

6 Chemical Equilibrium

6A The equilibrium constant

Answers to discussion questions

6A.2 Eqn 5E.9, in the form of the following expression, provides the general definition of the **activity** for species J, a_J : $\mu_J = \mu_J^\ominus + RT \ln a_J$ [5E.9] where μ_J^\ominus is the value of the chemical potential of J in the standard state, i.e., the state for which $a_J = 1$. In fact, the **standard state** of a substance at a specified temperature is its pure form at 1 bar. This means that the activity of a substance that is either a pure solid (e.g., copper, sodium chloride, naphthalene) or a pure liquid (e.g., bromine, water, methanol) equals 1 at, say, 25°C. Since the activity of a pure solid or liquid is equal to 1, it can be conveniently ignored when presenting an equilibrium constant expression.

Activities and **activity coefficients** are generally used to address questions that concern real, non-ideal mixtures. It is well worth remembering several useful activity forms. Of course, both activities, a_J , and activity coefficients, γ_J , of non-ideal mixtures are dimensionless and related by eqns that have the general form $a_J = \gamma_J \times$ (concentration of J).

Perfect Gas:	$a_J = p_J/p^\ominus$	(μ_J^\ominus depends upon T alone; $p^\ominus \equiv 1$ bar.)
Real Gas:	$a_J = \gamma_J p_J/p^\ominus$	(μ_J^\ominus depends upon T alone.)
Ideal solutions:	$a_J = x_J$	
Ideal-dilute solutions:	$a_B = [B]/c^\ominus$	where $c^\ominus \equiv 1 \text{ mol dm}^{-3}$
Solvent A of a non-ideal solution:	$a_A = \gamma_A x_A$	
Solute B of a non-ideal solution:	$a_B = \gamma_B [B]/c^\ominus$	

Solutions to exercises

6A.1(b) $2 \text{ A} \rightarrow \text{B}$

$n_J = n_J(0) + \nu_J \Delta \xi$ where ξ is the extent of reaction; ν_J is negative for reactants and positive for products.

$$n_A = 1.75 \text{ mol} - 2 \times (0.30 \text{ mol}) = \boxed{1.15 \text{ mol}}$$

$$n_B = 0.12 \text{ mol} + 1 \times (0.30 \text{ mol}) = \boxed{0.42 \text{ mol}}$$

6A.2(b) $2 \text{ A} \rightarrow \text{B}$ $\Delta_r G = -2.41 \text{ kJ mol}^{-1}$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} \quad [6A.1]$$

With the approximation that $\left(\frac{\partial G}{\partial \xi} \right)_{p,T} \approx \frac{\Delta G}{\Delta \xi}$, which is valid when $\Delta \xi$ is very small, we find that

$$\begin{aligned} \Delta G &\approx \Delta_r G \times \Delta \xi \\ &\approx (-2.41 \text{ kJ mol}^{-1}) \times (+0.051 \text{ mol}) = \boxed{-0.12 \text{ kJ}} \end{aligned}$$

6A.3(b) $2 \text{ NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ $\Delta_r G^\ominus = -4.73 \text{ kJ mol}^{-1}$

$$\begin{aligned}\Delta_r G &= \Delta_r G^\ominus + RT \ln Q \quad [6A.10] \\ &= (-4.73 \text{ kJ mol}^{-1}) + (2.4790 \text{ kJ mol}^{-1}) \times \ln Q \quad \text{at } 298.15 \text{ K}\end{aligned}$$

The above equation is used to calculate $\Delta_r G$ values at the given Q values in the following table.

Part	Q	$\ln Q$	$\Delta_r G / \text{kJ mol}^{-1}$
(i)	0.10	-2.303	-10.44
(ii)	1.0	0	-4.73
(iii)	10	2.303	+0.979
(iv)	100	4.605	+6.69

The above equation also indicates that a plot of $\ln Q$ against $\Delta_r G$ should be linear so points ii and iii, which straddle $\Delta_r G = 0$, can be used to perform a linear interpolation to find K from our equilibrium knowledge that $\ln Q = \ln Q_{\text{equilibrium}} = \ln K$ when $\Delta_r G = 0$. Performing the linear interpolation:

$$\begin{aligned}\ln Q &= \ln Q_{\text{ii}} + \left(\frac{\ln Q_{\text{iii}} - \ln Q_{\text{ii}}}{\Delta_r G_{\text{iii}} - \Delta_r G_{\text{ii}}} \right) \times (\Delta_r G - \Delta_r G_{\text{ii}}) \\ &= 0 + \left(\frac{2.303 - 0}{0.979 - (-4.73)} \right) \times \left(\frac{\Delta_r G}{\text{kJ mol}^{-1}} - (-4.73) \right) \\ &= 0.4034 \times \left(\frac{\Delta_r G}{\text{kJ mol}^{-1}} + 4.73 \right)\end{aligned}$$

Thus,

$$\begin{aligned}\ln K &= 0.4034 \times (0 + 4.73) \\ &= 1.908 \\ K &= e^{1.908} = \boxed{6.74} \text{ from a two-point interpolation}\end{aligned}$$

The two-point interpolation is in agreement with the result given by eqn 6A.8:

$$\begin{aligned}K &= e^{-\Delta_r G^\ominus / RT} \quad [6A.8] \\ &= e^{-(-4.73 \times 10^3 \text{ J mol}^{-1}) / \{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})\}} \\ &= 6.74\end{aligned}$$

6A.4(b) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad T = 298.15 \text{ K}, p = 1 \text{ bar} = p^\ominus, \alpha = 0.201$ at equilibrium

We draw up the following equilibrium table (Example 6A.2).

	$\text{N}_2\text{O}_4(\text{g})$	$\text{NO}_2(\text{g})$
Amount at equilibrium	$(1 - \alpha)n$	$2\alpha n$
Mole fraction	$\frac{1 - \alpha}{1 + \alpha}$	$\frac{2\alpha}{1 + \alpha}$
Partial pressure	$\frac{(1 - \alpha)p}{1 + \alpha}$	$\frac{2\alpha p}{1 + \alpha}$

$$\begin{aligned}K &= \left(\prod_{\text{equilibrium}} a_j^{v_j} \right) \quad [6A.13] = \left(\prod_{\text{equilibrium}} (p_j / p^\ominus)^{v_j} \right) \quad (\text{perfect gas assumption}) \\ &= \frac{(p_{\text{NO}_2} / p^\ominus)^2}{p_{\text{N}_2\text{O}_4} / p^\ominus} = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4} p^\ominus} = \frac{\left(\frac{2\alpha p}{1 + \alpha} \right)^2}{\left(\frac{(1 - \alpha)p}{1 + \alpha} \right) p^\ominus}\end{aligned}$$

$$= \frac{4p}{p^\ominus} \left\{ \frac{\alpha^2}{(1-\alpha) \times (1+\alpha)} \right\} = 4 \left\{ \frac{(0.201)^2}{(1-0.201) \times (1+0.201)} \right\}$$

$$= \boxed{0.168}$$

6A.5(b) (i) $\text{Br}_2(\text{g}) \rightleftharpoons 2 \text{Br}(\text{g})$ $T = 1600 \text{ K}$, $p = 1 \text{ bar} = p^\ominus$, $\alpha = 0.24$ at equilibrium

We draw up the following equilibrium table (Example 6A.2).

	$\text{Br}_2(\text{g})$	$\text{Br}(\text{g})$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\frac{1-\alpha}{1+\alpha}$	$\frac{2\alpha}{1+\alpha}$
Partial pressure	$\frac{(1-\alpha)p}{1+\alpha}$	$\frac{2\alpha p}{1+\alpha}$

$$K = \left(\prod_{\text{J}} a_{\text{J}}^{v_{\text{J}}} \right)_{\text{equilibrium}} \quad [6A.13] = \left(\prod_{\text{J}} (p_{\text{J}} / p^\ominus)^{v_{\text{J}}} \right)_{\text{equilibrium}} \quad (\text{perfect gas assumption})$$

$$= \frac{(p_{\text{Br}} / p^\ominus)^2}{p_{\text{Br}_2} / p^\ominus} = \frac{p_{\text{Br}}^2}{p_{\text{Br}_2} p^\ominus} = \frac{\left(\frac{2\alpha p}{1+\alpha} \right)^2}{\left(\frac{(1-\alpha)p}{1+\alpha} \right) p^\ominus}$$

$$= \frac{4p}{p^\ominus} \left\{ \frac{\alpha^2}{(1-\alpha) \times (1+\alpha)} \right\} = 4 \left\{ \frac{(0.24)^2}{(1-0.24) \times (1+0.24)} \right\}$$

$$= \boxed{0.244} \text{ at } 1600 \text{ K}$$

(ii) $\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ [6A.22]

$$\ln K_{2000 \text{ K}} = \ln K_{1600 \text{ K}} - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{2000 \text{ K}} - \frac{1}{1600 \text{ K}} \right)$$

$$= \ln(0.244) - \left(\frac{+112 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{2000 \text{ K}} - \frac{1}{1600 \text{ K}} \right) = 0.273$$

$$K_{2000 \text{ K}} = e^{0.273} = \boxed{1.3}$$

As expected, the temperature increase causes a shift to the right when the reaction is endothermic.

