

[92/297]

1980

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Tuesday, 13th May—9.30 a.m. to 12 noon



Dalziel High School
Chemistry Department

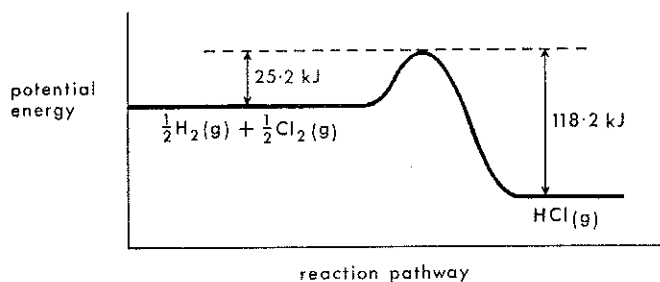


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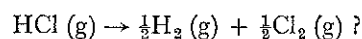
1. All noble gases are characterised in terms of electrons by the completion of the outermost orbital. This orbital is a(n)
- A s-orbital
 B p-orbital
 C d-orbital
 D s or p-orbital.

2. Going down the Group I elements from lithium to caesium, which of the following is true?
- A The electronegativity of the elements increases.
 B The melting point of the elements increases.
 C The ionic nature of the chlorides increases.
 D The first ionisation energy of the elements increases.

3. Consider the diagram below.

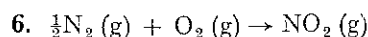


What is ΔH for the reaction

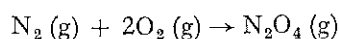


- A + 93 kJ
 B + 118.2 kJ
 C - 93 kJ
 D - 118.2 kJ
4. In the electrolysis of an aqueous solution of potassium sulphate 1 faraday of electricity was passed every 60 minutes. How long did it take to release 7.47 litres hydrogen gas? (Volume measured at s.t.p.)
- A 10 minutes
 B 20 minutes
 C 40 minutes
 D 1 hour 30 minutes

5. 50 cm³ of M sodium hydroxide were mixed with 50 cm³ of M sulphuric acid. Which of the following is nearest to the pH of the resultant solution?
- A 0
 B 1
 C 3
 D 7



$$\Delta G = + 51.8 \text{ kJ mol}^{-1}$$

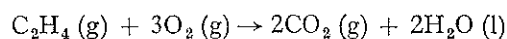


$$\Delta G = + 97.7 \text{ kJ mol}^{-1}$$

What is the free energy change ΔG for the conversion of nitrogen dioxide to one mole of dinitrogen tetroxide?

- A +45.9 kJ
 B -45.9 kJ
 C +5.9 kJ
 D -5.9 kJ
7. Which of the following contains the Avogadro Number of molecules?
- A 14 g nitrogen
 B 71 g chlorine
 C 58.5 g sodium chloride
 D 8 g helium

8. A mixture of 10 cm³ ethene and 40 cm³ oxygen (measured at s.t.p.) is exploded in a closed container. The overall reaction may be represented as follows



What would be the volume of gas at s.t.p. at the end of the reaction?

- A 10 cm³
 B 20 cm³
 C 30 cm³
 D 40 cm³

9. For a certain reaction

$$\Delta H = +7.3 \text{ kJ mol}^{-1} \text{ and } \Delta S = -0.002 \text{ kJ K}^{-1}\text{mol}^{-1}$$

This reaction will

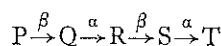
- A never be thermodynamically feasible
- B be thermodynamically feasible above some temperature
- C be thermodynamically feasible below some temperature
- D be thermodynamically feasible at all temperatures.

10. The heat of formation of water is -282 kJ mol^{-1} .

The heat of combustion of hydrogen is

- A $+282 \text{ kJ mol}^{-1}$
- B -282 kJ mol^{-1}
- C -141 kJ mol^{-1}
- D $+141 \text{ kJ mol}^{-1}$.

11. If the following represents a radioactive decay series



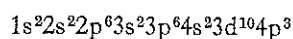
which of the following pairs must be isotopes?

- A P and R
- B Q and T
- C P and S
- D None of the above are isotopes.

12. An element has a melting point above 3800 K and forms a gaseous oxide. The type of bonding in the element is

- A metallic
- B covalent (non-polar)
- C ionic
- D covalent (polar).

13. The electronic configuration of an atom X is



The chemistry of X is therefore likely to be similar to that of

- A zinc
- B nitrogen
- C boron
- D chlorine.

14. The energy associated with electromagnetic radiation is

- A independent of the wavelength
- B proportional to the wavelength
- C proportional to the reciprocal of the wavelength
- D proportional to the square of the wavelength.

15. The position of the spots relative to the transmitted beam in an X-ray diffraction pattern is **not** affected by

- A the frequency of the X-rays
- B the co-ordination number of neighbours round each atom
- C the number of electrons on each atom
- D the distance between nearest neighbour atoms.

The processes in **questions 16, 17 and 18** may be placed in one of the following categories. A category may be used once, more than once, or not at all.

- A ΔH positive, ΔS positive
- B ΔH positive, ΔS negative
- C ΔH negative, ΔS positive
- D ΔH negative, ΔS negative

16. The melting of ice.

17. The burning of hydrogen and oxygen to form water.

18. The combination of phosphorus vapour and chlorine.

19. In which one of the following reactions does hydrogen behave as an oxidising agent?

- A $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$
- B $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
- C $2\text{Li} + \text{H}_2 \rightarrow 2\text{LiH}$
- D $\text{C}_2\text{H}_5\text{CHO} + \text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{OH}$

20. How many moles of iron(II) ions are oxidised by one mole potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, in acid solution? (You may wish to consult the Data Book.)

