

[92/306]

1981

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Monday, 11th May—9.30 a.m. to 12 noon



Dalziel High School
Chemistry Department



1981 CSYS

1. Which of the following electron configurations represents that of an atom in an excited state?

- A $1s^2 2s^2$
- B $1s^2 2s^2 2p^6$
- C $1s^2 2s^2 2p^6 4s^1$
- D $1s^2 2s^2 2p^6 3s^2 3p^2$

2. The bond dissociation energy of HBr is 364 kJ mol^{-1} . In which of the following processes are 364 kJ released?

- A $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g}) \rightarrow \text{HBr}(\text{g})$
- B $\text{HBr}(\text{g}) \rightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g})$
- C $\text{H}^+(\text{g}) + \text{Br}^-(\text{g}) \rightarrow \text{HBr}(\text{g})$
- D $\text{HBr}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{Br}^-(\text{g})$

3. The action of magnesium metal on dilute hydrochloric acid can be represented by the equation



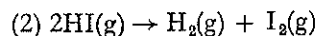
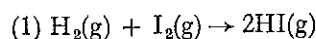
When excess magnesium is added to 500 cm^3 of hydrochloric acid, 1 mole of hydrogen gas is produced. What is the molarity of the hydrochloric acid?

- A 0.5
- B 1
- C 2
- D 4

4. When a ${}_{92}^{235}\text{U}$ atom loses an alpha particle followed by a beta particle it becomes

- A ${}_{91}^{233}\text{Pa}$
- B ${}_{89}^{299}\text{Ac}$
- C ${}_{91}^{231}\text{Pa}$
- D ${}_{89}^{231}\text{Ac}$

5. The activation energies for the reactions



are 165 kJ and 179 kJ respectively. The enthalpy change for reaction (2) is

- A -14 kJ
- B $+14 \text{ kJ}$
- C -344 kJ
- D $+344 \text{ kJ}$

6. What volume of 0.2 M sulphuric acid is required to make, by dilution with water, one litre of a solution with a $\text{H}^+(\text{aq})$ concentration of 0.1 M ?

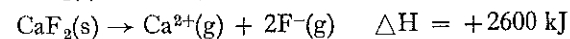
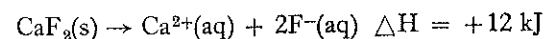
- A 100 cm^3
- B 125 cm^3
- C 250 cm^3
- D 500 cm^3

7. $\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2$

For the above reaction decide upon the probable signs of ΔS and ΔH at 298 K .

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

8. The equations below give some of the energy changes associated with the dissolving of calcium fluoride in water.



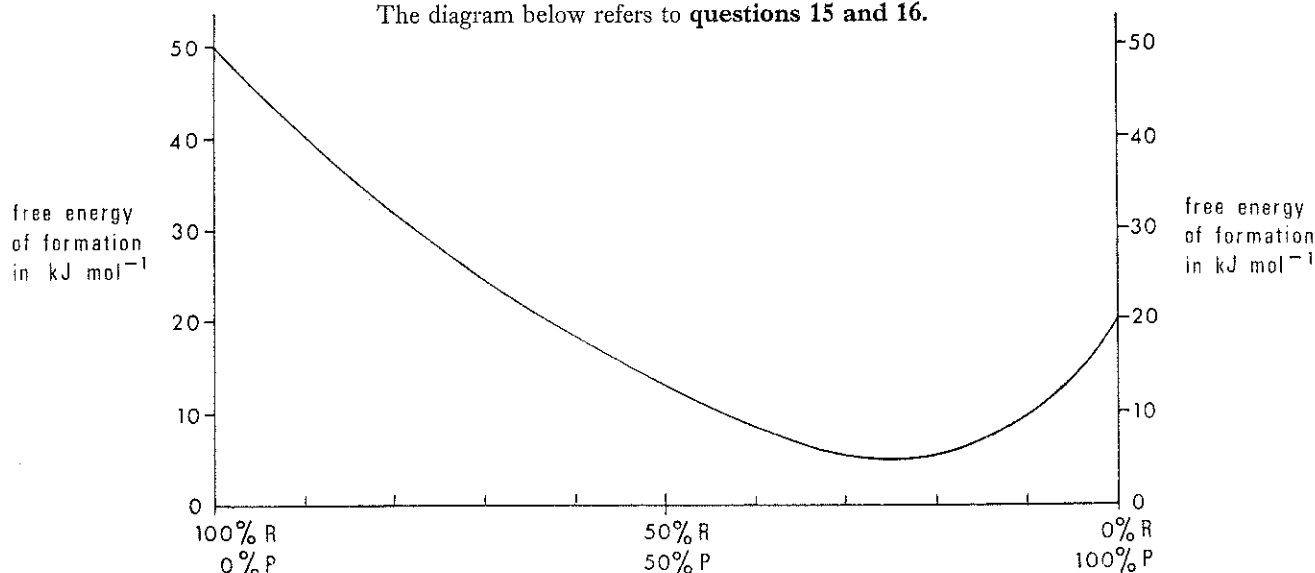
Which of the following energy terms has **not** been included?

