

1) At 2257 K and 1.00 atm total pressure, water is 1.77 per cent dissociated at equilibrium by way of the reaction $2 \text{H}_2\text{O}(\text{g}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$. Calculate (a) K , (b) $\Delta_r G^\ominus$, and (c) $\Delta_r G$ at this temperature.

We draw up the following equilibrium table (Example 7.2). α is the equilibrium extent of dissociation.

	H_2O	H_2	O_2
Amount at equilibrium	$(1 - \alpha)n$	αn	$\frac{1}{2}\alpha n$
Mole fraction	$\frac{1 - \alpha}{1 + \frac{1}{2}\alpha}$	$\frac{\alpha}{1 + \frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha}{1 + \frac{1}{2}\alpha}$
Partial pressure	$\frac{(1 - \alpha)p}{1 + \frac{1}{2}\alpha}$	$\frac{\alpha p}{1 + \frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha p}{1 + \frac{1}{2}\alpha}$

(a) $K = \left(\prod_{\text{J}} a_{\text{J}}^{\nu_{\text{J}}} \right)_{\text{equilibrium}}$ [7.16]; $a_{\text{J}} = \frac{p_{\text{J}}}{p^\ominus}$ [assume gases are perfect].

$$\begin{aligned}
 K &= \frac{(p_{\text{H}_2}/p^\ominus)^2 \times (p_{\text{O}_2}/p^\ominus)}{(p_{\text{H}_2\text{O}}/p^\ominus)^2} \quad [7.16] = \frac{(\alpha p / (1 + \frac{1}{2}\alpha)p^\ominus)^2 \times (\frac{1}{2}\alpha p / (1 + \frac{1}{2}\alpha)p^\ominus)}{((1 - \alpha)p / (1 + \frac{1}{2}\alpha)p^\ominus)^2} \\
 &= \frac{\alpha^3 p}{2(1 - \alpha)^2 \times (1 + \frac{1}{2}\alpha)p^\ominus} = \frac{(0.0177)^3}{2(1 - 0.0177)^2 \times (1 + \frac{1}{2} \times 0.0177)} \\
 &= 2.848 \times 10^{-6} = \boxed{2.85 \times 10^{-6}}.
 \end{aligned}$$

(b) $\Delta_r G^\ominus = -RT \ln K$ [7.8]

$$\begin{aligned}
 &= -(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (2257 \text{ K}) \times \ln(2.848 \times 10^{-6}) = 2.40 \times 10^5 \text{ J mol}^{-1} \\
 &= \boxed{+240 \text{ kJ mol}^{-1}}.
 \end{aligned}$$

(c) $\Delta_r G = \boxed{0}$ [the system is at equilibrium].

2) Dinitrogen tetroxide is 18.46 per cent dissociated at 25°C and 1.00 bar in the equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$. Calculate (a) K at 25°C, (b) $\Delta_r G^\ominus$, (c) K at 100°C given that $\Delta_r H^\ominus = +57.2 \text{ kJ mol}^{-1}$ over the temperature range.

We draw up the following equilibrium table.

	N_2O_4	NO_2
Amount at equilibrium	$(1 - \alpha)n$	$2\alpha n$
Mole fraction	$\frac{1 - \alpha}{1 + \alpha}$	$\frac{2\alpha}{1 + \alpha}$
Partial pressure	$\frac{(1 - \alpha)p}{1 + \alpha}$	$\frac{2\alpha p}{1 + \alpha}$

(a) Assuming the gases are perfect $a_J = \left(\frac{p_J}{p^\ominus}\right)$; hence

$$K = \frac{(p_{\text{NO}_2}/p^\ominus)^2}{(p_{\text{N}_2\text{O}_4}/p^\ominus)} [7.16] = \frac{4\alpha^2 p}{(1 - \alpha^2)p^\ominus} = \frac{4\alpha^2}{(1 - \alpha^2)} [p = p^\ominus],$$

$$K = \frac{(4) \times (0.1846)^2}{1 - (0.1846)^2} = \boxed{0.1411}.$$

(b) $\Delta_r G^\ominus = -RT \ln K [7.8] = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.2 \text{ K}) \times \ln(0.1411)$
 $= 4.855 \times 10^3 \text{ J mol}^{-1} = \boxed{+4.855 \text{ kJ mol}^{-1}}.$

(c) $\ln K(100^\circ\text{C}) = \ln K(25^\circ\text{C}) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{373.2 \text{ K}} - \frac{1}{298.2 \text{ K}} \right) [7.25],$

$$\ln K(100^\circ\text{C}) = \ln(0.1411) - \left(\frac{57.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-6.739 \times 10^{-4} \text{ K}^{-1}) = 2.678,$$

$$K(100^\circ\text{C}) = \boxed{14.556}.$$

3) From information in the *Data section*, calculate the standard Gibbs energy and the equilibrium constant at (a) 298 K and (b) 400 K for the reaction $\text{PbO(s)} + \text{CO(g)} \rightleftharpoons \text{Pb(s)} + \text{CO}_2\text{(g)}$. Assume that the reaction enthalpy is independent of temperature.

