[92/300] 1983

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Tuesday, 10th May—9.30 a.m. to 12.00 noon

Dalziel High School
Chemistry Department

1983 CSYS

TE&S 92/300 6/6/3/6326
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1. Select the arrangement of electrons that represents an atom in its ground state.

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

   B $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

   C $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

   D $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4d^2$

2. Which of the following compounds would be expected to have the highest boiling point?

   A $CH_3CH_2O\ CH_2CH_3$

   B $CH_3O\ CH_2CH_2CH_3$

   C $CH_3CH_2CH_2CH_2OH$

   D $CH_3CH_2CH_2CH_2CH_3$

3. $C(s) + O_2(g) \rightarrow CO_2(g)$
   $\Delta H = -396\ kJ\ mol^{-1}$

   $Pb(s) + \frac{1}{2}O_2(g) \rightarrow PbO(s)$
   $\Delta H = -210\ kJ\ mol^{-1}$

   $PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$
   $\Delta H = -74\ kJ\ mol^{-1}$

   What is the value of ΔH for the following reaction?

   $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

   A $+112\ kJ\ mol^{-1}$

   B $-112\ kJ\ mol^{-1}$

   C $+260\ kJ\ mol^{-1}$

   D $-260\ kJ\ mol^{-1}$

4. If the first and second ionisation energies of magnesium are 740 and 1450 kJ mol^{-1} respectively, what is the energy change for the following reaction?

   $Mg^{2+}(g) + 2e \rightarrow Mg(g)$

   A $+710\ kJ\ mol^{-1}$

   B $-710\ kJ\ mol^{-1}$

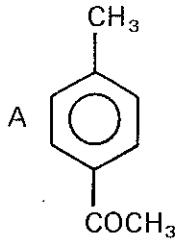
   C $+2190\ kJ\ mol^{-1}$

   D $-2190\ kJ\ mol^{-1}$

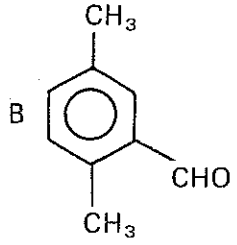
5. Spectral studies of an organic compound indicate a di-substituted benzene ring, two methyl groups and a molecular weight of 134.

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

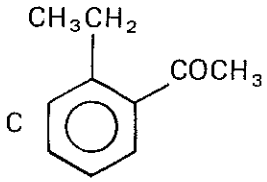
   A



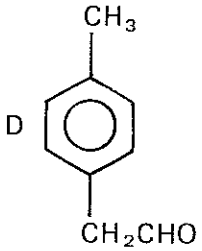
   B



   C



   D



6. $^{235}_{92}U$ is formed from X by a radioactive decay process involving the overall loss of one alpha and two beta particles. What is X?

   A $^{231}_{90}Th$

   B $^{239}_{92}U$

   C $^{239}_{93}Np$

   D $^{239}_{94}Pu$

7. Which of the following contains the Avogadro Number of molecules?

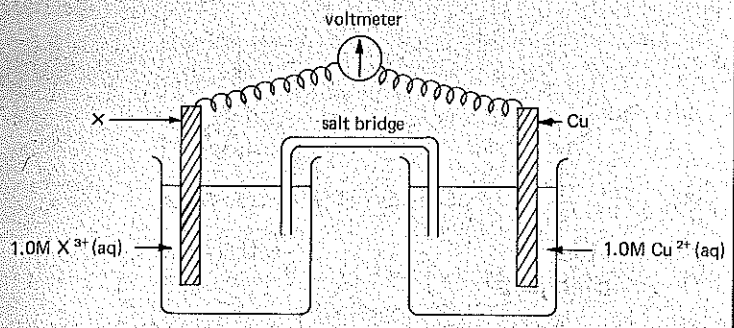
   A 8g helium

   B 14g nitrogen

   C 24g sodium hydride

   D 38g fluorine

8. Consider the following cell.



The E° values are as follows:

$X^{3+}(aq) + 3e \rightarrow X(s)$ $\quad E° = -1{\cdot}70$ V

$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ $\quad E° = +0{\cdot}34$ V

Will the reading on the voltmeter

A remain constant and suddenly drop to zero

B gradually fall until it eventually becomes zero

C gradually fall from 2·04 V to a final value of 1·70 V

D gradually fall from 1·70 V to a final value of 0·34 V?

9. Equal masses of radium chloride and radium bromide, each containing ^{226}Ra, have

A the same intensities of radiation and different half-lives

B different intensities of radiation and different half-lives

C the same intensities of radiation and the same half-lives

D different intensities of radiation and the same half-lives.

