Instructions

- Ensure that your name and student code are written in the spaces provided at the top of each page.
- You have 5 hours to work on the problems. Begin only when the START command is given.
- Use only the calculator provided.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be marked. Use the reverse of the sheets if you need scrap paper.
- Write any relevant calculations in the appropriate boxes when necessary. If you provide no working and only the correct result for a complicated calculation, you will receive no marks.
- **Numerical answers are meaningless without the appropriate units. You will be heavily penalised if units are not given where required. You should also take care to report answers to an appropriate number of significant figures.**
- Treat all gases as ideal.
- You must stop work immediately when the STOP command is given. A delay in doing this may lead to your disqualification from the exam.
- When you have finished the examination, you must put your papers into the envelope provided. Do not seal the envelope.
- Do not leave the examination hall until instructed by the supervisors.
- This examination has **42** pages.
- The official English version of this examination is available on request only for clarification.

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Physical constants

Name	**Symbol**	**Value**
Avogadro constant	N_A	6.0221×10^{23} mol^{-1}
Boltzmann constant	k_B	1.3807×10^{-23} J K^{-1}
Gas constant	R	8.3145 J K^{-1} mol^{-1}
Faraday constant	F	96485 C mol^{-1}
Speed of light	c	2.9979×10^{8} m s^{-1}
Planck constant	h	6.6261×10^{-34} J s
Standard pressure	$p°$	10^{5} Pa
Atmospheric pressure	p_{atm}	1.01325×10^{5} Pa
Zero of the Celsius scale		273.15 K
Standard acceleration of free fall	g	9.807 m s^{-2}
Bohr magneton	m_B	9.274015×10^{-24} J T^{-1}

Provide standard sheet of equations

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.102	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac$^+$															

*Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
$^+$Actinides	90 Th 232.01	91 Pa	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Problem 1 9% of the total

Estimating the Avogadro constant

1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**	**Total**
4	4	4	2	1	2	3	6	4	3	3	36

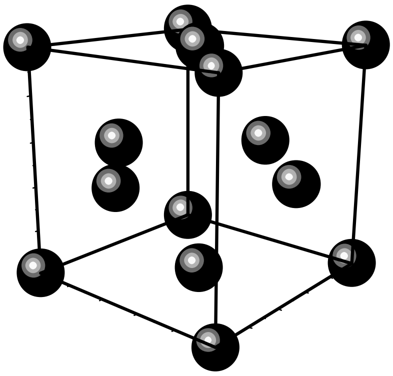
Many different methods have been used to determine the Avogadro constant. Three different methods are given below.

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.

a) Sketch the unit cell and calculate how many Au atoms the cell contains.

Unit cell:



2 points

Number of Au atoms in the unit cell:

8 × 1/8 from each corner = 1

6 × ½ from each face = 3

Total = 4 atoms

2 points

b) The density of Au is 1.93×10^{4} kg m^{-3}. Calculate the volume and mass of the cubic unit cell.

Volume:

volume = $(0.408 \text{ nm})^3 = 6.79 \times 10^{-29}$ m^3 (will accept 3 or 2 Sig Fig as long as accurate value is carried forward)

2 points, half a point off for wrong SFs, 1 point off for incorrect or missing units

Mass:

mass = density × volume = 1.31×10^{-24} kg (will accept 3 or 2 Sig Fig as long as accurate value is carried forward)

2 points, half a point off for wrong SFs, 1 point off for incorrect or missing units

c) Hence calculate the mass of a gold atom and the Avogadro constant, given that the relative atomic mass of Au is 196.97.

Mass of Au atom:

$m = 1.31\times10^{-24}$ kg / 4 = 3.28×10^{-25} kg

2 points, half a point off for wrong SFs, 1 point off for incorrect or missing units

Avogadro constant:

$N_A = 196.97\ \text{g mol}^{-1} / 3.28\times10^{-22}\ \text{g} = 6.01\times10^{23}\ \text{mol}^{-1}$

2 points, half a point off for wrong SFs, accepted with or without mol^{-1} units

Method B – from radioactive decay (Rutherford, 1911)

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

$$^{226}\text{Ra} \xrightarrow{t} {}^{222}\text{Rn} \xrightarrow{3.825\ \text{d}} {}^{218}\text{Po} \xrightarrow{3.10\ \text{m}} {}^{214}\text{Pb} \xrightarrow{26.8\ \text{m}} {}^{214}\text{Bi} \xrightarrow{19.9\ \text{m}}$$

$$^{214}\text{Po} \xrightarrow{164.3\ \mu\text{s}} {}^{210}\text{Pb} \xrightarrow{22.3\ \text{y}} {}^{210}\text{Bi} \xrightarrow{5.013\ \text{d}} {}^{210}\text{Po} \xrightarrow{138.4\ \text{d}} {}^{206}\text{Pb}$$

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.

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

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

2 points, half a point off for each error or omission

e) 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.

Answer:

^{210}Pb *1 point, 0 points for wrong or missing mass number*

f) 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.

$2.77\times10^{10}\ s^{-1} \times 163\times24\times60\times60\ s = 3.90\times10^{17}$

2 points

g) At the end of the 163 days the sample was found to contain 10.4 mm^3 of He, measured at 101325 Pa and 273 K. Calculate the Avogadro constant from these data.

Answer:

$n = pV / RT = 4.64 \times 10^{-7}$ mol

$N_A = 3.90\times10^{17} / 4.64\times10^{-7}$ mol $= 8.4\times10^{23}$ mol^{-1}

3 points

h) Given that the relative isotopic mass of ^{226}Ra measured by mass spectrometry is 226.25, use the textbook value of the Avogadro constant (6.022×10^{23} 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 (**e**).

