

[0500/269] 1986

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Friday, 16th May—9.30 a.m. to 12.00 noon



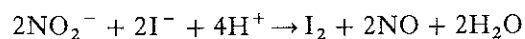
Dalziel High School
Chemistry Department



1986 CSYS

1. Which of the following represents the electron configuration of the highest energy level of an atom of a Group III element in the ground state?
- A $3s^23p^1$
 B $3s^23d^3$
 C $4s^23d^1$
 D $4s^24p^3$
2. The formation of iron(III) oxide may be given by
- $$2\text{Fe(s)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} \quad \Delta G_r^\circ = -741.0 \text{ kJ}$$
- The standard free energy change for the reaction
- $$\frac{4}{3}\text{Fe(s)} + \text{O}_2\text{(g)} \rightarrow \frac{2}{3}\text{Fe}_2\text{O}_3\text{(s)}$$
- will be
- A -494.0 kJ
 B -741.0 kJ
 C -988.0 kJ
 D -1111.5 kJ
3. Which of the following reactions would you expect to be exothermic?
- A $\text{Na(s)} \rightarrow \text{Na(g)}$
 B $\frac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{Cl(g)}$
 C $\text{Na(g)} \rightarrow \text{Na}^+\text{(g)} + \text{e}^-$
 D $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-\text{(g)}$
4. Which of the following contains the Avogadro constant of molecules?
- A 12 g carbon
 B 16 g oxygen
 C 40 g magnesium oxide
 D 160 g bromine
5. Which one of the following will produce an acidic solution in water?
- A Aluminium sulphate
 B Sodium sulphate
 C Potassium phenoxide
 D Ammonium ethanoate
6. How many moles of iron(II) ions can be oxidised by one mole of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, in acid solution? (You may wish to consult the Data Book.)
- A 1
 B 2
 C 3
 D 6
7. Which of the following reactions lead to an increase in entropy?
- (i) $\text{NaCl(s)} + \text{H}_2\text{O(l)} \rightarrow \text{NaCl(aq)}$
 (ii) $\text{Pb(s)} + \text{Br}_2\text{(l)} \rightarrow \text{PbBr}_2\text{(s)}$
 (iii) $\text{Na(s)} + \text{H}_2\text{O(l)} \rightarrow \text{NaOH(s)} + \text{H}_2\text{(g)}$
 (iv) $\text{CH}_2=\text{CH}_2\text{(g)} + \text{HCl(g)} \rightarrow \text{CH}_3\text{CH}_2\text{Cl(g)}$
- A (i) and (iii)
 B (i), (ii) and (iii)
 C (i), (iii) and (iv)
 D (ii) and (iii)
8. In a mass spectrum, which of the following would give a line at the same place as $[\text{}^{12}\text{C}^1\text{H}_4]^+$?
- A $[\text{}^{14}\text{N}_2]^+$
 B $[\text{}^{14}\text{N}^1\text{H}_2]^{2+}$
 C $[\text{}^{28}\text{Si}^1\text{H}_4]^{2+}$
 D $[\text{}^7\text{Li}^1\text{H}]^{2+}$
9. The reaction between nitrogen monoxide (NO) and hydrogen occurs by the following steps:
- $$2\text{NO} + \text{H}_2 \xrightarrow{\text{slow}} \text{N}_2 + \text{H}_2\text{O}_2$$
- $$\text{H}_2\text{O}_2 + \text{H}_2 \xrightarrow{\text{fast}} 2\text{H}_2\text{O}$$
- The order of this reaction will be
- A 1
 B 2
 C 3
 D 4

10. In the reaction

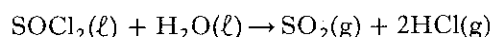


the rate of formation of iodine is doubled when $[\text{NO}_2^-]$ is doubled, halved when the $[\text{I}^-]$ is halved and increased by a factor of four when the $[\text{H}^+]$ is doubled.

The rate law for the reaction is

- A Rate = $k[\text{NO}_2^-]^2[\text{I}^-]^2[\text{H}^+]^4$
- B Rate = $k[\text{NO}_2^-][\text{I}^-]^{0.5}[\text{H}^+]^4$
- C Rate = $k[\text{NO}_2^-][\text{I}^-]^{0.5}[\text{H}^+]^2$
- D Rate = $k[\text{NO}_2^-][\text{I}^-][\text{H}^+]^2$.

11. For the reaction



the ΔS_{298}° and ΔH_{298}° values are

+336.1 J K⁻¹ mol⁻¹ and +49.4 kJ mol⁻¹ respectively. Which one of the following statements is true at 25 °C?

The reaction is

- A not feasible
- B feasible and would be exothermic
- C feasible and would be endothermic
- D feasible and would be stopped by increasing the temperature.

