

9 Chemical equilibrium

Solutions to exercises

Discussion questions

- E9.1(b)** The thermodynamic equilibrium constant involves activities rather than pressures. See eqn 9.18 and Example 9.1. For systems involving gases, the activities are the dimensionless fugacities. At low pressures, the fugacity may be replaced with pressures with little error, but at high pressures that is not a good approximation. The difference between the equilibrium constant expressed in activities and the constant expressed in pressures is dependent upon two factors: the stoichiometry of the reaction and the magnitude of the partial pressures. Thus there is no one answer to this question. For the example of the ammonia synthesis reaction, in a range of pressures where the fugacity coefficients are greater than one, an increase in pressure results in a greater shift to the product side than would be predicted by the constant expressed in partial pressures. For an exothermic reaction, such as the ammonia synthesis, an increase in temperature will shift the reaction to the reactant side, but the relative shift is independent of the fugacity coefficients. The ratio $\ln(K_2/K_1)$ depends only on $\Delta_r H$. See eqn 6.26.
- E9.2(b)** The physical basis of the dependence of the equilibrium constant on temperature as predicted by the van't Hoff equation can be seen when the expression $\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$ is written in the form $R \ln K = -\Delta_r H^\ominus/T + \Delta_r S^\ominus$. When the reaction is exothermic and the temperature is raised, $\ln K$ and hence K decrease, since T occurs in the denominator, and the reaction shifts to favor the reactants. When the reaction is endothermic, increasing T makes $\ln K$ less negative, or K more positive, and products are favored. Another factor of importance when the reaction is endothermic is the increasing entropy of the reacting system resulting in a more positive $\ln K$, favoring products.
- E9.3(b)** A typical pH curve for the titration of a weak base with a strong acid is shown in Figure 9.1. The stoichiometric point S occurs on the acidic side of $\text{pH} = 7$ because the salt formed by the neutralization reaction has an acid cation.
- E9.4(b)** Buffers work best when $S \approx A'$, that is when the concentrations of the salt and acid are not widely different. An abundant supply of A^- ions can remove by reaction any H_3O^+ supplied by the addition of an acid; likewise an abundant supply of HA can remove by reaction any OH^- supplied by addition of base.
- Indicators are weak acids which in their undissociated acid form have one colour, and in their dissociated anion form, another. In acidic solution, the indicator exists in the predominantly acid form (one colour), in basic solution in the predominantly anion form (the other colour). The ratio of the two forms is very pH sensitive because of the small value of $\text{p}K_a$ of the indicator, so the colour change can occur very rapidly with change in pH.

Numerical exercises

E9.5(b)
$$\Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1600 \text{ K}) \times \ln(0.255)$$
$$= +18.177 \text{ kJ mol}^{-1} = \boxed{+18.18 \text{ kJ mol}^{-1}}$$

E9.6(b)
$$\Delta_r G^\ominus = -RT \ln K$$
$$K = e^{-(\Delta_r G^\ominus/RT)} = \exp \left\{ -\frac{(0.178 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1173 \text{ K})} \right\}$$
$$= 0.982 = \boxed{0.98}$$

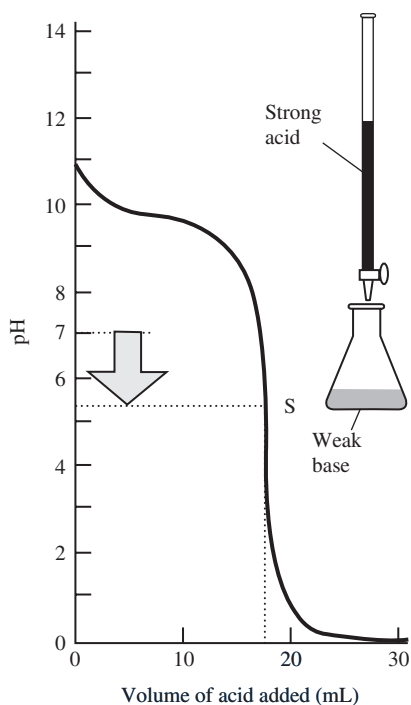
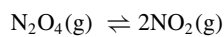


Figure 9.1

E9.7(b)



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

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

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

For $p = p^\ominus$, $K = \frac{4\alpha^2}{1 - \alpha^2}$

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

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

(c) $\Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.16841)$
 $= \boxed{4.41 \text{ kJ mol}^{-1}}$

E9.8(b)

(a) $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g}) \quad \alpha = 0.24$

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

Assuming both gases are perfect $a_J = \frac{p_J}{p^\ominus}$

$$K = \frac{(p_{\text{Br}}/p^\ominus)^2}{p_{\text{Br}_2}/p^\ominus} = \frac{4\alpha^2 p}{(1-\alpha^2)p^\ominus} = \frac{4\alpha^2}{1-\alpha^2} \quad [p = p^\ominus]$$

$$= \frac{4(0.24)^2}{1-(0.24)^2} = 0.244\bar{5} = \boxed{0.24}$$

$$\text{(b)} \quad \Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1600 \text{ K}) \times \ln(0.244\bar{5})$$

$$= \boxed{19 \text{ kJ mol}^{-1}}$$

$$\text{(c)} \quad \ln K(2273 \text{ K}) = \ln K(1600 \text{ K}) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{2273 \text{ K}} - \frac{1}{1600 \text{ K}} \right)$$

$$= \ln(0.244\bar{5}) - \left(\frac{112 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-1.851 \times 10^{-4})$$

$$= 1.08\bar{4}$$

$$K(2273 \text{ K}) = e^{1.08\bar{4}} = \boxed{2.96}$$

E9.9(b) $\nu(\text{CHCl}_3) = 1, \quad \nu(\text{HCl}) = 3, \quad \nu(\text{CH}_4) = -1, \quad \nu(\text{Cl}_2) = -3$

$$\text{(a)} \quad \Delta_r G^\ominus = \Delta_f G^\ominus(\text{CHCl}_3, \text{l}) + 3\Delta_f G^\ominus(\text{HCl}, \text{g}) - \Delta_f G^\ominus(\text{CH}_4, \text{g})$$

$$= (-73.66 \text{ kJ mol}^{-1}) + (3) \times (-95.30 \text{ kJ mol}^{-1}) - (-50.72 \text{ kJ mol}^{-1})$$

$$= \boxed{-308.84 \text{ kJ mol}^{-1}}$$

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} [8] = \frac{-(-308.84 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} = 124.58\bar{4}$$

$$K = \boxed{1.3 \times 10^{54}}$$

$$\text{(b)} \quad \Delta_r H^\ominus = \Delta_f H^\ominus(\text{CHCl}_3, \text{l}) + 3\Delta_f H^\ominus(\text{HCl}, \text{g}) - \Delta_f H^\ominus(\text{CH}_4, \text{g})$$

$$= (-134.47 \text{ kJ mol}^{-1}) + (3) \times (-92.31 \text{ kJ mol}^{-1}) - (-74.81 \text{ kJ mol}^{-1})$$

$$= -336.59 \text{ kJ mol}^{-1}$$

$$\ln K(50^\circ\text{C}) = \ln K(25^\circ\text{C}) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{323.2 \text{ K}} - \frac{1}{298.2 \text{ K}} \right) [9.28]$$

$$= 124.58\bar{4} - \left(\frac{-336.59 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-2.594 \times 10^{-4} \text{ K}^{-1}) = 114.08\bar{3}$$

$$K(50^\circ\text{C}) = \boxed{3.5 \times 10^{49}}$$

$$\Delta_r G^\ominus(50^\circ\text{C}) = -RT \ln K(50^\circ\text{C}) [18] = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (323.15 \text{ K}) \times (114.08\bar{3})$$

$$= \boxed{-306.52 \text{ kJ mol}^{-1}}$$

E9.10(b) Draw up the following table

	A	+	B	\rightleftharpoons	C	+	2D	Total
Initial amounts/mol	2.00		1.00		0		3.00	6.00
Stated change/mol					+0.79			
Implied change/mol	-0.79		-0.79		+0.79		+1.58	
Equilibrium amounts/mol	1.21		0.21		0.79		4.58	6.79
Mole fractions	0.178 $\bar{2}$		0.030 $\bar{9}$		0.116 $\bar{3}$		0.674 $\bar{5}$	0.9999

