AUSTRALIAN CHEMISTRY OLYMPIAD

QUALIFYING EXAMINATION

1988

General Instructions

(1) This paper is in **two** sections and candidates must answer each section according to the instructions. *ie.* Answer **ALL** questions in section A and **any three** (3) in section B.

(2) All answers must be written in the space provided in the answer book.

(3) Rough working must done on left-hand pages of the answer book.

(4) You are not permitted to refer to books or periodic tables and the only permitted aid is an electronic calculator.

(5) **Make sure your NAME, HOME ADDRESS and HOME TELEPHONE NUMBER are written on the cover sheet**. Your teacher will fill in the other information.

(6) You are permitted **10 minutes** to read the paper followed by **120 minutes** to work the questions.

(7) Data relevant to a question will be found at the end of the question.

SECTION A: It is intended that candidates devote not more than **30 minutes to this section.** Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be by clearly ticking the chosen answer box in **the answer book.** If you make a mistake, **correct it clearly** so that the examiners can read your answer.

Q1 0.0005 moles of metal bromide were dissolved in water and required 40.0 mL of 0.025 M silver nitrate solution to complete precipitation of silver bromide. These results are consistent with a bromide with the formula:

A. X_2Br
B. XBr
C. XBr_2
D. XBr_3
E. X_2Br_3

Q2 A small quantity of each of the following is added to separate samples of an aqueous solution of ethanoic (acetic) acid. Which would leave the lowest concentration of ethanoate (acetate) ions?

A. sodium hydrogen carbonate solution
B. dilute hydrochloric acid
C. magnesium
D. dilute sodium hydroxide solution
E. ethanol

Q3 What is the total number of isomeric carboxylic acids and esters having the molecular formula $C_4H_8O_2$?

A. 6
B. 5
C. 4
D. 3
E. 2

Q4 Some alkanes may be prepared by adding an alkyl iodide (iodoalkane) dropwise to sodium in a suitable inert solvent.

eg. $2CH_3I + 2Na \longrightarrow C_2H_6 + 2NaI$

If a mixture of iodomethane and iodoethane is used as a starting material, the product will contain

A. propane only.
B. ethane and butane.
C. ethane, propane and butane.
D. methane, ethane, propane and butane.
E. ethane, propane, 2-methylpropane.

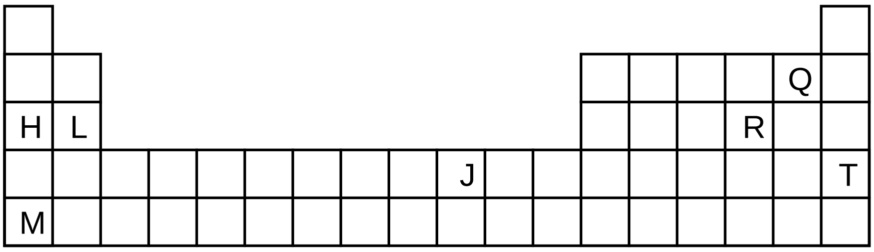
Q5 Which of the following is the most polar molecule? ie. has the highest permanent electric dipole, $CHCl_3$, SF_6, $SnCl_4$, BF_3, CO_2.

A. $CHCl_3$
B. SF_6
C. $SnCl_4$
D. BF_3
E. CO_2

Q6. When pure ammonium chloride is dissolved in pure water, the pH of the resulting solution is NOT 7. This is because

A. Ammonium ions accept protons from water molecules leaving free OH^- ions in solution.
B. Ammonium ions donate protons to water molecules forming H_3O^+ ions in solution.
C. Ammonium ions combine with water molecules to give the weak base, ammonium hydroxide.
D. Ammonium ions make the solution alkaline.
E. Chloride ions make the solution acidic.

Q7 The diagram below shows part of the skeleton of the Periodic Table in which elements are indicated by letters which are not their usual symbols.



Which one of the following statements is correct?

