

## Our country, our future

525/1

# **S6 CHEMISTRY**

Exam 23

### PAPER 1

**DURATION: 2 HOUR 45 MINUTES** 

#### **Instructions:**

- This paper consists of two sections A and B
- Section A is compulsory.
- Attempt only six questions in section B
- Answers must be written in the spaces provided only

| For I | For Examiner's Use Only |   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |
|-------|-------------------------|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|
| 1     | 2                       | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|       |                         |   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |

#### **SECTION A**

#### Answer all questions from this section.

1. (a) (i) The decay law is given the expression

$$-\frac{dN}{dt} = \lambda N$$

State what the symbols represent.

 $(01\frac{1}{2})$ 

λ rate constant

dt = change in tome

N amount of decaying substance available

(ii) Using the above expression derive the expression for the relation between half-life and the decay constant. (02)

Collecting like terms

$$-\frac{dN}{N} = \lambda dt$$

Integrating both sides

$$-\int \frac{dN}{N} = \lambda \int dt$$

$$-InN = \lambda t + C$$

$$t = 0, C - In N_0$$

Substituting for C and rearrangement

$$In\frac{N_0}{N} = \lambda t$$

When t = half-life  $t_{\frac{1}{2}}$ ; N =  $\frac{N_0}{2}$ 

$$\ln \frac{N_0}{\frac{N_0}{2}} = \lambda t_{\frac{1}{2}}$$

Half-life, 
$$t_{\frac{1}{2}} = \frac{In2}{\lambda} = \frac{0.693}{\lambda}$$

(b) (i) Nickel(<sup>63</sup>Ni) decays to copper (<sup>63</sup>Cu)

Name the particle emitted and write the equation for the reaction:

Name of particle; (01)

Beta particle

Equation

$$^{63}_{28}Ni \rightarrow ^{63}_{29}Cu + ^{0}_{-1}\beta$$

(ii) Calculate the time taken for  $\frac{15}{16}$  of nickel to be change to copper.

[The half-life for nickel is 120 years] (02)

Rate constant,  $\lambda = \frac{0.693}{120} \text{ yr}^{-1}$ 

Fraction of Ni undecayed =  $1 - \frac{15}{16} = \frac{1}{16}$ 

From 
$$In \frac{N_0}{N} = \lambda t$$
  
 $In \frac{1}{\frac{1}{16}} = \frac{0.693}{120} t$ 

t =480years

2. (a) State conditions for the reaction between aluminium oxide and sulphuric acid and write the equation for the reaction.

Conditions;

Dilute acid

Equation

$$Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(1)$$

(b) The resultant solution in (a) was mixed with aqueous sodium carbonate solution. State what would be observed and write equation for the reaction that takes place

Observation;  $(02\frac{1}{2})$ 

Effervescence and white precipitate

Equation;

$$2AI^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(I) \rightarrow 2AI(OH)_3(s) + 3CO_2(g)$$

3. The following experimental results were obtained for the reaction

$$A + 2B \longrightarrow products$$

| Ехр | Initial concent        | rations (mol $I^{-1}$ ) | Initial rate (mol I <sup>-1</sup> S <sup>-1</sup> ) |
|-----|------------------------|-------------------------|---|
|     | Α                      | В                       |   |
| 1   | 3.0 x 10 <sup>-2</sup> | 3.0 x 10 <sup>-2</sup>  | 2.7 x 10 <sup>-5</sup>                              |
| 2   | 3.0 x 10 <sup>-2</sup> | 6.0 x 10 <sup>-2</sup>  | 5.4 x 10 <sup>-5</sup>                              |
| 3   | 6.0 x 10 <sup>-2</sup> | 3.0 x 10 <sup>-2</sup>  | 10.8 x 10 <sup>-5</sup>                             |

(a) (i) Deduce the order of reactions with respect to

A;

2

В;

1

- (ii) Write the expression for the rate equation (0%) Rate =  $K[A]^2[B]$
- (b) The rate of reaction under certain conditions for temperature and pressure is x. Express the rate in terms of x when the following changes are made. (0 ½ each)
  - (i) The concentration B is halved while the concentration of A remains unchanged  $\frac{1}{2}$  x
  - (ii) The rate constant is doubled, by increasing temperature, but keeping the concentrations of A and B unchanged.