6A.6(b) $\text{CH}_4(\text{g}) + 3 \text{Cl}_2(\text{g}) \rightleftharpoons \text{CHCl}_3(\text{l}) + 3 \text{HCl}(\text{g})$

(i) Using data tables of the text *Resource section* at 25°C , we find

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

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

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

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

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

$$= -336.59 \text{ kJ mol}^{-1} \quad [\text{Used in part (ii)}]$$

$$\ln K = \frac{-\Delta_r G^\ominus}{RT} \quad [6A.14] = \frac{-(-308.84 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} = 124.6$$

$$K = e^{124.6} = \boxed{1.30 \times 10^{54}}$$

(ii) $\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ [6A.22]

$$\begin{aligned} \ln K_{50^\circ\text{C}} &= \ln K_{25^\circ\text{C}} - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{323.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ &= \ln(1.30 \times 10^{54}) - \left(\frac{-336.59 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{323.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) = 114.1 \end{aligned}$$

$$K_{50^\circ\text{C}} = e^{114.1} = \boxed{3.57 \times 10^{49}}$$

As expected, the temperature increase causes a shift to the left when the reaction is exothermic.

$$\Delta_r G^\ominus = -RT \ln K \quad [6A.14]$$

$$\Delta_r G_{50^\circ\text{C}}^\ominus = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (323.15 \text{ K}) \ln(3.57 \times 10^{49}) = \boxed{-307 \text{ kJ mol}^{-1}}$$

6A.7(b) $3 \text{ N}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2 \text{ HN}_3(\text{g})$ For this gas phase reaction $\Delta\nu = \sum_j \nu_j = 2 - 3 - 1 = -2$

$$\begin{aligned} K &= \left(\prod_j a_j^{\nu_j} \right)_{\text{equilibrium}} \quad [6A.13] = \left(\prod_j (\gamma_j p_j / p^\ominus)^{\nu_j} \right)_{\text{equilibrium}} = \left(\prod_j \gamma_j^{\nu_j} \right)_{\text{equilibrium}} \left(\prod_j (p_j / p^\ominus)^{\nu_j} \right)_{\text{equilibrium}} \\ &= K_\gamma K_p \quad \text{where} \quad K_\gamma = \left(\prod_j \gamma_j^{\nu_j} \right)_{\text{equilibrium}} \quad \text{and} \quad K_p = \left(\prod_j (p_j / p^\ominus)^{\nu_j} \right)_{\text{equilibrium}} \end{aligned}$$

Let us assume that the gases are perfect gases. Then, the activity coefficients equal 1 and $K_\gamma = 1$. Additionally,

$p_j = n_j RT / V = [J] RT$. Substitution gives

$$\begin{aligned} K &= K_p = \left(\prod_j ([J] RT / p^\ominus)^{\nu_j} \right)_{\text{equilibrium}} = \left(\prod_j ([J] / c^\ominus)^{\nu_j} \right)_{\text{equilibrium}} \left(\prod_j (c^\ominus RT / p^\ominus)^{\nu_j} \right)_{\text{equilibrium}} \\ &= K_c (c^\ominus RT / p^\ominus)^{\Delta\nu} \quad \text{where} \quad K_c = \left(\prod_j ([J] / c^\ominus)^{\nu_j} \right)_{\text{equilibrium}} \end{aligned}$$

$$K = K_c \times (c^\ominus RT / p^\ominus)^{-2} \quad \text{because } \Delta\nu = -2 \text{ for this reaction}$$

Since $c^\ominus R / p^\ominus = 0.0831451 \text{ K}^{-1}$, this expression may be written in the form

$$K = \boxed{(144.653 \text{ K}^2) \times K_c / T^2}$$

Anhydrous hydrogen azide, HN_3 , boils at 36°C and decomposes explosively. A dilute solution can be handled safely.

6A.8(b) Draw up the following table for the reaction equation: $\text{A} + \text{B} \rightleftharpoons \text{C} + 2 \text{D}$.

	A	B	C	D	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	0.1782	0.0309	0.1163	0.6745	0.9999

(i) Mole fractions are given in the table.

(ii) $K_x = \prod_j x_j^{\nu_j}$

$$K_x = \frac{(0.1163) \times (0.6745)^2}{(0.1782) \times (0.0309)} = \boxed{9.61}$$

(iii) $p_j = x_j p$. Assuming the gases are perfect, $a_j = p_j / p^\ominus$, so

$$K = \frac{(p_C/p^\ominus) \times (p_D/p^\ominus)^2}{(p_A/p^\ominus) \times (p_B/p^\ominus)} = K_x \left(\frac{p}{p^\ominus} \right) = K_x \quad \text{when } p = 1.00 \text{ bar}$$

$$K = K_x = \boxed{9.61}$$

(iv) $\Delta_r G^\ominus = -RT \ln K = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(9.61) = \boxed{-5.61 \text{ kJ mol}^{-1}}$

6A.9(b) The formation reaction is: $\text{U(s)} + \frac{3}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{UH}_3(\text{s})$.

$$K = \frac{1}{a_{\text{H}_2(\text{g})}^{3/2}} = \left(\frac{p^\ominus}{p_{\text{H}_2}} \right)^{3/2} \quad (a_{\text{U(s)}} = a_{\text{UH}_3(\text{s})} = 1 \text{ and, assuming perfect gas behavior, } a_{\text{H}_2(\text{g})} = p_{\text{H}_2}/p^\ominus.)$$

$$= \left(\frac{10^5 \text{ Pa}}{139 \text{ Pa}} \right)^{3/2} = 1.93 \times 10^4$$

$$\Delta_r G^\ominus = -RT \ln K \quad [6A.14]$$

$$= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K}) \times \ln(1.93 \times 10^4)$$

$$= \boxed{-41.0 \text{ kJ mol}^{-1}}$$

6A.10(b) $\text{P(s,wh)} + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{PH}_3(\text{g}) \quad \Delta_r G^\ominus = +13.4 \text{ kJ mol}^{-1}$

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \quad [6A.10] \quad \text{where } Q = \prod_j a_j^{\nu_j} \quad [6A.12b]$$

$$= \Delta_r G^\ominus + RT \ln \frac{p_{\text{PH}_3} / p^\ominus}{(p_{\text{H}_2} / p^\ominus)^{3/2}} \quad [\text{Perfect gas assumption}]$$

$$= (+13.4 \text{ kJ mol}^{-1}) + (8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times \ln \left(\frac{0.60}{1^{3/2}} \right)$$

$$= \boxed{+12.1 \text{ kJ mol}^{-1}}$$

Since $\Delta_r G > 0$, the spontaneous direction of reaction is toward the elements in their standard states.

6A.11(b) $\text{PbI}_2(\text{s}) \rightleftharpoons \text{PbI}_2(\text{aq}) \quad K_s = 1.4 \times 10^{-8}$

$$\Delta_r G^\ominus = -RT \ln K_s$$

$$= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times \ln(1.4 \times 10^{-8}) = +44.8 \text{ kJ mol}^{-1}$$

$$= \Delta_r G^\ominus(\text{PbI}_2, \text{aq}) - \Delta_r G^\ominus(\text{PbI}_2, \text{s})$$

$$\Delta_r G^\ominus(\text{PbI}_2, \text{aq}) = \Delta_r G^\ominus + \Delta_r G^\ominus(\text{PbI}_2, \text{s})$$

$$= (44.8 - 173.64) \text{ kJ mol}^{-1} = \boxed{-128.8 \text{ kJ mol}^{-1}}$$

Solutions to problems

6A.2 $\Delta_r G^\ominus(\text{H}_2\text{CO}, \text{g}) = \Delta_r G^\ominus(\text{H}_2\text{CO}, \text{l}) + \Delta_{\text{vap}} G^\ominus(\text{H}_2\text{CO}, \text{l})$ where $\Delta_r G^\ominus(\text{H}_2\text{CO}, \text{l}) = +28.95 \text{ kJ mol}^{-1}$

For $\text{H}_2\text{CO}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}(\text{g})$, $K(\text{vap}) = \frac{p}{p^\ominus}$ where $p = 1500 \text{ Torr} = 2.000 \text{ bar}$ and $p^\ominus = 1 \text{ bar}$

$$\begin{aligned}\Delta_{\text{vap}}G^\ominus &= -RT \ln K(\text{vap}) = -RT \ln \frac{p}{p^\ominus} \\ &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln\left(\frac{2.000 \text{ bar}}{1 \text{ bar}}\right) = -1.72 \text{ kJ mol}^{-1}\end{aligned}$$

Therefore, for the reaction $\text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}(\text{g})$,

$$\Delta_r G^\ominus = \{(+28.95) + (-1.72)\} \text{ kJ mol}^{-1} = +27.23 \text{ kJ mol}^{-1}$$

Hence, $K = e^{(-27.23 \times 10^3 \text{ J mol}^{-1}) / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = e^{-10.99} = \boxed{1.69 \times 10^{-5}}$.

6A.4[‡] A reaction proceeds spontaneously if its reaction Gibbs function is negative.

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \quad [6A.10]$$

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

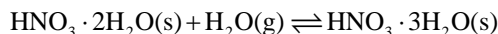
$$\begin{aligned}\text{(i)} \quad \Delta_r G / (\text{kJ mol}^{-1}) &= \{\Delta_r G^\ominus \text{ (i)} - RT \ln p_{\text{H}_2\text{O}}\} / \text{kJ mol}^{-1} = -23.6 - 1.58 \ln(1.3 \times 10^{-7}) \\ &= +1.5\end{aligned}$$

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

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

$$\begin{aligned}\text{(iv)} \quad \Delta_r G / (\text{kJ mol}^{-1}) &= \{\Delta_r G^\ominus \text{ (iv)} - RT \ln p_{\text{H}_2\text{O}}^3 p_{\text{HNO}_3}\} / (\text{kJ mol}^{-1}) \\ &= -112.8 - 1.58 \ln[(1.3 \times 10^{-7})^3 \times (4.1 \times 10^{-10})] \\ &= -3.5\end{aligned}$$

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(iv) – reaction(iii). $\Delta_r G$ for this reaction is

$$\Delta_r G = \Delta_r G(\text{iv}) - \Delta_r G(\text{iii}) = -2.2 \text{ kJ mol}^{-1}.$$

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

6B The response to equilibria to the conditions

Answers to discussion questions

6B.2 (1) Response to change in pressure. The equilibrium constant is independent of pressure, but the individual partial pressures of a gas phase reaction can change as the total pressure changes. This will happen when there is a difference, Δv , between the sums of the number of moles of gases on the product and reactant sides of the balanced chemical reaction equation.

$$\Delta v = \sum_J \nu_J = \sum_{J=\text{product gases}} \nu_J - \sum_{J=\text{reactant gases}} |\nu_J|$$

