Answers to AS spreads

Amount of substance

Page 6–7

1 **a** 24.3 g
   b 9.0 g
   c 27.0 g
2 **a** 48.6 g
   b 13.5 g
   c 54.0 g
   d 80.0 g
   e 30.3 g
3 **a** $32.1 \, \text{g mol}^{-1}$
   b $64.1 \, \text{g mol}^{-1}$
   c $44.0 \, \text{g mol}^{-1}$
   d $117.3 \, \text{g mol}^{-1}$
   e $17.0 \, \text{g mol}^{-1}$
4 **a** 0.75 mol
   b 1.5 mol
   c 2.0 mol
5 **a** $100 \, \text{g mol}^{-1}$
   b $44.0 \, \text{g mol}^{-1}$
   c $100 \, \text{g mol}^{-1}$

Avogadro constant

Page 8–9

1 **a** 6.02×10^{23}
   b 6.02×10^{23}
   c 6.02×10^{23}
2 **a** 6.02×10^{22}
   b 1.51×10^{24}
   c 4.52×10^{24}
3 **a** 6.02×10^{23}
   b 6.02×10^{23}
   c 6.02×10^{23}
4 **a** 1.204×10^{24}
   b 9.03×10^{23}
   c 1.204×10^{23}
5 1.204×10^{24}

Relative atomic mass

Page 10–11

1 10.8
2 69.8
3 39.14
4 46.6
5 32.09
6 79.98

Moles and gas volumes

Page 12–13

1 **a** 0.25 mol
   b 1.5 mol
   c 5.0 mol
   d 3.0 mol
   e 0.5 mol

2 a 0.33 mol
  b 3.0 mol
  c 0.075 mol
  d 0.5 mol
  e 0.15 mol
3 a 2.4 dm^3
  b 60 dm^3
  c 4.8 dm^3
  d 360 dm^3
  e 1.2 dm^3
4 a 5.34 g
  b 22.0 g
  c 160 g

Ideal gas equation

Page 14–15

1 a 373 K
  b 310 K
  c 173 K
  d 473 K
  e 73 K
2 a 1×10^{-4} m^3
  b 0.01 m^3
  c 0.15 m^3
  d 5×10^{-4} m^3
  e 0.02 m^3
3 a 100 Pa
  b 10 000 Pa
  c 2500 Pa
  d 100 000 Pa
  e 500 Pa
4 1.24×10^{-4} m^3
5 45.4 Pa
6 6020 K

Concentration

Page 16–17

1 4.0 mol dm^{-3}
2 2.5 mol dm^{-3}
3 0.025 mol dm^{-3}
4 a 0.0036 mol
  b 0.013 mol
  c 0.0025 mol
5 0.1 dm^3
6 5.0 dm^3
7 0.8 g

Titrations

Page 18–19

1 a 0.00625
  b 0.00625
  c 0.28 mol dm^{-3}
2 a 0.005
  b 0.005
  c 0.227 mol dm^{-3}
3 a 0.0005
  b 0.00025
  c 0.008 929 mol dm^{-3}
4 a 0.1
  b 0.1
  c 3.571 mol dm^{-3}
5 26.35

Mole calculations 1

Page 20–21

1 a 0.02
   b 0.02
   c 0.806 g
2 a 0.005
   b 0.005
   c 0.2925 g
3 a 0.005
   b 0.005
   c 0.373 g
4 a 0.05
   b 0.025
   c $0.6 \, dm^3$
5 a 0.002
   b 0.002
   c $0.048 \, dm^3$
6 a 0.02
   b 0.01
   c $0.24 \, dm^3$
7 a 5.93
   b 5.93
   c $142 \, dm^3$

Mole calculations 2

Page 22–23

1 a 0.02
   b 0.02
   c $200 \, cm^3$
2 a 0.020
   b 0.040
   c $20 \, cm^3$
3 a 0.01
   b 0.02
   c $20 \, cm^3$
4 a 0.040
   b 0.080
   c $1.60 \, mol \, dm^{-3}$
5 a 0.02
   b 0.04
   c $0.80 \, mol \, dm^{-3}$
6 a 0.05
   b 0.05
   c $1.00 \, mol \, dm^{-3}$
7 5.61
8 8.00
9 2.81

Empirical formula 1

Page 24–25

1 PCl_5
2 NH_3
3 $MgCO_3$
4 $CuSO_4$
5 Fe_2O_3
6 $FeCl_2$

Empirical formula 2

Page 26–27

1 a CH_2
   b C_6H_{12}

2 a NH_2
  b N_2H_4
3 a CH_2
  b C_7H_{14}
4 a HO
  b H_2O_2
5 C_2H_3

Water of crystallisation

Page 28–29

1 a 0.630
  b 0.005
  c 0.035
  d $MgSO_4.7H_2O$
2 a 1.260
  b 0.01
  c 0.07
  d $ZnSO_4.7H_2O$
3 a 1.800
  b 0.02
  c 0.10
  d $MgCl_2.5H_2O$
4 a $CoCl_2.6H_2O$
  b $Ca(NO_3)_2.4H_2O$
  c $Na_2SO_4.10H_2O$

