

41st



6 theoretical problems
3 practical problems

THE FORTY-FIRST INTERNATIONAL CHEMISTRY OLYMPIAD 18–27 JULY 2009, CAMBRIDGE, UNITED KINGDOM

THEORETICAL PROBLEMS

PROBLEM 1

Estimating the Avogadro constant

Many different methods have been used to determine the Avogadro constant. Three different methods are given below.

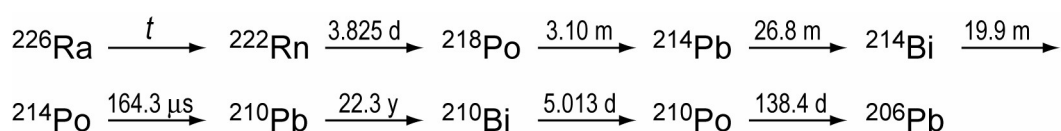
Method A – from X-ray diffraction data (modern)

The unit cell is the smallest repeating unit in a crystal structure. The unit cell of a gold crystal is found by X-ray diffraction to have the face-centred cubic unit structure (i.e. where the centre of an atom is located at each corner of a cube and in the middle of each face). The side of the unit cell is found to be 0.408 nm.

- 1.1 Sketch the unit cell and calculate how many Au atoms the cell contains.
- 1.2 The density of Au is $1.93 \cdot 10^4 \text{ kg m}^{-3}$. Calculate the volume and mass of the cubic unit cell.
- 1.3 Hence calculate the mass of a gold atom and the Avogadro constant, given that the relative atomic mass of Au is 196.97.

Method B – from radioactive decay (Rutherford, 1911)

The radioactive decay series of ^{226}Ra is as follows:



The times indicated are half-lives, the units are y = years, d = days, m = minutes. The first decay, marked t above, has a much longer half-life than the others.

1.4 In the table below, identify which transformations are α -decays and which are β -decays.

	α -decay	β -decay
$^{226}\text{Ra} \longrightarrow ^{222}\text{Rn}$		
$^{222}\text{Rn} \longrightarrow ^{218}\text{Po}$		
$^{218}\text{Po} \longrightarrow ^{214}\text{Pb}$		
$^{214}\text{Pb} \longrightarrow ^{214}\text{Bi}$		
$^{214}\text{Bi} \longrightarrow ^{214}\text{Po}$		
$^{214}\text{Po} \longrightarrow ^{210}\text{Pb}$		
$^{210}\text{Pb} \longrightarrow ^{210}\text{Bi}$		
$^{210}\text{Bi} \longrightarrow ^{210}\text{Po}$		
$^{210}\text{Po} \longrightarrow ^{206}\text{Pb}$		

- 1.5 A sample containing 192 mg of ^{226}Ra was purified and allowed to stand for 40 days. Identify the first isotope in the series (excluding Ra) that has not reached a steady state.
- 1.6 The total rate of α -decay from the sample was then determined by scintillation to be 27.7 GBq (where 1 Bq = 1 count s⁻¹). The sample was then sealed for 163 days. Calculate the number of α particles produced.
- 1.7 At the end of the 163 days the sample was found to contain 10.4 mm³ of He, measured at 101325 Pa and 273 K. Calculate the Avogadro constant from these data.
- 1.8 Given that the relative isotopic mass of ^{226}Ra measured by mass spectrometry is 226.25, use the textbook value of the Avogadro constant ($6.022 \cdot 10^{23} \text{ mol}^{-1}$) to calculate the number of ^{226}Ra atoms in the original sample, n_{Ra} , the decay rate constant, λ , and the half-life, t , of ^{226}Ra (in years). You need only consider the decays up to but not including the isotope identified in 1.5.

Method C – dispersion of particles (Perrin, 1909)

One of the first accurate determinations of the Avogadro constant was carried out by studying the vertical distribution under gravity of colloidal particles suspended in water. In one such experiment, particles with radius $2.12 \cdot 10^{-7}$ m and density $1.206 \cdot 10^3$ kg m⁻³ were suspended in a tube of water at 15 °C. After allowing sufficient time to equilibrate, the mean numbers of particles per unit volume observed at four heights from the bottom of the tube were:

height / 10 ⁻⁶ m	5	35	65	95
mean number per unit volume	4.00	1.88	0.90	0.48

1.9 Assuming the particles to be spherical, calculate:

- the mass, m , of a particle;
- the mass, $m_{\text{H}_2\text{O}}$, of the water it displaces;
- the effective mass, m^* , of the particle in water accounting for buoyancy (i.e. taking account of the upthrust due to the displaced volume of water).

Take the density of water to be 999 kg m⁻³.

At equilibrium, the number of particles per unit volume at different heights may be modelled according to a Boltzmann distribution:

$$\frac{n_h}{n_{h_0}} = \exp \left[-\frac{E_h - E_{h_0}}{RT} \right]$$

where

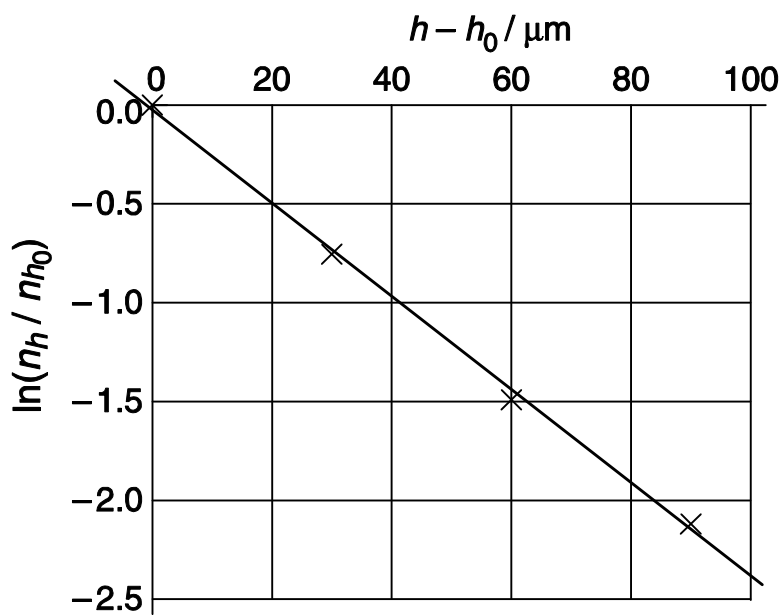
n_h is the number of particles per unit volume at height h ,

n_{h_0} is the number of particles per unit volume at the reference height h_0 ,

E_h is the gravitational potential energy per mole of particles at height h relative to the particles at the bottom of the tube,

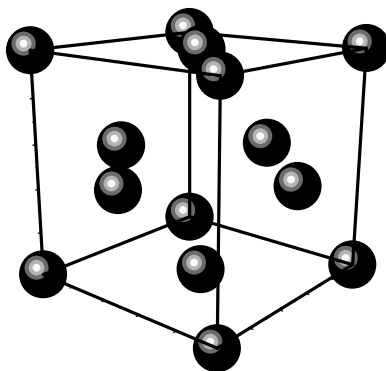
R is the gas constant, 8.3145 J K⁻¹ mol⁻¹.

A graph of $\ln(n_h / n_{h_0})$ against $(h - h_0)$, based on the data in the table above, is shown below. The reference height is taken to be 5 μm from the bottom of the tube.



