[0500/393] 1994

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Friday, 20th May—1.30 p.m. to 3.10 p.m.

Dalziel High School
Chemistry Department

1994 CSYS

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1. In which of the following is the number of molecules greatest?

   A 6×10^{23} molecules of hydrogen

   B 10 g carbon dioxide

   C 6 g hydrogen

   D 2 moles carbon dioxide

2. When electrons occupy degenerate orbitals, they do so in such a way as to maximise the number of parallel spins. This statement is known as

   A the Pauli exclusion principle

   B Heisenberg's uncertainty principle

   C the aufbau principle

   D Hund's rule.

3. Which of the following salts shows most ionic character?

   A Na^+Br^-

   B K^+Cl^-

   C Li^+I^-

   D Na^+Cl^-

4. Which of the following most accurately represents the quantity of electricity needed to deposit 54 g aluminium during the electrolysis of molten aluminium oxide?

   A 2 F

   B 3 F

   C 5 F

   D 6 F

5. Which of the following decreases when an aqueous solution of ethanoic acid (1 mol l^{-1}) is diluted? The

   A pH

   B $[H^+]$

   C pK_a

   D degree of dissociation.

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

   A an energy level within an atom

   B a principal quantum number

   C the energy released when an electron drops to a lower level

   D the energy absorbed from the visible part of the electromagnetic spectrum.

7. How many moles of iron(II) ions are oxidised by one mole of potassium dichromate, $K_2Cr_2O_7$, in acid solution?

   A 1

   B 2

   C 3

   D 6

8. 32 g sulphur were converted to the corresponding mass 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.

9. $Ba(OH)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaOH(aq)$

   50 cm^3 sodium sulphate (0·01 mol l^{-1}) were added to 50 cm^3 barium hydroxide (0·01 mol l^{-1}). The resulting solution consisted of 100 cm^3 of sodium hydroxide of concentration

   A 0·001 mol l^{-1}

   B 0·01 mol l^{-1}

   C 0·02 mol l^{-1}

   D 0·10 mol l^{-1}.

[Turn over

10. Which of the following reactions exhibits a positive entropy change? The

A formation of ice from water

B combination of ammonia and hydrogen chloride gases to give solid ammonium chloride

C polymerisation of ethene

D decomposition of solid ammonium nitrate into nitrogen oxide gas and steam.

11. The reaction expressed by the stoichiometric equation

$$Q + R \rightarrow X + Z$$

was found to be first order with respect to each of the reactants.

Which of the following statements is correct?

A Overall, the reaction is first order.

B If the initial concentrations of Q and R are halved, the rate of the reaction will be halved.

C The rate of the reaction decreases as the reaction proceeds.

D The rate of the reaction is independent of the concentration of either Q or of R.

Questions 12, 13 and 14 refer to the following shapes of molecules or ions.

A Linear

B Bent

C Planar trigonal

D Pyramidal

What is the shape of the following species?

12. CO_2

13. H_2S

14. H_3O^+

15. $Ti^{3+}(aq) + e^- \rightarrow Ti^{2+}(aq)$ $\quad E^\circ = -0{\cdot}37$ V

$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$ $\quad E^\circ = -0{\cdot}26$ V

It can be concluded that, for the reaction represented by the equation

$$V^{3+}(aq) + Ti^{2+}(aq) \rightleftharpoons V^{2+}(aq) + Ti^{3+}(aq),$$

the standard free energy change and the equilibrium constant for the **forward** (i.e. left to right) reaction will be

A negative and $K > 1$

B positive and $K > 1$

C negative and $K < 1$

D positive and $K < 1$.

16. The electron configuration of an atom of X is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$$

The chemistry of X is therefore likely to be similar to that of

A titanium

B calcium

C vanadium

D yttrium.

17. Why is it not practicable to find the concentration of a solution of ethylamine by titration with standard propanoic acid solution using an indicator?

A The pH change at the end point is small.

B An organic base neutralises an organic acid very slowly.

C The salt of the above acid and alkali is subject to hydrolysis by water.

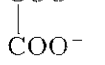
D An insoluble salt is formed.

18. Which of the following would **not** act as a ligand in the formation of a complex with a transition metal ion?

A O^{2-}

B $NH_2C_2H_4NH_2$

C $C_2H_5NH_3^+$

D 

19. Which solid would form a colourless aqueous solution?

A K_2CrO_4

B VCl_2

C $ZnSO_4.7H_2O$

D $NiSO_4.6H_2O$

20. Which of the following species can reduce a solution of nickel ions to nickel, assuming standard conditions?

A Pb(s)

B $Pb^{2+}(aq)$

C Zn(s)

D $Zn^{2+}(aq)$

21. Which of the following processes is **least** likely to be carried out on an industrial scale in Britain in the 1990s?