$n_{\mathrm{Ra}} = 0.192$ g $\times 6.022\times10^{23}$ mol^{-1} / 226.25 g mol^{-1} $= 5.11\times10^{20}$ atoms

1 point

$\lambda = 2.77\times10^{10}$ s^{-1} / 4 / $5.11\times10^{20} = 1.36\times10^{-11}$ s^{-1} (only ¼ of the decays are from ^{226}Ra)

3 points, 1 off for wrong or missing units, 1 off for missing factor of 4

$t = \ln 2 / \lambda = 5.12\times10^{10}$ s = 1620 years

2 points

$n_{\mathrm{Ra}} =$

$\lambda =$

$t =$

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 2.12×10^{-7} m and density 1.206×10^{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

i) Assuming the particles to be spherical, calculate: the mass, *m*, of a particle; the mass of the water it displaces, m_{H2O}; and 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}.

$V = 3.99\times10^{-20}$ m^3

$m = 4.81\times10^{-17}$ kg *2 points, 1 off for missing units*

$m_{H2O} = 3.99\times10^{-17}$ kg *1 point, ½ off for missing units*

$m^* = 8.3\times10^{-18}$ kg (accept 1 or 2 sig fig) *1 point, ½ off for missing units*

$m =$ $m_{H2O} =$

$m^* =$

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

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

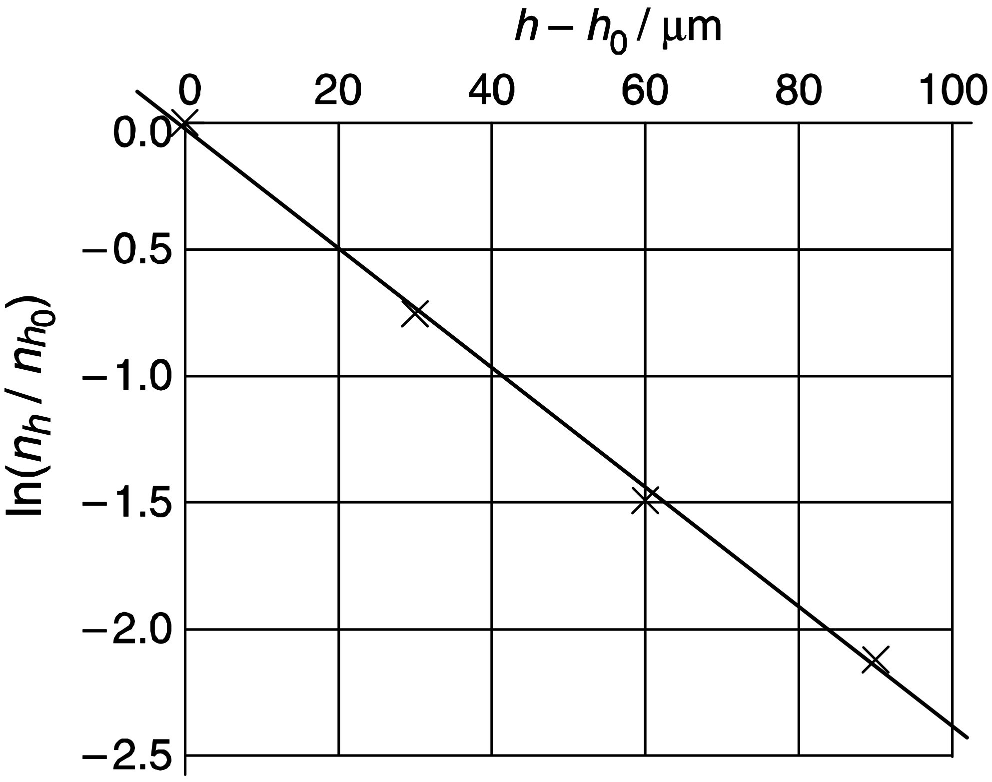
where n_h is the number of particles per unit volume at height h,

n_{h0} 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 $\ln(n_h / n_{h0})$ 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.



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

gradient = $-m^*N_Ag/(RT)$

3 points (1 point for basic equation, 1 point for using m, 1 point for N_A/R)*

k) Determine the Avogadro constant from these data.

Acceptable range of slopes is 0.0235 ± 0.002 μm

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

3 points (-1 point if slope is outside acceptable range)

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Problem 2 9% of the total

Interstellar production of H_2

2a	2b	2c	2d	2e	2f	2g	2h	2i	Total
2	2	4	2	6	6	3	2	6	33

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 H_2 molecules on the surface of dust particles. The dust particles absorb most of the excess energy and the newly formed H_2 rapidly desorbs. This question examines two kinetic models for H_2 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 $k_a = 1.4\times10^{-5}$ cm^3 s^{-1}. The typical number density of H atoms (number of H atoms per unit volume) in interstellar space is [H] = 10 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.]

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

Ans: 1.4×10^{-4} s^{-1}

2 points

Desorption of H atoms is first order with respect to the number of adsorbed atoms. The rate constant for the desorption step is $k_d = 1.9\times10^{-3}\ \mathrm{s}^{-1}$.

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

Ans: $1.4\times10^{-4}\ \mathrm{s}^{-1} = 1.9\times10^{-3}\ \mathrm{s}^{-1}\ N \Rightarrow N = 7.4\times10^{-2}$

2 points

The H atoms are mobile on the surface. When they meet they react to form H_2, 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.

$k_a = 1.4\times10^{-5}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$

$k_d = 1.9\times10^{-3}\ \mathrm{s}^{-1}$

$k_r = 5.1\times10^{4}\ \mathrm{s}^{-1}$

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 $k_r N^2$.

c) <u>Write down an equation</u> for the rate of change of N, including adsorption, desorption and reaction. Assuming steady state conditions, <u>determine</u> the value of N.