(a) Mole fractions are given in the table.

$$(b) \quad K_x = \prod_{\text{J}} x_{\text{J}}^{\nu_{\text{J}}}$$

$$K_x = \frac{(0.1163) \times (0.6745)^2}{(0.1782) \times (0.0309)} = \boxed{9.6}$$

(c) $p_{\text{J}} = x_{\text{J}} p$. Assuming the gases are perfect, $a_{\text{J}} = \frac{p_{\text{J}}}{p^{\ominus}}$, so

$$K = \frac{(p_{\text{C}}/p^{\ominus}) \times (p_{\text{D}}/p^{\ominus})^2}{(p_{\text{A}}/p^{\ominus}) \times (p_{\text{B}}/p^{\ominus})} = K_x \left(\frac{p}{p^{\ominus}} \right) = K_x \quad \text{when } p = 1.00 \text{ bar}$$

$$K = K_x = \boxed{9.6}$$

$$(d) \quad \Delta_{\text{r}} G^{\ominus} = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(9.609) \\ = \boxed{-5.6 \text{ kJ mol}^{-1}}$$

E9.11(b) At 1120 K, $\Delta_{\text{r}} G^{\ominus} = +22 \times 10^3 \text{ J mol}^{-1}$

$$\ln K(1120 \text{ K}) = \frac{-\Delta_{\text{r}} G^{\ominus}}{RT} = -\frac{(22 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1120 \text{ K})} = -2.363$$

$$K = e^{-2.363} = 9.41 \times 10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_{\text{r}} H^{\ominus}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Solve for T_2 at $\ln K_2 = 0$ ($K_2 = 1$)

$$\frac{1}{T_2} = \frac{R \ln K_1}{\Delta_{\text{r}} H^{\ominus}} + \frac{1}{T_1} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-2.363)}{(125 \times 10^3 \text{ J mol}^{-1})} + \frac{1}{1120 \text{ K}} = 7.36 \times 10^{-4}$$

$$T_2 = \boxed{1.4 \times 10^3 \text{ K}}$$

E9.12(b) Use $\frac{d(\ln K)}{d(1/T)} = \frac{-\Delta_{\text{r}} H^{\ominus}}{R}$

$$\text{We have } \ln K = -2.04 - 1176 \text{ K} \left(\frac{1}{T} \right) + 2.1 \times 10^7 \text{ K}^3 \left(\frac{1}{T} \right)^3$$

$$-\frac{\Delta_{\text{r}} H^{\ominus}}{R} = -1176 \text{ K} + 3 \times (2.1 \times 10^7 \text{ K}^3) \times \left(\frac{1}{T} \right)^2$$

$T = 450 \text{ K}$ so

$$-\frac{\Delta_{\text{r}} H^{\ominus}}{R} = -1176 \text{ K} + 3 \times (2.1 \times 10^7 \text{ K}^3) \times \left(\frac{1}{450 \text{ K}} \right)^2 = -865 \text{ K}$$

$$\Delta_{\text{r}} H^{\ominus} = +(865 \text{ K}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = \boxed{7.191 \text{ kJ mol}^{-1}}$$

Find $\Delta_r S^\ominus$ from $\Delta_r G^\ominus$

$$\begin{aligned}\Delta_r G^\ominus &= -RT \ln K \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K}) \times \left\{ -2.04 - \frac{1176 \text{ K}}{450 \text{ K}} + \frac{2.1 \times 10^7 \text{ K}^3}{(450 \text{ K})^3} \right\} \\ &= 16.55 \text{ kJ mol}^{-1} \\ \Delta_r G^\ominus &= \Delta_r H^\ominus - T \Delta_r S^\ominus \\ \Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{7.191 \text{ kJ mol}^{-1} - 16.55 \text{ kJ mol}^{-1}}{450 \text{ K}} = -20.79 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= \boxed{-21 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

E9.13(b) $\text{U(s)} + \frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{UH}_3(\text{s}), \quad \Delta_r G^\ominus = -RT \ln K$

At this low pressure, hydrogen is nearly a perfect gas, $a(\text{H}_2) = \left(\frac{p}{p^\ominus}\right)$. The activities of the solids are 1.

$$\text{Hence, } \ln K = \ln \left(\frac{p}{p^\ominus} \right)^{-3/2} = -\frac{3}{2} \ln \frac{p}{p^\ominus}$$

$$\begin{aligned}\Delta_r G^\ominus &= \frac{3}{2} RT \ln \frac{p}{p^\ominus} \\ &= \left(\frac{3}{2} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K}) \times \ln \left(\frac{1.04 \text{ Torr}}{750 \text{ Torr}} \right) \\ &\quad [p^\ominus = 1 \text{ bar} \approx 750 \text{ Torr}] \\ &= \boxed{-41.0 \text{ kJ mol}^{-1}}\end{aligned}$$

E9.14(b) $K_x = \prod_{\text{J}} x_{\text{J}}^{\nu_{\text{J}}}$ [analogous to 17]

The relation of K_x to K is established in *Illustration 9.4*

$$\begin{aligned}K &= \prod_{\text{J}} \left(\frac{p_{\text{J}}}{p^\ominus} \right)^{\nu_{\text{J}}} \left[9.18 \text{ with } a_{\text{J}} = \frac{p_{\text{J}}}{p^\ominus} \right] \\ &= \prod_{\text{J}} x_{\text{J}}^{\nu_{\text{J}}} \times \left(\frac{p}{p^\ominus} \right)^{\sum_{\text{J}} \nu_{\text{J}}} [p_{\text{J}} = x_{\text{J}} p] = K_x \times \left(\frac{p}{p^\ominus} \right)^{\nu} \left[\nu \equiv \sum_{\text{J}} \nu_{\text{J}} \right]\end{aligned}$$

Therefore, $K_x = K \left(\frac{p}{p^\ominus} \right)^{-\nu}$, $K_x \propto p^{-\nu}$ [K and p^\ominus are constants]

$$\nu = 1 + 1 - 1 - 1 = 0, \quad \text{thus } \boxed{K_x(2 \text{ bar}) = K_x(1 \text{ bar})}$$

E9.15(b) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) \quad K = 1.69 \times 10^{-3}$ at 2300 K

$$\text{Initial moles N}_2 = \frac{5.0 \text{ g}}{28.01 \text{ g mol}^{-1}} = 0.2380 \text{ mol N}_2$$

$$\text{Initial moles O}_2 = \frac{2.0 \text{ g}}{32.00 \text{ g mol}^{-1}} = 6.250 \times 10^{-2} \text{ mol O}_2$$

	N ₂	O ₂	NO	Total
Initial amount/mol	0.2380	0.0625	0	0.300
Change/mol	-z	-z	+2z	0
Equilibrium amount/mol	0.2380 - z	0.0625 - z	2z	0.300
Mole fractions	$\frac{0.2380 - z}{0.300}$	$\frac{0.0625 - z}{0.300}$	$\frac{2z}{0.300}$	(1)

$$K = K_x \left(\frac{p}{p^\ominus} \right)^\nu \left[\nu = \sum_J \nu_J = 0 \right], \text{ then}$$

$$K = K_x = \frac{(2z/0.300)^2}{\left(\frac{0.2380-z}{0.300} \right) \times \left(\frac{0.0625-z}{0.300} \right)}$$

$$= \frac{4z^2}{(0.2380 - z) \times (0.0625 - z)} = 1.69 \times 10^{-3}$$

$$4z^2 = 1.69 \times 10^{-3} \left\{ 0.01488 - 0.3005z + z^2 \right\}$$

$$= 2.514 \times 10^{-5} - (5.078 \times 10^{-4})z + (1.69 \times 10^{-3})z^2$$

$$4.00 - 1.69 \times 10^{-3} = 4.00 \quad \text{so}$$

$$4z^2 + (5.078 \times 10^{-4})z - 2.514 \times 10^{-5} = 0$$

$$z = \frac{-5.078 \times 10^{-4} \pm \left\{ (5.078 \times 10^{-4})^2 - 4 \times (4) \times (-2.514 \times 10^{-5}) \right\}^{1/2}}{8}$$

$$= \frac{1}{8}(-5.078 \times 10^{-4} \pm 2.006 \times 10^{-2})$$

$$z > 0 \quad [z < 0 \text{ is physically impossible}] \quad \text{so}$$

$$z = 2.444 \times 10^{-3}$$

$$x_{\text{NO}} = \frac{2z}{0.300} = \frac{2(2.444 \times 10^{-3})}{0.300} = \boxed{1.6 \times 10^{-2}}$$

E9.16(b) $\Delta_r G^\ominus = -RT \ln K$ [9.8]

Hence, a value of $\Delta_r G^\ominus < 0$ at 298 K corresponds to $K > 1$.