A Decane → octane + ethene

B Ethene + hydrogen → ethane

C Methane + oxygen → carbon dioxide + water

D Ethene + hydrogen chloride → chloroethane

22. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^\circ = -394 \text{ kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\quad \Delta H^\circ = -286 \text{ kJ mol}^{-1}$

$C_6H_{14}(\ell) + 9\frac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(\ell)$ $\quad \Delta H^\circ = -4160 \text{ kJ mol}^{-1}$

Using the above data, the standard enthalpy of formation of hexane is

A $-3480 \text{ kJ mol}^{-1}$

B $+3480 \text{ kJ mol}^{-1}$

C -206 kJ mol^{-1}

D $+206 \text{ kJ mol}^{-1}$.

23. A solution with a pH of 3·2 has a **hydroxide** ion concentration which lies between

A 10^{-2} and 10^{-3} mol l^{-1}

B 10^{-3} and 10^{-4} mol l^{-1}

C 10^{-10} and 10^{-11} mol l^{-1}

D 10^{-11} and 10^{-12} mol l^{-1}.

24. Which of the following pairs of numbers represents the oxidation number of Cr in K_2CrO_4 and CrO_2Cl_2 respectively?

A +6 and +2

B +6 and +6

C +4 and +6

D +3 and +4

25. Which of the following, when dissolved in distilled water, gives rise to a solution with a pH value greater than 7?

A Lithium chloride

B Potassium ethanoate

C Sodium sulphate

D Ammonium nitrate

[Turn over

26. A solid is fairly soluble in water and its solubility rises with increase in temperature.

Which of the following can be stated definitely about the process of dissolving the solid?

	ΔS°	ΔH°
A	negative	negative
B	negative	positive
C	positive	negative
D	positive	positive

27. Tin can exist in two different forms, "white tin" and "grey tin". For the change

"white tin" → "grey tin"

$\Delta H^\circ = 2{\cdot}5$ kJ mol^{-1}

$\Delta S^\circ = -6{\cdot}7$ J K^{-1} mol^{-1}

and hence, ΔG° at 298 K will be

A $-0{\cdot}5$ kJ mol^{-1}

B $-4{\cdot}2$ kJ mol^{-1}

C $+4{\cdot}5$ kJ mol^{-1}

D $+9{\cdot}2$ kJ mol^{-1}.

28. Silver(I) nitrate (0·1 mol l^{-1}) was added to 20 cm^3 of a metal complex solution (0·1 mol l^{-1}). Precipitation of silver(I) chloride took place and was complete after 20 cm^3 of the silver(I) nitrate solution had been added.
The complex could have been

A $K_2[PtCl_6]$

B $[Cr(H_2O)_6]Cl_3$

C $[PtCl(NH_3)_3]Cl$

D $[CrCl(H_2O)_5]Cl_2.H_2O$

29. Which of the following can **not** be determined by a single experiment? The enthalpy of

A formation of ethyne

B combustion of methanol

C solution of sodium hydroxide

D neutralisation of hydrochloric acid by sodium hydroxide.

30. Which is a correct statement about a catalyst? For a chemical reaction, it

A does not alter the value of the rate constant

B alters the value of the equilibrium constant

C alters the mechanism

D has no effect on the value of the activation energy.

31. Which of the following correctly describes an atom of nickel in its ground state?

A It has one empty d-orbital.

B It contains 12 electrons in p-orbitals.

C All orbitals with principal quantum number 3 are full.

D It contains no unpaired electrons.

32. Which of the following can be used **directly** to distinguish between an alkanal and an alkanone?

A Ammoniacal silver(I) nitrate solution

B Sodium hydrogensulphite

C 2,4-Dinitrophenylhydrazine

D Bromine water

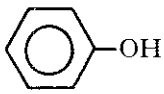
33. Alkenes may **not** be prepared by

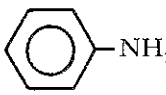
A thermal cracking of alkanes

B partial hydrogenation of alkynes

C dehydration of primary alcohols

D direct synthesis from carbon and hydrogen.

34. Consider  —OH in relation to C_2H_5OH

and  —NH_2 in relation to $C_2H_5NH_2$

The benzene ring makes

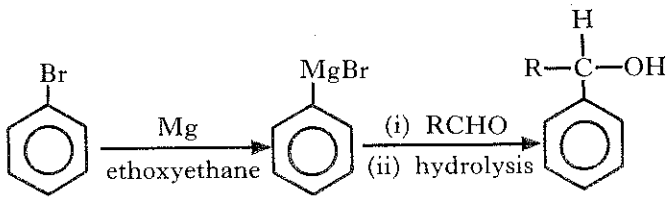
A OH less acidic and the NH_2 less basic

B OH more acidic and the NH_2 more basic

C OH less acidic and the NH_2 more basic

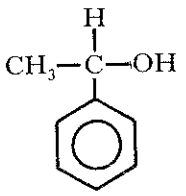
D OH more acidic and the NH_2 less basic.

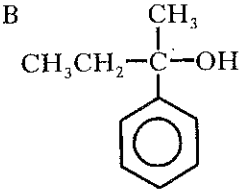
35.