2x

- (iii) If 90% of B is removed by precipitation, without affecting concentration of A.  $0.01^2x = 0.0001x$
- (c) Calculate the value of the rate constant and state its units. (02)

$$2.7 \times 10^{-5} = K \times (3.0 \times 10^{-2})^{2} (3.0 \times 10^{-2})$$

 $K = 1 \text{mol}^{-2} l^2$ 

4. Complete the following reaction equations and write the IUPAC names of the main organic product in each case. (01½)

Name of product;

1-methylcyclopropene

(b) 
$$\frac{C - H}{\frac{Conc \, HCl}{Zn/Hg}} \xrightarrow{CH_{3}}$$

Name of product;

Methylbenzene

(c) (CH<sub>3</sub>)<sub>3</sub>COH anhydrous ZnCl<sub>2</sub>/Conc HCl (CH<sub>3</sub>)<sub>3</sub>C-Cl

Name of product. 2-chloro-2-methylpropane

5. (a) Write half equation(s) to show the action of hydrogen peroxide as

(i) an oxidizing agent

(01 mark each)

$$H_2O_2 + 2H + 2e \rightarrow 2H_2O(I)$$

(ii) a reducing agent

$$H_2O_2 - 2e \rightarrow 2H^+(aq) + O_2(g)$$

- (b) State what is observed and in each case write equation of reaction that take place when hydrogen peroxide is added to the following mixtures; (01 ½ marks each)
- (i) Acidified potassium chromate (VI) solution

Observation

Blue solution

Equation

$$Cr_2O_7^{2-}(aq) + 4H_2O_2(I) + 2H+(aq) \rightarrow 2CrO(O_2)_2 + 5H_2O(I)$$

(ii) Iron (II) sulphate in dilute sulphuric acid

Observation

Green solution turns brown

Equation

$$H_2O_2$$
 (aq) +  $2F^{2+}$ (aq) +  $2H^{+}$ (aq)  $\rightarrow 2H_2O(I) + 2Fe^{3+}$ (aq)

(c) Give one reason why hydrogen peroxide is not used in estimation of concentration of iron (II) ions in volumetric analysis (01)

Fe 3+ catalyzes the decomposition of hydrogen peroxide

6. (a) Explain what is meant by the term first election affinity.

First electron affinity is energy change when 1 mole of electrons is added to gaseous atoms to form gaseous ions with single negative charge.

(b) State three factors that can affect electron affinity.

(01 ½)

(01)

- atomic radius

- electronegativity

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### - electropositivity

### (c) The first electron affinities of some elements of period 3 are given in the table below

| Element                 | Al   | Si    | Р      | S     |
|-------------------------|------|-------|--------|-------|
| First electron affinity | - 44 | - 134 | - 71.7 | - 200 |
| (kJmol <sup>-1</sup> )  |      |       |        |       |

Generally electronegativity increases from Aluminium to sulphur

Electron affinity increases from Al to S due to increase in electronegativity. P has abnormally low electron affinity because it has stable electron configuration that oppose addition of electrons

### 7. (a) The enthalpies of some reactions are given below

$$\Delta H^{\theta}/kJmol^{-1}$$

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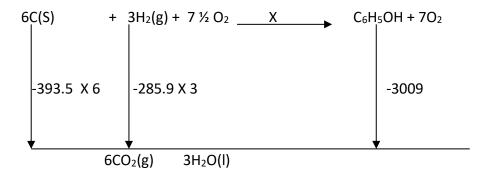
 $(0 \frac{1}{2})$ 

(i) 
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \Delta H^{\theta_1} = -393.5$$

(ii) 
$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2(I) \Delta H^{\theta_2} = -285.9$$

(iii) 
$$C_6H_5OH(s) + 7O_2(g) \longrightarrow 6CO_2(g), +3H_2O(I)$$
  $\Delta H_{3} = -3009$ 

Calculate the standard enthalpy of formation of phenol from its elements. (03)



$$X - 3009 = -393.5 X 6 - 285.9 X 3$$

 $X = 209.7 \text{kJmol}^{-1}$ 

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- (b) (i) From your answer in (a) state whether phenol is a stable compound or not. (0 ½ ) It is stable
  - (ii) Give a reason for your answer in b (i) above

    (01 mark)

    Its formation involves loss of energy
- (d) Write equation'(s) to show how phenol can be synthesized from chlorobenzene. (01  $\frac{1}{2}$  mark)

$$C_6H_5Cl$$
 NaOH, heat  $C_6H_5O^ H^+$   $C_6H_5OH$ 

8. (a) Neoprene is a synthetic polymer which has the following structure

$$\begin{array}{c|c} CH_2 - C = C - CH_2 \\ \hline H & CI \end{array}$$

- (i) Name the type of polymerization reaction which leads to formation of neoprene

  Addition polymerization
- (ii) Write the structure and name of monomer of neoprene. (01)

$$CH_2 = CH - C = CH_2$$
 2-chlorobut-2,3-diene | Cl

(b) When 350g of the monomer was polymerized  $9.89 \times 10^{-2}$  moles of neoprene was formed. Calculate the relative molecular mass of neoprene. (2)

Formula mass of neoprene =  $350/9.89 \times 10^{-2} = 3540$ 

(c) State one use of neoprene (0½)

Containers

#### **SECTION B**

#### Attempt only six questions in this section

(01)

10. (a) Explain what is meant by the term common ion effect.