Shape of simple molecules

Page 30–31

1 pyramidal 107°
2 tetrahedal 109.5°
3 trigonal bipyramidal 120° and 90°
4 non linear/bent 104.5°
5 octahedral 90°
6 trigonal planar 120°
7 trigonal planar

Oxidation number

Page 32–33

1 a +1
  b 0
  c +2 and −2
  d +1 and −1
  e +1 and −1
2 a +4 and −2
  b +1 and −2
  c +2 and −2
  d +1 and −2
  e +4 and −2
3 a −3
  b +5
  c +4
  d −2
  e +4
4 a +1
  b +6
  c +3
  d +1
  e +1

5 a $+4$

  b $+1$

  c $+2$

  d $+3$

  e $+2$

Oxidation and reduction

Page 34–35

1 0 to $+2$ so zinc is oxidised

2 a magnesium 0 to $+2$

  b oxygen 0 to -2

3 a zinc 0 to $+2$

  b oxygen 0 to -2

4 a magnesium 0 to $+2$

  b chlorine 0 to -1

5 magnesium is oxidised form 0 to $+2$

  hydrogen is reduced from $+1$ to 0

6 zinc is oxidised from 0 to $+2$

  hydrogen is reduced from $+1$ to 0

7 NO_3^-

Group 2

Page 36–37

1 a The oxidation number of strontium increases from 0 to $+2$ so the strontium is oxidised. The oxidation number of oxygen decreases from 0 to -2 so the oxygen is reduced.

  b The reducing agent is strontium. The oxidising agent is oxygen.

2 a The oxidation number of barium increases from 0 to $+2$ so the barium is oxidised. The oxidation number of oxygen decreases from 0 to -2 so the oxygen is reduced.

  b The reducing agent is barium. The oxidising agent is oxygen.

3 a The oxidation number of strontium increases from 0 to $+2$ so the strontium is oxidised. The oxidation number of one of the hydrogen atoms in water decreases from $+1$ to 0 so the hydrogen is reduced.

  b The reducing agent is strontium. The oxidising agent is water.

4 a The oxidation number of barium increases from 0 to $+2$ so the barium is oxidised. The oxidation number of oxygen decreases from 0 to -2 so the oxygen is reduced.

  b The reducing agent is barium. The oxidising agent is water.

5 a 0.005 mol

  b 0.005 mol

  c 120 cm^3

Group 7

Page 38–39

1 a The oxidation number of sodium increases from 0 to $+1$ so the sodium is oxidised. The oxidation number of fluorine decreases from 0 to -1 so the fluorine is reduced.

  b Sodium is the reducing agent. Fluorine is the oxidising agent.

2 a The oxidation number of potassium increases from 0 to $+1$ so the potassium is oxidised. The oxidation number of fluorine decreases from 0 to -1 so the fluorine is reduced.

  b Potassium is the reducing agent. Fluorine is the oxidising agent.

3 a The oxidation number of iodine increases from -1 to 0 so the iodine is oxidised. The oxidation number of bromine decreases from 0 to -1 so the bromine is reduced.

  b Iodide ion is the reducing agent. Bromine is the oxidising agent.

4 a The oxidation number of iodine increases from -1 to 0 so the iodine is oxidised. The oxidation number of chlorine decreases from 0 to -1 so the chlorine is reduced.

  b Iodide ion is the reducing agent. Chlorine is the oxidising agent.

5 The copper is simultaneously oxidised from $+1$ to $+2$ and reduced from $+1$ to 0

Enthalpy changes 1

Page 40–41

1 2090 J

2 8778 J

3 a 3344 J
   b 0.1 mol
   c $-33.44 \, \text{kJ mol}^{-1}$
4 a 4389 J
   b 0.15 mol
   c $-29.26 \, \text{kJ mol}^{-1}$
5 Insulate the cup

Enthalpy changes 2

Page 42–43

1 6270 J
2 9405 J
3 10 032 J
4 a 25.916 kJ
   b 0.03 mol
   c $-864 \, \text{kJ mol}^{-1}$
   d exothermic
5 a $5.016 \, \text{kJ mol}^{-1}$
   b 0.05 mol
   c $-100 \, \text{kJ mol}^{-1}$

Hess' Law 1

Page 44–45

1 $-137 \, \text{kJ mol}^{-1}$
2 $-128 \, \text{kJ mol}^{-1}$
3 $-1309 \, \text{kJ mol}^{-1}$
4 $+109 \, \text{kJ mol}^{-1}$

Hess' Law 2

Page 46–47

1 $+165 \, \text{kJ mol}^{-1}$
2 $-1324 \, \text{kJ mol}^{-1}$
3 $-727 \, \text{kJ mol}^{-1}$
4 $-85 \, \text{kJ mol}^{-1}$
5 $+101 \, \text{kJ mol}^{-1}$
6 $+132 \, \text{kJ mol}^{-1}$

Bond enthalpy 1

Page 48–49

1 a $-1317 \, \text{kJ mol}^{-1}$
   b $-125 \, \text{kJ mol}^{-1}$
   c $-483 \, \text{kJ mol}^{-1}$

Bond enthalpy 2

Page 50–51

1 $243 \, \text{kJ mol}^{-1}$
2 $347 \, \text{kJ mol}^{-1}$
3 $151 \, \text{kJ mol}^{-1}$