The requirement of an unchanged equilibrium constant implies that the side with the smaller number of moles of

gas be favored as pressure increases. To see this, we examine the general reaction equation $0 = \sum_J \nu_J J$ [6A.9] in the special case for which all reactants and products are perfect gases. In this case the activities equal the partial pressure of the gaseous species and, therefore,

$$a_{J(\text{gas})} = p_J/p^\ominus = x_J p/p^\ominus$$

where x_J is the mole fraction of gaseous species J . Substitution into eqn 6A.13 and simplification yields a useful equation.

$$\begin{aligned} K &= \left(\prod_J a_J^{\nu_J} \right)_{\text{equilibrium}} = \left(\prod_J x_J^{\nu_J} (p/p^\ominus)^{\nu_J} \right)_{\text{equilibrium}} \\ &= \left(\prod_J x_J^{\nu_J} \right)_{\text{equilibrium}} \left(\prod_J (p/p^\ominus)^{\nu_J} \right)_{\text{equilibrium}} = \left(\prod_J x_J^{\nu_J} \right)_{\text{equilibrium}} (p/p^\ominus)^{\Delta\nu} \\ &= K_x (p/p^\ominus)^{\Delta\nu} \quad \text{where} \quad K_x = \left(\prod_J x_J^{\nu_J} \right)_{\text{equilibrium}} \end{aligned}$$

K_x is not an equilibrium constant. It is a ratio of product and reactant concentration factors that has a form analogous to the equilibrium constant K . However, whereas K depends upon temperature alone, the concentration ratio K_x depends upon both temperature and pressure. Solving for K_x provides an equation that directly indicates its pressure dependence.

$$K_x = K (p/p^\ominus)^{-\Delta\nu}$$

This equation indicates that, if $\Delta\nu = 0$ (an equal number of gas moles on both sides of the balanced reaction equation), $K_x = K$ and the concentration ratio has no pressure dependence. An increase in pressure causes no change in K_x and no shift in the concentration equilibrium is observed upon a change in pressure.

However this equation indicates that, if $\Delta\nu < 0$ (fewer moles of gas on the product side of the balanced reaction equation), $K_x = K (p/p^\ominus)^{|\Delta\nu|}$. Because p is raised to a positive power in this case, an increase in pressure causes K_x to increase. This means that the numerator concentrations (products) must increase while the denominator concentrations (reactants) decrease. The concentrations shift to the product side to reestablish equilibrium when an increase in pressure has stressed the reaction equilibrium. Similarly, if $\Delta\nu > 0$ (fewer moles of gas on the reactant side of the balanced reaction equation), $K_x = K (p/p^\ominus)^{-|\Delta\nu|}$. Because p is raised to a negative power in this case, the concentrations now shift to the reactant side to reestablish equilibrium when an increase in pressure has stressed the reaction equilibrium.

(2) Response to change in temperature. The **van 't Hoff equation**, $\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$ [6B.2(a)], shows that K decreases with increasing temperature when the reaction is exothermic (i.e., $\Delta_r H^\ominus < 0$); thus the reaction shifts to the left. The opposite occurs in endothermic reactions (i.e., $\Delta_r H^\ominus > 0$). See text Section 6B.2 for a more detailed discussion.

Solutions to exercises

6B.1(b) At 1120 K, $\Delta_r G^\ominus = +22 \times 10^3 \text{ J mol}^{-1}$

$$\ln K_1(1120\text{K}) = -\frac{\Delta_r G^\ominus}{RT} \quad [6A.14] = -\frac{(22 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1120 \text{ K})} = -2.36\bar{3}$$

$$K = e^{-2.36\bar{3}} = 9.4\bar{1} \times 10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [6B.4]$$

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

$$\frac{1}{T_2} = \frac{R \ln K_1}{\Delta_r H^\ominus} + \frac{1}{T_1} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-2.36\bar{3})}{(125 \times 10^3 \text{ J mol}^{-1})} + \frac{1}{1120 \text{ K}} = 7.36\bar{3} \times 10^{-4}$$

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

6B.2(b) $\ln K = A + \frac{B}{T} + \frac{C}{T^3}$ where $A = -2.04$, $B = -1176 \text{ K}$, and $C = 2.1 \times 10^7 \text{ K}^3$

At 450 K:

$$\begin{aligned} \Delta_r G^\ominus &= -RT \ln K \quad [6A.14] = RT \times \left(A + \frac{B}{T} + \frac{C}{T^3} \right) \\ &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K}) \times \left(-2.04 - \frac{1176 \text{ K}}{450 \text{ K}} + \frac{2.1 \times 10^7 \text{ K}^3}{(450 \text{ K})^3} \right) \\ &= +16.6 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r H^\ominus &= -R \frac{d \ln K}{d(1/T)} \quad [6B.2(b)] \\ &= -R \frac{d}{d(1/T)} \left(A + \frac{B}{T} + \frac{C}{T^3} \right) = -R \times \left(B + \frac{3C}{T^2} \right) \\ &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left\{ (-1176 \text{ K}) + 3 \times \frac{2.1 \times 10^7 \text{ K}^3}{(450 \text{ K})^2} \right\} = \boxed{+7.19 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{7.19 \text{ kJ mol}^{-1} - 16.6 \text{ kJ mol}^{-1}}{450 \text{ K}} = \boxed{-20.9 \text{ J K}^{-1} \text{ mol}^{-1}}$$

6B.3(b) $\text{CH}_3\text{OH(g)} + \text{NOCl(g)} \rightarrow \text{HCl(g)} + \text{CH}_3\text{NO}_2\text{(g)}$ For this gas phase reaction $\Delta v = \sum_J \nu_J = 0$

$$\begin{aligned} K &= \left(\prod_J a_J^{\nu_J} \right)_{\text{equilibrium}} \quad [6A.13] = \left(\prod_J (\gamma_J p_J / p^\ominus)^{\nu_J} \right)_{\text{equilibrium}} = \left(\prod_J \gamma_J^{\nu_J} \right)_{\text{equilibrium}} \left(\prod_J (p_J / p^\ominus)^{\nu_J} \right)_{\text{equilibrium}} \\ &= K_\gamma K_p \quad \text{where} \quad K_\gamma = \left(\prod_J \gamma_J^{\nu_J} \right)_{\text{equilibrium}} \quad \text{and} \quad K_p = \left(\prod_J (p_J / p^\ominus)^{\nu_J} \right)_{\text{equilibrium}} \end{aligned}$$

Let us assume that the gases are perfect gases. Then, the activity coefficients equal 1 and $K_\gamma = 1$. Additionally,

$p_J = x_J p$. Substitution gives

$$\begin{aligned} K &= K_p = \left(\prod_J (x_J p / p^\ominus)^{\nu_J} \right)_{\text{equilibrium}} = \left(\prod_J x_J^{\nu_J} \right)_{\text{equilibrium}} \left(\prod_J (p / p^\ominus)^{\nu_J} \right)_{\text{equilibrium}} \\ &= K_x (p / p^\ominus)^{\Delta v} \quad \text{where} \quad K_x = \left(\prod_J x_J^{\nu_J} \right)_{\text{equilibrium}} \end{aligned}$$

For this reaction:

$$K = K_x \times (p / p^\ominus)^0 = K_x \quad \text{because } \Delta v = 0$$

K is independent of pressure so we conclude by the above eqn that for this reaction K_x is also independent of pressure. Thus, the percentage change in K_x upon changing the pressure equals zero for this reaction.



Initial moles: $n_{\text{N}_2} = \frac{5.0 \text{ g}}{28.013 \text{ g mol}^{-1}} = 0.1785 \text{ mol}$

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

	N_2	O_2	NO	Total
Initial amount/mol	$n_{\text{N}_2} = 0.1785$	$n_{\text{O}_2} = 0.0625$	0	$n = 0.2410$
Change/mol	$-z$	$-z$	$+2z$	0
Equilibrium amount/mol	$n_{\text{N}_2} - z$	$n_{\text{O}_2} - z$	$2z$	$n = 0.2410$
Mole fractions	$(n_{\text{N}_2} - z)/n$	$(n_{\text{O}_2} - z)/n$	$2z/n$	1

$$K = K_x \left(\frac{P}{P^\ominus} \right)^{\Delta v} = K_x \quad (\text{Because } \Delta v = \sum_j \nu_j = 0 \text{ for this reaction. See Exercise 6B.3(a) or (b)})$$

$$K = \frac{(2z)^2}{(n_{\text{N}_2} - z)(n_{\text{O}_2} - z)}$$

$$(1 - 4/K)z^2 - nz + n_{\text{N}_2}n_{\text{O}_2} = 0$$

$$z = \frac{n \pm \sqrt{n^2 - 4(1 - 4/K)n_{\text{N}_2}n_{\text{O}_2}}}{2(1 - 4/K)}$$

$$= \frac{0.2410 \pm \sqrt{0.2410^2 - 4(1 - 4/1.69 \times 10^{-3})(0.1785)(0.0625)}}{2(1 - 4/1.69 \times 10^{-3})}$$

$$= -2.223 \times 10^{-3} \text{ or } 2.121 \times 10^{-3}$$

$$= 2.121 \times 10^{-3} \text{ because the negative value is non-physical.}$$

$$x_{\text{NO}} = \frac{2z}{n} = \frac{2(2.121 \times 10^{-3})}{0.241} = \boxed{1.8 \times 10^{-2}}$$

6B.5(b) $\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ [6B.4]

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

$$= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{310 \text{ K}} - \frac{1}{325 \text{ K}} \right)^{-1} \times \ln \left(\frac{K_2}{K_1} \right)$$

$$= (55.85 \text{ kJ mol}^{-1}) \times \ln \left(\frac{K_2}{K_1} \right)$$

(a) $K_2/K_1 = 2.00$

$$\Delta_r H^\ominus = (55.85 \text{ kJ mol}^{-1}) \times \ln(2.00) = \boxed{38.71 \text{ kJ mol}^{-1}}$$

(b) $K_2/K_1 = 0.500$

$$\Delta_r H^\ominus = (55.85 \text{ kJ mol}^{-1}) \times \ln(0.500) = \boxed{-38.71 \text{ kJ mol}^{-1}}$$

6B.6(b) The reaction is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4(\text{s}) + 5 \text{H}_2\text{O}(\text{g})$.

