

A Level

Chemistry

Session: 1974 June
Type: Question paper
Code: 866

CHEMISTRY

866/1

ADVANCED LEVEL

PAPER 1

(Two hours and a half)

|| *Mathematical tables and a data book are available.* ||

In this paper, relative atomic mass may be read as atomic weight and relative molecular mass as molecular weight.

All working must be shown.

PART I [45 marks]

You are recommended not to spend more than about 60 or 70 minutes on this part of the paper.

Attempt all the eight questions.

1 [8 marks] (a) Show on a labelled sketch the shapes and spatial distributions of all the orbitals of principal quantum number 2.

(b) How are the electrons distributed between these orbitals in an atom of nitrogen?

.....
(c) Sketch or describe the shape you would predict for the molecule of nitrogen trichloride (NCl_3).

(d) Explain your answer to (c) above

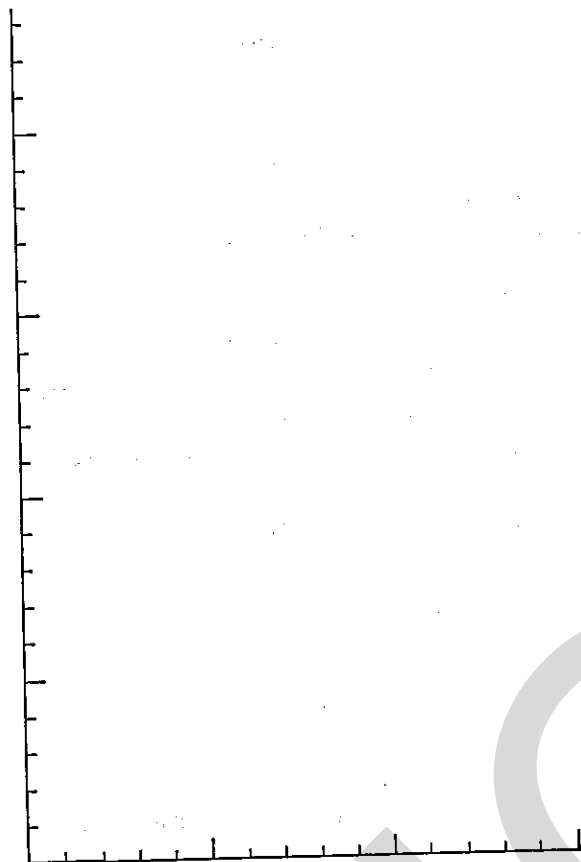
2 [4 marks] The following data refer to carbon dioxide.

	Critical point	Triple point
Temperature/ $^{\circ}\text{C}$	31	-57
Pressure/atm	73	5

Under 1 atm pressure, solid carbon dioxide sublimates at -78°C . The melting point of carbon dioxide increases by 20°C for an increase of 100 atm pressure.

(a) What is the melting point of carbon dioxide at 73 atm?

.....
(b) Construct a labelled pressure-temperature diagram (phase diagram) for carbon dioxide, with pressure on the y -axis and temperature on the x -axis.



3 [6 marks] A colloidal solution of arsenic(III) sulphide is prepared by the reaction between hydrogen sulphide (H_2S) and arsenic(III) oxide (As_2O_3). Particles of the colloid are negatively charged.

(a) Suggest a method of measuring the velocity of the particles in an electric field.

(b) Aqueous 0.01 M barium chloride (BaCl_2) is gradually added to the colloid. Deduce how the particle velocity measured in (a) will change.

4 [5 marks] (a) Write an expression for the solubility product of silver chloride, giving the units.

(b) At 25 °C, the solubility of silver chloride is 1.2×10^{-5} mol litre⁻¹. What is the solubility product of silver chloride at 25 °C?

Answer

(c) In a series of experiments, 50 cm³ of A (a solution of silver nitrate, AgNO_3) were added to 50 cm³ of B (0.1 M KCl). In each successive experiment, the concentration of A was increased. Calculate the concentration of A for which the first trace of silver chloride is precipitated on mixing A and B.

Answer

5 [5 marks] A quantity of electricity equal to the charge on one mole of electrons is passed through separate solutions of copper(II) sulphate and sulphuric acid.

(a) Calculate the masses of copper and hydrogen produced.