Percentage yields

Page 52–53

1 67.2%
2 91.7%
3 52.1%
4 80%
5 40%
6 20%

Atom economy

Page 54–55

1 100%

2 100%

3 83.0%

4 50.6%

5 30.9%

Percentage error in apparatus

Page 56–57

1 **a** 4.00%

   b 1.25%

   c 2.63%

2 **a** 5.00%

   b 3.33%

   c 0.602%

3 **a** 2.38%

   b 1.92%

   c 1.16%

4 **a** 8.33%

   b 4.76%

   c 2.66%

5 **a** 21.65 cm^3

   b 0.462%

Mass spectrometry ram

Page 58–59

1 87.8

2 24.3

3 40.1

4 55.9

Stretch yourself

   a Measure mass of all the isotopes and take into account abundance of each isotope.

   b Carbon 12 has a mass of 12 amu. $\frac{1}{12}$ of this is 1 amu.

Mass spectroscopy (fragmentation of organic compounds)

Page 60–61

1 Chloropropane $CH_3CH_2CH_2Cl$

2 $CH_3CH_2COCH_2CH_3$

3 $CH_3CH_2CH_2CH_2CH_3$

Stretch yourself

   a Two different molecular ions are found due to the different types of isotopes of chlorine Cl^{35} Cl^{37}. The ratios of the isotopes lead to the 3 to 1 ratio of molecular ions.

   b $CH_3CH_2Cl^+ \rightarrow CH_3CH_2^+ + Cl$

4 **a** $(CH_3CH_2)^+$

   b $(CH_3CH_2CH_2)^+$

   c $(CH_3CH_2CH_2CH_2)^+$

   d $(CH_3CH_2CH_2CH_2CH_3)^+$

5 **a** $(CH_3CH_2)^+$

   b $(CH_3CH_2CO)^+$

   c $(CH_3CH_2COCH_2CH_3)^+$

Entropy

Page 62–63

1 **a** Positive

   b Negative

2 a $270.32\,\mathrm{J\,K^{-1}\,mol^{-1}}$

   b $53.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$

   c $216.72\,\mathrm{J\,K^{-1}\,mol^{-1}}$

   d $4040.27\,\mathrm{J\,K^{-1}\,mol}$

   e $4257.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Reaction is feasible because of total entropy change being positive.

3 a Atomic mass and atomic radius increases down the group along with the number of filled orbitals.

   b The van der Waals forces of attraction increases down Group 0.

   c **i** The boiling points increase down Group 0.

      ii This is due to a higher enthalpy of vaporisation.

   d **i** This higher enthalpy of vaporisation leads to a larger entropy change of surroundings.

      ii At lower temperatures the entropy changes of surroundings has a smaller magnitude.

Stretch Yourself

van der Waals force increase down Group 0 and so do melting points and boiling points. This leads to an increase in enthalpy of vapourisation. This increases the entropy of the surroundings so the entropies of noble gases increase helium to xenon.

Gibbs free energy

Page 64–65

1 a $-685156.2\,\mathrm{J\,mol^{-1}}$ spontaneous

   b $-57551.8\,\mathrm{J\,mol^{-1}}$ spontaneous

2 a $-65.5\,\mathrm{kJ\,mol^{-1}}$

   b $-33.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$

   c $-55457.4\,\mathrm{J\,mol^{-1}}$

3 a $1408.7\,\mathrm{kJ\,mol^{-1}}$

Stretch yourself

i $\Delta H = -91\,\mathrm{kJ\,mol^{-1}}$

  $\Delta S = 220\,\mathrm{J\,K^{-1}\,mol^{-1}}$

ii When the reaction is no longer feasible $\Delta H = \mathrm{T}\Delta S$

$$\frac{91\,000}{220} = T$$

$$T = 413\,\mathrm{K}$$

Concentration–time graphs

Page 66–67

1
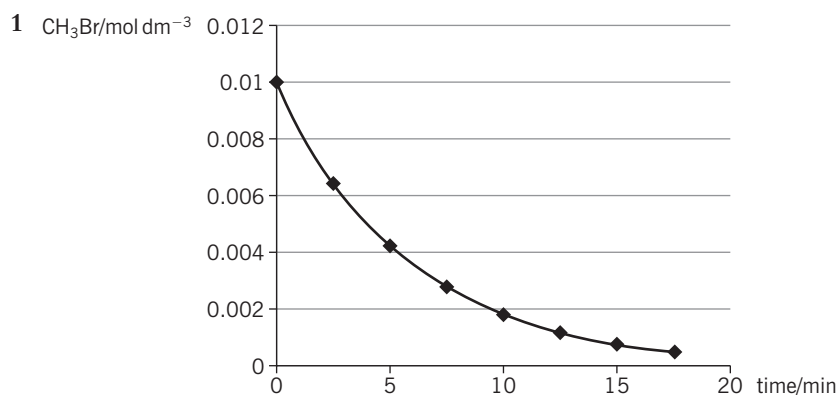
2 10 min: $-0.0004\,\mathrm{mol\,dm^{-3}\,min^{-1}}$

