

[92/291]

1979

CERTIFICATE OF SIXTH YEAR STUDIES

# CHEMISTRY

PAPER

Thursday, 10th May—9.30 a.m. to 12.30 p.m.



Dalziel High School



Chemistry Department

# 1979 CSYS

1. In some areas drinking water is deliberately over-chlorinated to make sure of killing bacteria. Sulphur dioxide is then added to remove excess chlorine. The latter reaction can be described as

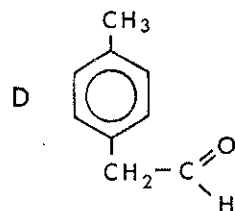
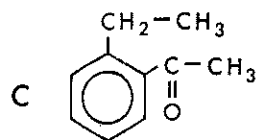
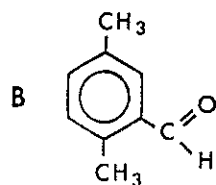
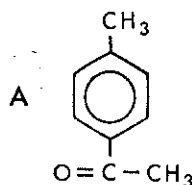
- A neutralisation
- B hydrolysis
- C dehydration
- D redox

2. In a mass spectrum which of the following could give a line at the same place as  $[^{12}\text{C}^1\text{H}_4]^+$ ?

- A  $[^{14}\text{N}_2]^+$
- B  $[^{14}\text{N}^1\text{H}_2]^{2+}$
- C  $[^{28}\text{Si}^1\text{H}_4]^{2+}$
- D  $[^7\text{Li}^1\text{H}]^{2+}$

3. Spectral studies of an organic compound indicated the presence of a di-substituted benzene ring, two methyl groups and a molecular weight of 134.

Which of the following is a possible structure for the compound?



4. Which of the following most nearly represents the quantity of electricity needed to deposit 50 g of aluminium?

- A 2 F
- B 3 F
- C 5 F
- D 6 F

5. The electron distributions, X and Y, for two uncharged atoms of sodium are as follows:



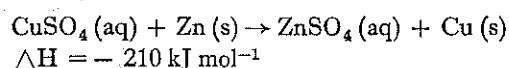
Which of the following statements is true?

- A Energy is absorbed in changing Y to X.
- B Atom Y will ionise more readily than X.
- C Atom X is in an excited state.
- D Both atoms have vacant 2d orbitals.

6. 32 g sulphur was converted to sulphur trioxide and then into the corresponding amount of sulphuric acid. The mass of sodium hydroxide required to neutralise the acid would be

- A 64 g
- B 80 g
- C 128 g
- D 160 g.

7. Consider the reaction



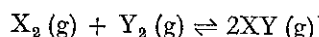
The heat evolved in kJ when 0.2 mole zinc is added to 300 ml M  $\text{CuSO}_4(\text{aq})$  is

- A -105
- B -63
- C -42
- D -21.

8. Which one of the following nuclear species is formed by the loss of one  $\beta$ -particle from  $^{82}\text{Br}$ ?

- A  $^{81}\text{Kr}$
- B  $^{82}\text{Br}$
- C  $^{82}\text{Se}$
- D  $^{82}\text{Kr}$

9. Consider the equilibrium



For the reaction from left to right  $\Delta H = -x$  kJ

As the temperature of the mixture is increased which of the following statements will be true?

- A The rate of the reverse reaction will be increased by more than the rate of the forward reaction.
- B The rate of the forward reaction will be increased by more than the rate of the reverse reaction.
- C The rates of both forward and reverse reactions will be increased by the same amount.
- D No prediction is possible about relative increases in rates of forward and reverse reactions.

10. Which of the following are listed in order of increasing wavelength?

- A radio; gamma; yellow; I.R.
- B X-rays; green; U.V.; radio.
- C gamma; I.R.; U.V.; radio.
- D X-rays; blue; orange; radio.

11. Which of the following contains approximately  $1.8 \times 10^{24}$  ions? One mole of the chloride of

- A rubidium
- B strontium
- C aluminium
- D sulphur.

12. For a cell in which the following reaction occurs

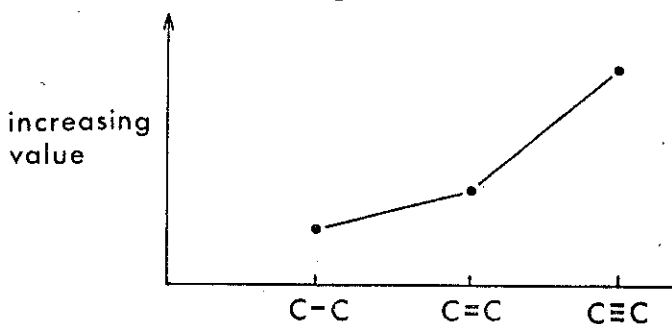


the  $E^\circ$  value is 1.5 V.

The  $\Delta G^\circ$  for the reaction is

- A + 289.5 kJ
- B + 144.8 kJ
- C - 144.8 kJ
- D - 289.5 kJ (F = 96 500 coulombs)

13. Which property of the three chemical bonds is represented by the diagram?



- A Bond strength
- B Bond polarity
- C Bond length
- D Ease of rotation about the bond

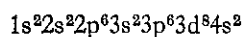
14. Which one of the following reactions **must** be exothermic?