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

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = 0$$

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

We now estimate that the values of both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ are not too different then the values at 25 °C and calculate each with standard values found in the text *Resource section*.

$$\Delta_r H^\ominus = \sum_j \nu_j \Delta_{f,j} H^\ominus = \{(-771.36) + (5) \times (-241.82) - (-2279.7)\} \text{ J mol}^{-1} = +299.2 \text{ kJ mol}^{-1}$$

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

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

Question: What would the decomposition temperature be for decomposition defined as the state at which $K = 1/2$?

6B.7(b) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ Vapor pressures: $p_{427^\circ\text{C}} = 608 \text{ kPa}$ and $p_{459^\circ\text{C}} = 1115 \text{ kPa}$

The gases originate from the dissociation of the solid alone so $p_{\text{NH}_3} = p_{\text{HCl}} = 1/2 p$.

(i) Equilibrium constants

$$K = (p_{\text{NH}_3} / p^\ominus) \times (p_{\text{HCl}} / p^\ominus) \quad [\text{Perfect gas assumption}]$$

$$= (1/2 p / p^\ominus) \times (1/2 p / p^\ominus)$$

$$= 1/4 (p / p^\ominus)^2$$

$$K_{427^\circ\text{C}} = 1/4 (608 \text{ kPa} / 100 \text{ kPa})^2 = \boxed{9.24}$$

$$K_{459^\circ\text{C}} = 1/4 (1115 \text{ kPa} / 100 \text{ kPa})^2 = 31.08$$

(ii) $\Delta_r G^\ominus = -RT \ln K$ [6A.14]

$$\Delta_r G_{427^\circ\text{C}}^\ominus = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (700.15 \text{ K}) \times \ln(9.24) = \boxed{-12.9 \text{ kJ mol}^{-1}}$$

(iii) $\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ [6B.4]

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

$$= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{700.15 \text{ K}} - \frac{1}{732.15 \text{ K}} \right)^{-1} \times \ln \left(\frac{31.08}{9.24} \right)$$

$$= \boxed{162 \text{ kJ mol}^{-1}}$$

(iv) $\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{(162 \text{ kJ mol}^{-1}) - (-12.9 \text{ kJ mol}^{-1})}{700.15 \text{ K}} = \boxed{+250 \text{ J K}^{-1} \text{ mol}^{-1}}$

Solutions to problems

6B.2 $\text{U}(\text{s}) + 3/2 \text{H}_2(\text{g}) \rightleftharpoons \text{UH}_3(\text{s})$

$$K = a_{\text{H}_2}^{-3/2} = (p_{\text{H}_2}/p^\ominus)^{-3/2} \text{ [perfect gas]}$$

$$= (p/p^\ominus)^{-3/2} \quad [p_{\text{H}_2} = p]$$

$$\Delta_f H^\ominus = RT^2 \frac{d \ln K}{dT} \text{ [6B.2(a)]} = RT^2 \frac{d}{dT} \ln(p/p^\ominus)^{-3/2} = -\frac{3}{2} RT^2 \frac{d}{dT} (\ln p/\text{Pa} - \ln p^\ominus/\text{Pa})$$

$$= -\frac{3}{2} RT^2 \frac{d}{dT} (\ln p/\text{Pa})$$

$$= -\frac{3}{2} RT^2 \frac{d}{dT} (A + B/T + C \ln(T/K)) = -\frac{3}{2} RT^2 \times \left(\frac{-B}{T^2} + \frac{C}{T} \right)$$

$$= \boxed{\frac{3}{2} R \times (B - CT)} \quad \text{where } B = -1.464 \times 10^4 \text{ K} \quad \text{and} \quad C = -5.65$$

$$d(\Delta_f H^\ominus) = \Delta_f C_p^\ominus dT \text{ [from eqn 2B.6(a) applied to chemical reactions, 2C.7(a)]}$$

or $\Delta_f C_p^\ominus = \left(\frac{\partial \Delta_f H^\ominus}{\partial T} \right)_p = -\frac{3}{2} CR = \boxed{70.5 \text{ J K}^{-1} \text{ mol}^{-1}}$

6B.4 $\text{CaCl}_2 \cdot \text{NH}_3(\text{s}) \rightleftharpoons \text{CaCl}_2(\text{s}) + \text{NH}_3(\text{g}) \quad K = \frac{p}{p^\ominus} \text{ and } \Delta_f H^\ominus = +78 \text{ kJ mol}^{-1}$

$$\Delta_r G^\ominus = -RT \ln K = -RT \ln \frac{p}{p^\ominus}$$

$$= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln \left(\frac{1.71 \text{ kPa}}{100.0 \text{ kPa}} \right) \quad [p^\ominus = 1 \text{ bar} = 100.0 \text{ kPa}]$$

$$= +13.5 \text{ kJ mol}^{-1} \text{ at } 400 \text{ K}$$

$$\frac{\Delta_r G^\ominus(T_2)}{T_2} - \frac{\Delta_r G^\ominus(T_1)}{T_1} = \Delta_f H^\ominus \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ [6B.4 and 6A.14]}$$

Therefore, taking $T_1 = 400 \text{ K}$ and letting $T = T_2$ be any temperature in the range 350 K to 470 K,

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

$$= (78 \text{ kJ mol}^{-1}) + \left(\frac{(13.5 - 78) \text{ kJ mol}^{-1}}{400} \right) \times \left(\frac{T}{\text{K}} \right)$$

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

6B.6 The equilibrium we need to consider is $\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g})$ ($M_{\text{I}} = 126.90 \text{ g mol}^{-1}$). It is convenient to express the equilibrium constant in terms of α , the degree of dissociation of I_2 , which is the predominant species at low temperatures. Recognizing that the data n_{I_2} is related to the total iodine mass, m_{I} , by $n_{\text{I}_2} = m_{\text{I}}/M_{\text{I}_2}$ we draw the following table.

	I	I ₂	Total
Equilibrium amounts	$2\alpha n_{\text{I}_2}$	$(1-\alpha)n_{\text{I}_2}$	$(1+\alpha)n_{\text{I}_2}$
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

$$K = \frac{(p_1 / p^\ominus)^2}{p_{1_2} / p^\ominus} = \frac{p_1^2}{p_{1_2} p^\ominus} = \frac{4\alpha^2 (p / p^\ominus)}{1 - \alpha^2}$$

We also know that

$$pV = n_{\text{total}}RT = (1 + \alpha)n_{1_2}RT$$

Implying that $\alpha = \frac{pV}{n_{1_2}RT} - 1$ where $V = 342.68 \text{ cm}^3$. The provided data along with calculated values of α and $K(T)$ are summarized in the following table.

T / K	973	1073	1173
p / atm	0.06244	0.07500	0.09181
$10^4 n_{1_2} / \text{mol}$	2.4709	2.4555	2.4366
α	0.08459	0.1887	0.3415
K	1.82×10^{-3}	1.12×10^{-2}	4.91×10^{-2}

Since $\Delta_r H^\ominus$ is expected to be approximately a constant over this temperature range and since $\Delta_r H^\ominus = -R \left(\frac{d \ln K}{d(1/T)} \right)$ [6B.2(b)], a plot of $\ln K$ against $1/T$ should be linear with slope $= -\Delta_r H^\ominus / R$. The linear regression fit to the plot is found to be $\ln K = 13.027 - (18809 \text{ K})/T$ with $R^2 = 0.999969$. Thus,

$$\Delta_r H^\ominus = -(-18809 \text{ K})R = \boxed{+156 \text{ kJ mol}^{-1}}$$

6B.1 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ $\Delta_r H^\ominus = -285.83 \text{ kJ mol}^{-1}$ and $\Delta_r S^\ominus = -163.343 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298.15 K

Let the temperatures of interest be $T_1 = 298.15 \text{ K}$ and T_2 . $\Delta_r G(T_2)$ at 1 bar can be calculated from the reaction thermodynamic properties at T_1 with the following relations.

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p(T) dT \quad [2\text{C.7(a) and (b)}; \Delta_r C_p(T) = \sum_j \nu_j C_{p,j}]$$

$$\Delta_r S(T_2) = \Delta_r S(T_1) + \int_{T_1}^{T_2} \frac{\Delta_r C_p(T)}{T} dT \quad [3\text{A.19 applied to reaction equations}]$$

$$\Delta_r G(T_2) = \Delta_r H(T_2) - T_2 \Delta_r S(T_2)$$

The computation is most easily performed using the function capability and numeric integrations of either the scientific calculator or a computer software package. The following is a Mathcad Prime 2 worksheet for the calculation of $\Delta_r G$ for $273.15 \text{ K} \leq T_2 \leq 373.15 \text{ K}$ at 1 bar.

