

[0500/269]

1987

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Monday, 11th May—9.30 a.m. to 12.00 noon

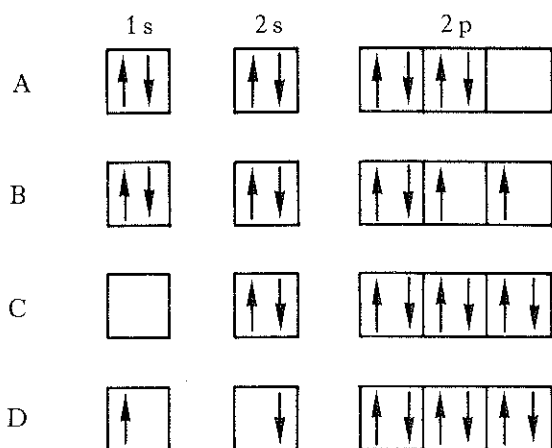


Dalziel High School
Chemistry Department



1987 CSYS

1. The electron configuration of an atom of oxygen in the ground state is



2. At temperatures below 84 K at atmospheric pressure, argon exists as a crystalline solid. Argon atoms are held together in the solid mainly by

- A covalent bonding
- B ionic bonding
- C hydrogen bonding
- D van der Waal's forces.

3. The electron configuration of an atom X is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

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

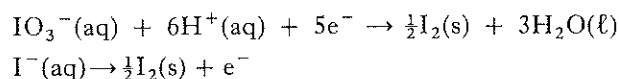
- A zinc
- B aluminium
- C phosphorus
- D chlorine.

4. A chemical system in dynamic equilibrium is one in which

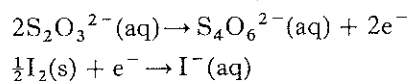
- A ΔG° is zero
- B ΔG is zero
- C activation energy of forward reaction = activation energy of the reverse reaction
- D ΔH for the forward reaction = ΔH for the reverse reaction.

Questions 5 and 6 refer to the following.

Iodate ions (IO_3^-) are reduced to iodine by iodide ions.



The iodine formed above can be estimated by reaction with thiosulphate ions ($\text{S}_2\text{O}_3^{2-}$).



5. How many moles of I_2 are produced by completely reducing one mole of IO_3^- by iodide ions?

- A 0.5
- B 1
- C 2.5
- D 3

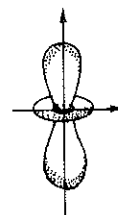
6. How many moles of $\text{S}_2\text{O}_3^{2-}$ will react with one mole of I_2 ?

- A 1
- B 2
- C 3
- D 4

7. Which of the following are emitted during the radioactive decay of ${}_{92}^{238}\text{U}$ to ${}_{82}^{206}\text{Pb}$?

- A 6 alpha and 8 beta particles only
- B 8 alpha and 2 beta particles only
- C 8 alpha and 6 beta particles only
- D 10 alpha and 8 beta particles only

- 8.



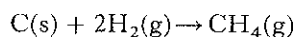
The above is a diagrammatic representation of

- A any p-orbital
- B a specific p-orbital
- C any d-orbital
- D a specific d-orbital.

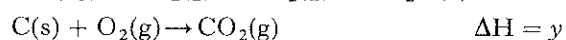
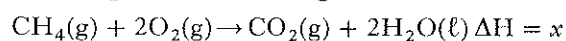
9. Which of the following conditions ensures that a reaction will be thermodynamically feasible at any temperature?

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

10. The formation of methane is represented by the equation

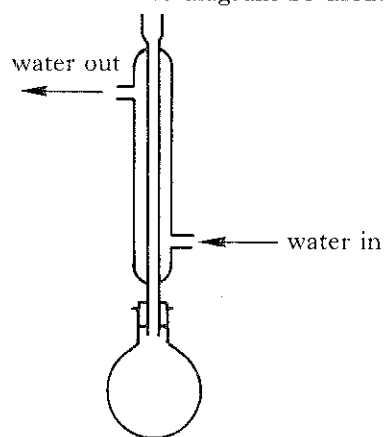


The enthalpy changes (in kJ mol^{-1}) for the following reactions are as given



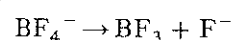
The enthalpy change (in kJ mol^{-1}) for the formation of methane is

- A $y + 2z - x$
 B $x + y + z$
 C $y + x - 2z$
 D $2z - y + x$
11. For which one of the following purposes would the apparatus shown in the diagram be used?