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

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

$N = 5.2\times10^{-5}$

4 points (2 for equation, 2 for solution)

$N =$

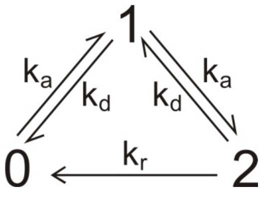
d) <u>Calculate</u> the rate of production of H_2 per dust particle in this model

Ans: $\frac{1}{2}k_r N^2 = 7.0\times10^{-5}\ \mathrm{s}^{-1}$

2 points (1 point if missing factor of ½)

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 = $k_a[H]x_m$

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

Reaction ($m \rightarrow m - 2$): rate = ½ $k_r m(m-1)x_m$

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

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

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

$$\frac{dP_2}{dt} = k_a[\mathrm{H}]P_1 - (2k_d + k_r)P_2$$

(remember P is changed to x)

2 points for each equation

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f) 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.

$$\frac{P_2}{P_1} = \frac{k_a[\mathrm{H}]}{(2k_d + k_r)} \approx \frac{k_a[\mathrm{H}]}{k_r} = 2.7\times10^{-9}$$

$$\frac{P_1}{P_0} = \frac{k_a[\mathrm{H}](2k_d + k_r)}{k_d(2k_d + k_r) + k_r k_a[\mathrm{H}]} \approx \frac{k_a[\mathrm{H}]}{k_d + k_a[\mathrm{H}]} = 6.9\times10^{-2}$$

2 points for each equation (either exact or approximate forms) and 1 point for each numerical value

g) Evaluate the steady state fractions x_0, x_1 and x_2

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

$P_0 = 0.94,$

$P_1 = 0.064,$

$P_2 = 1.8\times10^{-10}$

1 point for each value

h) Evaluate the rate of production of H_2 per dust particle in this model

$k_r x_2 = 9.0\times10^{-6}\ \mathrm{s}^{-1}$.

2 points

i) 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 $9.4 \times 10^{-6}\ \mathrm{s}^{-1}$. 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.	ü	(ü)	
The rate-determining step is desorption of H_2 molecules.			ü
The rate determining step is the bimolecular reaction of H atoms on the surface.			ü
The rate determining step is adsorption of the second H atom.		ü	
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).	ü		
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at			ü

least a factor of two).			

1 point for each row

Problem 3 11% of the total

Protein Folding

3a	3b	3c	3d	3e	3f	3g	3h	Total
2.5	3.5	1	6	2	4	2	2	23

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

$$\text{Folded} \rightleftharpoons \text{Unfolded}$$

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 sample of the protein Chymotrypsin Inhibitor 2 (CI2) was measured as a function of temperature over the range 58 to 66 °C:

Temp /°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.

a) 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.

2.5 points (1 point for equation; 1/2 point removed for each incorrect value)

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

b) Give an expression for the equilibrium constant, *K*, in terms of *x*, and hence calculate the value of *K* at each temperature.

3.5 points (1 for equation, ½ point off for each incorrect value)

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

c) Estimate the value of T_m for this protein (to the nearest 1°C).

Ans: 61 °C

1 point

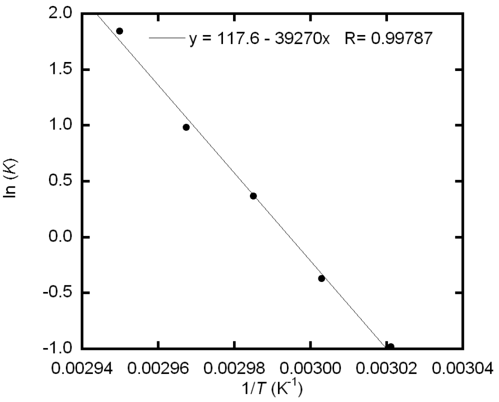
T_m =

Assuming that the values of $\Delta H°$ and $\Delta S°$ for the protein unfolding reaction are constant with temperature then:

$$\ln K = -\frac{\Delta H°}{RT} + C$$

where C is a constant.

d) Plot a suitable graph and hence determine the values of $\Delta H°$ and $\Delta S°$ for the protein unfolding reaction.



ΔH^o = 330 kJ mol^{-1}

ΔS^o = 980 J mol^{-1} K $^{-1}$

6 points (full marks if gradient in range -37000 to -41000; 1 mark for gradient in range -35000 to -37000 or -41000 to -43000; zero marks for gradient if temp is in ^{o}C) 2 for graph, 2 each for DH^o and DS^o, 1 point off each value for incorrect or missing units).

ΔH° =

ΔS° =

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 question:

ΔH° = 130 kJ mol^{-1}

ΔS° = 250 J K^{-1} mol^{-1}

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

ΔH^o = 330000 J mol^{-1} and ΔS^o= 980 J mol^{-1} K^{-1} then ΔG^o = 35000 J mol^{-1} at 25 ^{o}C

hence $K = 6.9 \times 10^{-7}$

2 points

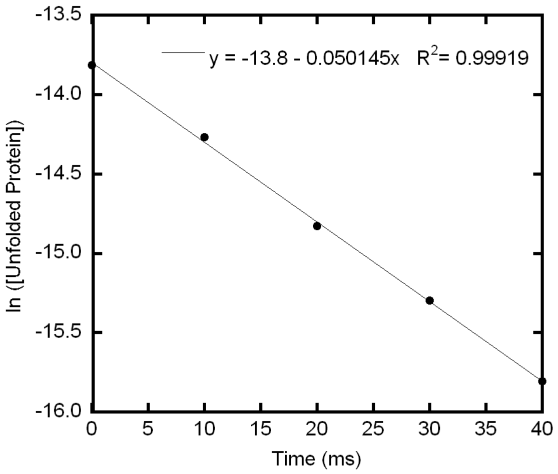
K =

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

The first order rate constant for the CI2 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 CI2 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

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



k_f = 50 s^{-1}

4 points (2 points for plotting graph of ln(concn of unfolded protein) vs time, 2 for calculation of rate constant within the range 48 to 53 s^{-1} , 1 mark off for incorrect or missing units)

k_f =

If you have been unable to calculate the values for k_f, you should use the following incorrect value for the subsequent parts of the question:

k_f = 60 s^{-1}.

---

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

$k_u = 3.5 \times 10^{-5}$ s^{-1}

2 points (1 point off for incorrect or missing units)

k_u =

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

Ans: 61 kJ mol^{-1}.

