AUSTRALIAN
SCIENCE
OLYMPIADS

2007 National Qualifying Exam – Chemistry

Solutions

Section A (Multiple Choice)

Question #	Answer	Question #	Answer	Question #	Answer
Q1	B	Q6	B	Q11	C
Q2	B	Q7	D	Q12	B
Q3	C	Q8	D	Q13	B
Q4	D	Q9	C	Q14	E
Q5	E	Q10	A	Q15	E

Question 16

Transition metal ions are often brightly coloured and can exist in a wide range of oxidation states. Vanadium is particularly diverse: an oft-used chemistry demonstration involves swirling a vanadium(V) solution with zinc in a flask, which causes the solution to change colour from yellow to blue to green and finally, pale violet.

(a) Complete the following table.

Species	**Colour**	**Oxidation State**
V *(s)*	*Silver / metallic / grey*	0
V^{2+} *(aq)*	pale violet	+2
V^{3+} *(aq)*	green	*+3*
VO^{2+} *(aq)*	deep blue	*+4*
VO_3^- *(aq)*	yellow	*+5*

The vanadous ion (V^{2+}) is used in a redox titration to determine the concentration of an unknown solution containing the Fe^{3+} ion. Iron(III) is reduced to iron(II), and the solution is acidic throughout the determination.

(b) What are the two half equations and the balanced full equation for this reaction? The first one has been done for you.

$$V^{2+} \longrightarrow V^{3+} + e^{-}$$

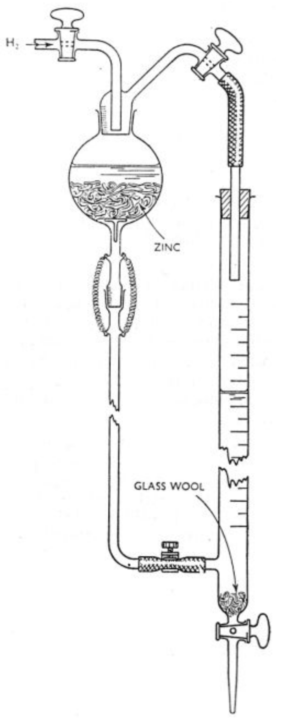
$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

$$V^{2+} + Fe^{3+} \rightarrow V^{3+} + Fe^{2+}$$

Fiona, an earnest young analytical chemist, decided to make some 0.500 mol L^{-1} vanadous sulfate (VSO_4) solution. She had a bottle of vanadyl sulfate ($VOSO_4.2H_2O$), which she stirred with an excess of zinc metal (amalgamated with a small amount of mercury(II) catalyst). Since it was getting late, Fiona decided to filter the solution and leave it out on the bench, with the intention to perform the titration the next day. Disaster struck! Fiona returned to find her perfectly prepared pale violet solution had a slight green tinge.

(c) Write a possible equation for the reaction of the V^{2+} ion with air.

$$V^{2+} \rightarrow V^{3+} + e^{-} \quad \text{(responsible for green)}$$
$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \quad \text{(oxygen from air)}$$
$$4V^{2+} + O_2 + 4H^{+} \rightarrow 4V^{3+} + 2H_2O$$



Fiona did a little background reading and found the apparatus shown in the diagram at the right was used for the titration. The setup allows the V^{2+} ion to be conveniently produced and stored *in situ*. The whole apparatus is filled with hydrogen gas to prevent reaction with air.

Fiona also learnt that even a small amount of *dissolved* oxygen could affect the titration. To her unknown iron(III) solution, she added saturated sodium carbonate solution, forming a rusty yellow precipitate, followed by dilute hydrochloric acid solution, forming bubbles of colourless gas. The effervescence completely removes any dissolved oxygen in the solution.

(d) What is the chemical formula of the rusty yellow precipitate and the colourless gas?

Precipitate
$Fe(OH)_3$ (half marks for $Fe_2(CO_3)_3$)

Gas *CO_2*

25.00 mL aliquots of an iron(III) solution of unknown concentration were titrated against the standard 0.500 mol L^{-1} V^{2+} solution. The average titre, i.e. the average volume of the solution containing the V^{2+} ions needed to completely react with the solution containing the Fe^{3+} ions, was 22.14 mL.

(e) Calculate the mass of $VOSO_4.2H_2O$ required to make 250 mL of the standard solution.

$$M_w\ (VOSO_4.2H_2O) = 50.94 + 7*16.00 + 32.06 + 4*1.01 = 199.04\ g/mol$$
$$n\ (VOSO_4.2H_20) = c.V = 0.25 * 0.5 = 0.125\ mol$$
$$m\ (VOSO_4.2H_2O) = 24.9\ g$$

(f) Calculate the concentration of the iron(III) solution.

$$n\ (V^{2+}) = c.V = 0.02214*0.5 = 0.01107\ mol$$
$$n\ (Fe^{2+}) = n\ (V^{2+})$$
$$[Fe^{3+}] = n / V = 0.01107 / 0.025 = 0.443\ mol/L$$

The indicator used in the titration is potassium thiocyanate, KSCN. The thiocyanate ions, SCN^{-}, form an intense blood red complex ion with Fe^{3+} in solution.

