}
\]

\[
K = \left( \prod \text{q}_j^a \right)_{\text{equilibrium}} = \left( \prod (p_j/p^*)^{\alpha_j} \right)_{\text{equilibrium}} \tag{6.13}
\]

(Perfect gas assumption)

\[
= \frac{(p_{\text{H}_2} p^*)^2(p_{\text{O}_2} p^*)^2}{(p_{\text{H}_2}\text{O}^*)^2} = \frac{p_{\text{H}_2} p_{\text{O}_2}}{p_{\text{H}_2}\text{O}^*} = \left( \frac{\alpha p}{1+\frac{1}{2} \alpha} \right)^2 \left( \frac{\frac{1}{2} \alpha p}{1+\frac{1}{2} \alpha} \right)^2 \left( \frac{(1-\alpha)p}{1+\frac{1}{2} \alpha} \right)^2 \
\]

\[
= \frac{p}{2p^*} \left( \frac{\alpha^3}{(1-\alpha)^2(1+\frac{1}{2} \alpha)^2} \right) = \frac{1}{2} \left( \frac{(0.0177)^3}{(1-0.0177)^2(1+\frac{1}{2} \times 0.0177)} \right) = 2.85 \times 10^{-5}
\]
4. At 25°C, the density of a 50 per cent by mass ethanol–water solution is 0.914 g cm\(^{-3}\). Given that the partial molar volume of water in the solution is 17.4 cm\(^3\) mol\(^{-1}\), calculate the partial molar volume of the ethanol.

Let A denote water and B ethanol. The total volume of the solution is

\[ V = n_A V_A + n_B V_B. \]

We are given \(V_A\), we need to determine \(n_A\) and \(n_B\) in order to solve for \(V_B\).

Assume we have 100 cm\(^3\) of solution; then the mass of solution is

\[ m = d \times V = (0.914 \text{ g cm}^{-3}) \times (100 \text{ cm}^3) = 91.4 \text{ g} \]

of which 45.7 g is water and 45.7 g ethanol.

\[
100 \text{ cm}^3 = \left( \frac{45.7 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (17.4 \text{ cm}^3 \text{ mol}^{-1}) + \left( \frac{45.7 \text{ g}}{46.07 \text{ g mol}^{-1}} \right) \times V_B
\]

\[ = 44.13 \text{ cm}^3 + 0.9920 \text{ mol} \times V_B, \]

\[ V_B = \frac{55.87 \text{ cm}^3}{0.9920 \text{ mol}} = \frac{56.3 \text{ cm}^3 \text{ mol}^{-1}}{\text{.}} \]

Let A denote water and B ethanol. The total volume of the solution is

\[ V = n_A V_A + n_B V_B. \]

We are given \(V_A\), we need to determine \(n_A\) and \(n_B\) in order to solve for \(V_B\).

Assume we have 100 cm\(^3\) of solution; then the mass of solution is

\[ m = d \times V = (0.914 \text{ g cm}^{-3}) \times (100 \text{ cm}^3) = 91.4 \text{ g} \]

of which 45.7 g is water and 45.7 g ethanol.

\[
100 \text{ cm}^3 = \left( \frac{45.7 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (17.4 \text{ cm}^3 \text{ mol}^{-1}) + \left( \frac{45.7 \text{ g}}{46.07 \text{ g mol}^{-1}} \right) \times V_B
\]

\[ = 44.13 \text{ cm}^3 + 0.9920 \text{ mol} \times V_B, \]

\[ V_B = \frac{55.87 \text{ cm}^3}{0.9920 \text{ mol}} = \frac{56.3 \text{ cm}^3 \text{ mol}^{-1}}{\text{.}} \]