- A One in which  $\Delta G$  is negative
- B One in which  $\Delta S$  is positive
- C One in which both  $\Delta G$  and  $\Delta S$  are negative
- D One in which both  $\Delta G$  and  $\Delta S$  are positive

15. Which of the following could **not** exist in isomeric forms?

- A  $\text{C}_3\text{H}_6$
- B  $\text{C}_3\text{H}_7\text{Br}$
- C  $\text{C}_2\text{H}_4\text{Cl}_2$
- D  $\text{C}_3\text{H}_8$

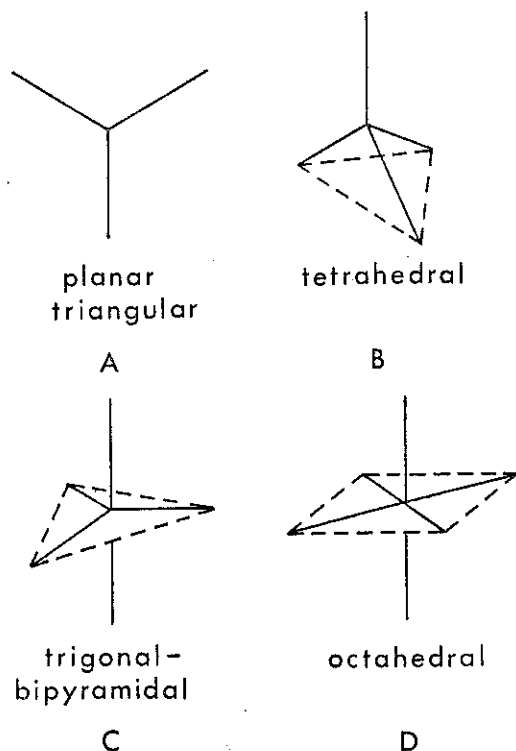
16. A nickel atom has the electronic configuration



The number of unpaired electrons in a gaseous  $Ni^{2+}$  ion is

- A 0  
 B 1  
 C 3  
 D 5.
17. Successive additions of 5 ml of a 0.1 M solution of the chloride of a metal X were made to 20 ml of a 0.1 M solution of phosphoric acid. After the sixth addition no further precipitate was formed. The formula of the chloride was
- A  $XCl$   
 B  $XCl_2$   
 C  $XCl_3$   
 D impossible to determine from the data given.

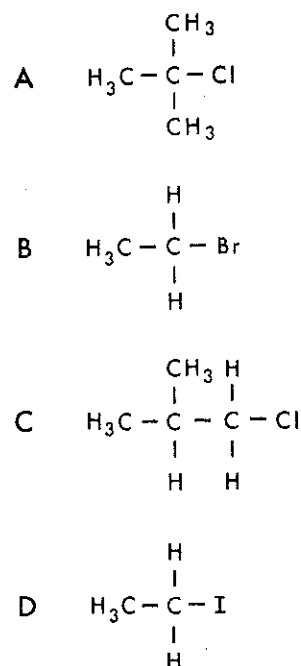
Questions 18 and 19 refer to the following lettered headings which indicate different arrangements of electron pairs.



Which arrangement will be found in the following molecules? Note: A letter may be used more than once.

18.  $IF_5$   
 19.  $SiH_3^+$

20. Which of the following molecules is most likely to hydrolyse to the alcohol via a  $S_N1$  mechanism?



21. A white crystalline compound, soluble in water, was found to react with both dilute hydrochloric acid and sodium hydroxide solution. Which of the following might it have been?
- A  $C_6H_5NH_2$   
 B  $CH_2NH_2COOH$   
 C  $C_2H_5NH_2$   
 D  $C_2H_5NH_3Cl$
22. Excess zinc is added to 50 ml of each of the following acids. When each reaction is complete which would be expected to release the **least** amount of hydrogen?
- A 1 M hydrochloric acid  
 B 2 M oxalic acid  
 C 1 M sulphuric acid  
 D 2 M ethanoic acid
23. Assuming complete dissociation an aqueous solution of sulphuric acid with  $pH = 1$  has a molarity of
- A 0.05  
 B 0.1  
 C 0.5  
 D 1.0.

24. Which of the following aqueous solutions has the lowest pH?

- A 1 M CH<sub>3</sub>COOH
- B 0.1 M CH<sub>3</sub>COOH
- C 1 M CH<sub>2</sub>ClCOOH
- D 0.1 M CH<sub>2</sub>ClCOOH

25. For water

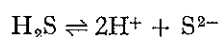
$$K_w = \frac{[H^+][OH^-]}{[H_2O]}$$

The magnitude of  $K_w$  is temperature dependent.

Which of the following is a correct deduction about the effect of temperature change on water?

- A The concentrations of H<sup>+</sup> and OH<sup>-</sup> remain equal and the pH remains 7.
- B The concentrations of H<sup>+</sup> and OH<sup>-</sup> can be unequal but the pH remains 7.
- C The concentrations of H<sup>+</sup> and OH<sup>-</sup> can be unequal and the pH can differ.
- D The concentrations of H<sup>+</sup> and OH<sup>-</sup> remain equal but the pH can differ.

26. Hydrogen sulphide gas ionises only slightly in aqueous solution:



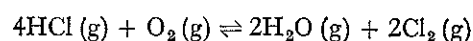
If the gas is added to a solution of Zn<sup>2+</sup> ions, zinc sulphide is only precipitated if the concentration of S<sup>2-</sup> ions is above a certain value. Which of the following added substances would raise the concentration of these ions in a solution of H<sub>2</sub>S gas?

- A Sodium chloride
- B Sodium ethanoate
- C Sodium sulphate
- D Sodium nitrate

27. Propanone and ethyl magnesium iodide, when allowed to react together, give a product which, on hydrolysis, yields

- A 2-methylbutan-1-ol
- B 2-methylbutan-2-ol
- C 2-methylbutan-3-ol
- D 2-methylbutan-4-ol.

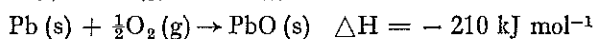
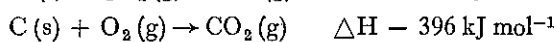
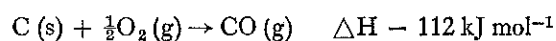
28. Under certain conditions chlorine may be obtained by the reaction



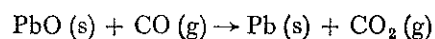
For the reaction of HCl with O<sub>2</sub> the enthalpy change is negative. Which of the following operations will increase the equilibrium concentration of chlorine?