Copper: Hydrogen:

(b) Calculate a value for the Avogadro constant, L , given that 0.16 g of copper is deposited by the passage of a current of 0.50 A for 16 min.

Answer

6 [6 marks] The pure compound E (which is a red-brown powder), when treated with dilute sulphuric acid, gave a blue solution, leaving a pinkish residue. With nitric acid, E yielded a similar blue solution with no residue and evolved a brown gas.

(a) Give the name and formula of E

(b) Write a balanced equation for the reaction of E with

(i) dilute sulphuric acid,

(ii) nitric acid.

To the blue solution is added potassium tartrate and an excess of aqueous sodium hydroxide. When this mixture is warmed with acetaldehyde, E is again precipitated.

(c) Explain in words this sequence of reactions.

7 [5 marks] A compound G ($C_5H_{11}Br$), on heating with ethanolic sodium hydroxide, gave a mixture of two hydrocarbons (C_5H_{10}). Hydrolysis of G with dilute sodium hydroxide gave J ($C_5H_{12}O$) which was resistant to oxidation.

- Write a full structural formula for J.
- Write full structural formulae for the two hydrocarbons (C_5H_{10}).
- Write the full structural formula for G.

8 [6 marks] Write full structural formulae for the hydrocarbons L and M described below, giving your reasoning.

- L (C_4H_8), on ozonolysis, gives a compound C_3H_6O , which is resistant to oxidation.

(b) M (C_4H_8) gives an off-white precipitate on passing through a solution containing diamminesilver ions (Tollens' reagent).

PART II (54 marks)

Answer any six questions.

Each question carries nine marks.

9 (a) Sketch the line spectrum of hydrogen (Lyman series only, wavelength increasing from left to right).

- Explain the atomic processes that give rise to the lines in this spectrum.
- Explain how the spectrum can be used to determine the ionisation energy of hydrogen.
- The charge on the oxygen nucleus is eight times that on the hydrogen nucleus and yet the first ionisation energies of hydrogen and oxygen are almost identical ($\sim 1300 \text{ kJ mol}^{-1}$). Suggest reasons for this.

10 The water in a certain locality contains temporary hardness and freezes at -0.01°C .

- Identify a substance that might be responsible for causing the temporary hardness.
- Calculate the concentration (mol litre^{-1}) of this substance in the local water.
- Calculate the volume of 0.03 M sodium hydroxide required to precipitate all the temporary hardness in 1 litre of the local water.

[The freezing point depression constant for water, $K = 18.6^\circ\text{C}$ per 100 g of solvent.]

11 The graph (Fig. 1) shows the variation of the molar conductivity of aqueous solutions of sodium chloride and of acetic acid.

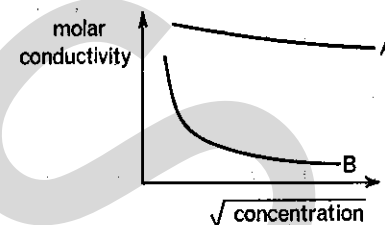


Fig. 1

- Which curve (A or B) refers to the sodium chloride solution?
- Copy the figure and, on your copy, insert a line appropriate to the behaviour of aqueous hydrochloric acid.
- Explain the shapes and relative positions of the three lines sketched in (b) above.

12 Fig. 2 illustrates the experimental arrangement of the cell

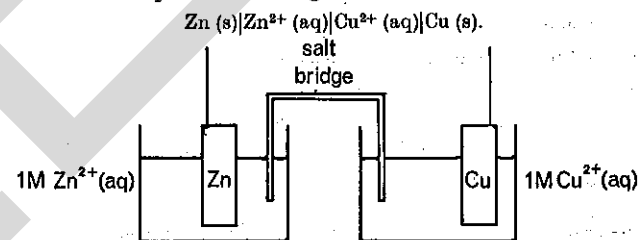


Fig. 2

The standard electrode potentials for the half cells are as follows:

	E^\ominus/V
$\text{Cu}^{2+}(\text{aq}) \text{Cu}(\text{s})$	+0.34
$\text{Zn}^{2+}(\text{aq}) \text{Zn}(\text{s})$	-0.77

(a) Write the equations for the half-cell reactions and calculate the e.m.f. of the cell under standard conditions.

The e.m.f. of the cell is measured whilst aqueous sodium hydroxide is run, with stirring, into the zinc half-cell. The variation of e.m.f. with volume of alkali is shown in Fig. 3.