(g) What colour change occurs at the end point of the titration?

Blood Red (due to $[FeSCN]^{2+}$) → Green (due to V^{3+})

Fiona also discovered the possibility of the following reaction between the vanadous ions and hydrogen ions in solution:

$$2V^{2+}\,(aq) + 2H^{+}\,(aq) \longrightarrow 2V^{3+}\,(aq) + H_2\,(g)$$

Fortunately this reaction is very slow under normal conditions. Fiona remembered that solution-phase reactions usually occur in two steps: the reactants first associate, or come together, and then react to form products.

$$(1) \quad A + B \rightleftharpoons A.B$$

$$(2) \quad A.B \longrightarrow C$$

(h) Explain why the reaction might be slow?

V^{2+} and H^{+} are both positively charged and repel each other.

This means that reaction (1) will be slow.

To improve the accuracy of the titration, the solution of V^{2+} ions was standardised against potassium permanganate solution ($KMnO_4$). In the reaction with permanganate ion, V^{2+} is converted into VO_3^{-}, and MnO_4^{-} is converted into Mn^{2+}.

(i) Give the equation for the reaction between V^{2+} ion and the MnO_4^{-} ion.

$$V^{2+} + 3H_2O \rightarrow VO_3^{-} + 6H^{+} + 3e^{-} \quad (x5)$$

$$MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O \quad (x3)$$

$$5V^{2+} + MnO_4^{-} + 3H_2O \rightarrow 5VO_3^{-} + 3Mn^{2+} + 6H^{+}$$

(j) 25.00 mL aliquots of the solution containing V^{2+} ions required an average of 25.34 mL of a 0.283 mol L^{-1} $KMnO_4$ solution. Calculate the true concentration of the V^{2+} ion in the solution.

$$n\,(MnO_4^{-}) = c.V = 0.02534 * 0.283 = 7.171*10^{-3}\text{ mol}$$

$$n\,(V^{2+}) = (5/3)*\,n\,(MnO_4^{-}) = 1.195*10^{-2}\text{ mol}$$

$$[V^{2+}] = n\,/\,V = 1.195*10^{-2}\,/\,0.025 = 0.478\text{ mol/L}$$

(k) Using the answer obtained in (j), what is the true concentration of the Fe^{3+} ion in the solution?

$$n\,(V^{2+}) = c.V = 0.02214*0.4781 = 0.01059\text{ mol}$$

$$n\,(Fe^{2+}) = n\,(V^{2+})$$

$$[Fe^{3+}] = n\,/\,V = 0.01059\,/\,0.025 = 0.423\text{ mol/L}$$

Q17

Mass spectrometry is an important tool in the determination of the structures of organic compounds.

The process begins with the ionisation of the sample to form a positively charged ion, the *molecular ion*. At this stage, the molecular ion commonly fragments to form additional cations. These cations are passed through a magnetic field where they are observed to follow a curved path. The radius of curvature of the path is dependent upon the mass to charge ratio (m/z) of individual ions. Measurement of the radius of curvature thus gives an accurate measure of the *m*/*z* ratio for each ion. The abundance of ions detected for each *m*/*z* is plotted as a graph of the mass spectrum.

Since ions with a multiple positive charge are much less abundant than those with a single positive charge, the detected *m/z* ratio is effectively equal to the mass of the ion, *m*.

(a) The empirical formula of a compound may be calculated from percentage composition data. An unknown compound consisting of carbon, hydrogen and oxygen only was analysed to contain 54.5% carbon and 9.15% hydrogen.

(i) Calculate the empirical formula of the unknown compound.

C: 54.5/12.01 = 4.54; H: 9.15/1.008 = 9.08; O: 36.35/16.00 = 2.27

C_2H_4O

(ii) Deduce the molecular formula of the unknown compound given it has a molecular mass of 88 g mol^{-1}.

$M(C_2H_4O) = 44$ g mol^{-1}

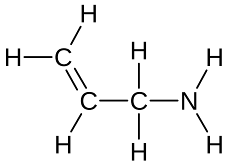
$C_4H_8O_2$

The molecular mass of a compound is readily obtained from mass spectrometry. However, compounds with different molecular formulae may have molecular masses that are identical to the nearest unit value. *High resolution mass spectrometry* overcomes this issue by providing molecular mass measurements with great precision (often to several decimal places).

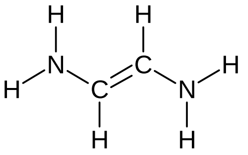
(b) The *m*/*z* of a molecular ion containing only carbon, hydrogen and oxygen was determined to be 58.0417 units by high resolution mass spectrometry.