- A 6
- B 3
- C 2
- D 1

21. Which of the following would you expect to show the **least** ionic character?

- A Lead(II) chloride
- B Lead(IV) chloride
- C Tin(II) chloride
- D Tin(IV) chloride

22. In which of the following would the term hydrolysis **not** be appropriate? Describing the

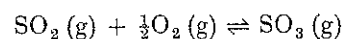
- A acidity of ammonium sulphate solution
- B conversion of an ester to an acid and an alcohol
- C instability of aluminium chloride in a moist atmosphere
- D action of concentrated sulphuric acid on copper sulphate crystals.

23. In the equilibrium system $\text{P} + \text{Q} \rightleftharpoons \text{R} + \text{S}$, the concentration of R at equilibrium was 0.6 mol l^{-1} . The initial concentrations of P and Q were each 1.0 mol l^{-1} , and those of R and S zero.

The value of the equilibrium constant was

- A 0.16
- B 0.44
- C 2.25
- D 6.25

24. Consider the equilibrium reaction

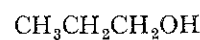
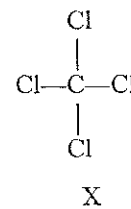
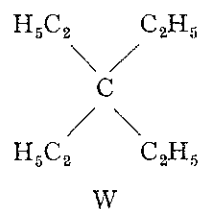


For the forward reaction $\Delta H = -97 \text{ kJ}$.

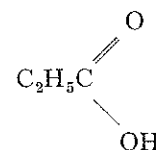
Which of the following changes would **not** increase the equilibrium yield of sulphur trioxide?

- A An increase in pressure
- B An increase in the concentration of sulphur dioxide
- C A decrease of temperature
- D The introduction of a catalyst

25.



Y



Which of the above compounds would be expected to be completely miscible with water?

- A W and X
- B X only
- C Y and Z
- D Z only

26. A Lewis base may be regarded as a substance which is capable of donating an unshared pair of electrons to form a covalent bond. Which of the following could act as a Lewis base?

- A BCl_3
- B NH_4^+
- C PH_3
- D Co^{3+}

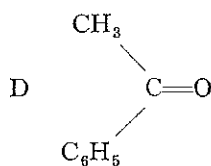
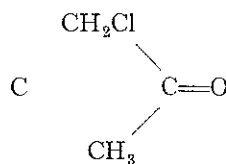
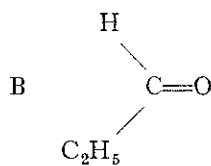
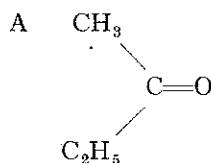
27. When ethene reacts with bromine in the presence of potassium chloride, $\text{CH}_2\text{BrCH}_2\text{Cl}$ and $\text{CH}_2\text{BrCH}_2\text{Br}$ are both formed. The first of these two compounds is produced because chloride ion

- A competes with ethene to form an ionic intermediate
- B competes with bromide ion attacking a carbocation ion
- C attacks the $\text{CH}_2\text{BrCH}_2\text{Br}$ which had originally formed, displacing the less reactive Br^-
- D reacts with bromine to give chlorine which then attacks the ethene.

28. A compound X (molecular weight < 100) gave:

- (i) on combustion carbon dioxide and water only
- (ii) a secondary alcohol on reduction.

X is most likely to be



29. The lattice energy of a salt is 769 kJ mol^{-1} and its hydration energy is -765 kJ mol^{-1} .

This salt

- A will not dissolve in water
- B if soluble, will dissolve in water with practically no temperature change
- C has a high heat of solution
- D will dissolve in water because of an increase in entropy.

30. A cyclic silicate ion has the general formula $(\text{Si}_n\text{O}_{3n})^{2n-}$. In the mineral $\text{Ca}_2\text{XSi}_3\text{O}_9$, X could be

- A sodium
- B barium
- C aluminium
- D carbon.

31. Which one of the following statements concerning germanium tetrachloride is correct?

- A Its molecules are square planar and it reacts with water.
- B Its molecules are square planar and it does not react with water.
- C Its molecules are tetrahedral and it reacts with water.
- D Its molecules are tetrahedral and it does not react with water.

32. Three drops of dilute hydrochloric acid are added to 10 cm^3 solution containing ethanoic acid, sodium ethanoate and universal pH indicator.

Which of the following statements is true?

- A Most of the hydrogen ions from the hydrochloric acid combine with ethanoate ions so that the pH remains almost the same.
- B Hydrochloric acid reacts to form sodium chloride and the pH becomes 7.
- C Hydrochloric acid increases the degree of hydrolysis of sodium ethanoate and the pH rises slightly.
- D The pH decreases sharply.

33. Which of the following factors favour charge transfer from ligand to metal in a transition metal complex?

- A High reducing power of ligand
- B Low oxidation state of the metal
- C Large ionisation energy of ligand
- D Large radius of metal ion

34. In which of the following compounds of nickel is the metal in the highest oxidation state?

- A NiO
- B K_2NiF_6
- C $\text{K}_4[\text{Ni}_2(\text{CN})_6]$
- D $[\text{Ni}(\text{NH}_3)_6] [\text{BF}_4]_2$

35. The colour change from light blue to dark blue when excess ammonia is added to copper(II) sulphate solution is due to

- A a change in the oxidation state of copper
- B the removal of the degeneracy of the d-orbitals
- C a change from octahedral to tetrahedral coordination
- D an alteration in the ligand field strength.

