

# CHAPTER 6 Chemical equilibrium

## TOPIC 6A The equilibrium constant

### Discussion questions

**6A.1** Explain how the mixing of reactants and products affects the position of chemical equilibrium.

**6A.2** What is the justification for not including a pure liquid or solid in the expression for an equilibrium constant?

### Exercises

**6A.1(a)** Consider the reaction  $A \rightarrow 2B$ . Initially, 1.50 mol A is present and no B. What are the amounts of A and B when the extent of reaction is 0.60 mol?

**6A.1(b)** Consider the reaction  $2A \rightarrow B$ . Initially, 1.75 mol A and 0.12 mol B are present. What are the amounts of A and B when the extent of reaction is 0.30 mol?

**6A.2(a)** When the reaction  $A \rightarrow 2B$  advances by 0.10 mol (that is,  $\Delta\xi = +0.10$  mol) the Gibbs energy of the system changes by  $-6.4$  kJ mol<sup>-1</sup>. What is the Gibbs energy of reaction at this stage of the reaction?

**6A.2(b)** When the reaction  $2A \rightarrow B$  advances by 0.051 mol (that is,  $\Delta\xi = +0.051$  mol) the Gibbs energy of the system changes by  $-2.41$  kJ mol<sup>-1</sup>. What is the Gibbs energy of reaction at this stage of the reaction?

**6A.3(a)** The standard Gibbs energy of the reaction  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$  is  $-32.9$  kJ mol<sup>-1</sup> at 298 K. What is the value of  $\Delta_r G$  when  $Q =$  (i) 0.010, (ii) 1.0, (iii) 10.0, (iv) 100 000, (v) 1 000 000? Estimate (by interpolation) the value of  $K$  from the values you calculate. What is the actual value of  $K$ ?

**6A.3(b)** The standard Gibbs energy of the reaction  $2NO_2(g) \rightarrow N_2O_4(g)$  is  $-4.73$  kJ mol<sup>-1</sup> at 298 K. What is the value of  $\Delta_r G$  when  $Q =$  (i) 0.10, (ii) 1.0, (iii) 10, (iv) 100? Estimate (by interpolation) the value of  $K$  from the values you calculate. What is the actual value of  $K$ ?

**6A.4(a)** At 2257 K and 1.00 bar total pressure, water is 1.77 per cent dissociated at equilibrium by way of the reaction  $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ . Calculate  $K$ .

**6A.4(b)** For the equilibrium,  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ , the degree of dissociation,  $\alpha$ , at 298 K is 0.201 at 1.00 bar total pressure. Calculate  $K$ .

**6A.5(a)** Dinitrogen tetroxide is 18.46 per cent dissociated at 25 °C and 1.00 bar in the equilibrium  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ . Calculate  $K$  at (i) 25 °C, (ii) 100 °C given that  $\Delta_r H^\ominus = +56.2$  kJ mol<sup>-1</sup> over the temperature range.

**6A.5(b)** Molecular bromine is 24 per cent dissociated at 1600 K and 1.00 bar in the equilibrium  $Br_2(g) \rightleftharpoons 2Br(g)$ . Calculate  $K$  at (i) 1600 °C, (ii) 2000 °C given that  $\Delta_r H^\ominus = +112$  kJ mol<sup>-1</sup> over the temperature range.

**6A.6(a)** From information in the *Resource section*, calculate the standard Gibbs energy and the equilibrium constant at (i) 298 K and (ii) 400 K for the reaction  $PbO(s) + CO(g) \rightleftharpoons Pb(s) + CO_2(g)$ . Assume that the reaction enthalpy is independent of temperature.

**6A.6(b)** From information in the *Resource section*, calculate the standard Gibbs energy and the equilibrium constant at (i) 25 °C and (ii) 50 °C for the reaction  $CH_4(g) + 3Cl_2(g) \rightleftharpoons CHCl_3(l) + 3HCl(g)$ . Assume that the reaction enthalpy is independent of temperature.

**6A.7(a)** Establish the relation between  $K$  and  $K_c$  for the reaction  $H_2CO(g) \rightleftharpoons CO(g) + H_2(g)$ .

**6A.7(b)** Establish the relation between  $K$  and  $K_c$  for the reaction  $3N_2(g) + H_2(g) \rightleftharpoons 2HN_3(g)$ .

**6A.8(a)** In the gas-phase reaction  $2A + B \rightleftharpoons 3C + 2D$ , it was found that, when 1.00 mol A, 2.00 mol B, and 1.00 mol D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.90 mol C at a total pressure of 1.00 bar. Calculate (i) the mole fractions of each species at equilibrium, (ii)  $K_x$ , (iii)  $K$ , and (iv)  $\Delta_r G^\ominus$ .

**6A.8(b)** In the gas-phase reaction  $A + B \rightleftharpoons C + 2D$ , it was found that, when 2.00 mol A, 1.00 mol B, and 3.00 mol D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.79 mol C at a total pressure of 1.00 bar. Calculate (i) the mole fractions of each species at equilibrium, (ii)  $K_x$ , (iii)  $K$ , and (iv)  $\Delta_r G^\ominus$ .