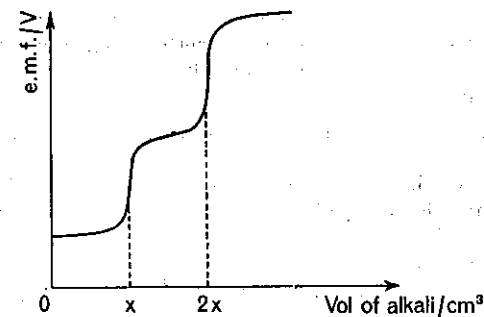


Fig. 3

- (b) Write balanced equations to describe the reactions occurring in the zinc half-cell.
- (c) Explain why the addition of aqueous sodium hydroxide causes a general increase in the e.m.f.
- (d) What do you think is the significance of the two volumes $x \text{ cm}^3$ and $2x \text{ cm}^3$ of aqueous alkali?

13 The following table shows the heat changes for a number of reactions.

Reaction	$\Delta H/\text{kJ mol}^{-1}$
$\text{Na (s)} + \frac{1}{2}\text{Cl}_2 \text{ (g)} \rightarrow \text{Na}^+\text{Cl}^- \text{ (s)}$	-411
$\text{Na (s)} \rightarrow \text{Na (g)}$	+109
$\text{Na (g)} \rightarrow \text{Na}^+ \text{ (g)} + \text{e}^-$	+494
$\frac{1}{2}\text{Cl}_2 \text{ (g)} \rightarrow \text{Cl (g)}$	+121
$\text{Cl (g)} + \text{e}^- \rightarrow \text{Cl}^- \text{ (g)}$	-364

(a) For which of the above reactions does the heat of reaction correspond to

- (i) a heat of atomisation,
 (ii) an ionisation energy?

(b) (i) Define, and (ii) calculate, the lattice energy of sodium chloride.

(c) The numerical values of the lattice energies of the other sodium halides are

Compound	NaF	NaBr	NaI
Lattice energy/ kJ mol^{-1}	899	719	670

Suggest a possible reason for this trend.

14 Write a balanced equation in each case for the reaction of hot concentrated sulphuric acid with each of the following, and name the products:

- (a) potassium nitrate, (c) potassium oxalate,
 (b) potassium bromide, (d) sulphur.

15 Two substances Q and R each have the elemental composition C = 60.0%; H = 13.3%; O = 26.7% (by mass).

0.60 g of each substance occupied a volume of 0.336 litre at 137 °C and standard pressure.

- (a) Calculate the empirical formula and the relative molecular mass of Q and R.
 (b) What is their molecular formula?

With sodium, Q was unreactive but R produced an inflammable gas. R also reacted with warm, acidified potassium dichromate, giving a product which, when isolated by distillation, gave a precipitate of silver with aqueous diamminesilver ions (Tollens' reagent).

(c) Identify Q and R.

(d) Write simplified equations for the reactions of R as described above.

16 An ester ($\text{C}_8\text{H}_{12}\text{O}_2$) was heated with aqueous sodium hydroxide until no more alkali was consumed and the solution then partly distilled. The distillate gave a positive iodoform reaction. The residue was neutralised with dilute nitric acid; addition of aqueous silver nitrate then precipitated a silver salt containing 59.7% of silver (by mass).

Draw the full structural formula for the ester, explaining your reasoning.

CHEMISTRY

866/2

ADVANCED LEVEL

PAPER 2

(Two hours and a half)

Answer five questions, including one question from each of the Sections A, B, and C.

Mathematical tables, a data book and squared paper are available.

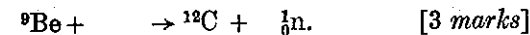
In this paper, relative molecular mass may be read as molecular weight and relative atomic mass as atomic weight.