A. The greatest ionic character of compounds formed by reaction of pairs of the listed elements would be exhibited by the compound with the formula, M_2Q.
B. The J^{2+} ion is coloured and has an electronic configuration of $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7$.
C. The carbonate of compound H is insoluble in water.
D. Element R is a gas at room temperature.
E. Element T is an inert gas with an electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6\ 3d^{10}, 4s^2, 4p^6$.

Q8 Iodate ions (IO_3^-) can be reduced to iodine by iodide ions. The half-equations which represent the redox reactions are:

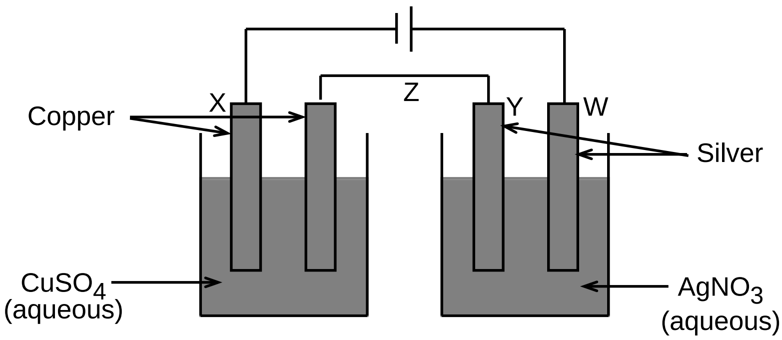
$$IO_3^-\,(aq) + 6H^+\,(aq) + 5e \longrightarrow \tfrac{1}{2} I_2\,(s) + 3H_2O\,(l)$$

$$I^-\,(aq) \longrightarrow \tfrac{1}{2} I_2\,(s) + e$$

How many moles of iodine are produced for every mole of iodate ions consumed in the reaction ?

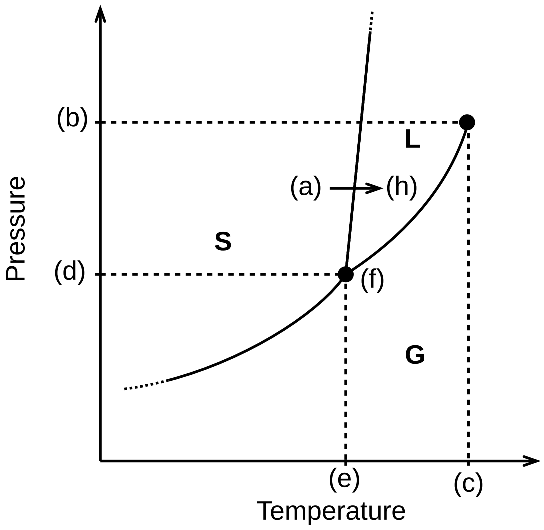
A. 0.5
B. 1
C. 2.5
D. 3
E. 5

Q9 During electrolysis in the cell below, 1.05 g copper is deposited on electrode X. Which one of the following statements is correct? (Relative atomic masses Cu = 63, Ag = 108).



- **A .** The mass of silver electrode W decreases by 3.60 g.
- **B .** The mass of silver deposited on electrode Y during the electrolysis is 1.80 g.
- **C .** Z is a salt-bridge.
- **D .** The concentration of copper ions in solution decreases during the electrolysis.
- **E .** The flow of negative charge is from right to left in Z.

Q10. The phase properties of a pure substance X are represented by the graph shown below.



For this system which one of the following statements is true?

- **A .** The boiling point of the substance at atmospheric pressure is **(c).**
- **B .** The phase transition shown as **(a)** $\rightarrow$ **(h)** represents a sublimation process.
- **C .** At pressure **(d)** the substance melts at temperature **(e).**
- **D .** The point represented by **(f)** is the triple point for the substance.
- **E .** The point represented by **(f)** is the critical point for the substance.