(i) In the following structures, circle those with a molecular mass of 58 g mol^{-1}. **B, D, E**

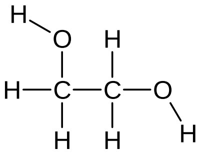
A



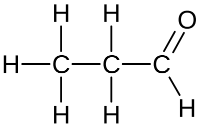
B



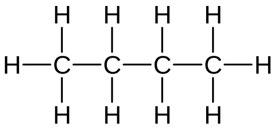
C



D



E



(ii) By considering the following table of atomic masses, identify the structure in part (i) which could give rise to a molecular ion peak of 58.0417 units.

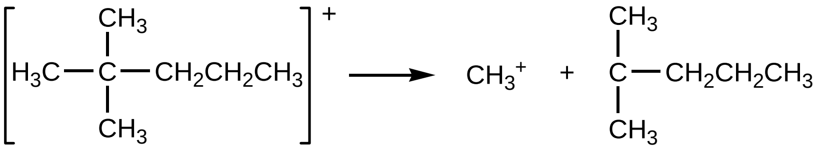
Atom	Relative atomic mass (amu)
^{12}C	12.0000
^{16}O	15.9949
^{1}H	1.0078
^{14}N	14.0031

B: 58.053 D: 58.0417 E: 58.078

D

Fragmentation of a molecular ion often occurs according to predictable patterns. In general, fragmentation involves the breaking of weak bonds and formation of stable fragment ions. The location where bonds are commonly broken include:

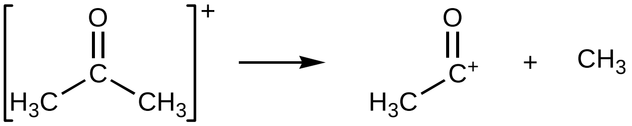
- At branch points, for example:



- Adjacent to heteroatoms (atoms other than carbon and hydrogen), for example:

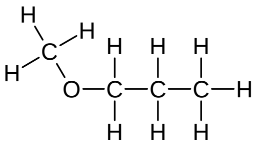
$$[H_3CCH_2-O-CH_2CH_3]^+ \longrightarrow H_3CCH_2^+ + O-CH_2CH_3$$

- Adjacent to carbonyl groups (C=O), for example:

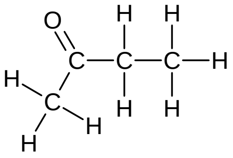


(c) Indicate on each of these molecules the two bonds most liable to break upon fragmentation of the molecular ion.

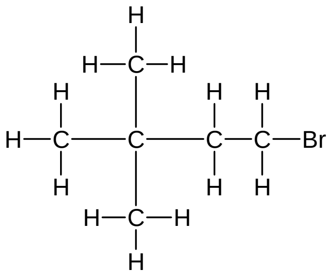
(i) **Adjacent to O**



(ii) **Adjacent to C=O**

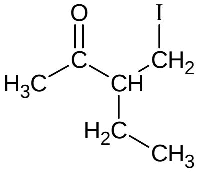


(iii) **Methyl; Br**



The fragmentation of a molecular ion into lower molecular mass fragments may result in the observation of peaks corresponding to lower *m*/*z*

(d) The following compound was analysed by mass spectrometry. Propose structures for each fragment corresponding to observed *m*/*z* peaks in the obtained spectrum.



(i) *m*/*z* = 15 **$[CH_3]^+$**	(ii) *m*/*z* = 29 **$[CH_2CH_3]^+$**	**(**iii) *m*/*z* = 43 **$[COCH_3]^+$**	(iv) *m*/*z* = 127 **$[I]^+$**

(e) A four-carbon compound containing only carbon, hydrogen and oxygen displayed a molecular ion peak at *m*/*z* 74.0729 when subjected to high resolution mass spectrometry. Significant fragment peaks were also observed at *m*/*z* 15, 17 and 57.

(i) Provide the molecular formula for this compound.

$C_4H_{10}O$

(ii) Provide a possible structure for the fragments corresponding to each of the peaks.

m/*z* = 15 $[CH_3]^+$	*m*/*z* = 17 $[OH]^+$	*m*/*z* = 57 $[C_4H_9]^+$ (any acceptable structure)

(iii) Propose a possible structure for the compound, based on your answers from (ii).

butan-1-ol, butan-2-ol, 2-methylpropan-2-ol

Some elements exist in nature as a mixture of more than one isotope of high natural abundance. Bromine appears as two abundant isotopes: ^{79}Br (49.3% abundance) and ^{81}Br (50.7% abundance). A compound containing one bromine atom will give rise to two molecular peaks depending on which isotope it contains. One peak will result from molecular ions containing ^{79}Br, and the other will result from molecular ions containing ^{81}Br. The two peaks differ by two *m*/*z* units. The relative intensities of these two peaks correspond to the natural abundance of the isotopes (49.3 : 50.7).