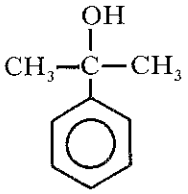


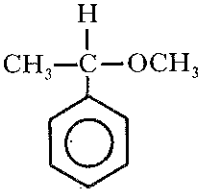
R = alkyl group or hydrogen

Using bromobenzene above and treating with propanone at (i), subsequent hydrolysis would result in the formation of

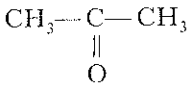
A 

B 

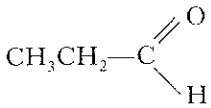
C 

D 

36. Which of the following compounds is most likely to show an infra-red absorption at 2725 cm^{-1}?

A 

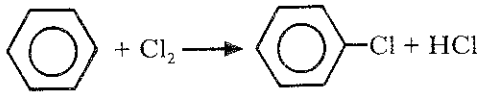
B $HOCH_2CH{=}CH_2$

C 

D $CH_3{-}O{-}CH{=}CH_2$

37. Which of the following does **not** involve a nucleophilic substitution of the organic compound?

A $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$

B 

C $C_2H_5CH_2Br + CN^- \rightarrow C_2H_5CH_2CN + Br^-$

D $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$

38. For a given chemical change involving two reactants P and Q,

rate of reaction $\propto$ [P] [Q].

If the equation representing the overall reaction is

$P + 2Q \rightarrow S + T$

the mechanism could be

A	$2Q \rightarrow R + S$	fast
	$R + P \rightarrow T$	slow
B	$P + Q \rightarrow R + S$	slow
	$R + Q \rightarrow T$	fast
C	$P \rightarrow R + S$	fast
	$2Q + R \rightarrow T$	slow
D	$P + Q \rightarrow R + S$	fast
	$R + Q \rightarrow T$	slow

39. Which of the following is exothermic?

A $K(s) \rightarrow K(g)$

B $K(g) \rightarrow K^+(g) + e^-$

C $\frac{1}{2}Br_2(l) \rightarrow Br(g)$

D $Br(g) + e^- \rightarrow Br^-(g)$

40. Which of the following is **not** correct?

A The pH of hydrochloric acid (0·1 mol l^{-1}) is 1.

B An aqueous solution of 0·1 mole of ethanoic acid and 0·1 mole potassium ethanoate is a good buffer.

C The pH of hydrochloric acid (0·1 mol l^{-1}) is less than that of ethanoic acid (0·1mol l^{-1}).

D The K_a value of ethanoic acid is greater than that of hydrochloric acid.

[Turn over

41. The boxes in the grid below contain the names for certain enthalpy changes.

A enthalpy of solution	B enthalpy of electron gain (affinity)	C enthalpy of sublimation
D enthalpy of lattice making	E enthalpy of hydration	F enthalpy of lattice breaking

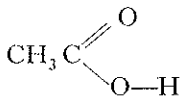
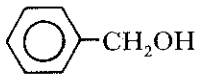
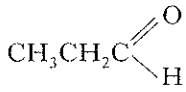
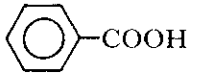
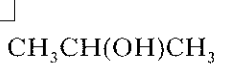
(*a*) Identify the enthalpy change for $Li^+(g) + Cl^-(g) \xrightarrow{H_2O} Li^+(aq) + Cl^-(aq)$.

(*b*) Identify the enthalpy change for $Cl(g) + e^- \longrightarrow Cl^-(g)$.

(*c*) Identify the enthalpy change for $Li^+Cl^-(s) \xrightarrow{H_2O} Li^+(aq) + Cl^-(aq)$.

(*d*) Identify the enthalpy change for $Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g)$.

42. The boxes in the grid below contain the formulae for certain organic species.

A 	B 	C 
D 	E 	F 

(*a*) Identify the species **not** exhibiting hydrogen bonding.

(*b*) Identify the species which are isomers.

(*c*) Identify the species which will give a positive Benedict's (Fehling's) test.

(*d*) Identify the species which on oxidation would produce a compound which is an isomer of D.

Marks

1. The mechanism for the bromination of methane is outlined below. Copy the mechanism and complete it by filling in the missing words or symbols for (*a*) to (*h*).