**6A.9(a)** The standard reaction Gibbs energy of the isomerization of borneol ( $C_{10}H_{17}OH$ ) to isoborneol in the gas phase at 503 K is  $+9.4$  kJ mol<sup>-1</sup>. Calculate the reaction Gibbs energy in a mixture consisting of 0.15 mol of borneol and 0.30 mol of isoborneol when the total pressure is 600 Torr.

**6A.9(b)** The equilibrium pressure of  $H_2$  over solid uranium and uranium hydride,  $UH_3$ , at 500 K is 139 Pa. Calculate the standard Gibbs energy of formation of  $UH_3(s)$  at 500 K.

**6A.10(a)** The standard Gibbs energy of formation of  $NH_3(g)$  is  $-16.5$  kJ mol<sup>-1</sup> at 298 K. What is the reaction Gibbs energy when the partial pressures of the  $N_2$ ,  $H_2$ , and  $NH_3$  (treated as perfect gases) are 3.0 bar, 1.0 bar, and 4.0 bar, respectively? What is the spontaneous direction of the reaction in this case?

**6A.10(b)** The standard Gibbs energy of formation of  $PH_3(g)$  is  $+13.4$  kJ mol<sup>-1</sup> at 298 K. What is the reaction Gibbs energy when the partial pressures of the  $H_2$  and  $PH_3$  (treated as perfect gases) are 1.0 bar and 0.60 bar, respectively? What is the spontaneous direction of the reaction in this case?

**6A.11(a)** For  $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$ ,  $K = 3.9 \times 10^{-11}$  at 25 °C and the standard Gibbs energy of formation of  $CaF_2(s)$  is  $-1167$  kJ mol<sup>-1</sup>. Calculate the standard Gibbs energy of formation of  $CaF_2(aq)$ .

**6A.11(b)** For  $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$ ,  $K = 1.4 \times 10^{-8}$  at 25 °C and the standard Gibbs energy of formation of  $PbI_2(s)$  is  $-173.64$  kJ mol<sup>-1</sup>. Calculate the standard Gibbs energy of formation of  $PbI_2(aq)$ .

### Problems

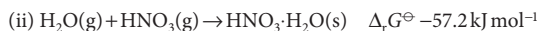
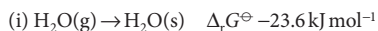
**6A.1** The equilibrium constant for the reaction  $I_2(s) + Br_2(g) \rightleftharpoons 2IBr(g)$  is 0.164 at 25 °C. (a) Calculate  $\Delta_r G^\ominus$  for this reaction. (b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25 °C, respectively. Find the partial pressure of  $IBr(g)$  at equilibrium. Assume that all the bromine is in the liquid form and that the vapour pressure of iodine is negligible. (c) In fact,

solid iodine has a measurable vapour pressure at 25 °C. In this case, how would the calculation have to be modified?

**6A.2** Calculate the equilibrium constant of the reaction  $CO(g) + H_2(g) \rightleftharpoons H_2CO(g)$  given that, for the production of liquid formaldehyde,  $\Delta_r G^\ominus = +28.95$  kJ mol<sup>-1</sup> at 298 K and that the vapour pressure of formaldehyde is 1500 Torr at that temperature.

**6A.3** A sealed container was filled with 0.300 mol  $\text{H}_2(\text{g})$ , 0.400 mol  $\text{I}_2(\text{g})$ , and 0.200 mol  $\text{HI}(\text{g})$  at 870 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that  $K=870$  for the reaction  $\text{H}_2(\text{g})+\text{I}_2(\text{g})\rightleftharpoons 2\text{HI}(\text{g})$ .

**6A.4\*** Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. Standard reaction Gibbs energies are as follows:



Which solid is thermodynamically most stable at 190 K if  $p_{\text{H}_2\text{O}}=0.13 \mu\text{bar}$  and  $p_{\text{HNO}_3}=0.41 \text{ nbar}$  *Hint*: Try computing  $\Delta_r G$  for each reaction under the prevailing conditions; if more than one solid form spontaneously, examine  $\Delta_r G$  for the conversion of one solid to another.

**6A.5** Express the equilibrium constant of a gas-phase reaction  $\text{A} + 3\text{B} \rightleftharpoons 2\text{C}$  in terms of the equilibrium value of the extent of reaction,  $\xi$ , given that initially A and B were present in stoichiometric proportions. Find an expression for  $\xi$  as a function of the total pressure,  $p$ , of the reaction mixture and sketch a graph of the expression obtained.

## TOPIC 6B The response to equilibria to the conditions

### Discussion questions

**6B.1** Suggest how the thermodynamic equilibrium constant may respond differently to changes in pressure and temperature from the equilibrium constant expressed in terms of partial pressures.