- A Heat of hydration
- B Ionisation energy
- C Heat of solution
- D Lattice energy

9. 11.2 litres oxygen are sparked with 11.2 litres hydrogen, all measurements being made at s.t.p.
Approximately how many molecules of the two gases react?
- A 3×10^{23}
B 4.5×10^{23}
C 6×10^{23}
D 9×10^{23}
10. Sodium vapour street lamps emit yellow light because
- A sodium vapour filters out all the light from the filament except yellow
B electrons in sodium are absorbing energy corresponding to yellow light as they move to higher energies
C sodium vapour is burning and giving out a yellow glow
D electrons in sodium are giving out energy corresponding to yellow light as they move to lower energies.
11. Consider the reaction
- $$\text{Cu(s)} + 2\text{AgNO}_3(\text{aq}) \rightarrow \text{Cu(NO}_3)_2(\text{aq}) + 2\text{Ag(s)}$$
- $$\Delta H = -72 \text{ kJ}$$
- The heat change in kJ when 0.1 mole copper is added to 100 cm³ of 1.0 M AgNO₃ is
- A - 3.6
B - 7.2
C - 14.4
D - 21.6.
12. Which one of the following substances would be most suitable for extinguishing an incendiary bomb made of magnesium?
- A Water
B Carbon dioxide
C Sulphur dioxide
D Bromochlorodifluoromethane
13. In each of the following compounds the bonding is shown between carbon and one other element. In which compound is the bond polarised such that carbon has a partial **negative** charge?
- A C₂H₅—Br
B H₃Si—CH₃
C CH₃CH=O
D CH₃C≡N
14. Which of the following would be expected to have the highest entropy at 298 K?
- A Ag
B Hg
C Mg
D Na

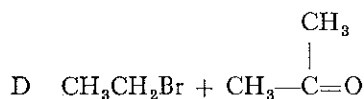
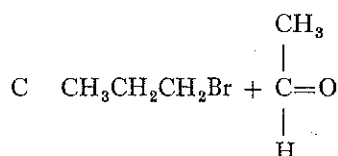
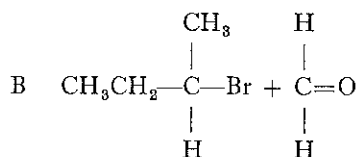
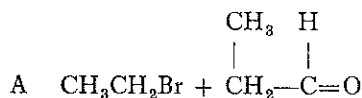
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The diagram below refers to questions 15 and 16.