$Br_2 \xrightarrow{(a)} (b)$ initiation

$(c) + CH_4 \longrightarrow HBr + (d)$
$(e) + Br_2 \longrightarrow CH_3Br + (f)$ } (*g*)

$CH_3^{\cdot} + Br^{\cdot} \longrightarrow CH_3Br$
$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow C_2H_6$ } (*h*)

(4)

2. Brass is an alloy consisting mainly of copper and zinc. To determine the percentage of copper in a sample of brass, 2·63 g of the brass were dissolved in concentrated nitric acid and the solution diluted to 250 cm^3 in a standard flask. Excess potassium iodide was added to 25·0 cm^3 of this solution, iodine being produced according to the equation:

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

The iodine formed was titrated with 0·10 mol l^{-1} sodium thiosulphate solution, $Na_2S_2O_3(aq)$, the volume required for complete reaction being 24·8 cm^3.

$$\underset{\text{colourless}}{I_2(aq)} + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + \underset{\text{colourless}}{S_4O_6^{2-}(aq)}$$

(*a*) Which species in the first equation is oxidised? **1**

(*b*) How could the end-point for the titration be made more obvious? **1**

(*c*) How many moles of sodium thiosulphate were required in the titration? **1**

(*d*) Calculate the percentage by mass of copper in the sample of brass. **3**

(6)

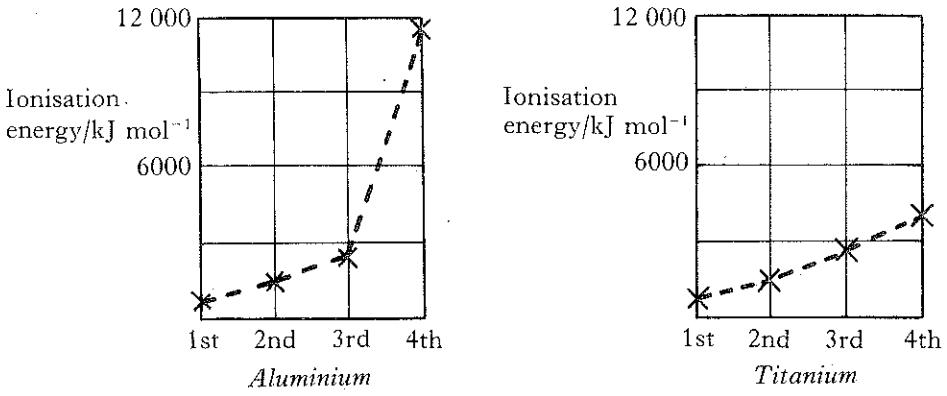
Marks

3. (*a*) The electron configuration of an aluminium atom may be written:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$$

Write the corresponding electron configuration for the Ti^{3+} ion. 1

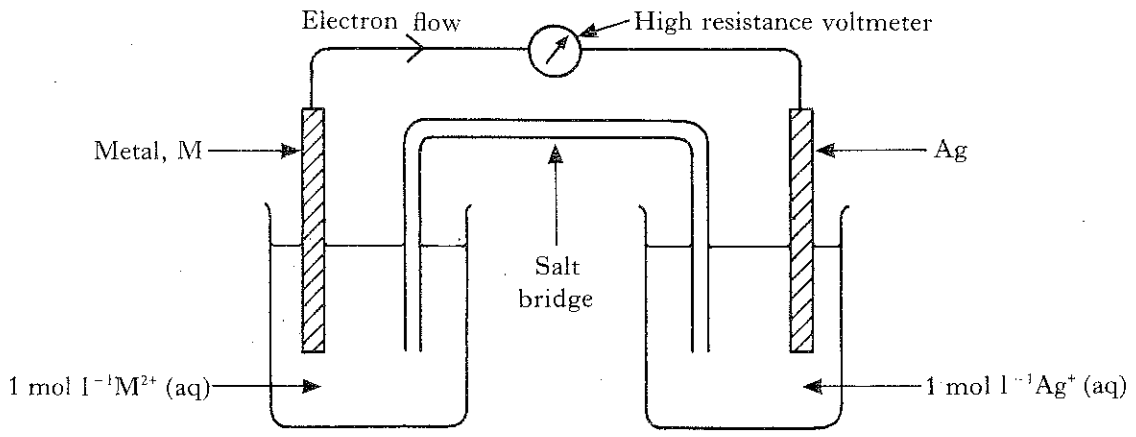
(*b*) The graphs show the first four ionisation energies for aluminium and titanium.



Why is there a sharp increase in the graph for aluminium but only gradual increases in the graph for titanium? 2

(3)

4.



The emf of the above cell operating under standard conditions is 1·03V.

(*a*) Calculate the standard reduction potential for the half-cell reaction

$$M^{2+}(aq) + 2e^- \rightarrow M(s)$$ 1

(*b*) Calculate the free energy change for this cell operating under standard conditions. 2

(*c*) Why is a **low** resistance voltmeter not used to measure the emf of the cell? 1

(*d*) Name a solution which could be used in the salt bridge of the above cell. 1

(5)

[Turn over

Marks

5. *MANUFACTURE OF 98% SULPHURIC ACID FROM SULPHUR TRIOXIDE*

In theory, sulphuric acid is made by allowing sulphur trioxide to react with water, but this is unsatisfactory on an industrial scale. The following method is used.

Sulphur trioxide gas is passed into the bottom of an absorption tower, where it reacts with previously manufactured 98% sulphuric acid trickling from the top of the tower to form 99·5% sulphuric acid called oleum. Waste gases are removed from the top of the tower.