**6B.2** Account for Le Chatelier's principle in terms of thermodynamic quantities.

**6B.3** Explain the molecular basis of the van 't Hoff equation for the temperature dependence of  $K$ .

### Exercises

**6B.1(a)** The standard reaction enthalpy of  $\text{Zn}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2(\text{g})$  is approximately constant at  $+224 \text{ kJ mol}^{-1}$  from 920 K up to 1280 K. The standard reaction Gibbs energy is  $+33 \text{ kJ mol}^{-1}$  at 1280 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

**6B.1(b)** The standard enthalpy of a certain reaction is approximately constant at  $+125 \text{ kJ mol}^{-1}$  from 800 K up to 1500 K. The standard reaction Gibbs energy is  $+22 \text{ kJ mol}^{-1}$  at 1120 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

**6B.2(a)** The equilibrium constant of the reaction  $2\text{C}_2\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$  is found to fit the expression  $\ln K = A + B/T + C/T^2$  between 300 K and 600 K, with  $A = -1.04$ ,  $B = -1088 \text{ K}$ , and  $C = 1.51 \times 10^5 \text{ K}^2$ . Calculate the standard reaction enthalpy and standard reaction entropy at 400 K.

**6B.2(b)** The equilibrium constant of a reaction is found to fit the expression  $\ln K = A + B/T + C/T^3$  between 400 K and 500 K with  $A = -2.04$ ,  $B = -1176 \text{ K}$ , and  $C = 2.1 \times 10^7 \text{ K}^3$ . Calculate the standard reaction enthalpy and standard reaction entropy at 450 K.

**6B.3(a)** Calculate the percentage change in  $K_x$  for the reaction  $\text{H}_2\text{CO}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$  when the total pressure is increased from 1.0 bar to 2.0 bar at constant temperature.

**6B.3(b)** Calculate the percentage change in  $K_x$  for the reaction  $\text{CH}_3\text{OH}(\text{g}) + \text{NOCl}(\text{g}) \rightleftharpoons \text{HCl}(\text{g}) + \text{CH}_3\text{NO}_2(\text{g})$  when the total pressure is increased from 1.0 bar to 2.0 bar at constant temperature.

**6B.4(a)** The equilibrium constant for the gas-phase isomerization of borneol ( $\text{C}_{10}\text{H}_{17}\text{OH}$ ) to isoborneol at 503 K is 0.106. A mixture consisting of 7.50 g of borneol and 14.0 g of isoborneol in a container of volume 5.0 dm<sup>3</sup> is heated to 503 K and allowed to come to equilibrium. Calculate the mole fractions of the two substances at equilibrium.

### Problems

**6B.1** Consider the dissociation of methane,  $\text{CH}_4(\text{g})$ , into the elements  $\text{H}_2(\text{g})$  and C(s, graphite). (a) Given that  $\Delta_r H^\ominus(\text{CH}_4, \text{g}) = -74.85 \text{ kJ mol}^{-1}$  and that

\* These problems were supplied by Charles Trapp and Carmen Giunta.

**6B.4(b)** The equilibrium constant for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  is  $1.69 \times 10^{-3}$  at 2300 K. A mixture consisting of 5.0 g of nitrogen and 2.0 g of oxygen in a container of volume 1.0 dm<sup>3</sup> is heated to 2300 K and allowed to come to equilibrium. Calculate the mole fraction of NO at equilibrium.

**6B.5(a)** What is the standard enthalpy of a reaction for which the equilibrium constant is (i) doubled, (ii) halved when the temperature is increased by 10 K at 298 K?

**6B.5(b)** What is the standard enthalpy of a reaction for which the equilibrium constant is (i) doubled, (ii) halved when the temperature is increased by 15 K at 310 K?

**6B.6(a)** Estimate the temperature at which  $\text{CaCO}_3$  (calcite) decomposes.

**6B.6(b)** Estimate the temperature at which  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  undergoes dehydration.

**6B.7(a)** The dissociation vapour pressure of a salt  $\text{A}_2\text{B}(\text{s}) \rightleftharpoons \text{A}_2(\text{g}) + \text{B}(\text{g})$  at 367 °C is 208 kPa but at 477 °C it has risen to 547 kPa. Calculate (i) the equilibrium constant, (ii) the standard reaction Gibbs energy, (iii) the standard enthalpy, (iv) the standard entropy of dissociation, all at 422 °C. Assume that the vapour behaves as a perfect gas and that  $\Delta_r H^\ominus$  and  $\Delta_r S^\ominus$  are independent of temperature in the range given.

**6B.7(b)** The dissociation vapour pressure of  $\text{NH}_4\text{Cl}$  at 427 °C is 608 kPa but at 459 °C it has risen to 1115 kPa. Calculate (i) the equilibrium constant, (ii) the standard reaction Gibbs energy, (iii) the standard enthalpy, (iv) the standard entropy of dissociation, all at 427 °C. Assume that the vapour behaves as a perfect gas and that  $\Delta_r H^\ominus$  and  $\Delta_r S^\ominus$  are independent of temperature in the range given.

$\Delta_r S^\ominus = -80.67 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298 K, calculate the value of the equilibrium constant at 298 K. (b) Assuming that  $\Delta_r H^\ominus$  is independent of temperature, calculate  $K$  at 50 °C. (c) Calculate the degree of dissociation,  $\alpha$ , of methane

at 25 °C and a total pressure of 0.010 bar. (d) Without doing any numerical calculations, explain how the degree of dissociation for this reaction will change as the pressure and temperature are varied.