Chlorine and sulfur likewise exist as several isotopes. This is shown in the following table:

Isotope	Natural Abundance (%)
$^{35}C\ell$	75.8
$^{37}C\ell$	24.2
^{32}S	95.0
^{33}S	0.75
^{34}S	4.2

(f) For each of the following compounds, provide the expected *m/z* values corresponding to the peaks for the **molecular** ion, and state the relative intensity of the peaks in each case.

(i) $CH_3CH_2CH_2—SH$

m/z	**Relative Intensity**
76	95.0 %
77	0.75 %
78	4.2 %

(ii) $C\ell — CH_2CH_2\ CH_2CH_2 — C\ell$

m/z	**Relative Intensity**
126	57.5 %
128	36.7 %
130	5.86 %

(iii) $Br — CH_2CH_2 — C\ell$

m/z	**Relative Intensity**
142	37.4 %
144	50.4 %
146	12.3 %

Question 18 (NQE 2007) Answers and Marking Scheme

A

1 mark total

1 mark if:

- 1atm
- 101.3 kPa or 101300 Pa
- 760 torr or 760mmHg

½ marks if:

- “atmospheric pressure”
- 100kPa, 1 bar, 1000mbar, etc

B:

½ marks for each correctly circled answer, to a maximum of 2 marks

	Pressure	
Temperature	1 atm	2 atm
253 K	Gaseous / **Non-gaseous**	Gaseous / **Non-gaseous**
283 K	**Gaseous** / Non-gaseous	Gaseous / **Non-gaseous**

C:

I:

$$p(C_6H_6) = \chi_{C_6H_6} p^*_{C_6H_6} = \frac{0.530}{0.530 + 1.12} \times 36.6kPa = 11.8kPa$$

II:

$$p(C_7H_9) = \chi_{C_7H_9} p^*_{C_7H_9} = \frac{1.12}{0.530 + 1.12} \times 12.28kPa = 8.34kPa$$

Maximum 2 marks for each of I and II

Deduct ½ marks for each of the following (n.b. no negative marking)

- Incorrect number of sig figs and/or slight numerical error
- Calculation error (with sufficient working)
- Absent formulae and absent sufficient numerical working
- Absence of units

III:

$$p_T = 11.8 + 8.34 = 20.1kPa$$

- 1 mark maximum
- No marks deducted for wrong number of sig figs as long as value correct as per ci and cii
- Marks not deducted for omission of working

D:

$$\chi_{C6H6(g)} = \frac{11.8}{11.8+8.34} = 0.585$$

- 1 mark maximum
- No marks deducted for wrong number of sig figs as long as value correct as per ci and cii
- Marks not deducted for omission of working

E:

$$1-\frac{p_b}{p} = \frac{\Delta_{vap}H}{R(T_b)^2}(T-T_b)$$

I:

$$1-\frac{101.3}{p} = \frac{29960}{8.314(332.4)^2}(320-332.4) = -0.4044$$

$$\frac{101.3}{p} = 1.4044$$

$$p = \frac{101.3}{1.4044} = 72.1kPa \text{ or } 72.13kPa$$

II:

$$1-\frac{101.3}{p} = \frac{29960}{8.314(332.4)^2}(340-332.4) = 0.2479$$

$$\frac{101.3}{p} = 1-0.2479 = 0.7521$$

$$p = \frac{101.3}{0.7521} = 135kPa \text{ or } 134.7kPa$$

F:

$$1-\frac{1}{2} = \frac{29960}{8.314(332.4)^2}(T-332.4)$$

$$(T-332.4) = \frac{1}{2}\times\frac{8.314(332.4)^2}{29960} = 15.33$$

T = 347.7K

2 marks for each of EI, EII and F

½ marks deducted for each of the following

- Calculation error (with sufficient working)
- Absent formulae and absent sufficient numerical working
- Absence of units

G

I:

Moles of solute particles = $1\times\frac{160}{FW(glu\cos e)}=1\times\frac{160}{12.01\times 6+16.00\times 6+1.008\times 12}$

$=1\times\frac{160}{180.156}=0.8881mol$

Moles of solvent particles = $1\times\frac{500}{FW(H_2O)}=1\times\frac{500}{16.00\times 1+1.008\times 2}=1\times\frac{500}{18.016}=27.75mol$

Mole fraction is hence = $\frac{0.8881}{0.8881+27.75}=3.101\times 10^{-2}$

II:

Moles of solute particles = $2\times\frac{50}{FW(NaCl)}=2\times\frac{50}{22.99+35.45}=2\times 0.856=1.71mol$

Moles of solvent particles = $1\times\frac{500}{FW(H_2O)}=1\times\frac{500}{16.00\times 1+1.008\times 2}=1\times\frac{500}{18.016}=27.75mol$

Mole fraction is hence = $\frac{1.71}{1.71+27.75}=5.80\times 10^{-2}$

2 marks maximum for each of GI and GII
½ marks deduction for each of:

- Incorrect number of sig figs and/or slight numerical error
- Calculation error (with sufficient working)
- Absent formulae and absent sufficient numerical working
- Omission of factor of 2 for NaCl

H

i) NaCl (because lower formula weight hence more solute particles per unit mass)

ii) $CaCl_2$ (because 3 particles per empirical formula of chloride salt c.f. 2 particles for carbonate salt)

iii) 0.75mol glucose (although acetic acid is expected to ionize, less than half should ionize, hence glucose will yield more particles in this case)

1 mark maximum with explanation that yields correct meaning (0 marks if correct selection but wrong or absent reason)

J

- Mention that ‘vapour pressure’ is an equilibrium constant of an equilibrium process
- Forward rate is determined by escape of molecules from liquid to gas phase at the surface of the liquid
- This rate is proportional to the amount of molecules present at the surface, which is that of its mole fraction.