- A Heating the reaction vessel
- B Decreasing the total pressure
- C Increasing the concentration of oxygen
- D Adding a manganese catalyst

29. The following heats of reaction are known:



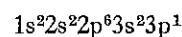
$\Delta H$  for the reaction



is

- A -74 kJ mol<sup>-1</sup> ×
- B -435 kJ mol<sup>-1</sup>
- C -494 kJ mol<sup>-1</sup>
- D -718 kJ mol<sup>-1</sup>.

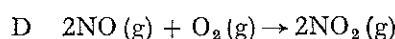
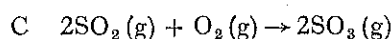
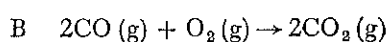
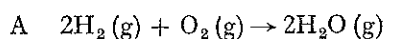
30. An atom has the electronic configuration



What is the charge on the most probable aqueous ion formed by this element?

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

31. Which of the following reactions has the lowest activation energy?



32. Which one of the following metal ions has the **fewest** unpaired electrons in its **high spin** octahedral compounds?
- A  $\text{Cr}^{3+}$   
 B  $\text{Co}^{2+}$   
 C  $\text{V}^{3+}$   
 D  $\text{Mn}^{2+}$
33. In each of the following compounds carbon is bonded directly to the element which is underlined in the formula. In which compound is the bond polarised so that carbon has a partial **negative** charge?
- A  $\text{C}_2\text{H}_5\text{Br}$   
 B  $\text{CH}_3\text{CHO}$   
 C  $\text{H}_3\text{SiCH}_3$   
 D  $\text{CH}_3\text{CN}$
34. What volume of water would require to be added to 100 ml of 0.2 M  $\text{H}_3\text{PO}_4$  to produce a solution with  $\text{H}^+$  concentration of 0.1 M? (Assume complete dissociation.)
- A 100 ml  
 B 200 ml  
 C 500 ml  
 D 600 ml
35. When a Tutton salt, general formula  $\text{M}(\text{H}_2\text{O})_6\text{K}_2(\text{SO}_4)_2$ , is dissolved in water the solution contains the ions  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{K}^+$  and  $\text{SO}_4^{2-}$ .  
 The relative concentrations of  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{K}^+$  and  $\text{SO}_4^{2-}$  in dilute solution are respectively
- A 1 : 1 : 1  
 B 2 : 1 : 2  
 C 1 : 2 : 2  
 D 6 : 2 : 2.
36. Two identical bottles, X and Y, contain respectively 5 g of neon and 5 g of argon at the same temperature.  
 Relative atomic masses: Ne = 20; Ar = 40  
 The number of atoms of gas in bottle Y
- A is equal to the number of atoms of gas in bottle X  
 B is twice the number of atoms of gas in bottle X  
 C is one half the number of atoms of gas in bottle X  
 D cannot be related to the number in X from the information given.
37. In the equilibrium system  $\text{W} + \text{X} \rightleftharpoons \text{Y} + \text{Z}$ , the value of the equilibrium constant was 9. The initial concentrations of W and X were each 1 mole litre<sup>-1</sup>.  
 At equilibrium the concentration of X in mol l<sup>-1</sup> was
- A 0.25  
 B 0.75  
 C 3.0  
 D 9.0.
38. Which one of the following compounds is **least** likely to act as a ligand towards a transition metal ion?
- A  $(\text{CH}_3)_2\text{O}$   
 B  $(\text{CH}_3)_2\text{S}$   
 C  $(\text{CH}_3)_3\text{P}$   
 D  $(\text{CH}_3)_4\text{Si}$
39. In a complex chemical reaction the rate determining step is always
- A the last step  
 B the fastest step  
 C the first step  
 D the slowest step.

40. The heats of combustion of the following compounds are:-

Compound	Heat of Combustion $\text{kJ mol}^{-1}$
propane	2200
propan-1-ol	2000
propan-2-ol	1980

The Heat of Combustion of propanone will probably be

- A greater than all the above three  
 B between that of propane and that of propan-1-ol  
 C between that of propan-1-ol and propan-2-ol  
 D less than any of the above three.
41. Animal manure and calcium hydroxide should never be applied to soil simultaneously because
- A the soil would become too acidic for plants to grow  
 B the soil would become too alkaline for the plants to grow  
 C an insoluble calcium compound would form depriving the plants of calcium  
 D a gaseous compound of nitrogen would be formed depriving the plants of some nitrogen.
42. Dilute sulphuric acid is electrolysed using platinum electrodes.
- What volume of gas at s.t.p. is produced at the positive electrode after the passage of one Faraday of electricity?
- A 5.6 litres  
 B 11.2 litres  
 C 22.4 litres  
 D 44.8 litres

43. An ester on hydrolysis yields two compounds X and Y. X is neutral and has a mole weight of 60. Y is an acid and has a mole weight of 60. The ester has the formula

- A  $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$   
 B  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$   
 C  $\text{CH}_3\text{COOCH}_2\text{CH}_3$   
 D  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$

44. Four sets of atoms and ions with formal charges are listed below. Which set consists of atoms and ions each with the same number of electrons in the outer shell?

- A B,  $\text{C}^{2-}$ ,  $\text{N}^-$ , O,  $\text{F}^+$   
 B  $\text{B}^{3-}$ ,  $\text{C}^{2-}$ ,  $\text{N}^-$ , O,  $\text{F}^+$   
 C  $\text{B}^{3-}$ ,  $\text{C}^{2-}$ ,  $\text{N}^-$ , O,  $\text{F}^-$   
 D  $\text{B}^{3-}$ ,  $\text{C}^{2-}$ ,  $\text{N}^-$ ,  $\text{O}^-$ ,  $\text{F}^+$

45. Which one of the following is the most alkaline in 0.1 M aqueous solution?

- A KCl  
 B  $\text{CH}_3\text{COOK}$   
 C  $\text{NH}_4\text{Cl}$   
 D  $\text{CH}_3\text{COONH}_4$

To answer questions 46 to 50 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.