**6B.2** The equilibrium pressure of  $\text{H}_2$  over  $\text{U}(\text{s})$  and  $\text{UH}_3(\text{s})$  between 450 K and 715 K fits the expression  $\ln(p/\text{Pa}) = A + B/T + C \ln(T/\text{K})$ , with  $A = 69.32$ ,  $B = -1.464 \times 10^4 \text{ K}$ , and  $C = -5.65$ . Find an expression for the standard enthalpy of formation of  $\text{UH}_3(\text{s})$  and from it calculate  $\Delta_f C_p^\ominus$ .

**6B.3** The degree of dissociation,  $\alpha$ , of  $\text{CO}_2(\text{g})$  into  $\text{CO}(\text{g})$  and  $\text{O}_2(\text{g})$  at high temperatures was found to vary with temperature as follows:

$T/\text{K}$	1395	1443	1498
$\alpha/10^{-4}$	1.44	2.50	4.71

Assuming  $\Delta_f H^\ominus$  to be constant over this temperature range, calculate  $K$ ,  $\Delta_f G^\ominus$ ,  $\Delta_f H^\ominus$ , and  $\Delta_f S^\ominus$ . Make any justifiable approximations.

**6B.4** The standard reaction enthalpy for the decomposition of  $\text{CaCl}_2 \cdot \text{NH}_3(\text{s})$  into  $\text{CaCl}_2(\text{s})$  and  $\text{NH}_3(\text{g})$  is nearly constant at  $+78 \text{ kJ mol}^{-1}$  between 350 K and 470 K. The equilibrium pressure of  $\text{NH}_3$  in the presence of  $\text{CaCl}_2 \cdot \text{NH}_3$  is 1.71 kPa at 400 K. Find an expression for the temperature dependence of  $\Delta_f G^\ominus$  in the same range.

**6B.5** Acetic acid was evaporated in a container of volume  $21.45 \text{ cm}^3$  at 437 K and at an external pressure of 101.9 kPa, and the container was then sealed. The mass of acid present in the sealed container was 0.0519 g. The experiment was repeated with the same container but at 471 K, and it was found that

0.0380 g of acetic acid was present. Calculate the equilibrium constant for the dimerization of the acid in the vapour and the enthalpy of vaporization.

**6B.6** The dissociation of  $\text{I}_2$  can be monitored by measuring the total pressure, and three sets of results are as follows:

$T/\text{K}$	973	1073	1173
$100p/\text{atm}$	6.244	6.500	9.181
$10^4 n_1$	2.4709	2.4555	2.4366

where  $n_1$  is the amount of I atoms per mole of  $\text{I}_2$  molecules in the mixture, which occupied  $342.68 \text{ cm}^3$ . Calculate the equilibrium constants of the dissociation and the standard enthalpy of dissociation at the mean temperature.

**6B.7\*** The 1980s saw reports of  $\Delta_f G^\ominus(\text{SiH}_2)$  ranging from 243 to 289  $\text{kJ mol}^{-1}$ . If the standard enthalpy of formation is uncertain by this amount, by what factor is the equilibrium constant for the formation of  $\text{SiH}_2$  from its elements uncertain at (a) 298 K, (b) 700 K?

**6B.8** Find an expression for the standard reaction Gibbs energy at a temperature  $T'$  in terms of its value at another temperature  $T$  and the coefficients  $a$ ,  $b$ , and  $c$  in the expression for the molar heat capacity listed in Table 2B.1. Evaluate the standard Gibbs energy of formation of  $\text{H}_2\text{O}(\text{l})$  at 372 K from its value at 298 K.

**6B.9** Derive an expression for the temperature dependence of  $K_c$  for a gas-phase reaction.

## TOPIC 6C Electrochemical cells

### Discussion questions

**6C.1** Explain why reactions that are not redox reactions may be used to generate an electric current.

**6C.2** Explain the role of a salt bridge.

**6C.3** Why is it necessary to measure the cell potential under zero-current conditions?

**6C.4** Can you identify other contributions to the cell potential when a current is being drawn from the cell?

### Exercises

**6C.1(a)** Write the cell reaction and electrode half-reactions and calculate the standard potential of each of the following cells:

- $\text{Zn}|\text{ZnSO}_4(\text{aq})||\text{AgNO}_3(\text{aq})|\text{Ag}$
- $\text{Cd}|\text{CdCl}_2(\text{aq})||\text{HNO}_3(\text{aq})|\text{H}_2(\text{g})|\text{Pt}$
- $\text{Pt}|\text{K}_3[\text{Fe}(\text{CN})_6](\text{aq}), \text{K}_4[\text{Fe}(\text{CN})_6](\text{aq})||\text{CrCl}_3(\text{aq})|\text{Cr}$

**6C.1(b)** Write the cell reaction and electrode half-reactions and calculate the standard potential of each the following cells:

- $\text{Pt}|\text{Cl}_2(\text{g})|\text{HCl}(\text{aq})||\text{K}_2\text{CrO}_4(\text{aq})|\text{Ag}_2\text{CrO}_4(\text{s})|\text{Ag}$
- $\text{Pt}|\text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq})||\text{Sn}^{4+}(\text{aq}), \text{Sn}^{2+}(\text{aq})|\text{Pt}$
- $\text{Cu}|\text{Cu}^{2+}(\text{aq})||\text{Mn}^{2+}(\text{aq}), \text{H}^+(\text{aq})|\text{MnO}_2(\text{s})|\text{Pt}$