15. What is the value of ΔG for the reaction $R \rightarrow P$?
- A -30 kJ mol^{-1}
 B $+30 \text{ kJ mol}^{-1}$
 C -70 kJ mol^{-1}
 D $+70 \text{ kJ mol}^{-1}$
16. The equilibrium constant for the reaction is
- A 0.25
 B 0.3
 C 3
 D 4.
17. At its boiling point, the entropy of vapourisation of a liquid is $88 \text{ J K}^{-1} \text{ mol}^{-1}$. The heat of vapourisation of the liquid is 26.4 kJ mol^{-1} . If at boiling point $\Delta G = 0$, then the boiling point of the liquid is
- A $30 \text{ }^\circ\text{C}$
 B 30 K
 C $300 \text{ }^\circ\text{C}$
 D 300 K .
18. Though insoluble in water, silver chloride is soluble in aqueous ammonia solution because
- A silver chloride is a covalent molecule
 B the solvation energy of Ag^+ is greater with water than with ammonia
 C the ammonia forms a soluble complex with the silver ion
 D aqueous ammonia is basic whereas water is neutral.
19. What is the change in the three dimensional arrangement of the bonds round the P atom in the following reaction?
- $$\text{PH}_3 + \text{H}^+ \rightarrow \text{PH}_4^+$$
- A Planar to pyramidal
 B Tetrahedral to square planar
 C Pyramidal to tetrahedral
 D Pyramidal to square planar
20. Which of the following compounds has the highest degree of ionic character?
- A Lithium hydride
 B Hydrogen chloride
 C Silicon chloride
 D Phosphorus hydride
21. The infra-red spectrum of a compound X shows that it contains the bonds C—H, C=O and C—O. Which of the following compounds is most likely to be X?
- A Ethyl ethanoate
 B Methoxymethane (Dimethyl ether)
 C Propanal
 D Propanone

22. To prepare the alcohol $\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{CH}_2\text{OH}$ by a Grignard synthesis which of the following sets of starting materials, with magnesium, would be required?



23. From which of the following observations could it most reasonably be concluded that a certain hydrocarbon is an alkene?

- A On complete hydrogenation 22.4 litres of hydrogen (at s.t.p.) react per mole of hydrocarbon.
 B It decolourises bromine water fairly rapidly.
 C It has a formula corresponding to C_nH_{2n} .
 D It burns to form carbon dioxide and water only.

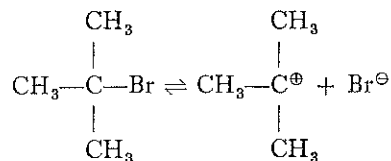
24. Which of the following is **not** an isomer of butan-1-ol?

- A Ethoxyethane (diethyl ether)
 B 2-Methylpropan-1-ol
 C Butanone
 D Methoxypropane (methyl propyl ether)

25. Which one of the following species has nucleophilic properties?

- A Cl^-
 B Br^+
 C CH_3^+
 D NH_3

26. The rate determining step for the hydrolysis of 2-bromo-2-methylpropane by hydroxide ions is as follows:



Which of the following statements is **false**?

For this hydrolysis

- A increasing the concentration of the alkyl halide will increase the rate
 B increasing the concentration of hydroxide ions has no effect on the rate
 C increasing the concentration of bromide ions will decrease the rate
 D increasing the polarity of the solvents will decrease the rate.

27. The hydride of one of the first twenty elements in the Periodic Table

- (i) does not react spontaneously with air at room temperature;
 (ii) dissolves in water to give an alkaline solution only;
 (iii) is produced with great difficulty by direct combination of its elements;
 (iv) has a characteristic pungent odour.

The hydride is

- A nitrogen hydride
 B sodium hydride
 C sulphur hydride
 D silicon hydride.

28. Under which one of the following conditions will the lattice energy of an ionic crystal, MX, have the largest numerical value?

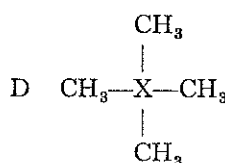
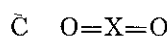
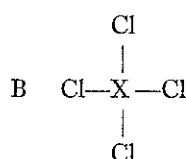
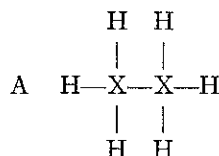
- A M has a small ionisation energy.
 B X has a small electron affinity.
 C M^+ has a small radius, X^- has a large radius.
 D M^+ has a small radius, X^- has a small radius.

[Turn over

29. What is the value of x in the mineral $\text{Ca}_2 \text{Mg}_x (\text{Si}_4 \text{O}_{11})_2 (\text{OH})_2$, assuming that the silicate ion is $(\text{Si}_4 \text{O}_{11})^{6-}$?