(a) $\Delta_r G^\ominus / (\text{kJ mol}^{-1}) = (2) \times (-33.56) - (-166.9) = +99.8, \quad K < 1$

(b) $\Delta_r G^\ominus / (\text{kJ mol}^{-1}) = (-690.00) - (-33.56) - (2) \times (-120.35) = -415.74, \quad \boxed{K > 1}$

E9.17(b) Le Chatelier's principle in the form of the rules in the first paragraph of Section 9.4 is employed. Thus we determine whether $\Delta_r H^\ominus$ is positive or negative using the $\Delta_f H^\ominus$ values of Table 2.6.

(a) $\Delta_r H^\ominus / (\text{kJ mol}^{-1}) = (2) \times (-20.63) - (-178.2) = +136.9$

(b) $\Delta_r H^\ominus / (\text{kJ mol}^{-1}) = (-813.99) - (-20.63) - (2) \times (-187.78) = -417.80$

Since (a) is endothermic, an increase in temperature favours the products, which implies that a reduction in temperature favours the reactants; since (b) is exothermic, an increase in temperature favours the reactants, which implies that a reduction in temperature favours the products (in the sense of K increasing).

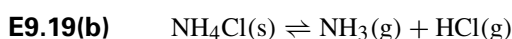
$$\text{E9.18(b)} \quad \ln \frac{K'}{K} = \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T} - \frac{1}{T'} \right) \quad \text{so} \quad \Delta_r H^\ominus = \frac{R \ln \left(\frac{K'}{K} \right)}{\left(\frac{1}{T} - \frac{1}{T'} \right)}$$

$$T = 310 \text{ K}, \quad T' = 325 \text{ K}; \quad \text{let } \frac{K'}{K} = \kappa$$

$$\text{Now } \Delta_r H^\ominus = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}{\left(\frac{1}{310 \text{ K}} - \frac{1}{325 \text{ K}} \right)} \times \ln \kappa = 55.84 \text{ kJ mol}^{-1} \ln \kappa$$

$$\text{(a)} \quad \kappa = 2, \quad \Delta_r H^\ominus = (55.84 \text{ kJ mol}^{-1}) \times (\ln 2) = \boxed{39 \text{ kJ mol}^{-1}}$$

$$\text{(b)} \quad \kappa = \frac{1}{2}, \quad \Delta_r H^\ominus = (55.84 \text{ kJ mol}^{-1}) \times \left(\ln \frac{1}{2} \right) = \boxed{-39 \text{ kJ mol}^{-1}}$$



$$p = p(\text{NH}_3) + p(\text{HCl}) = 2p(\text{NH}_3) \quad [p(\text{NH}_3) = p(\text{HCl})]$$

$$\text{(a)} \quad K = \prod_{\text{J}} a_{\text{J}}^{\nu_{\text{J}}} [17]; \quad a(\text{gases}) = \frac{p_{\text{J}}}{p^\ominus}; \quad a(\text{NH}_4\text{Cl, s}) = 1$$

$$K = \left(\frac{p(\text{NH}_3)}{p^\ominus} \right) \times \left(\frac{p(\text{HCl})}{p^\ominus} \right) = \frac{p(\text{NH}_3)^2}{p^{\ominus 2}} = \frac{1}{4} \times \left(\frac{p}{p^\ominus} \right)^2$$

$$\text{At } 427^\circ\text{C (700 K)}, \quad K = \frac{1}{4} \times \left(\frac{608 \text{ kPa}}{100 \text{ kPa}} \right)^2 = \boxed{9.24}$$

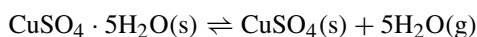
$$\text{At } 459^\circ\text{C (732 K)}, \quad K = \frac{1}{4} \times \left(\frac{1115 \text{ kPa}}{100 \text{ kPa}} \right)^2 = 31.08$$

$$\text{(b)} \quad \Delta_r G^\ominus = -RT \ln K [8] = (-8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (700 \text{ K}) \times (\ln 9.24) \\ = \boxed{-12.9 \text{ kJ mol}^{-1}} \quad (\text{at } 427^\circ\text{C})$$

$$\text{(c)} \quad \Delta_r H^\ominus \approx \frac{R \ln \frac{K'}{K}}{\left(\frac{1}{T} - \frac{1}{T'} \right)} [26] \\ \approx \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{31.08}{9.24} \right)}{\left(\frac{1}{700 \text{ K}} - \frac{1}{732 \text{ K}} \right)} = \boxed{+161 \text{ kJ mol}^{-1}}$$

$$\text{(d)} \quad \Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{(161 \text{ kJ mol}^{-1}) - (-12.9 \text{ kJ mol}^{-1})}{700 \text{ K}} = \boxed{+248 \text{ J K}^{-1} \text{ mol}^{-1}}$$

E9.20(b) The reaction is

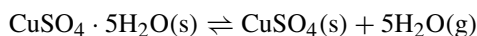


For the purposes of this exercise we may assume that the required temperature is that temperature at which the $K = 1$ which corresponds to a pressure of 1 bar for the gaseous products. For $K = 1$, $\ln K = 0$, and $\Delta_r G^\ominus = 0$.

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = 0 \quad \text{when } \Delta_r H^\ominus = T \Delta_r S^\ominus$$

Therefore, the decomposition temperature (when $K = 1$) is

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus}$$



$$\Delta_r H^\ominus = [(-771.36) + (5) \times (-241.82) - (-2279.7)] \text{kJ mol}^{-1} = +299.2 \text{kJ mol}^{-1}$$

$$\Delta_r S^\ominus = [(109) + (5) \times (188.83) - (300.4)] \text{J K}^{-1} \text{mol}^{-1} = 752.8 \text{J K}^{-1} \text{mol}^{-1}$$

$$\text{Therefore, } T = \frac{299.2 \times 10^3 \text{J mol}^{-1}}{752.8 \text{J K}^{-1} \text{mol}^{-1}} = \boxed{397 \text{K}}$$

Question. What would the decomposition temperature be for decomposition defined as the state at which $K = \frac{1}{2}$?

E9.21(b) (a) The half-way point corresponds to the condition

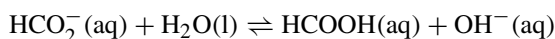
$$[\text{acid}] = [\text{salt}], \quad \text{for which } \text{pH} = \text{p}K_a$$

$$\text{Thus } \text{p}K_a = 4.82 \text{ and } K_a = 10^{-4.82} = \boxed{1.5 \times 10^{-5}}$$

(b) When $[\text{acid}] = 0.025 \text{M}$

$$\text{pH} = \frac{1}{2}\text{p}K_a - \frac{1}{2}\log[\text{acid}] = \frac{1}{2}(4.82) - \frac{1}{2}(-1.60) = \boxed{3.21}$$

E9.22(b) (a) The HCO_2^- ion acts as a weak base.