1 mark if each of these points are made to a maximum of 3 marks (or an alternate, sufficiently thorough reason is given)

K

$$1-\frac{p_b}{p}=\frac{\Delta_{vap}H}{R(T_b)^2}\left(T-T_b\right)$$

With respect to the solvent we need to make the following substitutions:

$p_b = (1-\chi_{solute})\times p_b^*$

$p = (1-\chi_{solute})\times p^*$ =101.3kPa = p_b^*

Hence $\frac{p_b}{p}=\frac{(1-\chi_{solute})\times p_b^*}{p_b^*}=(1-\chi_{solute})$, therefore $1-\frac{p_b}{p}=\chi_{solute}$

(2 marks)

We let $K=\frac{R(T_b)^2}{\Delta_{vap}H}$, hence T - T$_b$ = Kχ

(1 mark)

L:

$$K=\frac{R(T_b)^2}{\Delta_{vap}H}=\frac{8.314(373.15)^2}{40650}=28.48$$

I:

$T-T_b = 28.48\times 3.101\times 10^{-2} = 0.8831$

$T = 374.03$

II:

$T-T_b = 28.48\times 5.80\times 10^{-2} = 1.65$

$T = 374.80$

2 marks total for the whole question

- 1 mark for correct determination of K
- ½ mark each for correct boiling point elevations (yes, 5 sig figs)

30 marks total

Q19

Ionic compounds, such as $NaC\ell$, dissolve in water to give hydrated Na^+ and $C\ell^-$ ions.

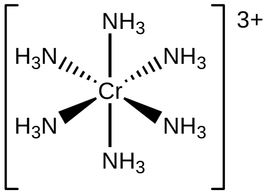
$$NaC\ell\,(s) \xrightarrow{H_2O} Na^+\,(aq) + C\ell^-\,(aq)$$

The compound $[Ag(NH_3)_2]C\ell$ similarly dissolves in water to give a cation $[Ag(NH_3)_2]^+$ (known as a **complex ion**) and the $C\ell^-$ ion.

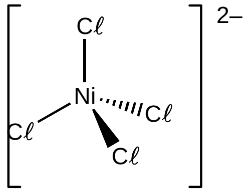
$$[Ag(NH_3)_2]C\ell\,(s) \xrightarrow{H_2O} [Ag(NH_3)_2]^+\,(aq) + C\ell^-\,(aq)$$

A complex ion is a transition metal ion surrounded by **ligands**. Ligands are neutral molecules or ions which behave as Lewis bases, donating an unshared pair of electrons to the metal ion (Lewis acid) to form a covalent metal-ligand bond. The resulting complexes are known as coordination compounds. A square bracket is placed around the formula of the complex ion.

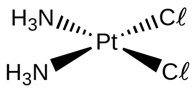
The charge of a complex ion is the sum of the charges on the central metal and on its surrounding ligands. In $[Ag(NH_3)_2]^+$ the charge on the complex ion is +1. The charge on the complex ion can now be used to determine the oxidation state of silver. Because the NH_3 ligands are neutral molecules, the oxidation state of silver must be +1.



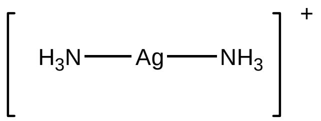
Octahedral



Tetrahedral



Square planar



Linear

The number of atoms directly bonded to the metal atom in a complex ion is called the **coordination number**. The atom of the ligand bound directly to the metal is called the **donor atom**. Nitrogen, for example is the donor atom in the $[Ag(NH_3)_2]^+$ complex ion. The silver ion in $[Ag(NH_3)_2]^+$ has a coordination number of 2. The most common coordination number is six (octahedral geometry), closely followed by 4 (tetrahedral or square planar geometry) then 2 (linear geometry).

(a) What is the oxidation state and coordination number of the central metal in each of the following compounds?