2 points (1 point off for incorrect or missing units)

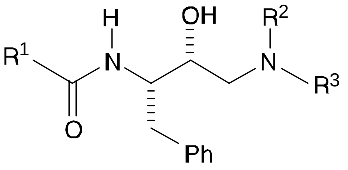
Activation energy =

Problem 4 9% of the total

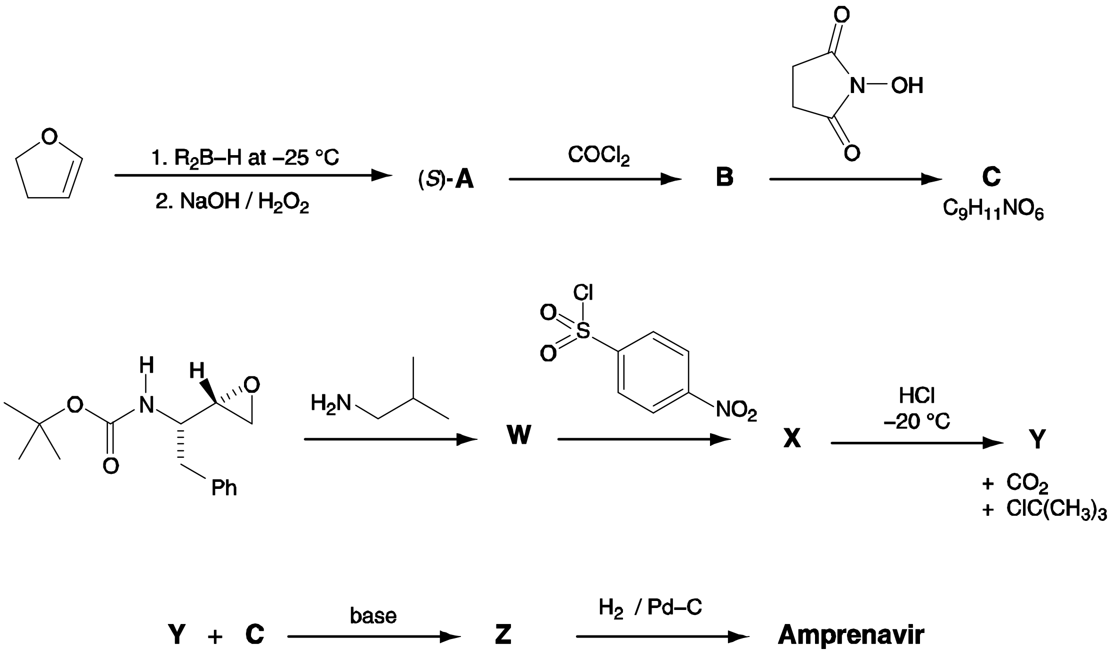
Synthesis of Amprenavir

4a A	4a B	4a C	4a W	4a X	4a Y	4a Z	4b	Total
4	3	2	3	3	2	3	3	23

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.

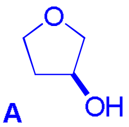


The reagent $R_2B\text{–}H$ used in the first step is chiral. Product **A** is formed as the (*S*)-enantiomer.

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

Suggest structures for **a)** the intermediates **A**, **B**, **C**, **W**, **X**, **Y** and **Z**, and **b)** for *Amprenavir*. Your answers should clearly show the stereochemistry at each centre.

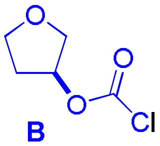
A



A

4 points .1 off for wrong regiochem, 1 off for stereochemical errors. No marks for boron-containing species. 2 off for peroxides

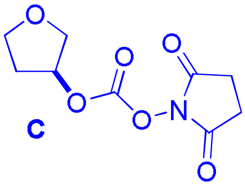
B



B

3 points (2 points for carbonate, reasonable answer but this won't react in the next step, 1 point off if stereochemistry changed from A)

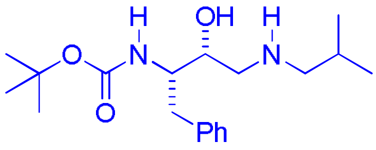
C



C

2 points (no marks for reaction via nitrogen or carbonyl oxygen, 1 point off for new errors in stereochemistry)

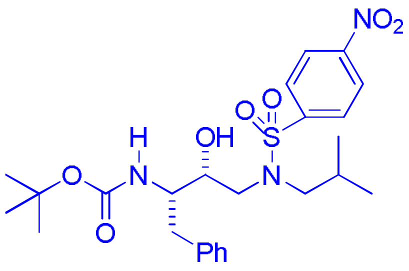
W



W

3 points (1 off for wrong regiochemistry, 1 off for stereochemical errors, 0 marks for attack on the carbonyl, 0 marks for deprotonation)

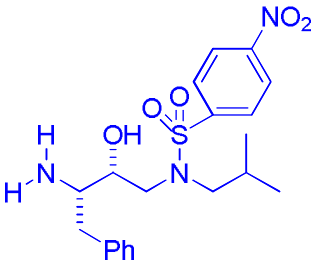
X



X

3 points (2 points if attack by OH, 1 off for new stereochemical errors)

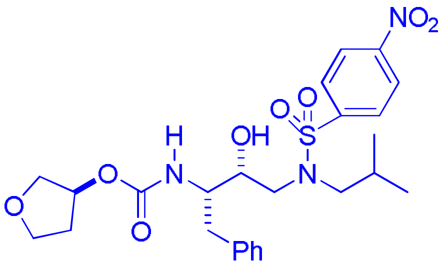
Y



Y

2 points (full credit for either amine or corresponding ammonium salt, 1 off for new stereochemical errors)

Z



Z

3 points (1 off for ring opening at succinamide, 1 off for new stereochemical errors)

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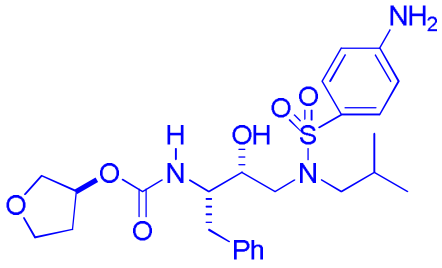
Amprenavir