1.10 Derive an expression for the gradient (slope) of the graph.

1.11 Determine the Avogadro constant from these data.

SOLUTION**1.1** Unit cell:

Number of Au atoms in the unit cell:

$$8 \times 1/8 \text{ from each corner} = 1$$

$$6 \times 1/2 \text{ from each face} = 3$$

Total = 4 atoms

1.2 Volume:

$$V = (0.408 \text{ nm})^3 = 6.79 \cdot 10^{-29} \text{ m}^3$$

Mass:

$$m = \rho V = 1.93 \cdot 10^4 \text{ kg m}^{-3} \times 6.79 \cdot 10^{-29} \text{ m}^3 = 1.31 \cdot 10^{-24} \text{ kg}$$

1.3 Mass of Au atom:

$$m = \frac{1.31 \cdot 10^{-24} \text{ kg}}{4} = 3.28 \cdot 10^{-25} \text{ kg}$$

Avogadro constant:

$$N_A = \frac{196.97 \text{ g mol}^{-1}}{3.28 \cdot 10^{-22} \text{ g}} = 6.01 \cdot 10^{23} \text{ mol}^{-1}$$

1.4

	α -decay	β -decay
$^{226}\text{Ra} \longrightarrow ^{222}\text{Rn}$	✓	
$^{222}\text{Rn} \longrightarrow ^{218}\text{Po}$	✓	
$^{218}\text{Po} \longrightarrow ^{214}\text{Pb}$	✓	
$^{214}\text{Pb} \longrightarrow ^{214}\text{Bi}$		✓
$^{214}\text{Bi} \longrightarrow ^{214}\text{Po}$		✓
$^{214}\text{Po} \longrightarrow ^{210}\text{Pb}$	✓	
$^{210}\text{Pb} \longrightarrow ^{210}\text{Bi}$		✓
$^{210}\text{Bi} \longrightarrow ^{210}\text{Po}$		✓
$^{210}\text{Po} \longrightarrow ^{206}\text{Pb}$	✓	

1.5 Answer: ^{210}Pb

1.6 $2.77 \cdot 10^{10} \text{ s}^{-1} \times 163 \times 24 \times 60 \times 60 \text{ s} = 3.90 \cdot 10^{17}$

1.7 Answer:

$$n = \frac{pV}{RT} = 4.64 \cdot 10^{-7} \text{ mol}$$

$$N_A = \frac{3.90 \cdot 10^{17}}{4.64 \cdot 10^{-7} \text{ mol}} = 8.4 \cdot 10^{23} \text{ mol}^{-1}$$

1.8 $n_{\text{Ra}} = \frac{0.192 \text{ g} \times 6.022 \cdot 10^{23} \text{ mol}^{-1}}{226.25 \text{ g mol}^{-1}} = 5.11 \cdot 10^{20} \text{ atoms}$

$$\lambda = \frac{2.77 \cdot 10^{10} \text{ s}^{-1}}{5.11 \cdot 10^{20} \times 4} = 1.36 \cdot 10^{-11} \text{ s}^{-1}$$

(only $\frac{1}{4}$ of the decays are from ^{226}Ra)

$$t = \frac{\ln 2}{\lambda} = 5.12 \cdot 10^{10} \text{ s} = 1620 \text{ years}$$

1.9 $V = 3.99 \cdot 10^{-20} \text{ m}^3$

$$m = 4.81 \cdot 10^{-17} \text{ kg}$$

$$m_{\text{H}_2\text{O}} = 3.99 \cdot 10^{-17} \text{ kg}$$

$$m^* = 8.3 \cdot 10^{-18} \text{ kg}$$

1.10 $\text{gradient} = \frac{-m^* N_A g}{RT}$

1.11 Acceptable range of slopes is $0.0235 \pm 0.002 \mu\text{m}$

Hence $N_A = (6.9 \pm 0.8) \cdot 10^{23} \text{ mol}^{-1}$ (error range needs widening here).

PROBLEM 2

Interstellar production of H₂

If two atoms collide in interstellar space the energy of the resulting molecule is so great that it rapidly dissociates. Hydrogen atoms only react to give stable H₂ molecules on the surface of dust particles. The dust particles absorb most of the excess energy and the newly formed H₂ rapidly desorbs. This question examines two kinetic models for H₂ formation on the surface of a dust particle.

In both models, the rate constant for adsorption of H atoms onto the surface of dust particles is $k_a = 1.4 \cdot 10^{-5} \text{ cm}^3 \text{ s}^{-1}$. The typical number density of H atoms (number of H atoms per unit volume) in interstellar space is $[\text{H}] = 10 \text{ cm}^{-3}$.

[Note: In the following, you may treat numbers of surface-adsorbed atoms and number densities of gas-phase atoms in the same way as you would normally use concentrations in the rate equations. As a result, the units of the rate constants may be unfamiliar to you. Reaction rates have units of numbers of atoms or molecules per unit time.]

2.1 Calculate the rate at which H atoms adsorb onto a dust particle. You may assume that this rate is constant throughout.

Desorption of H atoms is first order with respect to the number of adsorbed atoms. The rate constant for the desorption step is $k_d = 1.9 \cdot 10^{-3} \text{ s}^{-1}$.

2.2 Assuming that only adsorption and desorption take place, calculate the steady-state number, N , of H atoms on the surface of a dust particle.

The H atoms are mobile on the surface. When they meet they react to form H₂, which then desorbs. The two kinetic models under consideration differ in the way the reaction is modelled, but share the same rate constants k_a , k_d , and k_r , for adsorption, desorption, and bimolecular reaction, as given below.

$$k_a = 1.4 \cdot 10^{-5} \text{ cm}^3 \text{ s}^{-1}$$

$$k_d = 1.9 \cdot 10^{-3} \text{ s}^{-1}$$

$$k_r = 5.1 \cdot 10^4 \text{ s}^{-1}$$

Model A

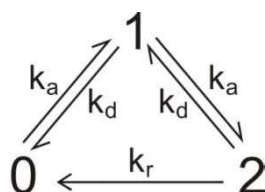
Reaction to form H_2 is assumed to be second order. On a dust particle the rate of removal of H atoms by reaction is $k_r N^2$.

2.3 Write down an equation for the rate of change of N , including adsorption, desorption and reaction. Assuming steady state conditions, determine the value of N .

2.4 Calculate the rate of production of H_2 per dust particle in this model.

Model B

Model B attempts to analyse the probability that the dust particles carry 0, 1 or 2 H atoms. The three states are linked by the following reaction scheme. The assumption is made that no more than 2 atoms may be adsorbed simultaneously.



x_0 , x_1 and x_2 are the fractions of dust particles existing in state 0, 1 or 2, respectively. These fractions may be treated in the same way as concentrations in the following kinetic analysis. For a system in state m with fraction x_m , the rates of the three possible processes are

Adsorption ($m \rightarrow m + 1$): rate = $k_a [\text{H}] x_m$

Desorption ($m \rightarrow m - 1$): rate = $k_d m x_m$

Reaction ($m \rightarrow m - 2$): rate = $\frac{1}{2} k_r m(m-1) x_m$

2.5 Write down equations for the rates of change, dx_m/dt , of the fractions x_0 , x_1 and x_2 .

2.6 Assuming steady-state conditions, use the above rate equations to find expressions for the ratios x_2/x_1 and x_1/x_0 , and evaluate these ratios.

2.7 Evaluate the steady state fractions x_0 , x_1 and x_2 .

[If you were unable to determine the ratios in 2.6, use $x_2/x_1 = a$ and $x_1/x_0 = b$ and give the result algebraically.]

2.8 Evaluate the rate of production of H_2 per dust particle in this model.

- 2.9** It is currently not possible to measure the rate of this reaction experimentally, but the most recent computer simulations of the rate give a value of $9.4 \cdot 10^{-6} \text{ s}^{-1}$. Which of the following statements apply to each model under these conditions? Mark any box you consider to be appropriate.

Statement	Model A	Model B	Neither model
The rate determining step is adsorption of H atoms.			
The rate-determining step is desorption of H ₂ molecules.			
The rate determining step is the bimolecular reaction of H atoms on the surface.			
The rate determining step is adsorption of the second H atom.			
The implicit assumption that reaction can take place regardless of the number of atoms adsorbed leads to substantial error (at least a factor of two).			
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at least a factor of two).			

SOLUTION

2.1 Answer: $1.4 \cdot 10^{-4} \text{ s}^{-1}$

2.2 Answer: $1.4 \cdot 10^{-4} \text{ s}^{-1} = 1.9 \cdot 10^{-3} \text{ s}^{-1} N \Rightarrow N = 7.4 \cdot 10^{-2}$

2.3 $\frac{dN}{dt} = 0 = k_a[H] - k_d N - k_r N^2$

$$N = \frac{-k_d + \sqrt{k_d^2 + 4 k_r k_a [H]}}{2 k_r}$$

$$N = 5.2 \cdot 10^{-5}$$

2.4 Answer: $\frac{1}{2} k_r N^2 = 7.0 \cdot 10^{-5} \text{ s}^{-1}$

2.5

$$\frac{dP_0}{dt} = -k_a [H] P_0 + k_d P_1 + k_r P_2$$

$$\frac{dP_1}{dt} = k_a [H] P_0 - (k_a [H] + k_d) P_1 + 2 k_d P_2$$

$$\frac{dP_2}{dt} = k_a [H] P_1 - (2 k_d + k_r) P_2 \quad (\text{remember P is changed to x})$$