The oleum is then transferred to a diluter where it is carefully diluted with water to form 98% acid, some of which is recycled to the absorption tower and the rest is fed into storage tanks.

Construct a flow chart to represent the processes outlined in the passage. **(4)**

6. An anhydrous chloride of iron is a volatile red solid which dissolves in ethoxyethane (diethyl ether). It also dissolves in water forming an aqueous solution from which a salt can be crystallised. The percentage composition by mass of the salt is shown in the table below.

Element	% by Mass
Iron	20·7
Chlorine	39·4
Hydrogen	4·4
Oxygen	35·5

(*a*) Comment on the nature of the bonding in the anhydrous chloride of iron, giving a reason for your answer. **2**

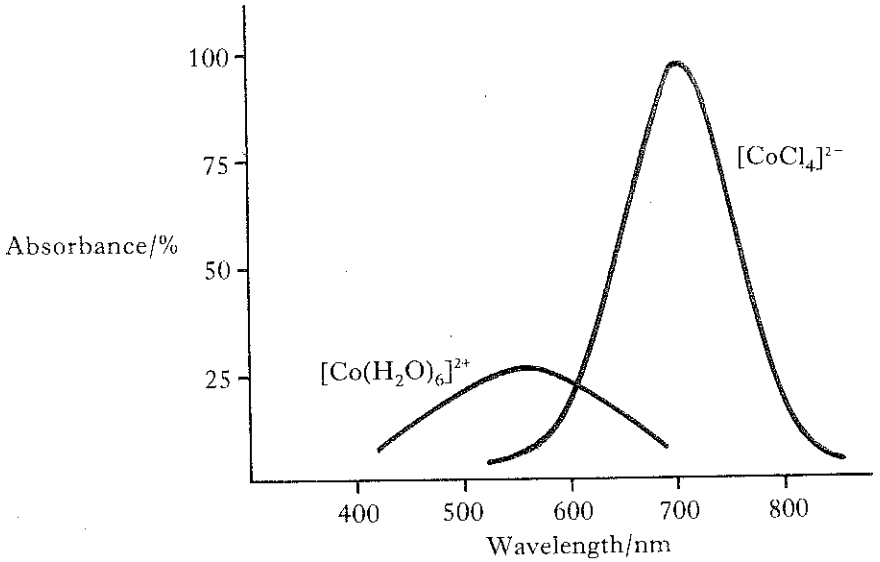
(*b*) Calculate the empirical formula for the crystalline salt. **3**

(*c*) Suggest the **formula** which would be used, along with the name, on the label of a bottle of the crystalline salt. **1**

(6)

Marks

7. The following diagram shows the simplified visible spectra of two complex ions. The complex ions are in aqueous solutions of equal concentration.



The $[CoCl_4]^{2-}$ solution has an intense (deep) blue colour while the $[Co(H_2O)_6]^{2+}$ solution has a much less intense (pale) pink colour. The hexaaquacobalt(II) ion can be converted into $[Co(NH_3)_6]^{2+}$ by the addition of excess ammonia solution. A solution of this new ion has an intense (deep) red colour.

(*a*) Why can chloride ions and water and ammonia molecules act as ligands? 1

(*b*) Name the ions (i) $[CoCl_4]^{2-}$ and

(ii) $[Co(NH_3)_6]^{2+}$ 2

(*c*) Copy the diagram above (no graph paper needed) and add a curve to show where a $[Co(NH_3)_6]^{2+}$ ion solution of the same concentration will absorb in the visible region. 2

(5)

[Turn over

Marks

8. (*a*) Calculate the pH of a solution of ethanoic acid of concentration 0·01 mol l^{-1}.

(K_a ethanoic acid = $1{\cdot}7 \times 10^{-5}$) **3**

(*b*) A mixture of ethanoic acid and sodium ethanoate solution constitutes a buffer solution. Show how this buffer solution is able to resist a change in pH when small quantities of the following are added:

(i) hydrochloric acid;

(ii) sodium hydroxide solution.

(Use of equations may be helpful.) **4**

(*c*) The simplified equation for the pH of a buffer solution is

$$pH = pK_a - \log \frac{[acid]}{[salt]}$$

A buffer solution was prepared from ethanoic acid (0·25 mol l^{-1}) and sodium ethanoate solution (0·15 mol l^{-1}).