- A To separate liquids of boiling points 60°C and 70°C
 B To separate a low boiling liquid from a solid
 C To minimise the escape of a low boiling solvent in which an exothermic reaction is occurring
 D To control the temperature of a highly endothermic reaction

12. What is the change in the three-dimensional arrangement of the bonds round the B atom in the following reaction?



- A Square planar to trigonal planar
 B Tetrahedral to trigonal planar
 C Tetrahedral to pyramidal
 D Square planar to pyramidal

Questions 13 and 14 refer to the analysis of a salt whose formula is $\text{Pt}(\text{NH}_3)_x\text{Cl}_y$

13. 0.02 moles of this salt required 20.0 cm^3 4.0 M nitric acid for exact neutralisation. The number of moles of NH_3 per mole of salt, x , is

- A 2
 B 4
 C 6
 D 8

14. 0.02 moles of the salt was dissolved in nitric acid and excess silver (I) nitrate solution was added. The precipitate formed was filtered, washed and dried. It weighed 5.74 g. The number of moles of chloride ions (per mole of the salt) is

- A 1
 B 2
 C 3
 D 4

15. The pH of a solution of a strong monoprotic acid is 2.17. The concentration of the acid in mol l^{-1} is between

- A 0.0001 and 0.001
 B 0.001 and 0.01
 C 0.01 and 0.10
 D 0.10 and 1.00

[Turn over

16. Which of the following, when dissolved in distilled water, would be expected to give a solution with a pH less than 7?
- Methylamine (aminomethane)
 - Sodium sulphate
 - Potassium ethanoate
 - Ammonium sulphate
17. In which set of circumstances will the lattice energy of an ionic crystal, MX, have the largest numerical value?
- M has a small ionisation energy.
 - X has a small electron affinity.
 - M^+ has a small radius, X^- has a small radius.
 - M^+ has a small radius, X^- has a large radius.
18. A suggested mechanism for the reaction
- $$2A + B \rightarrow A_2B$$
- is a two-step process
- $$A + B \rightarrow AB \text{ (slow)}$$
- $$AB + A \rightarrow A_2B \text{ (fast)}$$
- This mechanism is consistent with the rate expression
- rate = $k[A]^2[B]$
 - rate = $k[A][B]$
 - rate = $k[A][AB]$
 - rate = $k[AB]$
19. For the reaction
- $$(\text{CH}_3)_3\text{CI}(\text{g}) \rightarrow (\text{CH}_3)_2\text{C}=\text{CH}_2(\text{g}) + \text{HI}(\text{g})$$
- the rate = $k[(\text{CH}_3)_3\text{CI}]$
- If all concentrations are in mol l^{-1} , the units of k will be
- s^{-1}
 - $\text{mol l}^{-1} \text{s}^{-1}$
 - $\text{l mol}^{-1} \text{s}^{-1}$
 - $\text{l}^2 \text{mol}^{-2} \text{s}^{-1}$
20. Ethers are more volatile than isomeric alcohols because
- ethers contain less oxygen
 - alcohols have stronger covalent bonding
 - ethers have lower molecular weights
 - alcohols exhibit more hydrogen bonding.
21. In the equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, the forward reaction is endothermic. Which one of the following causes an increase in the value of the equilibrium constant?
- The removal of NO_2
 - An increase in pressure
 - An increase in temperature
 - A decrease in temperature
22. (1) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
 (2) $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- The activation energies for the reactions, as written, are 165 kJ and 179 kJ respectively. The enthalpy change for reaction (2) is
- +14 kJ
 - 14 kJ
 - +344 kJ
 - 344 kJ
23. A solid compound, $\text{C}_2\text{H}_8\text{NCl}$, reacted with sodium hydroxide solution. The gas evolved was bubbled into water. The resulting solution
- had a pH value greater than 7,
 - gave a blue precipitate with copper(II) sulphate solution.
- Which of the following gases is most likely to have been liberated from $\text{C}_2\text{H}_8\text{NCl}$?
- Ammonia
 - Methylamine (aminomethane)
 - Ethylamine (aminoethane)
 - Nitrogen
24. Which of the following is **not** an isomer of butan-1-ol?
- Ethoxyethane
 - 2-methylpropan-1-ol
 - Butanone
 - Methoxypropane

Questions 25 and 26 refer to the following grid.

$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{Cl} & \text{H} \end{array}$	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{O}-\text{H} & \text{H} \end{array}$
$\begin{array}{c} \text{H} & & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{O} & \text{H} \end{array}$	$\begin{array}{c} \text{H} & & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}=\text{C} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$
$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$

25. Which compound will react with aqueous sodium hydroxide solution to give an isomer of the compound in box 5?

- A 1
B 3
C 4
D 6

26. The following reaction sequence was performed:

reduction; then dehydration;
then reaction with HCl.

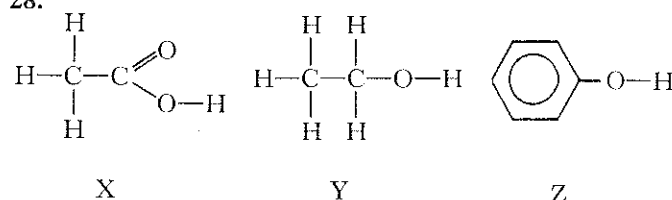
To which of the following could this sequence be applied?

