

[0519/422] 1990

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Friday, 4th May—9.30 a.m. to 12.00 noon



Dalziel High School
Chemistry Department



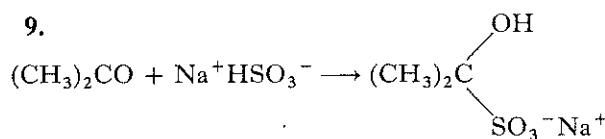
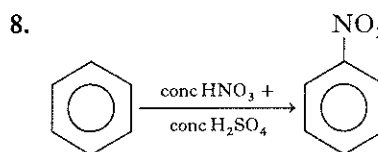
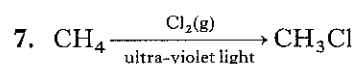
1990 CSYS

1. Electrons are accommodated in orbital types within atoms in the order
- A 1s 2s 2p 3s 3p 4s 4p 3d
 B 1s 2s 2p 3p 3s 3d 4s 4p
 C 1s 2s 2p 3s 3p 3d 4s 4p
 D 1s 2s 2p 3s 3p 4s 3d 4p
2. Which of the following statements about the molecule PF₅ is **incorrect**?
- A It has a trigonal bipyramidal structure.
 B It contains five identical covalent bonds.
 C It has bond angles of equal value.
 D It contains phosphorus with an oxidation state of +5.
3. In which of the following processes are ΔH° and ΔS° both positive?
- A The explosion of nitroglycerine
 B The dissolution of sulphuric acid in water
 C The dimerisation of nitrogen dioxide
 D The evaporation of ethoxyethane
4. $2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^{-}(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{s})$
 $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{s}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{I}^{-}(\text{aq})$
 50 cm³ of an aqueous solution of Cu²⁺ (0.02 M) are added to excess aqueous KI solution. What volume of 0.1 M Na₂S₂O₃ is required to react completely with the liberated iodine?
- A 5 cm³
 B 10 cm³
 C 25 cm³
 D 50 cm³
5. A reaction in dynamic equilibrium is one in which
- A ΔG is always zero
 B ΔG° is always zero
 C activation energy of the forward reaction = activation energy of the reverse reaction
 D ΔH for the forward reaction = ΔH for the reverse reaction.

6. One mole of barium chloride (BaCl₂) contains
- A 3 moles of atoms
 B 1 mole of positive ions
 C 1 mole of molecules
 D 2 moles of ions.

The reactions in **questions 7, 8 and 9** may be described as one of the following types. Select the appropriate type in each case. A type may be used once, more than once, or not at all.

- A Electrophilic substitution
 B Electrophilic addition
 C Free radical substitution
 D Nucleophilic addition

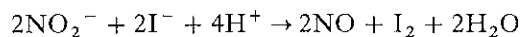


10. A white crystalline compound, soluble in water, was found to react with both dilute hydrochloric acid and sodium hydroxide solution. Which of the following might it have been?
- A Aniline
 B Aminoethanoic acid
 C Ethylamine
 D Ethylammonium chloride
11. A solution of a weak alkali is to be standardised. Which of the following properties must be possessed by an acid to be suitable as a primary standard for this purpose?
- A It must have exactly the same molarity as the alkali.
 B It must have a high purity and stability.
 C It must have about the same strength as the alkali.
 D One mole of the acid must neutralise one mole of the alkali.

12. Which of the following has the greatest number of lone pairs of electrons?

- A NH_2^-
- B NH_4^+
- C CH_3^-
- D H_3O^+

13. Iodide ions are oxidised by acidified nitrite ions according to the equation

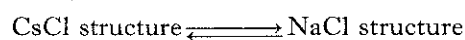


A mixture of sodium nitrite and sodium iodide solutions was divided into two parts. Ethanoic acid was added to one part and ethanoic acid saturated with sodium ethanoate was added to the other.

Which of the following is the most likely explanation for the slower formation of iodine in the second case?

- A Sodium ethanoate removes iodine.
- B Sodium ethanoate reduces the concentration of sodium iodide.
- C Sodium ethanoate reacts with sodium nitrite.
- D Sodium ethanoate decreases the ionisation of ethanoic acid.