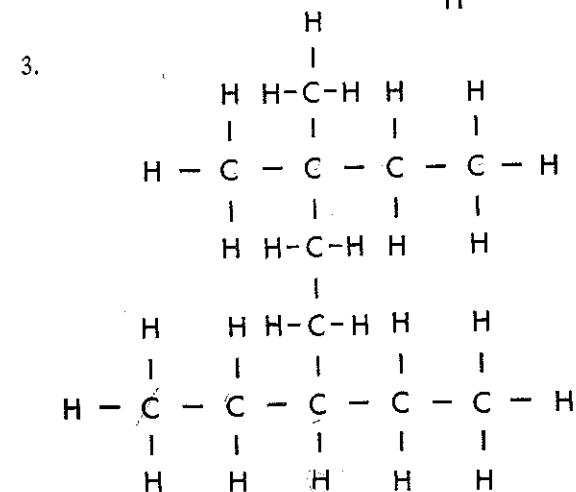
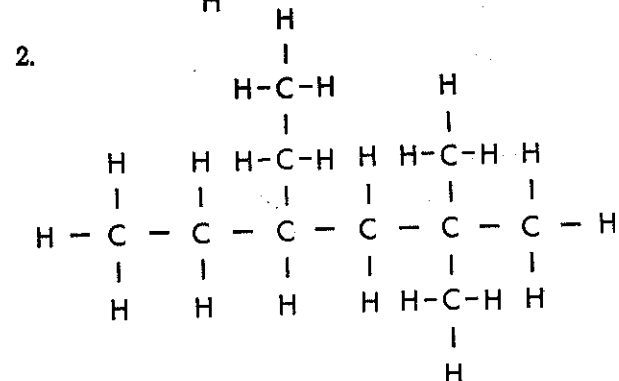
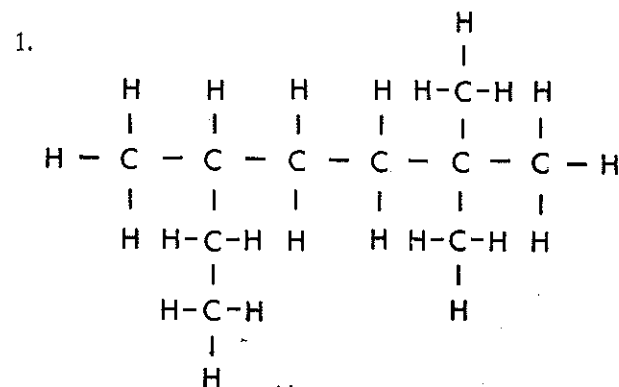
If only 3 is correct, select C.

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

46. Which are true statements?

- $C_6H_5OH$  is a stronger acid than  $CH_3OH$ .
- $C_6H_5NH_2$  is a stronger base than  $C_6H_5OH$ .
- $C_6H_5NH_2$  is a stronger base than  $CH_3NH_2$ .

47. The following structural formula(e) may represent 4-ethyl-2,2-dimethylhexane:-



48. The table on page 30 of the Data Book should be used in connection with this question.

- In equimolar solutions, sulphur dioxide is a more powerful reducing agent than  $Sn^{2+}(aq)$ .
- Copper metal will dissolve in a molar solution of  $Fe^{3+}(aq)$ .
- The permanganate ion  $[MnO_4^-](aq)$  is a more powerful oxidising agent than  $Fe^{3+}(aq)$ .

49. Consider the following information regarding dissociation constants,  $K_a$ .

Ethanoic acid	$1.8 \times 10^{-5}$
Chloroethanoic acid	$1.4 \times 10^{-3}$
Bromoethanoic acid	$2.1 \times 10^{-3}$

Which of the following is/are correct?

- The introduction of chlorine/bromine into ethanoic acid molecules makes the acid stronger.
- Assuming that the number of ions is the main factor, ethanoic acid is the poorest conductor of electricity when molar solutions of the three acids are compared.
- The pH values of molar solutions of these acids lie between 3 and 6.

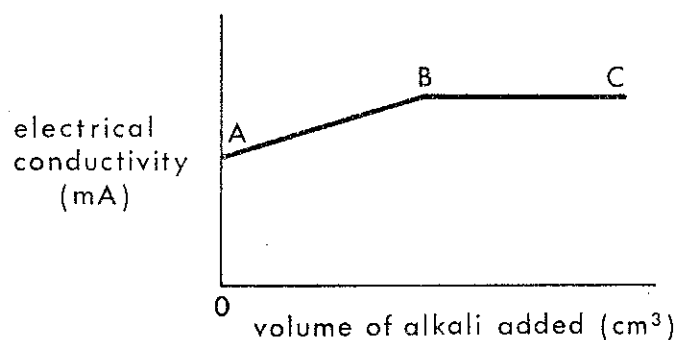
50. The energy of the radiation absorbed to produce a peak in the I.R. spectrum of a compound is related to which of the following?

- The height of the peak.
- The wavelength of the radiation.
- The wave number of the radiation.

[END OF QUESTION PAPER]



1. (a) Explain what is meant by the statement  
 "The ionic product for water at 25 °C is  $10^{-14} \text{ mol}^2 \text{ l}^{-2}$ " (1)
- (b) Calculate the pH of a solution of 0.01 M potassium hydroxide. (2)
- (c) In an experiment, 50 cm<sup>3</sup> of 0.1 M hydrochloric acid is added to 50 cm<sup>3</sup> of 0.05 M potassium hydroxide solution. What is the pH of the resulting solution? (4)
- (d)



The graph shows the changes in current occurring as a solution of ammonia is added to a solution of ethanoic acid.