- A 4
- B 5
- C 6
- D 10

30. In three of the following molecules at room temperature X could represent either C or Si. In which one could it not?



31. The ionic product for water, K_w , has the value of $10^{-14} \text{ mol}^2 \text{ l}^{-2}$ at 25°C .

Assuming sodium hydroxide to be completely ionised in aqueous solution, the concentration of hydrogen ions in a 0.1 M solution of sodium hydroxide at 25°C will be

- A $10^{+14} \text{ mol l}^{-1}$
- B $10^{+13} \text{ mol l}^{-1}$
- C $10^{-13} \text{ mol l}^{-1}$
- D $10^{-14} \text{ mol l}^{-1}$

32. Which of the following acids is the strongest?

- A $\text{CH}_3\text{CBr}_2\text{COOH}$
- B $\text{CH}_3\text{CHBrCOOH}$
- C $\text{CH}_2\text{BrCH}_2\text{COOH}$
- D $\text{CH}_3\text{CH}_2\text{COOH}$

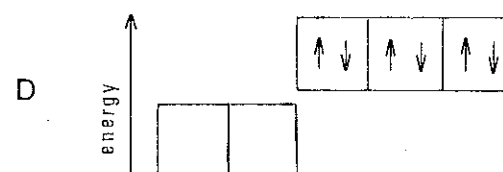
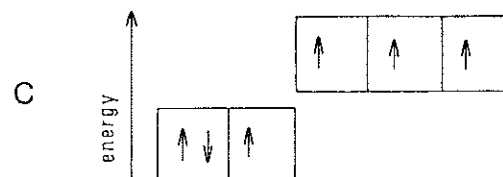
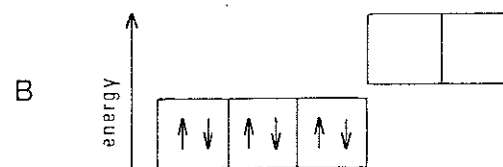
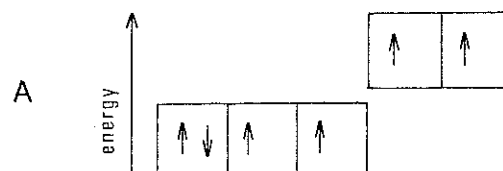
33. The pH ranges over which some common indicators change colour are given below. Which of these indicators would be the most suitable for the titration of ethanoic acid with sodium hydroxide?

- A Screened methyl orange 3.1 — 4.5
- B Litmus solution 5.0 — 8.0
- C Bromothymol blue 6.0 — 7.6
- D Phenolphthalein 8.3 — 10.0

34. A reaction in dynamic equilibrium is one in which

- A the concentration of the product is always independent of reaction conditions
- B the enthalpy changes for the forward and the backward reactions are equal
- C the activation energies for the forward and the backward reactions are equal
- D the rates of the forward and the backward reactions are equal.

35. The cobalt(III) ion has six 3d electrons. Which diagram represents their arrangement in the presence of a strong octahedral ligand field?



36. The formula for chloropentaamminecobalt(III) chloride is

- A $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{3+}(\text{Cl}^-)_3$
- B $[\text{Co}(\text{NH}_4)_5\text{Cl}]^{7+}(\text{Cl}^-)_7$
- C $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{Cl}^-)_2$
- D $[\text{Co}(\text{NH}_4)_5\text{Cl}]^{2+}(\text{Cl}^-)_2$

37. Which of the following elements can exhibit the highest oxidation number?

- A Scandium
- B Titanium
- C Vanadium
- D Chromium

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. Consider the following possibility.

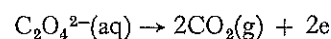
A compound X, molecular formula $\text{C}_3\text{H}_6\text{O}$, reacted with bromine to form $\text{C}_3\text{H}_6\text{OBr}_2$. On treating X with a suitable oxidising agent, the substance formed had the formula $\text{C}_3\text{H}_4\text{O}$ and reacted with ammoniacal silver nitrate solution to form a silver mirror.

Which of the following is/are correct?

- 1 X is an alcohol.
- 2 X is a primary alcohol.
- 3 X is an unsaturated alcohol.

39. The reaction between permanganate ions and ethanedioate (oxalate) ions in acidic solution has a negative ΔG value.

The ethanedioate ions are oxidised thus



Which of the following can be said with certainty about the reaction?

- 1 The products will appear to be colourless.
- 2 One mole of permanganate ions will oxidise 2.5 moles ethanedioate ions.
- 3 The reaction will take place instantaneously at 20°C .