14. At room temperature, caesium chloride has a structure in which each ion is surrounded by 8 oppositely charged ions (caesium chloride structure). Above 445°C , the structure found is one in which each ion is surrounded by 6 oppositely charged ions (sodium chloride structure).



Which of the following is true of the reaction from left to right?

- A $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$
- B $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$
- C $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$
- D $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$

15. What is the change in the three dimensional arrangement of the bonds round the P atom in the following reaction?



- A Pyramidal to planar
- B Square planar to tetrahedral
- C Tetrahedral to pyramidal
- D Square planar to pyramidal

16. $\text{S}(\text{s}) + 3\text{F}_2(\text{g}) \rightleftharpoons \text{SF}_6(\text{g})$

$$\Delta G^\circ = -983.2 \text{ kJ mol}^{-1}$$

(left to right)

Which of the following can be deduced with certainty from the above?

- A Sulphur and fluorine will react rapidly to form SF_6 .
- B At equilibrium, the yield of SF_6 will be large.
- C The reaction will not occur to any significant extent.
- D SF_6 is thermodynamically unstable.

17. In which of the following are the ions isoelectronic?

- A Sc^{2+} and Ca^{2+}
- B Na^+ and Cl^-
- C Rb^+ and Br^-
- D Sr^{2+} and I^-

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

- A Describing the instability of aluminium chloride in a moist atmosphere
- B Describing the alkalinity of sodium ethanoate solution
- C Describing the action of water on ethyl ethanoate
- D Describing the action of 2,4-dinitrophenylhydrazine on propanone

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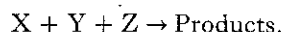
19. You have been asked to calculate the mean bond enthalpy (energy) of a (C=C) double bond. Which of the following sets of information would allow you to do this?

	<i>Enthalpy of formation of</i>	<i>Enthalpy of combustion of</i>	<i>Enthalpy of sublimation of</i>	<i>(Mean) bond enthalpy of</i>
A	ethene	ethene		C—H, H—H
B	benzene	benzene		C—H, H—H
C	ethene		carbon	C—H, H—H
D	benzene		carbon	C—H, H—H

20. The position of equilibrium in a chemical reaction is dependent on

- A the state of subdivision of the reactants
 B the temperature at which the reaction takes place
 C the presence or absence of a catalyst
 D the time to reach a state of equilibrium.

21. The following data refer to initial reaction rates obtained with initial concentrations of reactants expressed in arbitrary but consistent units for the reaction

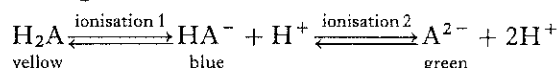


	[X]	[Y]	[Z]	Initial Rate
Experiment 1	1.0	1.0	1.0	0.3
Experiment 2	1.0	2.0	1.0	0.6
Experiment 3	2.0	2.0	1.0	1.2
Experiment 4	2.0	1.0	2.0	0.6

These data fit the rate equation

- A Rate = $k[X][Y][Z]$
 B Rate = $k[X][Y]^2$
 C Rate = $k[X][Y]$
 D Rate = $k[X]$.
22. Which one of the following pairs could be used to produce a buffer solution?
- A Ethanoic acid and methanoic acid
 B Ammonia and ammonium chloride
 C Hydrochloric acid and sodium chloride
 D Ammonia and methylamine

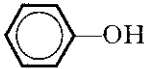
23. An indicator (H_2A) is a weak acid, and undergoes two ionisations:



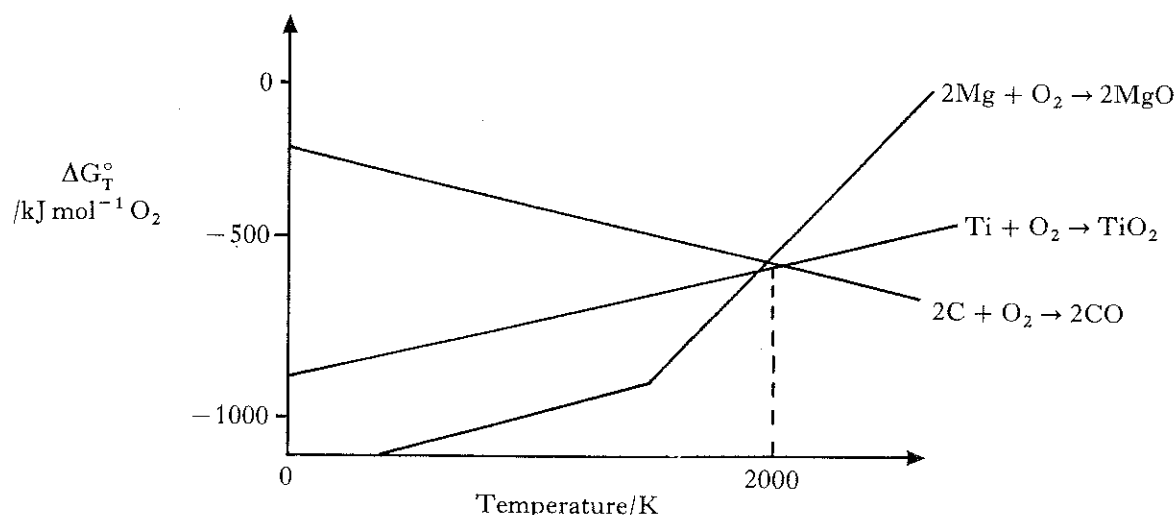
The colours of the species are shown. The dissociation constants for the two ionisations are given by:

$$pK_1 = 3.2 \text{ and } pK_2 = 5.9.$$

Given that for an indicator $pK = pH$ at the point where colour change occurs, the indicator will be

- A yellow in a solution of $pH = 3$, and green in a solution of $pH = 5$
 B blue in a solution of $pH = 3$, and green in a solution of $pH = 5$
 C blue in a solution of $pH = 3$, and blue in a solution of $pH = 5$
 D yellow in a solution of $pH = 3$, and blue in a solution of $pH = 5$.
24. Which of the following is the weakest acid?
- A $ClCH_2COOH$
 B C_2H_5OH
 C CH_3COOH
 D 

25.



From the graph above, it can be deduced that

- A magnesium can be used to reduce titanium oxide **below** 2000 K, and carbon can be used to reduce titanium oxide **below** 2000 K
- B magnesium can be used to reduce titanium oxide **above** 2000 K, and carbon can be used to reduce titanium oxide **below** 2000 K
- C magnesium can be used to reduce titanium oxide **below** 2000 K, and carbon can be used to reduce titanium oxide **above** 2000 K
- D magnesium can be used to reduce titanium oxide **above** 2000 K, and carbon can be used to reduce titanium oxide **above** 2000 K.

26. The element chromium has the ground state electron arrangement $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. Ammonium dichromate, $(NH_4)_2Cr_2O_7$, is bright orange. The colour of this compound results from

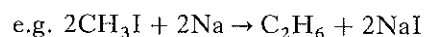
- A charge transfer between chromium and oxygen
- B electronic transitions in the ammonium ion
- C $3p \rightarrow 3d$ electronic transitions in the chromium atom
- D $3d \rightarrow 3d$ electronic transitions in the chromium atom.

27. Two isomeric esters, X and Y, have the molecular formula $C_4H_8O_2$. Ester X on hydrolysis with sodium hydroxide solution gives CH_3CH_2COONa , and ester Y on similar treatment gives CH_3CH_2OH .

The esters are

- | | X | Y |
|---|-------------------|------------------|
| A | methyl butanoate | ethyl propanoate |
| B | butyl methanoate | ethyl propanoate |
| C | methyl propanoate | ethyl ethanoate |
| D | propyl methanoate | ethyl ethanoate. |

28. Some alkanes may be prepared by adding an iodoalkane dropwise to a suspension of sodium in a suitable solvent.

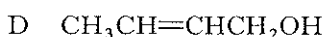
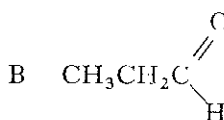
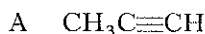


When a mixture of iodomethane and iodoethane is used as starting material, the product will contain

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

29. When 0.5 mole of organic compound X was dissolved in a suitable solvent and allowed to react with hydrogen in the presence of a nickel catalyst, 22.4 litres of hydrogen at s.t.p. were required for complete reaction.