12. Dilute sulphuric acid is electrolysed using platinum electrodes. How many litres of gas corrected to s.t.p. is produced at the positive electrode after the passage of one faraday of electricity?

- A 5.6
- B 11.2
- C 22.4
- D 44.8

13. Which of the following most accurately describes how the atoms of sulphur are held together in the solid state?

- A Covalent bonding
- B Polar covalent bonding
- C van der Waals bonding
- D Covalent and van der Waals bonding

14. Silicon carbide (SiC) has a similar structure to diamond with silicon and carbon atoms alternating through the lattice.

Which of the following is correct?

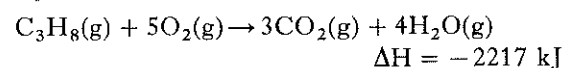
In solid silicon carbide

- A there are CSi_4 molecules each of which contains one carbon atom surrounded by four silicon atoms
- B each carbon atom is surrounded tetrahedrally by four silicon atoms
- C silicon and carbon atoms are packed into a cubic lattice with six silicon atoms around each carbon and six carbon atoms around each silicon atom
- D silicon and carbon atoms are closely packed together as densely as possible.

15. Which of the following is an essential property of a solvent to be used for recrystallisation purposes?

- A Immiscibility with water (insoluble in water)
- B A low boiling point
- C Ability to dissolve more solute when hot than when cold
- D Ability to dissolve more solute when cold than when hot

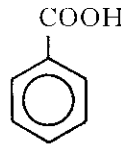
16. Propane burns in oxygen according to the equation



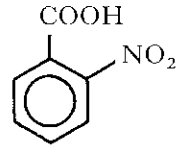
A particular stove, operating on propane, has a heat output of 22.17 kJ min⁻¹. Which one of the following statements applies to each minute that the stove operates?

- A 0.05 g of oxygen is consumed.
- B 0.44 g of propane is consumed.
- C 1.8×10^{24} molecules of CO_2 are produced.
- D 0.72 kg of water is produced.

[Turn over

17. All noble gases are characterised in terms of electrons by the completion of the outermost orbital. This orbital is a(n)
- s-orbital
 - p-orbital
 - d-orbital
 - s or p-orbital.
18. In the determination of nickel in a nickel (II) salt, 1 mole of EDTA is equivalent to 1 mole of nickel.
What is the molarity of a nickel (II) solution if 20 cm³ of it react with 2×10^{-3} moles EDTA?
- 0.002
 - 0.01
 - 0.02
 - 0.1
19. Which of the following statements referring to the structures of sodium chloride and caesium chloride is correct?
- There are eight chloride ions surrounding each sodium ion.
 - There are six chloride ions surrounding each caesium ion.
 - The chloride ions are arranged octahedrally round the sodium ions.
 - The chloride ions are arranged tetrahedrally round the caesium ions.
20. Sodium vapour street lamps emit yellow light because
- sodium vapour filters out all the light from the filament except yellow
 - sodium electrons are absorbing energy corresponding to yellow light as they move to higher energies
 - sodium vapour is burning and giving out a yellow glow
 - sodium electrons are giving out energy corresponding to yellow light as they move to lower energies.
21. What is the change in the three dimensional arrangement of the bonds round the P atom in the following reaction?
- $$\text{PF}_3 + \text{F}_2 \rightarrow \text{PF}_5$$
- Trigonal planar to pyramidal
 - Pyramidal to tetrahedral
 - Pyramidal to square planar
 - Pyramidal to trigonal bipyramidal
22. Which one of the following molecules contains three atoms in a straight line?
- BF₃
 - CH₄
 - H₂O
 - SF₆
23. One mole of each of the following substances is completely hydrogenated. Which requires the largest number of moles of hydrogen molecules?
- Benzene
 - Cyclohexene
 - Hex-1-ene
 - Ethyne
- 24.
- 

pK_a = 4.2



pK_a = 2.2
- From the decrease in pK_a value it can be deduced that the nitro group
- attracts electrons so increases proton donation by the carboxyl group
 - attracts electrons so decreases proton donation by the carboxyl group
 - repels electrons so increases proton donation by the carboxyl group
 - repels electrons so decreases proton donation by the carboxyl group.