2.6

$$\frac{P_2}{P_1} = \frac{k_a [H]}{(2 k_d + k_r)} \approx \frac{k_a [H]}{k_r} = 2.7 \cdot 10^{-9}$$

$$\frac{P_1}{P_0} = \frac{k_a [H] (2 k_d + k_r)}{k_d (2 k_d + k_r) + k_r k_a [H]} \approx \frac{k_a [H]}{k_d + k_a [H]} = 6.9 \cdot 10^{-2}$$

2.7

$$P_0 = 0.94,$$

$$P_1 = 0.064,$$

$$P_2 = 1.8 \cdot 10^{-10}$$

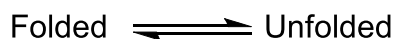
2.8 $k_r x_2 = 9.0 \cdot 10^{-6} \text{ s}^{-1}$

2.9

Statement	Model A	Model B	Neither model
The rate determining step is adsorption of H atoms.	✓	(✓)	
The rate-determining step is desorption of H ₂ molecules.			✓
The rate determining step is the bimolecular reaction of H atoms on the surface.			✓
The rate determining step is adsorption of the second H atom.		✓	
The implicit assumption that reaction can take place regardless of the number of atoms adsorbed leads to substantial error (at least a factor of two).	✓		
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at least a factor of two).			✓

PROBLEM 3**Protein Folding**

The unfolding reaction for many small proteins can be represented by the equilibrium:



You may assume that the protein folding reaction takes place in a single step. The position of this equilibrium changes with temperature; the melting temperature T_m is defined as the temperature at which half of the molecules are unfolded and half are folded.

The intensity of the fluorescence signal at a wavelength of 356 nm of a 1.0 μM ($\text{M} = \text{mol dm}^{-3}$) sample of the protein Chymotrypsin Inhibitor 2 (CI2) was measured as a function of temperature over the range 58 to 66 $^{\circ}\text{C}$:

Temperature / $^{\circ}\text{C}$	58	60	62	64	66
Fluorescence intensity (arbitrary units)	27	30	34	37	40

A 1.0 μM sample in which all of the protein molecules are folded gives a fluorescence signal of 21 units at 356 nm. A 1.0 μM sample in which all of the protein molecules are unfolded gives a fluorescence signal of 43 units.

- 3.1 Assuming that the fluorescence intensity from each species is directly proportional to its concentration, calculate the fraction, x , of unfolded molecules present at each temperature.
- 3.2 Give an expression for the equilibrium constant, K , in terms of x , and hence calculate the value of K at each temperature.
- 3.3 Estimate the value of T_m for this protein (to the nearest 1 $^{\circ}\text{C}$).

Assuming that the values of ΔH° and ΔS° for the protein unfolding reaction are constant with temperature then:

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + C$$

where C is a constant.

3.4 Plot a suitable graph and hence determine the values of ΔH° and ΔS° for the protein unfolding reaction.

[If you have been unable to calculate values for ΔH° and ΔS° , you should use the following incorrect values for the subsequent parts of the problem:

$$\Delta H^\circ = 130 \text{ kJ mol}^{-1}; \quad \Delta S^\circ = 250 \text{ J K}^{-1} \text{ mol}^{-1}.$$

3.5 Calculate the equilibrium constant for the unfolding reaction at 25 °C.

[If you have been unable to calculate a value for K , you should use the following incorrect value for the subsequent parts of the problem: $K = 3.6 \cdot 10^{-6}$]

The first order rate constant for the Cl2 protein folding reaction can be determined by following the fluorescence intensity when a sample of unfolded protein is allowed to refold (typically the pH of the solution is changed). The concentration of protein when a 1.0 μM sample of unfolded Cl2 was allowed to refold was measured at a temperature of 25 °C:

time / ms	0	10	20	30	40
concentration / μM	1	0.64	0.36	0.23	0.14

3.6 Plot a suitable graph and hence determine the value of the rate constant for the protein folding reaction, k_f , at 25 °C.

[If you have been unable to calculate the value for k_f , you should use the following incorrect value for the subsequent parts of the question: $k_f = 60 \text{ s}^{-1}$.]

3.7 Determine the value of the rate constant for the protein *unfolding* reaction, k_u , at 25 °C.

3.8 At 20 °C the rate constant for the protein folding reaction is 33 s^{-1} . Calculate the activation energy for the protein folding reaction.

SOLUTION

3.1

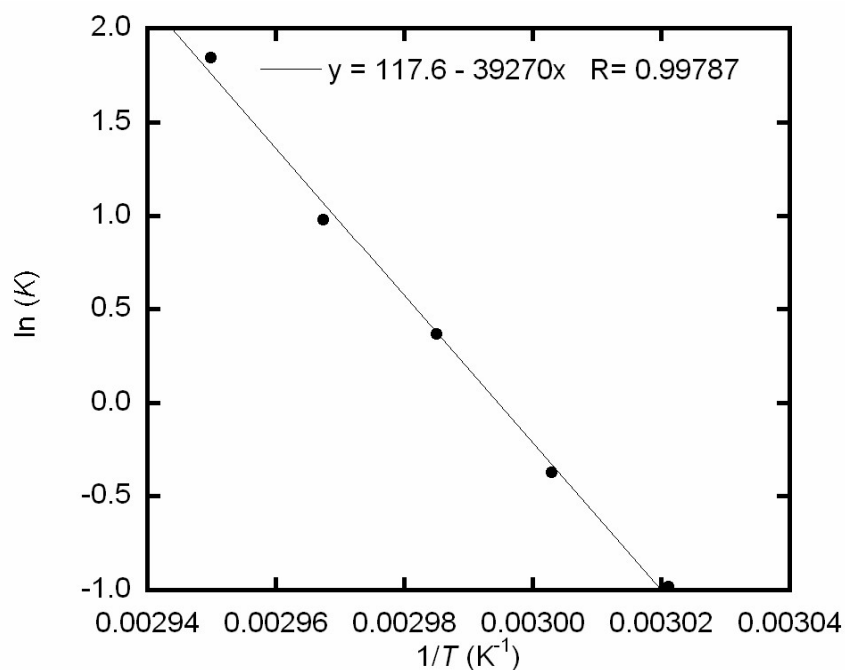
Temp / °C	58	60	62	64	66
x	0.27	0.41	0.59	0.73	0.86

3.2

Temp / °C	58	60	62	64	66
K	0.38	0.69	1.4	2.7	6.3

3.3 Answer: $T_m = 61\text{ °C}$

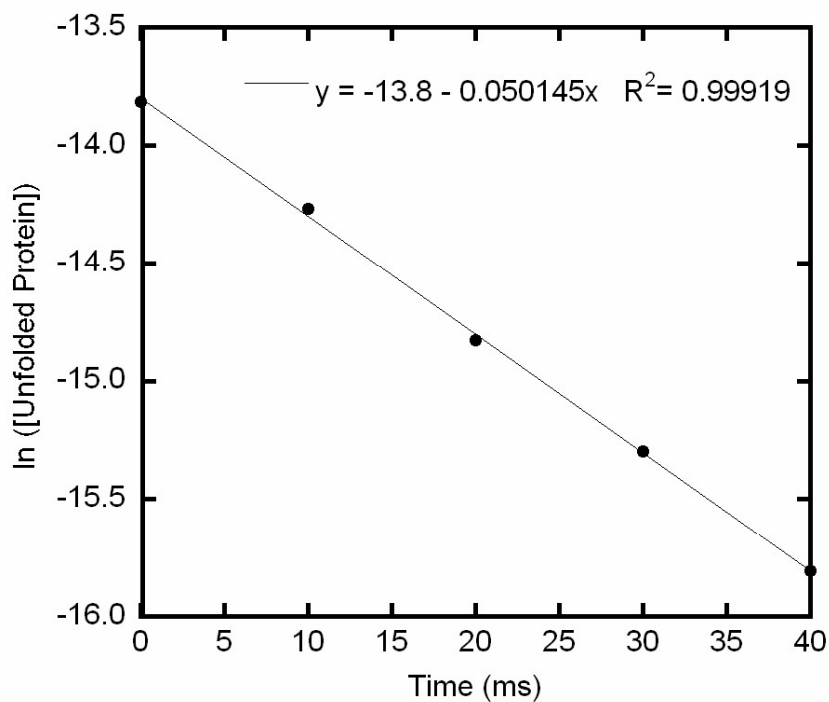
3.4



Answers: $\Delta H^\circ = 330\text{ kJ mol}^{-1}$; $\Delta S^\circ = 980\text{ J mol}^{-1}\text{ K}^{-1}$

3.5 $\Delta H^\circ = 330000\text{ J mol}^{-1}$ and $\Delta S^\circ = 980\text{ J mol}^{-1}\text{ K}^{-1}$ then $\Delta G^\circ = 35000\text{ J mol}^{-1}$ at 25 °C , hence $K = 6.9 \cdot 10^{-7}$.