Data:

$$T_1 := 298.15 \cdot \text{K}$$

$$\text{kJ} := 1000 \cdot \text{J}$$

$$\Delta H_{f_water_298} := -285.83 \cdot \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{f_water_298} := -163.343 \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p_water}(T) := 75.29 \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p_hydrogen}(T) := \left(27.28 + 3.26 \cdot 10^{-3} \cdot \text{K}^{-1} \cdot T + \frac{0.50 \cdot 10^5 \cdot \text{K}^2}{T^2} \right) \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p_oxygen}(T) := \left(29.96 + 4.18 \cdot 10^{-3} \cdot \text{K}^{-1} \cdot T - \frac{1.67 \cdot 10^5 \cdot \text{K}^2}{T^2} \right) \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Computational equations:

$$\Delta C_p(T) := C_{p_water}(T) - C_{p_hydrogen}(T) - \frac{1}{2} \cdot C_{p_oxygen}(T)$$

$$\Delta H_{f_water}(T_2) := \Delta H_{f_water_298} + \int_{T_1}^{T_2} \Delta C_p(T) dT$$

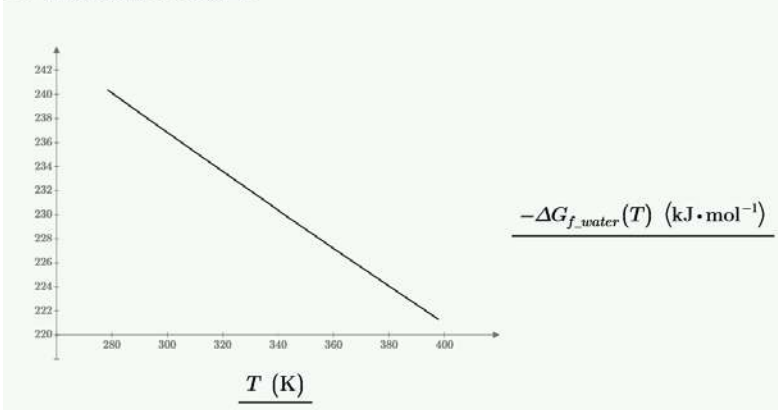
$$\Delta S_{f_water}(T_2) := \Delta S_{f_water_298} + \int_{T_1}^{T_2} \frac{\Delta C_p(T)}{T} dT$$

$$\Delta G_{f_water}(T_2) := \Delta H_{f_water}(T_2) - T_2 \cdot \Delta S_{f_water}(T_2)$$

Computation: $\Delta G_{f_water}(372 \cdot K) = -225.334 \text{ kJ} \cdot \text{mol}^{-1}$

Thus, with numerical integrations we have found that $\Delta_f G^\ominus = \boxed{-225.334 \text{ kJ mol}^{-1}}$. The worksheet also makes it very easy to examine, even plot, changes in the reaction thermodynamic properties. The following worksheet plot shows the variation of the formation Gibb's energy with temperature. The plot shows a decrease with temperature in a near-linear manner. Can you explain why?

$T := 273 \cdot K, 278 \cdot K .. 398 \cdot K$



6C Electrochemical cells

Answers to discussion questions

6C.2 A salt bridge connecting two half-cells is usually a U-tube filled with potassium chloride in agar jelly. It provides the mobile electrolyte for completing the circuit of an electrochemical cell. In its absence, the cell cannot generate an electrical current through the single wire that connects the two electrodes and the circuit is said to be "open". No electron can leave or enter either half-cell, because this act would cause the net electronic charge of the half-cell to be non-zero. The strong electrostatic force prevents this from happening and causes macroscopic objects to normally have a zero net electrical charge. However, a salt bridge provides an anion to the anodic half-cell for every electron that leaves while simultaneously providing a cation to the cathodic half-cell for every electron that enters. This is a "closed" electrical circuit in which the net charge of each half-cell remains zero but an electric current can be generated.

6C.4 When a current is being drawn from an electrochemical cell, the cell potential is altered by the formation of charge double layers at the surface of electrodes and by the formation of solution chemical potential gradients

(concentration gradients). Resistive heating of the cell circuits may occur and junction potentials between dissimilar materials both external and external to the cell may change.

Solutions to exercises

6C.1(b) The cell notation specifies the right and left electrodes. Note that for proper cancellation we must equalize the number of electrons in half-reactions being combined. For the calculation of the standard cell potentials we have used $E_{\text{cell}}^{\ominus} = E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus}$, with standard electrode potentials from data tables.

		E^{\ominus}
(i)	R: $\text{Ag}_2\text{CrO}_4(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq})$	+0.45 V
	L: $\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	+1.36 V
	Overall(R-L): $\text{Ag}_2\text{CrO}_4(\text{s}) + 2 \text{Cl}^-(\text{aq}) \rightarrow 2 \text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq}) + \text{Cl}_2(\text{g})$	-0.91 V
(ii)	R: $\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.15 V
	L: $2 \text{Fe}^{3+}(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Fe}^{2+}(\text{aq})$	+0.77 V
	Overall (R-L): $\text{Sn}^{4+}(\text{aq}) + 2 \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2 \text{Fe}^{3+}(\text{aq})$	-0.62 V
(iii)	R: $\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.23 V
	L: $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34 V
	Overall (R-L): $\text{Cu}(\text{s}) + \text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+0.89 V

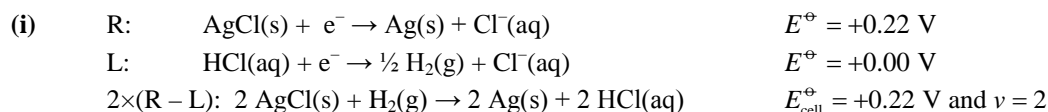
Comment. Those cells for which $E_{\text{cell}}^{\ominus} > 0$ may operate as spontaneous galvanic cells under standard conditions. Those for which $E_{\text{cell}}^{\ominus} < 0$ may operate as nonspontaneous electrolytic cells. Recall that $E_{\text{cell}}^{\ominus}$ informs us of the spontaneity of a cell under standard conditions only. For other conditions we require E_{cell} .

6C.2(b) The conditions (concentrations, etc.) under which these reactions occur are not given. For the purposes of this exercise we assume standard conditions. The specification of the right and left electrodes is determined by the direction of the reaction as written. As always, in combining half-reactions to form an overall cell reaction we must write half-reactions with equal number of electrons to ensure proper cancellation. We first identify the half-reactions, and then set up the corresponding cell.

		E^{\ominus}
(i)	R: $2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$	-0.83 V
	L: $2 \text{Na}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Na}(\text{s})$	-2.71 V
and the cell is		
	$\text{Na}(\text{s}) \mid \text{NaOH}(\text{aq}) \mid \text{H}_2(\text{g}) \mid \text{Pt}$	+1.88 V
(ii)	R: $\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	+0.54 V
	L: $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0
and the cell is		
	$\text{Pt} \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq}), \text{I}^-(\text{aq}) \mid \text{I}_2(\text{s}) \mid \text{Pt}$	+0.54 V
(iii)	R: $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0
	L: $2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83 V
and the cell is		
	$\text{Pt} \mid \text{H}_2(\text{g}) \mid \text{OH}^-(\text{aq}) \parallel \text{H}^+(\text{aq}) \mid \text{H}_2(\text{g}) \mid \text{Pt}$	+0.83 V

Comment. All of these cells have $E_{\text{cell}}^{\ominus} > 0$, corresponding to a spontaneous cell reaction under standard conditions. If $E_{\text{cell}}^{\ominus}$ had turned out to be negative, the spontaneous reaction would have been the reverse of the one given, with the right and left electrodes of the cell also reversed.

6C.2(b) Pt|H₂(g, p^{\ominus})|HCl(aq, 0.010 mol kg⁻¹)|AgCl(s)|Ag



The cell reaction is spontaneous toward the right under standard conditions because $E_{\text{cell}}^{\ominus} > 0$. The Nernst equation for the above cell reaction is:

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{\nu F} \ln Q \quad [6C.4]$$

$$Q = \frac{(a_{\text{HCl(aq)}})^2}{a_{\text{H}_2(\text{g})}} = \frac{(a_{\text{H}^+(\text{aq})} a_{\text{Cl}^-(\text{aq})})^2}{a_{\text{H}_2(\text{g})}} = \frac{(\gamma_{\pm}^2 (b_{\text{HCl}} / b^{\ominus})^2)^2}{p / p^{\ominus}} = \gamma_{\pm}^4 (b_{\text{HCl}} / b^{\ominus})^4 \quad (\text{i.e., } p = p^{\ominus})$$

Thus,

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{2F} \ln \left\{ \gamma_{\pm}^4 (b_{\text{HCl}} / b^{\ominus})^4 \right\} \quad \text{or} \quad \boxed{E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{2RT}{F} \ln \left\{ \gamma_{\pm} (b_{\text{HCl}} / b^{\ominus}) \right\}}$$

(ii) $\Delta_r G^{\ominus} = -\nu F E_{\text{cell}}^{\ominus} = -2 \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (0.22 \text{ V}) = \boxed{-42 \text{ kJ mol}^{-1}}$

(iii) The ionic strength and mean activity coefficient are:

$$I = \frac{1}{2} \sum_i z_i^2 (b_i / b^{\ominus}) \quad [5F.9] = \frac{1}{2} \{1(0.010) + 1(0.010)\} = 0.010$$

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2} \quad [5F.8] = -1 \times (0.509) \times (0.010)^{1/2} = -0.0509$$

$$\gamma_{\pm} = 0.889$$

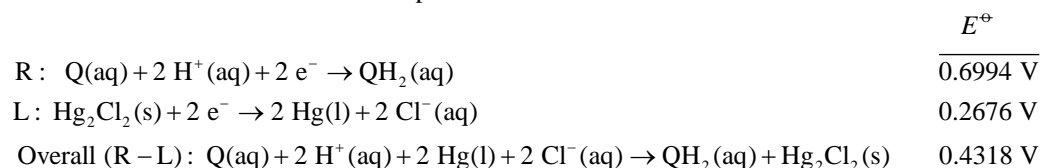
Therefore,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{2RT}{F} \ln \left\{ \gamma_{\pm} (b_{\text{HCl}} / b^{\ominus}) \right\} \\ &= 0.22 \text{ V} - \frac{2 \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}{9.6485 \times 10^5 \text{ C mol}^{-1}} \ln \left\{ (0.889) \times (0.010) \right\} = 0.22 \text{ V} + 0.24 \text{ V} \\ &= \boxed{+0.46 \text{ V}} \end{aligned}$$

Solutions to problems

6C.2 Cell: Hg|Hg₂Cl₂(s)|HCl(aq)|Q·QH₂|Au $E_{\text{cell}} = +0.190 \text{ V}$ and $\nu = 2$

The electrode half-reactions and their standard potentials are



The reaction quotient is directly related to the pH, a relation that is simplified by noting that for an HCl solution $b_{\text{H}^+} = b_{\text{Cl}^-}$ while for the Q·QH₂ equimolecular complex of quinone $b_{\text{Q}} = b_{\text{QH}_2}$.

$$Q = \frac{a_{\text{QH}_2}}{a_{\text{Q}} a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}$$