25. Which of the following does **not** apply to the reaction between methane and chlorine?

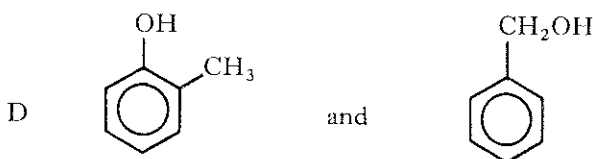
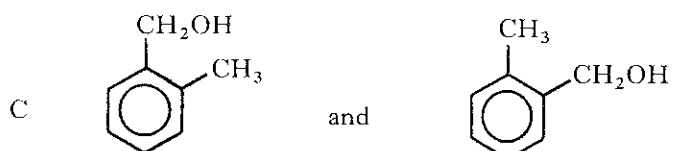
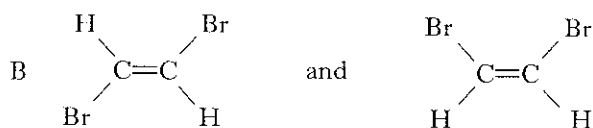
The reaction

- A is exothermic
- B involves free radicals
- C involves heterolytic fission
- D involves homolytic fission.

26. Ethanoic acid is allowed to react with PCl_5 forming an organic compound X. On allowing X to react with sodium ethanoate the main organic product is

- A ethyl ethanoate
- B ethanoic acid
- C ethanoic anhydride
- D ethoxyethane.

27. Which of the following have the same physical and chemical properties?

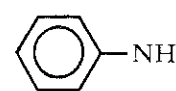


28. A colourless liquid did not react with ammoniacal silver (i) nitrate solution but gave a brightly coloured crystalline solid when treated with 2,4-dinitrophenylhydrazine solution.

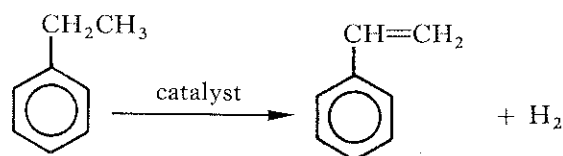
Which of the following could be the liquid?

- A $\text{C}_2\text{H}_5\text{CHO}$
- B $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
- C $\text{C}_2\text{H}_5\text{OH}$
- D $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$

29. Which of the following is the strongest base?

- A NH_3
- B CH_3CONH_2
- C $\text{CH}_3\text{CH}_2\text{NH}_2$
- D 

30. Phenylethene can be produced by the dehydrogenation of ethylbenzene.



ΔH_{298}° is positive

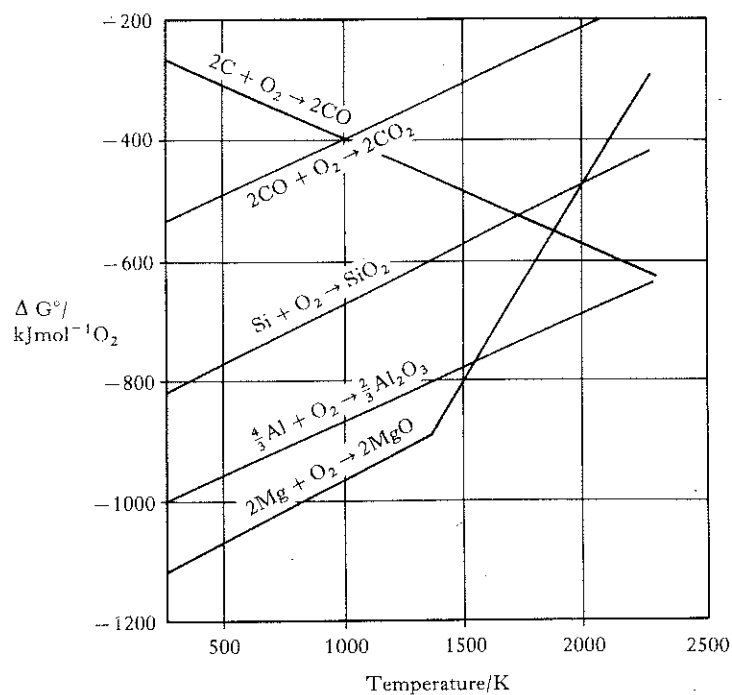
The reaction is carried out in the gaseous state. The conditions which should give the highest yield of phenylethene are

- A high temperature and low pressure
- B high temperature and high pressure
- C low temperature and low pressure
- D low temperature and high pressure.

[Turn over

31. The purple colour of an aqueous solution of potassium permanganate is due to
- emission of energy and the promotion of d electrons in the permanganate ion
 - absorption of energy when electrons are transferred from the oxygen to the manganese atom
 - absorption of the red and blue components of white light
 - emission of energy when electrons are transferred from the oxygen to the manganese atom.

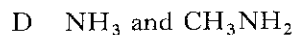
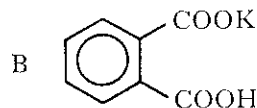
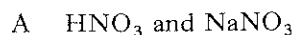
The Ellingham diagram below refers to **questions 32 and 33**.