3.6



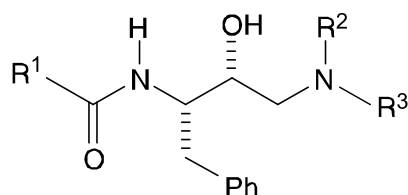
Answer: Rate constant for the protein folding reaction, $k_f = 50 \text{ s}^{-1}$.

3.7 Answer: Rate constant for the protein *unfolding* reaction, $k_u = 3.5 \cdot 10^{-5} \text{ s}^{-1}$.

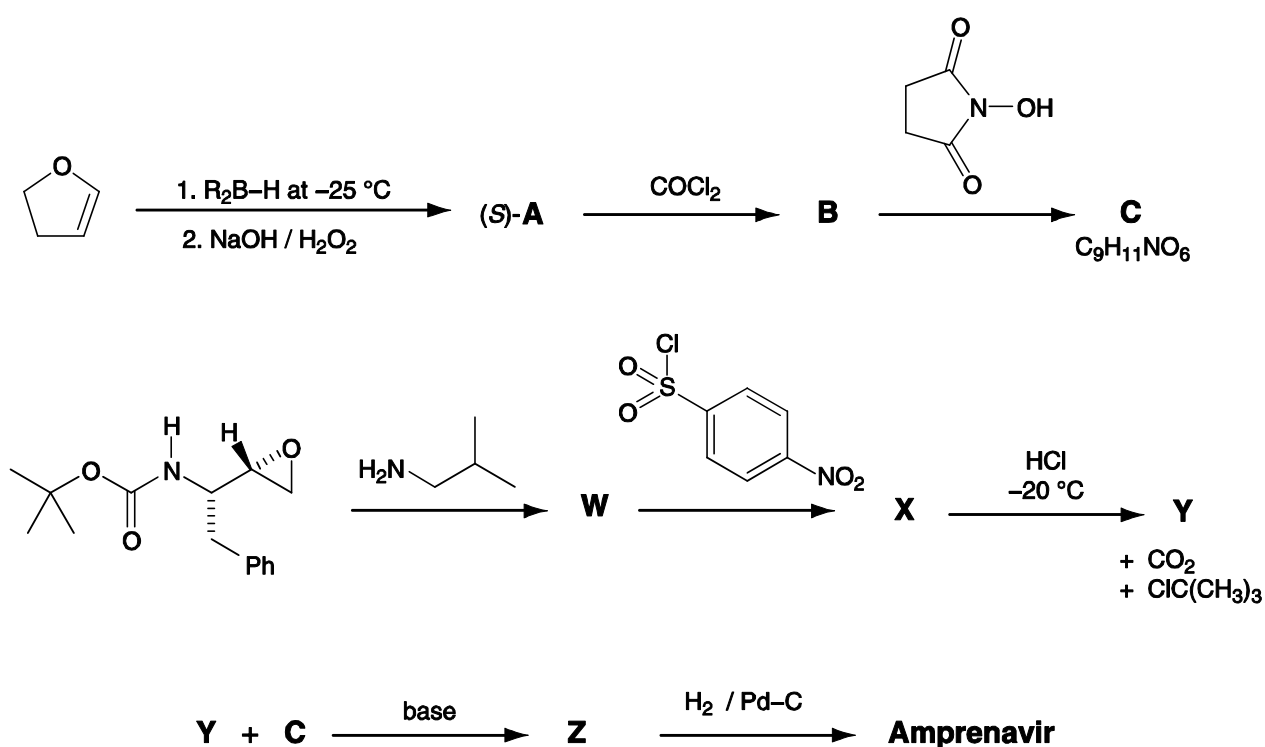
3.8 Answer: Activation energy = 61 kJ mol^{-1} .

PROBLEM 4**Synthesis of Amprenavir**

One class of anti-HIV drugs, known as *protease inhibitors*, works by blocking the active site of one of the enzymes used in assembly of the viruses within the host cell. Two successful drugs, *saquinavir* and *amprenavir*, contain the structural unit shown below which mimics the transition state within the enzyme. In the structure, R^1 , R^2 and R^3 may represent any atom or group other than hydrogen.



Amprenavir may be synthesised as shown in the convergent scheme below.



The reagent R_2B-H used in the first step is chiral.

Product **A** is formed as the (*S*)-enantiomer.

Three of the signals in the ^1H NMR spectrum of Amprenavir disappear on shaking with D_2O : δ 4.2 (2H), δ 4.9 (1H) and δ 5.1 (1H).

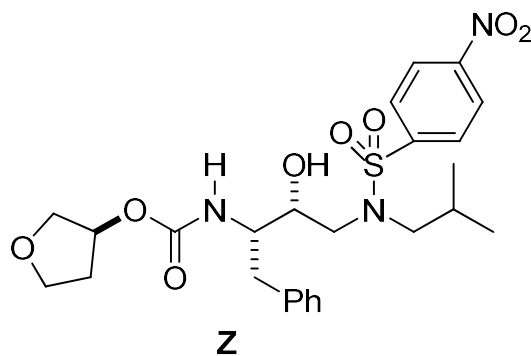
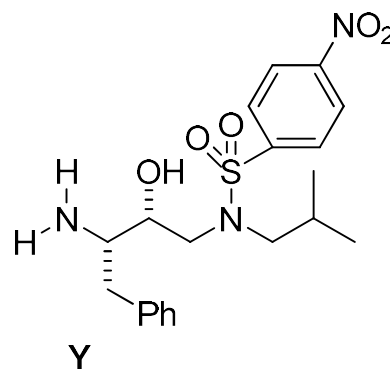
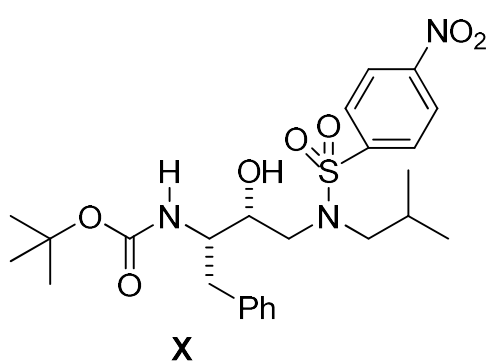
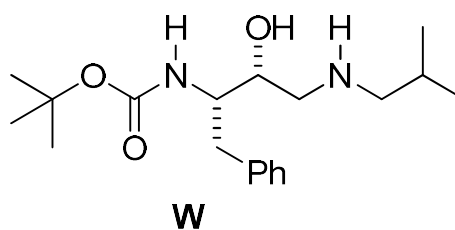
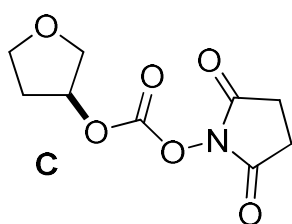
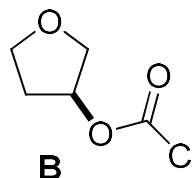
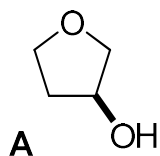
4.1 Suggest structures for:

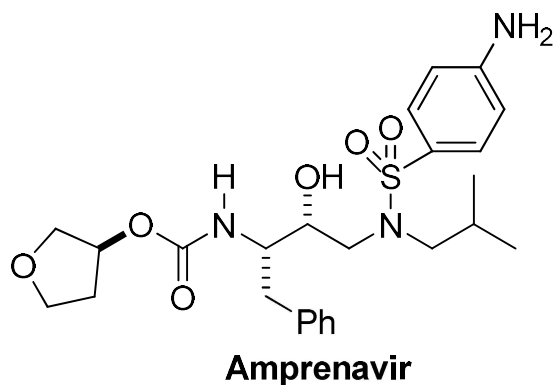
- the intermediates **A**, **B**, **C**, **W**, **X**, **Y** and **Z**,
- Amprenavir*.

Your answers should clearly show the stereochemistry at each centre.