**6C.2(a)** Devise cells in which the following are the reactions and calculate the standard cell potential in each case:

- $\text{Zn}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu}(\text{s})$
- $2 \text{AgCl}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{aq}) + 2 \text{Ag}(\text{s})$
- $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$

**6C.2(b)** Devise cells in which the following are the reactions and calculate the standard cell potential in each case:

- $2 \text{Na}(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{aq})$
- $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$

**6C.3(a)** Use the Debye–Hückel limiting law and the Nernst equation to estimate the potential of the cell  $\text{Ag}|\text{AgBr}(\text{s})|\text{KBr}(\text{aq}, 0.050 \text{ mol kg}^{-1})||\text{Cd}(\text{NO}_3)_2(\text{aq}, 0.010 \text{ mol kg}^{-1})|\text{Cd}$  at 25 °C.

**6C.3(b)** Consider the cell  $\text{Pt}|\text{H}_2(\text{g}, p^\ominus)|\text{HCl}(\text{aq})|\text{AgCl}(\text{s})|\text{Ag}$ , for which the cell reaction is  $2 \text{AgCl}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2 \text{Ag}(\text{s}) + 2 \text{HCl}(\text{aq})$ . At 25 °C and a molality of  $\text{HCl}$  of  $0.010 \text{ mol kg}^{-1}$ ,  $E_{\text{cell}} = +0.4658 \text{ V}$ . (i) Write the Nernst equation for the cell reaction. (ii) Calculate  $\Delta_r G$  for the cell reaction. (iii) Assuming that the Debye–Hückel limiting law holds at this concentration, calculate  $E^\ominus(\text{Cl}^-, \text{AgCl}, \text{Ag})$ .

## Problems

**6C.1** A fuel cell develops an electric potential from the chemical reaction between reagents supplied from an outside source. What is the cell potential of a cell fuelled by (a) hydrogen and oxygen, (b) the combustion of butane at 1.0 bar and 298 K?

**6C.2** Although the hydrogen electrode may be conceptually the simplest electrode and is the basis for our reference state of electrical potential in electrochemical systems, it is cumbersome to use. Therefore, several substitutes for it have been devised. One of these alternatives is the quinhydrone electrode (quinhydrone, Q·QH<sub>2</sub>, is a complex of quinone, C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>=Q, and hydroquinone, C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>H<sub>2</sub>=QH<sub>2</sub>). The electrode half-reaction is Q(aq) + 2 H<sup>+</sup>(aq) + 2 e<sup>-</sup> → QH<sub>2</sub>(aq), E<sup>⊖</sup> = +0.6994 V. If the cell Hg|Hg<sub>2</sub>Cl<sub>2</sub>(s)|HCl(aq)|Q·QH<sub>2</sub>|Au is prepared, and the measured cell potential

is +0.190 V, what is the pH of the HCl solution? Assume that the Debye–Hückel limiting law is applicable.

**6C.3** Fuel cells provide electrical power for spacecraft (as in the NASA space shuttles) and also show promise as power sources for automobiles. Hydrogen and carbon monoxide have been investigated for use in fuel cells, so their solubilities in molten salts are of interest. Their solubilities in a molten NaNO<sub>3</sub>/KNO<sub>3</sub> mixture were found to fit the following expressions:

$$\log s_{\text{H}_2} = -5.39 - \frac{980}{T/\text{K}} \quad \log s_{\text{CO}} = -5.98 - \frac{980}{T/\text{K}}$$

where  $s$  is the solubility in mol cm<sup>-3</sup> bar<sup>-1</sup>. Calculate the standard molar enthalpies of solution of the two gases at 570 K.

## TOPIC 6D Electrode potentials

### Discussion questions

**6D.1** Describe a method for the determination of the standard potential of a redox couple.

**6D.2** Devise a method for the determination of the pH of an aqueous solution.

### Exercises

**6D.1(a)** Calculate the equilibrium constants of the following reactions at 25 °C from standard potential data:

- (i) Sn(s) + Sn<sup>4+</sup>(aq) ⇌ 2 Sn<sup>2+</sup>(aq)  
 (ii) Sn(s) + 2 AgCl(s) ⇌ SnCl<sub>2</sub>(aq) + 2 Ag(s)

**6D.1(b)** Calculate the equilibrium constants of the following reactions at 25 °C from standard potential data:

- (i) Sn(s) + CuSO<sub>4</sub>(aq) ⇌ Cu(s) + SnSO<sub>4</sub>(aq)  
 (ii) Cu<sup>2+</sup>(aq) + Cu(s) ⇌ 2 Cu<sup>+</sup>(aq)

**6D.2(a)** The potential of the cell Ag|AgI(s)|AgI(aq)|Ag is +0.9509 V at 25 °C. Calculate (i) the solubility product of AgI and (ii) its solubility.

**6D.2(b)** The potential of the cell Bi|Bi<sub>2</sub>S<sub>3</sub>(s)|Bi<sub>2</sub>S<sub>3</sub>(aq)|Bi is -0.96 V at 25 °C. Calculate (i) the solubility product of Bi<sub>2</sub>S<sub>3</sub> and (ii) its solubility.