Calculate the pH of the buffer solution. **2**

(9)

9. The following passage has been adapted from *Chemistry Now — Generating Power in a Green World.*

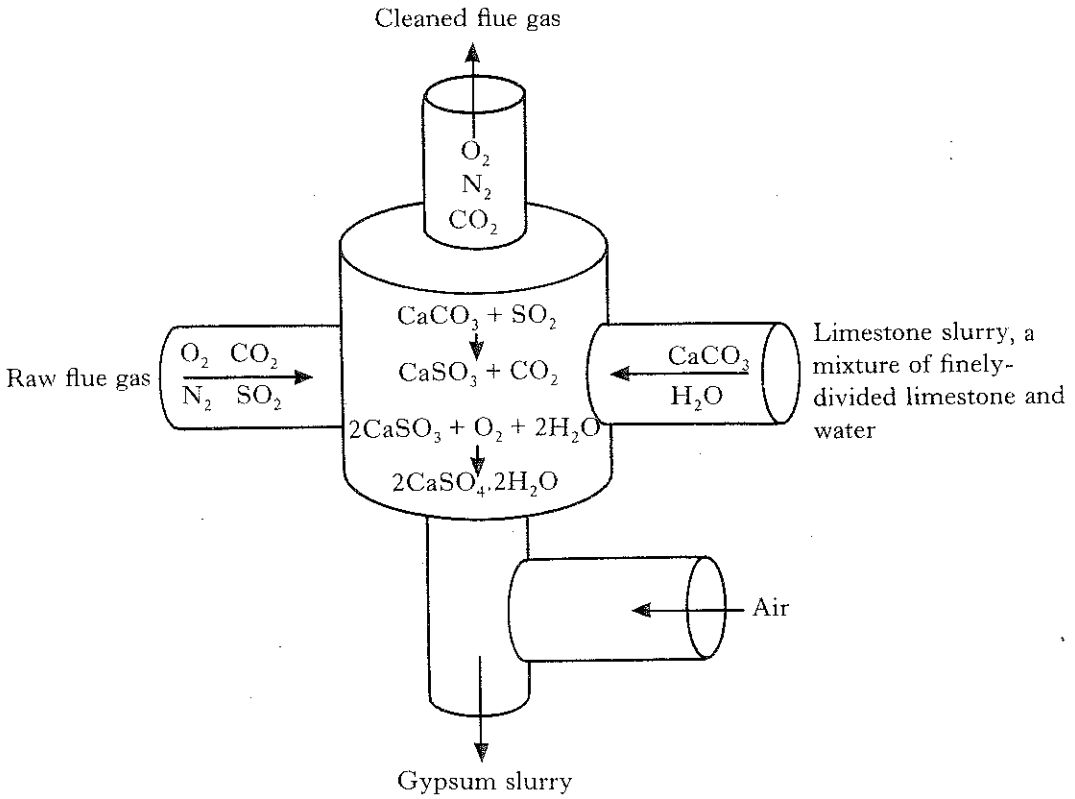
About half the sulphur in British coals occurs as pyrite (FeS_2) and this can be reduced in quantity during the cleaning operation which takes place in a coal preparation plant. Most of the non-pyritic sulphur occurs organically bound to the coal molecules and can not be removed during this cleaning operation.

During combustion, virtually all of the sulphur is converted to SO_2 and emissions can be significantly reduced by (*a*) treatment during combustion, or (*b*) by flue gas desulphurisation (FGD).

Technique (*a*) involves the direct injection of limestone into the combustion zone while technique (*b*) involves the SO_2 in the flue gases being removed by a limestone slurry (mixture of finely divided limestone and water) in a large "scrubber".

The FGD unit being installed at Drax Power Station will remove 90% of the SO_2 from the flue gases while each year consuming 6 million tonnes of limestone and manufacturing 1·1 million tonnes of gypsum. Gypsum has a number of industrial uses including wallboard manufacturing or it can be disposed of in an environmentally acceptable way such as landfill. Although limestone is required for the process, the product gypsum replaces natural gypsum that would otherwise need to be mined. The installation of FGD technology results in 10% addition to the capital and operating costs of a power station and results in slightly increased emissions of CO_2, because of its release from the limestone, and a drop in power station efficiency.

The chemistry involved is shown in the diagram of the FGD unit below.



Marks

(*a*) Why is the limestone introduced into the FGD unit as a slurry? **1**

(*b*) The production of gypsum ($CaSO_4 . 2H_2O$) from limestone is a two-step process. What chemical names could be given to these two processes? **2**

(*c*) Discuss the environmental and economic advantages and disadvantages of FGD. **3**

(6)

[Turn over

10. Mercury(II) chloride is reduced by oxalate ions ($C_2O_4^{2-}$) according to the equation

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2Cl^-(aq) + 2CO_2(g) + 2HgCl(s)$$

The following data were obtained in a series of four experiments at the same temperature. The rate is measured by the decrease in concentration of $HgCl_2(aq)$ per minute.