Amprenavir

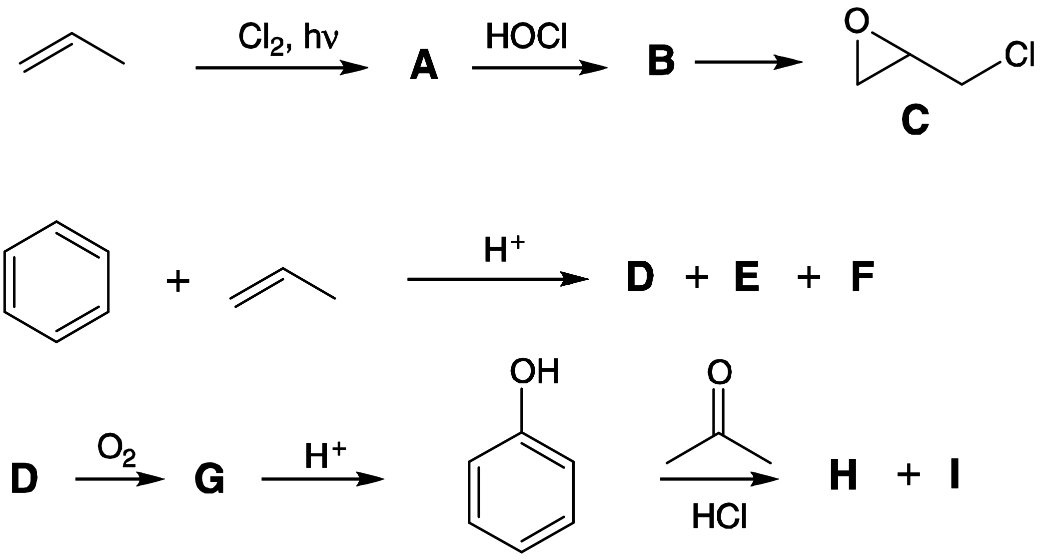
3 points (2 mark for reducing NO_2 and the aromatic ring attached to it, 1 mark for reducing sulphonamide, no marks for reducing the phenyl group or any other functional groups, 1 point off for new stereochemical errors)

Problem 5 10% of the total

Epoxy resins

5a A	5a B	5b	5c D	5c E	5c F	5d G	5e H	5f	5g I	5h J	5h K	5h L	5i M	5j N	5k O	Total
2	2	1	2	2	2	3	3	1	2	2	2	2	2	4	3	35

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**. **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.

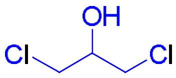
a) Draw the structures of **A** and **B**:

A

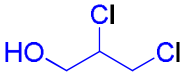
A

2 points (1 point for 1,2-dichloropropane)

B



and / or **B**



2 points (no marks for diol)

b) Give the formula of a suitable reagent for the conversion of **B** into epichlorohydrin **C**:

NaOH, or the formula of another suitable base

1 point

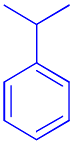
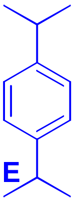
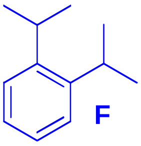
The synthesis of **H** commences with the reaction of benzene with propene in the presence of an acid catalyst which gives **D** as the major product and **E** and **F** as minor products.

c) 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 ^{13}C NMR spectrum

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

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

D	**E**	**F**
 D *2 points (no marks just for molecular formula, no marks for non-aromatic product)*	 E *2 points (no marks for incorrect isomer, no marks for non-aromatic product)*	 F *2 points (no marks for incorrect isomer, no marks for non-aromatic product)*

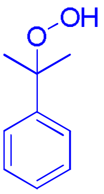
Bubbling oxygen through a hot solution of **D** gives **G** which on exposure to acid gives phenol (hydroxybenzene) and acetone (propanone).

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 ^{1}H 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 δ = 7.78.

d) Draw the structure of **G**.

G

G



3 points (1 point for a sensible oxidant, 1 point for an exchangeable OH on sensible structure, 1 point if structure fits the NMR data.)

Exposure of phenol and acetone to hydrochloric acid gives compound **H**. The ^{13}C NMR spectrum for **H** is shown in Fig. 1. The ^{1}H NMR spectrum is shown in Fig. 2 together with a four-fold expansion of the region 6.5 – 7.1 ppm. The ^{1}H 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 (*).