## Problems

**6D.1** The potential of the cell Pt|H<sub>2</sub>(g,  $p^\ominus$ )|HCl(aq,  $b$ )|Hg<sub>2</sub>Cl<sub>2</sub>(s)|Hg(l) has been measured with high precision with the following results at 25 °C:

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
$E/\text{V}$	0.60080	0.56825	0.54366	0.52267	0.50532

Determine the standard cell potential and the mean activity coefficient of HCl at these molalities. (Make a least-squares fit of the data to the best straight line.)

**6D.2** The standard potential of the AgCl/Ag, Cl<sup>-</sup> couple fits the expression

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

Calculate the standard Gibbs energy and enthalpy of formation of Cl<sup>-</sup>(aq) and its entropy at 298 K.

## Integrated activities

**6.1\*** Thorn et al. (*J. Phys. Chem.* **100**, 14178 (1996)) carried out a study of Cl<sub>2</sub>O(g) by photoelectron ionization. From their measurements, they report  $\Delta_f H^\ominus(\text{Cl}_2\text{O}) = +77.2 \text{ kJ mol}^{-1}$ . They combined this measurement with literature data on the reaction Cl<sub>2</sub>O(g) + H<sub>2</sub>O(g) → 2 HOCl(g), for which  $K = 8.2 \times 10^{-3}$  and  $\Delta_r S^\ominus = +16.38 \text{ J K}^{-1} \text{ mol}^{-1}$ , and with readily available thermodynamic data on water vapour to report a value for  $\Delta_f H^\ominus(\text{HOCl})$ . Calculate that value. All quantities refer to 298 K.

**6.2** Given that  $\Delta_r G^\ominus = -212.7 \text{ kJ mol}^{-1}$  for the reaction in the Daniell cell at 25 °C, and  $b(\text{CuSO}_4) = 1.0 \times 10^{-3} \text{ mol kg}^{-1}$  and  $b(\text{ZnSO}_4) = 3.0 \times 10^{-3} \text{ mol kg}^{-1}$ , calculate (a) the ionic strengths of the solutions, (b) the mean ionic activity coefficients in the compartments, (c) the reaction quotient, (d) the standard cell potential, and (e) the cell potential. (Take  $\gamma_+ = \gamma_- = \gamma_{\pm}$  in the respective compartments.)

**6.3** Consider the cell,  $\text{Zn(s)}|\text{ZnCl}_2(0.0050 \text{ mol kg}^{-1})|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg(l)}$ , for which the cell reaction is  $\text{Hg}_2\text{Cl}_2(\text{s}) + \text{Zn(s)} \rightarrow 2 \text{Hg(l)} + 2 \text{Cl}^-(\text{aq}) + \text{Zn}^{2+}(\text{aq})$ . Given that  $E^\ominus(\text{Zn}^{2+}, \text{Zn}) = -0.7628 \text{ V}$ ,  $E^\ominus(\text{Hg}_2\text{Cl}_2, \text{Hg}) = +0.2676 \text{ V}$ , and that the cell potential is  $+1.2272 \text{ V}$ , (a) write the Nernst equation for the cell. Determine (b) the standard cell potential, (c)  $\Delta_r G$ ,  $\Delta_r G^\ominus$ , and  $K$  for the cell reaction, (d) the mean ionic activity and activity coefficient of  $\text{ZnCl}_2$  from the measured cell potential, and (e) the mean ionic activity coefficient of  $\text{ZnCl}_2$  from the Debye-Hückel limiting law. (f) Given that  $(\partial E_{\text{cell}}/\partial T)_p = -4.52 \times 10^{-4} \text{ V K}^{-1}$ , calculate  $\Delta_r S$  and  $\Delta_r H$ .

**6.4** Careful measurements of the potential of the cell  $\text{Pt}|\text{H}_2(\text{g}, p^\ominus)|\text{NaOH}(\text{aq}, 0.0100 \text{ mol kg}^{-1}), \text{NaCl}(\text{aq}, 0.01125 \text{ mol kg}^{-1})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$  have been reported. Among the data is the following information:

$\theta/^\circ\text{C}$	20.0	25.0	30.0
$E_{\text{cell}}/\text{V}$	1.04774	1.04864	1.04942

Calculate  $\text{p}K_w$  at these temperatures and the standard enthalpy and entropy of the autoprotolysis of water at  $25.0^\circ\text{C}$ .

**6.5** Measurements of the potential of cells of the type  $\text{Ag}|\text{AgX}(\text{s})|\text{MX}(b_1)|\text{M}_x\text{Hg}|\text{MX}(b_2)|\text{AgX}(\text{s})|\text{Ag}$ , where  $\text{M}_x\text{Hg}$  denotes an amalgam and the electrolyte is an  $\text{LiCl}$  in ethylene glycol, are given below. Estimate the activity coefficient at the concentration marked \* and then use this value to calculate activity coefficients from the measured cell potential at the other concentrations. Base your answer on the Davies equation (eqn 5F.11) with  $A = 1.461$ ,  $B = 1.70$ ,  $C = 0.20$ , and  $I = b/b^\ominus$ . For  $b_2 = 0.09141 \text{ mol kg}^{-1}$ :