- (i) Which ions are present in the solution at A? (1)
- (ii) Explain why the current rises from A to B. (5)
- (iii) Beyond B, excess ammonia solution is being added and yet the current does not rise. Explain why this is so. (3)
- (e) (i) Draw a graph showing the changes in pH occurring during a titration such as in (d). (2)
- (ii) Mark on the graph the end-point of the reaction. (1)
- (iii) Why is it difficult to follow this reaction using an indicator? (1)

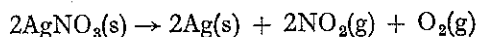
[Turn over

- Marks*
2. (a) What is meant by the term "electrophile" or "electrophilic reagent"? (1)
- (b) Why are such reagents attracted to the double bond of an alkene? (1)
- (c) A bromine molecule can be said to split "homolytically" or "heterolytically". What exactly is meant by these terms? (2)
- (d) If an alkene such as propene is allowed to react with bromine dissolved in a saturated solution of sodium chloride, several products can be identified. Write equations for a possible mechanism for this reaction and so suggest what the structural formulae of these products might be. (5)
- (e) A Grignard reagent can be made by treating bromoethane with magnesium turnings under strictly anhydrous conditions. Write an equation to represent this reaction. (1)
- (f) What effect does the formation of this compound have on the carbon atom adjacent to the magnesium? (1)
- (g) What product would form if
- (i) moisture came in contact with this Grignard reagent; (1)
- (ii) the reagent was made to react with methanal? (3)
- (h) One way of keeping the ether dry for this reaction is to store it over a molecular sieve. This is a three dimensional silicate structure. Suggest an industrial use made of such substances. (2)
- (i) Consider the following bond energies:

<i>Bond</i>	<i>Energy (kJ mol<sup>-1</sup>)</i>
C-C	337
C-H	414
C-O	331
Si-Si	200
Si-H	319
Si-O	454

Comment on the possible connection between these bond energies and the occurrence and stability of various naturally occurring compounds of silicon and of carbon. (3)

3. (a) Silver nitrate can be made to decompose, according to the following equation, by being heated.

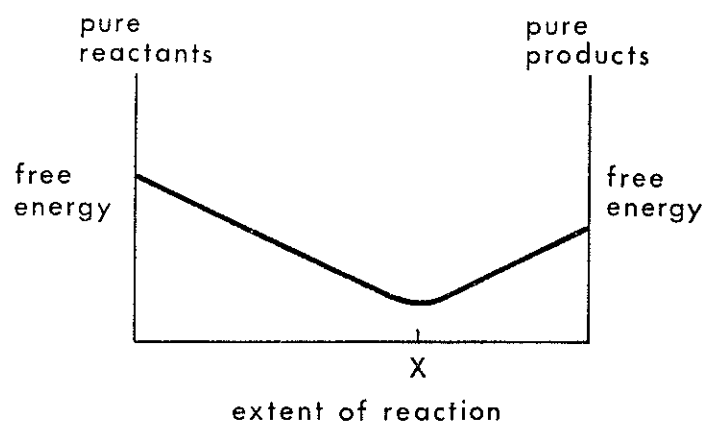


- (i) For what values of free energy change ( $\Delta G$ ) will this reaction occur spontaneously? (1)  
 (ii) From the table of values given below, calculate the minimum temperature at which the decomposition of silver nitrate will take place spontaneously.

Substance	Standard Heat of Formation $\Delta H_f$ (kJ mol <sup>-1</sup> )	Standard Entropy S (J K <sup>-1</sup> mol <sup>-1</sup> )
AgNO <sub>3</sub>	-123.6	141.5
Ag	0	42.9
NO <sub>2</sub>	33.98	241.4
O <sub>2</sub>	0	205.8

(6)

(b)



If, as in the above graph, the free energy of a mixture of reactants and products of a given reaction is plotted against their composition in the mixture, the graph shows a minimum at X.

What information can be deduced from the position of X? (2)

- (c) (i) A 100-litre container at 600 K contains at equilibrium  $2.5 \times 10^{-2}$  moles of ammonia gas and 1.00 mole each of nitrogen gas and hydrogen gas.

Calculate the numerical value of K, the equilibrium constant. (5)

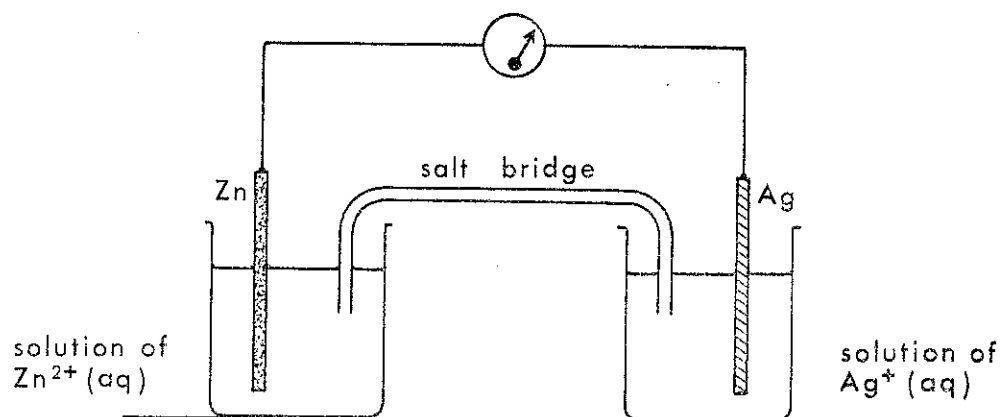
- (ii) The effect of increasing the pressure in the reaction producing ammonia gas is to give an equilibrium mixture containing a relatively higher proportion of ammonia. Explain why an increase in pressure does not produce a similar increase in the yield of hydrogen iodide vapour from hydrogen and iodine vapour. (4)