Then, since $[\text{HCOOH}] \approx [\text{OH}^-]$ and $[\text{HCO}_2^-] \approx S$, the nominal concentration of the salt,

$$K_b \approx \frac{[\text{OH}^-]^2}{S} \quad \text{and} \quad [\text{OH}^-] = (SK_b)^{1/2}$$

Therefore $\text{pOH} = \frac{1}{2}\text{p}K_b - \frac{1}{2}\log S$

However, $\text{pH} + \text{pOH} = \text{p}K_w$, so $\text{pH} = \text{p}K_w - \text{pOH}$

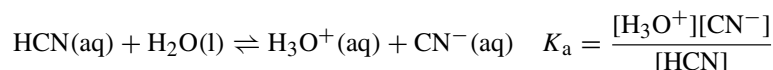
and $\text{p}K_a + \text{p}K_b = \text{p}K_w$, so $\text{p}K_b = \text{p}K_w - \text{p}K_a$

$$\begin{aligned} \text{Thus } \text{pH} &= \text{p}K_w - \frac{1}{2}(\text{p}K_w - \text{p}K_a) + \frac{1}{2}\log S = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log S \\ &= \frac{1}{2}(14.00) + \frac{1}{2}(3.75) + \frac{1}{2}\log(0.10) = \boxed{8.37} \end{aligned}$$

(b) The same expression is obtained

$$\begin{aligned} \text{pH} &= \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log S \\ &= \frac{1}{2}(14.00) + \frac{1}{2}(4.19) + \frac{1}{2}\log(0.20) = \boxed{8.74} \end{aligned}$$

(c) 0.150 M $\text{HCN}(\text{aq})$



Since we can ignore water autoprotolysis, $[\text{H}_3\text{O}^+] = [\text{CN}^-]$, so

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{A}$$

where $A = [\text{HCN}]$, the nominal acid concentration.

Thus $[\text{H}_3\text{O}^+] \approx (AK_a)^{1/2}$ and $\text{pH} \approx \frac{1}{2}\text{p}K_a - \frac{1}{2}\log A$

$$\text{pH} = \frac{1}{2}(9.31) - \frac{1}{2}\log(0.150) = \boxed{5.07}$$

E9.23(b) The pH of a solution in which the nominal salt concentration is S is

$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log S$$

The volume of solution at the stoichiometric point is

$$V = (25.00 \text{ mL}) + (25.00 \text{ mL}) \times \left(\frac{0.100 \text{ M}}{0.175 \text{ M}}\right) = 39.286 \text{ mL}$$

$$S = (0.100 \text{ M}) \times \left(\frac{25.00 \text{ mL}}{39.286 \text{ mL}}\right) = 6.364 \times 10^{-2} \text{ M}$$

$\text{p}K_a = 1.96$ for chlorous acid.

$$\begin{aligned} \text{pH} &= \frac{1}{2}(14.00) + \frac{1}{2}(1.96) + \frac{1}{2}\log(6.364 \times 10^{-2}) \\ &= \boxed{7.38} \end{aligned}$$

E9.24(b) When only the salt is present, use $\text{pH} = \frac{1}{2}\text{p}K_a + \frac{1}{2}\text{p}K_w + \frac{1}{2}\log S$

$$\text{pH} = \frac{1}{2}(4.19) + \frac{1}{2}(14.00) + \frac{1}{2}\log(0.15) = 8.68 \quad (\text{a})$$

When $A \approx S$, use the Henderson–Hasselbalch equation

$$\text{pH} = \text{p}K_a - \log \frac{A}{S} = 4.19 - \log \frac{A}{0.15} = 3.366 - \log A \quad (\text{b})$$

When so much acid has been added that $A \gg S$, use

$$\text{pH} = \frac{1}{2}\text{p}K_a - \frac{1}{2}\log A \quad (\text{c})$$

We can make up a table of values

$A/(\text{mol L}^{-1})$	0	0.06	0.08	0.10	0.12	0.14	0.6	0.8	1.0
pH	8.68	4.59	4.46	4.36	4.29	4.21	2.21	2.14	2.09
Formula	(a)	(b)				(c)			

These values are plotted in Fig. 9.2.

E9.25(b) According to the Henderson–Hasselbalch equation the pH of a buffer varies about a central value given by $\text{p}K_a$. For the $\frac{[\text{acid}]}{[\text{salt}]}$ ratio to be neither very large nor very small we require $\text{p}K_a \approx \text{pH}$ (buffer)

(a) For $\text{pH} = 4.6$, use aniline and anilinium ion, $\text{p}K_a = 4.63$.

(b) For $\text{pH} = 10.8$, use ethylammonium ion and ethylamine, $\text{p}K_a = 10.81$

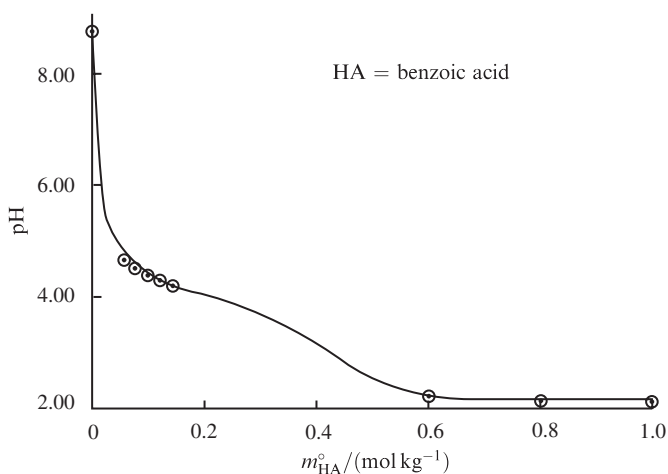
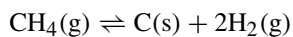


Figure 9.2

Solutions to problems

Solutions to numerical problems

P9.2



This reaction is the reverse of the formation reaction.

(a) $\Delta_r G^\ominus = -\Delta_f G^\ominus$
 $\Delta_f G^\ominus = \Delta_f H^\ominus - T \Delta_f S^\ominus$
 $= -74\,850 \text{ J mol}^{-1} - 298 \text{ K} \times (-80.67 \text{ J K}^{-1} \text{ mol}^{-1})$
 $= -5.08 \times 10^4 \text{ J mol}^{-1}$
 $\ln K = \frac{\Delta_r G^\ominus}{-RT} [9.8] = \frac{5.08 \times 10^4 \text{ J mol}^{-1}}{-8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = -20.508$
 $K = \boxed{1.24 \times 10^{-9}}$

(b) $\Delta_r H^\ominus = -\Delta_f H^\ominus = 74.85 \text{ kJ mol}^{-1}$
 $\ln K(50^\circ\text{C}) = \ln K(298 \text{ K}) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right) [9.28]$
 $= -20.508 - \left(\frac{7.4850 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-2.597 \times 10^{-4}) = -18.170$
 $K(50^\circ\text{C}) = \boxed{1.29 \times 10^{-8}}$

(c) Draw up the equilibrium table

	$\text{CH}_4(\text{g})$	$\text{H}_2(\text{g})$
Amounts	$(1 - \alpha)n$	$2\alpha n$
Mole fractions	$\frac{1 - \alpha}{1 + \alpha}$	$\frac{2\alpha}{1 + \alpha}$
Partial pressures	$\left(\frac{1 - \alpha}{1 + \alpha} \right) p$	$\frac{2\alpha p}{1 + \alpha}$

$$K = \prod_J a_J^{\nu_J} [9.18] = \frac{\left(\frac{p_{\text{H}_2}}{p^\ominus}\right)^2}{\left(\frac{p_{\text{CH}_4}}{p^\ominus}\right)}$$

$$1.24 \times 10^{-9} = \frac{(2\alpha)^2}{1 - \alpha^2} \left(\frac{p}{p^\ominus}\right) \approx 4\alpha^2 p \quad [\alpha \ll 1]$$

$$\alpha = \frac{1.24 \times 10^{-9}}{4 \times 0.010} = \boxed{1.8 \times 10^{-4}}$$

(d) Le Chatelier's principle provides the answers:

As pressure increases, α decreases, since the more compact state (less moles of gas) is favoured at high pressures. As temperature increases the side of the reaction which can absorb heat is favoured. Since $\Delta_r H^\ominus$ is positive, that is the right-hand side, hence α increases. This can also be seen from the results of parts (a) and (b), K increased from 25°C to 50°C, implying that α increased.