10. A catalyst is normally added to a reaction mixture to

A give a better yield at equilibrium

B provide an alternative reaction mechanism

C slow down an unwanted side-reaction

D reduce the enthalpy change for the reaction.

The processes in questions 11 and 12 may be placed in one of the following categories. A category may be used once, more than once, or not at all.

A ΔH positive, ΔS positive

B ΔH positive, ΔS negative

C ΔH negative, ΔS positive

D ΔH negative, ΔS negative

11. The evaporation of water from a puddle.

12. The combination of sodium vapour with chlorine.

13. In a complex chemical reaction the rate determining step is always

A the last step

B the fastest step

C the first step

D the slowest step.

14. How many moles of iodine molecules are produced when excess potassium iodide is oxidised by 1 mole of potassium permanganate in acidic solution?

A 0·5

B 1

C 2·5

D 5

15. One mole of barium chloride ($BaCl_2$) contains

A 3 moles of atoms

B 1 mole of molecules

C 1 mole of positive ions

D 2 moles of positive ions.

16. The bond angle in a molecule of ammonia is

A 90°

B 107·3°

C 109·5°

D 120°.

[Turn over

17. 0·0710 g of an unknown chloride gives 0·1435 g of silver(I) chloride when treated with excess aqueous silver(I) nitrate solution. What is the percentage of chloride ion in this unknown?

A 5

B 20

C 25

D 50

18. The complete combustion of 0·224 litres (at s.t.p.) of a volatile organic compound in excess oxygen produced 0·04 mole carbon dioxide. How many carbon atoms are there in one molecule of the volatile organic compound?

A 5

B 4

C 3

D 2

19. Which fluoride would be expected to undergo further reaction with fluorine?

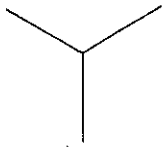
A CaF_2

B CF_4

C IF_5

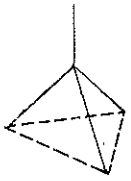
D SF_6

Questions 20 and 21 refer to the following arrangements of electron pairs.



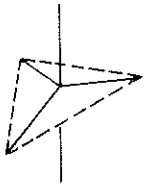
planar triangular

A



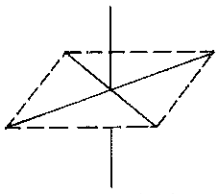
tetrahedral

B



trigonal – bipyramidal

C



octahedral

D

Which arrangement will be found in the following molecules?

Note: A letter may be used more than once.

20. PCl_5

21. SiH_3^+

22. The boiling point of propanoic acid (141 °C) is higher than that of its isomer methyl ethanoate (57 °C) because

A propanoic acid is more stable than methyl ethanoate

B propanoic acid ionises but methyl ethanoate does not

C hydrogen bonding occurs in propanoic acid

D hydrogen bonding occurs in methyl ethanoate.

23. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Adding PCl_3 to the above system will

A increase the value of the equilibrium constant

B decrease the value of the equilibrium constant

C increase the concentration of PCl_5 and decrease the concentration of Cl_2

D decrease the concentration of PCl_5 and increase the concentration of Cl_2.

24. 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 → Products,

	[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].

25. Which of the following will **not** react with HCl?

A Aminoethanoic acid

B Triethylamine

C Tetraethylammonium bromide

D Diethylamine

26. A substance (C_7H_8O) is slightly soluble in water, but very soluble in sodium hydroxide solution. It does not react with sodium carbonate solution. It is most likely to be

A carboxylic

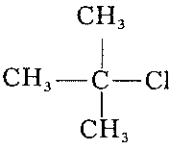
B phenolic

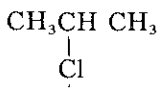
C ketonic

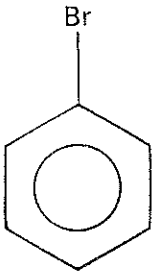
D aldehydic.