36. The transition metal salts $\text{Mn}^{2+}(\text{F}^-)_2$, $\text{Fe}^{2+}(\text{F}^-)_2$, $\text{Co}^{2+}(\text{F}^-)_2$ have identical crystal structures because the metal ions

- A have the same nuclear charge
- B have the same number of d electrons
- C have similar radii
- D are all paramagnetic.

37. Which of the following has the electronic structure $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$?

(You may wish to consult the Data Book.)

- A Cr^{2+}
- B V^{2+}
- C Mn^{3+}
- D Ti^{4+}

To answer questions 38 to 40 use the following code.

If all the responses 1, 2 and 3 are correct, select A.

If only 1 and 2 are correct, select B.

If only 3 is correct, select C.

If some other response, or combination of responses of those given is correct, select D.

38. A bottle of liquid is marked C_6H_{12} . Assuming the formula to be correct, which of the following statements can be made with certainty about the liquid?

- 1 It is an unsaturated open chain compound.
- 2 It will decolourise bromine water.
- 3 It will burn.

39. The following compounds can exist in isomeric forms:

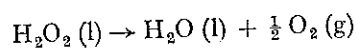
- 1 $\text{CH}_3\text{CH}_2\text{CH}_3$
- 2 CH_3CHCl_2
- 3 $\text{CH}_3\text{CH}=\text{CH}_2$.

40. In a line spectrum the frequency of each emission line represents

- 1 the energy change when an electron moves to a lower energy level
- 2 the kinetic energy possessed by an electron in an atom
- 3 an energy level within an atom.

[END OF QUESTION PAPER]

1. The decomposition of hydrogen peroxide at 298 K and 1 atmosphere pressure may be represented as follows



The following data relate to this reaction.

$$\text{Enthalpy change, } \Delta H = -98 \text{ kJ mol}^{-1}$$

$$\text{Activation energy} = 76 \text{ kJ mol}^{-1}$$

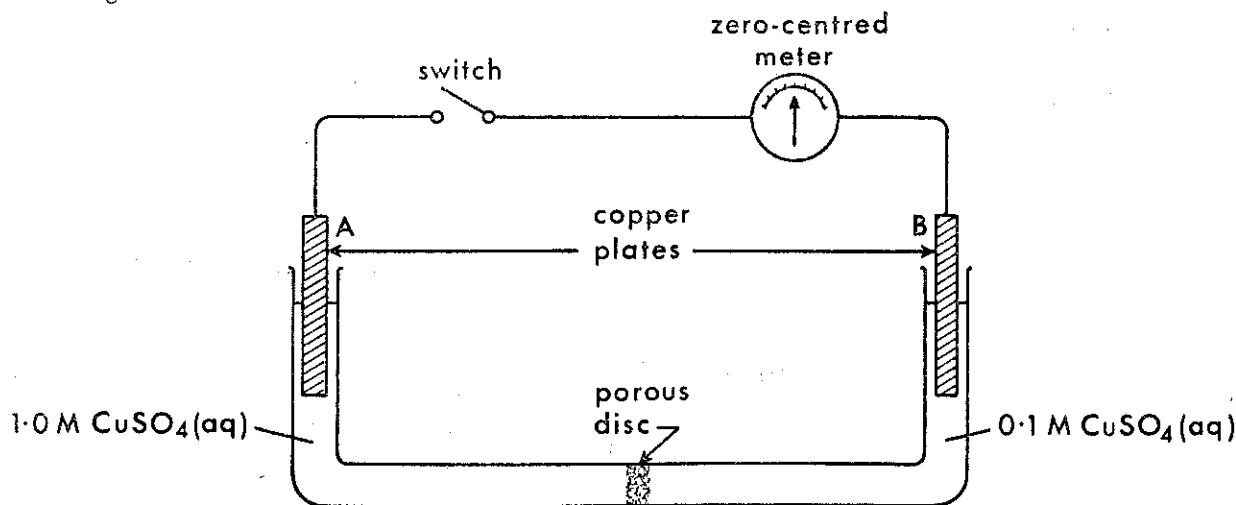
Substance	Entropy, S ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{H}_2\text{O}_2(\text{l})$	102
$\text{H}_2\text{O}(\text{l})$	70
$\text{O}_2(\text{g})$	205

Answer the following questions concerning this reaction at 298 K and 1 atmosphere pressure.

- (a) Calculate the entropy change, ΔS . 1
- (b) Calculate the free energy change, ΔG . 3
- (c) Which of the energy values—activation energy, enthalpy change, free energy change—gives most information concerning its
- (i) thermodynamic feasibility, 2
- (ii) rate of reaction?
- (d) The decomposition can be catalysed by manganese(IV) oxide. Which of the energy values mentioned in (c) above is affected by the catalyst? 1
- (7)

2. Answer EITHER A OR B.

- A. When the switch was closed in the circuit shown in the diagram below, a very small current was registered on the meter.



- (a) Write down ion-electron equations for the reactions occurring at both metal plates and deduce the direction of current through the meter. 2
- (b) The controlling factor in this process is entropy rather than enthalpy. Justify this statement. 2
- (c) Suppose that the above cell is altered by replacing copper plate B and 0.1 M CuSO_4 (aq) by a tin plate and 1.0 M SnCl_2 (aq) respectively.

What effect, if any, will this have on the direction of the electric current? Explain your answer. 2

(6)

OR

- B. In an experiment to find the percentage of iron in a sample of iron wire, 0.700 g of the wire was dissolved in excess dilute sulphuric acid under conditions where the reaction could be described by the equation



- (a) One drop of the resulting solution was added to ammonium thiocyanate solution and no colour change was observed. Why was this test carried out? 1
- (b) The iron(II) solution was then titrated against 0.1 M potassium permanganate solution and 24.0 cm^3 of the latter were required for complete reaction.