(i) $[Rh(NH_3)_5C\ell](NO_3)_2$

Oxidation state: +3 **1 mark**

Coordination number: 6 **0.5 marks**

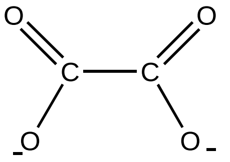
(ii) $Cs_2[NiC\ell_4]$

Oxidation state: +2 **1 mark**

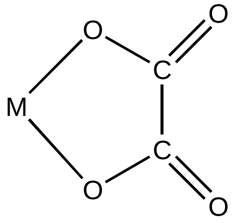
Coordination number: 4 **0.5 marks**

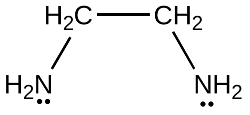
NH_3 is an example of a **unidentate** ligand and has one donor atom which donates one pair of electrons to the metal ion. Other examples of unidentate ligands are the halide ions and CN^-, NO_2^-, OH^-, CO, SCN^- and H_2O.

Bidentate ligands have two donor atoms each of which typically donates one pair of electrons to metal ions. If both donor atoms are bound to the same metal ion the complex is also known as a **chelate**. Three examples are shown on the next page:

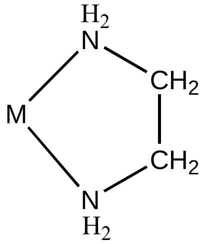


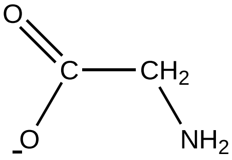
oxalate (**ox**) ion



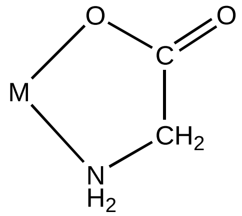


ethylenediamine (**en**)



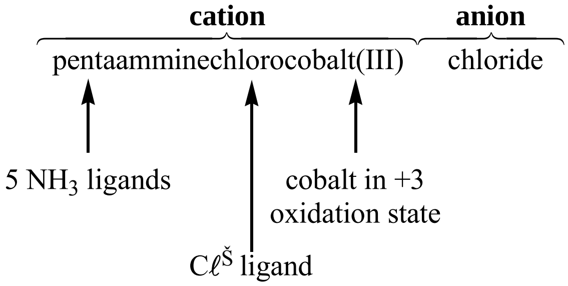


glycinate (**gly**) ion



When complexes were first discovered and few were known, they were named after the chemist who originally prepared them. A few of these names still persist; for example, the dark red substance $NH_4[Cr(NH_3)_2(NCS)_4]$ is still known as Reinecke's salt. Once the structures of complexes were more fully understood, it was possible to name them more systematically. For example:

$[Co(NH_3)_5C\ell]C\ell_2$



The rules for naming coordination compounds are:

(i) The cation is named before the anion.

(ii) When naming the complex ion, the ligands are named **as prefixes** (i.e. before the metal ion).

(iii) When naming anionic ligands ($C\ell^-$) an **o** is added to the root name of the anion. For example the anionic ligand, $C\ell^-$, would be named as chloro. Neutral ligands retain the name of the molecule, except for the following: H_2O is aqua, NH_3 is ammine and CO is carbonyl.

(iv) The prefixes mono-, di-, tri-, tetra-, penta-, hexa-, etc, are used to denote the number of simple (typically unidentate) ligands; bis-, tris-, tetrakis-, etc for more complicated (bidentate) ligands or ones that already contain di-, tri, etc.

(v) Ligands are named in alphabetical order. Prefixes do not affect the order.

(vi) The oxidation state of the metal ion is designated by a Roman numeral in parentheses after the name of the metal ion.

Q19 continues on the next page.

(vii) Negatively charged complex ions have the suffix **–ate** added to the name of the metal – usually that from which the atomic symbol is derived. For example: nickel becomes nickelate, iron becomes ferrate and copper becomes cuprate.

(b) Give the formula for each of the following compounds.

(i) aquacyanobis(ethylenediamine)cobalt(III) chloride

$[Co(H_2O)(CN)(en)_2]C\ell_2$ **2 marks**

(ii) sodium diaquadioxalatoruthenate(III)

$Na[Ru(H_2O)_2(C_2O_4)_2]$ **2 marks**

(c) Give the name of each of the following coordination compounds.

(i) $[Cr(H_2O)_4C\ell_2]C\ell$

tetraaquadichlorochromium(III) chloride **2 marks**

(ii) $K_2[Ni(CN)_4]$

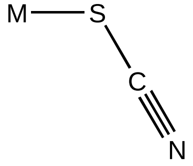
potassium tetracyanonickelate(II) **2 marks**

(iii) $[Co(en)_3]C\ell_3$

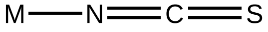
tris(ethylenediamine)cobalt(III) chloride **2 marks**

Structural isomerism

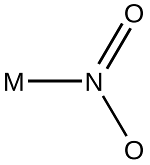
Many different types of structural isomerism are known in coordination chemistry. **Linkage isomerism** is an interesting type that arises when a particular ligand is capable of coordinating to a metal in two different ways. Ligands of this type are called **ambidentate** ligands. The nitrite ion, NO_2^-, for example, can coordinate through either a nitrogen or oxygen atom. When it coordinates through the nitrogen atom, the NO_2^- ligand is called *nitro*; when it coordinates through the oxygen atom, it is called *nitrito*. Another ligand capable of coordinating through either of two donor atoms is the thiocyanate ion, SCN^-, whose potential donor atoms are N (*isothiocyanato*) and S (*thiocyanato*). When writing chemical formula of coordination compounds containing ligands of this type, the symbol for donor atom of the ambidentate ligand is written first. For example, $[Co(NH_3)_5(NO_2)]C\ell$, for N-bound NO_2^- and $[Co(NH_3)_5(ONO)]C\ell$ for O-bound NO_2^-.