27. Which halide will be most resistant to attack by nucleophilic reagents?

A CH_3CH_2Br

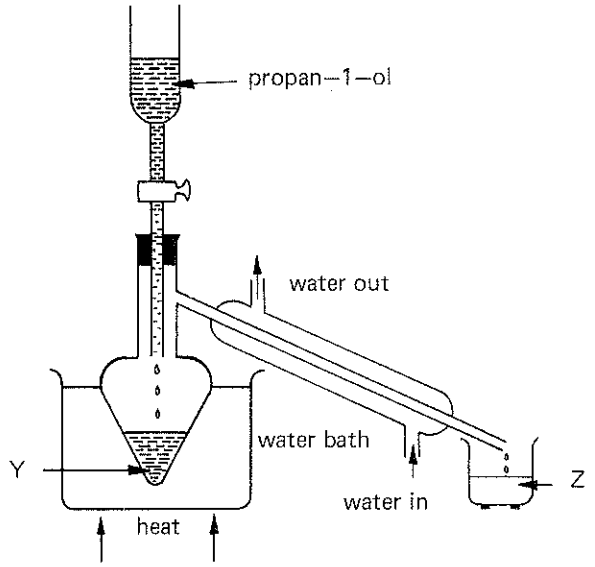
B 

C 

D 

[Turn over

Questions 28 and 29 refer to the diagram below.



The above apparatus was used in an attempt to prepare reasonably pure propanoic acid by the oxidation of propan-1-ol. The following information is available.

Compound	*Formula*	*Boiling Point/°C*
propan-1-ol	C_3H_7OH	97
propanal	C_2H_5CHO	49
propanoic acid	C_2H_5COOH	140
propanone	CH_3COCH_3	56
propyl propanoate	$C_2H_5COOC_3H_7$	123

28. Solution Y contained

A aqueous copper(II)

B aqueous iron(II)

C acidified aqueous chromium(III)

D acidified aqueous dichromate(VI).

29. Substance Z was **not** propanoic acid. It was probably

A propanal

B propan-1-ol

C propanone

D propyl propanoate.

30. The compound of molecular formula $C_3H_6O_2$ could **not** be

A propanoic acid

B methyl ethanoate

C ethyl methanoate

D ethyl ethanoate.

31. Which of the following statements about an ethanoic acid/sodium ethanoate buffer solution is correct?

A It is effective because ethanoic acid and sodium ethanoate are both strong electrolytes.

B It has a pH greater than 7·0.

C The total molar concentration of ethanoate ions is much higher than the molar concentration of sodium ethanoate.

D When hydrogen ions are added more ethanoic acid is produced.

32. An indicator used in an acid-alkali titration changes colour at pH 4·4. The concentration of hydroxide ions in the solution at the end point shown by this indicator lies between

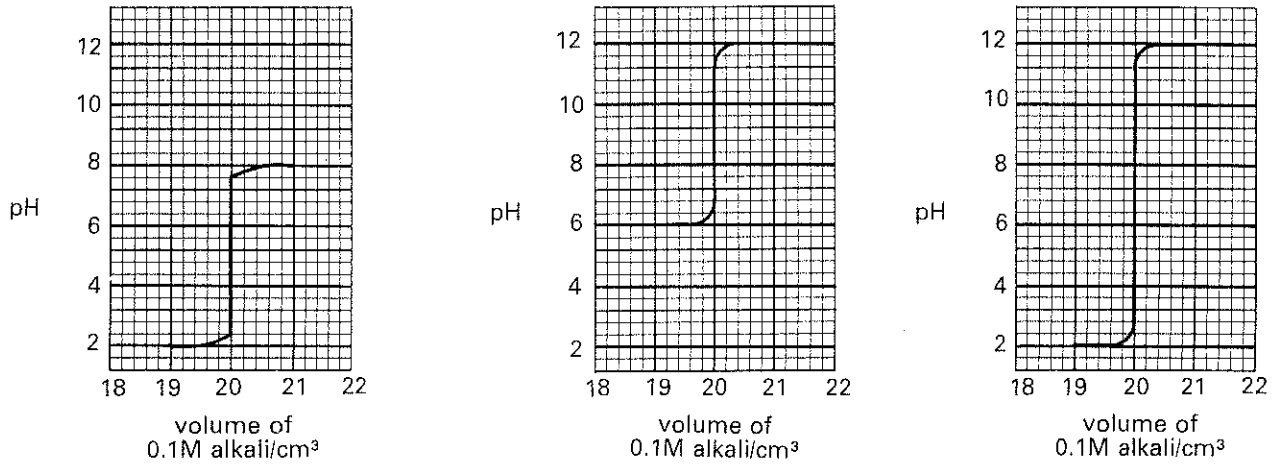
A 10^{-3} and 10^{-4} mol 1^{-1}

B 10^{-4} and 10^{-5} mol 1^{-1}

C 10^{-9} and 10^{-10} mol 1^{-1}

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

33.