Q11. A strong diprotic acid is dissolved in water at 25^{o}C to yield a solution of pH 2.63. The concentration of acid in this solution in mol L^{-1} is between:

A. 0.1 and 0.5.
B. 0.05 and 0.1.
C. 0.01 and 0.05.
D. 0.005 and 0.01.
E. 0.001 and 0.005.

Q12. Under which set of conditions is the ionic product of water, K_W, constant at a given temperature in aqueous systems?

A. in dilute acidic but not dilute alkaline solutions.
B. in dilute alkaline but not dilute acidic solutions.
C. in both dilute acidic and alkaline solutions.
D. only at the equivalence point of a strong acid-strong alkali titration.
E. only in pure water.

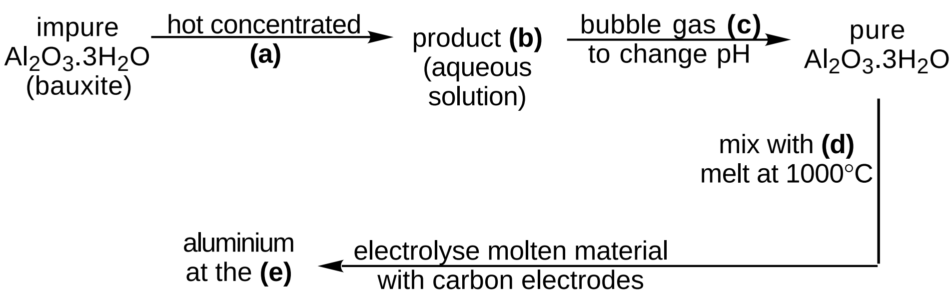
Q13. When an aluminium atom is bombarded with α-particles , phosphorus may be formed according to the following equation.

$$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P + X$$

In this process the particle X emitted is a

A. β -particle
B. hydrogen atom.
C. γ-ray.
D. proton.
E. neutron.

Q14. In 1886 an American student, Charles Hall devised a relatively inexpensive process to produce aluminium metal. This process (called the Hall-Heroult process) is now employed to produce over 20 megatonnes of aluminium annually. The basic process may be summarised as follows:



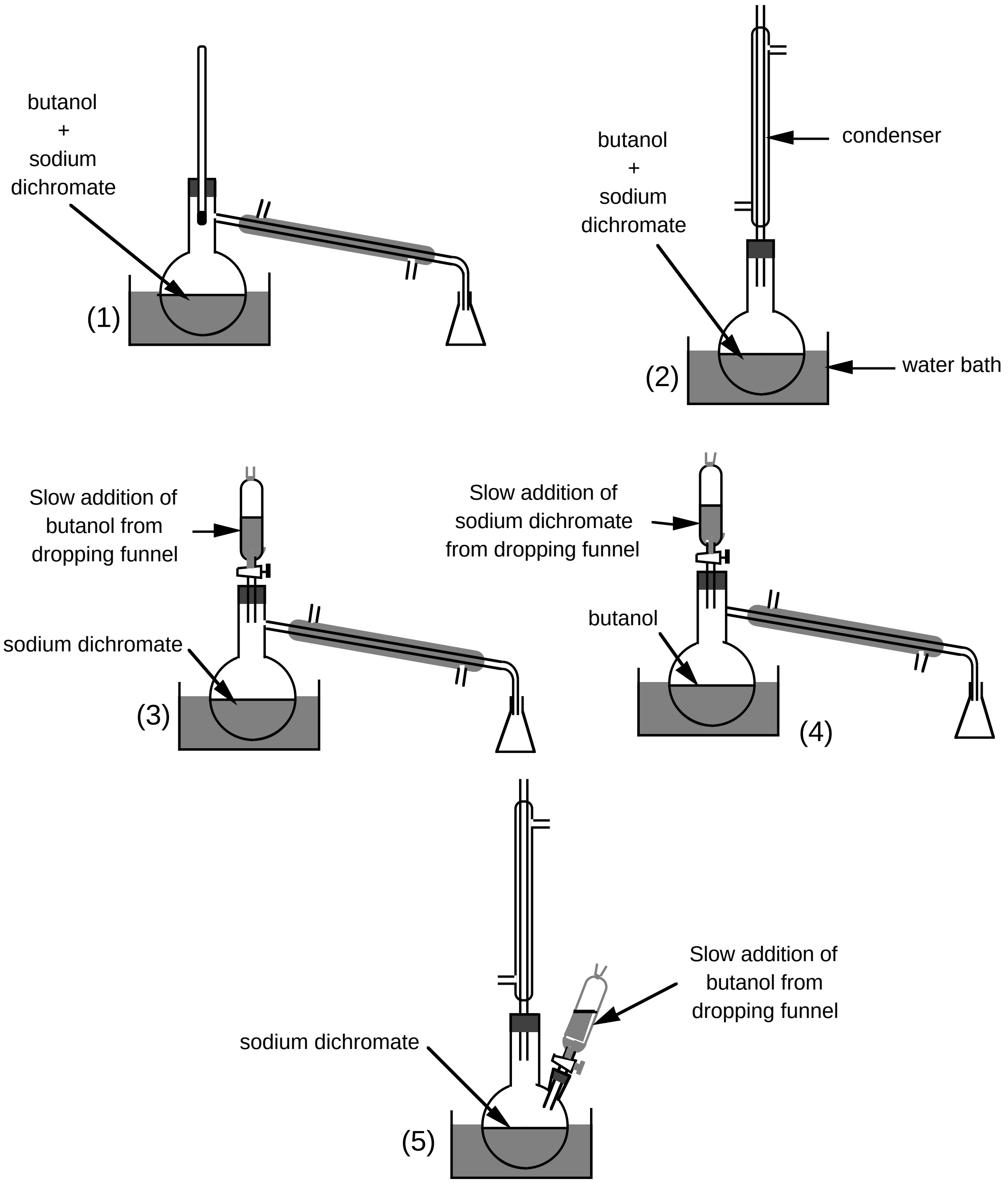
Which of the following entries correctly summarises the reagents, electrodes and products of the process?

	(a)	(b)	(c)	(d)	(e).
A.	NaOH	Al^{3+}	HF	Na_3AlF_6	Cathode
B.	NaOH	$NaAlO_2$	CO_2	NaF	Anode
C.	H_2SO_4	$Al_2(SO_4)_3$	NH_3	Na_3AlF_6	Cathode
D.	NaOH	$NaAlO_2$	CO_2	Na_3AlF_6	Cathode
E.	NaF	$NaAlF_4$	F_2	CaF_2	Anode

Note: $NaAlO_2$ when hydrated has the formula $NaAl(OH)_4$.

Q15 Aliphatic aldehydes are frequently prepared by oxidising primary alcohols with sodium dichromate in 5M aqueous sulfuric acid at 100^{o}C. However, over oxidation of the aldehyde to the carboxylic acid readily occurs and this necessitates careful choice of the experimental method.

Given the boiling points of butanal (74.8^{o}C), butan-1-ol (117^{o}C) and butanoic acid (163.3^{o}C) suggest which of the following arrangements of apparatus would be most useful to a chemist seeking the maximum yield of butanal from butan-1-ol? [Note. in each case the reaction flask is heated at 100^{o}C on a water bath and sodium dichromate is dissolved in 5M aqueous sulfuric acid.]



A. 1
B. 2
C. 3
D. 4
E. 5

<u>SECTION B</u>: Candidates should answer any **three** (3) of the four questions in this section. Be sure that **ALL** relevant working is shown in your answers to numerical questions. You should devote 90 minutes to this section.