  20 min: $-0.0002\,\mathrm{mol\,dm^{-3}\,min^{-1}}$
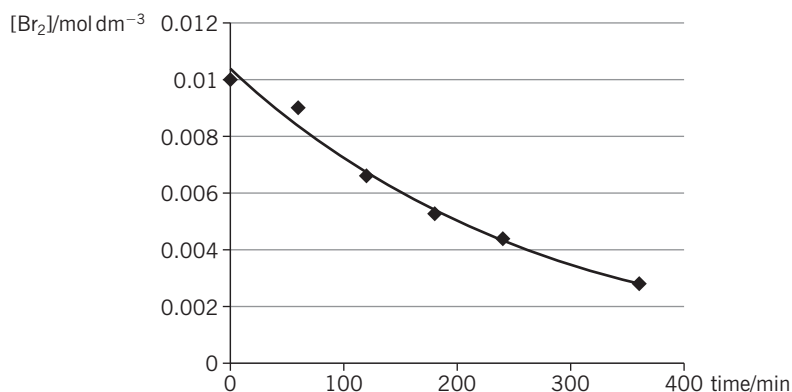
3 1

Half-life

1 Concentration/time graph
   The reaction is first order
   Approximately half life is 180 seconds

[Br$_2$]/mol dm^{-3}

2 a When concentration of H$_2$ doubles the rate doubles
   b [H$_2$] is a first order
   c When concentration of NO doubles the rate quadruples
   d [NO] is second order

Stretch yourself

a Approximately 10%

b

0	100%
5800	50%
11600	25%
17400	12.5%

c Approximately 7000 years use graph to determine

Rate by inspection 1

1 a [A] is second order [B] is zero order [C] is zero order
   b Rate = k[A]^2
   c Total order is 2

2 a [X] is zero order [Y] is 2nd order [Z] is 1st order
   b Rate = k[Y]^2[Z]
   c Total order is 3

3 a O$_2$ + 2CO → 2CO$_2$
   b The first step is the rate determining step because [NO$_2$] is the only reactant that effects the rate with an order 2.

Rate by inspection 2

1 Rate = k[NO]^2[H$_2$]

2 Rate = k[A]^3

3 a [A] doubled rate would double
   b [B] doubled rate would quadruple
   c It increases the rate by a factor of 8 times.

Stretch yourself

k = mol^{-2} dm^6 s^{-1}

4 It increases by factor of 8.

5 The rate of reaction will increase by a factor of 4.

6 The concentration will half so the rate will decrease by a factor of 8.

Rates: rate constant

Page 74–75

1 a $k = mol^{-1} dm^3 s^{-1}$
  b $k = 1.15 \times 10^{-3} mol^{-1} dm^3 s^{-1}$
2 a $k = mol^{-1} dm^3 s^{-1}$
  b $17.25 \, mol^{-1} dm^3 s^{-1}$
3 a $[NO] = \dfrac{rate}{k[H_2]}$

  b $[NO] = \dfrac{0.0138}{(17.25 \times 0.02)} = 0.04 \, mol \, dm^{-3}$
  c It would increase the value of the rate constant

Stretch yourself
a $[A] = 1, [B] = 1, [C] = 0$ order
b Rate = k[A][B]
c $K = 0.154 \, mol^{-1} dm^3 s^{-1}$

Experiment	[A]	[B]	[C]	Rate $mol \, dm^{-3} s^{-1}$
1	0.1	0.2	0.1	0.00308
2	0.2	0.2	0.1	0.00616
3	0.3	0.2	0.1	0.00924
4	0.1	0.4	0.1	0.00616
5	0.1	0.6	0.1	0.00924
6	0.1	0.2	0.2	0.00308
7	0.1	0.2	0.3	0.00308

Equilibrium equations

Page 76–77

1 a $k_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

  b $mol^{-1} dm^3$
  c $k_c = 341\,333 \, mol^{-1} dm^3$
  d The yield of sulfur trioxide would decrease.
2 a $k_c = \dfrac{[NO]^2}{[N_2O_4]}$

  b Units are $mol \, dm^{-3}$
  c $k_c = 5 \, mol \, dm^{-3}$
  d k_c will increase with temperature
3 a $k_c = [CH_3COOCH_3][H_2O]/[CH_3OH][CH_3COOH]$
  b no units
  c 4.33 moles
  d $[CH_3COOCH_3] = 2.17 \, mol \, dm^{-3}$, $[H_2O] = 2.17 \, mol \, dm^{-3}$, $[CH_3COOH] = 0.34 \, mol \, dm^{-3}$, $[CH_3OH] = 1.17 \, mol \, dm^{-3}$
  e $k_c = 11.8$ 2 d.p.

Stretch yourself
If N_2 increases NH_3 must increase 4 fold

Equilibrium calculations given equilibrium concentrations

Page 78–79

1 a $k_c = \dfrac{[HOOCCH_2NH_2][H^+]}{[[HOOCCH_2NH_3]}$

  b $mol \, dm^{-3}$
  c $1 \, mol \, dm^{-3}$
2 a $k_c = \dfrac{[O_2]^3}{[O_3]^2}$

  b $mol \, dm^{-3}$
  c $1.4 \, mol \, dm^{-3}$
  d 2.8 moles at equilibrium
  e $134.4 \, g$

Stretch Yourself

a 1000 moles of N_2, 1000 moles of H_2

b 529.41 moles of NH_3 at equilibrium (2 d.p.)

c 264.71 moles N_2 used up

d 794.12 moles H_2 used up

e 735.29 moles N_2 left at

f Concentration at $[N_2] = 147.06 \, \text{mol dm}^{-3}$ $[H_2] = 41.18 \, \text{mol dm}^{-3}$ $[NH_3] = 105.88 \, \text{mol dm}^{-3}$

g $k_c = [CH_3COOCH_3][H_2O]/[CH_3OH][CH_3CH_2COOH]$

h 3 mol of methanol, 8 mol of methyl ethanoate and 6 mol of water.

i 4

j 1.33 mol of reactants. 2.67 mol of products.