- (iii) The yield of ammonia from nitrogen and hydrogen is greater at lower rather than higher temperatures. What can you deduce about the change in heat content occurring in the forward reaction? (2)

[Turn over

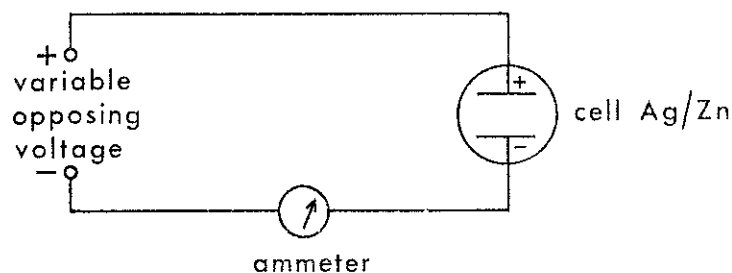
Marks  
(2)

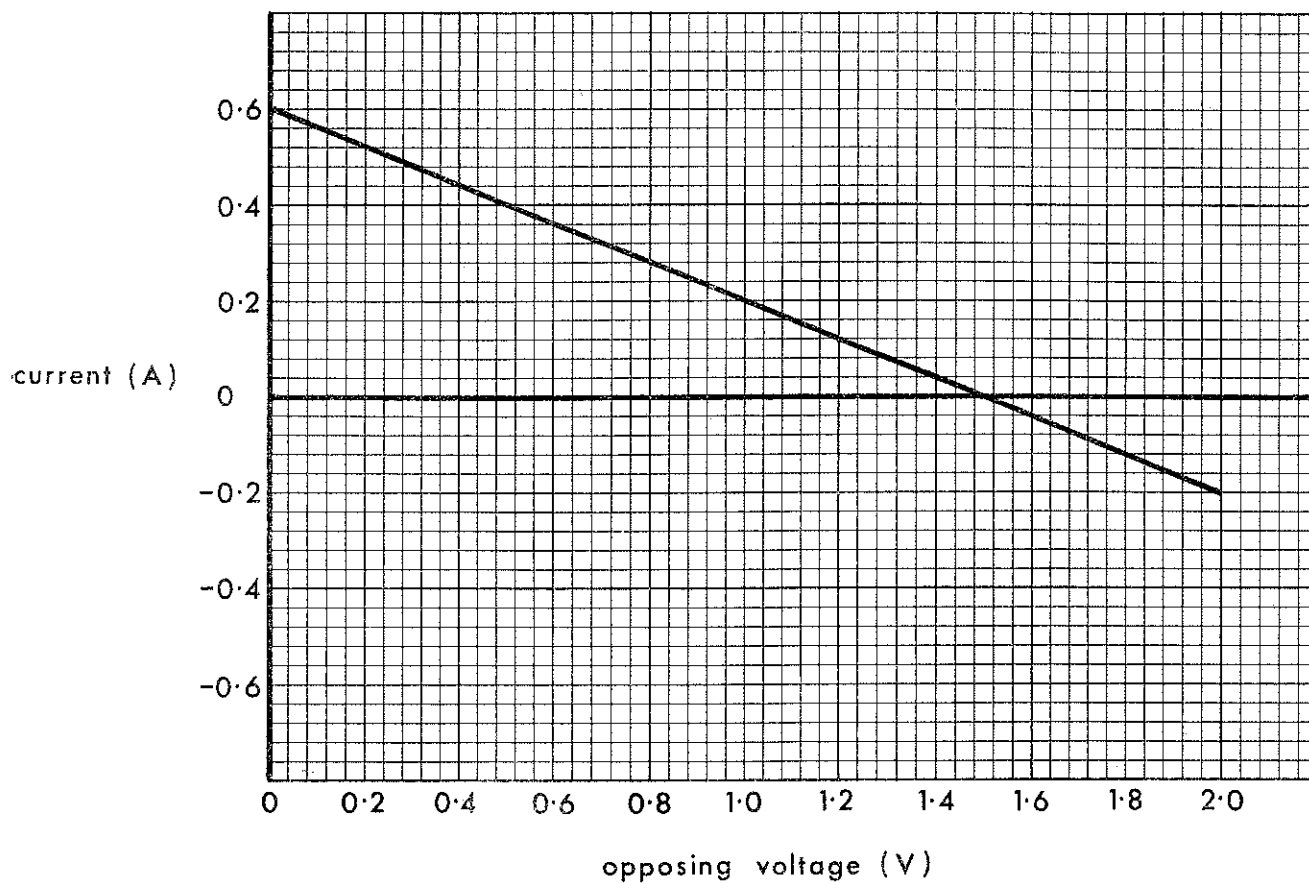
4. (a) In thermodynamics, what is meant by the term "reversible conditions"?  
(b) A chemical reaction can often be made to take place in the form of an electrical cell.



In the above cell, the two half cells are linked in two ways—by a conductor and meter and by a salt bridge.

- (i) What is the function of the conductor? (1)  
(ii) What is the function of the salt bridge? (1)  
(iii) Why is it better in this case to use ammonium nitrate instead of sodium chloride in the salt bridge? (2)  
(iv) If the solution in each beaker was molar with respect to  $Zn^{2+}(aq)$  and  $Ag^+(aq)$  ions, what would be the e.m.f. of the cell? (2)
- (c) The same reaction took place in a thermos flask. In such a reaction, the temperature of  $100\text{ cm}^3$  of  $0.2\text{ M}$  silver nitrate solution rose by  $8.5\text{ }^\circ\text{C}$  when  $0.01$  mole of zinc powder was added. The same rise of temperature was produced when an electric current released  $3570$  joules of energy in the solution in the flask. Assuming negligible heat loss to the thermometer and the surroundings, calculate the change in heat content for the displacement caused by one mole of the zinc powder.  
Comment on the various errors likely to exist in this method. (5)
- (d) A cell identical to the one above was introduced into the following circuit. An opposing voltage was applied and the current in the circuit measured for various external voltages as shown on the graph.