16. (a) A chemist opened a cupboard to find four bottles containing water solutions, each of which had lost its label. Bottles 1, 2 and 3 contained colourless solutions, whilst Bottle 4 contained a blue solution. The labels from the bottles were lying scattered on the floor of the cupboard. They were:-

copper(II) sulfate
lead nitrate
hydrochloric acid
sodium carbonate

By mixing samples of the contents of the bottles, in pairs, the chemist made the following observations:

Bottle 1 + Bottle 2	white precipitate
Bottle 1 + Bottle 3	white precipitate
Bottle 1 + Bottle 4	white precipitate
Bottle 2 + Bottle 3	colourless gas evolved
Bottle 2 + Bottle 4	no visible reaction
Bottle 3 + Bottle 4	blue precipitate

(i) For each bottle identify the contents. Briefly explain the reason(s) for each identification that you have reached. Support your answers with appropriate equations.

(ii) Using any other apparatus or reagents that you wish, describe an additional chemical test which could be used to confirm the identity of the contents of **EACH** bottle. Support your tests with appropriate equations.

(b) An impure sample of the mineral azurite was analysed for copper by three analytical procedures.

A. Gravimetric analysis as copper (II) oxide.
B. Electrochemical deposition of metallic copper on a platinum cathode.
C. Indirect volumetric analysis by reaction with iodide ion (see below),

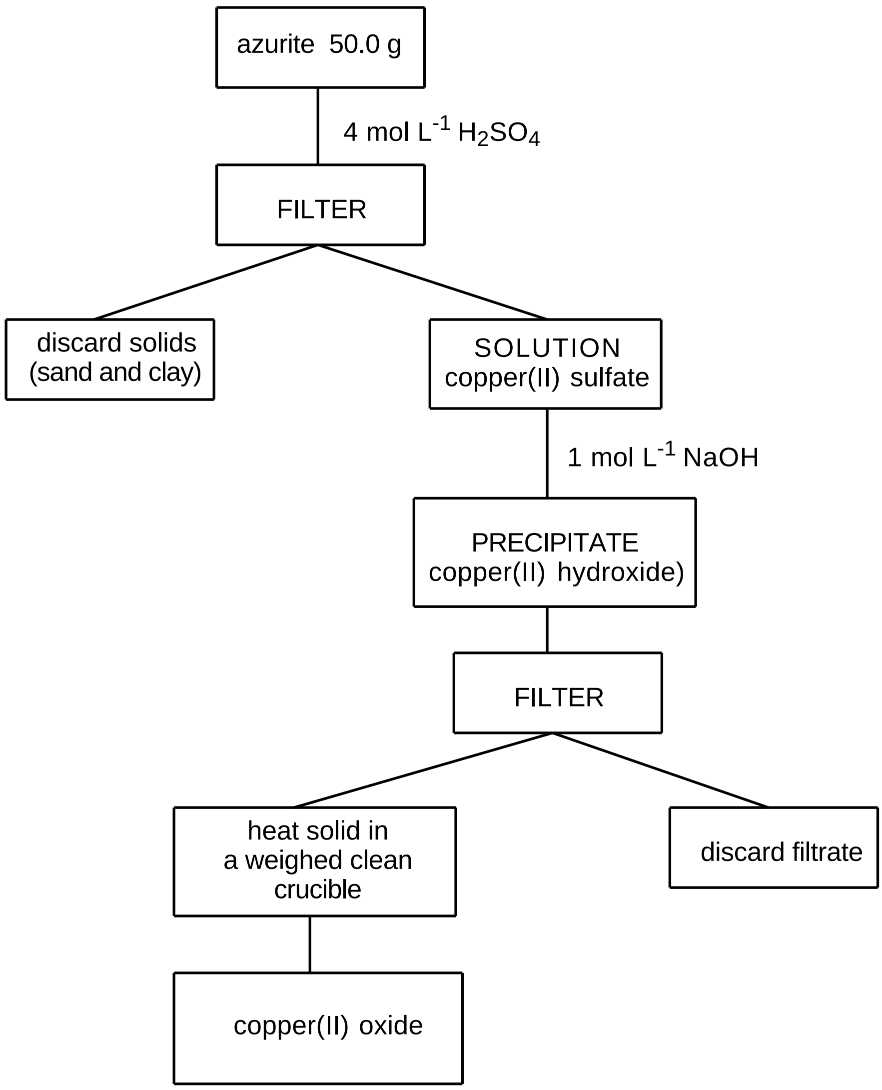
$$2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

and subsequent titration of the liberated iodine with a standard solution of sodium thiosulfate.

$$I_2(aq) + 2Na_2S_2O_3(aq) \longrightarrow Na_2S_4O_6(aq) + 2NaI(aq)$$

The most accurate procedure showed that the azurite sample contained 12.70% copper.