Equilibrium calculations given moles at equilibrium

Page 80–81

1 a $k_c = \dfrac{[PCl_5]}{[PCl_3][Cl_2]}$

  b $k_c = \text{mol}^{-1}\,\text{dm}^3$

  c $k_c = \dfrac{0.5}{(0.05 \times 0.05)} = 20\,\text{mol}^{-1}\,\text{dm}^3$

2 a $k_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

  b $\text{mol}^{-2}\,\text{dm}^6$

  c $[NH_3] = 0.50\,\text{mol dm}^{-3}$, $[H_2] = 0.67\,\text{mol dm}^{-3}$, $[N_2] = 0.25\,\text{mol dm}^{-3}$

  d $k_c = 3.32\,\text{mol}^{-2}\,\text{dm}^6$(2 d.p.)

3 a $k_c = \dfrac{[NO_2]^2}{[N_2O_4]}$

  b $k_c = \text{mol dm}^{-3}$

  c $[NO_2] = 1.60\,\text{mol dm}^{-3}$, $[N_2O_4] = 2.0\,\text{mol dm}^{-3}$

  d $k_c = \dfrac{[1.6]^2}{[2]} = 1.28\,\text{mol dm}^{-3}$

Stretch yourself

a $k_c = \dfrac{[0.1]^2}{[0.1][0.1]^2}$ does not equal $2.0 \times 10^{-6}\,\text{mol dm}^{-3}$

b So not in equilibrium

c K_c the equilibrium constant is dependent on temperature.

d Equilibrium will be achieved quicker but the equilibrium position will not be affected.

e The concentration of reactants will decrease but the products will increase because the forwards reaction is exothermic.

f A high temperature will achieve a low yield but a high rate. It is essential to compromise between yield and rate.

Equilibrium equations given moles at start of reaction

Page 82–83

1 a The ratio is 1 mole N_2: 3 mol H_2: 2 mol NH_3

  b At equilibrium there is 12 moles N_2, 21 moles H_2 and 6 moles of NH_3

  c $k_c = \dfrac{[NH_3]^2}{[N_2][H]^3}$ units $\text{mol}^{-3}\,\text{dm}^9$

  d $k_c = 3.239 \times 10^{-4}\,\text{mol}^{-3}\,\text{dm}^9$

2 a 0.0126 moles $CuSO_4.7H_2O$ react

  b At equilibrium there is 0.0126 moles $CuSO_4$ and 0.0882 moles H_2O and 0.00490 moles $CuSO_4.7H_2O$

  c $k_c = \dfrac{[CuSO_4][H_2O]^7}{[CuSO_4.7H_2O]} = 7.93 \times 10{-7}\,\text{mol}^7\,\text{dm}^{-21}$

  d $k_c = 3.99 \times 10^{-11}\,\text{mol}^5\,\text{dm}^{-15}$

3 a Concentration of each reactant $[CH_3CH_2CH_2OH] = 8.0\,\text{mol dm}^{-3}$, $[HCOOH] = 10.0\,\text{mol dm}^{-3}$

  b 0.1875 moles of methanoic acid with 0.1875 moles of propanol reacts to form 0.1875 moles of propyl methanoate and water. Therefore at equilibrium will be 0.0125 moles of propanol, 0.0625 moles of methanoic acid and 0.1875 moles of both products.

  c $[CH_3CH_2CH_2OH] = 0.5\,\text{mol dm}^{-3}$, $[HCOOH] = 2.5\,\text{mol dm}^{-3}$ and $[HCOOCH_2CH_2CH_3] = 7.5\,\text{mol dm}^{-3}$, $[H_2O] = 7.5\,\text{mol dm}^{-3}$

  d $K_c = 45$

Stretch yourself

a 0.50 mol

b 2.5 mol

c The equilibrium would move to oppose the change, as in Le Chatelier's principle, producing more products. K_c would stay the same.

d At equilibrium there would be 1 mole of ethanol, 9 moles of ethyl ethanoate and 6 moles of water.

e K_c would now equal 27.