P9.3 $\text{U(s)} + \frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{UH}_3(\text{s}) \quad K = (p/p^\ominus)^{-3/2}$ [Exercise 9.13(b)]

$$\begin{aligned} \Delta_f H^\ominus &= RT^2 \frac{d \ln K}{dT} [9.26] = RT^2 \frac{d}{dT} \left(-\frac{3}{2} \ln p/p^\ominus \right) \\ &= -\frac{3}{2} RT^2 \frac{d \ln p}{dT} \\ &= -\frac{3}{2} RT^2 \left(\frac{14.64 \times 10^3 \text{ K}}{T^2} - \frac{5.65}{T} \right) \\ &= -\frac{3}{2} R(14.64 \times 10^3 \text{ K} - 5.65T) \\ &= \boxed{-(2.196 \times 10^4 \text{ K} - 8.48T)R} \end{aligned}$$

$$d(\Delta_f H^\ominus) = \Delta_r C_p^\ominus dT \quad [\text{from 2.44}]$$

$$\text{or } \Delta_r C_p^\ominus = \left(\frac{\partial \Delta_f H^\ominus}{\partial T} \right)_p = \boxed{8.48R}$$

P9.5 $\text{CaCl}_2 \cdot \text{NH}_3(\text{s}) \rightleftharpoons \text{CaCl}_2(\text{s}) + \text{NH}_3(\text{g}) \quad K = \frac{p}{p^\ominus}$

$$\begin{aligned} \Delta_r G^\ominus &= -RT \ln K = -RT \ln \frac{p}{p^\ominus} \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln \left(\frac{12.8 \text{ Torr}}{750 \text{ Torr}} \right) \quad [p^\ominus = 1 \text{ bar} = 750.3 \text{ Torr}] \\ &= +13.5 \text{ kJ mol}^{-1} \quad \text{at } 400 \text{ K} \end{aligned}$$

Since $\Delta_r G^\ominus$ and $\ln K$ are related as above, the dependence of $\Delta_r G^\ominus$ on temperature can be determined from the dependence of $\ln K$ on temperature.

$$\frac{\Delta_r G^\ominus(T)}{T} - \frac{\Delta_r G^\ominus(T')}{T'} = \Delta_r H^\ominus \left(\frac{1}{T} - \frac{1}{T'} \right) [26]$$

Therefore, taking $T' = 400$ K,

$$\begin{aligned}\Delta_r G^\ominus(T) &= \left(\frac{T}{400 \text{ K}}\right) \times (13.5 \text{ kJ mol}^{-1}) + (78 \text{ kJ mol}^{-1}) \times \left(1 - \frac{T}{400 \text{ K}}\right) \\ &= (78 \text{ kJ mol}^{-1}) + \left(\frac{(13.5 - 78) \text{ kJ mol}^{-1}}{400}\right) \times \left(\frac{T}{\text{K}}\right)\end{aligned}$$

That is, $\Delta_r G^\ominus(T)/(\text{kJ mol}^{-1}) = \boxed{78 - 0.161(T/\text{K})}$

P9.7

The equilibrium we need to consider is $\text{A}_2(\text{g}) \rightleftharpoons 2\text{A}(\text{g})$. A = acetic acid

It is convenient to express the equilibrium constant in terms of α , the degree of dissociation of the dimer, which is the predominant species at low temperatures.

	A	A ₂	Total
At equilibrium	$2\alpha n$	$(1 - \alpha)n$	$(1 + \alpha)n$
Mole fraction	$\frac{2\alpha}{1 + \alpha}$	$\frac{1 - \alpha}{1 + \alpha}$	1
Partial pressure	$\frac{2\alpha p}{1 + \alpha}$	$\left(\frac{1 - \alpha}{1 + \alpha}\right)p$	p

The equilibrium constant for the dissociation is

$$K_p = \frac{\left(\frac{p_A}{p^\ominus}\right)^2}{\frac{p_{A_2}}{p^\ominus}} = \frac{p_A^2}{p_{A_2} p^\ominus} = \frac{4\alpha^2 \left(\frac{p}{p^\ominus}\right)}{1 - \alpha^2}$$

We also know that

$$pV = n_{\text{total}} RT = (1 + \alpha)n RT, \quad \text{implying that } \alpha = \frac{pV}{nRT} - 1 \quad \text{and} \quad n = \frac{m}{M}$$

In the first experiment,

$$\alpha = \frac{pVM}{mRT} - 1 = \frac{(764.3 \text{ Torr}) \times (21.45 \times 10^{-3} \text{ L}) \times (120.1 \text{ g mol}^{-1})}{(0.0519 \text{ g}) \times (62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}) \times (437 \text{ K})} - 1 = 0.392$$

$$\text{Hence, } K = \frac{(4) \times (0.392)^2 \times \left(\frac{764.3}{750.1}\right)}{1 - (0.392)^2} = \boxed{0.740}$$

In the second experiment,

$$\alpha = \frac{pVM}{mRT} - 1 = \frac{(764.3 \text{ Torr}) \times (21.45 \times 10^{-3} \text{ L}) \times (120.1 \text{ g mol}^{-1})}{(0.038 \text{ g}) \times (62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}) \times (471 \text{ K})} - 1 = 0.764$$

$$\text{Hence, } K = \frac{(4) \times (0.764)^2 \times \left(\frac{764.3}{750.1}\right)}{1 - (0.764)^2} = \boxed{5.71}$$

The enthalpy of dissociation is

$$\Delta_r H^\ominus = \frac{R \ln \frac{K'}{K}}{\left(\frac{1}{T} - \frac{1}{T'}\right)} [9.28, \text{ Exercise 9.18(a)}] = \frac{R \ln \left(\frac{5.71}{0.740}\right)}{\left(\frac{1}{437 \text{ K}} - \frac{1}{471 \text{ K}}\right)} = +103 \text{ kJ mol}^{-1}$$

The enthalpy of dimerization is the negative of this value, or $\boxed{-103 \text{ kJ mol}^{-1}}$ (i.e. per mole of dimer).

P9.9 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

The mole fractions are given in the table.

$$K_x = \prod_{\text{J}} x_{\text{J}}^{\nu_{\text{J}}} \quad [\text{analogous to eqn 9.18 and Illustration 9.4}]$$

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

$$p_{\text{J}} = x_{\text{J}} p, \quad p = 1 \text{ bar}, \quad p^{\ominus} = 1 \text{ bar}$$

Assuming that the gases are perfect, $a_{\text{J}} = \frac{p_{\text{J}}}{p^{\ominus}}$, hence

$$K = \frac{(p_{\text{C}}/p^{\ominus})^3 \times (p_{\text{D}}/p^{\ominus})^2}{(p_{\text{A}}/p^{\ominus})^2 \times (p_{\text{B}}/p^{\ominus})}$$

$$= \frac{x_{\text{C}}^3 x_{\text{D}}^2}{x_{\text{A}}^2 x_{\text{B}}} \times \left(\frac{p}{p^{\ominus}}\right)^2 = K_x \quad \text{when } p = 1.00 \text{ bar} = \boxed{0.33}$$

P9.10 The equilibrium $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$ is described by the equilibrium constant

$$K = \frac{x(\text{I})^2}{x(\text{I}_2)} \times \frac{p}{p^{\ominus}} = \frac{4\alpha^2 \left(\frac{p}{p^{\ominus}}\right)}{1 - \alpha^2} \quad [\text{Problem 9.7}]$$