40. The nitrate, NO_3^- , ion is colourless because it

- 1 absorbs all visible radiation
- 2 does not absorb electromagnetic radiation
- 3 absorbs ultra-violet radiation only.

[END OF QUESTION PAPER]

1. Here are some data for the allotropes (polymorphs) of carbon at 298 K and 1 atmosphere pressure:

<i>Substance</i>	<i>Heat of formation</i> ΔH_f (kJ mol ⁻¹)	<i>Entropy</i> S (J K ⁻¹ mol ⁻¹)
Graphite	0	5.7
Diamond	1.9	2.4

- (a) What is meant by "entropy"? 1
- (b) Comment on the zero value in the above table. 1
- (c) Suggest why graphite and diamond have different entropy values. 1
- (d) (i) Calculate the enthalpy change, ΔH , and the entropy change, ΔS , for the conversion of graphite to diamond. 2
- (ii) "The conversion of graphite to diamond should **not** be thermodynamically feasible at any temperature." Comment on this statement. 2
- (7)**
2. The reaction between zinc and copper(II) sulphate solution under standard conditions (298 K, 1 atmosphere pressure, molar solutions) can be represented as follows:
- $$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$$
- (a) Draw a labelled diagram of a cell based on the above reaction, functioning under standard conditions. 2
- (b) Calculate the e.m.f. of this cell, using your Data Book. 1
- (c) Calculate the free energy change of this cell under these conditions. 3
- (6)**

3. Answer EITHER A OR B.

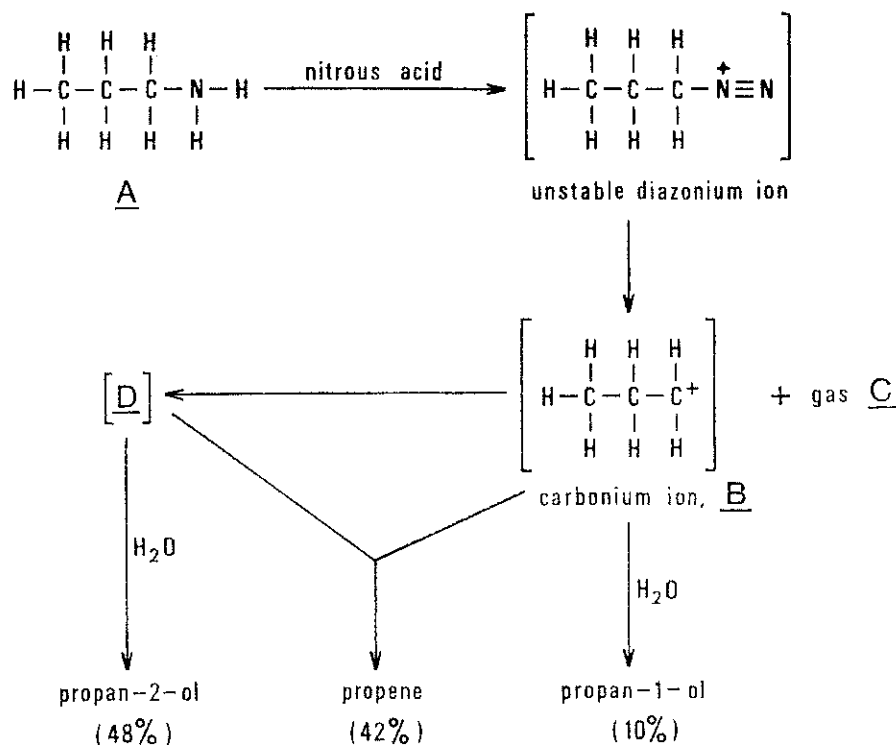
- A. 0.41 g of iron powder was added to 50 cm³ of hot 0.1 M iron(III) chloride solution. After a short time, the yellow colour changed to pale green. A drop of this solution was added to a solution containing thiocyanate ions, which give a deep blood red colour with iron(III) ions. No colour was observed. The remaining iron powder was filtered off, and found to weigh 0.27 g.
- (a) How many moles of iron reacted? 2
- (b) How many moles of iron were in the iron(III) chloride solution? 1
- (c) Using the figures from (a) and (b) above, and setting out your working clearly, write a balanced equation for the initial reaction. 2
- (d) Next day, another sample of the pale green solution was again tested with thiocyanate. A deep red colour was obtained.
- (i) Suggest what has happened to the pale green solution, and explain briefly. 2
- (ii) Suggest a reagent (not already used) which could reverse the overnight change. 1
- (8)