$b_1/(\text{mol kg}^{-1})$	0.0555	0.09141	0.1652	0.2171	1.040	1.350*
$E/\text{V}$	-0.0220	0.0000	0.0263	0.0379	0.1156	0.1336

**6.6\*** The table below summarizes the potential of the cell  $\text{Pd}|\text{H}_2(\text{g}, 1 \text{ bar})|\text{BH}(\text{aq}, b), \text{B}(\text{aq}, b)|\text{AgCl}(\text{s})|\text{Ag}$ . Each measurement is made at equimolar concentrations of 2-aminopyridinium chloride (BH) and 2-aminopyridine (B). The data are for  $25^\circ\text{C}$  and it is found that  $E^\ominus = 0.22251 \text{ V}$ . Use the data to determine  $\text{p}K_a$  for the acid at  $25^\circ\text{C}$  and the mean activity coefficient ( $\gamma_\pm$ ) of BH as a function of molality ( $b$ ) and ionic strength ( $I$ ). Use the Davies equation (eqn 5F.11) with  $A = 0.5091$  and  $B$  and  $C$  are parameters that depend upon the ions. Draw a graph of the mean activity coefficient with  $b = 0.04 \text{ mol kg}^{-1}$  and  $0 \leq I \leq 0.1$ .

$b/(\text{mol kg}^{-1})$	0.01	0.02	0.03	0.04	0.05
$E_{\text{cell}}(25^\circ\text{C})/\text{V}$	0.74452	0.72853	0.71928	0.71314	0.70809
$b/(\text{mol kg}^{-1})$	0.06	0.07	0.08	0.09	0.10
$E_{\text{cell}}(25^\circ\text{C})/\text{V}$	0.70380	0.70059	0.69790	0.69571	0.69338

*Hint:* Use mathematical software or a spreadsheet.

**6.7** Here we investigate the molecular basis for the observation that the hydrolysis of ATP is exergonic at  $\text{pH} = 7.0$  and  $310 \text{ K}$ . (a) It is thought that the exergonicity of ATP hydrolysis is due in part to the fact that the standard entropies of hydrolysis of polyphosphates are positive. Why would an increase in entropy accompany the hydrolysis of a triphosphate group into a diphosphate and a phosphate group? (b) Under identical conditions, the Gibbs energies of hydrolysis of  $\text{H}_4\text{ATP}$  and  $\text{MgATP}^{2-}$ , a complex between the  $\text{Mg}^{2+}$  ion and  $\text{ATP}^{4-}$ , are less negative than the Gibbs energy of hydrolysis of  $\text{ATP}^{4-}$ . This observation has been used to support the hypothesis that electrostatic repulsion between adjacent phosphate groups is a factor that controls the exergonicity of ATP hydrolysis. Provide a rationale for the hypothesis and discuss how the experimental evidence supports it. Do these electrostatic effects contribute to the  $\Delta_r H$  or  $\Delta_r S$  terms that determine the exergonicity of the reaction? *Hint.* In the  $\text{MgATP}^{2-}$  complex, the  $\text{Mg}^{2+}$  ion and  $\text{ATP}^{4-}$  anion form two bonds: one that involves a negatively charged oxygen belonging to the terminal phosphate group of  $\text{ATP}^{4-}$  and another that involves a negatively charged oxygen belonging to the phosphate group adjacent to the terminal phosphate group of  $\text{ATP}^{4-}$ .

**6.8** To get a sense of the effect of cellular conditions on the ability of ATP to drive biochemical processes, compare the standard Gibbs energy of hydrolysis of ATP to ADP with the reaction Gibbs energy in an environment at  $37^\circ\text{C}$  in which  $\text{pH} = 7.0$  and the ATP, ADP, and  $\text{P}_i^-$  concentrations are all  $1.0 \text{ mmol dm}^{-3}$ .

**6.9** Under biochemical standard conditions, aerobic respiration produces approximately 38 molecules of ATP per molecule of glucose that is completely oxidized. (a) What is the percentage efficiency of aerobic respiration under biochemical standard conditions? (b) The following conditions are more likely to be observed in a living cell:  $p_{\text{CO}_2} = 5.3 \times 10^{-2} \text{ atm}$ ,  $p_{\text{O}_2} = 0.132 \text{ atm}$ ,  $[\text{glucose}] = 5.6 \text{ pmol dm}^{-3}$ ,  $[\text{ATP}] = [\text{ADP}] = [\text{P}_i] = 0.10 \text{ mmol dm}^{-3}$ ,  $\text{pH} = 7.4$ ,  $T = 310 \text{ K}$ . Assuming that activities can be replaced by the numerical values of molar concentrations, calculate the efficiency of aerobic respiration under these physiological conditions. (c) A typical diesel engine operates between  $T_c = 873 \text{ K}$  and  $T_h = 1923 \text{ K}$  with an efficiency that is approximately 75 per cent of the theoretical limit of  $1 - T_c/T_h$  (see Topic 3A). Compare the efficiency of a typical diesel engine with that of aerobic respiration under typical physiological conditions (see part b). Why is biological energy conversion more or less efficient than energy conversion in a diesel engine?