- A 3 → 2 → 4 → 1
B 2 → 3 → 4 → 1
C 4 → 6 → 2 → 1
D 3 → 2 → 1 → 6

27. Which of the following could react together under mild conditions to produce ethanoic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$?

- A CH_3COOH and CH_3COONa
B CH_3COCl and CH_3COONa
C CH_3COCl and CH_3OH
D CH_3COOH and CH_3COCl

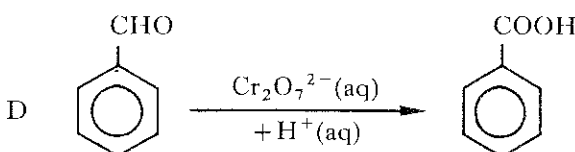
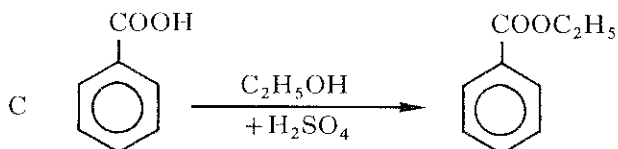
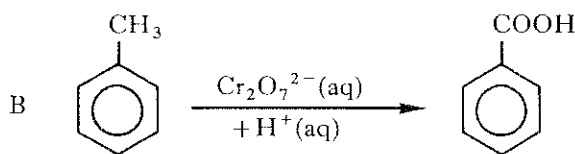
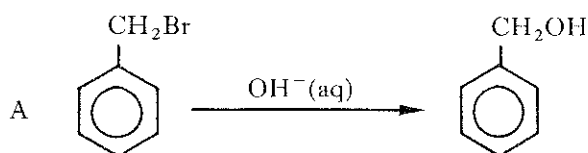
28.



Which of the following lists the above in **ascending** order of K_a value?

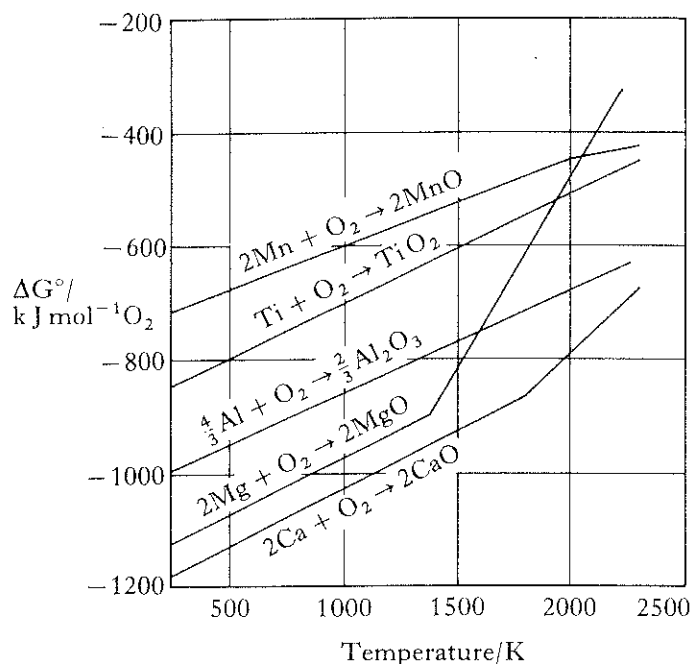
- A X Y Z
B Y Z X
C Z X Y
D X Z Y

29. Which of the following reactions is **not** easily carried out with the corresponding aliphatic compound?



[Turn over

Questions 30 and 31 refer to the following diagram.



30. Which is responsible for the similarity in the slopes of all of the graphs at the lower temperatures?

- A All metals exhibit metallic bonding when solid.
- B The lattice enthalpies of the metal oxides are similar.
- C The entropy change is similar for the oxidation of each of the metals.
- D Reaction rate increases steadily with increasing temperature.

31. The reduction of MgO to Mg is thermodynamically feasible at 1500 K using

- A manganese
- B titanium
- C aluminium
- D calcium.

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

- A When hydrogen ions are added, more ethanoic acid is produced.
- B It has a pH higher than 7.0.
- C It is effective because ethanoic acid and sodium ethanoate are both strong electrolytes.
- D The total molar concentration of ethanoate ions is much higher than the molar concentration of sodium ethanoate.

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

- | | |
|--------------------------|----------|
| A Screened methyl orange | 3.1–4.5 |
| B Methyl red | 4.2–6.3 |
| C Bromothymol blue | 6.0–7.6 |
| D Phenolphthalein | 8.3–10.0 |

34. A solution of a chemical absorbs energy only from the blue region of the visible spectrum. Which of the following is the most likely colour of the solution?