OR

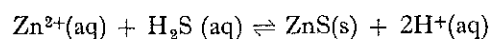
- B. Vanadium compounds of oxidation state +5 in aqueous solution are pale yellow and contain VO₂⁺ and VO³⁺ ions. Two separate 10 cm³ portions, (I) and (II), were treated as follows:
- (I) Sulphur dioxide was bubbled through until there was no further colour change. The resulting pale blue solution was boiled to drive out excess sulphur dioxide. After acidification with sulphuric acid, the solution was titrated with 0.02 M potassium permanganate. 17.1 cm³ were required to convert the vanadium back to its original oxidation state.
- (II) The addition of excess granulated zinc and concentrated sulphuric acid produced a lilac solution. After filtration, it was titrated with 0.02 M potassium permanganate and 51.2 cm³ were required to convert the vanadium back to its original oxidation state.
- (a) What is the oxidation state of the vanadium before reaction with permanganate
- (i) in (I), 2
- (ii) in (II)? 2
- Explain your answers.
- (b) Write an ionic equation showing how VO₂⁺ and VO³⁺ can be interconverted in aqueous solution. Which of these two ions will be present in larger quantities in strongly acidic solution? 3
- (c) Give one reason why sulphuric acid has to be present before titration with potassium permanganate. 1
- (8)
4. The lunar module which landed the first man on the moon in 1969 used methylhydrazine as fuel, with dinitrogen tetroxide (N₂O₄) as oxidant. Methylhydrazine has the formula CH₃NHNH₂.
- (a) Write an expanded structural formula for methylhydrazine. 1
- (b) Write an equation which represents the heat of formation of methylhydrazine. 2
- (c) The oxidation reaction in the rocket gives rise to gaseous products at the high temperature at which it is operated. Suggest **three** major gaseous products formed. 3
- (6)
5. Using data available on pages 38 and 39 of the Data Book, calculate the energy in kJ mol⁻¹ associated with the spectral line of cadmium. (4)

[Turn over

6. The reaction of a primary amine with nitrous acid is thought to proceed by the mechanism summarised below. Reaction intermediates are shown in square brackets, and the yield of the final products are shown as percentages.



- (a) Name compound A. 1
- (b) Identify substance C. 1
- (c) B undergoes partial isomerisation to yield D. What is the structure of D? 1
- (d) Suggest a reason for the much higher yield of propan-2-ol compared with propan-1-ol. 1
- (e) Explain briefly the formation of propene from intermediates B and D. 1
- (f) Suggest an experiment which would confirm the presence of a carbonium ion as intermediate in this reaction. Explain briefly. 2
- (7)
7. Boron fluoride readily forms addition compounds,
e.g. $\text{BF}_3 + \text{NH}_3 \rightarrow \text{BF}_3\text{NH}_3$
- (a) Show clearly, by means of a sketch in each case, the three-dimensional shape of a molecule of
- (i) BF_3
- (ii) NH_3 . 2
- (b) Suggest how the bond between the two molecules can form. 2
- (4)
8. Consider the following equilibrium situation:



The reaction is used as a qualitative test for Zn^{2+} , and as much Zn^{2+} as possible is converted to ZnS by bubbling H_2S gas into Zn^{2+} ions in water.

- (a) Write an expression for the equilibrium constant for the reaction. 2
- (b) Explain whether each of the following would increase or decrease, or leave unchanged, the amount of Zn^{2+} converted to ZnS:
- (i) dissolving a little solid sodium hydroxide in the solution;
- (ii) increasing the pressure of H_2S gas;
- (iii) boiling the solution. 6
- (8)

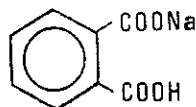
9. Answer EITHER A OR B.