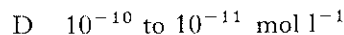
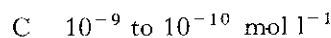
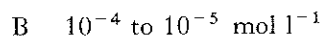
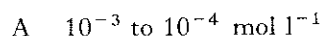
32. The value of ΔG° for the reaction $2C + O_2 \rightarrow 2CO$ decreases as temperature increases. What is the **main** reason for this decrease?
- ΔS° is positive.
 - ΔS° is negative.
 - ΔH° is positive.
 - ΔH° is negative.

33. The reduction of silicon dioxide is thermodynamically feasible using
- magnesium at temperatures over 2000 K
 - aluminium between 500 and 2000 K
 - carbon monoxide between 500 and 2000 K
 - carbon at a temperature of 1000 K.

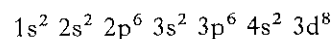
34. Which of the following could be used to produce an aqueous buffer solution?



35. An indicator used in an acid-alkali titration changes colour at pH 4.4. What is the range of concentration of hydroxide ions in the solution at the end point shown by this indicator?



36. A nickel atom has the electron configuration



The number of unpaired electrons in a gaseous Ni^{3+} ion is



37. Which one of the following pairs of numbers represents the oxidation numbers of titanium in K_2TiO_3 and TiO_2 respectively?

- A 2 and 2
- B 4 and 2
- C 2 and 4
- D 4 and 4

To answer Questions 38 to 40 use the following code.

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

If only 1 and 2 are correct, select B.

If only 3 is correct, select C.

Otherwise select D.

38. In modern electron theory it is accepted that

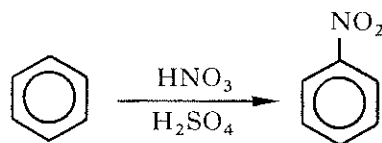
- 1 each succeeding electron shell, in the lower energy shells, contains an additional orbital type
- 2 orbitals of the same type in different shells differ only in size and energy
- 3 the total number of electrons which may occupy any one orbital is two.

39. Which of the following can be determined by a single experiment?

The

- 1 enthalpy of combustion of ethanol
- 2 first ionisation energy of helium
- 3 lattice energy of magnesium chloride.

40.

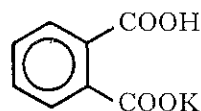


The above reaction involves

- 1 substitution
- 2 electrophilic attack
- 3 free radicals.

[END OF QUESTION PAPER]

1. Volumetric analysis procedures require the use of primary standards such as potassium hydrogen phthalate—



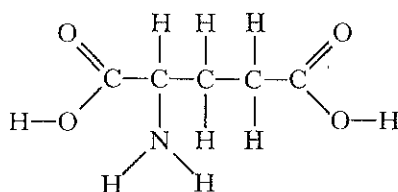
because they meet certain requirements.

(a) What is meant by a primary standard? 1

(b) Give **two** necessary requirements of a primary standard. 2

(3)

2. Glutamic acid has the structure



(a) How many moles of

(i) HCl,

(ii) NaOH,

would react with one mole of glutamic acid? 2

(b) Monosodium glutamate is a common flavour enhancer added to tinned foods.

(i) Draw the full structural formula for monosodium glutamate. 1

(ii) The use of such food additives is a matter of public concern.

Discuss briefly why this is so. 2

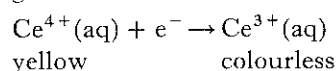
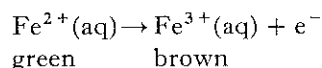
(5)

3. Answer EITHER A OR B

A. The following reagents can be obtained as crystalline solids:

Reagent	Formula
X	$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
Y	$\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$

Solutions of these reagents react as follows:



1.50 g of tablets containing iron (II) gluconate, used to treat iron deficiency in the body, were dissolved in dilute sulphuric acid. The solution was titrated against 0.12 M solution of reagent Y. The end point was reached when 25 cm³ of the reagent were added.

- (a) Calculate the percentage of iron (by mass) present in the iron (II) gluconate tablets. 4
- (b) Explain why reagent X is coloured both in aqueous solution and in the solid state. 2
- (c) The concentration of Ce⁴⁺(aq) could be measured by colorimetry. 1
- What colour of filter would be used in this technique? (7)

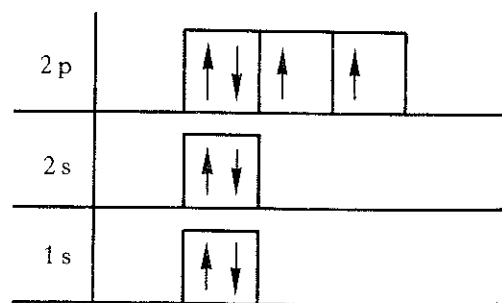
OR

B. A metal chloride (6.05 g) was dissolved in water and the solution made up to a final volume of 100 cm³. A solution of silver (I) nitrate containing 34 g l⁻¹ was titrated against 20 cm³ of the metal chloride solution. The end point was detected when 50 cm³ of the silver (I) nitrate solution had been added.