- A Red
- B Green
- C Yellow
- D Blue

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

- A CN^-
- B NH_4^+
- C NH_3
- D $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

36. The colour change from green to blue when excess ammonia is added to aqueous nickel (II) sulphate solution is due to
- A a change from octahedral to tetrahedral coordination
 - B a change in the oxidation state of nickel
 - C the removal of the degeneracy of the d-orbitals
 - D an alteration in the ligand field strength at nickel.
37. Which of the following elements can exhibit the highest oxidation number?
- A Manganese
 - B Cobalt
 - C Titanium
 - D Iron

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.

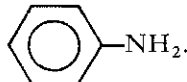
If only 3 is correct, select C.

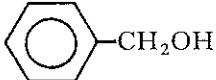
Otherwise select D.

38. Which of the following statements about benzene is/are true?
- 1 It is susceptible to attack by electrophilic reagents.
 - 2 Its molecules are planar.
 - 3 The C—C bond is greater in length than the C—C bond in ethane.
39. Which of the following statements about the atomic emission spectrum of hydrogen is/are correct?
- 1 Each series of lines in the spectrum eventually converge.
 - 2 The lines arise from electron transitions between one energy level and another.
 - 3 The lines arise from absorption of energy from the visible part of the electromagnetic spectrum.

40. Which of the following statements is/are true?

1 Infra-red spectra will not easily distinguish between $C_2H_5CONH_2$ and $C_2H_5NH_2$.

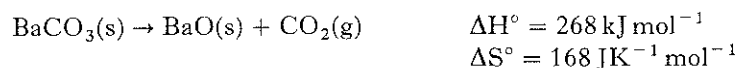
2 $C_2H_5NH_2$ is a weaker base than .

3 Both C_2H_5OH and 

react with sodium.

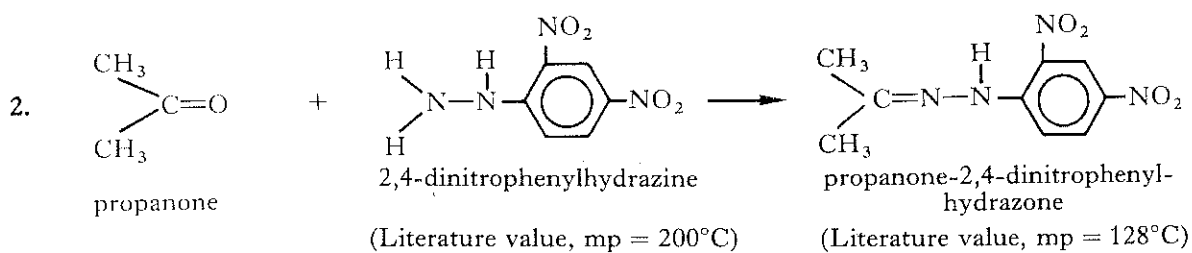
[END OF QUESTION PAPER]

1. Here are data for a reaction.



- (a) Calculate the temperature at which the decomposition of barium carbonate is thermodynamically feasible. 3
- (b) Is decomposition more favourable above or below this temperature? 1

(4)



1.16 g of propanone was added slowly to Brady's reagent (2,4 dinitrophenylhydrazine solution) and well mixed. The yellow solid derivative was filtered off and then recrystallised from ethanol. The crystals were filtered, washed with a little ethanol, dried and weighed. Only 60% of the theoretical yield was obtained. The melting point of the propanone-2,4-dinitrophenylhydrazone was found to be 125°C.

- (a) Name the two functional groups which react in this experiment. 2
- (b) What type of reaction has taken place? 1
- (c) Calculate the theoretical yield of the propanone-2,4-dinitrophenylhydrazone derivative. 2
- (d) Suggest why only 60% of the theoretical yield was obtained in the experiment. 1
- (e) Suggest a reason for the difference in the melting point of the propanone-2,4-dinitrophenylhydrazone derivative found experimentally and the literature value. 1
- (f) A yellow crystalline substance was thought to be either 2,4-dinitrophenylhydrazine or propanone-2,4-dinitrophenylhydrazone. 1
 How would you verify experimentally which it was? 1

(8)

3. Car exhausts contribute to air pollution by producing oxides of nitrogen and carbon monoxide.
- (a) Explain the origin of these gases in car exhaust fumes. 2
 - (b) Give a possible consequence of polluting the atmosphere with oxides of nitrogen. 1
 - (c) Cars with high compression engines need petrol with high octane numbers so that the petrol burns smoothly in the cylinders. Different hydrocarbons have different burning characteristics so that the petrol composition affects the octane rating. At present octane numbers are raised by adding lead compounds. Legislation is reducing the concentration of lead compounds allowed since these also cause pollution.
 - (i) How can oil companies raise octane numbers without adding lead compounds? 1
 - (ii) Why are lead compounds still used? 1
 - (d) Using catalysts in car exhaust systems can reduce the emission of gaseous pollutants but the catalysts would be "poisoned" by the use of the lead compounds. 1
Explain briefly how catalysts become "poisoned". (6)

[Turn over

4. Answer EITHER A OR B

A. When studying the kinetics of reactions, various techniques are used for measuring the concentrations of the species involved. Colorimetric methods are often convenient.