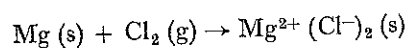
Calculate

- (i) the number of moles of iron(II) ions in the solution, and hence, 2
- (ii) the percentage of iron in the iron wire. 2
- (c) Why would unsatisfactory results be obtained in this experiment if hydrochloric acid were used instead of sulphuric acid? 1

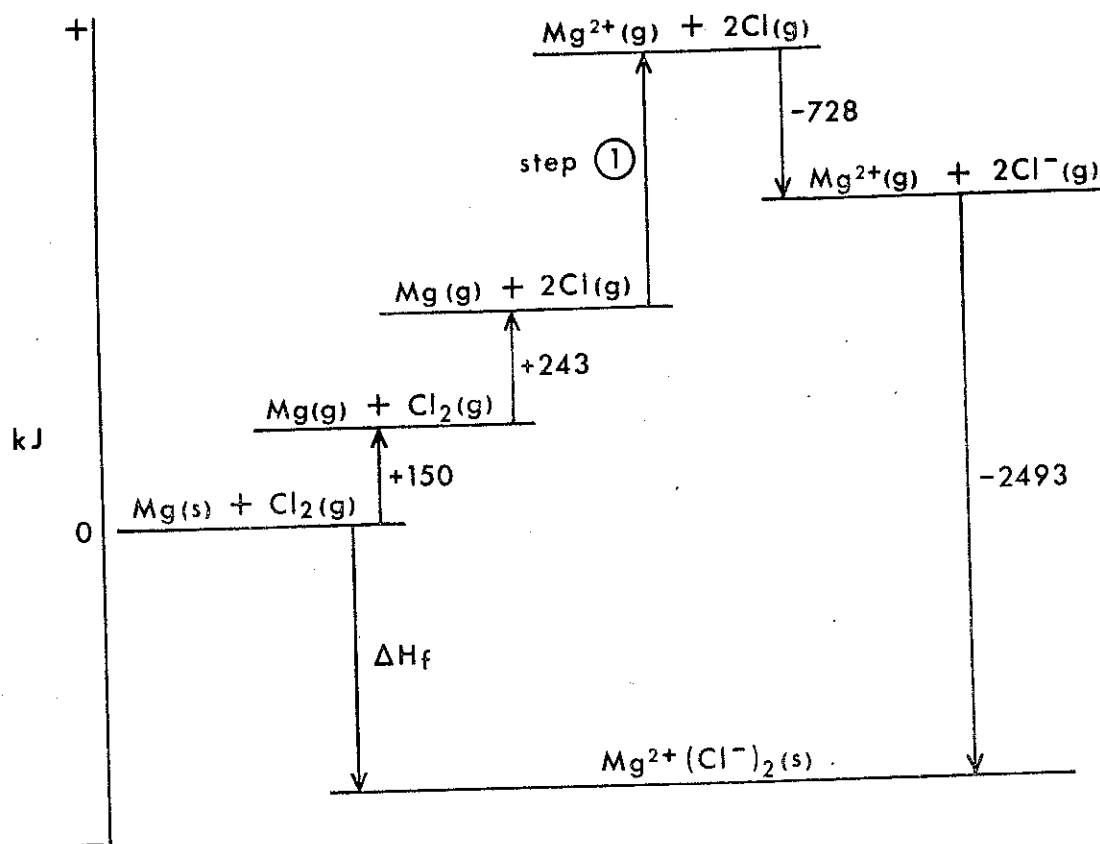
(6)

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3. The diagram below shows the enthalpy changes in kJ at 298 K and 1 atmosphere pressure for the reaction



The diagram is **not** drawn to scale.



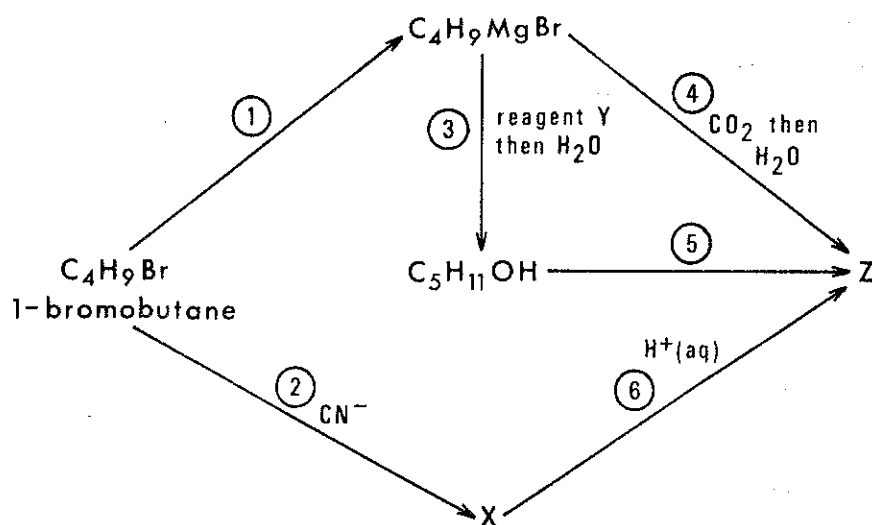
- (a) Refer to page 28 of the Data Book to calculate the enthalpy change for step ①. 1
- (b) Calculate ΔH_f , the heat of formation of solid magnesium chloride. 2
- (c) $\text{Mg}^{2+} \text{ (g)} + \text{H}_2\text{O (l)} \rightarrow \text{Mg}^{2+} \text{ (aq)} \quad \Delta H = -1920 \text{ kJ mol}^{-1}$
- $\text{Cl}^{-} \text{ (g)} + \text{H}_2\text{O (l)} \rightarrow \text{Cl}^{-} \text{ (aq)} \quad \Delta H = -364 \text{ kJ mol}^{-1}$

Use this data and relevant data from the diagram to calculate the heat of solution of magnesium chloride. 2

(5)

4. Answer EITHER A OR B.

- A. The following reaction scheme illustrates three methods of synthesising a certain organic compound, Z, starting from 1-bromobutane.