Fig. 1

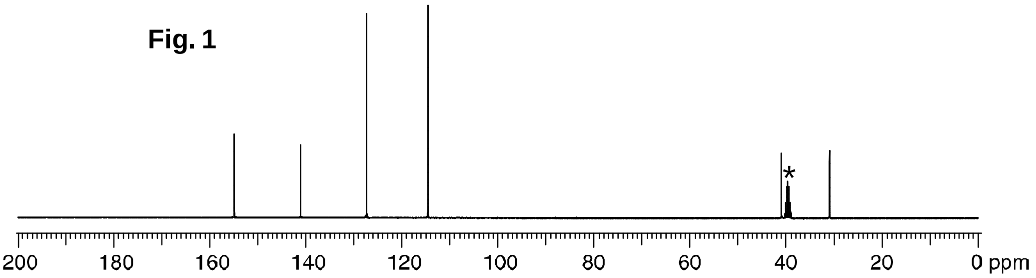


Fig. 2

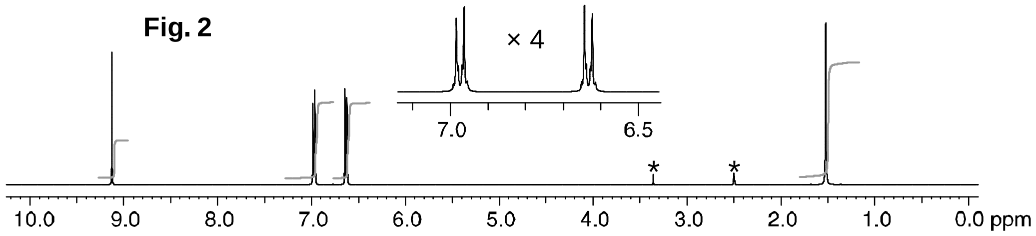
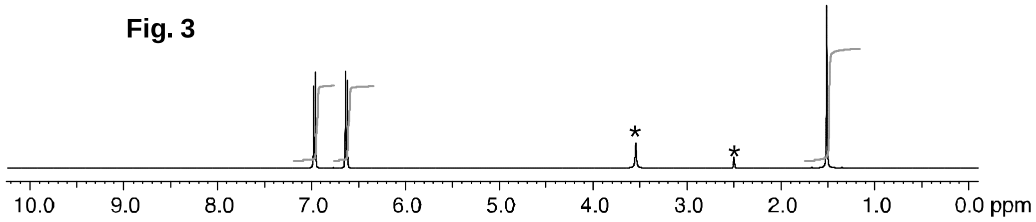
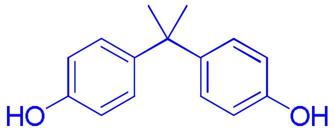


Fig. 3



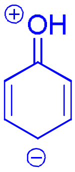
e) Draw the structure of **H**.

H



3 points

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

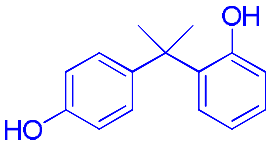


1 point

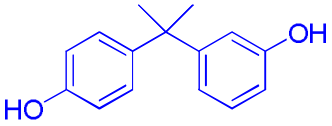
A second compound, **I**, is also formed in the reaction of phenol with acetone. The ^{13}C NMR spectrum of **I** has 12 signals. The ^{1}H NMR spectrum has the following signals: δ 7.50-6.51 (8H, m), 5.19 (1H, s), 4.45 (1H, s), 1.67 (6H, s); addition of D_2O results in the disappearance of the signals at δ = 5.19 and 4.45

g) Draw a structure for **I**.

I



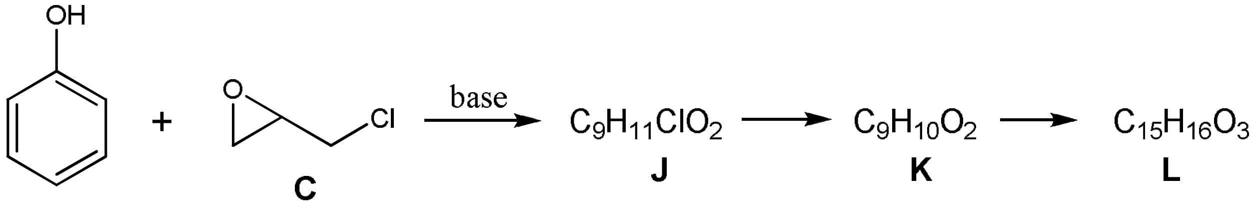
I



also fits the data

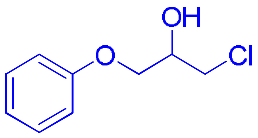
2 points (1 point for meta-para product)

Excess phenol reacts with epichlorohydrin **C** in the presence of base to give compound **L** which has 6 signals in its ^{13}C 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**.



h) Draw the structures of **J**, **K** and **L**.

J

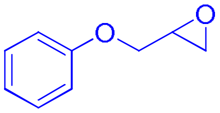


J

2 points

-1 point for regiochemical errors

K

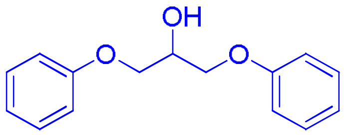


K

2 points

-1 point for regiochemical errors

L



L

2 points

no marks for 1,2-bisphenoxy product

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.

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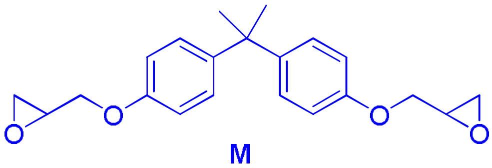
i) Draw the structure of **M**.

M



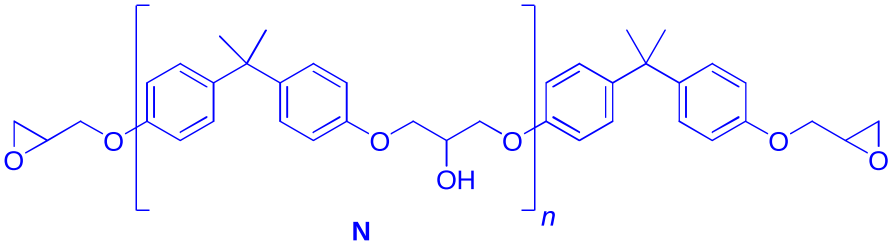
M

2 points

Treatment of **H** with a small excess of epichlorohydrin and base gives **N**. **N** has the form: **endgroup1-[repeat unit]$_n$-endgroup2** where *n* is approximately 10 – 15. **N** does not contain chlorine atoms and contains one OH group per repeat unit.

j) Draw the structure of **N** in the form indicated above (**endgroup1-[repeat unit]$_n$-endgroup2**).

N



N

4 points (2 for correct repeat unit, 1 for each correct end group).