In the gravimetric method a 50.0 g sample of azurite, was crushed, excess
4 mol L^{-1} H_2SO_4 added, and the procedures outlined in the flow diagram below carried out.



(i) Calculate the mass of copper (II) oxide which would be formed if the gravimetric procedure commenced with 50.0 g of the mineral.

(ii) If instead of the gravimetric analysis, an aliquot(sample) comprising 1/40th of the total solution of copper (II) sulfate had been subjected to electrochemical analysis using a voltage of 2 volts and a current of 1 ampere, how many minutes would have elapsed before all the copper was deposited on the cathode?

(iii) If instead of the gravimetric analysis, an aliquot(sample) comprising 1/100th of the copper(II) sulfate had been adjusted to pH 5 and analysed via the iodometric procedure, what volume of 0.0500M sodium thiosulfate would have been required to consume all the iodine liberated?

(iv) Which of the above analytical methods (A-C) would yield the most accurate results? Explain your answer.

DATA: Relative atomic masses: Cu=63.55, I=126.9, Na=22.99, O=16.00, S=32.06.
1 faraday = 96,486 coulombs.
1 coulomb =1 amp sec.

17. For the following reaction, in which reactants and products are in the gas phase,

$$I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$$

the magnitude of equilibrium constant K_c is 280 at 150°C.

(a) Write an expression for the equilibrium constant and give the units of K_c.

(b) For gas phase reactions an alternative equilibrium constant K_p may be defined in terms of the partial pressures of the reactants and products. In the case of the reaction above

$$K_p = \frac{(P_{IBr})^2}{(P_{I_2}).(P_{Br_2})}$$

Assuming that all components in the equilibrium behave as ideal gases, deduce the relationship between K_p and K_c and give the value of K_p at 150°C.

(c) A sample of IBr is placed in an evacuated closed vessel. After reaching equilibrium at 150°C, the partial pressure of IBr was measured as 20.2kPa (0.20 atm). What are the pressures of $I_2(g)$ and $Br_2(g)$ in the vessel at that point? How would these three values change if 10.1kPa (0.1 atm) of helium was pumped into the vessel?

(d) Assuming the forward and reverse reactions are elementary (ie. single step), what would the rate law expressions be for the forward and reverse reactions?

(e) How would the presence of a catalyst affect the ratio of the forward and reverse rate constants?

(f) Given that the rates of both the forward and reverse reactions are increased by irradiation of the system with white light,

(i) decide if light is acting as a catalyst.

(ii) explain whether or not this observation is consistent with the assumption of elementary reactions.

(g) Given that the bond dissociation energies for the species involved are

I_2	+151.5 $kJmol^{-1}$
Br_2	+192.9 $kJmol^{-1}$
IBr	+177.8 $kJmol^{-1}$

estimate the heat of formation (standard enthalpy) for 1 mole of IBr (g) from the elements.

(h) Given that the equilibrium constant K_c can be related to the standard enthalpy of formation ($\Delta H°$) and entropy of formation ($\Delta S°$) by the relationship

$$\ln K_c = 2.303 \log K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

where T is temperature in Kelvin and R is the universal gas constant.

Calculate the value of the $\frac{\Delta S°}{R}$ term in the above equation and explain its significance in the determination of K_c at 150°C.

DATA: $R = 8.314\ JK^{-1}mol^{-1}$.