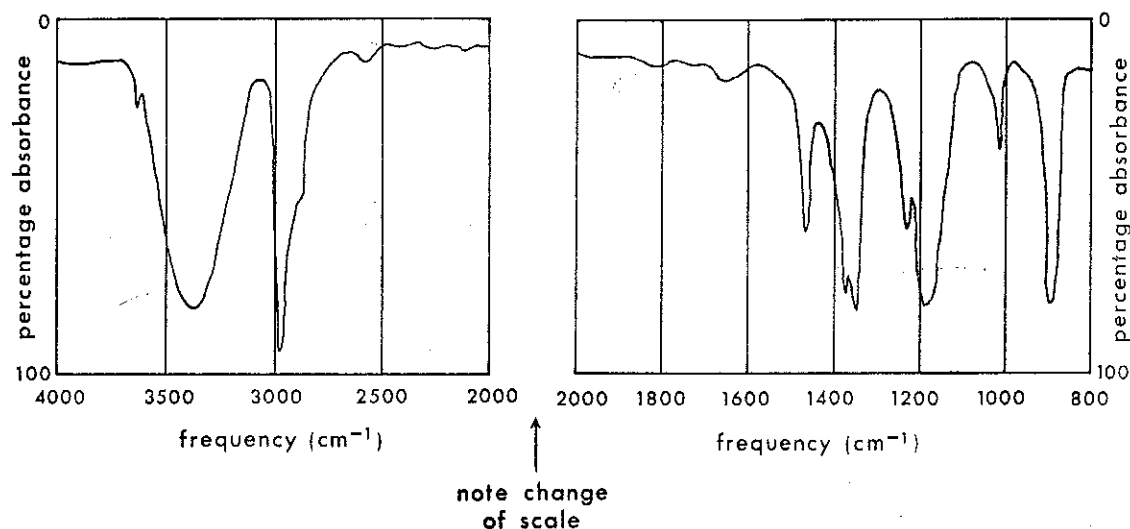
- (a) Describe briefly how reaction ① can be carried out. 2
- (b) Give the formula of the carbon compound X. 1
- (c) (i) What is reagent Y in reaction ③? 1
- (ii) Is the alcohol produced by reaction ③ primary, secondary or tertiary? 1
- (iii) Give a suitable reagent and conditions for reaction ⑥. 1
- (d) Name and give the extended structural formula of Z. 2
- (e) Identify one of the reactions in the above scheme which occurs by a nucleophilic substitution. 1
- (9)**

[Turn over

OR

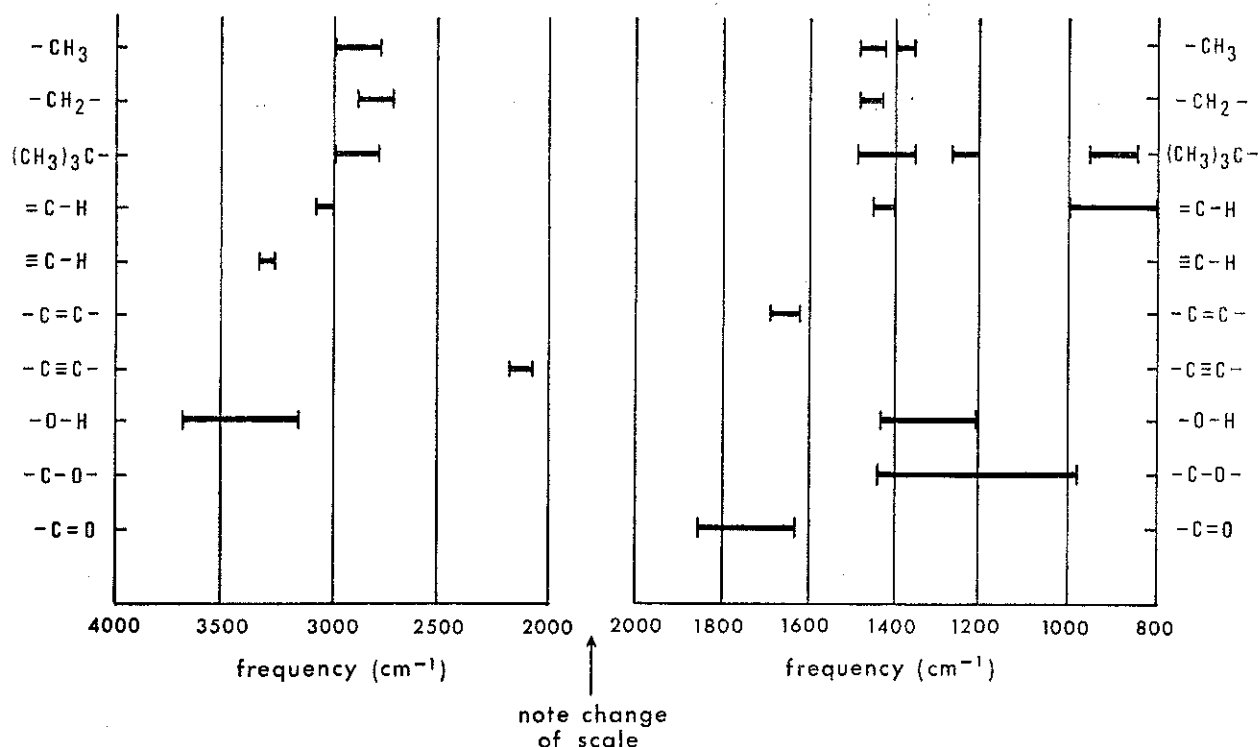
B. The following data concerns compound Q.