The Debye–Hückel limiting law makes use of the mean activity coefficient for the compound M_pX_q defined by $a_j = \gamma_{\pm} b_j$. Thus, $a_{\text{OH}_2} / a_{\text{O}} = 1$, $a_{\text{H}^+} = a_{\text{Cl}^-}$, and the reaction quotient becomes

$$Q = a_{\text{H}^+}^{-4}$$

The definition of pH provides the relation to the reaction quotient.

$$\text{pH} \equiv -\log(a_{\text{H}^+}) = -\frac{\ln(a_{\text{H}^+})}{\ln(10)} = -\frac{\ln(Q^{-1/4})}{\ln(10)} = \frac{\ln(Q)}{4 \ln(10)} \quad \text{or} \quad \ln(Q) = 4 \ln(10) \text{ pH}$$

The Nernst equation [6C.4] at 25 °C is now used to relate cell potentials to the pH.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{25.693 \times 10^{-3} \text{ V}}{\nu} \ln Q \\ &= E_{\text{cell}}^{\ominus} - \frac{25.693 \times 10^{-3} \text{ V}}{\nu} (4 \ln(10) \text{ pH}) \\ \text{pH} &= \frac{\nu}{0.23664 \text{ V}} (E_{\text{cell}}^{\ominus} - E_{\text{cell}}) \\ &= \frac{2}{0.23664 \text{ V}} \times (0.4318 - 0.190) \text{ V} \\ &= \boxed{2.04} \end{aligned}$$

6D Electrode potentials

Answers to discussion questions

6D.2 The pH of an aqueous solution can in principle be measured with any electrode having an emf that is sensitive to $\text{H}^+(\text{aq})$ concentration (activity). In principle, the hydrogen gas electrode is the simplest and most fundamental. A cell is constructed with the hydrogen electrode being the right-hand electrode and any reference electrode with known potential as the left-hand electrode. A common choice is the saturated calomel electrode. The pH can then be obtained by measuring the emf (zero-current potential difference), E_{cell} , of the cell. The hydrogen gas electrode is not convenient to use, so in practice glass electrodes are used because of ease of handling (see Impact I6.2).

Solutions to exercises

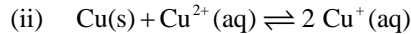
6D.1(b) In each case the equilibrium constant is calculated with the expression $\ln K = \frac{\nu F E_{\text{cell}}^{\ominus}}{RT}$ [6C.5].

(i) $\text{Sn}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightleftharpoons \text{Cu}(\text{s}) + \text{SnSO}_4(\text{aq})$



$$\ln K = \frac{\nu F E_{\text{cell}}^{\ominus}}{RT} \quad [6C.5] = \frac{(2) \times (0.48 \text{ V})}{25.693 \text{ mV}} = 37.4$$

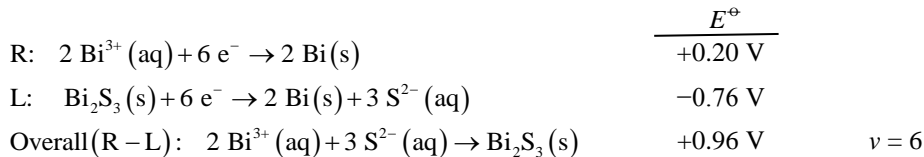
$$K = e^{37.4} = \boxed{1.7 \times 10^{16}}$$



$$\ln K = \frac{\nu F E_{\text{cell}}^{\ominus}}{RT} \quad [6\text{C.5}] = \frac{(1) \times (-0.36 \text{ V})}{25.693 \text{ mV}} = -14.0$$

$$K = e^{-14.0} = \boxed{8.3 \times 10^{-7}}$$

6D.2(b) $\text{Bi}|\text{Bi}_2\text{S}_3(\text{s})|\text{Bi}_2\text{S}_3(\text{aq})|\text{Bi}$



(i) $\ln K = \frac{\nu F E_{\text{cell}}^{\ominus}}{RT} \quad [6\text{C.5}] = \frac{6(0.96 \text{ V})}{(25.693 \times 10^{-3} \text{ V})} = 224$

$$K = e^{224} = 1.9 \times 10^{97}$$

The solubility equilibrium is written as the reverse of the cell reaction. Therefore, the solubility product of $\text{Bi}_2\text{S}_3(\text{s})$ is $K_{\text{sp}} = K^{-1} = 1 / 1.9 \times 10^{97} = \boxed{5.3 \times 10^{-98}}$.

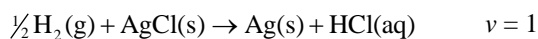
(ii) The solubility product of $\text{Bi}_2\text{S}_3(\text{s})$ is very small. Consequently, the molar solubility, s , of $\text{Bi}_2\text{S}_3(\text{s})$ must also be very low and we can reasonably take the activity coefficients of the aqueous ions to equal 1.

$$K_{\text{sp}} = [\text{Bi}^{2+}]^2 [\text{S}^{2-}]^3 / (c^{\ominus})^5 = (2s)^2 (3s)^3 / (c^{\ominus})^5 = 108 (s/c^{\ominus})^5$$

$$s = (K_{\text{sp}} / 108)^{1/5} c^{\ominus} = (5.3 \times 10^{-98} / 108)^{1/5} \text{ mol dm}^{-3} = \boxed{1.4 \times 10^{-20} \text{ mol dm}^{-3} \text{ or } 7.2 \text{ ag dm}^{-3}}$$

Solutions to problems

6D.2 The method of the solution is first to determine $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and $\Delta_f S^{\ominus}$ at 25 °C for the cell reaction



and then, from the values of these quantities and the known values of $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and S^{\ominus} , for all the species other than $\text{Cl}^-(\text{aq})$, to calculate $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and S^{\ominus} for $\text{Cl}^-(\text{aq})$.

Since $E_{\text{cell}}^{\ominus} = E_{\text{AgCl/Ag,Cl}^-}^{\ominus} - E_{\text{H}^+/\text{H}_2}^{\ominus} = E_{\text{AgCl/Ag,Cl}^-}^{\ominus} - 0 = E_{\text{AgCl/Ag,Cl}^-}^{\ominus}$, we have (R.G. Bates and V.E. Bowers, *J. Res. Nat. Bur. Stand.*, **53**, 283 (1954)):

$$E_{\text{cell}}^{\ominus} / \text{V} = 0.23659 - 4.8564 \times 10^{-4} (\theta/^{\circ}\text{C}) - 3.4205 \times 10^{-6} (\theta/^{\circ}\text{C})^2 + 5.869 \times 10^{-9} (\theta/^{\circ}\text{C})^3$$

and we proceed with the calculation of the electrochemical and thermodynamic reaction properties at 25 °C.

$$\begin{aligned} E_{\text{cell}}^{\ominus} / \text{V} &= (0.23659) - (4.8564 \times 10^{-4}) \times (25.00) - (3.4205 \times 10^{-6}) \times (25.00)^2 + (5.869 \times 10^{-9}) \times (25.00)^3 \\ &= +0.22240 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta_r G^{\ominus} &= -\nu F E_{\text{cell}}^{\ominus} \\ &= -1 \times (96.485 \text{ kC mol}^{-1}) \times (0.22240 \text{ V}) = -21.46 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned}
\Delta_r S^\ominus &= -\left(\frac{\partial \Delta_r G^\ominus}{\partial T}\right)_p = \nu F \left(\frac{\partial E_{\text{cell}}^\ominus}{\partial T}\right)_p \quad [6C.6] = \nu F \left(\frac{\partial E_{\text{cell}}^\ominus}{\partial \theta}\right)_p \frac{^\circ\text{C}}{\text{K}} \quad [d\theta/^\circ\text{C} = dT/\text{K}] \\
&= \nu F \left\{ (-4.8564 \times 10^{-4} / ^\circ\text{C}) - 2 \times (3.4205 \times 10^{-6} \theta / (^\circ\text{C})^2) + 3 \times (5.869 \times 10^{-9} \theta^2 / (^\circ\text{C})^3) \right\} \frac{^\circ\text{C V}}{\text{K}} \\
&= 1 \times (96.485 \text{ kC mol}^{-1}) \times \left\{ \begin{aligned} &(-4.8564 \times 10^{-4}) - 2 \times (3.4205 \times 10^{-6}) \times (25) \\ &+ 3 \times (5.869 \times 10^{-9}) \times (25)^2 \end{aligned} \right\} \frac{\text{V}}{\text{K}} \\
&= -62.30 \text{ J K}^{-1} \text{ mol}^{-1} \\
\Delta_r H^\ominus &= \Delta_r G^\ominus + T \Delta_r S^\ominus \\
&= -(21.46 \text{ kJ mol}^{-1}) + (298.15 \text{ K}) \times (-62.30 \text{ J K}^{-1} \text{ mol}^{-1}) = -40.03 \text{ kJ mol}^{-1}
\end{aligned}$$

The cell reaction Gibbs's energy is related to formation Gibbs's energies by

$$\begin{aligned}
\Delta_r G^\ominus &= \Delta_f G^\ominus(\text{H}^+) + \Delta_f G^\ominus(\text{Cl}^-) - \Delta_f G^\ominus(\text{AgCl}) \\
&= \Delta_f G^\ominus(\text{Cl}^-) - \Delta_f G^\ominus(\text{AgCl}) \quad [\Delta_f G^\ominus(\text{H}^+) = 0]
\end{aligned}$$

Hence, $\Delta_f G^\ominus(\text{Cl}^-) = \Delta_r G^\ominus + \Delta_f G^\ominus(\text{AgCl})$

$$\begin{aligned}
&= (-21.46 - 109.79) \text{ kJ mol}^{-1} \\
&= \boxed{-131.25 \text{ kJ mol}^{-1}}
\end{aligned}$$

Similarly, $\Delta_f H^\ominus(\text{Cl}^-) = \Delta_r H^\ominus + \Delta_f H^\ominus(\text{AgCl})$

$$\begin{aligned}
&= (-40.03 - 127.07) \text{ kJ mol}^{-1} \\
&= \boxed{-167.10 \text{ kJ mol}^{-1}}
\end{aligned}$$