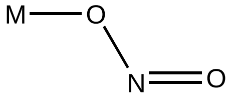
thiocyanato



isothiocyanato



nitro



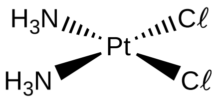
nitrito

Stereoisomerism

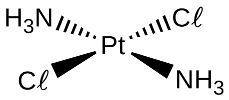
Stereoisomers have the same chemical bonds but different spatial arrangements. The term covers geometric isomers and optical isomers.

Geometric isomerism

In the square planar complex $[Pt(NH_3)_2C\ell_2]$, for example, the chloro ligands can be either adjacent or opposite to each other as shown on the next page.



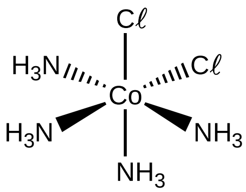
cis



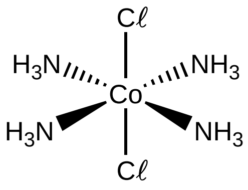
trans

Geometric isomers have different properties, such as colour, solubility and melting points. They may also have very different chemical reactivities. For example, *cis*-$[Pt(NH_3)_2C\ell_2]$, also called *cisplatin*, is effective in the treatment of certain cancers, whereas the trans isomer is ineffective.

Geometric isomerism is also possible in octahedral complexes when two or more different ligands are present. For example, the cis and trans isomers of the tetraamminedichlorocobalt(III) ion are shown below.



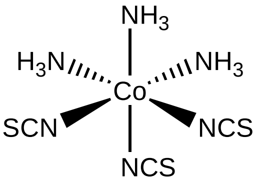
cis



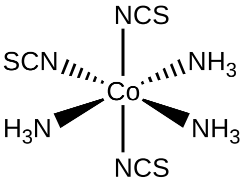
trans

A similar type of isomerism occurs for octahedral complexes when there are two sets of three identical ligands since each trio of donor atoms can occupy either adjacent positions at the corners of an octahedral face (**fac**ial) or positions around the meridian of the octahedron (**mer**idional).

For example, *fac*- and *mer*-$[Co(NCS)_3(NH_3)_3]$:



fac



mer

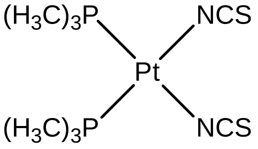
(d) Consider the following coordination compound: $[Pd(NCS)_2\{P(CH_3)_3\}_2]$ where $P(CH_3)_3$ is a neutral, unidentate ligand called trimethylphosphine.

(i) Name the above compound.

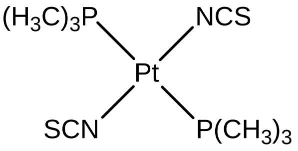
diisothiocyanatobis(trimethylphosphine)palladium(II) **[1 mark]**

(ii) Indicate how many geometric isomers are possible and sketch the structure of each of them.

$[Pt(NCS)_2\{P(CH_3)_3\}_2]$ – 2 geometric isomers



cis



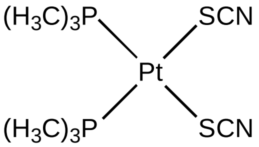
trans

[1 mark for 2 geometric isomers, 1 mark for each correct structure. Total of 3 marks]

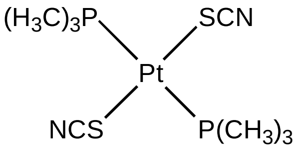
(iii) Would you expect the above compound to exhibit linkage isomerism? If so, name the linkage isomer and sketch **one** of its stereoisomers.

Yes, 2 linkage isomers.

$[Pt(SCN)_2\{P(CH_3)_3\}_2]$ – dithiocyanatobis(trimethylphosphine)platinum(II)



or



cis

trans

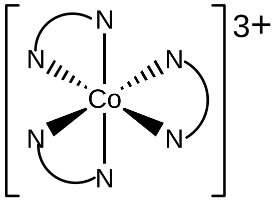
[1 mark for saying Yes, 1 mark for the correct structure. Total of 2 marks]

Optical isomerism

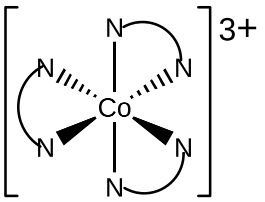
Optical isomers, called **enantiomers**, are mirror images that cannot be superimposed on each other – like a left and a right hand.