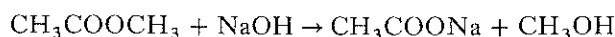
(a) Outline the procedure for a colorimetric method. 2

In some cases titrimetric methods are used. To "stop" the reaction before the titration, a sample is added to either

(i) a large volume of cold solvent, or

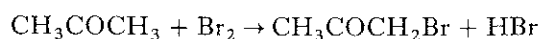
(ii) a known volume of a "quenching agent" which reacts immediately with one of the reagents.

(b) For the reaction



suggest a suitable quenching agent. 1

(c) The reaction



has the following rate law:

$$\text{rate} = k[\text{CH}_3\text{COCH}_3]^1[\text{Br}_2]^0.$$

What is the order of this reaction? 1

(d) The kinetics of a reaction can be studied by measuring the concentration (c) of a reactant at various times (t) after the reaction has started.

Kinetics data prove that a reaction is first order if a plot of $\log_{10}c$ against t is a straight line.

The results show data from an experiment. Find out, using a graph, if the data fits a first order reaction.

Time, t/s	Concentration of reactant, $c/\text{mol l}^{-1}$
0	2.0
100	1.7
200	1.5
300	1.3
400	1.1

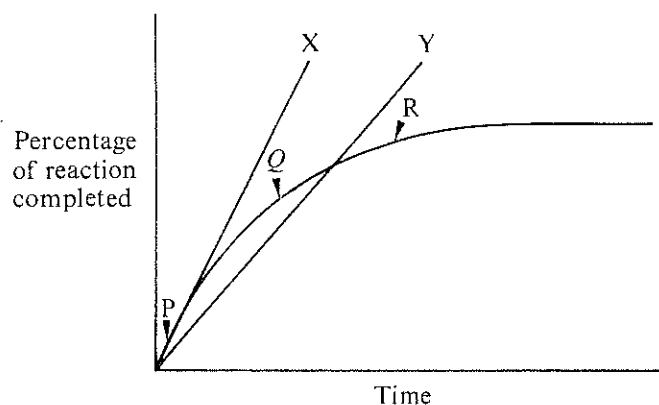
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(7)

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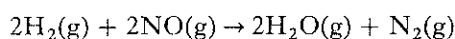
Marks

B. The study of kinetics is the study of reaction rates. Since the rate of a reaction varies as the reaction proceeds, initial reaction rates are often used.

(a)



- (i) At what stage, P, Q or R, is the reaction fastest? 1
- (ii) What causes the rate of the reaction to change? 1
- (iii) Which line, X or Y, represents the initial rate of the reaction? 1
- (b) The table below gives information about the reaction of hydrogen and nitrogen oxide at 800°C.



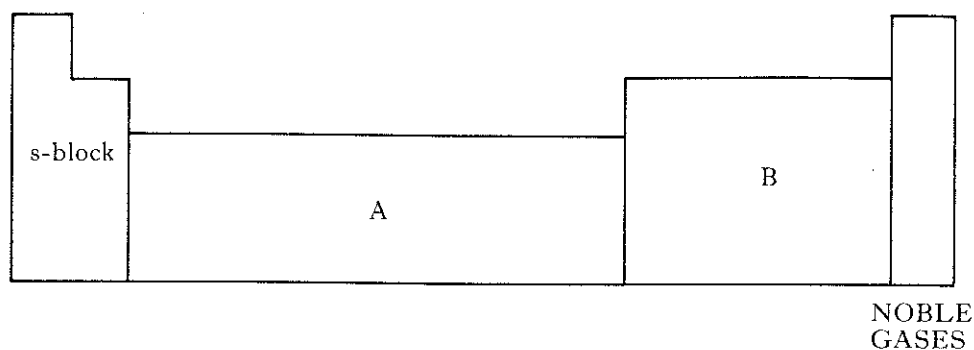
Experiment	Initial concentration of		Initial rate of production of N_2 / $\text{mol l}^{-1} \text{s}^{-1}$
	NO / mol l^{-1}	H_2 / mol l^{-1}	
1	6×10^{-3}	1×10^{-3}	3×10^{-3}
2	6×10^{-3}	2×10^{-3}	6×10^{-3}
3	1×10^{-3}	6×10^{-3}	0.5×10^{-3}
4	2×10^{-3}	6×10^{-3}	2.0×10^{-3}

- (i) Write the rate equation for the reaction. Explain how you derived it. 2
- (ii) Calculate the rate constant, k , for the reaction, giving the correct units. 2
- (7)