Calculating pH

Page 84–85

1 a 2.4

  b 3.3

  c 0.08

2 pH 3.1

3 a 0.0001 or 10^{-4} mol dm^{-3}

  b 0.0000001 or 10^{-7} mol dm^{-3}

  c 0.00000158 or 1.58×10^{-6} mol dm^{-3}

  d 6.31×10^{-10} mol dm^{-3} or 0.000000000631 mol dm^{-3}

Stretch yourself

Sulfuric acid	H_2SO_4	$K_a 1 = $ Large	$K_a 2 = 1.2 \times 10^{-2}$

The second dissociation of HSO_4^-, $\rightarrow H^+ + SO_4^-$

Is very weak in comparison

Assume 0.1 mols of hydrogen ions from first dissociation

For second dissociation

$$K_a = \frac{[H^+]^2}{HSO_4^-}$$

$1.2 \times 10^{-2} \times 0.1 = [H^+]^2$

$[H^+] = 0.0346$ mol dm^{-3} extra hydrogen ions

A monoprotic acid of the same concentration would have pH

pH $= -\log [0.1] = 1$

Sulfuric acid

pH $= -\log [0.1346] = 0.87$

4 pH $= 2.4$ ∴ $[H^+] = 3.98 \times 10^{-3}$ mol dm^{-3}

  moles $H^+ = 0.01$ volume $= 2.512$ dm^{-3}

  Add 2412 cm^3 of water

Acid dissociation constant

Page 86–87

1 a $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

  b $K_a = \dfrac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$

  c $K_a = \dfrac{[CH_3CHClCH_2COO^-][H^+]}{[CH_3CHClCH_2COOH]}$

2 a 3.8

  b 4.2

  c 4.0

Stretch yourself

a $K_a = \dfrac{[H^+][F^-]}{[HF]}$

b $pK_a = -\log K_a = 3.13$ (2 d.p.)

c Hydrofluoric acid is readily absorbed through the skin into blood and other tissues – skin contact may be fatal. Acts as a systemic poison, even when highly diluted. May cause tissue necrosis and degeneration of bones, requiring amputation. Causes severe burns, potentially deep within tissue.

Reaction may be delayed and less extreme in diluted form.

The ionisation of water

1 a $0.1 \, \text{mol m}^{-3}$ or $10^{-1} \, \text{mol dm}^{-3}$

   b $0.04 \, \text{mol dm}^{-3}$ or $4 \times 10^{-2} \, \text{mol dm}^{-3}$

   c $10^{-10} \, \text{mol dm}^{-3}$

   d $2 \times 10^{-11} \, \text{mol dm}^{-3}$

2 a $10^{-12} \, \text{mol}^2 \, \text{dm}^{-6}$

   b $10^{-22} \, \text{mol}^2 \, \text{dm}^{-6}$

   c $4 \times 10^{-10} \, \text{mol}^2 \, \text{dm}^{-6}$

Stretch yourself

The ionic product of water increases with temperature as the equilibrium moves to favour the dissociation into hydrogen ions. This increased concentration of hydrogen ions decreases the pH of water.

3 a In pure water every water molecule H_2O that dissociates produces one $[H^+]$ and one $[OH^-]$

   b Without the addition of hydrogen ions the electrical conductivity is weak, because of the low number of both hydrogen and hydroxide ions.

   c Increasing the temperature will increase the dissociation of water because dissociation is an endothermic process and, according to Le Chatelier's principle, the equilibrium will move from left to right to oppose the increase in temperature. This increase in dissociation will increase K_w.

pH of strong bases

1 a 12.0

   b 11.6

   c 9.70

   d 14.5

2 a 14.7

   b 13.9

Stretch Yourself

a $K_b = \dfrac{[C_5H_5NH^+][OH^-]}{[C_5H_5NH]}$

b 9.62

c $[OH^-]$ increases so $[H^+]$ decreases and pH increases.

d $H^+ = 2.51 \times 10^{-10} \, \text{mol dm}^{-3}$

   OH^- 0.000 042 426

   pOH = 4.4

   pH = 9.6

e The higher the temperature the larger the concentration of OH^- ions, therefore the higher the pH.

pH Of Buffers

1 a $pK_a = 9.886$

   pH = 8.76

   b pH = 9.18

   c $pK_a = 4.187$

   pH = 3.79

   d pH = 3.49

   e $pK_a = 4.770$

   pH = 3.47

   f pH = 3.54

   g $pK_a = 9.310$

   pH = 7.83

   h pH = 8.18

   i $pK_a = 3.347$

   pH = 2.22

   j pH = 2.83

2 a M_r CH$_3$COOH = 60
No. of moles = 0.1166667
Concentration CH$_3$COOH = 0.58 mol dm^{-3}
M_r CH$_3$COONa = 82
No. of moles CH$_3$COONa = 0.1707
Concentration = 0.85 mol dm^{-3}
pK_a = 4.770
pH = 4.6

b M_r HCN = 27
M_r NaCN = 49
[HCN] = 1.852 mol dm^{-3}
[NaCN] = 2.041 mol dm^{-3}
pK_a = 9.310
pH = 9.35

Stretch yourself

[H$^+$] = 3.1622 × 10^{-5} mol dm^{-3}
[H$^+$] propanoic acid = 39.1 cm^3
[HA] sodium propanoate = 160.9 cm^3

Born Haber Cycle 1

Page 94–95

The diagram shows the Born-Haber cycle for Al_2O_3:

$2Al^{3+}_{(g)} + 6e^- + 3O_{(g)}$

$\Delta H_{\text{bond energy of oxygen}} \times$
$2Al^{3+}_{(g)} + \frac{3}{2}O_2 + 6e^-$

$2 \times \Delta H_{\text{first electron affinity}}$
$Al^{3+}_{(g)} + 3O^- + 3e^-$