SECTION A

1 Give the relative masses and charges of the three fundamental atomic particles. [6 marks]

Outline with the aid of one example the nature of isotopes. [6 marks]

Complete the following equation:



A sample of a radioactive substance gave 40 000 counts per second at time zero and 5 000 counts per second after 24 hours. What is the half-life of the decay? How long would it now take for the number of counts per second to fall to 1 250? [5 marks]

2 Explain, with the aid of suitable boiling-point/composition curves, what is meant by (a) fractional distillation, (b) azeotropic mixture. [11 marks]

From the following data, calculate the maximum mass of aniline ($\text{C}_6\text{H}_5\text{NH}_2$) that can be steam distilled using 1 000 g of steam, assuming an atmospheric pressure of 760 mm.Hg. What is the temperature of this steam distillation? [9 marks]

Temperature/°C	Vapour pressure/mmHg	
	Water	Aniline
92	567	28.3
94	611	30.8
96	658	33.5
98	707	36.4
100	760	39.5
102	815	42.8

3 Use the idea of an energy barrier to explain how and why the rate of a chemical reaction is affected by (a) a rise in temperature, (b) the presence of a heterogeneous catalyst.

[6 + 5 marks]

The gaseous equilibrium mixture present in a 1 litre vessel at a constant temperature was found to contain 0.50 mole of sulphur dioxide, 0.10 mole of oxygen, and 4.6 moles of sulphur trioxide. Calculate the equilibrium constant, K_c , at that temperature. How many moles of oxygen must be forced into the vessel at the same temperature in order to increase the amount of sulphur trioxide present at equilibrium to 4.7 moles?

[9 marks]

4 Describe the determination of the relative molecular mass of a gas by a method of direct weighing, e.g. Regnault's method.

[10 marks]

For a fixed mass of gas at a constant temperature, outline (a) the predicted effect of increasing pressure on the volume of an ideal gas, (b) the effect of increasing pressure on the volume of a real gas. Account for any differences.

[10 marks]

SECTION B

5 Outline the preparation of a pure sample of nitric oxide (NO).

[4 marks]

With the aid of diagrams, give the electronic structures of nitric oxide, nitrogen dioxide and dinitrogen tetroxide. Comment on any unusual features.

[8 marks]

How, and under what conditions, does nitric oxide react with (a) iron(II) sulphate, (b) copper, (c) potassium hydroxide,

(d) chlorine?

[8 marks]

6 Account for the variation in the radii of the following ions.

Ion	Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁻	P ³⁻	S ²⁻	Cl ⁻
Radius/nm	0.095	0.065	0.050	0.271	0.212	0.184	0.181

[6 marks]

What would you predict about the size of (a) the K⁺ ion, (b) the Si⁴⁺ ion? Give your reasons.

[4 marks]

The first four ionisation energies of one of the above elements are 576, 1810, 2740, and 11 600 kJ mole⁻¹ (138, 434, 656, and 2770 kcal mole⁻¹). Identify this element, giving your reasons. Why is there a greater difference between the first and second ionisation energies than between the second and third?

[4 marks]

Discuss the following solubilities (given in moles per 1000 g of water at 20 °C) in terms of the energy changes involved in dissolution.

[6 marks]

Salt	CaCl ₂	SrCl ₂	BaCl ₂
Solubility	6.73	3.39	1.73

7 How does the electronic structure of a transition element differ from the structure of elements in the main groups of the Periodic Table? Describe the electronic structure of either chromium (atomic number 24) or manganese (atomic number 25) and discuss briefly how the valency of the element is determined by this structure.

[8 marks]

Give three characteristic properties (other than that relating to valency) of transition metals or their compounds. Illustrate your answer by reference to either chromium or manganese.

[9 marks]

Give the full electronic structure of either the chromate ion or the permanganate ion.

[3 marks]

SECTION C

8 Give full structural formulae for the three carbonyl-containing compounds having the composition (by mass) C = 66.7%; H = 11.1%; O = 22.2% and a relative molecular mass of 72.

[7 marks]

What would you observe when each of these three compounds is treated separately with the following reagents

- aqueous 2,4-dinitrophenylhydrazine,
- iodine in aqueous alkali,
- a solution of silver oxide in aqueous ammonia?

Account for your observations. [13 marks]

9 Describe the preparation of a pure sample of diethyl ether starting from ethanol. [10 marks]

Diethyl ether is frequently used for the extraction of organic substances from aqueous solution. Give **three** properties of diethyl ether which make it particularly suitable for this task and **two** properties which make the operation potentially dangerous. [5 marks]

How, and under what conditions, does diethyl ether react with (i) hydrogen iodide, (ii) concentrated sulphuric acid? [5 marks]

10 Identify the compounds A–D, explaining your reasoning and accounting for the observations.

(i) A, C_8H_9NO , is neutral. Hydrolysis with concentrated aqueous sodium hydroxide gives a solution of a salt, $C_2H_3O_2Na$, and a compound, C_6H_7N , which gives a violet colour with aqueous bleaching powder and with aqueous bromine forms a compound $C_6H_4Br_3N$.