Which one of the following reactions can **not** be represented by any of the above curves?

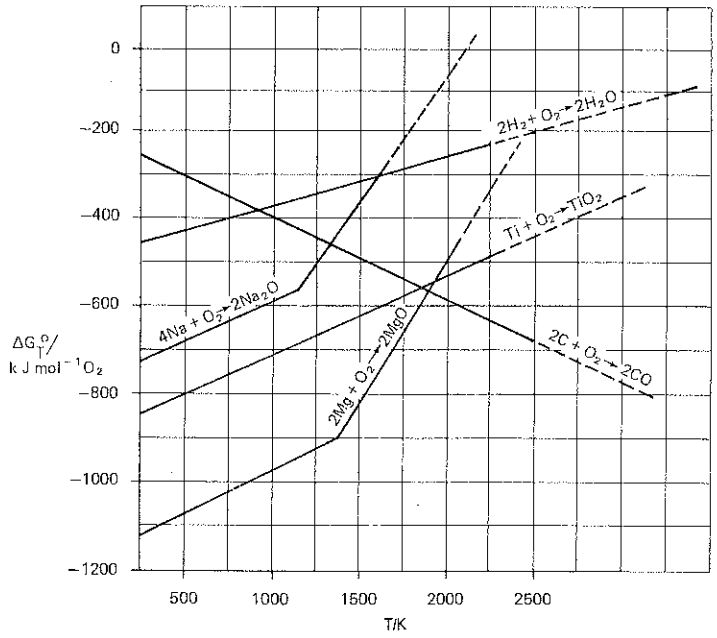
A Potassium hydroxide and nitric acid

B Ethylamine and hydrochloric acid

C Ammonia and propanoic acid

D Sodium hydroxide and ethanoic acid

34.



The reduction of TiO_2 to Ti is thermodynamically feasible at 1500 K using

A hydrogen

B magnesium

C carbon

D sodium.

[Turn over

35. The purple colour of an aqueous solution of potassium permanganate is due to

A emission of energy and the promotion of d electrons in the permanganate ion

B emission of energy when electrons are transferred from the oxygen to the manganese atom

C absorption of the red and blue components of white light

D absorption of energy when electrons are transferred from the oxygen to the manganese atom.

36. On the basis of d → d transitions, the hydrated transition metal ion most likely to be colourless is

A Ti^{4+}

B Co^{3+}

C Cr^{2+}

D V^{4+}.

37. The metal undergoes oxidation in

A $MnO_4^{2-} \rightarrow MnO_2$

B $VO^{2+} \rightarrow VO_2^{+}$

C $Co(NH_3)_6^{3+} \rightarrow Co(NH_3)_6^{2+}$

D $Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-}$.

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. A possible mechanism for the reaction of chlorine with methane is

$Cl_2 \rightarrow 2Cl^{\cdot}$ $\triangle H = +243$ kJ mol^{-1} (Initiation Step)

$Cl^{\cdot} + CH_4 \rightarrow HCl + H_3C^{\cdot}$ $\triangle H = -8{\cdot}4$ kJ mol^{-1} (Propagation Step)

$H_3C^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$ $\triangle H = -92{\cdot}3$ kJ mol^{-1} (Propagation Step).

The reaction of chlorine with methane can be described as

1 free radical

2 chain

3 endothermic.

39. The electronic arrangement, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$, represents

1 Co^{2+}

2 Ni^{3+}

3 Mn.

40. All the atoms are in the same plane in

1 $CH_2{=}CHCl$

2 $CH_2{=}CHCH_2Cl$

3 C_6H_5Cl.

[END OF QUESTION PAPER]

Marks

1. The data in the table below apply at 298 K and 1 atmosphere pressure.

Substance	$\triangle H_f^\circ$/kJ mol^{-1}	S°/J K^{-1} mol^{-1}
$NH_3(g)$	− 46·2	193·0
$HCl(g)$	− 92·3	187·0
$NH_4Cl(s)$	−315·0	94·6

(a) Calculate the standard free energy change for the following reaction,

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$ **4**

(b) What is the value of the standard free energy change for the reverse reaction? **1**

(c) In the light of your answer to *(b)*, account for the fact that ammonium chloride can be decomposed into ammonia and hydrogen chloride. **2**

(7)

2. Answer **EITHER A OR B.**

A. The percentage of calcium carbonate in a sample of limestone can be determined by back titration as follows.

2·0 g of limestone were dissolved in 60·0 cm^3 of 0·5 M hydrochloric acid. After the reaction was completed, insoluble impurities were removed by filtration and the amount of unreacted acid was determined by titration with 0·1 M sodium hydroxide solution. On first adding the alkali a white precipitate formed, which immediately dissolved in the unreacted acid.