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

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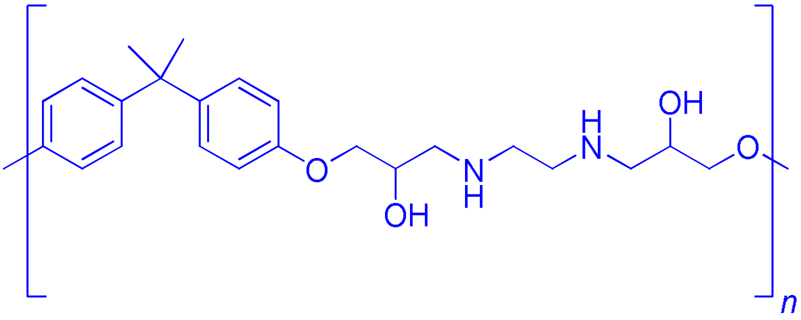


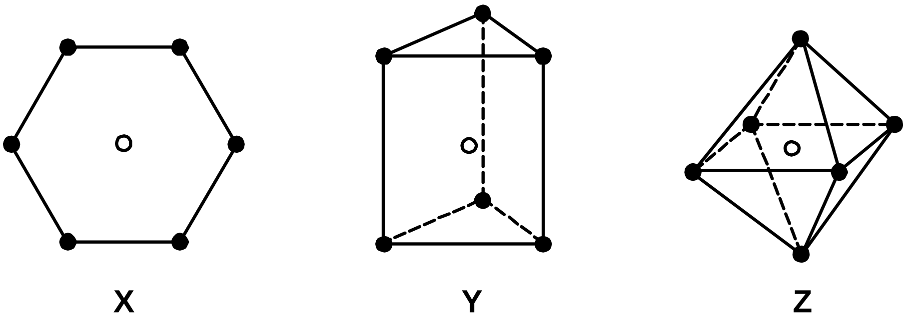
3 points

Problem 6 12% of the total

Transition metal complexes

6a	6b	6c	6d	6e	6f	6g	6h	6i	6j	6k	6l	Total
18	5	4	6	5	2	3	2	4	4	2	6	61

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.

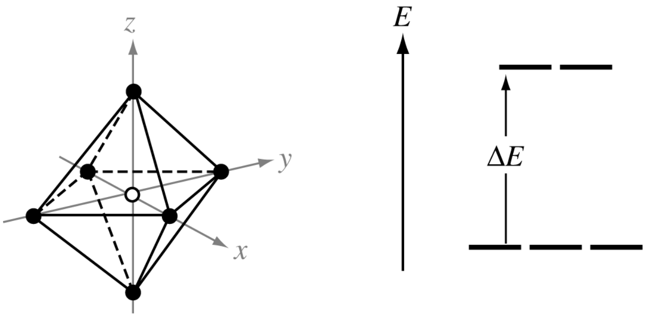
a) Fill in the table below to indicate how many geometrical isomers may be formed for each structure **X**, **Y**, and **Z** as the monodentate ligands A are substituted by monodentate ligands B or by symmetrical bidentate ligands, denoted C—C. Bidentate ligand C—C can only link between two atoms on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

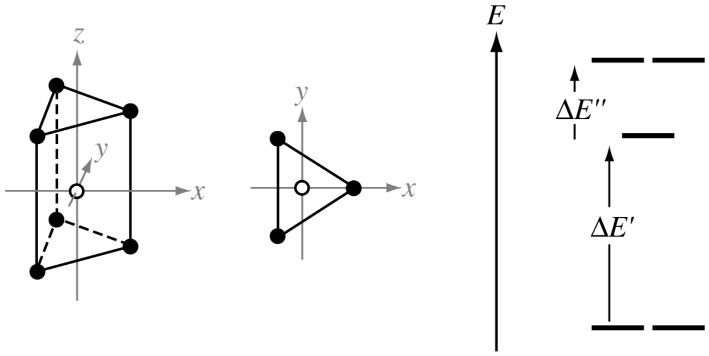
In each case write the number of geometrical isomers in the space provided. If one of the isomers exists as a pair of enantiomers, include an asterisk, *, in the box. If two exist as two pairs of enantiomers, include two asterisks and so on. For example, if you think there are five geometrical isomers 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_5B	1	1	1
MA_4B_2	3	3*	2
MA_3B_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*

18 points (1 mark off for each box containing any error)

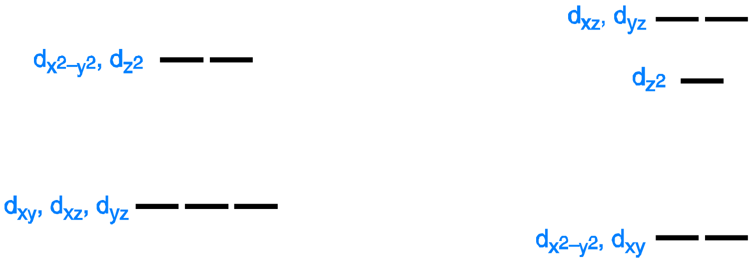
There are no known complexes that adopt the hexagonal planar geometry **X**, but structures are known for both the trigonal prismatic geometry **Y** and the octahedral geometry **Z**. In these complexes, the orbitals derived from the metal d orbitals have different energies depending on the geometry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





The separations in energy, Δ*E*, Δ*E’* and Δ*E”* depend on the particular complex.

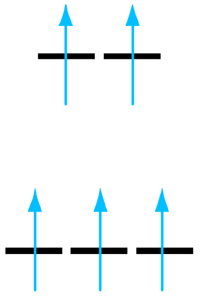
b) For each of the splitting patterns shown below label which d orbitals are which.



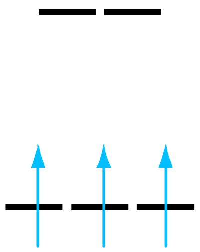
5 points in total. Half a mark off for each error

The two complexes $[Mn(H_2O)_6]^{2+}$ and $[Mn(CN)_6]^{2-}$ 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.

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



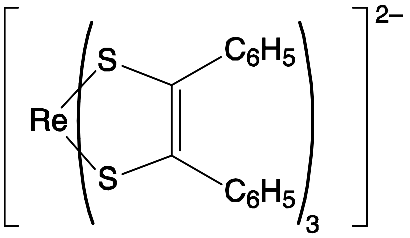
$[Mn(H_2O)_6]^{2+}$



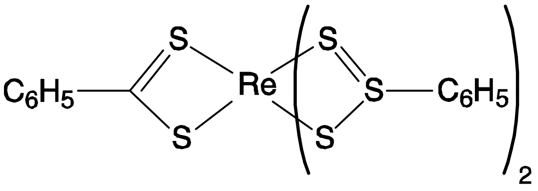
$[Mn(CN)_6]^{2-}$

4 points in total. 1 point for the correct number of electrons in each diagram.
1 point for correct arrangement for each.