If $p^0 = \frac{nRT}{V}$, then $p = (1 + \alpha)p^0$, implying that

$$\alpha = \frac{p - p^0}{p^0}$$

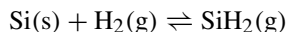
We therefore draw up the following table

	973 K	1073 K	1173 K	
p/atm	0.06244	0.07500	0.09181	
$10^4 n_1$	2.4709	2.4555	2.4366	
p^0/atm	0.05757	0.06309	0.06844	$\left[p^0 = \frac{nRT}{V}\right]$
α	0.08459	0.1888	0.3415	
K	$\boxed{1.800 \times 10^{-3}}$	$\boxed{1.109 \times 10^{-2}}$	$\boxed{4.848 \times 10^{-2}}$	

$$\Delta H^{\ominus} = RT^2 \times \left(\frac{d \ln K}{dT}\right) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1073 \text{ K})^2 \times \left(\frac{-3.027 - (-6.320)}{200 \text{ K}}\right)$$

$$= \boxed{+158 \text{ kJ mol}^{-1}}$$

P9.13 The reaction is



The equilibrium constant is

$$K = \exp\left(\frac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right) \exp\left(\frac{-\Delta_r S^\ominus}{R}\right)$$

Let h be the uncertainty in $\Delta_r H^\ominus$, so that the high value is $h+$ the low value. The K based on the low value is

$$\begin{aligned} K_{\text{low } H} &= \exp\left(\frac{-\Delta_r H_{\text{low}}^\ominus}{RT}\right) \exp\left(\frac{\Delta_r S^\ominus}{R}\right) = \exp\left(\frac{-\Delta_r H_{\text{high}}^\ominus}{RT}\right) \exp\left(\frac{h}{RT}\right) \exp\left(\frac{\Delta_r S^\ominus}{R}\right) \\ &= \exp\left(\frac{h}{RT}\right) K_{\text{high } H} \end{aligned}$$

$$\text{So } \frac{K_{\text{low } H}}{K_{\text{high } H}} = \exp\left(\frac{h}{RT}\right)$$

$$\text{(a) At 298 K, } \frac{K_{\text{low } H}}{K_{\text{high } H}} = \exp\left(\frac{(289 - 243) \text{ kJ mol}^{-1}}{(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}\right) = \boxed{1.2 \times 10^8}$$

$$\text{(b) At 700 K, } \frac{K_{\text{low } H}}{K_{\text{high } H}} = \exp\left(\frac{(289 - 243) \text{ kJ mol}^{-1}}{(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (700 \text{ K})}\right) = \boxed{2.7 \times 10^3}$$

Solutions to theoretical problems

P9.16

$$K = \frac{p(\text{NO}_2)^2}{p(\text{N}_2\text{O}_4)p^\ominus} \quad \text{with } p(\text{NO}_2) + p(\text{N}_2\text{O}_4) = p$$

$$\text{Since } p(\text{NO}_2)^2 + p(\text{NO}_2)K - pK = 0 \quad [p \equiv p/p^\ominus]$$

$$p(\text{NO}_2) = \frac{\left(1 + \frac{4p}{K}\right)^{1/2} - 1}{\left(\frac{2}{K}\right)}$$

We choose the root with the positive sign because p must be positive.

For equal absorptions

$$l_1 p_1(\text{NO}_2) = l_2 p_2(\text{NO}_2), \quad \text{or} \quad \rho p_1 = p_2 \quad [\rho = l_1/l_2]$$

Therefore

$$\rho \left(1 + \frac{4p_1}{K}\right)^{1/2} - \rho = (1 + 4p_2/K)^{1/2} - 1$$

$$\rho \left(1 + \frac{4p_1}{K}\right)^{1/2} = \rho - 1 + \left(1 + \frac{4p_2}{K}\right)^{1/2}$$

$$\rho^2 \left(1 + \frac{4p_1}{K}\right) = (\rho - 1)^2 + \left(1 + \frac{4p_2}{K}\right) + 2(\rho - 1) \times \left(1 + \frac{4p_2}{K}\right)^{1/2}$$

$$\rho - 1 + \frac{2(p_1\rho^2 - p_2)}{K} = (\rho - 1) \times \left(1 + \frac{4p_2}{K}\right)^{1/2}$$

$$\left(\rho - 1 + \frac{2(p_1\rho^2 - p_2)}{K}\right)^2 = (\rho - 1)^2 \times \left(1 + \frac{4p_2}{K}\right)$$

$$\frac{(p_1\rho^2 - p_2)^2}{K^2} + \frac{(\rho - 1) \times (p_1\rho^2 - p_2) - (\rho - 1)^2 p_2}{K} = 0$$

Hence, $K = \frac{(p_1\rho^2 - p_2)^2}{\rho(\rho - 1) \times (p_2 - p_1\rho)p^\ominus}$ [reinstating p^\ominus]

Since $\rho = \frac{395 \text{ mm}}{75 \text{ mm}} = 5.27$

$$p^\ominus K = \frac{(27.8p_1 - p_2)^2}{22.5(p_2 - 5.27p_1)}$$

We can therefore draw up the following table

Absorbance	p_1/Torr	p_2/Torr	$p^\ominus K/\text{Torr}$
0.05	1.00	5.47	110.8
0.10	2.10	12.00	102.5
0.15	3.15	18.65	103.0

Mean: 105

Hence, since $p^\ominus = 750 \text{ Torr (1 bar)}$, $K = \boxed{0.140}$

P9.18

The five conditions are:

(a) Electrical neutrality: $[\text{BH}^+] + [\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-]$

(b) Conservation of B groups: $[\text{B}] + [\text{BH}^+] = \frac{B_0 V_B}{V_A + V_B}$

where V_B is the (fixed) initial volume of base and V_A is the volume of titrant (acid) added.

(c) Concentration of A^- groups: $[\text{A}^-] = \frac{A_0 V_A}{V_A + V_B}$

(d) Protonation equilibrium of B: $[\text{B}]K_b = [\text{BH}^+][\text{OH}^-]$

(e) Autoprotolysis equilibrium: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

First we express condition (b) in terms of $[\text{BH}^+]$ and $[\text{OH}^-]$ by using condition (d) to eliminate $[\text{B}]$

$$[\text{BH}^+] = \frac{B_0 K_b V_B}{(V_A + V_B)([\text{OH}^-] + K_b)}$$

Next we use this relation and condition (c), and at the same time we use condition (e) to eliminate $[\text{H}_3\text{O}^+]$

$$\frac{B_0 K_b V_B}{(V_A + V_B)([\text{OH}^-] + K_b)} + \frac{K_w}{[\text{OH}^-]} = \frac{A_0 V_A}{V_A + V_B} + [\text{OH}^-]$$

Now we multiply through by $\left(\frac{V_A + V_B}{V_B}\right)[\text{OH}^-]$, expand the fraction $\left(\frac{V_A + V_B}{V_B}\right)$, and collect

terms in $\nu = \frac{V_A}{V_B}$ and obtain $\nu = \frac{B_0 K_b [\text{OH}^-] + (K_w - [\text{OH}^-]^2)([\text{OH}^-] + K_b)}{([\text{OH}^-] + K_b)([\text{OH}^-]^2 + A_0 [\text{OH}^-] - K_w)}$

If desired, this formula for ν can be rewritten in terms of $[\text{H}_3\text{O}^+]$ and pH by using relation (e) and the definition $\text{pH} = -\log[\text{H}_3\text{O}^+]$, or $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

Solutions to applications

P9.20

Refer to Box 9.2 for information necessary to the solution of this problem. The biological standard value of the Gibbs energy for ATP hydrolysis is $\approx -30 \text{ kJ mol}^{-1}$. The standard Gibbs energy of combustion of glucose is $-2880 \text{ kJ mol}^{-1}$.