$$(a) \Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus(J) \quad [7.12(b)].$$

$$\nu(\text{Pb}) = 1, \quad \nu(\text{CO}_2) = 1, \quad \nu(\text{PbO}) = -1, \quad \nu(\text{CO}) = -1.$$

The equation is

$$0 = \text{Pb(s)} + \text{CO}_2\text{(g)} - \text{PbO(s)} - \text{CO(g)}.$$

$$\begin{aligned} \Delta_r G^\ominus &= \Delta_f G^\ominus(\text{Pb, s}) + \Delta_f G^\ominus(\text{CO}_2, \text{g}) - \Delta_f G^\ominus(\text{PbO, s, red}) - \Delta_f G^\ominus(\text{CO, g}) \\ &= (-394.36 \text{ kJ mol}^{-1}) - (-188.93 \text{ kJ mol}^{-1}) - (-137.17 \text{ kJ mol}^{-1}) \\ &= \boxed{-68.26 \text{ kJ mol}^{-1}}. \end{aligned}$$

$$\ln K = \frac{-\Delta_r G^\ominus}{RT} \quad [7.8] = \frac{+68.26 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 27.55; \quad K = \boxed{9.2 \times 10^{11}}.$$

$$\begin{aligned} (b) \quad \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{Pb, s}) + \Delta_f H^\ominus(\text{CO}_2, \text{g}) - \Delta_f H^\ominus(\text{PbO, s, red}) - \Delta_f H^\ominus(\text{CO, g}) \\ &= (-393.51 \text{ kJ mol}^{-1}) - (-218.99 \text{ kJ mol}^{-1}) - (-110.53 \text{ kJ mol}^{-1}) \\ &= \boxed{-63.99 \text{ kJ mol}^{-1}}. \end{aligned}$$

$$\begin{aligned} \ln K(400\text{K}) &= \ln K(298) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{400 \text{ K}} - \frac{1}{298 \text{ K}} \right) \quad [7.25] \\ &= 27.55 - \left(\frac{-63.99 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-8.557 \times 10^{-4} \text{ K}^{-1}) = 20.96, \end{aligned}$$

$$K(400\text{K}) = \boxed{1.3 \times 10^9}.$$

$$\begin{aligned} \Delta_r G^\ominus(400 \text{ K}) &= -RT \ln K(400\text{K}) \quad [7.8] = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times (20.96) \\ &= -6.97 \times 10^4 \text{ J mol}^{-1} = \boxed{-69.7 \text{ kJ mol}^{-1}}. \end{aligned}$$

4) In the gas-phase reaction $2 A + B \rightleftharpoons 3 C + 2 D$, it was found that when 1.00 mol A, 2.00 mol B, and 1.00 mol D were mixed and allowed to come to equilibrium at 25°C, the resulting mixture contained 0.90 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x , (c) K , and (d) $\Delta_r G^\ominus$.

Draw up the following equilibrium table.

	A	B	C	D	Total
Initial amounts/mol	1.00	2.00	0	1.00	4.00
Stated change/mol			+0.90		
Implied change/mol	-0.60	-0.30	+0.90	+0.60	
Equilibrium amounts/mol	0.40	1.70	0.90	1.60	4.60
Mole fractions	0.087	0.370	0.196	0.348	1.001

(a) The mole fractions are given in the table.

(b) $K_x = \prod_j x_j^{\nu_j}$ [analogous to eqn 7.16 and *Illustration 7.5*],

$$K_x = \frac{(0.196)^3 \times (0.348)^2}{(0.087)^2 \times (0.370)} = 0.326 = \boxed{0.33}$$

(c) $p_J = x_J p$, $p = 1 \text{ bar}$, $p^\ominus = 1 \text{ bar}$.

Assuming that the gases are perfect, $a_J = \frac{p_J}{p^\ominus}$; hence

$$K = \frac{(p_C/p^\ominus)^3 \times (p_D/p^\ominus)^2}{(p_A/p^\ominus)^2 \times (p_B/p^\ominus)}$$

$$= \frac{x_C^3 x_D^2}{x_A^2 x_B} \times \left(\frac{p}{p^\ominus}\right)^2 = K_x \quad \text{when } p = 1.00 \text{ bar} = \boxed{0.33}$$

(d) $\Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 0.326)$
 $= \boxed{+2.8 \times 10^3 \text{ J mol}^{-1}}$

5) The standard reaction Gibbs energy of the isomerization of borneol ($C_{10}H_{17}OH$) to isoborneol in the gas phase at 503 K is $+9.4 \text{ kJ mol}^{-1}$. Calculate the reaction Gibbs energy in a mixture consisting of 0.15 mol of borneol and 0.30 mol of isoborneol when the total pressure is 600 Torr.