- ① Its molecular formula is $C_4H_{10}O$.
- ② Its infra-red spectrum is—



The following chart shows the infra-red absorption regions for a number of groups in aliphatic compounds. (— indicates the range of frequencies where absorption may occur, **not** the breadth of an absorption peak.)

Characteristic absorptions of various groups



③ Compound Q is resistant to oxidation while three of its isomers (belonging to the same homologous series as Q) are readily oxidised.

Use the data given above to answer the following.

- (a) To which homologous series does compound Q belong?
Explain your answer. 3
- (b) Draw the extended structural formula of Q and give its systematic name. Give **two** reasons for selecting this isomer rather than another from within the same homologous series. 4
- (c) Draw the extended structural formula of an isomer of compound Q that belongs to *another* homologous series.
Give **two** regions of the infra-red spectrum where you would expect this other isomer to absorb. The two absorptions should be caused by different groups within the molecule. 2
(9)

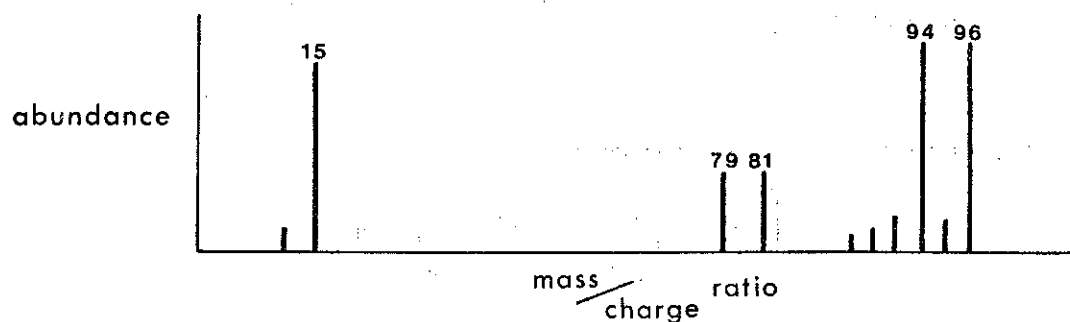
5. (a) Show by diagrams the three dimensional shapes of
(i) the SiF_4 molecule,
(ii) the SiF_5^- ion,
(iii) the SiF_6^{2-} ion. 3
- (b) Xenon combines with fluorine to form a number of fluorides of which xenon tetrafluoride, XeF_4 , is one.
The XeF_4 molecule has a square planar structure.
Draw a diagram to illustrate its structure and suggest why this molecule has this shape. 2
(5)

6. Answer **EITHER A OR B.**

- A Predict the mass/charge ratios of the **five** peaks in the mass spectrum arising from chlorine gas. Assume that all the particles in the mass spectrometer are singly charged. (3)

OR

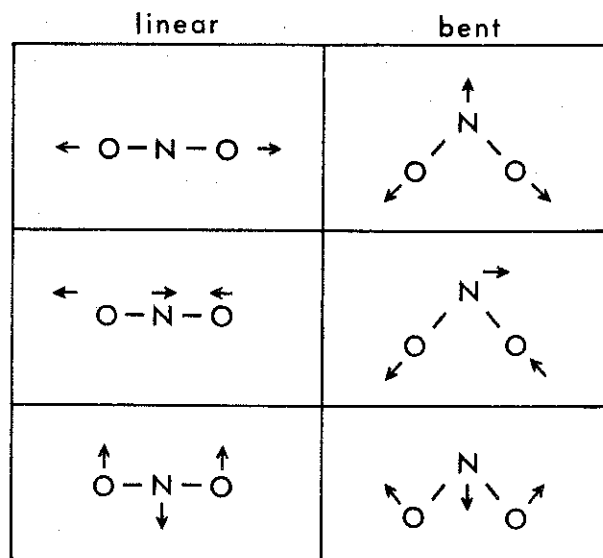
- B The mass spectrum of CH_3Br is shown below. It is **not** drawn to scale.



- (a) Given that the atomic weight of bromine is 80, which species give rise to the peaks at mass/charge ratios of 15, 79, 81 and 96? 2
- (b) What happens to the molecules within the mass spectrometer to account for the small peaks at mass/charge ratios of 91, 92 and 93? 1
(3)

7. The NO_2 molecule could be either linear or bent in shape.

The expected vibrations for these two possible shapes are given below.



There are **three** separate absorptions in the infra-red spectrum of this molecule.

Is the NO_2 molecule linear or bent? Explain your answer clearly.

(5)

8. In classical mechanics the energy of bodies can be varied continuously. Yet to explain the emission spectrum of the hydrogen atom, it was postulated that the energy of an electron in the field of the atomic nucleus must be "quantised".

(a) What is meant by "quantised"?

1

(b) What feature of the hydrogen emission spectrum led to this conclusion?

1

(c) Explain how this idea of the atom accounted for the hydrogen spectrum.

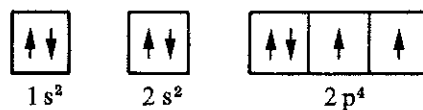
2

(d) If classical mechanics could account for the energy of electrons, what type of emission spectrum would be observed for hydrogen?