SOLUTION

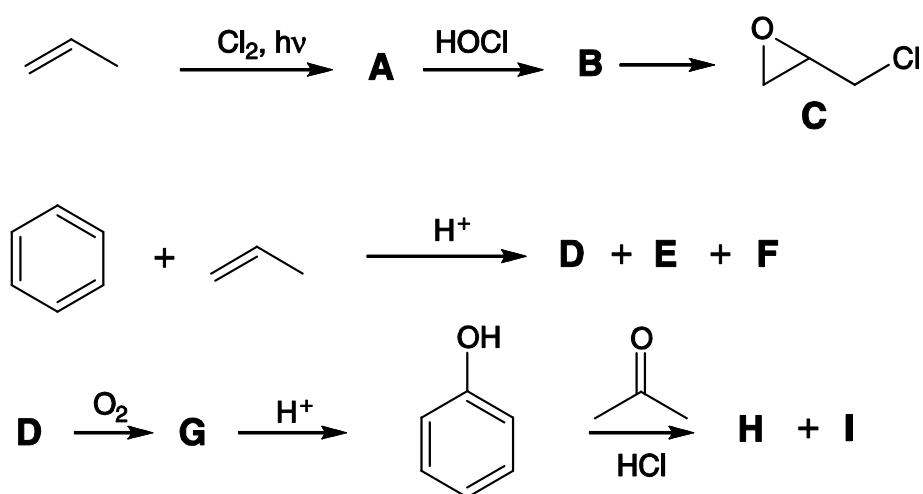
4.1





PROBLEM 5**Epoxy resins**

The synthesis of epoxy resins is a multi-billion dollar industry worldwide. Epoxy resins are high performance adhesives synthesised from the reaction of a bis-epoxide with a diamine. The bis-epoxide is made from **H** and epichlorohydrin, **C**. Compounds **C** and **H** can be synthesised according to the schemes below.



The synthesis of epichlorohydrin **C** begins with the reaction of propene with chlorine in the presence of light.

5.1 Draw the structures of **A** and **B**.

5.2 Give the formula of a suitable reagent for the conversion of **B** into epichlorohydrin **C**.

The synthesis of **H** commences with the reaction of benzene with propene in the presence of an acid catalyst which gives **D** as the major product and **E** and **F** as minor products.

5.3 Draw the structures of **D**, **E**, and **F** from the following data:

D: Elemental composition: C 89.94 %, H 10.06 %; 6 signals in the ¹³C NMR spectrum.

E: Elemental composition: C 88.82 %, H 11.18 %; 4 signals in the ¹³C NMR spectrum.

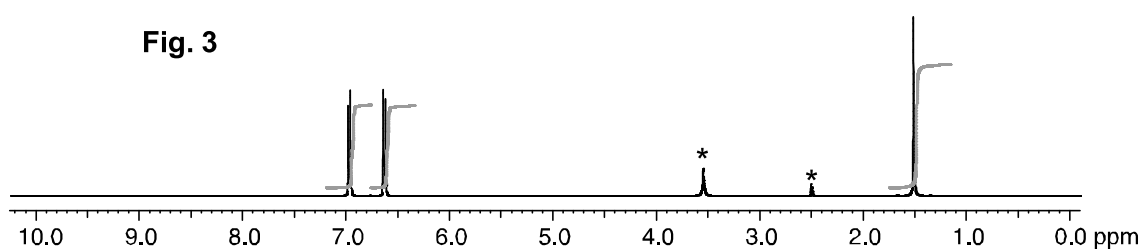
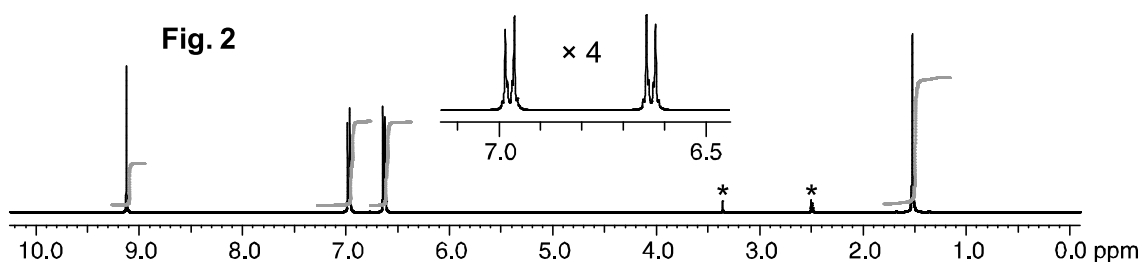
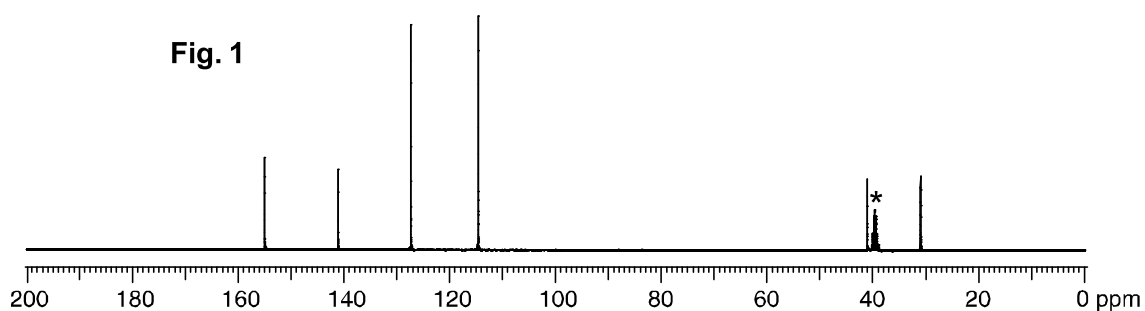
F: Elemental composition: C 88.82 %, H 11.18 %; 5 signals in the ¹³C NMR spectrum.

Bubbling oxygen through a hot solution of **D** gives **G** which on exposure to acid gives phenol (hydroxybenzene) and acetone (propanone). **G** turns starch iodide paper from

white to dark blue. **G** has 6 signals in the ^{13}C NMR spectrum and the following signals in the ^1H NMR spectrum: δ 7.78 (1H, s), 7.45 – 7.22 (5H, m), 1.56 (6H, s); addition of D_2O results in the disappearance of the signal at $\delta = 7.78$.

5.4 Draw the structure of **G**.

Exposure of phenol and acetone to hydrochloric acid gives compound **H**. The ^{13}C NMR spectrum for **H** is shown in Fig. 1. The ^1H NMR spectrum is shown in Fig. 2 together with a four-fold expansion of the region 6.5 – 7.1 ppm. The ^1H NMR spectrum after the addition of a drop of D_2O , is shown in Fig. 3. Peaks due to the solvent are marked with an asterisk (*).



5.5 Draw the structure of **H**.

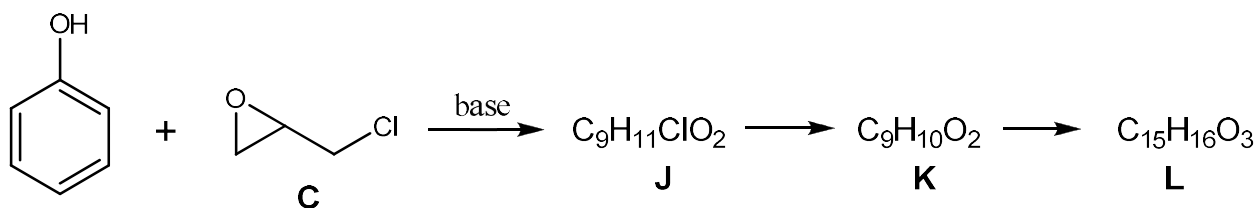
5.6 Draw one resonance structure of phenol which explains the regioselective formation of **H**.

A second compound, **I**, is also formed in the reaction of phenol with acetone. The ^{13}C NMR spectrum of **I** has 12 signals. The ^1H NMR spectrum has the following signals:

δ 7.50 – 6.51 (8H, m), 5.19 (1H, s), 4.45 (1H, s), 1.67 (6H, s); addition of D₂O results in the disappearance of the signals at δ = 5.19 and 4.45

5.7 Draw a structure for **I**.

Excess phenol reacts with epichlorohydrin **C** in the presence of base to give compound **L** which has 6 signals in its ¹³C NMR spectrum. If the reaction is stopped before completion compounds **J** and **K** can also be isolated. Compound **L** is formed from compound **K** and compound **K** is formed from compound **J**.



5.8 Draw the structures of **J**, **K** and **L**.

Treatment of **H** with a large excess of epichlorohydrin **C** and base gives a monomeric bis-epoxide **M**. **M** contains no chlorine atoms or OH groups.

5.9 Draw the structure of **M**.

Treatment of **H** with a small excess of epichlorohydrin and base gives **N**. **N** has the form: endgroup 1-[repeat unit]_n-endgroup 2 where *n* is approximately 10 – 15. **N** does not contain chlorine atoms and contains one OH group per repeat unit.