Marks

- From this graph, calculate the change in free energy of the reaction occurring in the cell.  
 (Show the steps in your reasoning and calculations clearly.) (6)
- (e) State the thermodynamic expression which relates changes in free energy with change in heat content for the reaction. (1)

[Turn over

5. (a) The following table gives the measured wavelengths of lines in the ultra-violet region of the hydrogen emission spectrum (Lyman series) and the calculated differences in wavelengths between successive lines.

$\lambda$ (nm)	$\Delta\lambda$ (nm)
102.6	
97.3	5.3
95.0	2.3
93.8	1.2
93.1	0.7

Using the square ruled paper provided, plot a graph of  $\lambda$  against  $\Delta\lambda$  and by extrapolation obtain a value for  $\lambda$  when  $\Delta\lambda = 0$ .

From this estimated wavelength, calculate a value for the ionisation energy of hydrogen. (5)

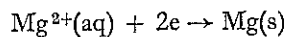
- (b) What is meant by the term "degeneracy of d-orbitals"? (1)
- (c) Explain why there is a loss of d-orbital degeneracy when, for example, an ion of titanium combines with six water molecules. (3)
- (d)  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  absorbs light of wavelength 500 nm. Explain how this absorption of light arises. (3)
- (e) Explain what change in wavelength of absorption you might expect if the  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ions were converted into  $\text{Ti}(\text{CN})_6^{3-}$  ions. (3)
- (f) What two effects, in complex compounds, have to be considered in determining the distribution of d-electrons? (2)
- (g) Explain the difference you might expect to observe in the degree of paramagnetism exhibited by a substance containing  $\text{Co}(\text{NH}_3)_6^{3+}$  ions and one containing  $\text{CoF}_6^{3-}$  ions. (3)

6. (a) State the Second Law of thermodynamics. (1)

(b) Discuss the law in the light of the observation that a random solution of sodium thio-sulphate can spontaneously crystallise to give well ordered crystals. (4)

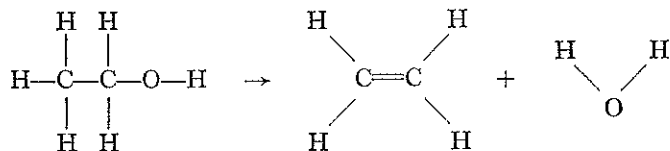
What can you deduce about the change in heat content of such a crystallisation?

(c) For the following reaction the Standard Reduction Potential is  $-2.37$  V. (4)



The reverse of this process can be considered as consisting of four steps. Represent these as equations and name the energy change involved in each step. (4)

(d) (i) Using the table of bond energies given on p. 31 of the Data Book, estimate the change in heat content when one mole of ethanol is converted to ethene and water. (4)



(ii) This reaction is usually brought about by passing ethanol vapour over a catalyst,  $\text{Al}_2\text{O}_3$ . What effect would this have on the  $\Delta H$  for the reaction? (1)

(e)

Name	Boiling Point ( $^{\circ}\text{C}$ )
A Ethanol	78
B Dimethyl ether (Methoxymethane)	-24
C Propan-1-ol	97
D Propan-2-ol	82
E Methyl-ethyl ether (Methoxyethane)	6

(i) Explain why the boiling points of isomers A and B are so different. (3)

(ii) What difference would you expect in the viscosity of isomers C and E? (1)

(iii) Explain why the boiling points of C and D are slightly different. (2)

7. (a)

Marks

Compound	Lattice Energy (kJ mol <sup>-1</sup> )	Compound	Lattice Energy (kJ mol <sup>-1</sup> )	Compound	Lattice Energy (kJ mol <sup>-1</sup> )
LiF	1021	LiCl	845	CaF <sub>2</sub>	2594
NaF	900	NaCl	770	CaO	3523
KF	795	KCl	699	MgF <sub>2</sub>	2887
RbF	762	RbCl	674	MgO	3933
CsF	720	CsCl	649	MgS	3255

By studying the values of the lattice energies in the above table and using the information on p. 29 of the Data Book, deduce the main factors affecting the magnitude of the lattice energy of a compound.

(Show clearly how you have come to your conclusions.) (3)

- (b) Measurements of bond angles show that the angles between the C-H bonds in methane are 109° whereas those between the N-H bonds in ammonia are 107° and that between the O-H bonds in water is only 105°.

How can these differences in bond angles be explained in terms of electron distribution? (4)

- (c) (i) Why can phosphorus form two covalent chlorides of formulae PCl<sub>3</sub> and PCl<sub>5</sub> whereas nitrogen forms only NCl<sub>3</sub>? (3)

(ii) Draw and name the shape you would expect the PCl<sub>5</sub> molecule to have. (2)

- (d) The transition element vanadium can also form a range of compounds in which its oxidation number varies.

(i) Why is such behaviour typical of transition elements? (1)

(ii) What is the oxidation number of vanadium in the compound NH<sub>4</sub>VO<sub>3</sub> (ammonium metavanadate)? (1)

- (iii) The commonest way to effect the stepwise reduction of a solution of ammonium metavanadate is to add zinc metal to the warm acidified solution.