- (a) If we assume that each mole of ATP formed during the aerobic breakdown of glucose produces -30 kJ mol^{-1} , then

$$\text{efficiency} = \frac{38 \times (-30 \text{ kJ mol}^{-1})}{-2880 \text{ kJ mol}^{-1}} \times 100\% \approx \boxed{40\%}$$

- (b) For the oxidation of glucose under the biological conditions of $p_{\text{CO}_2} = 5.3 \times 10^{-2} \text{ atm}$, $p_{\text{O}_2} = 0.132 \text{ atm}$, and $[\text{glucose}] = 5.6 \times 10^{-2} \text{ mol L}^{-1}$ we have

$$\Delta_r G' = \Delta_r G^\ominus + RT \ln Q$$

$$\text{where } Q = \frac{(p_{\text{CO}_2}/p^\ominus)^6}{[\text{glucose}] \times (p_{\text{O}_2}/p^\ominus)^9} = \frac{(5.3 \times 10^{-2})^6}{5.6 \times 10^{-2} \times (0.132)^9} \\ = 32.5$$

Then

$$\Delta_r G' = -2880 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 310 \text{ K} \times \ln(32.5) \\ = \boxed{-2871 \text{ kJ mol}^{-1}}$$

which is not much different from the standard value.

For the ATP \rightarrow ADP conversion under the given conditions

$$\Delta_r G' = \Delta_r G^\oplus + RT \ln \left(\frac{Q'}{Q^\oplus} \right)$$

$$\text{where } Q^\oplus = \frac{[\text{ADP}][\text{Pi}][\text{H}_3\text{O}^+]}{[\text{ATP}]} = \frac{1 \times 1 \times 10^{-7}}{1} = 10^{-7}$$

$$\text{and } Q' = \frac{1.0 \times 10^{-4} \times 1.0 \times 10^{-4} \times 10^{-7.4}}{1.0 \times 10^{-4}} = 10^{-11.4}$$

then

$$\Delta_r G' = -30 \text{ kJ mol}^{-1} + RT \ln(10^{-4.4}) \\ = -30 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 310 \text{ K} \times (-10.1) \\ = \boxed{-56 \text{ kJ mol}^{-1}}$$

With this value for $\Delta_r G'$, the efficiency becomes

$$\text{efficiency} = \frac{38 \times (-56 \text{ kJ mol}^{-1})}{-2871 \text{ kJ mol}^{-1}} = \boxed{74\%}$$

(c) The theoretical limit of the diesel engine is

$$\epsilon = 1 - \frac{T_c}{T_h} = 1 - \frac{873 \text{ K}}{1923 \text{ K}} = 55\%$$

75% of the theoretical limit is 41%.

We see that the biological efficiency under the conditions given is greater than that of the diesel engine. What limits the efficiency of the diesel engine, or any heat engine, is that heat engines must convert heat ($q \approx \Delta_c H$) into useful work ($W_{\text{add,max}} = \Delta_r G$). Because of the second law, a substantial fraction of that heat is wasted. The biological process involves $\Delta_r G$ directly and does not go through a heat step.

P9.22 (a) The equilibrium constant is given by

$$K = \exp\left(\frac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right) \exp\left(\frac{\Delta_r S^\ominus}{R}\right)$$

$$\text{so } \ln K = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}$$

A plot of $\ln K$ against $1/T$ should be a straight line with a slope of $-\Delta_r H^\ominus/R$ and a y-intercept of $\Delta_r S^\ominus/R$ (Fig. 9.3).

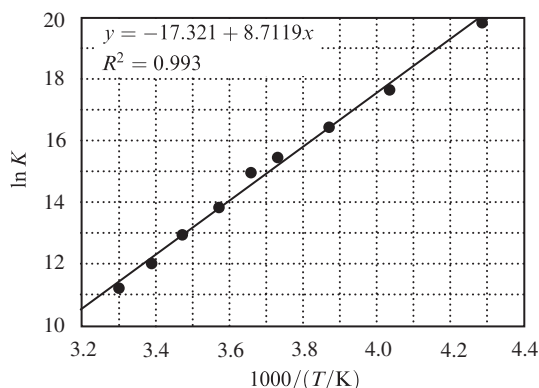


Figure 9.3

$$\begin{aligned} \text{So } \Delta_r H^\ominus &= -R \times \text{slope} = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \times (8.71 \times 10^3 \text{ K}) \\ &= \boxed{-72.4 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\text{and } \Delta_r S^\ominus = R \times \text{intercept} = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-17.3) = \boxed{-144 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\begin{aligned} \text{(b) } \Delta_r H^\ominus &= \Delta_f H^\ominus((\text{ClO})_2) - 2\Delta_f H^\ominus(\text{ClO}) \text{ so } \Delta_f H^\ominus((\text{ClO})_2) = \Delta_r H^\ominus + 2\Delta_f H^\ominus(\text{ClO}), \\ \Delta_f H^\ominus((\text{ClO})_2) &= [-72.4 + 2(101.8)] \text{ kJ mol}^{-1} = \boxed{131.2 \text{ kJ mol}^{-1}} \\ S^\ominus((\text{ClO})_2) &= [-144 + 2(226.6)] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{309.2 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

P9.24 A reaction proceeds spontaneously if its reaction Gibbs function is negative.

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

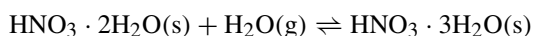
Note that under the given conditions, $RT = 1.58 \text{ kJ mol}^{-1}$.

$$(1) \Delta_r G/(\text{kJ mol}^{-1}) = \Delta_r G^\ominus(1) - RT \ln p_{\text{H}_2\text{O}} = -23.6 - 1.58 \ln 1.3 \times 10^{-7} = +1.5$$

$$\begin{aligned} (2) \Delta_r G/(\text{kJ mol}^{-1}) &= \Delta_r G^\ominus(2) - RT \ln p_{\text{H}_2\text{O}} p_{\text{HNO}_3} \\ &= -57.2 - 1.58 \ln[(1.3 \times 10^{-7}) \times (4.1 \times 10^{-10})] = +2.0 \end{aligned}$$

$$\begin{aligned}
 (3) \quad \Delta_r G / (\text{kJ mol}^{-1}) &= \Delta_r G^\ominus(3) - RT \ln p_{\text{H}_2\text{O}}^2 p_{\text{HNO}_3} \\
 &= -85.6 - 1.58 \ln[(1.3 \times 10^{-7})^2 \times (4.1 \times 10^{-10})] = -1.3 \\
 (4) \quad \Delta_r G / (\text{kJ mol}^{-1}) &= \Delta_r G^\ominus(4) - RT \ln p_{\text{H}_2\text{O}}^3 p_{\text{HNO}_3} \\
 &= -85.6 - 1.58 \ln[(1.3 \times 10^{-7})^3 \times (4.1 \times 10^{-10})] = -3.5
 \end{aligned}$$

So both the dihydrate and trihydrate form spontaneously from the vapour. Does one convert spontaneously into the other? Consider the reaction



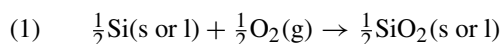
which may be considered as reaction (4) – reaction (3). Therefore $\Delta_r G$ for this reaction is

$$\Delta_r G = \Delta_r G(4) - \Delta_r G(3) = -2.2 \text{ kJ mol}^{-1}$$

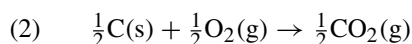
We conclude that the dihydrate converts spontaneously to the trihydrate, the most stable solid (at least of the four we considered).

P9.26

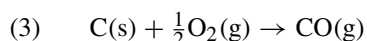
(a) The following four equilibria are needed for the construction of the Ellingham diagram for the smelting reduction of silica with graphite (Box 9.1).