60·0 cm^3 of the 0·1 M sodium hydroxide solution were required to neutralise the unreacted acid.

(a) What is meant by a back titration? **1**

(b) Calculate the number of moles of hydrochloric acid that had reacted with the limestone. **3**

(c) Calculate the percentage of calcium carbonate in the sample of limestone. **3**

(d) What is the white precipitate? **1**

(8)

OR

B. When nickel(II) ions in solution are reacted with dimethylglyoxime ($C_4H_8N_2O_2$) in ethanol, a red complex of nickel(II) ions and dimethylglyoxime is precipitated.

The equation for this reaction is

$$Ni^{2+}(aq) + 2(C_4H_8N_2O_2) \rightarrow Ni(C_4H_7N_2O_2)_2(s) + 2H^+(aq)$$

0·281g of a nickel(II) salt ($NiSO_4.7H_2O$) were dissolved in water and completely reacted with dimethylglyoxime. The red precipitate weighed 0·289g.

(a) What is the name given to this type of chemical analysis? **1**

(b) Calculate the

(i) mass of nickel(II) ions in the complex, **3**

(ii) percentage of nickel in the original salt. **1**

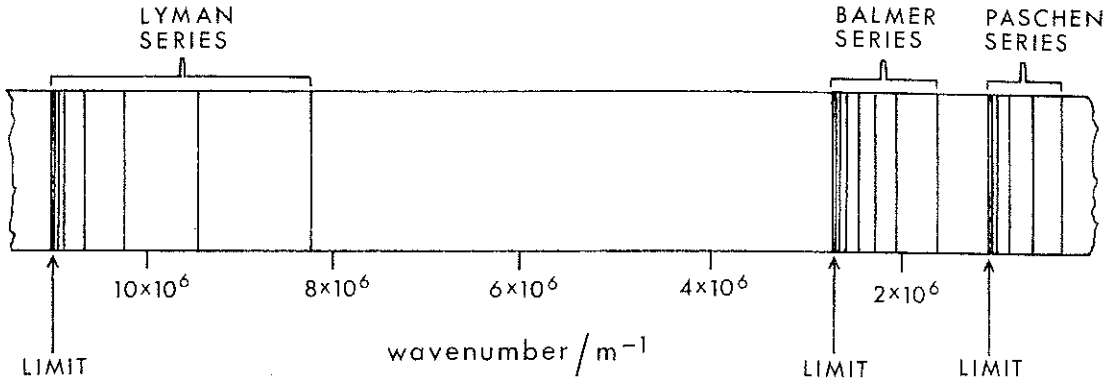
(c) Nickel(II) ions can also be determined by a complexometric titration method.

(i) Name a suitable reagent for this method. **1**

(ii) Give one advantage and one disadvantage of this method compared with the precipitation method given above. **2**

(8)

3. *Marks*



The diagram represents a section of the line emission spectrum for hydrogen.

(a) If the spectrum of hydrogen is viewed through a spectroscope only one set of lines is seen.

(i) Why is this?

(ii) Which series is seen? 2

(b) Explain how any particular line in this spectrum is produced. 3

(c) The last line or convergence limit of the Lyman series has a wavenumber of approximately 11×10^6 m^{-1}. Using data available on page 18 of the Data Booklet, calculate the energy equivalent of this in kJ mol^{-1}. 3

(d) What does the energy referred to in *(c)* correspond to? 1

(9)

4. Ethane-1,2-diol can be made as follows:

Method (1)

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[180\ ^\circ C]{\text{Ag catalyst}} CH_2\text{—}CH_2 \text{ (epoxide)} \xrightarrow{+H_2O} CH_2OHCH_2OH$$

Method (2)

$$5CH_2{=}CH_2 + 2H_2O + 2MnO_4^- + 6H^+ \rightarrow 5CH_2OHCH_2OH + 2Mn^{2+}$$

(a) Give one advantage and one disadvantage for each of the above methods, if used for the industrial production of ethane-1,2-diol. 2

(b) Although methanol has many of the properties of ethane-1,2-diol and is cheaper to produce, ethane-1,2-diol is preferred commercially as the main ingredient of anti-freeze.