18. (a) In a colony of honey bees, the queen bee excretes a substance that keeps the sterile female workers subservient and also acts as a sex attractant for the drones. Microanalysis of this "queen bee substance", Q, gives 65.2% C, 8.75% H, with the remainder being oxygen. Q is acidic and careful titration of a 43.7 mg sample of Q with 0.0100 M aqueous sodium hydroxide (phenolphthalein indicator) gave a 23.7 mL titre. The volatility of Q was indicative of a relative molecular mass in the vicinity of 200.

What is the molecular formula of Q? What combinations of functional groups may be present in acidic compounds of this formula?

(b) Q reacts with hydrogen gas in the presence of finely divided platinum metal to give a substance A. Further reduction of A with sodium borohydride ($NaBH_4$) in ethanol gives substance B which is easily dehydrated on warming with strong sulfuric acid to a major alkene product C (along with some minor isomeric alkenes).

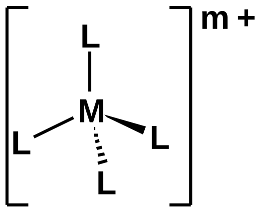
What functional groups are consistent with the above reactions?

(c) Cleavage of the alkene linkage in C by oxidative ozonolysis gives only two fragments, identified as acetic acid (CH_3COOH) and a straight chain aliphatic dicarboxylic acid D. Similar oxidative cleavage of Q itself also yields two fragments, oxalic acid (HOOC-COOH) and a substance E which contains a carboxylic acid group.

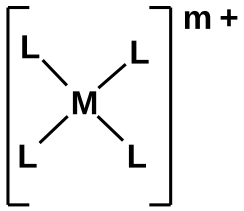
From this information deduce the full structure of the queen bee substance, Q, along with all the other compounds A-E. How many stereochemical isomers are possible for Q? Draw them.

DATA: Relative atomic masses: C = 12.01, O = 16.00, H = 1.01.

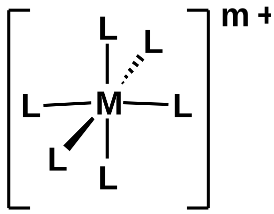
19. Transition metal ions, M^{n+} , are known to bind a variety of charged and neutral species, known as LIGANDS, and abbreviated as L, to give complex ions of the type $ML_n{}^{m+}$. Examples of neutral ligands are NH_3 and H_2O, and of anionic ligands Cl^- and Br^-. Two of the most commonly formed types of complex ions are $ML_4{}^{m+}$ and $ML_6{}^{m+}$ in which the central metal ion is surrounded by four or six ligands, respectively. (The number of ligands bound to the metal ion is referred to as the COORDINATION NUMBER of the complex ion.) In complex ions of the type $ML_4{}^{m+}$ the ligands adopt a tetrahedral(A) or square-planar(B) geometry whereas for $ML_6{}^{m+}$ an octahedral(C) arrangement of ligands about the metal ion is observed:



A

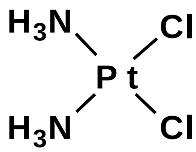


B

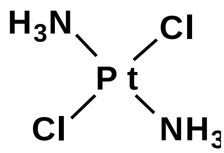


C

For example $[Cu(NH_3)_4]^{2+}$ has type A, $Pt(NH_3)_2Cl_2$ has type B and $[Co(H_2O)_6]^{2+}$ type C structure. The second example also exists in two isomeric forms:



cis



trans

The cis isomer is marketed as <u>cisplatin</u> and is one of the most potent anti-tumour drugs known whereas the trans isomer shows no significant biological activity. How many isomers can you draw for each of the following complex ions? (Illustrate your answer with suitable diagrams.)

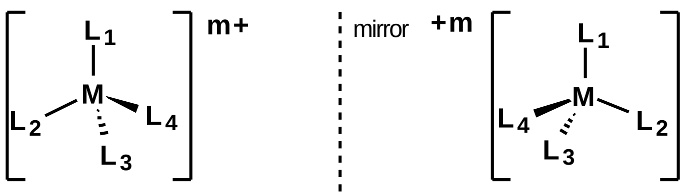
(a) Square-planar $[M(L_1)_2(L_2)_2]^{m+}$.