$\Delta H_{\text{third ionisation energy}}$
$2Al^{2+}_{(g)} + \frac{3}{2}O_2 + 4e^-$

$2 \times \Delta H_{\text{second electron affinity}}$
$Al^{3+}_{(g)} + 3O^{2-}$

$\Delta H_{\text{second ionisation energy}} \times 2$
$2Al^+_{(s)} + \frac{3}{2}O_2 + 2e^-$

$\Delta H_{\text{first ionisation energy}} \times 2$
$2Al_{(g)} + \frac{3}{2}O_{2(g)}$

$\Delta H_{\text{atomisation}}$
$2Al_{(s)} + \frac{3}{2}O_{2(g)}$

$\Delta H_{\text{lattice}}$
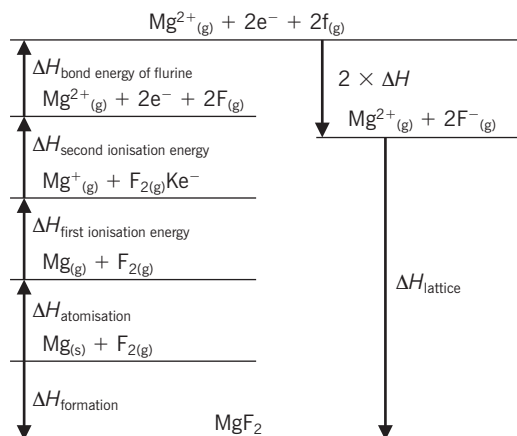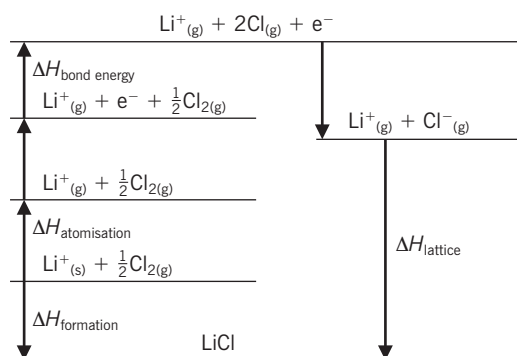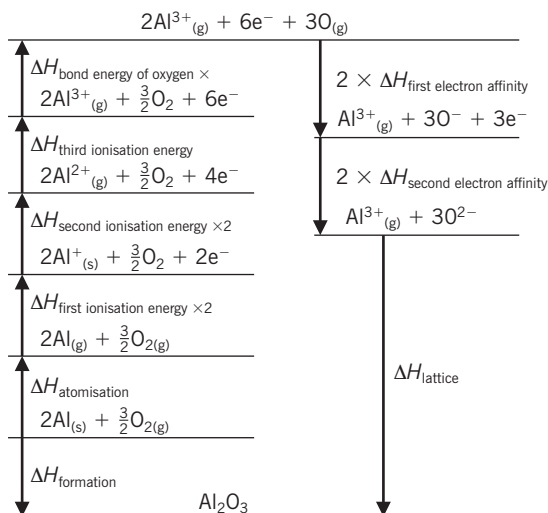
$\Delta H_{\text{formation}}$
Al_2O_3

Born Haber Cycles 2

Page 96–97

			$\Delta H/\text{kJ mol}^{-1}$	
1	A	$K(s) + \frac{1}{2}Br_2(l) \rightarrow K^+Br^-(s)$	−392	Enthalpy change of formation
2	B	$K(s) \rightarrow K(g)$	+90	Enthalpy change of atomisation
3	C	$K(g) \rightarrow K+(g) + e^-$	+420	First ionisation energy of potassium
4	D	$\frac{1}{2}Br_2(l) \rightarrow Br(g)$	+112	Bond enthalpy of bromine
5	E	$Br(g) + e^- \rightarrow Br^-(g)$	−342	First electron affinity of bromine

$H_{le} = H_a - (H_b + H_c + H_d - H_e) = -672 \text{ kJ mol}^{-1}$
NaBr would have a higher lattice enthalpy due to smaller Na ionic radius. KF would have higher lattice enthalpy due to smaller ionic radius of F.

Stretch yourself
$\Delta H \text{ MgCl}_2 = -113 \text{ kJ mol}^{-1}$
$2MgCl \rightarrow Mg + MgCl_2 \; \Delta H = -398 \text{ kJ mol}^{-1}$ so $MgCl_2$ stable with respect to $MgCl$.

Enthalpies of solution

Page 98–99

2 -30 kJ mol^{-1}
4 $+17 \text{ kJ mol}^{-1}$
6 -120 kJ mol^{-1}
8 $+960 \text{ kJ mol}^{-1}$

Stretch yourself
$H_{sol} \text{ BaCl}_2 = +55 \text{ KJ mol}^{-1}$
$H_{sol} \text{ BaF}_2 = +65 \text{ kJ mol}^{-1}$
BaF_2 is less soluble because it requires more energy more endothermic process in order to dissolve.