(ii) B, C_2H_5NO , is neutral. With cold aqueous alkali there is no reaction but, on refluxing, ammonia is slowly evolved.

(iii) C, C_7H_7Cl , on refluxing with aqueous potassium permanganate, filtration, and acidification of the filtrate, gives a compound $C_7H_6O_2$.

(iv) D, $C_3H_3NO_2$, is acidic. On refluxing with aqueous alkali, ammonia is slowly liberated. [4 × 5 marks]

(Two hours and a half)

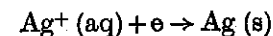
Answer five questions, of which not more than two may be selected from one section.

The answers to questions in Sections A, B and C are to be given up separately.

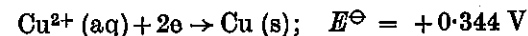
Mathematical tables, a data book and squared paper are available.

SECTION A

1 Explain what is meant by the statement that the standard electrode potential, E^\ominus , for the silver electrode



is +0.799 V at 25 °C. Give the cell reaction and the standard cell potential for a cell formed from standard silver and copper electrodes



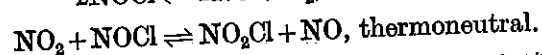
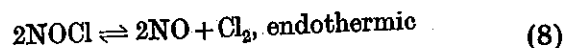
with the electrolytes separated by a porous barrier. How will a decrease in the silver ion concentration affect the cell potential? (11)

The electrolysis of a solution containing a silver salt gave silver and hydrogen at the cathode in the ratio by moles of 4:1 at a current density of 0.012 A cm⁻². What cathode area will be necessary to deposit silver at the rate of 0.01 mol min⁻¹ under these conditions? (9)

2 Comment *critically* on the following arguments.

(a) If two homogeneous mixtures of liquid M with liquid N have different compositions but have the same boiling point (at the same pressure), they must give equilibrium vapours of identical composition. (5)

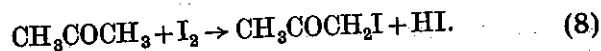
(b) When nitrosyl chloride, NOCl, and nitrogen dioxide, NO₂, interact at moderate temperatures, the only significant equilibria are those shown below.



It can therefore be concluded that the ratio $[\text{NO}_2]/[\text{NO}_2\text{Cl}]$ will not vary as the temperature changes.

(c) The presence of a dipole in a molecule has little effect on the intermolecular force because, on average, the interaction between a pair of molecules is as likely to be repulsive as attractive. (7)

3 Define *order of reaction* and explain briefly how it might be determined for the acid-catalysed reaction between acetone and iodine in aqueous solution:



In glass vessels, nitric acid vapour decomposes by reaction on the glass and by a gas-phase reaction. With the information given below, show how the ratio of the gas-phase rate/surface rate will change for an increase in (i) the temperature, (ii) the partial pressure of HNO_3 , and (iii) the volume of a spherical reaction vessel.

Surface reaction: zero order, low activation energy

Gas-phase reaction: first order, high activation energy. (6)

The rate of decomposition of NH_3 on a Pt catalyst at a high temperature depends on the partial pressures of NH_3 and H_2 present in the manner shown below. Deduce the orders of reaction with respect to NH_3 and to H_2 and comment on the result.

Partial pressure of NH_3/mmHg	100	160	100
Partial pressure of H_2/mmHg	50	50	75
Reaction rate/ mmHg min^{-1}	0.072	0.115	0.048

 (6)

SECTION B

4 The atomic number of the element vanadium, V, is 23. Certain features of the chemistry of this element are presented in Fig. 1. Consider the diagram carefully and then give

brief answers to the questions that follow.