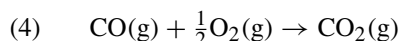
$$\begin{aligned}
 \Delta_1 G(T) &= 0.5 [GH_{\text{SiO}_2(\text{l})}(T) - GH_{\text{Si}(\text{l})}(T) - GH_{\text{O}_2}(T)] \text{ if } T > \text{mpSiO}_2 \\
 &= 0.5 [GH_{\text{SiO}_2(\text{s})}(T) - GH_{\text{Si}(\text{l})}(T) - GH_{\text{O}_2}(T)] \text{ if } \text{mpSi} \leq T \leq \text{mpSiO}_2 \\
 &= 0.5 [GH_{\text{SiO}_2(\text{s})}(T) - GH_{\text{Si}(\text{s})}(T) - GH_{\text{O}_2}(T)] \text{ if } T < \text{mpSi}
 \end{aligned}$$



$$\Delta_2 G(T) = 0.5 [GH_{\text{CO}_2(\text{g})}(T) - GH_{\text{C}(\text{s})}(T) - GH_{\text{O}_2}(T)]$$

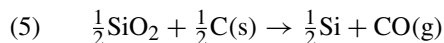


$$\Delta_3 G(T) = GH_{\text{CO}(\text{g})}(T) - GH_{\text{C}(\text{s})}(T) - \frac{1}{2}GH_{\text{O}_2}(T)$$



$$\Delta_4 G(T) = GH_{\text{CO}_2(\text{g})}(T) - GH_{\text{CO}(\text{g})}(T) - \frac{1}{2}GH_{\text{O}_2}(T)$$

$\Delta_3 G(T)$ alone lies above $\Delta_1 G(T)$ and then only above 1900 K. Thus, the smelting reaction.



$$(\Delta_5 G(T) = \Delta_3 G(T) - \Delta_1 G(T))$$

will have an equilibrium that lies to the right at temperatures higher than the temperature for which $\Delta_5 G(T) = 0$. Algebra or the root function can be used to show that this temperature equals 1892 K. The minimum smelting temperature of silica is about 1892 K. Furthermore, $\Delta_2 G$ never lies above $\Delta_1 G$ so we do not expect appreciable amounts of CO_2 is formed during smelting of silica.

(b) This problem is related to P8.18. Begin by making the definition $GH(T) = G(T) - H_{\text{SER}} = a + bT$. Write the important equilibria and calculate equilibrium contents at 2000 K. Silica and

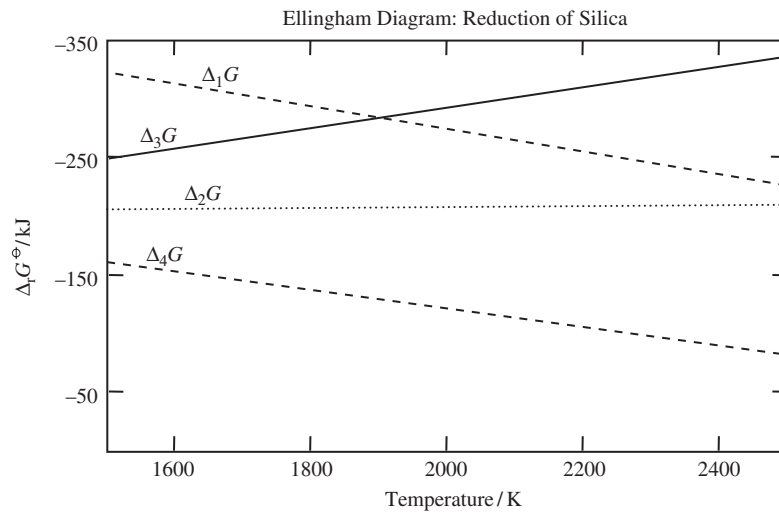


Figure 9.4

silicon are molten at this temperature. We assume that carbon forms an ideal solution with molten silicon and make the initial estimate:

$$\{\text{initial estimate of carbon mole fraction in molten Si}\} = x_{\text{est}} = 0.02$$

according to eqn 7.27,

$$\Delta_{\text{mix}}G(\text{C}) = RTx_{\text{est}} \ln x_{\text{est}} \quad \text{and} \quad \Delta_{\text{mix}}G(\text{Si}) = RT(1 - x_{\text{est}}) \ln(1 - x_{\text{est}})$$

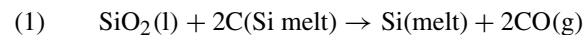
There are three unknowns (x_{C} , P_{CO} , P_{SiO}) so we select three independent equilibria that involve the silicon melt and solve them self-consistently with the ideal solution estimate. The estimate is used to calculate the small mixing Gibbs energy only.

$$GH_{\text{C in melt}} = GH_{\text{graphite}} + \Delta_{\text{mix}}G(\text{C}) \equiv GH_{\text{C}}$$

$$GH_{\text{Si in melt}} = GH_{\text{Si(l)}} + \Delta_{\text{mix}}G(\text{Si}) \equiv GH_{\text{Si}}$$

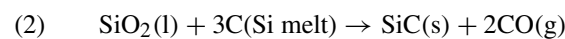
The independent equilibria are used to calculate a new estimate for the mole fraction of carbon in silicon, x_{C} . The new value is used in a repeat calculation in order to have a better estimate for x_{est} . This iteration procedure is repeated until the estimate and the calculated value of x_{C} agree to within 1%.

With the initial estimate:



$$\Delta_1G = GH_{\text{Si}} + 2GH_{\text{CO}(\text{g})} - GH_{\text{SiO}_2(\text{l})} - 2GH_{\text{C}} = -37.69 \text{ kJ mol}^{-1}$$

$$K_1 = e^{-\Delta_1G/RT} = 9.646 \quad \text{and} \quad x_{\text{Si}}P_{\text{CO}}^2 = K_1x_{\text{C}}^2$$



$$\Delta_2G = GH_{\text{SiC}(\text{s})} + 2GH_{\text{CO}(\text{g})} - GH_{\text{SiO}_2(\text{l})} - 3GH_{\text{C}} = -85.72 \text{ kJ mol}^{-1}$$

$$K_2 = e^{-\Delta_2G/RT} = 173.26 \quad \text{and} \quad P_{\text{CO}}^2 = K_2x_{\text{C}}^3$$

Dividing the equilibrium constant expression of Reaction (1) by the one for Reaction (2), and using $x_C = 1 - x_{Si}$, gives

$$(1 - x_{Si})(x_{Si}) = K_1/K_2$$

Solving for x_{Si} gives:

$$x_{Si} = \frac{1}{2} \left\{ 1 + \sqrt{1 - 4K_1/K_2} \right\} = 0.9408$$

$$x_C = 1 - x_{Si} = 0.0592$$

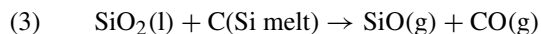
The initial estimate of x_C (0.02) and the calculated value do not agree to within 1%, so the calculation is repeated (iterated) with the new estimate: $x_{est} = 0.0592$. After several additional iterations, it is found that with $x_{est} = 0.0695$ the calculated value is $x_C = 0.0698$. Since these do agree to within 1%, the calculation is self-consistent and further iteration is unnecessary.

The equilibrium expression for reaction (2) gives:

$$P_{CO} = \sqrt{K_2 x_C^3} \text{ bar} = \sqrt{(125.66)(0.0698)^3} \text{ bar}$$

$$P_{CO} = 0.207 \text{ bar}$$

The third equilibrium is used to acquire P_{Si} , it is:



$$\Delta_3 G = GH_{\text{SiO}(g)} + GH_{\text{CO}(g)} - GH_{\text{SiO}_2(l)} - GH_C = -8.415 \text{ KJ mol}^{-1}$$

$$K_3 = e^{-\Delta G_3/RT} = 1.659$$

$$P_{\text{SiO}} = \left(\frac{K_3 x_C}{P_{\text{CO}}} \right) \text{ bar}^2 = \frac{1.659(0.0698)}{0.207} \text{ bar}$$

$$P_{\text{SiO}} = 0.559 \text{ bar}$$