[Turn over

5. Answer EITHER A OR B.

A. This is a block diagram of the Periodic Table.



- (a) How are A and B designated and why? 2
- (b) Which block contains both metals and non-metals? 1
- (c) The size of the atoms decreases going from left to right across a given row in the Periodic Table.
Why is this so? 1
- (d) The trend mentioned in (c) above is less pronounced in block A than it is in the s-block.
Suggest a reason for this. 1
- (e) What happens to the size of the atoms as we go down a vertical group in the s-block?
Why is this so? 2
- (f) The Noble Gases were formerly called the Inert Gases.
Why was the name changed? 1
- (8)**

OR

- B. (a) Draw diagrams to represent a 2s orbital and the three 2p orbitals. 3
- (b) What does an orbital diagram represent? 1
- (c) What is the significance of the number 2 in the terms 2s and 2p? 1
- (d) The three 2p orbitals are often degenerate. What does the term "degenerate" mean in this context? 1
- (e) Draw an energy level diagram to represent the relative energies of the 1s, 2s and 2p orbitals in an isolated atom. 2
- (8)**

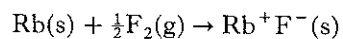
6. All the questions below are about the compounds shown in the grid. The answer to each question will be a number (or group of numbers) corresponding to the box(es) in the grid. A box may be used more than once in different answers. Correct boxes and no more are required to obtain each mark.

ethanal 1	methyl ethanoate 2	ethene 3
methylpropane 4	methylamine 5	ethanoyl chloride 6
phenylethene 7	phenyl ethanoate 8	butane 9

- (a) Which boxes contain a substance which gives ethanoic acid on hydrolysis? 1
- (b) Which boxes contain substances which would readily react together to form an amide? 1
- (c) Which boxes contain a monomer which could form an addition polymer? 1
- (d) Which boxes contain a set of isomers? 1
- (e) Which box contains a substance which on oxidation gives a product which reacts with PCl_5 to give the substance in box 6? 1
- (f) The compound in box 8 has a structural feature not found in the compounds in either box 4 or box 7. Three other compounds in the grid have this feature. In which boxes are they? 1
- (6)

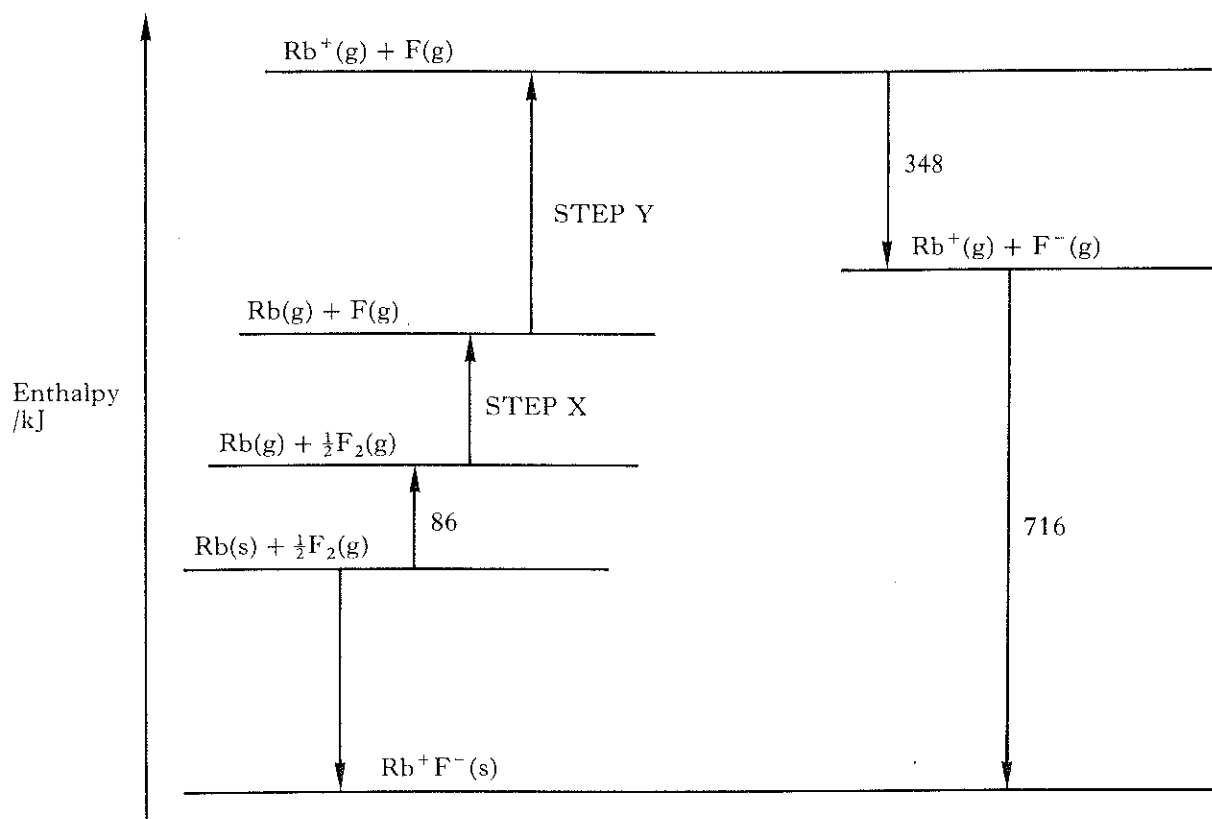
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7. The diagram below shows the enthalpy/energy changes for the reaction

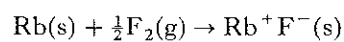


at 298 K and 1 atmosphere pressure.