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.

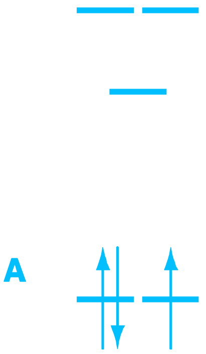


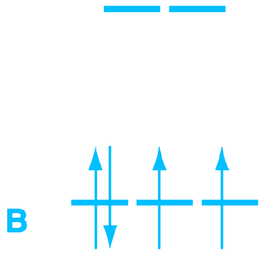
A



B

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





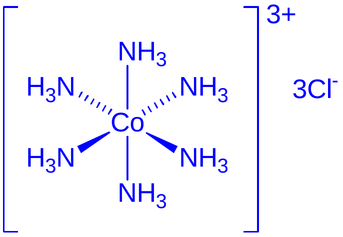
6 points in total: 1 for correct total number of electrons in each complex, 1 for correct number of unpaired electrons in each complex, 1 for correct splitting diagrams (i.e. trigonal prismatic for A and octahedral for B).

Octahedral complexes are far more common than trigonal prismatic. Werner isolated five compounds **C** – **G** containing Co(III), Cl, and NH_3 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 $AgNO_3$; compounds **C**, **D**, and **E** react with different stoichiometric ratios of aqueous $AgNO_3$; **E** and **F** react with the same stoichiometric ratio of aqueous $AgNO_3$.

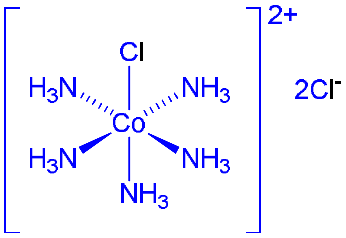
	C	**D**	**E**	**F**	**G**
molar conductivity	510	372	249	249	~0

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

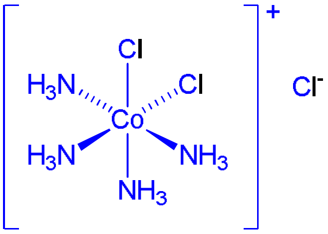
C *1 point*



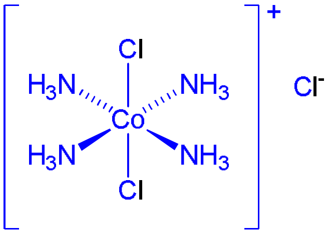
D 1 point



E *1 point*

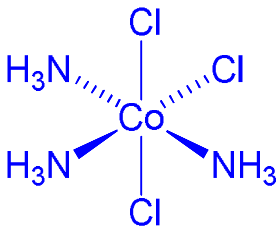


F *1 point*

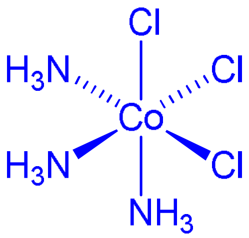


E and F could be either way round

G *1 point*



or



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 H_2O, or HO^- or O^{2-}. 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 cm^3 of 0.100 M silver nitrate to exchange all of the chloride.

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

mol of Ag^+ = mol of Cl^- = 2.28×10^{-3}

mass of Cl = 8.0826×10^{-2} g

% Cl = 28.1 by mass

2 points

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 cm^3 of 0.500 M aqueous HCl. The residual HCl required 24.8 cm^3 of 0.500 M aqueous KOH to be neutralized.

The remaining suspension of cobalt(III) oxide was allowed to cool, approximately 1g of potassium iodide was added, and then the mixture was acidified with aqueous HCl. The liberated iodine was then titrated with 0.200 M aqueous sodium thiosulfate and required 21.0 cm^3 for complete reaction.

g) Calculate the percentage, by mass, of ammonia in **H**.

mol of KOH = 0.0124

mol of HCl neutralised by ammonia = 0.025 – 0.0124 = 0.0126 mol

mass of ammonia = 17.034 × 0.0126 g = 0.2146 g

% ammonia = 100 × 0.2146 / 0.7934 = 27.1%

3 point

h) Give the equation for the reaction of cobalt(III) oxide with potassium iodide in aqueous acid.

$Co_2O_3 + 2KI + 6HCl \longrightarrow 2Co^{2+} + I_2 + 3H_2O + 6Cl^{-} + 2K^{+}$

2 point

i) Calculate the percentage, by mass, of cobalt in **H**.

mol of thiosulfate used = 0.200 × 21/1000 = 4.20×10^{-3} mol

mol of I_2 2.10 mmol 1 mol of I_2 from 2 mol Co atoms

mass of Co = 4.20×10^{-3} 58.93 = 0.2475 g

% Co by mass = 0.2475 / 0.7934 = 31.2 %

4 point

j) Calculate the identity of the oxygen species contained in **H**. Show your working.

assuming 100 g of complex, there is 13.6 g unaccounted for

molar ratio of Co : NH3 : Cl = 0.529 : 1.591 : 0.7927 = 2 : 6 : 3

missing species is either O^{2-}, OH^{-} or H2O with similar molar mass ≈ 17 g mol^{-1}

molar fraction of missing oxygen species ≈ 13.6 / 17 = 0.8 i.e. the same as the Cl

considering charge balance, 2(+3) + 6(0) + 3(-1) = +3 so need -3 to balance

i.e. must be OH^{-}.   4 points.

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k) Give the empirical formula of **H**.

$Co_2 N_6 H_{21} O_3 Cl_3$

2point

l) Suggest a structure for the chiral compound **H**.

6 points Structure must fit the empirical formula worked out above, contain only octahedral cobalt, and be chiral otherwise zero marks. 4 marks deducted if chloride is directly coordinated to cobalt, or if any single ammonia molecule is coordinated to more than one cobalt atom.