For the entropy of Cl^- in solution we use

$$\Delta_r S^\ominus = S^\ominus(\text{Ag}) + S^\ominus(\text{H}^+) + S^\ominus(\text{Cl}^-) - \frac{1}{2}S^\ominus(\text{H}_2) - S^\ominus(\text{AgCl})$$

with $S^\ominus(\text{H}^+) = 0$. Then,

$$\begin{aligned}
S^\ominus(\text{Cl}^-) &= \Delta_r S^\ominus - S^\ominus(\text{Ag}) + \frac{1}{2}S^\ominus(\text{H}_2) + S^\ominus(\text{AgCl}) \\
&= \{(-62.30) - (42.55) + \frac{1}{2} \times (130.68) + (96.2)\} \text{ J K}^{-1} \text{ mol}^{-1} \\
&= \boxed{+56.7 \text{ J K}^{-1} \text{ mol}^{-1}}
\end{aligned}$$

Integrated activities

6.3 (a) $I = \frac{1}{2} \left\{ \left(\frac{b}{b^\ominus}\right)_+ z_+^2 + \left(\frac{b}{b^\ominus}\right)_- z_-^2 \right\} [5F.9] = 4 \left(\frac{b}{b^\ominus}\right)$

For CuSO_4 , $I = (4) \times (1.0 \times 10^{-3}) = \boxed{4.0 \times 10^{-3}}$

For ZnSO_4 , $I = (4) \times (3.0 \times 10^{-3}) = \boxed{1.2 \times 10^{-2}}$

(b) $\log \gamma_\pm = -|z_+ z_-| A I^{1/2} [5F.8]$

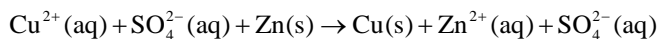
$$\log \gamma_\pm(\text{CuSO}_4) = -(4) \times (0.509) \times (4.0 \times 10^{-3})^{1/2} = -0.1288$$

$$\gamma_\pm(\text{CuSO}_4) = \boxed{0.74}$$

$$\log \gamma_\pm(\text{ZnSO}_4) = -(4) \times (0.509) \times (1.2 \times 10^{-2})^{1/2} = -0.2230$$

$$\gamma_\pm(\text{ZnSO}_4) = \boxed{0.60}$$

(c) The reaction in the Daniell cell is



Hence,
$$Q = \frac{a(\text{Zn}^{2+})a(\text{SO}_4^{2-}, \text{R})}{a(\text{Cu}^{2+})a(\text{SO}_4^{2-}, \text{L})}$$

$$= \frac{\gamma_+ b_+(\text{Zn}^{2+})\gamma_- b_-(\text{SO}_4^{2-}, \text{R})}{\gamma_+ b_+(\text{Cu}^{2+})\gamma_- b_-(\text{SO}_4^{2-}, \text{L})} \left[b \equiv \frac{b}{b^\ominus} \text{ here and below} \right]$$

where the designations R and L refer to the right and left sides of the equation for the cell reaction and all b are assumed to be unitless, that is, b/b^\ominus .

$$b_+(\text{Zn}^{2+}) = b_-(\text{SO}_4^{2-}, \text{R}) = b(\text{ZnSO}_4)$$

$$b_+(\text{Cu}^{2+}) = b_-(\text{SO}_4^{2-}, \text{L}) = b(\text{CuSO}_4)$$

Therefore,

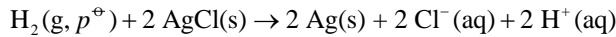
$$Q = \frac{\gamma_{\pm}^2(\text{ZnSO}_4)b^2(\text{ZnSO}_4)}{\gamma_{\pm}^2(\text{CuSO}_4)b^2(\text{CuSO}_4)} = \frac{(0.60)^2 \times (3.0 \times 10^{-3})^2}{(0.74)^2 \times (1.0 \times 10^{-3})^2} = 5.9\bar{2} = \boxed{5.9}$$

(d)
$$E_{\text{cell}}^\ominus = -\frac{\Delta_r G^\ominus}{\nu F} [6C.3] = \frac{-(-212.7 \times 10^3 \text{ J mol}^{-1})}{(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1})} = \boxed{+1.102 \text{ V}}$$

(e)
$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{25.693 \times 10^{-3} \text{ V}}{\nu} \ln Q = (1.102 \text{ V}) - \left(\frac{25.693 \times 10^{-3} \text{ V}}{2} \right) \ln(5.9\bar{2})$$

$$= (1.102 \text{ V}) - (0.023 \text{ V}) = \boxed{+1.079 \text{ V}}$$

6.4 Pt|H₂(g, p^\ominus)|NaOH(aq, 0.01000 mol kg⁻¹), NaCl(aq, 0.01125 mol kg⁻¹)|AgCl(s)|Ag(s)



where $\nu = 2$ [Activities of solids equal 1 and $p_{\text{H}_2} = p^\ominus$.]

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{2F} \ln \{a_{\text{H}^+} a_{\text{Cl}^-}\}^2 \quad [6C.4 \text{ and } 6A.12(\text{b})]$$

$$= E_{\text{cell}}^\ominus - \frac{RT}{F} \ln \{a_{\text{H}^+} a_{\text{Cl}^-}\} = E_{\text{cell}}^\ominus - \frac{RT}{F} \ln \frac{K_w a_{\text{Cl}^-}}{a_{\text{OH}^-}} = E_{\text{cell}}^\ominus - \frac{RT}{F} \ln \frac{K_w \gamma_{\pm} b_{\text{Cl}^-}}{\gamma_{\pm} b_{\text{OH}^-}}$$

$$= E_{\text{cell}}^\ominus - \frac{RT}{F} \ln \frac{K_w b_{\text{Cl}^-}}{b_{\text{OH}^-}} = E_{\text{cell}}^\ominus - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \frac{b_{\text{Cl}^-}}{b_{\text{OH}^-}}$$

$$= E_{\text{cell}}^\ominus + \ln 10 \frac{RT}{F} \times \text{p}K_w - \frac{RT}{F} \ln \frac{b_{\text{Cl}^-}}{b_{\text{OH}^-}} \quad \left(\text{p}K_w = -\log K_w = \frac{-\ln K_w}{\ln 10} \right)$$

Hence,
$$\text{p}K_w = \frac{E_{\text{cell}} - E_{\text{cell}}^\ominus}{\ln 10 RT / F} + \frac{\ln \left(\frac{b_{\text{Cl}^-}}{b_{\text{OH}^-}} \right)}{\ln 10}$$

$$= (5039.75 \text{ V}^{-1}) \times \left(\frac{E_{\text{cell}} - E_{\text{cell}}^\ominus}{T / \text{K}} \right) + \frac{\ln(0.0100 / 0.01125)}{\ln 10}$$

$$= (5039.75 \text{ V}^{-1}) \times \left(\frac{E_{\text{cell}} - E_{\text{cell}}^\ominus}{T / \text{K}} \right) - 0.05115$$

Using information of the data tables, we find that

$$E_{\text{cell}}^\ominus = E_{\text{R}}^\ominus - E_{\text{L}}^\ominus = E^\ominus(\text{AgCl}, \text{Ag}) - E^\ominus(\text{H}^+/\text{H}_2) = +0.22 \text{ V} - 0 = +0.22 \text{ V}.$$

This value does not have the precision needed for computations with the high precision data of this problem. Consequently, we will use the more precise value found in the *CRC Handbook of Chemistry and Physics* (71st ed): $E_{\text{cell}}^{\ominus} = 0.22233 \text{ V}$. We then draw up the following table.

$\theta / ^{\circ}\text{C}$	20.0	25.0	30.0
$E_{\text{cell}} / \text{V}$	1.04774	1.04864	1.04942
$\text{p}K_{\text{w}}$	14.14	13.92	13.70

Inspection of the table reveals that for each 5 K increase in temperature the value of $\text{p}K_{\text{w}}$ decreases by 0.22 and, consequently, $d(\text{p}K_{\text{w}})/dT = -0.22 / 5.0 \text{ K} = -0.044 \text{ K}^{-1}$. Thus, at 25 $^{\circ}\text{C}$:

$$\begin{aligned} \frac{d \ln K_{\text{w}}}{dT} &= \frac{\Delta_{\text{w}} H^{\ominus}}{RT^2} \quad [6\text{B.2(a)}] \\ \Delta_{\text{w}} H^{\ominus} &= RT^2 \frac{d \ln K_{\text{w}}}{dT} = \ln 10 \times RT^2 \frac{d \log K_{\text{w}}}{dT} = -\ln 10 \times RT^2 \frac{d \text{p}K_{\text{w}}}{dT} \\ &= -\ln 10 \times (8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})^2 \times (-0.044 \text{ K}^{-1}) \\ &= \boxed{+74.9 \text{ kJ mol}^{-1}} \\ \Delta_{\text{w}} G^{\ominus} &= -RT \ln K_{\text{w}} = \ln 10 \times RT \times \text{p}K_{\text{w}} = \boxed{+79.5 \text{ kJ mol}^{-1}} \\ \Delta_{\text{w}} S^{\ominus} &= \frac{\Delta_{\text{w}} H^{\ominus} - \Delta_{\text{w}} G^{\ominus}}{T} = \boxed{-15.4 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

6.5[†] Electrochemical Cell Equation: $\frac{1}{2} \text{H}_2(\text{g}, 1 \text{ bar}) + \text{AgCl}(\text{s}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}(\text{s})$

with $a(\text{H}_2) = 1 \text{ bar} = p^{\ominus}$ and $a_{\text{Cl}^-} = \gamma_{\text{Cl}^-} b$.