Which of the following could be X?



30. When an aluminium atom of mass number 27 is bombarded by alpha particles, a phosphorus atom of mass number 30 is formed. In this process, the other particle produced is a
- hydrogen atom
 - neutron
 - beta particle
 - proton.
31. Two mechanisms have been proposed for the hydrolysis of 2-bromo-2-methylpropane. One of these has only one step
- $$(\text{CH}_3)_3\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$$
- The other has two steps
- $$(\text{CH}_3)_3\text{CBr} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^- \quad (\text{Slow})$$
- $$(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} \quad (\text{Fast})$$
- The reaction is observed to follow first order kinetics. The rate expression is
- Rate = $k[(\text{CH}_3)_3\text{CBr}]$
 - Rate = $k[(\text{CH}_3)_3\text{CBr}][\text{OH}^-]$
 - Rate = $k[(\text{CH}_3)_3\text{C}^+]$
 - Rate = $k[(\text{CH}_3)_3\text{C}^+][\text{OH}^-]$.
32. When a solution of iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, is irradiated with ultra-violet light, the following reaction occurs.
- $$2\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}_2(\text{CO})_n + n\text{CO}$$
- If a solution containing 0.01 mole of iron pentacarbonyl undergoes complete conversion, 112 cm^3 of carbon monoxide (measured at s.t.p.) is released. The value of n is
- 1
 - 4
 - 6
 - 9.
33. If, in a 0.1 M solution of a monoprotic acid, 1% of the acid molecules dissociate, the pH of the solution is
- 1
 - 2
 - 3
 - 4.
34. One mole of an ionic compound was added to one litre of water. The mixture was stirred and the solid dissolved at room temperature. Which of the following statements **must** be true?
- There was a decrease in free energy in forming the solution.
 - The dissolving resulted in no change in entropy of the system.
 - There was no change in enthalpy as the solid dissolved.
 - The resulting solution is one molar.
35. Three isomers with the empirical formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ have been isolated. Analysis of one isomer in solution showed that one third of the total chlorine content was precipitated as silver(I) chloride by the addition of excess silver(I) nitrate solution. The formula of this isomer is
- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} (\text{Cl}^-)_3$
 - $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} (\text{Cl}^-)_2 \cdot \text{H}_2\text{O}$
 - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+ \text{Cl}^- \cdot 2\text{H}_2\text{O}$
 - $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
36. Molybdenum is a metal in the second transition series. Which of the following is **not** true?
- Molybdenum will exhibit a number of different oxidation states.
 - Molybdenum will form complexes with a variety of ligands.
 - Molybdenum will have no half-filled d orbitals in its electron configuration.
 - Molybdenum will form coloured compounds.
37. If the wavelength of visible light from a tunable laser is increased,
- the wavenumber increases
 - the velocity increases
 - the frequency increases
 - the colour changes towards red.

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.

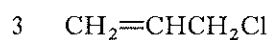
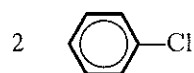
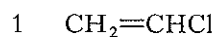
If only 3 is correct, select C.

Otherwise select D.

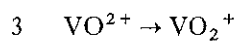
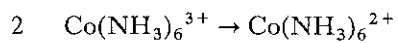
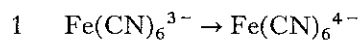
38. In a line spectrum, the frequency of each emission line represents

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

39. All atoms are in the same plane in

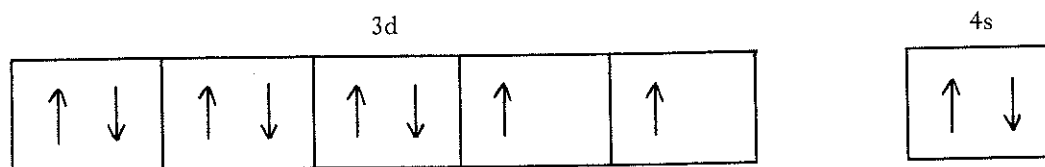


40. The metal undergoes oxidation in



[END OF QUESTION PAPER]

1. (a) The 3d and 4s electrons for the nickel atom can be represented as follows:



Draw the corresponding diagrams for Fe^{2+} and Fe^{3+} .