Reaction	Standard Reduction Potential E° (V)
V <sup>2+</sup> (aq) + 2e → V(s)	-1.2
V <sup>3+</sup> (aq) + e → V <sup>2+</sup> (aq)	-0.25
VO <sup>2+</sup> (aq) + 2H <sup>+</sup> + e → V <sup>3+</sup> (aq) + H <sub>2</sub> O	+0.36
VO <sub>3</sub> <sup>-</sup> (aq) + 4H <sup>+</sup> + e → VO <sup>2+</sup> (aq) + 2H <sub>2</sub> O	+1.0

Using the information given above and on p. 30 of the Data Book, calculate to what extent tin metal might bring about the reduction of ammonium metavanadate. (3)

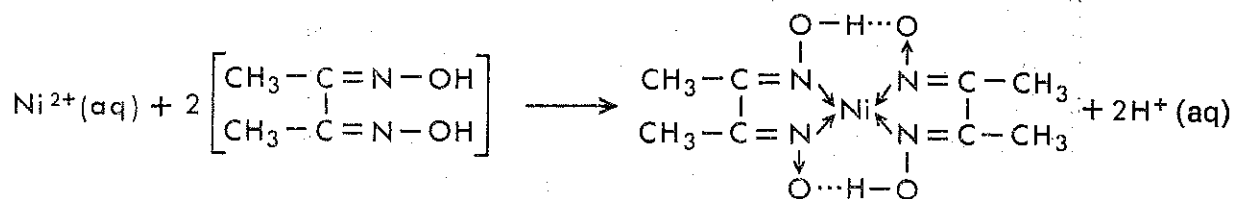
- (e) Consider the following.

Oxidation Number of Vanadium in Compound	Colour of Ion
+5	Yellow
+4	Blue
+3	Green
+2	Violet

- (i) What colour might you expect the end-product of the reaction with tin to be? (1)
- (ii) Why might you find in practice that your forecast was not accurate? (2)

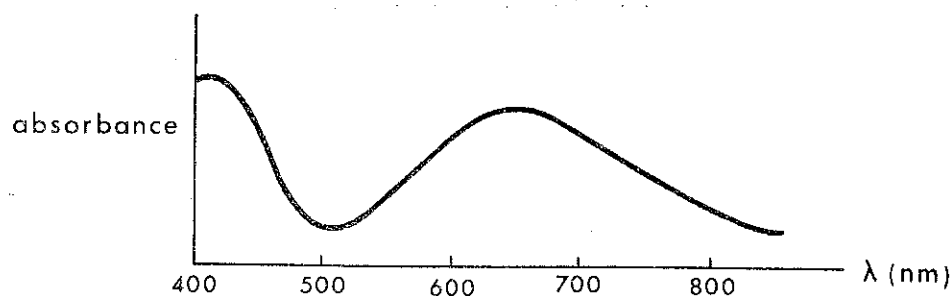


8. (a) Estimation of nickel ions can be achieved by precipitation of a complex of nickel with dimethyl glyoxime, viz



In such an estimation, 0.450 g of impure hydrated nickel sulphate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) was dissolved in 40 cm<sup>3</sup> of 1 M hydrochloric acid which was then diluted to about 200 cm<sup>3</sup>. The solution was heated to 75 °C and 50 cm<sup>3</sup> of a 0.1 M solution of dimethylglyoxime in ethanol was added. Ammonia solution was then added dropwise with stirring until a permanent red precipitate formed. A test showed that precipitation was complete. The precipitate was collected in a pre-weighed sintered glass crucible. It was then washed several times with small volumes of water and dried to constant mass at 120 °C.

- (i) Why is dimethylglyoxime a good reagent for the gravimetric analysis of nickel? (1)
  - (ii) Suggest why the addition of ammonia solution helps to give an accurate result. (2)
  - (iii) Describe how you would dry the precipitate "to constant mass". (2)
  - (iv) In the experiment described, the final precipitate was found to weigh 0.478 g. Calculate the percentage purity of the original hydrated nickel sulphate. (4)
- (b) The following graph shows the absorption of various wavelengths of light by a solution of nickel(II) chloride.



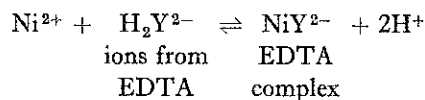
- (i) Explain what colour you would expect the solution to be. (You may find the table of Flame Colours in the Data Book helpful.) (1)
- (ii) If you wanted to use the colour of this solution as a means of estimating the concentration of  $\text{Ni}^{2+}$  in a solution, how would you go about finding out if this was possible? (4)  
(You may assume that a suitable colorimeter is available.)

[Turn over

- (c) Estimation of  $\text{Ni}^{2+}$  ions in solution can be effected by titration with a solution of EDTA [ethylene diamine tetra acetic (ethanoic) acid].

Metal ions complex with EDTA in the ratio of 1 mole of ions to 1 mole of EDTA. Solochrome Black is an indicator which also forms a complex with  $\text{Mg}^{2+}$  ions but the complex is less stable than the one with EDTA. Solochrome Black is sensitive to changes in pH.

The complex formation with  $\text{Ni}^{2+}$  and EDTA can be represented as follows:



The estimation of  $\text{Ni}^{2+}$  is done by a back titration. A portion ( $20 \text{ cm}^3$ ) of standard  $0.05 \text{ M}$  EDTA is added to  $5.0 \text{ cm}^3$  of a solution of a nickel salt. The mixture is then diluted to about  $100 \text{ cm}^3$  and  $4 \text{ cm}^3$  of a buffer pH 10 added. A small portion of Solochrome Black is added and standard  $0.05 \text{ M}$  magnesium sulphate solution added until the colour changes from blue to purple.

- (i) What is meant by the term "back titration"? (1)
- (ii) What is a buffer and what is the purpose of adding a buffer to the mixture? (2)
- (iii) What do you think causes the purple colour at the end point? (1)
- (iv) If  $8.0 \text{ cm}^3$  of  $0.05 \text{ M}$  magnesium sulphate solution were needed to reach the end point, how many moles of  $\text{Ni}^{2+}$  were present in the original sample taken? (2)

[END OF QUESTION PAPER]