(b) Square-planar $[ML_1L_2L_3L_4]^{m+}$.

(c) Octahedral $[M(L_1)_4(L_2)_2]^{m+}$.

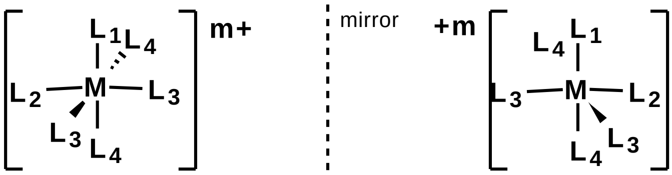
(d) Octahedral $[M(L_1)_3(L_2)_2L_3]^{m+}$.

The isomerism referred to above is termed GEOMETRIC isomerism. A second type of isomerism is OPTICAL isomerism*. Complex ions displaying the latter have the following in common: The isomers are <u>mirror images</u> of each other and they are <u>non-superimposable</u> (ie when the isomers are placed one on top of the other the spatial arrangements of their respective ligands are *always* different: Examine your own hands, they exhibit the same type of isomerism). Tetrahedral complex ions of the type $[ML_1L_2L_3L_4]^{m+}$ can in principle exhibit optical isomerism:



* When plane polarised light is passed through a solution containing an optical isomer of a complex ion the plane of polarisation is rotated through an angle of α°. For any pair of optical isomers one isomer will rotate the plane $+\alpha^\circ$ and the other $-\alpha^\circ$. Isomers which exhibit this phenomenon are said to be optically active, hence the term optical isomerism.

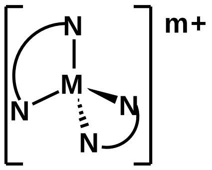
Similarly, octahedral complex ions containing four different ligands exhibit optical isomerism:



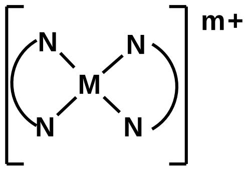
(e) How many other isomers can you draw for the octahedral complex ion $[ML_1L_2(L_3)_2(L_4)_2]^{m+}$ shown above? Which ones are optical isomers? (Illustrate your answer with suitable diagrams.)

All of the ligands mentioned so far are termed MONODENTATE as they form a single two-electron bond with the metal ion; the ligand provides both electrons. Molecules which can form two such bonds with a metal ion are referred to as BIDENTATE ligands.

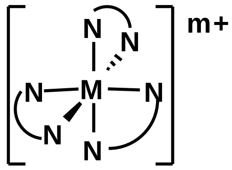
e.g. $H_2NCH_2CH_2NH_2$ is abbreviated as (N‿N) and $H_2NCH_2CH_2NMe_2$ as (N‿N').
These can also form type A, B or C geometries around suitable metel ions:



A

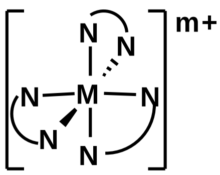


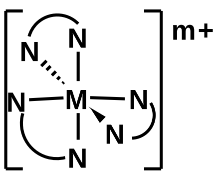
B



C

For example $[Cu(N‿N)_2]^{2+}$ has type A, $[Ni(N‿N)_2]^{2+}$ has type B and $[Co(N‿N)_3]^{3+}$ has type C structure. The last example also exists in two optically active isomeric forms





How many isomers can you draw for each of the following complex ions? (Illustrate your answer with suitable diagrams.)

(f) Square-planar $[M(N‿N')L_1L_2]^{m+}$.

(g) Square-planar $[M(N‿N')_2]^{m+}$.

(h) Octahedral $[M(N‿N)_2(L_1)_2]^{m+}$.

(i) Tetrahedral $[M(N‿N')_2]^{m+}$.

(j) Octahedral $[M(N‿N')_3]^{m+}$.