The diagram is not drawn to scale.



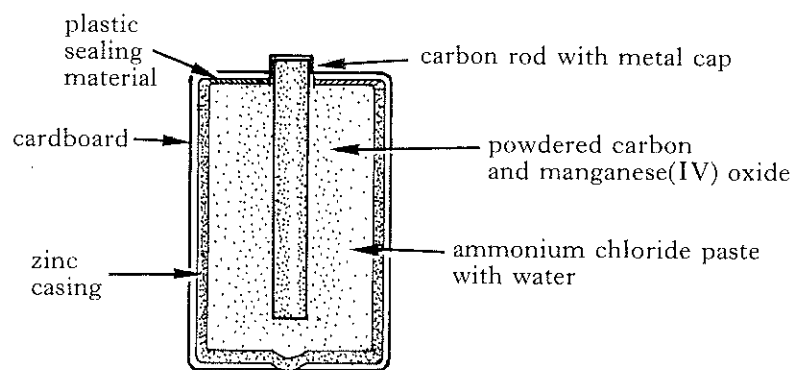
- (a) Using the appropriate information in the Data Booklet, find values for step X and step Y. 2
- (b) Calculate the value of ΔH° for the reaction



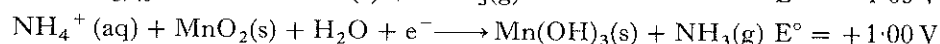
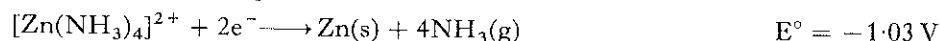
Show your working clearly.

3
(5)

8. This is a diagram of a common "dry" cell.

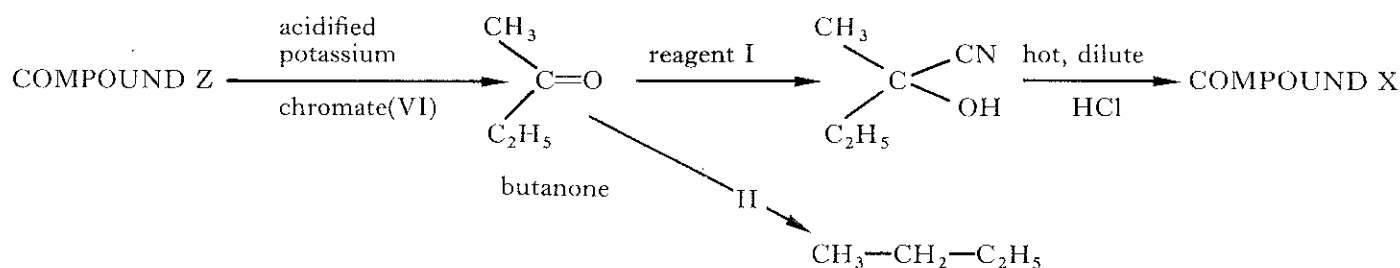


The two half-cell reactions making up the cell are quite complex. The Standard Reduction Potentials for the probable equations are:



- (a) What is the theoretical cell potential difference from these half-cell reactions? 1
- (b) Calculate the standard free energy change (per mole of zinc) for the cell, using this theoretical potential difference. 3
- (c) Suggest a reason for the fact that the actual cell potential difference is 1.5 V. 1
- (d) What is the function of the carbon rod? 1
- (6)**