Weak acid Equilibrium: $\text{BH}^+ \rightleftharpoons \text{B} + \text{H}^+$ with $b_{\text{BH}^+} = b_{\text{B}} = b$

$$K_{\text{a}} = a_{\text{B}} a_{\text{H}^+} / a_{\text{BH}^+} = \gamma_{\text{B}} b a_{\text{H}^+} / (\gamma_{\text{BH}^+} b) = \gamma_{\text{B}} a_{\text{H}^+} / \gamma_{\text{BH}^+}$$

Thus, $a_{\text{H}^+} = \gamma_{\text{BH}^+} K_{\text{a}} / \gamma_{\text{B}}$.

Ionic strength (neglect b_{H^+} because $b_{\text{H}^+} \ll b$): $I = \frac{1}{2} \{ z_{\text{BH}^+}^2 b_{\text{BH}^+} + z_{\text{Cl}^-}^2 b_{\text{Cl}^-} \} = b$.

According to the Nernst equation [6C.4]

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{RT}{F} \ln \left(\frac{a_{\text{H}^+} a_{\text{Cl}^-}}{p(\text{H}_2) / p^{\ominus}} \right) = E_{\text{cell}}^{\ominus} - \frac{RT \ln(10)}{F} \log(a_{\text{H}^+} a_{\text{Cl}^-}) \\ \frac{F}{RT \ln(10)} (E_{\text{cell}} - E_{\text{cell}}^{\ominus}) &= -\log(a_{\text{H}^+} \gamma_{\text{Cl}^-} b) = -\log \left(\frac{K_{\text{a}} \gamma_{\text{BH}^+} \gamma_{\text{Cl}^-} b}{\gamma_{\text{B}}} \right) \\ &= \text{p}K_{\text{a}} - \log(b) - 2\log(\gamma_{\pm}) \quad \text{where} \quad \gamma_{\pm}^2 \equiv \gamma_{\text{BH}^+} \gamma_{\text{Cl}^-} / \gamma_{\text{B}} \end{aligned}$$

Substitution of the Davies equation,

$$\log \gamma_{\pm} = -\frac{A |z_+ z_-| I^{1/2}}{1 + BI^{1/2}} + CI \quad [5\text{F.11(b)}],$$

gives

$$\frac{F}{RT \ln(10)} (E_{\text{cell}} - E_{\text{cell}}^{\ominus}) = \text{p}K_{\text{a}} - \log(b) + \frac{2A\sqrt{b}}{1 + B\sqrt{b}} - 2Cb \quad \text{where} \quad A = 0.5091.$$

The expression to the left of the above equality is experimental data that is a function of b . The parameters $\text{p}K_{\text{a}}$, B , and C on the right side are systematically varied with a mathematical regression software package like Mathcad until the right side fits the left side in a least squares sense. The results are: $\boxed{\text{p}K_{\text{a}} = 6.736}$, $\boxed{B = 1.997}$, and $\boxed{C = -0.121}$.

The mean activity coefficient is calculated with the equation $\gamma_{\pm} = 10^{\left(\frac{-AI^{1/2}}{1+BI^{1/2}} + Cb\right)}$ for desired values of b and I . Figure I6.1 shows a γ_{\pm} against I plot for $b = 0.04 \text{ mol kg}^{-1}$ and $0 \leq I \leq 0.1$.

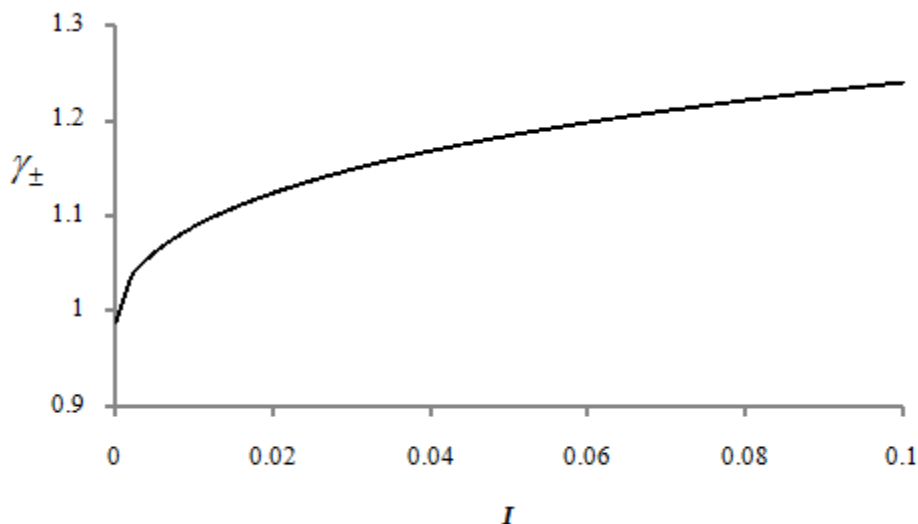


Figure I6.1

6.6 $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$ [6A.10]

In Equation 6A.10 molar solution concentrations are used with 1 M standard states ($c^\ominus = 1 \text{ mol dm}^{-3}$). The standard state (\ominus) pH equals zero in contrast to the biological standard state (\oplus) of pH 7. For the ATP hydrolysis



we can calculate the standard state free energy given the biological standard free energy of about -31 kJ mol^{-1} (Impact On Biochemistry I6.1).

$$\Delta_r G^\oplus = \Delta_r G^\ominus + RT \ln Q^\oplus \quad [6A.10]$$

$$\Delta_r G^\ominus = \Delta_r G^\oplus - RT \ln Q^\oplus$$

$$= -31 \text{ kJ mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K}) \ln(10^{-7} \text{ M/1 M})$$

$$= +11 \text{ kJ mol}^{-1}$$

This calculation shows that under standard conditions the hydrolysis of ATP is not spontaneous! It is endergonic.

The calculation of the ATP hydrolysis free energy with the cell conditions pH = 7, $[\text{ATP}] = [\text{ADP}] = [\text{P}_i^-] = 1.0 \times 10^{-3} \text{ M}$, is interesting.

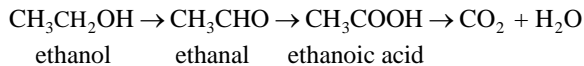
$$\Delta_r G = \Delta_r G^\oplus + RT \ln Q = \Delta_r G^\oplus + RT \ln \left(\frac{[\text{ADP}] \times [\text{P}_i^-] \times [\text{H}^+]}{[\text{ATP}] \times (1 \text{ M})^2} \right)$$

$$= +11 \text{ kJ mol}^{-1} + (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K}) \ln(10^{-3} \times 10^{-7})$$

$$= -48 \text{ kJ mol}^{-1}$$

The concentration conditions in biological cells make the hydrolysis of ATP spontaneous and very exergonic. A maximum of 48 kJ of work is available to drive coupled chemical reactions when a mole of ATP is hydrolyzed.

6.7 Yes, a bacterium can evolve to utilize the ethanol/nitrate pair to exergonically release the free energy needed for ATP synthesis. The ethanol reductant may yield any of the following products.

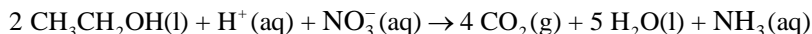
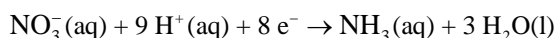
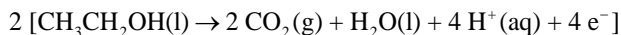


The nitrate oxidant may receive electrons to yield any of the following products.



nitrate nitrite dinitrogen ammonia

Oxidation of two ethanol molecules to carbon dioxide and water can transfer 8 electrons to nitrate during the formation of ammonia. The half-reactions and net reaction are:



$\Delta_r G^\ominus = -2331.29 \text{ kJ}$ for the reaction as written (a data table calculation). Of course, enzymes must evolve that couple this exergonic redox reaction to the production of ATP, which would then be available for carbohydrate, protein, lipid, and nucleic acid synthesis.

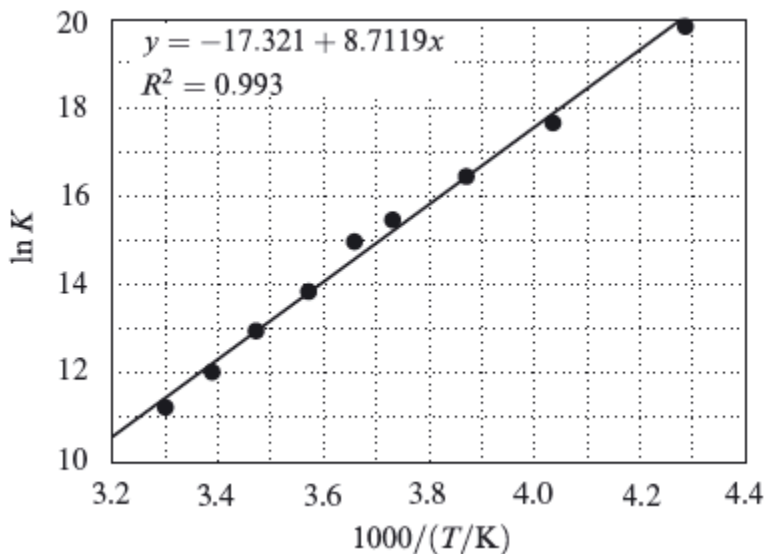
6.8[†] (a) The equilibrium constant is given by

$$K = \exp\left(\frac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right) \exp\left(\frac{\Delta_r S^\ominus}{R}\right) \quad [6A.18]$$

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. I6.2).

Figure I6.2



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

$$= \boxed{-72.4 \text{ kJ mol}^{-1}}$$

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

(b)
$$\Delta_r H^\ominus = \Delta_f H^\ominus((\text{ClO})_2) - 2 \Delta_f H^\ominus(\text{ClO}) \quad \text{so} \quad \Delta_f H^\ominus((\text{ClO})_2) = \Delta_r H^\ominus + 2 \Delta_f H^\ominus(\text{ClO}).$$

$$\Delta_f H^\ominus((\text{ClO})_2) = [-72.4 + 2(101.8)] \text{ kJ mol}^{-1} = \boxed{+131.2 \text{ kJ mol}^{-1}}$$

$$S^{\ominus}((\text{ClO})_2) = [-144 + 2(226.6)] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{+309.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$