1

(5)

9. The following represents the electronic configuration of an oxygen atom.



In what way does this diagrammatic representation illustrate

(a) Hund's Rule of Maximum Multiplicity,

2

(b) the Pauli Exclusion Principle?

2

(4)

10. Answer EITHER A OR B.

Marks

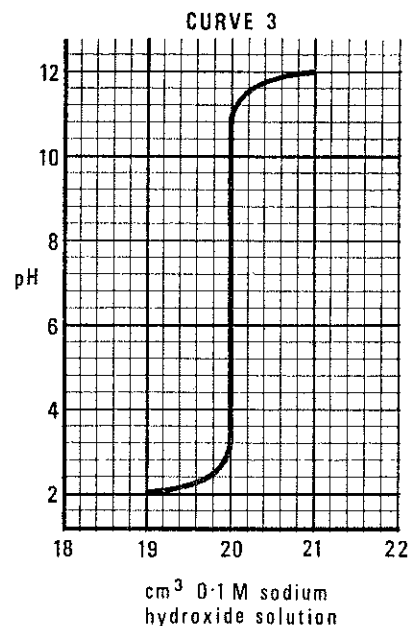
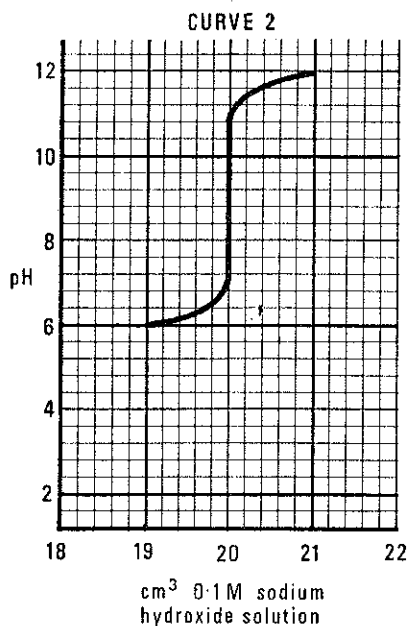
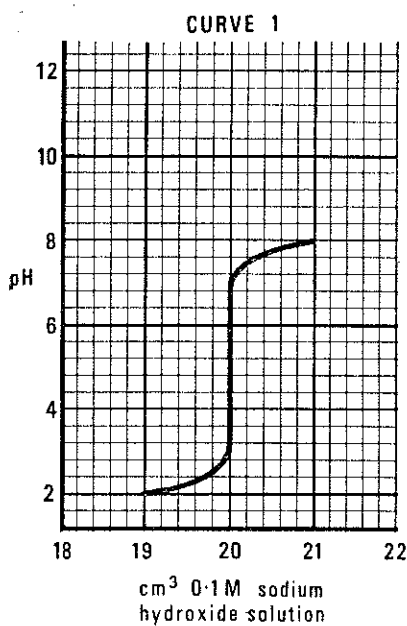
A

Name of acid	Dissociation in water	Dissociation Constant (at 298 K)
Hydrogen sulphide	$H_2S \rightleftharpoons H^+ + HS^-$	8.9×10^{-8}
Ethanoic	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.7×10^{-5}
Chloroethanoic	$CH_2ClCOOH \rightleftharpoons H^+ + CH_2ClCOO^-$	1.3×10^{-3}
Hypochlorous	$HClO \rightleftharpoons H^+ + ClO^-$	3.7×10^{-8}
Chromic	$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$	1.0×10^1
Propanoic	$C_2H_5COOH \rightleftharpoons H^+ + C_2H_5COO^-$	1.3×10^{-5}

- (a) Which of the above is the weakest acid in water? 1
- (b) If the acids were listed in order of strength, strongest first, where on the list would water be placed? 1
- (c) Name an acid from the above table which can undergo a second stage of dissociation. Give the equation for this stage. 2
- (d) Why are the dissociation constants of ethanoic acid and chloroethanoic acid different? 3
- (7)

OR

- B (a) The dissociation constant of butanoic acid is 1.5×10^{-5} .
Calculate the pH of a 0.1 M solution of butanoic acid. 3
- (b) Which of the following curves would represent the addition of 0.1 M sodium hydroxide solution to 20 cm³ of 0.1 M butanoic acid? 1

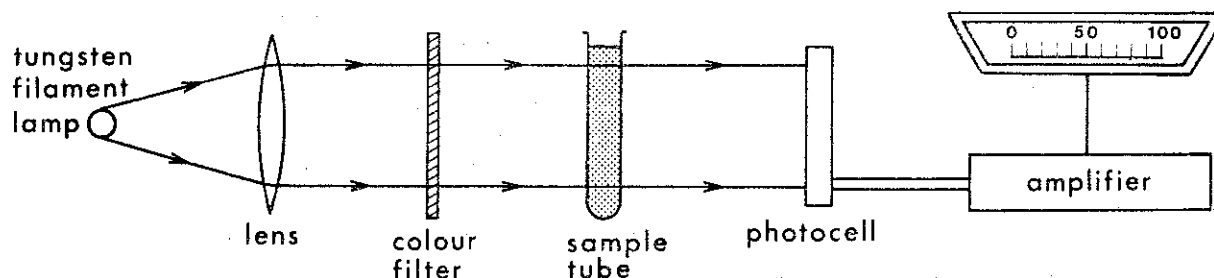


- (c) What criterion is employed in choosing a suitable indicator for the reaction in (b)? 1
- (d) If the titration in (b) were carried out using 0.1 M ammonia solution, the use of an indicator would not be suitable for determining the end-point. Why not? 1
- (e) Suggest an alternative technique for determining the end-point in (d). 1
- (7)