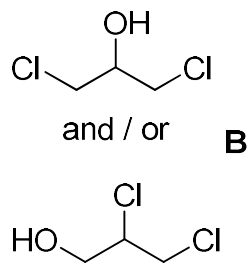
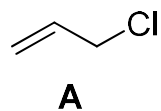
5.10 Draw the structure of **N** in the form indicated above:

(endgroup 1-[repeat unit]_{*n*}-endgroup 2).

5.11 Draw the repeat unit of the polymeric epoxy resin **O** formed from the reaction of the bis-epoxide **M** with ethane-1,2-diamine.

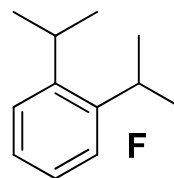
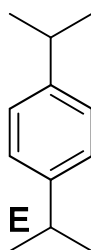
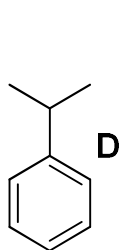
SOLUTION

5.1

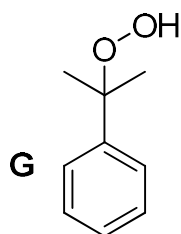


5.2 NaOH, or the formula of another suitable base.

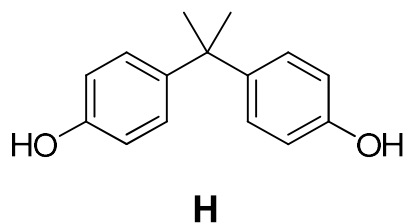
5.3



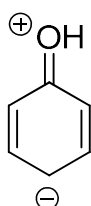
5.4



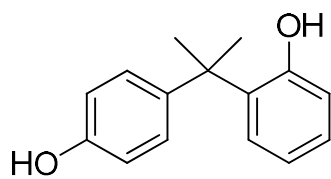
5.5



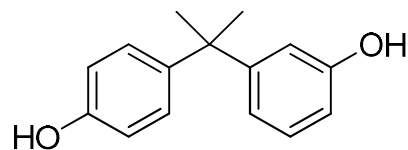
5.6



5.7

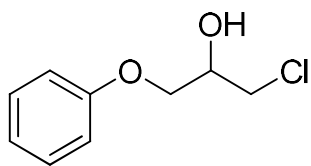


I

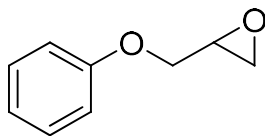


also fits the data

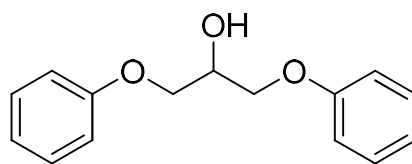
5.8



J

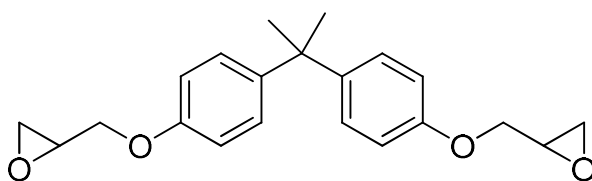


K



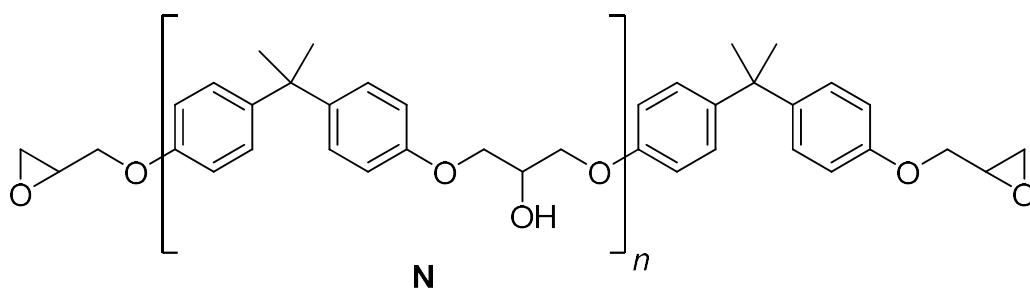
L

5.9



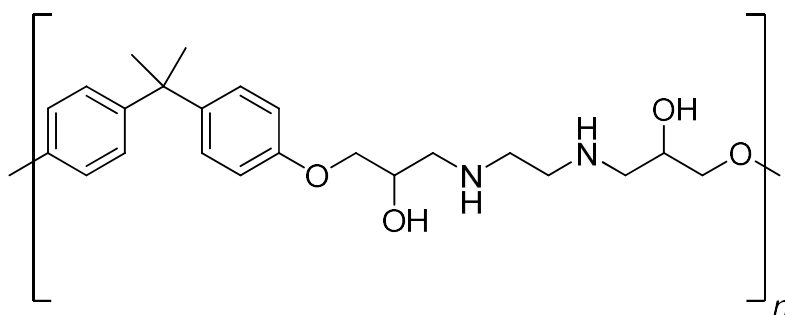
M

5.10



N

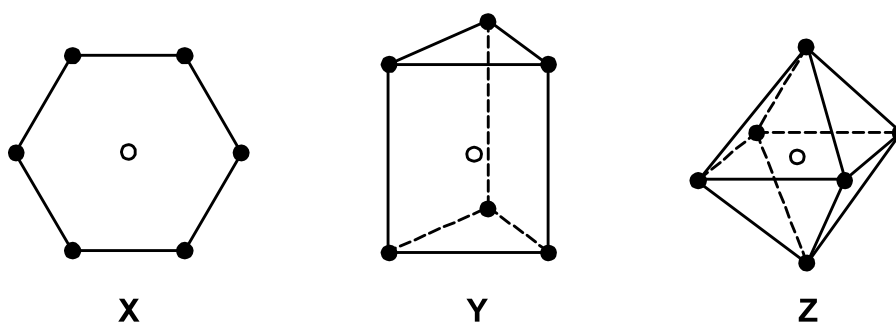
5.11



PROBLEM 6

Transition metal complexes

Alfred Werner used the technique of 'isomer counting' to deduce the structure of metal complexes with coordination number six. Three of the shapes he considered are shown below.



In each structure, the empty circle shows the location of the central metal atom and the filled circles show the location of the ligands. Structure **X** is hexagonal planar, structure **Y** is trigonal prismatic and structure **Z** is octahedral.

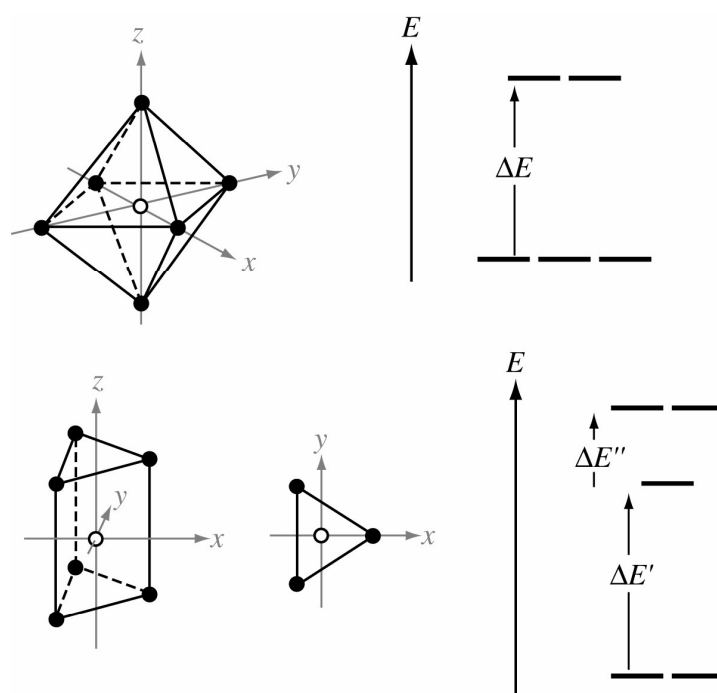
For each of the three shapes, there is just one structure when all of the ligands are the same, i.e. when the complex has the general formula MA_6 where A is the ligand. However, when achiral ligands A are substituted by one or more achiral ligands, it may be possible for each structure to form geometrical isomers. It might also be possible for one or more of the geometrical isomers to be optically active and exist as pairs of enantiomers.

6.1 Fill in the table below to indicate how many geometrical isomers may be formed for each structure **X**, **Y**, and **Z** as the monodentate ligands A are substituted by monodentate ligands B or by symmetrical bidentate ligands, denoted C–C. Bidentate ligand C–C can only link between two atoms on adjacent positions, i.e. those positions connected by a line in the structures **X**, **Y**, and **Z**.