2

- (b) How do these electron arrangements account for the relative stabilities of the two iron ions?

2

(4)

2. The formulae of certain substances are shown below. All the questions relate to these substances. The answer to each question will be a letter (or group of letters) corresponding to the box(es) in the grid.

A box may be used more than once in different answers.

Correct boxes, and no more, are required to obtain each mark.

A	KBr	B	C(graphite)	C	MgO
D	C_2H_2	E	SiO_2	F	PF_5
G	CCl_4	H	SF_6	I	CO_2

Which box(es) contain(s):

- (a) a giant three-dimensional structure held by covalent bonds;
 (b) a linear molecule;
 (c) a tetrahedral molecule;
 (d) a giant three-dimensional structure held by ionic bonds;
 (e) a trigonal bipyramidal structure;
 (f) an octahedral structure?

(6)

3. Answer **EITHER A OR B.**

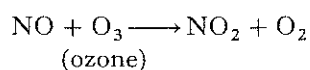
- A.** (a) Explain what you understand by
(i) nucleophilic reagents,
(ii) electrophilic reagents. 2
- (b) Ammonia adds readily to C=O bonds, whereas bromine does not. How do you account for this? 3
- (c) Aqueous sodium hydroxide does not react with benzene to form phenol. Suggest an explanation for this. 2
- (7)**

OR

- B.** (a) In some text books, zinc is not regarded as a transition element. Explain in terms of electronic structure why this should be so. 1
- (b) Mention **two** characteristics of transition elements which are not shown by zinc. 2
- (c) Name **three** different transition elements which can act as catalysts, giving the reaction or process which each catalyses. 3
- (d) What is thought to be a reason for so many catalysts being derived from transition elements? 1
- (7)**

[Turn over

4. The following exothermic reaction takes place in the upper atmosphere where the temperature is much lower than on the Earth's surface.

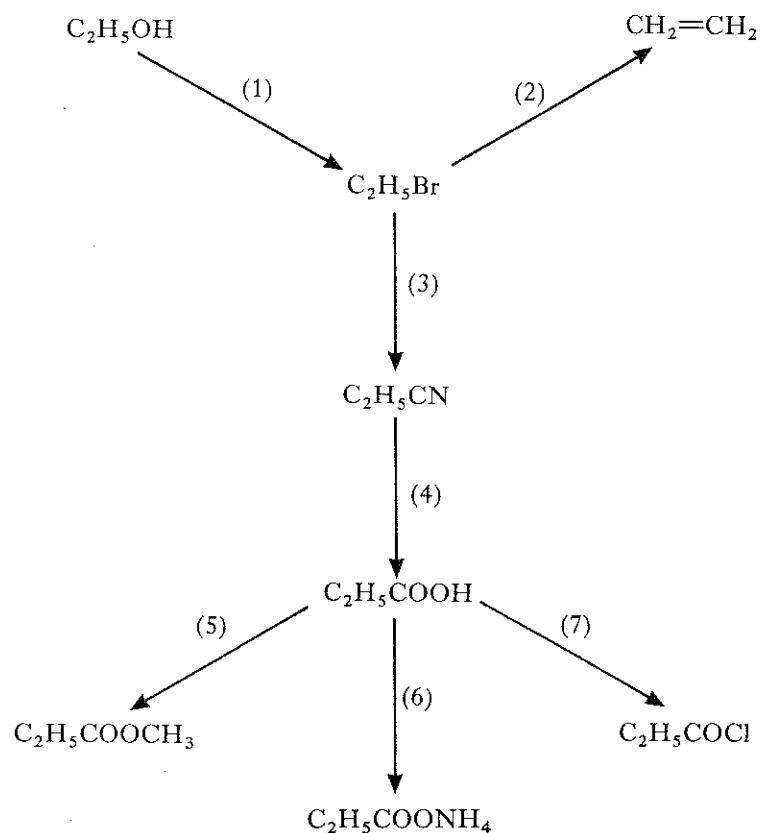


In a laboratory-simulated study carried out at room temperature, the following results were recorded.