Suggest two reasons why this is so. 2

(4)

5. Consider the following reaction sequence:

$$CH_3CHO \xrightarrow[HCN]{(1)} X \xrightarrow{(2)} CH_3CH(OH)COOH$$

(a) Draw a structural formula for X. 1

(b) For step (2) name

(i) the reagent, and 1

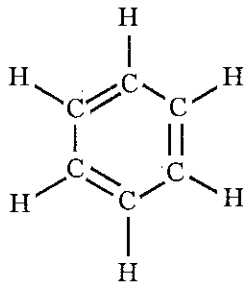
(ii) the type of reaction. 1

(3)

[Turn over

Marks

6. *(a)* In 1865 Kekulé suggested the following structure for benzene:



(i) Why is Kekulé's structure now unacceptable to many chemists? **1**

(ii) Give the structure which is generally accepted today and explain it. **2**

(b) In the nitration of benzene to produce nitrobenzene, a mixture of concentrated nitric and sulphuric acids is used rather than concentrated nitric acid alone.

The mixture of the two acids reacts as follows:

$$2H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Why is the mixture of the two acids used rather than the concentrated nitric acid on its own? **3**

(6)

7. Answer **EITHER A OR B.**

A. In acid solution iodine and propanone react as follows:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

The rate of this reaction can be determined by mixing various proportions of iodine, propanone and hydrochloric acid and withdrawing samples at known time intervals. The amount of unreacted iodine in the sample can be estimated by titration with sodium thiosulphate.

A typical set of results is given below:

Mixture	*Volume of 2·00 M Propanone/ cm^3*	*Volume of 0·01 M Iodine/ cm^3*	*Volume of 2·00 M HCl/ cm^3*	*Volume of Water/ cm^3*	*Relative Rate of Consumption of Iodine*
A	20	20	20	40	1
B	40	20	20	20	2
C	60	20	20	0	3
D	20	40	20	20	1
E	20	10	20	50	1
F	20	20	40	20	2
G	20	20	60	0	3

Marks

(a) What is the relationship between the **initial** reaction rate and the concentration of

(i) propanone, **1**

(ii) hydrogen ions, **1**

(iii) iodine? **1**

(b) What is the order of reaction with respect to

(i) propanone, **1**

(ii) hydrogen ions, **1**

(iii) iodine? **1**

(c) What is the overall order of reaction? **1**

(d) What is a possible disadvantage of withdrawing samples to measure the progress of the reaction? **1**

(e) Suggest an alternative method of estimating the iodine which need not involve the withdrawal of samples. **1**

(9)

OR

B. The following set of results was obtained for the reaction in which hydrogen peroxide is being catalytically decomposed by manganese(IV) oxide, according to the equation

$$H_2O_2(aq) \rightarrow H_2O(1) + \tfrac{1}{2}O_2(g)$$

$[H_2O_2]$/ mol 1^{-1}	Time/s	Reaction Rate $-\frac{d[H_2O_2]}{dt} \times 10^4$/ mol $1^{-1}s^{-1}$
0·36	0	3·30
0·28	200	2·46
0·19	600	1·70
0·10	1200	1·00
0·07	1800	0·56

(a) (i) Using the squared paper provided, draw a graph of reaction rate against $[H_2O_2]$ and use your graph to determine the order of the reaction with respect to the concentration of hydrogen peroxide, giving a reason for your answer. **4**

(ii) From your graph, or the above data, determine the rate constant for the reaction, giving the units in which it is measured. **3**

(b) Why does the reaction

(i) slow down with time, **1**

(ii) take place more slowly in the absence of the catalyst? **1**

(9)

[Turn over

Marks

8. *(a)* Calculate the pH of a 0·3 M solution of ethanoic acid, given that the dissociation constant, K_a, for ethanoic acid at 298 K is $1{\cdot}7 \times 10^{-5}$. **3**

(b) If solid sodium ethanoate is added to the 0·3 M solution of ethanoic acid what will happen to the