9. Study this reaction sequence.

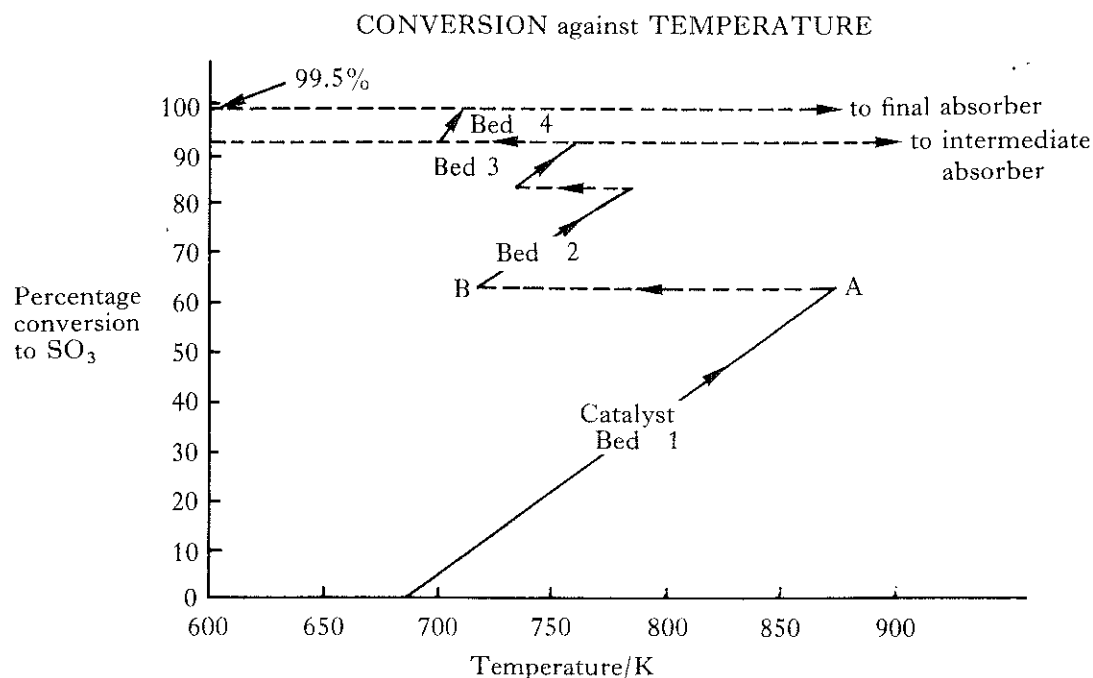


- (a) Name reagent I. 1
- (b) Draw the full structural formula for X. 1
- (c) Name the type of reaction taking place at II. 1
- (d) Name compound Z. 1
- (4)**

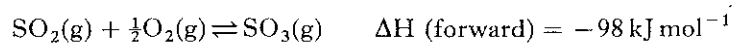
[Turn over

10. The Contact Process, using 4 or 5 catalyst beds in series, can achieve about 98% conversion of SO₂ to SO₃ with the SO₃ absorbed after the final catalyst bed.

Most modern plants use a "double absorption" process. The data shown here is from a Double Absorption Contact Plant. In these plants the SO₃ is removed at two different points.

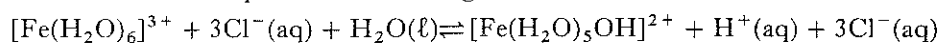


The equation for the reaction is



- (a) During the reaction, the entropy decreases. Suggest why. 1
 - (b) What effect will an increase in temperature have on the position of the equilibrium? Explain your answer. 2
 - (c) What happens to the reaction mixture between A and B? 1
 - (d) From the graph, what is the maximum temperature which allows nearly 100% conversion? 1
 - (e) (i) Apart from cooling, what happens to the gases between the 3rd and 4th catalyst beds? 1
 (ii) Why does this help to achieve a very high overall conversion to SO₃? 1
 - (f) Most plants operate at atmospheric pressure. Explain why some plants operating above atmospheric pressure achieve 99.85% conversions. 2
- (9)**

11. Solutions of some complex ions are acidic. For example, an aqueous solution of iron (III) chloride has a pH of 3.0. One of the processes occurring is



- (a) Name the two ligands in the complex structure on the right of the equation above and explain how they act as ligands. 2
- (b) Draw a diagram showing the shape of the complex ion on the right of the equation and name its shape. 2
- (c) It is more difficult to remove a proton from $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ than from $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. Explain why this is so. 1

(5)

12. Answer **EITHER A OR B.**

A (a) Write an expression which relates the dissociation constant of ethanoic acid to the concentration of the species present in an aqueous solution of the acid. 1

- (b) If the dissociation constant (K_a) of ethanoic acid at 25°C is $1.74 \times 10^{-5} \text{ mol l}^{-1}$, calculate the hydrogen ion concentration of a 0.1 M aqueous solution of ethanoic acid at this temperature.

Make clear any assumptions you make during your calculation. 4

(5)

OR

B (a) What is a buffer solution? 1

- (b) Show how an aqueous solution of benzoic acid and sodium benzoate can act as a buffer by considering what happens when

(i) a little dilute hydrochloric acid is added to the solution, and

(ii) a little dilute sodium hydroxide solution is added to the solution. 4

(5)

[Turn over

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

- A. In aromatic compounds, the presence of the benzene ring modifies the properties of the functional groups attached to it. Discuss this with reference to phenol, phenylamine (aniline), benzenecarboxylic acid (benzoic acid) and compare the properties of these compounds with those of the corresponding aliphatic compounds. (4)

OR

- B. Ellingham diagrams are very useful in helping a chemist to choose a method for extracting a metal from its ore. Discuss this.
Kinetic factors are also important.
Discuss these. (4)

OR

- C. Outline how you would calculate the percentage purity of a sample of sodium chloride using a gravimetric technique. Mention any relevant precautions. (4)

[END OF QUESTION PAPER]