Relative Concentration NO	Relative Concentration O ₃	Relative Rate
1	1	1
2	1	2
1	2	2

- (a) What is the overall order of the reaction? 1
- (b) Write out the rate expression for the reaction. 1
- (c) The reaction in the upper atmosphere is slower than the laboratory reaction for the same relative concentrations of NO and O₃. Account for this observation. 1
- (d) From the above equation, comment on the statement that "NO catalyses the decomposition of ozone". 1
- (e) In the above reaction, NO removes ozone from the upper atmosphere. Suggest one possible man-made source of oxides of nitrogen which could contribute to this effect. 1
- (f) (i) Chlorofluorocarbon (CFC) compounds also remove ozone from the upper atmosphere. Draw a possible structural formula for a chlorofluorocarbon compound. 2
- (ii) Give a source of these compounds mentioned in (i) above. 2
- (7)**

5. Study the organic reactions below.



The reagents necessary to bring about the above conversions are numbered. Copy the numbers into your book and, alongside each number, put the appropriate reagent. (7)

6. From the information supplied below, calculate the lattice energy of potassium bromide. (You are advised to show your working.)

<i>Reaction</i>	$\Delta H^0 / kJ mol^{-1}$
$K(s) + \frac{1}{2} Br_2(l) \longrightarrow K^+ Br^-(s)$	- 390
$K(s) \longrightarrow K(g)$	+ 90
$K(g) \longrightarrow K^+(g) + e^-$	+ 420
$\frac{1}{2} Br_2(l) \longrightarrow Br(g)$	+ 110
$Br(g) + e^- \longrightarrow Br^-(g)$	- 340

(3)

[Turn over

7. Answer EITHER A OR B.

- A. In aqueous solution, Fe^{2+} forms a deep red complex with the colourless compound phenanthroline. The intensity of the colour for a particular concentration of Fe^{2+} is independent of pH in the range 2 to 9.

With the aid of a single-beam colorimeter, an analysis of a series of solutions of Fe^{2+} with phenanthroline yielded the following results.

Concentration of $\text{Fe}^{2+} / \text{g l}^{-1}$	Reading on Colorimeter
0.003	31
0.005	47
0.009	84
0.015	140
Solvent water	3
Unknown	64

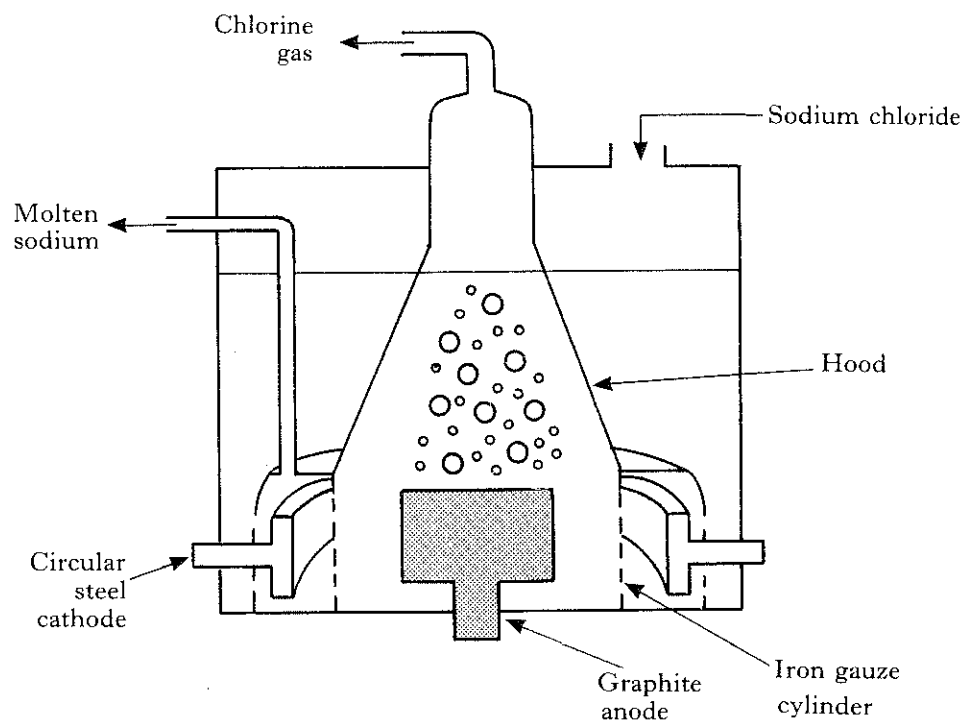
- (a) What colour transmission filter should be used in the colorimeter? 1
- (b) Evaluate the concentration of Fe^{2+} in the unknown solution. 3
- (c) Suggest a reason why the solvent gave a reading. 1
- (d) Suggest one condition which should be fulfilled in preparing the above solutions. 1
- (e) Name one process responsible for the colour of transition metal complexes. 1
- (7)