Let B = borneol and I = isoborneol.

$$\Delta_r G = \Delta G^\ominus + RT \ln Q \quad [7.11], \quad Q = \frac{p_I}{p_B} \quad [7.13(b)].$$

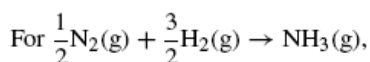
$$p_B = x_B p = \frac{0.15 \text{ mol}}{0.15 \text{ mol} + 0.30 \text{ mol}} \times 600 \text{ Torr} = 200 \text{ Torr}; \quad p_I = p - p_B = 400 \text{ Torr}.$$

$$Q = \frac{400 \text{ Torr}}{200 \text{ Torr}} = 2.00.$$

$$\Delta_r G = (+9.4 \text{ kJ mol}^{-1}) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (503 \text{ K}) \times (\ln 2.00) = \boxed{+12.3 \text{ kJ mol}^{-1}}.$$

6) The standard Gibbs energy of formation of $NH_3(g)$ is $-16.5 \text{ kJ mol}^{-1}$ at 298 K. What is the reaction Gibbs energy when the partial pressure of the N_2 , H_2 , and NH_3 (treated as perfect gases) are 3.0 bar, 1.0 bar, and 4.0 bar, respectively? What is the spontaneous direction of the reaction in this case?

$$\Delta_r G = \Delta G^\ominus + RT \ln Q \quad [7.11]; \quad Q = \prod_J a_J^{n_J} \quad [7.13(b)].$$



$$Q = \frac{\left(\frac{p(NH_3)}{p^\ominus}\right)}{\left(\frac{p(N_2)}{p^\ominus}\right)^{1/2} \left(\frac{p(H_2)}{p^\ominus}\right)^{3/2}} \quad \left[a_J = \frac{p_J}{p^\ominus} \text{ for perfect gases} \right]$$

$$= \frac{p(NH_3)p^\ominus}{p(N_2)^{1/2} p(H_2)^{3/2}} = \frac{4.0}{(3.0)^{1/2} \times (1.0)^{3/2}} = \frac{4.0}{\sqrt{3.0}}.$$

Therefore, $\Delta_r G = (-16.45 \text{ kJ mol}^{-1}) + RT \ln \frac{4.0}{\sqrt{3.0}} = (-16.45 \text{ kJ mol}^{-1}) + (2.07 \text{ kJ mol}^{-1})$

$$= \boxed{-14.38 \text{ kJ mol}^{-1}}$$

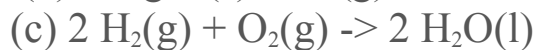
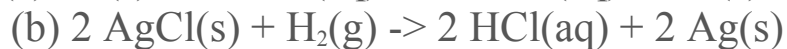
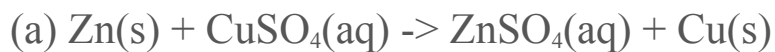
Since $\Delta_r G < 0$, the spontaneous direction of reaction is $\boxed{\text{toward products}}$.

7) Write the cell reaction and electrode half-reactions and calculate the standard emf of each the following cells:



		E^\ominus
(a)	R: $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s})$	$+0.80\text{V}$
	L: $\text{Zn}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76V
	Overall (R - L): $2\text{Ag}^+(\text{aq}) + \text{Zn}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Zn}^{2+}(\text{aq})$	$+1.56\text{V}$
(b)	R: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
	L: $\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40V
	Overall (R - L) : $\text{Cd}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Cd}^{2+}(\text{aq}) + \text{H}_2(\text{g})$	$+0.40\text{V}$
(c)	R: $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74V
	L: $3[\text{Fe}(\text{CN})_6]^{3-}(\text{aq}) + 3\text{e}^- \rightarrow 3[\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$	$+0.36\text{V}$
	Overall (R - L) : $\text{Cr}^{3+}(\text{aq}) + 3[\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) \rightarrow \text{Cr}(\text{s}) + 3[\text{Fe}(\text{CN})_6]^{3-}(\text{aq})$	-1.10V

8) Devise cells in which the following are the reactions and calculate the standard emf in each case:



	E^\ominus
(a) R: $2\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$	$\overline{+0.34\text{V}}$
L: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}$	-0.76 V
Hence the cell is $\text{Zn(s)} \text{ZnSO}_4(\text{aq}) \text{CuSO}_4(\text{aq}) \text{Cu(s)}$	+1.10 V
(b) R: $\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq})$	+0.22 V
L: $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g})$	0
and the cell is $\text{Pt} \text{H}_2(\text{g}) \text{H}^+(\text{aq}) \text{AgCl(s)} \text{Ag(s)}$	
or $\text{Pt} \text{H}_2(\text{g}) \text{HCl(aq)} \text{AgCl(s)} \text{Ag(s)}$	+0.22 V
(c) R: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$	+1.23 V
L: $4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2(\text{g})$	0
and the cell is $\text{Pt} \text{H}_2(\text{g}) \text{H}^+(\text{aq}), \text{H}_2\text{O(l)} \text{O}_2(\text{g}) \text{Pt}$	+1.23 V