In each case write the number of geometrical isomers in the space provided. If one of the isomers exists as a pair of enantiomers, include an asterisk, *, in the box. If two exist as two pairs of enantiomers, include two asterisks and so on. For example, if you think there are five geometrical isomers of a particular structure, three of which exist as pairs of enantiomers, write 5 ***

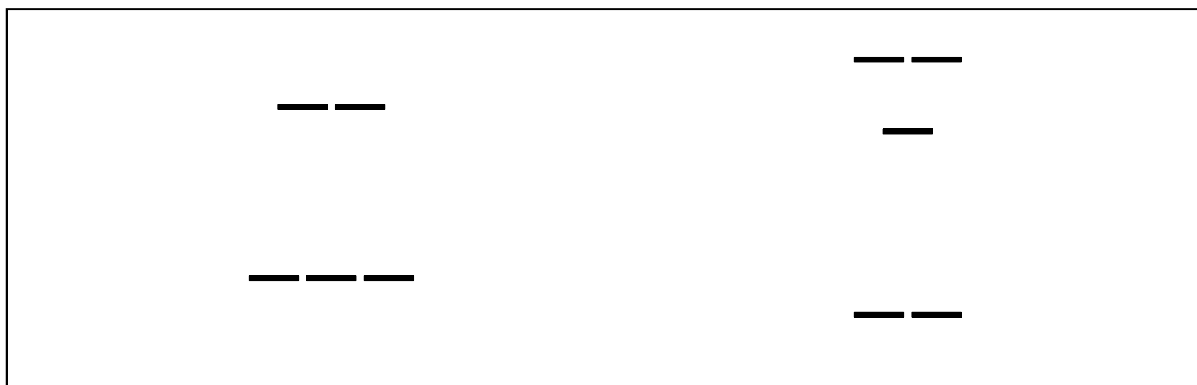
	Number of predicted geometrical isomers		
	Hexagonal planar X	Trigonal Prismatic Y	Octahedral Z
MA ₆	1	1	1
MA ₅ B			
MA ₄ B ₂			
MA ₃ B ₃			
MA ₄ (C-C)			
MA ₂ (C-C) ₂			
M(C-C) ₃			

There are no known complexes that adopt the hexagonal planar geometry **X**, but structures are known for both the trigonal prismatic geometry **Y** and the octahedral geometry **Z**. In these complexes, the orbitals derived from the metal d orbitals have different energies depending on the geometry of the complex. The splitting patterns for the trigonal prismatic geometry and for the octahedral geometry are shown below.



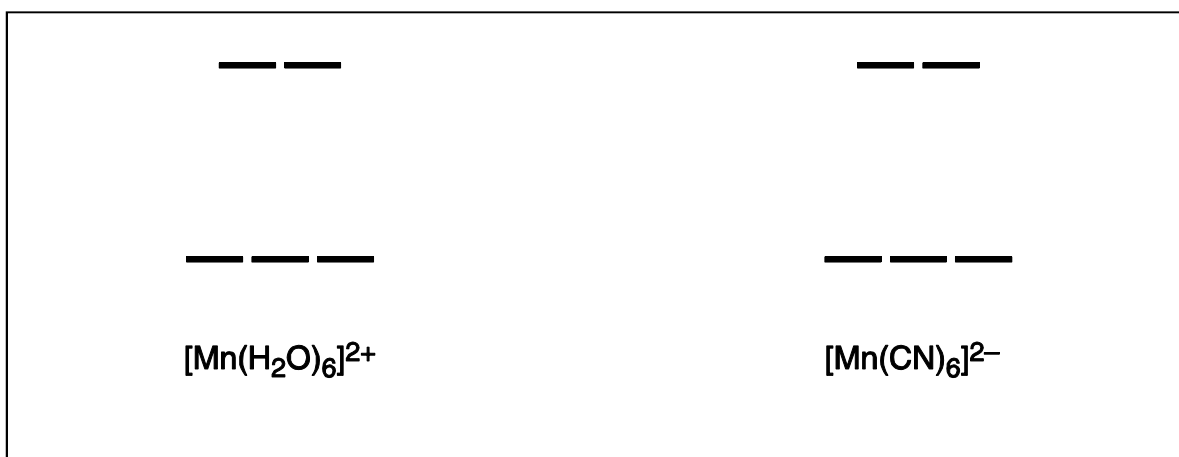
The separations in energy, ΔE , $\Delta E'$ and $\Delta E''$ depend on the particular complex.

6.2 For each of the splitting patterns shown below label which d orbitals are which.

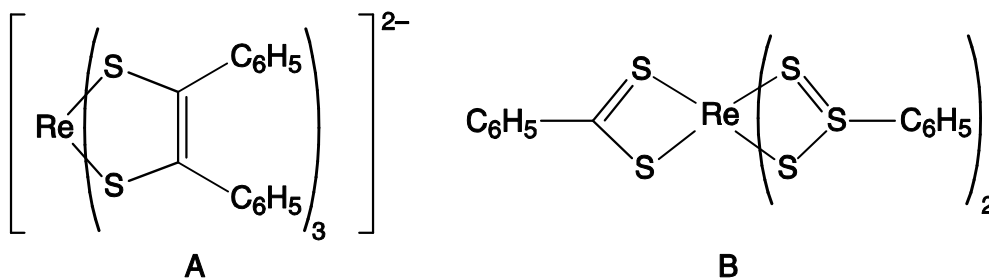


The two complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mn}(\text{CN})_6]^{2-}$ are both octahedral. One has a magnetic moment of 5.9 BM, the other has a magnetic moment of 3.8 BM but you must decide which is which.

6.3 On the diagram below, draw the electronic arrangements for each of the complexes.



The magnetic moments of complexes **A** and **B** shown below have been measured and found to be 1.9 and 2.7 BM but you must decide which is which.



6.4 Draw the orbital splitting diagrams for the two complexes, including the arrangements of the electrons.

Octahedral complexes are far more common than trigonal prismatic. Werner isolated five compounds **C** – **G** containing Co(III), Cl, and NH₃ only, each of which contained one octahedral complex. (There is actually a sixth compound but Werner could not isolate it.) Werner's five compounds had the molar conductivities shown below. The conductivities are extrapolated to infinite dilution and are expressed in arbitrary units. Compound **G** does not react with aqueous AgNO₃; compounds **C**, **D**, and **E** react with different stoichiometric ratios of aqueous AgNO₃; **E** and **F** react with the same stoichiometric ratio of aqueous AgNO₃.

	C	D	E	F	G
molar conductivity	510	372	249	249	~0

6.5 As far as you are able, suggest a structure for each of the compounds **C** – **G**.

Werner was also the first person to separate the enantiomers of an octahedral compound, **H**, which contained no carbon atoms. The compound, **H**, is composed of only cobalt, ammonia, chloride and an oxygen species which could be either H₂O, or HO⁻ or O²⁻. The compound contains octahedrally coordinated cobalt ions. All of the chloride is easily removed from the compound by titration with aqueous silver nitrate. A 0.2872 g sample of **H** (containing no water of crystallization) required 22.8 cm³ of a silver nitrate solution ($c = 0.100 \text{ mol dm}^{-3}$) to exchange all of the chloride.

6.6 Calculate the percentage, by mass, of chloride in **H**.

H is stable to acids, but is hydrolysed in alkali. A 0.7934 g sample of **H** (containing no water of crystallization) was heated with excess aqueous sodium hydroxide. Cobalt(III) oxide was formed and ammonia gas given off. The ammonia produced was distilled off and absorbed into 50.0 cm³ of aqueous HCl ($c_{\text{HCl}} = 0.500 \text{ mol dm}^{-3}$). The residual HCl required 24.8 cm³ of aqueous KOH solution ($c_{\text{KOH}} = 0.500 \text{ mol dm}^{-3}$) to be neutralized.

The remaining suspension of cobalt(III) oxide was allowed to cool, approximately 1 g of potassium iodide was added, and then the mixture was acidified with aqueous HCl. The liberated iodine was then titrated with aqueous solution of sodium thiosulfate ($c = 0.200 \text{ mol dm}^{-3}$) and required 21.0 cm³ for complete reaction.