OR

- B. 20 cm^3 of 0.1M ammonium oxalate solution was acidified with dilute sulphuric acid, heated to 60°C , and titrated with potassium permanganate solution. 20 cm^3 of the latter brought about the complete oxidation of the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, to carbon dioxide.

- (a) Write the ion-electron half equation for the oxidation of oxalate ions. 1
- (b) Why was it necessary to heat the oxalate solution to 60°C ? 1
- (c) How would you recognise the end point of the titration? 1
- (d) How many moles of $\text{C}_2\text{O}_4^{2-}$ react with one mole of MnO_4^- ? 2
- (e) What was the molarity of the potassium permanganate solution? 2
- (7)

8. (a) What is meant by the electron affinity of an element? 1
- (b) For carbon and nitrogen, the electron affinities are $-121.2 \text{ kJ mol}^{-1}$ and -4.0 kJ mol^{-1} respectively. 2
- By referring to electron configurations, account for the difference in these values. (3)
9. Study the diagram of the Downs cell for the extraction of sodium which operates at 7 V and 20,000 A, and then answer the questions which follow.

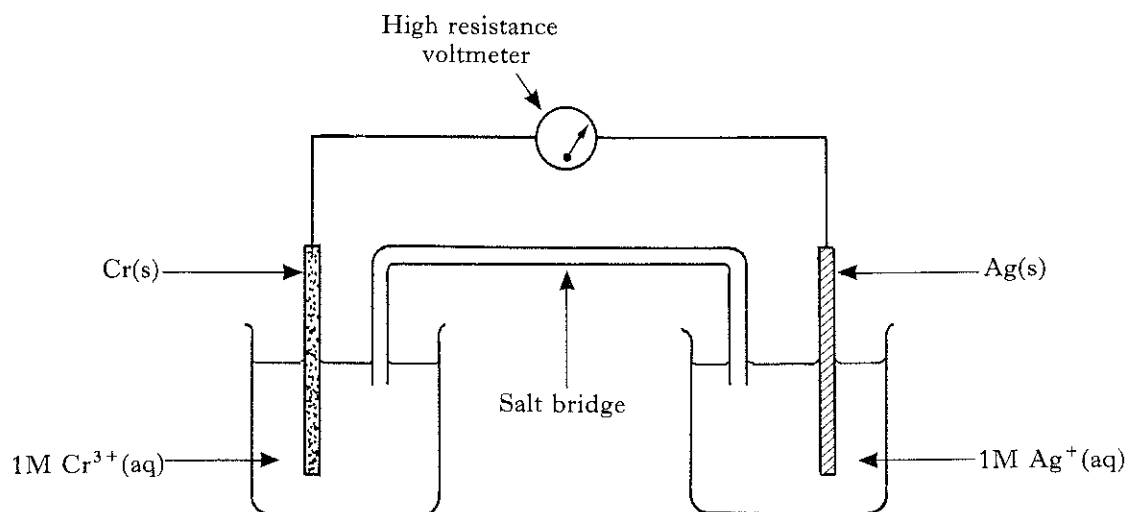


- (a) Write the equation for the reaction taking place at the graphite anode. 1
- (b) Steel is a better conductor than graphite. Apart from possible cost factors, why then is the anode made of graphite? 1
- (c) Suggest a reason why a mixture of sodium chloride and calcium chloride is used, rather than sodium chloride on its own. 1
- (d) What economic factor in the manufacture of sodium is most likely to affect the price of sodium? 1
- (e) State why purification of the sodium will be necessary. 1
- (f) In an operating cell, how is the sodium chloride/calcium chloride kept molten? 1
- (g) Why is the cell designed with a hood and a gauze cylinder? 1
- (h) Give an industrial use for
- (i) sodium metal, 1
- (ii) chlorine gas. (8)

[Turn over

10. Answer EITHER A OR B.

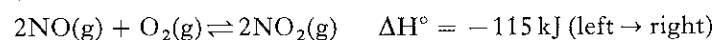
A.