Enantiomers are said to be optically active because when plane polarised light is passed through a solution containing one of them the plane is rotated. The **dextrorotatory** [or dextro] isomer causes the plane to rotate to the right (clockwise). That is, it has a positive rotation ($+\alpha^o$) while the **levorotatory** [or levo] isomer causes the plane to rotate in the opposite direction but having the same magnitude ($-\alpha^o$). Enantiomers have the same physical and chemical properties except in the presence of plane polarised light or other optically active compounds. This is an important method of identification.

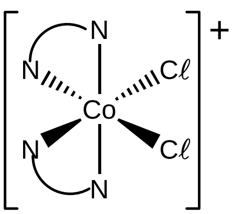
Enantiomers are called **chiral.** The most common types of chiral transition metal complexes are six-coordinate complexes of the type ML_3 and MX_2L_2 (where L is a bidentate ligand). For example, the complex ion $[Co(en)_3]^{3+}$ has two enantiomeric forms whereas $[CoC\ell_2(en)_2]^+$ has three stereoisomeric forms.



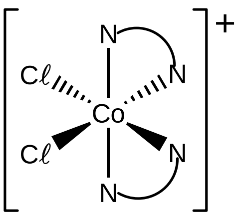
Λ



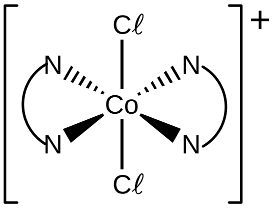
Δ



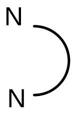
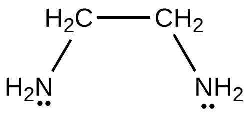
cis-Λ



cis-Δ



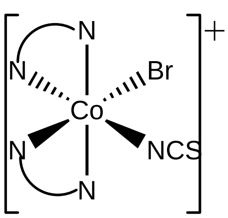
trans

where  represents 

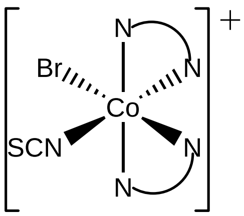
The enantiomeric species are assigned Λ (lambda) and Δ (delta) configurations on the basis of the helicity of the complexes. A Λ configuration refers to a left-handed helicity. That is, the optical isomer can be viewed as having a left-handed (or anticlockwise) screw into the plane of the page. The Δ configuration has a right-handed helicity.

Non-mirror image stereoisomers are referred to as **diastereoisomers** and, in contrast to enantiomers, do have different physical and chemical properties. Thus, in the case of the complex ion, $[CoC\ell_2(en)_2]^+$, the *cis*-Λ (or *cis*-Δ) isomer and the trans isomer are diastereoisomers.

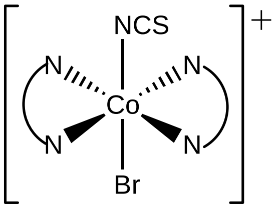
(e) Draw and name all of the possible isomers of the following complex ion: $[CoBr(NCS)(en)_2]^+$.



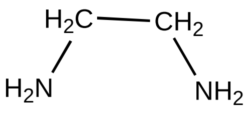
cis-Λ



cis-Δ



trans

where  = 

cis-(Λ)-, cis-(Δ)- and trans-bromobis(ethylenediamine)isothiocyanatocobalt(III) ion.

1 mark for each correct structure and 1 mark for each correct name. Total of 6 marks.]

(f) What type of structural isomerism could be exhibited by the complex ion in (e) above?

Linkage isomerism.

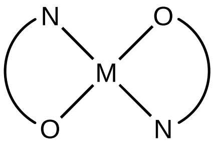
For example, cis-(Λ)-, cis-(Δ)- and trans-bromobis(ethylenediamine)thiocyanatocobalt(III) ion.

[1 mark for linkage isomerism. Name is not required. Total of 1 mark.]

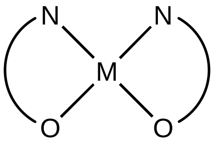
(g) What type of isomerism, if any, could be exhibited by a **four-coordinate** complex of the type $[M(H_2NCH_2CO_2)_2]$? Sketch the isomers.

Geometric isomerism

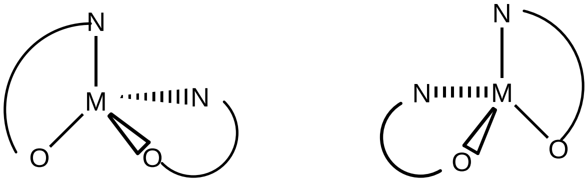
Optical isomerism

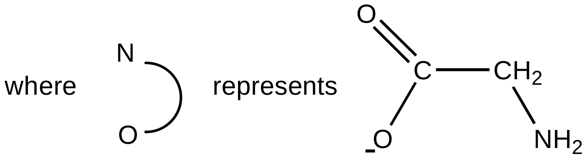


trans



cis





[1 mark for each correct structure. Total of 4 marks.]