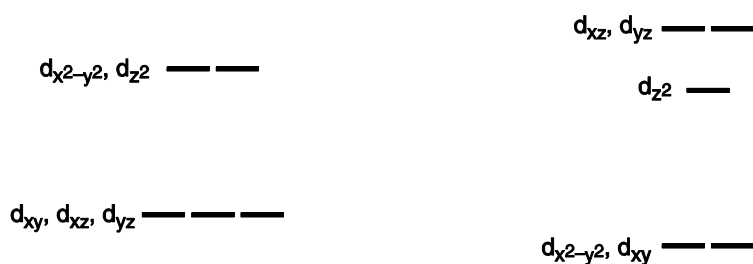
- 6.7 Calculate the percentage, by mass, of ammonia in **H**.
- 6.8 Give the equation for the reaction of cobalt(III) oxide with potassium iodide in aqueous acid.
- 6.9 Calculate the percentage, by mass, of cobalt in **H**.
- 6.10 Calculate the identity of the oxygen species contained in **H**. Show your working.
- 6.11 Give the empirical formula of **H**.
- 6.12 Suggest a structure for the chiral compound **H**.
-

SOLUTION

6.1

	Number of predicted geometrical isomers		
	Hexagonal planar X	Trigonal Prismatic Y	Octahedral Z
MA ₆	1	1	1
MA ₅ B	1	1	1
MA ₄ B ₂	3	3*	2
MA ₃ B ₃	3	3*	2
MA ₄ (C-C)	1	2	1
MA ₂ (C-C) ₂	2	4*	2*
M(C-C) ₃	1	2	1*

6.2



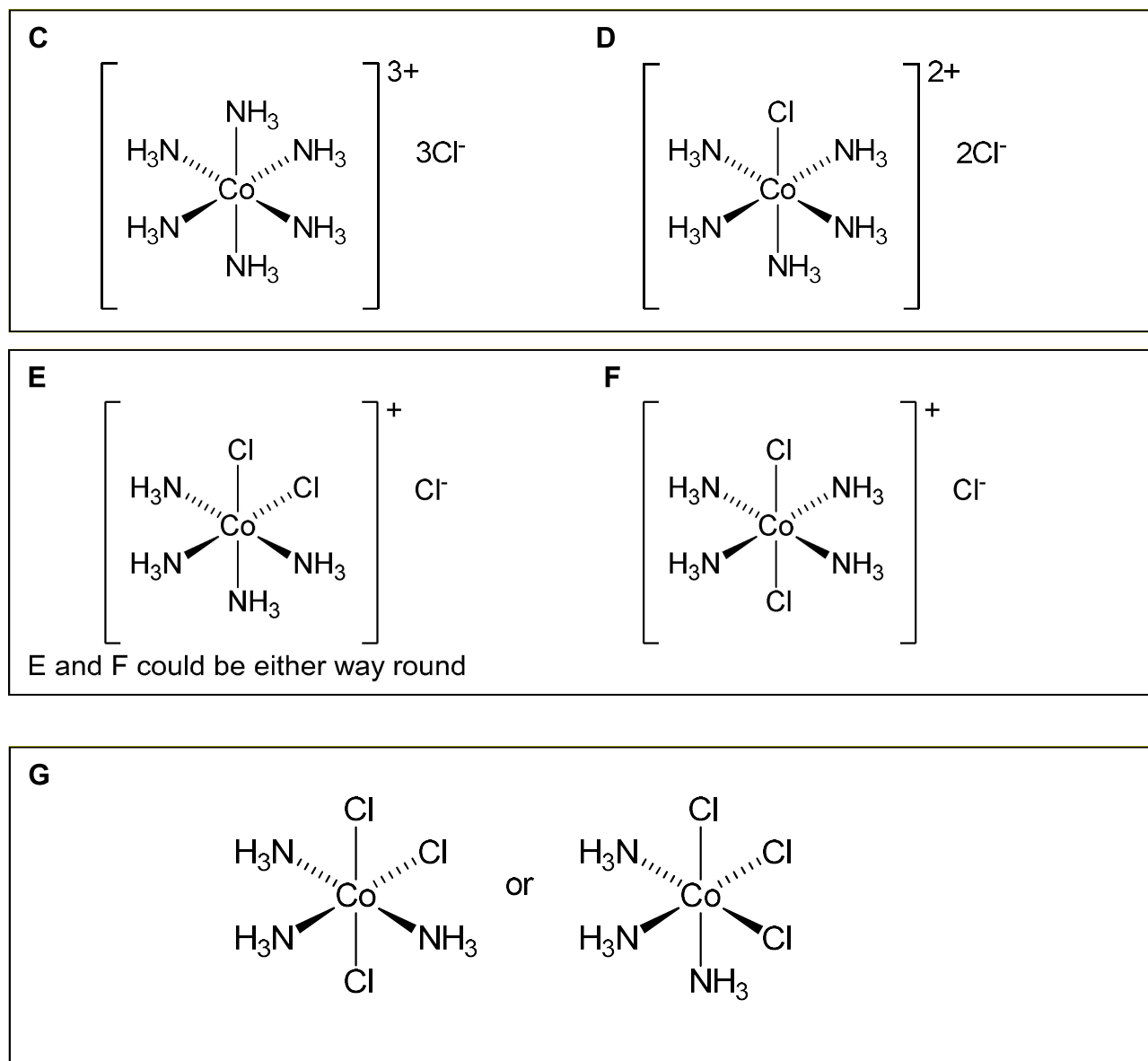
6.3



6.4



6.5



$$6.6 \quad n(\text{Ag}^+) = 0.100 \text{ mol dm}^{-3} \times 0.0228 \text{ dm}^3 = 2.28 \cdot 10^{-3} \text{ mol}$$

$$n(\text{Cl}^-) = 2.28 \cdot 10^{-3} \text{ mol}$$

$$m(\text{Cl}) = 8.083 \cdot 10^{-2} \text{ g}$$

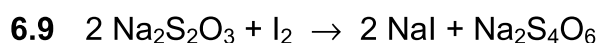
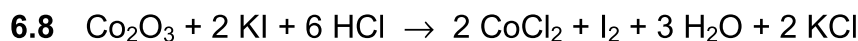
$$\% \text{ Cl} = \frac{8.083 \cdot 10^{-2} \text{ g}}{0.2872 \text{ g}} \times 100 = 28.1$$

$$6.7 \quad n(\text{KOH}) = 0.0124 \text{ mol}$$

$$n(\text{HCl}) \text{ neutralised by ammonia} = 0.025 \text{ mol} - 0.0124 \text{ mol} = 0.0126 \text{ mol}$$

$$m(\text{NH}_3) = 17.034 \text{ g mol}^{-1} \times 0.0126 \text{ mol} = 0.2146 \text{ g}$$

$$\% \text{NH}_3 = \frac{0.2146 \text{ g}}{0.7934 \text{ g}} \times 100 = 27.1 \%$$



$$n(\text{Na}_2\text{S}_2\text{O}_3) = 0.200 \text{ mol dm}^{-3} \times 0.021 \text{ dm}^3 = 4.20 \cdot 10^{-3} \text{ mol}$$

$$n(\text{I}_2) = 2.10 \cdot 10^{-3} \text{ mol}$$

$$n(\text{Co}^{2+}) = 4.20 \cdot 10^{-3} \text{ mol}$$

$$m(\text{Co}) = 4.20 \cdot 10^{-3} \text{ mol} \times 58.93 \text{ g mol}^{-1} = 0.2475 \text{ g}$$

$$\% \text{Co by mass} = \frac{0.2475 \text{ g}}{0.7934 \text{ g}} \times 100 = 31.2$$

6.10 Assuming 100 g of complex, there is 13.6 g unaccounted. for molar ratio of

$$n(\text{Co}) : n(\text{NH}_3) : n(\text{Cl}) = \frac{31.2}{58.93} : \frac{27.1}{17.034} : \frac{28.1}{35.453} = 0.529 : 1.591 : 0.7926 = 2 : 6 : 3.$$

Missing species is either O^{2-} , OH^- or H_2O with similar molar mass $\approx 17 \text{ g mol}^{-1}$.

Molar fraction of missing oxygen species $\approx 13.6 / 17 = 0.8$ i.e. the same as the Cl.

Considering charge balance, $2(+3) + 6(0) + 3(-1) = +3$, it is needed -3 to balance i.e. the missing species must be OH^- .

6.11 Empirical formula of H: $\text{Co}_2 \text{N}_6 \text{H}_{21} \text{O}_3 \text{Cl}_3$

6.12 Structure must fit the empirical formula worked out above, contain only octahedral cobalt, and be chiral. Some marks deducted if chloride is directly coordinated to cobalt, or if any single ammonia molecule is coordinated to more than one cobalt atom.