- (a) Calculate the molarity of the silver (I) nitrate solution. 1
- (b) What mass of metal is present in the metal chloride sample? 4
- (c) Use the experimental results to establish that the metal chloride is rubidium chloride. 2
- (7)

[Turn over

4.



The electron configuration of an oxygen atom may be represented as shown above.

(a) Explain how this structural representation agrees with

(i) the Pauli exclusion principle,

(ii) Hund's Rule of maximum multiplicity.

2

(b) The three 2p orbitals are degenerate.

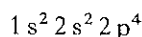
(i) What does this mean?

1

(ii) How do the three 2p orbitals differ from each other?

1

(c) The electron configuration of oxygen may also be represented as



Draw the electron configuration of the Mn^{2+} ion in this way.

1

(5)

5. Answer **EITHER A OR B**.

A. As an ionic solute crystallises it forms a *more orderly* structure, yet there can sometimes be an *increase* in entropy during crystallisation of some ionic solutions.

Explain the apparent contradiction in these cases.

(2)

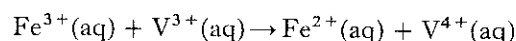
OR

B. Endothermic reactions are those which involve an *increase* in enthalpy. Many pupils are surprised when they find that such reactions cause a *drop* in temperature.

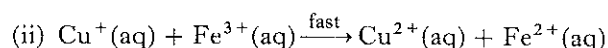
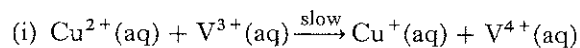
Explain why there is no real contradiction in this case.

(2)

6. The reaction between iron(III) ions and vanadium(III) ions is first order with respect to both species.



In the presence of copper (II) ions the reaction proceeds much more rapidly and there is evidence to suggest the following mechanism:



(a) Write the rate expression for the reaction between iron (III) ions and vanadium (III) ions.

1

(b) What is the order of reaction with respect to iron (III) ions when copper (II) ions are present?

Explain your answer.

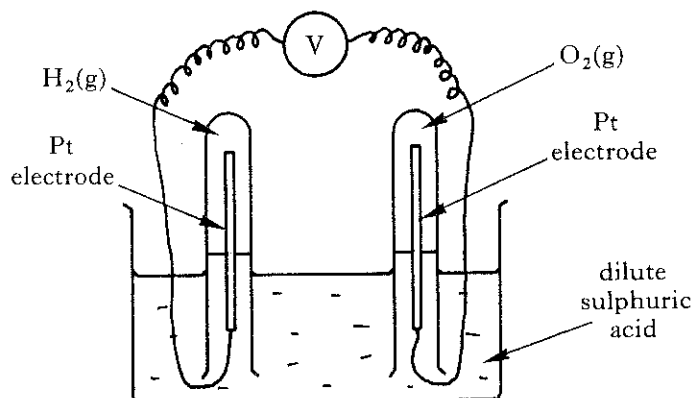
2

(c) In addition to the observation that copper (II) ions alter the rate, what indication is there that the copper (II) ions are acting as a catalyst for the reaction?

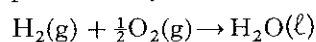
1

(4)

7. A simple fuel cell can be constructed as follows:



The overall cell reaction can be represented by:



for which

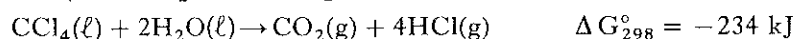
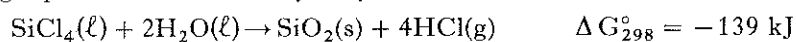
$$\Delta G_{298}^{\circ} = -237 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ} = -286 \text{ kJ mol}^{-1}$$

- (a) Use the data book to write half-equations for the reactions occurring at each electrode during the operation of the cell. 2
- (b) Calculate the standard voltage of the fuel cell. 2
- (c) Calculate ΔS_{298}° for the cell reaction and explain why there is a significant entropy change. 3
- (d) In the 1980s research is likely to continue into the development of the electric car. Discuss some of the advantages and disadvantages of such a vehicle. 2

(9)