(i) value of K_a, **2**

(ii) pH of the solution? **2**

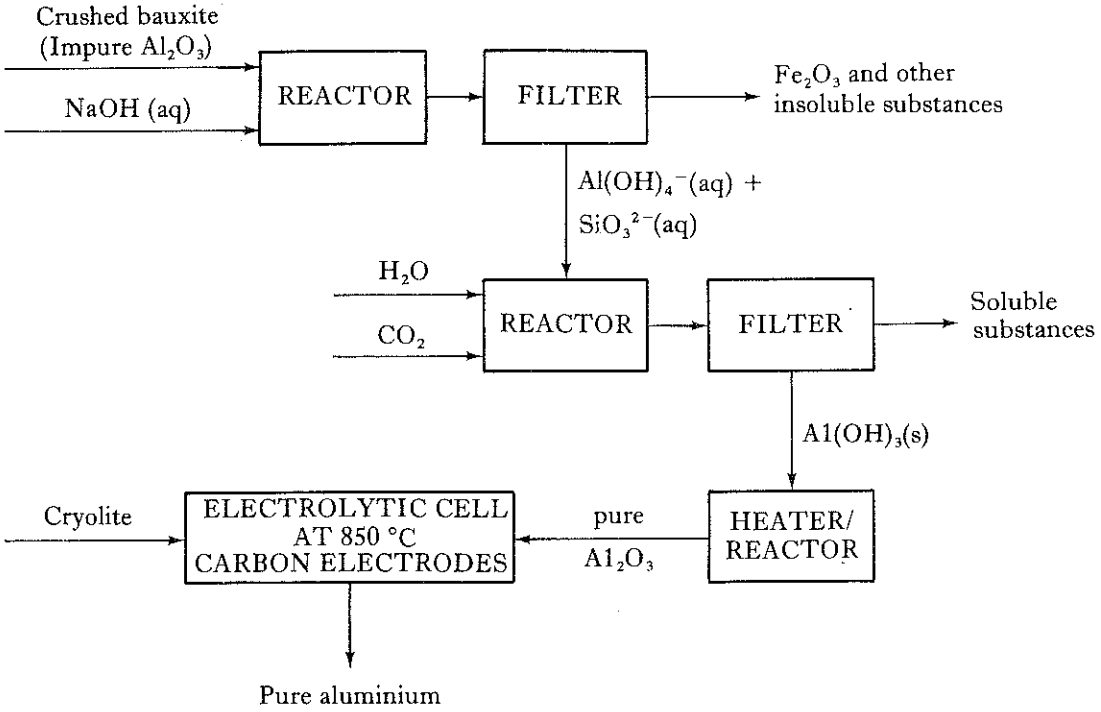
Explain your answer in each case.

(c) Buffering action in living systems is usually provided by a mixture of $H_2PO_4^-$ and HPO_4^{2-} ions. How does such a mixture act as a buffer? **2**

(9)

9. Answer **EITHER A OR B.**

A. Before aluminium can be extracted from bauxite, the ore must first be purified. The diagram summarises the various stages of the production of aluminium from bauxite.



(a) Why does aluminium oxide dissolve in NaOH(aq) in the first reactor but iron(III) oxide does not? **1**