- A. (a) What is meant by the pH of a solution? 1
 (b) What happens to the value of the pH of an 0.1 M solution of a strong acid (such as hydrochloric) when 10 cm³ of it are diluted to 100 cm³ with distilled water? 1
 (c) Show, by calculation, what happens to the pH of an 0.1 M solution of a weak monoprotic acid (such as ethanoic) when it is diluted as in (b) above. 4

(6)

OR

B. A solution of sodium hydrogen phthalate can act as a buffer solution. Its structure is:



- (a) What is a buffer solution? 1
 (b) To explain how it acts as a buffer, show what happens to a solution of sodium hydrogen phthalate when
 (i) a little acid is added to it, and
 (ii) a little alkali is added to it. 4
 (c) Give another example of a buffer solution. 1

(6)

10. The following tables give some data for the elements of Group IV:

	<i>m.p.</i> (K)	<i>b.p.</i> (K)	<i>Ionisation Energies</i> (kJ mol ⁻¹)			
			1st	2nd	3rd	4th
C { diamond	4000					
graphite	3820	5100	1090	2360	4640	6220
Si	1680	2630	792	1590	3250	4350
Ge	1210	3100	785	1541	3314	4423
Sn	505	2540	715	1420	2960	3930
Pb	601	2010	722	1460	3100	4080

<i>Bond Energies</i> (kJ mol ⁻¹)			
C-C	337	C-O	331
Si-Si	200	Si-O	454
Ge-Ge	189		
Sn-Sn	164		

	<i>E°</i> (volts)
Ge ⁴⁺ + 2e → Ge ²⁺	-0.30
Sn ⁴⁺ + 2e → Sn ²⁺	+0.15
Pb ⁴⁺ + 2e → Pb ²⁺	+1.70

Select data, as appropriate, from the above tables to support the following statements.

- (a) The metallic character of the elements increases going down the group. 1
 (b) The ability of the elements to form chains of atoms decreases going down the group. 1
 (c) The +4 oxidation state of the elements becomes less stable going down the group. 1
 (d) The chemistry of carbon is dominated by carbon-carbon bonds, whereas silicon chemistry is dominated by silicon-oxygen bonds. 2

(5)

[Turn over

11. Answer EITHER A OR B.

A. Aluminium oxide is colourless, yet the presence of a small proportion of titanium(III) ions gives it the blue colour of sapphire. In this structure, the titanium(III) ions are in the octahedral field of the oxide ions, and the d-orbitals are split.

- (a) By means of a sketch, show clearly the environment of a titanium(III) ion in the above structure. 1
 (b) Explain "split" in this context. 1
 (c) Explain how the presence of the titanium ion gives aluminium oxide a blue colour. 4

(6)

OR

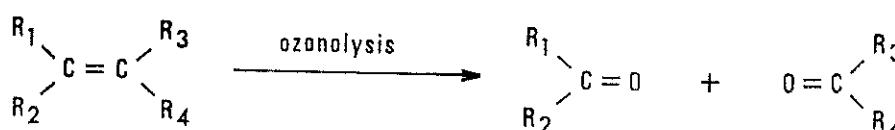
- B. (a) What is meant by saying that a substance is paramagnetic? 1
 (b) Describe briefly how you would find out if a substance is paramagnetic. 1
 (c) Put the following substances in order, the most paramagnetic first. Set out your reasoning clearly.



4

(6)

12. Ozonolysis can be used to determine the structure of an alkene. The process can be summarised as follows



(R₁, R₂, R₃, R₄ are alkyl groups or hydrogen)

An alkene, X, on ozonolysis, gave only methanal and butanone.

- (a) Give the structural formulae of methanal and butanone. 1
 (b) Deduce the structural formula and name of alkene X. 2

(3)

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. There is, however, no specific requirement that you must adopt these suggestions **and they should not** limit the structure and content of your answer. You should also remember that the Data Book may be a useful source of information.

However, while you have freedom to decide how and 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. The determination of chemical structure using electromagnetic radiation.

You might include in your essay reference to:

- how wavelength, frequency and energy vary across the electromagnetic spectrum;
 how the regions of this spectrum you have studied interact with matter;
 structure determination and chemical analysis.

OR

B. Organic halogen compounds.

You might include in your essay reference to how an alkyl halide is made, and how it reacts;
 the social and economic importance of these compounds.

OR

C. The Periodic Table

You might include in your essay reference to its build-up in terms of electron arrangements;
 major trends observed in the table in the elements and their compounds;
 its predictive value in chemistry.

(10)

[END OF QUESTION PAPER]