8. The following equations are for two hydrolyses:

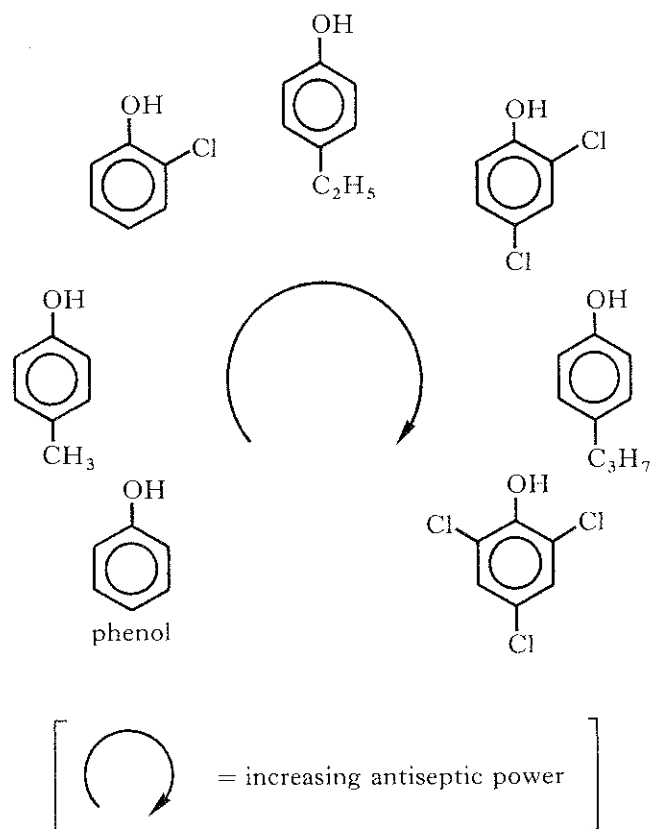


- (a) **From this information alone** what predictions can be made about their
- feasibility,
 - position of equilibrium,
 - rate?
- (b) In practice, the addition of water to tetrachlorosilane (SiCl_4) results in an immediate vigorous hydrolysis. The addition of water to tetrachloromethane has no effect even with prolonged boiling. Suggest an explanation for this difference. 1

(4)

[Turn over

9. The effectiveness of phenol as an antiseptic was improved by structural modifications:

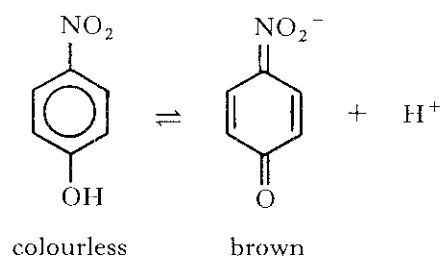


- (a) Suggest why, apart from its lower antiseptic power, it was found necessary to discontinue the use of phenol as an antiseptic. 1
- (b) Describe the trends which appear to have improved the antiseptic quality of phenol. 2
- (c) Sketch the structural formula of a molecule likely to exceed the antiseptic power of the final molecule in the sequence given. 1

(4)

10. The compound $C_6H_4(NO_2)OH$ behaves as a simple acid/base indicator.

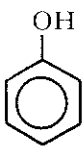
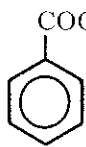
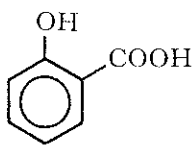
It exists in the equilibrium:



Explain how this system operates as an indicator. (2)

11. Answer EITHER A OR B.

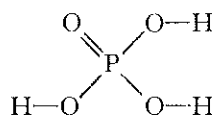
A. Consider the data for three compounds:

	Compound X	Compound Y	Compound Z
			
K_a	1.0×10^{-10}	6.3×10^{-5}	—
pK_a	10.0	—	2.99

- (a) Write an equation showing the ionisation for which the given pK_a value of compound Z applies. 1
- (b) Calculate (i) pK_a for compound Y, 2
(ii) K_a for compound Z. 2
- (c) Calculate the pH of a 0.0001 M solution of compound X. 2
- (d) Hydrogen bonding occurs between molecules in samples of compound Y. 1
(i) What effect does this produce in an infra-red spectrum of the compound? 1
(ii) Suggest **one** other property of compound Y which is affected by hydrogen bonding. 1
- (e) It has been suggested that there is an *intramolecular* hydrogen bond in compound Z. 1
Draw the full structural formula of compound Z and indicate this hydrogen bonding. 1
- (8)**

OR

B. A hydrogen atom bonded to phosphorus is not as readily ionised as a hydrogen atom bonded to oxygen. This is important in the chemistry of acids of phosphorus, e.g., H_3PO_4 is a triprotic acid with the full structural formula:



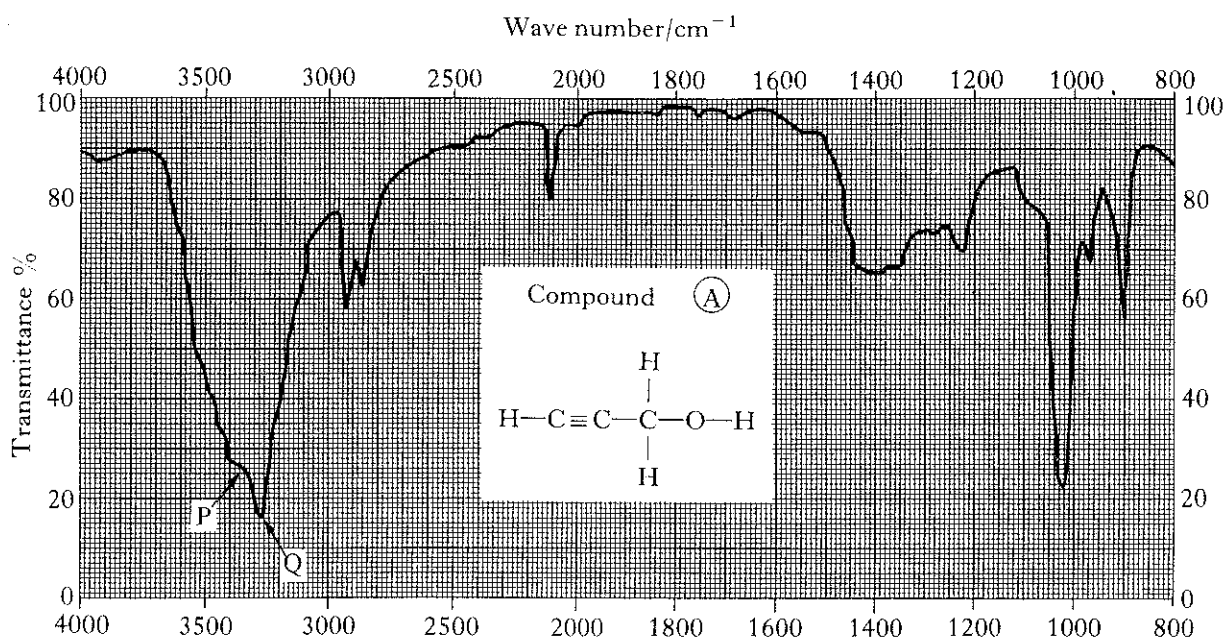
- (a) What is meant by the term "triprotic"? 1
- (b) Suggest full structural formulae for (i) H_3PO_2 a monoprotic acid, 2
(ii) H_3PO_3 a diprotic acid. 2
- (c) The following equilibria occur in aqueous hydrofluoric acid. 2
Equilibrium ①: $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
Equilibrium ②: $HF(aq) + F^-(aq) \rightleftharpoons HF_2^-(aq)$
(i) Write expressions for the equilibrium constants K_1 and K_2 for equilibria ① and ② respectively. 2
(ii) Calculate the concentration of hydrogen ions in a solution of 1 M $HF(aq)$ where $K_1 = 7.0 \times 10^{-4} \text{ mol l}^{-1}$. 2
(iii) State the units for K_2 . 1
- (8)**

12. The bonds of functional groups on organic molecules absorb radiation of different wave number, making identification of functional groups possible.

The table below shows the range of radiation absorbed by the bonds indicated with thicker lines.

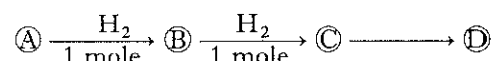
Bond Type	Wave number/cm ⁻¹
O—H	3600–3200
C≡C—H	3300–3260
C=C—H	3100–3000
C—C—H	2950–2850
C≡C	2250–2100
C=O	1850–1650
C=C	1650–1600
C—O	1250–1050

A typical infra-red spectrum is shown here:



Note that peak Q is due to the absorbance of infra-red radiation by the bond C—H in C≡C—H.