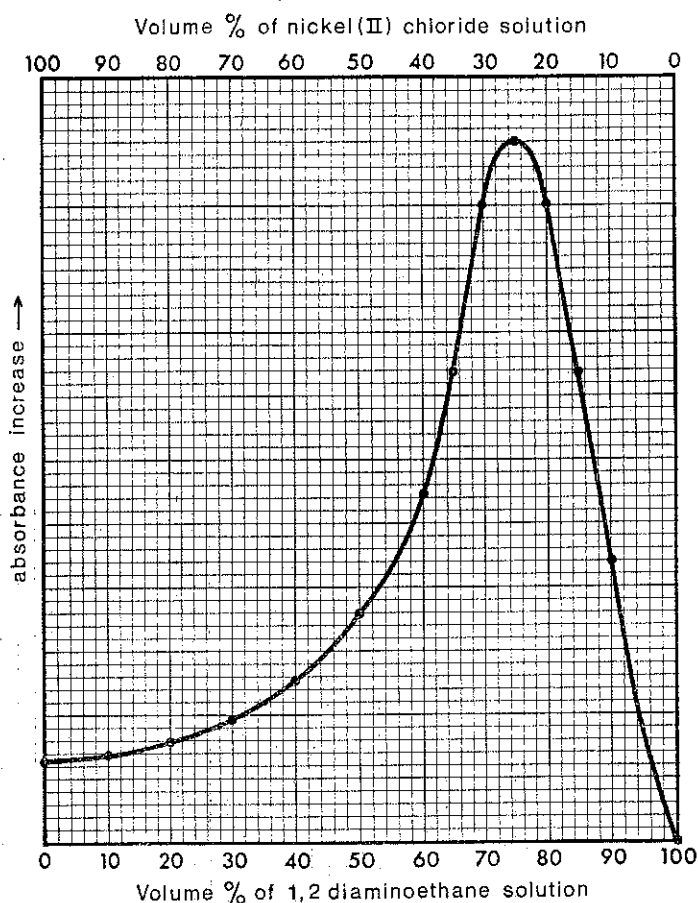
11. The following experiment was carried out to determine the formula of the purple complex formed between nickel(II) ions and 1,2-diaminoethane molecules, $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$.

Solutions of nickel(II) chloride and 1,2-diaminoethane of equal molarities were prepared. From these a range of solutions of equal volume was prepared containing different proportions of each. Each of the resulting solutions was then placed, in turn, in a colorimeter fitted with a filter which transmitted green light.

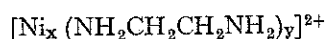
Diagrammatic section through a colorimeter



In this way the relative absorbance of each solution was determined and the following graph drawn.



- (a) The formula of the complex may be represented by



Examine the graph. What are the likely values of x and y?

Explain your reasoning briefly.

- (b) Suggest why 1,2-diaminoethane molecules should complex with Ni^{2+} ions.

- (c) Explain the use of the green-coloured filter in the colorimeter.

3

2

2

(7)

12. The visible spectra of rhodium(III) complexes resemble those of cobalt(III) complexes. There are, in general, two absorption bands towards the blue end of the visible spectrum which, together with any additional absorption in the blue region due to charge-transfer transitions, are responsible for the characteristic orange, red, yellow or brown colours of rhodium(III) compounds. All the rhodium(III) complexes are diamagnetic. This includes even the $[\text{RhF}_6]^{3-}$ ion.

—adapted from *Advanced Inorganic Chemistry* by Cotton and Wilkinson.

- (a) What is a charge-transfer transition? 1
- (b) What other type of transition (apart from charge-transfer) could give rise to the absorptions in the visible spectrum? 1
- (c) The rhodium(III) ion has six d electrons and its complexes are diamagnetic. Use the symbols

\square = a d-orbital

\uparrow or \downarrow = a d electron

- to indicate the arrangement of electrons within the d electron energy levels of a rhodium(III) octahedral complex which gives rise to this diamagnetism. 1
- (d) What does the lack of paramagnetism within these complexes indicate about the degree of splitting of the d electron energy levels? 1
- (e) Explain why paramagnetism would be more likely to occur where the ligand in the complex is F^- rather than CN^- . 3

(7)

[Turn over

13. In this question you are being asked to write an essay on *ONE* topic from a choice of three. Under each topic there are a number of sub-headings which may help you to answer the question. These sub-headings are suggestions only and are offered by way of general guidance. You should not regard them in any sense as being prescriptive, exhaustive or restrictive and they should not limit either the structure of your answer or the range of sub-topics which you consider related to your choice of main topic. You should also remember that the Data Book may be a useful source of information.

However, while you have freedom to decide what you are going to write, you are asked to pay particular attention in this question to the organisation and presentation of answers. Examiners will be scrutinising the essay to assess not only its scientific content but also its organisation and presentation of material. In this last connection the essential point is due regard for normal English usage.

- (a) Chemical equilibrium.

You might include in your essay reference to—
the establishment of equilibrium and the properties of an equilibrium system;
the mathematical approach to understanding equilibrium;
factors which influence the position of equilibrium.

OR

- (b) Family likenesses and disparities in the Group IV Elements.

You might include in your essay reference to—
physical properties of the elements;
chemical properties of the elements and their compounds;
formation of chain structures in compounds.

OR

- (c) A petrochemical plant for processing North Sea Oil.

It is proposed to construct such a plant in Scotland to process the ever-increasing quantities of oil which are expected to come ashore from North Sea oil fields in the future. It is suggested that the following might be discussed:

factors to be considered in siting such a plant;
the local environmental, economic and social implications of the plant;
the products of the plant and how they might be produced;
the impact of the plant on the national economy.

(10)

[END OF QUESTION PAPER]