Experiment	Initial concentration of $HgCl_2(aq)$/mol l^{-1}	Initial concentration of $C_2O_4^{2-}(aq)$/mol l^{-1}	Initial rate $\times 10^4$ /mol l^{-1} min^{-1}
1	0·128	0·304	1·82
2	0·064	0·608	3·66
3	0·128	0·608	7·31
4	0·064	0·304	0·90

Marks

(*a*) Write an ion-electron half equation for the oxidation part of the reaction. **1**

(*b*) From the data given above, deduce the overall rate equation for the reaction. **2**

(*c*) Using the results for Experiment 1 and your answer to (*b*), calculate the rate constant at the given temperature, giving the correct units. **2**

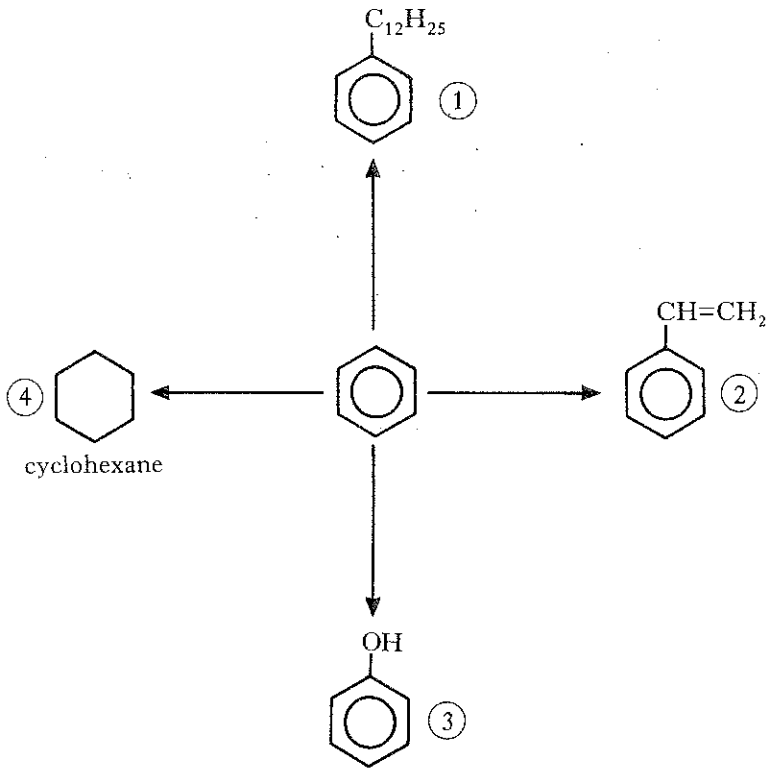
(*d*) Calculate the initial rate of the reaction when the initial concentration of each reactant is 0·1 mol l^{-1}. **1**

(*e*) (i) Draw a graph, which need not be to scale, to show how the concentration of $HgCl_2(aq)$ changes as the reaction proceeds (graph paper not required).

(ii) Draw a line on your graph to represent the initial rate of the reaction. **2**

(8)

11. Benzene is one of the most important aromatic feedstocks in the chemical industry. It can be made during the catalytic reforming of the naphtha fraction from crude oil and separated from the mixture of products. The diagram below shows four of the industrially important synthetic routes from benzene.



Marks

(*a*) What do you understand by the term "catalytic reforming"? **1**

(*b*) The preparation of compound (1) can be achieved in a single step.
Compounds (2) and (3) require more than one step in their preparation, but the first step in both involves the same type of reaction as that for the preparation of compound (1).
Name the **type** of reaction involved **and** name the **type** of organic compound used along with benzene. **2**

(*c*) Name the **type** of reaction involved in the conversion of benzene to compound (4). **1**

(*d*) Compound (1) is used as a feedstock for making an important domestic product. Name the product. **1**

(*e*) Compounds (2) and (3) are used in making plastics.

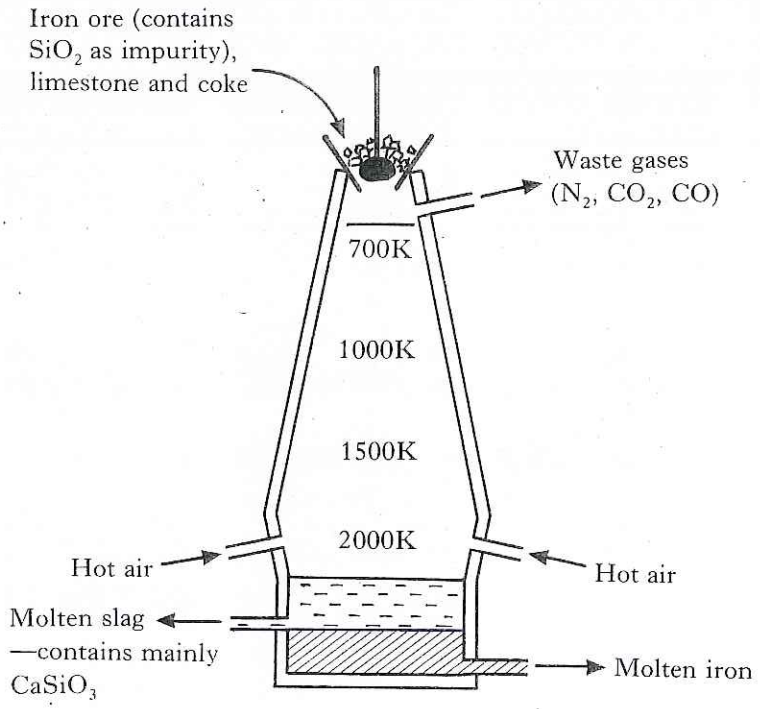
(i) Draw the structure of part of a polymer made by linking three molecules of compound (2). **2**