Factors that affect lattice enthalpy

Page 100–101

1 a NaCl and KBr NaCl has higher lattice enthalpy because of smaller ionic radius of Na^+ and Cl^-
  b K_2S and Na_2S Na_2S has a higher lattice because of smaller ionic radius of Na^+
  c $MgCl_2$ and RbCl $MgCl_2$ has a higher lattice enthalpy because of greater ionic charge of Mg^{2+}
  d $MgSO_4$ and MgO MgO has a higher lattice enthalpy because of smaller ionic radius of O^{2-}
2 a $XCO_3(s) \rightarrow XO(s) + CO_2(g)$
  b The carbonates decrease in thermal stability from $MgCO_3$ to $BaCO_3$
  c Thermal stability decrease down group 2 carbonates because of larger ionic radius reducing the lattice enthalpy.

Stretch yourself

As the ionic radius increases down Group 2 both the lattice enthalpy and the enthalpy of hydration decrease. However, for large anions ions such as sulfate the increase in size of the cation makes less difference to the lattice enthalpy than it does to the enthalpy of hydration , and so the solubility of the sulfates decreases down the group. For smaller anions such as hydroxide the decrease in lattice enthalpy is more significant than the decrease in enthalpy of hydration, and so the solubility of the hydroxides increases down the group.

Calculating the cell potential

Page 102–103

1 i Na: $Na^+ \parallel Cl_2 : 2Cl^-$
Na being oxidised and Cl_2 being reduced
$E_{cell} = +4.22V$

ii Na: $Na^+ \parallel Br_2: 2Br^-$
Na is oxidised and Br_2 is reduced
$E_{cell} = +3.8V$

iii Fe: $Fe^{2+} \parallel 2H^+: H_2$
Fe is oxidised and H^+ is reduced
$E_{cell} = +0.44V$

iv Na: $Na^+ \parallel Fe^{2+}; Fe$
Na is oxidised and Fe^{2+} is reduced
$E_{cell} = +2.27V$

v Al: $Al^{3+} \parallel Fe^{2+}: Fe$
Al is oxidised and Fe^{2+} is reduced
$E_{cell} = + 1.23V$

vi $2Br^-: Br_2 \parallel Cl_2: 2Cl^-$
Br^- is oxidised and Cl_2 is reduced
$E\ cell = +0.42V$

Stretch yourself

$H_2 | 2H^+ \parallel Br_2 | 2Br^-$
Hydrogen is oxidised to H_1 ions. In this case hydrogen ions will increase and therefore pH will decrease if left on.
$Fe | Fe^{2+} \parallel 2H^+/H_2$
Hydrogen ions will decrease in this case so pH will increase if cell is left on.

Redox titrations

Page 104–105

1 a $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$
 b $2Al + 3F_2 \rightarrow Al_2F_6$
 c $2Na + 2H^+ \rightarrow 2Na^+ + H_2$
 d $2H_2 + O_2 \rightarrow 2H_2O$
2 a Mn in MnO_4^- is +7
 b Cr in $Cr_2O_7^{2-}$ is +6
 c Cu in Cu_2O is +1
 d Cr in $Cr2(SO_4)_3$ is +3
Balanced redox equations
3 a $3Cu + 8H^+ + 2NO_3 \rightarrow 3Cu^{2+} + 2NO + 4H_2O$
 b $6Na + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Na^+ + 2Cr^{3+} + 7H_2O$

Stretch yourself
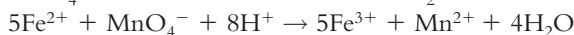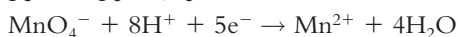
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
Concentration Fe^{2+} ions = $0.124\ mol\ dm^{-3}$
a $2MnO_4^-(aq) + 6H^+(aq) + 5H_2C_2O_4(aq) = 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$
b $M_r(H_2C_2O_4.2H_2O) = 126.0$
total mol $H_2C_2O_4.2H_2O$ (or $C_2O_4^{-2}$) = 1.50 / 126 = 0.011 904,
but mol of $H_2C_2O_4.2H_2O^-$ in titration = 0.001 190 4 (1/10 used, 25 of 250 cm^3),
mol MnO_4^- = mol of $C_2O_4^{-2}$ / 2.5 (2:5 or 1:2.5 ratio),
mol MnO_4^- = 0.001 190 4 / 2.5 = 0.000 476 19 (in 12.5 cm^3),
scaling up to 1 dm^3 the molarity of MnO_4^- = 0.000 482 4 × 1000 / 12.50 = $0.038\ 0\ mol\ dm^{-3}$
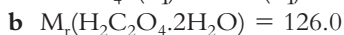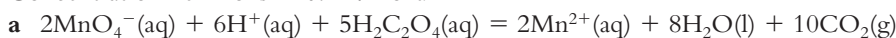
Redox titrations 2

Page 106–107

1 Concentration of bleach B is $0.01 \, mol \, dm^{-3}$ and concentration of bleach C is $0.0295 \, mol \, dm^{-3}$

2 Two other factors that need to be considered when choosing the best bleach is the viscosity of the bleach and the chemical half life how long the bleach continues to be active

Stretch yourself

a Thiosulfate $0.069 \, mol \, dm^{-3}$

b The initial concentration of $0.01 \, mol \, dm^{-3}$ was more suitable because it required a larger volume to titrate. The other small titre of $3.5 \, cm^3$ would have a much larger and significant percentage error.