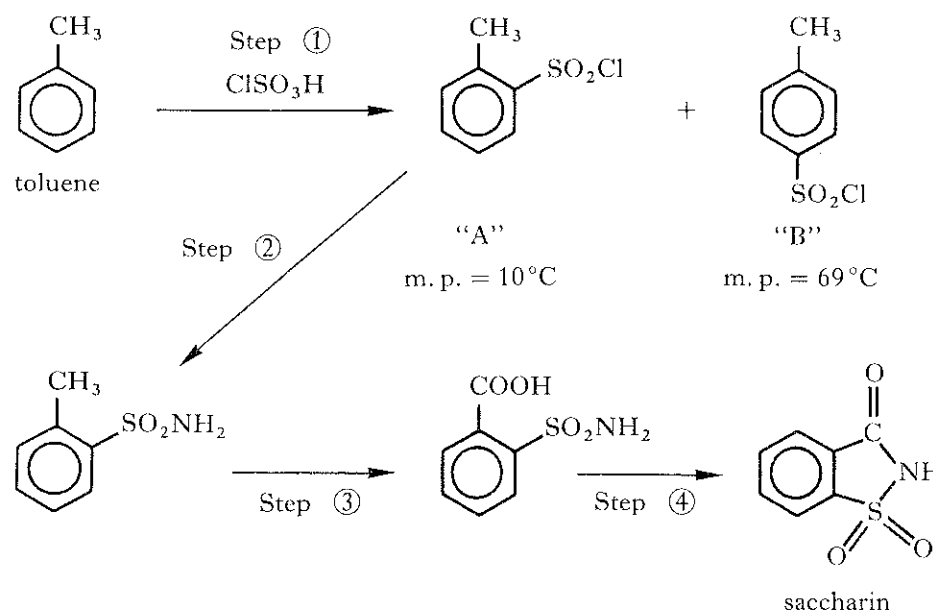
A series of reactions is performed with compound **A** as the starting material:



- (a) (i) How would the spectrum of compound **B** differ from that of compound **A**? 1
 (ii) How would the spectrum of compound **C** differ from that of compound **B**? 1
- (b) The spectrum of compound **D** ($\text{C}_3\text{H}_6\text{O}$) shows no peaks P and Q but a new peak is present at wave number 1740 cm^{-1} .
 (i) Draw the full structural formula for **D**. 1
 (ii) Suggest a suitable reagent for converting **C** to **D**. 1
- (c) In practice, it is highly unlikely that one mole of compound **D** could be obtained by carrying out this series of reactions on one mole of compound **A**.
 Suggest **two** possible reasons for this. 2
- (d) Compounds **B** and **D** are isomers. A third isomer has a similar infra-red spectrum to that of compound **D**.
 Identify this isomer. 1

(7)

13. A possible synthesis of saccharin is outlined below:



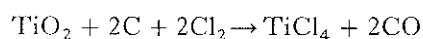
- (a) (i) What is the systematic name of toluene? 1
 (ii) What type of attack on toluene occurs in step ①? 1
 (iii) Throughout this series of reactions the aromatic ring remains intact.
 Account for this stability. 1
- (b) Suggest a suitable method for separating the compound "A" from compound "B". 1
- (c) What type of reaction is involved in
 (i) step ③, 2
 (ii) step ④? 2

(6)

[Turn over

14. Titanium was first extracted in 1910. It occurs as titanium dioxide in the ore, rutile. Large scale production of the metal was not carried out until the middle of the twentieth century but it is now expanding rapidly.

- (a) Reduction of the oxide by heating with carbon is feasible but uneconomic.
- (i) Suggest a reason for this. 1
- (ii) What undesirable property would be imparted to the titanium as a result of incompletely-removed carbon? 1
- (b) The first stage in the extraction involves roasting the oxide with carbon in a stream of chlorine. The equation for the reaction is



<i>Compound</i>	m.p./K	b.p./K
TiO ₂	2098	very high
TiCl ₄	248	401

Use the data to explain

- (i) how the TiCl₄ can be separated from unused reactants;
- (ii) why TiCl₄ cannot be electrolysed to produce the metal. 2
- (c) The metal can be produced by heating TiCl₄ with magnesium in an atmosphere of argon.
- (i) Write the balanced equation for this reaction. 1
- (ii) Why is the argon atmosphere required? 1
- (iii) How could the magnesium be recovered? 1

(7)

15. Answer **EITHER A OR B OR C.**

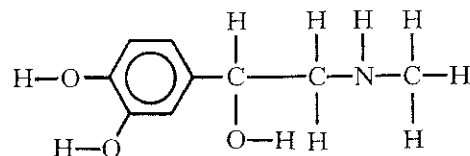
- A. "In the chemical industry, the siting of a manufacturing plant and the conditions used to operate the chemical reactions within it are decided by social and economic factors. Other important considerations are energy requirements and environmental effects."

Discuss this statement with reference to any **one** common industrial process.

(4)

OR

- B. "The structural formula of the hormone adrenaline is shown below.



This formula does not indicate the true shape of the molecule. For example, in the terminal methyl group the bonds are arranged tetrahedrally around the carbon atom."

Discuss other parts of the molecule in this way.

(4)

OR

- C. "Wool and silk have been important fibres for many centuries. Nylon and chemically-related synthetic fibres now make a significant contribution to the textile industries."

Discuss the similarities and differences in structures and properties of the nylons and the natural fibres.

Comment on factors which may affect the relative proportion of the market gained by natural and synthetic fibres in the future.

(4)

[END OF QUESTION PAPER]