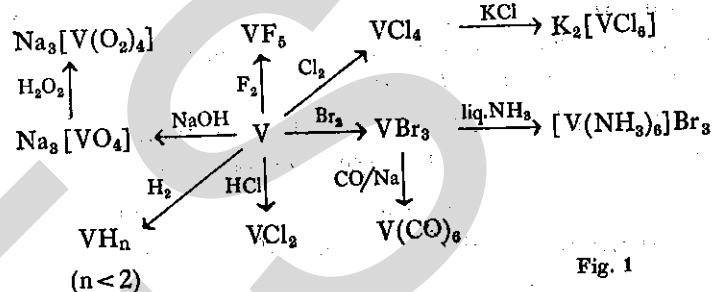


Fig. 1

- (a) Deduce the electronic configuration of vanadium. (1)
- (b) Suggest why the compound VBr_3 is paramagnetic but the vanadate ion in Na_3VO_4 is not. (2)
- (c) How many integral oxidation states of vanadium are represented in Fig. 1? (1)
- (d) Account for the fact that the compound VF_5 is colourless whereas VCl_2 is green. (2)
- (e) Suggest a reason why the colours of the compounds VCl_4 , VBr_3 and VCl_2 differ. (2)
- (f) What do you deduce about the oxidising power of the halogens towards vanadium? (2)
- (g) Compare the action of chlorine on vanadium with that of hydrogen chloride. (2)
- (h) Does VCl_4 react as an acid or as a base with potassium chloride? Explain your answer. (2)
- (i) List four features of vanadium as shown in Fig. 1 that are **not** also shown by arsenic (atomic number 33). Give a reason why a comparison of vanadium with arsenic might be considered appropriate. (4)
- (j) Explain what is meant by the *co-ordination number* of an element, illustrating your answer by reference to vanadium. (4)

5 The table below contains information concerning the elements beryllium, calcium and barium as follows:

- (i) M ; the atomic symbol,
- (ii) $\Delta H_A/\text{kJ mol}^{-1}$; ΔH_A , the heat of atomisation, is the

energy change associated with the process $M(s) \rightarrow M(g)$,

(iii) $\Delta H_I/\text{kJ mol}^{-1}$; ΔH_I , the heat of ionisation, is the energy change associated with the formation of the dipositive ion $M(g) \rightarrow M^{2+}(g)$,

(iv) $\Delta H_H/\text{kJ mol}^{-1}$; ΔH_H , the heat of hydration, is the energy change associated with the process $M^{2+}(g) \rightarrow M^{2+}(aq)$,

(v) m.p./K; the melting point of the dihalide, MCl_2 ,

(vi) r/pm ; the radius of the dipositive ion, M^{2+} .

[N.B. $1 \text{ pm} = 10^{-12} \text{ m}$.]

M	ΔH_A	ΔH_I	ΔH_H	m.p.	r
Be	+322	+2657	-2455	678	31
Ca	+177	+1736	-1565	1055	99
Ba	+176	+1467	-1275	1235	135

Consider the information carefully and then answer the following questions.

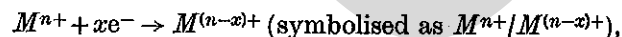
(a) Estimate ΔH_F , the heat of formation, of each divalent ion $M^{2+}(aq)$ from the solid metal $M(s)$. (7)

(b) Suggest an explanation of the variation in the melting points of the dihalides and compare the values shown for BeCl_2 and BaCl_2 with those for LiCl (879 K) and CsCl (911 K) respectively. (3)

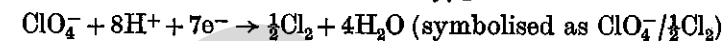
(c) Explain why, with reference to aqueous solutions, you would expect beryllium to be a weaker reducing agent than calcium. (3)

(d) Beryllium sulphate is highly soluble in water, calcium sulphate is soluble in excess dilute sulphuric acid but barium sulphate is almost completely insoluble under all conditions. How do you account for these observations? (2)

6 In the table below, E_A^\ominus and E_B^\ominus are standard electrode potentials for aqueous solutions 1.0 M with respect to HCl and NaOH respectively: they are the potentials for the reactions



where, for example, the reaction



is defined as having a large, positive potential.

E_A^\ominus/V		E_B^\ominus/V	
$\text{NO}_3^-/\frac{1}{2}\text{N}_2$	+1.2	$\text{NO}_3^-/\frac{1}{2}\text{N}_2$	+0.9
$\frac{1}{2}\text{N}_2/\text{NH}_4^+$	+0.3	$\frac{1}{2}\text{N}_2/\text{NH}_3$	+0.1
$\text{PO}_4^{3-}/\frac{1}{4}\text{P}_4$	-0.4	$\text{PO}_4^{3-}/\frac{1}{4}\text{P}_4$	-1.5
$\frac{1}{4}\text{P}_4/\text{PH}_3$	-0.1	$\frac{1}{4}\text{P}_4/\text{PH}_3$	-0.3

Use this information, where appropriate, to give brief answers to the following questions.