(b) Name another impurity in bauxite. **1**

(c) Why is cryolite added to the electrolytic cell? **1**

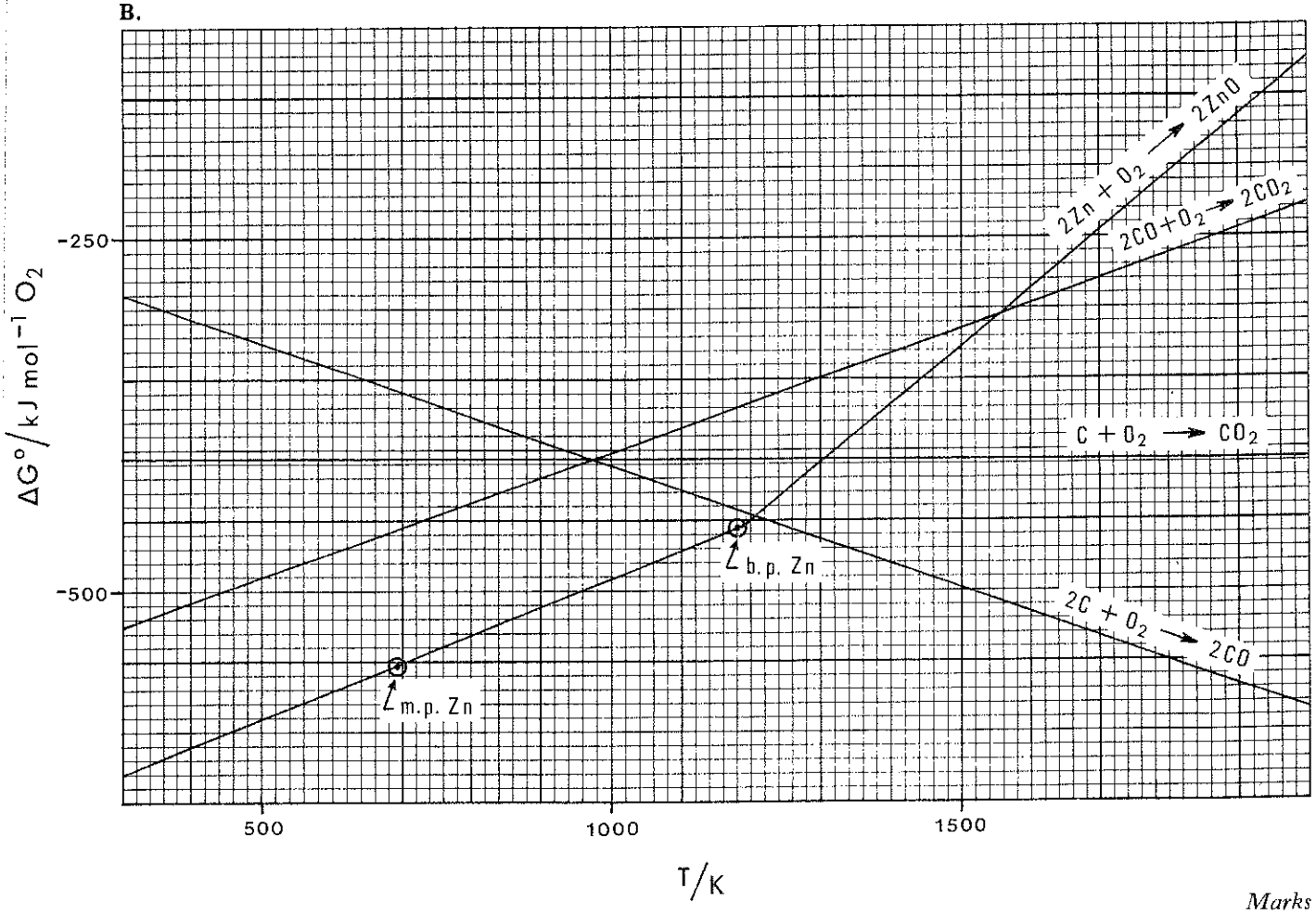
(d) Why are the carbon anodes replaced regularly? **1**

(e) What factor is likely to have the greatest effect on the economics of this process? **1**

(f) Vast quantities of aluminium exist in the form of clay. Suggest why this is not used instead of the relatively more expensive mineral bauxite. **1**

(6)

OR
B.



Marks

The Ellingham diagram shows the variation of ΔG° with temperature T for a number of reactions. The reaction $2ZnO \rightarrow 2Zn + O_2$ could be brought about by various reducing agents.

(a) What is the minimum temperature at which the reduction of zinc oxide becomes thermodynamically feasible using

(i) $2C + O_2 \rightarrow 2CO$ **1**

(ii) $2CO + O_2 \rightarrow 2CO_2$ **1**

(iii) $C + O_2 \rightarrow CO_2$? **1**

(b) Why might *(a)*(i) be considered the most suitable choice? In fact, *(a)*(ii) is selected. Give reasons for this. **3**

(6)

10. At 333 K nickel reacts with carbon monoxide to form a complex, $Ni(CO)_4$, which melts at 248 K, boils at 316 K and decomposes at 473 K as follows:

$$Ni(CO)_4 \rightarrow Ni + 4CO$$

(a) What is the oxidation number (state) of nickel in the complex? **1**

(b) Draw a labelled diagram of an apparatus which could be used in the laboratory to prepare and collect a sample of the complex, $Ni(CO)_4$, starting from nickel and carbon monoxide.

Indicate one precaution which should be taken during the experiment. **4**

(c) Use the information above and your answer to *(b)* to decide the additional steps which would have to be taken on an industrial scale

(i) to obtain pure nickel from scrap nickel; **1**

(ii) to keep production costs to a minimum in (i). **1**

(7)

Marks

11. Write an essay on **ONE** of the following topics. Each topic has suggestions which may help you to answer the question but there is no need to use them unless you so wish. The Data Booklet may be a useful additional source of information.

The essay will be assessed for scientific content, organisation, presentation and English usage.

(a) Corrosion of Metals.

(Thermodynamic, kinetic, industrial and economic aspects)

OR

(b) The Shapes of Molecules and Complex Ions.

(Range of shapes and factors that determine these)

OR

(c) The $\rangle C=O$ group in organic chemistry.

(Bonding, presence of this group in several homologous series, properties of the group in these series)

(12)

[END OF QUESTION PAPER]