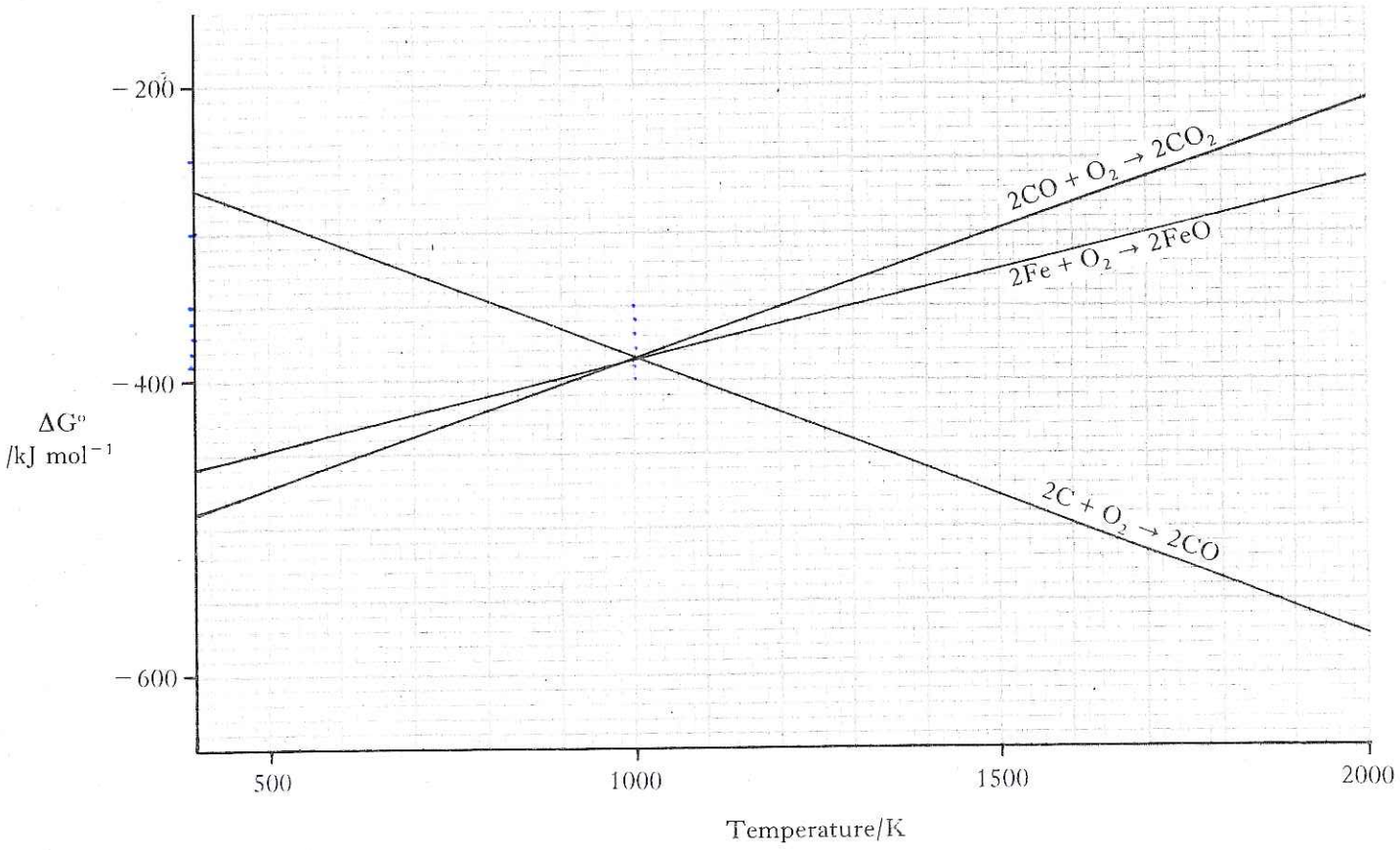
(ii) Compound (3) reacts with methanal to form a plastic. Name the type of polymerisation involved. **1**

(8)

[Turn over

12. The diagrams show the Blast Furnace for the extraction of iron from iron ore and an appropriate Ellingham diagram.





Marks

12. (continued)

(*a*) Calculate the standard free energy change for the reduction of iron(II) oxide by carbon at 1900 K. 2

(*b*) At what temperatures will it be thermodynamically feasible for carbon monoxide to reduce iron(II) oxide? 1

(*c*) Explain why the reduction by carbon monoxide is more efficient than by carbon. 1

(*d*) Give a reason for adding limestone to the furnace. 1

(*e*) To achieve maximum economy, suggest a use for the waste gases. 1

(6)

[END OF QUESTION PAPER]