(a) What is the effect of alkaline media on the stability of (i) the nitrate ion, (ii) the phosphate ion? (3)

(b) Would you describe as oxidising or reducing agents (i) phosphine in acid, (ii) phosphorus in alkali, (iii) nitrate ion in acid? Explain your answers. (6)

(c) Compare the action of acid upon ammonia with that upon phosphine. How do you account for the difference? (4)

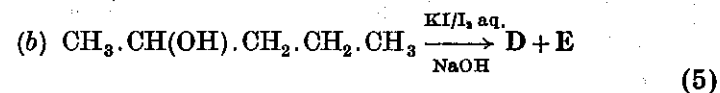
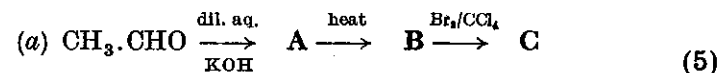
(d) The data suggest that nitrogen is thermodynamically unstable with respect to the NH_4^+ ion in acid solution. Suggest a reason why this conversion does not occur at all readily. (2)

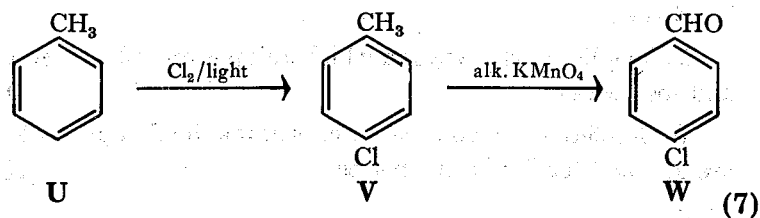
(e) Compare the stability of the +5 oxidation state of nitrogen with that of phosphorus. Account for the difference. (3)

(f) Suggest a reason why phosphorus does not form an ion PO_3^- (analogous to NO_3^-) but instead forms the ion PO_4^{3-} . (2)

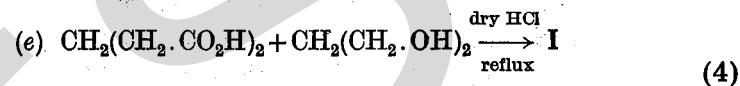
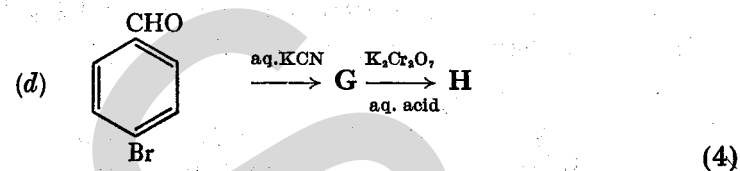
SECTION C

7 Give the formulae of the products A–I you would expect to be formed in each of the reactions indicated below, and write the equation for each reaction.





Formulate a more efficient route **either** for obtaining **T** from **R** or for obtaining **W** from **U**. (6)



8 Dehydration of the straight-chain pentanols **L**, **M** and **N** can give the C_5H_{10} isomers **O**, **P**, and **Q** as shown below.

Alcohol **L** gives **O** and **P**.

Alcohol **M** gives **O**, **P**, and **Q**.

Alcohol **N** gives **Q** alone.

Identify the alcohols and compounds **O**, **P**, and **Q**, and write their structural formulae. (6)

Show how far treatment of **O**, **P**, and **Q** with ozone and cleavage of the ozonides (ozonolysis) would allow identification of these compounds. (6)

Explain clearly in terms of hybrid orbitals how the isomerism of **O** and **P** arises, and suggest how they might be distinguished. (5)

What other type of isomerism is displayed by alcohol **M**?

What effect, if any, does this form of isomerism have on the dehydration reaction? (3)

9 Consider each step of the conversions **R** \rightarrow **T** and **U** \rightarrow **W** below. State for each step whether the reagents and conditions given will bring about the indicated conversion and, if not, what the product will be. Modify the reagents or conditions if this will allow the step to be accomplished.