- (a) What is the e.m.f. of the above cell operating under standard conditions? 1
- (b) What is the free energy change for the cell operating under standard conditions? 3
- (c) Why is a high resistance voltmeter used to measure the e.m.f. of the cell? 1
- (d) Why can the salt bridge not be replaced by a metal bridge? 1
- (e) Why would you not use sodium chloride solution in the salt bridge? 1
- (7)

OR

B. For the equilibrium,



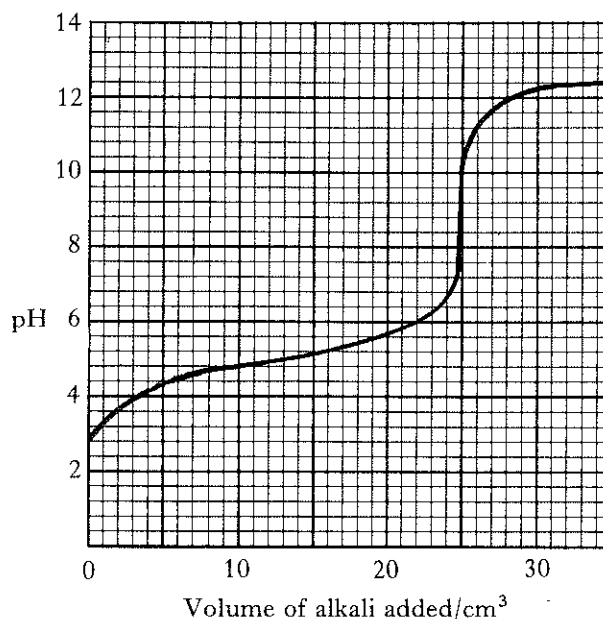
established in a closed vessel at a fixed temperature, the equilibrium constant has a value of 15 l mol^{-1} .

- (a) Write an expression for the equilibrium constant K . 2
- (b) What does the magnitude of K indicate? 1
- (c) What effect will increasing the temperature have on the value of the equilibrium constant K ? Explain your answer. 2
- (d) Calculate the equilibrium concentration of NO_2 when the equilibrium concentrations of NO and O_2 are both 0.1 mol l^{-1} . 2
- (7)

11. An ionic solid dissolves in water with the absorption of heat. In view of the fact that ΔH° is positive, account for the fact that this process is thermodynamically feasible. (3)
- 12 (a) Sketch the shapes of NH_3 and BCl_3 molecules, showing clearly all the bond angles and their values. 2
- (b) Since both nitrogen and boron have three bonding electrons, why do NH_3 and BCl_3 not have the same molecular shapes? 2

(4)

13.





The curve above shows the pH change when a solution of 0.1M sodium hydroxide is added to 20 cm³ of a solution of a monoprotic acid.

- (a) What is the molarity of the acid? 1
- (b) Is the acid weak or strong? Justify your answer. 2
- (c) What factor must be considered when an indicator for a particular titration is selected? 1
- (d) Copy the graph in your book (no graph paper required) and show, by a dotted line starting from the pH axis, the curve you would expect if the alkali were replaced by 0.1M ammonia solution. 2
- (e) Comment on the use of an indicator for the titration in (d) above. 1

(7)

[Turn over

14. Answer **A OR B OR C**.

- A. Explain why  is a more appropriate representation of the structure of benzene than .

What physical and chemical evidence supports your reasoning? (4)

OR

- B. Choose **two** examples of chemical pollution, describe the effects and suggest possible solutions. (4)

OR

- C. Discuss **three** methods available for separating mixtures of substances and comment on each method. (4)

[END OF QUESTION PAPER]