**6.10** In anaerobic bacteria, the source of carbon may be a molecule other than glucose and the final electron acceptor is some molecule other than  $\text{O}_2$ . Could a bacterium evolve to use the ethanol/nitrate pair instead of the glucose/ $\text{O}_2$  pair as a source of metabolic energy?

**6.11** The standard potentials of proteins are not commonly measured by the methods described in this chapter because proteins often lose their native structure and function when they react on the surfaces of electrodes. In an alternative method, the oxidized protein is allowed to react with an appropriate electron donor in solution. The standard potential of the protein is then determined from the Nernst equation, the equilibrium concentrations of all species in solution, and the known standard potential of the electron donor. We illustrate this method with the protein cytochrome *c*. The one-electron reaction between cytochrome *c*, *cyt*, and 2,6-dichloroindophenol, *D*, can be followed spectrophotometrically because each of the four species in solution has a distinct absorption spectrum. We write the reaction as  $\text{cyt}_{\text{ox}} + \text{D}_{\text{red}} \rightleftharpoons \text{cyt}_{\text{red}} + \text{D}_{\text{ox}}$ , where the subscripts 'ox' and 'red' refer to oxidized and reduced states, respectively. (a) Consider  $E_{\text{cyt}}^\ominus$  and  $E_{\text{D}}^\ominus$  to be the standard potentials of cytochrome *c* and *D*, respectively. Show that, at equilibrium, a plot of  $\ln([\text{D}_{\text{ox}}]_{\text{eq}}/[\text{D}_{\text{red}}]_{\text{eq}})$  versus  $\ln([\text{cyt}_{\text{ox}}]_{\text{eq}}/[\text{cyt}_{\text{red}}]_{\text{eq}})$  is linear with slope of 1 and *y*-intercept  $F(E_{\text{cyt}}^\ominus - E_{\text{D}}^\ominus)/RT$ , where equilibrium activities are replaced by the numerical values of equilibrium molar concentrations. (b) The following data were obtained for the reaction between oxidized cytochrome *c* and reduced *D* in a  $\text{pH} 6.5$  buffer at  $298 \text{ K}$ . The ratios  $[\text{D}_{\text{ox}}]_{\text{eq}}/[\text{D}_{\text{red}}]_{\text{eq}}$  and  $[\text{cyt}_{\text{ox}}]_{\text{eq}}/[\text{cyt}_{\text{red}}]_{\text{eq}}$  were adjusted by titrating a solution containing oxidized cytochrome *c* and reduced *D* with a solution of sodium ascorbate, which is a strong reductant. From the data and the standard potential of *D* of  $0.237 \text{ V}$ , determine the standard potential cytochrome *c* at  $\text{pH} 6.5$  and  $298 \text{ K}$ .

$[\text{D}_{\text{ox}}]_{\text{eq}}/[\text{D}_{\text{red}}]_{\text{eq}}$	0.00279	0.00843	0.0257	0.0497	0.0748	0.238	0.534
$[\text{cyt}_{\text{ox}}]_{\text{eq}}/[\text{cyt}_{\text{red}}]_{\text{eq}}$	0.0106	0.0230	0.0894	0.197	0.335	0.809	1.39

**6.12\*** The dimerization of  $\text{ClO}$  in the Antarctic winter stratosphere is believed to play an important part in that region's severe seasonal depletion of ozone. The following equilibrium constants are based on measurements on the reaction  $2 \text{ClO}(\text{g}) \rightarrow (\text{ClO})_2(\text{g})$ .

$T/\text{K}$	233	248	258	268	273	280
$K$	$4.13 \times 10^8$	$5.00 \times 10^7$	$1.45 \times 10^7$	$5.37 \times 10^6$	$3.20 \times 10^6$	$9.62 \times 10^5$
$T/\text{K}$	288	295	303			
$K$	$4.28 \times 10^5$	$1.67 \times 10^5$	$6.02 \times 10^4$			

(a) Derive the values of  $\Delta_r H^\ominus$  and  $\Delta_r S^\ominus$  for this reaction. (b) Compute the standard enthalpy of formation and the standard molar entropy of  $(\text{ClO})_2$  given  $\Delta_r H^\ominus(\text{ClO}, \text{g}) = +101.8 \text{ kJ mol}^{-1}$  and  $S_{\text{m}}^\ominus(\text{ClO}, \text{g}) = 266.6 \text{ J K}^{-1} \text{ mol}^{-1}$ .

6.13<sup>†</sup> Suppose that an iron catalyst at a particular manufacturing plant produces ammonia in the most cost-effective manner at 450 °C when the pressure is such that  $\Delta_r G$  for the reaction  $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$  is equal to  $-500 \text{ J mol}^{-1}$ . (a) What pressure is needed? (b) Now suppose that a new catalyst is developed that is most cost-effective at 400 °C when the pressure gives the same value of  $\Delta_r G$ . What pressure is needed when the new

catalyst is used? What are the advantages of the new catalyst? Assume that (i) all gases are perfect gases or that (ii) all gases are van der Waals gases. Isotherms of  $\Delta_r G(T, p)$  in the pressure range  $100 \text{ atm} \leq p \leq 400 \text{ atm}$  are needed to derive the answer. (c) Do the isotherms you plotted confirm Le Chatelier's principle concerning the response of equilibrium changes in temperature and pressure?