This is the reduction in solubility of ionic salt in a solution that contain a common ion

(b) Silver chromate is sparingly soluble in water.

Write

(i) Equation for solubility of silver chromate in water (1 ½)

 $Ag_2CrO_4$  (aq)  $\leftrightarrow$   $2Ag^+$ (aq) +  $CrO_4^{2-}$ (aq)

(ii) The expression for solubility product, Ksp for silver chromate. (0 ½)

 $Ksp = [Ag^{+}]^{2}[CrO_{4}^{2-}]$ 

(c) A saturated solution of silver chromate contains  $2.4 \times 10^{-2}$ g per liter at  $20^{\circ}$ C

Calculate the value for the solubility product Ksp for silver chromate at 20°C. (02)

Formula mass of  $Ag_2CrO_4 = 108 \times 2 + 52 + 16 \times 4 = 332$ 

Molarity of silver chromate =  $\frac{2.4 \times 10^{-2}}{332}$  = 7.2 x 10<sup>-5</sup> moldm<sup>-3</sup>

 $[Ag^{+}] = 7.2 \times 10^{-5} \times 2 = 1.4 \times 10^{-4} \text{moldm}^{-3}$ 

 $[CrO42-] = 7.2 \times 10^{-5} \text{moldm}^{-3}$ 

 $Ksp = (1.4 \times 10^{-4})^2 (7.2 \times 10^{-5}) = 1.41 \times 10^{-12} \text{mol}^3 \text{dm}^{-9}$ 

- (d) Chloride ions in solution can be determined by titration with silver nitrate in the presence of chromate ions. The end point is indicated by a red precipitate of silver chromate.
- (i) Explain why silver chromate does not precipitate until the end point is reached. (01)

Sliver chromate is more soluble than silver chloride

(ii) Calculate the solubility of silver chloride in g/dm<sup>-3</sup> of 0.1M KCl. (3marks)

[Solubility product for silver chloride is  $1.6 \times 10^{-10} \text{ mol}^2 \text{ l}^{-2}$ ]

#### Solution

Let solubility in mole per liter be x

 $[Ag^+] = x$ 

 $[Cl^{-}] = 0.1 + x \approx 0.1$  because x is very small

$$\Rightarrow$$
 0.1x = 1.6 x 10<sup>-10</sup>  
x = 1.6 x 10<sup>-9</sup>moldm<sup>-3</sup>

Formula mass of AgCl = 108 + 35.4 = 143.5

Concentration of AgCl in  $gdm^{-3} = 143.5 \times 1.6 \times 10^{-9} = 2.3 \times 10^{-7} gdm^{-3}$ 

(a) A compound Y contains carbon, hydrogen and nitrogen. On combustion, 0.72g of Y produced
 1.615g of carbon dioxide and 0.42g produced 84cm³ of nitrogen at 15°C and 760mmHg.
 Calculate the empirical formula of Y.

Mass of carbon in 1.615g of 
$$CO_2 = \frac{1 \times 1.615}{44} = 0.44g$$

Volume of nitrogen produced by 0.72g of Y at  $15^{\circ}$ C and 760mmHg =  $\frac{0.72 \times 84}{0.42}$  = 144cm<sup>3</sup>

Volume of nitrogen at stp

$$\frac{{}^{760V}_{273}}{{}^{273}} = \frac{{}^{144}_{(273+15)}}{{}^{(273+15)}}$$
$$V = \frac{{}^{144}_{(273)}}{{}^{288}} = 136.5cm^3$$

Mass of nitrogen in 136.5cm<sup>3</sup>

22400cm3 contain 28

$$136.5 \text{cm}^3 \text{ contain } \frac{136.5 \times 28}{22400} = 0.17g$$

Mass of hydrogen = 0.72 - (0.44 + 0.17) = 0.11g

| Elements          | С                               | Н    | N     |  |
|-------------------|---------------------------------|------|-------|--|
| Mass              | 0.44                            | 0.11 | 0.17  |  |
| RAM               | 12                              | 1    | 14    |  |
| Moles             | 0.037                           | 0.11 | 0.012 |  |
| Mole ratio        | 3                               | 9    | 1     |  |
| Empirical formula | C <sub>3</sub> H <sub>9</sub> N |      |       |  |

(b) When Y was vaporized, it took 38 seconds to diffuse through the same porous partition under similar conditions whereas oxygen takes 28 seconds. Calculate the molecular formula of Y (03)

$$\frac{\text{Rate of Y}}{\text{Rate of oxygen}} = \sqrt{\frac{RFm \text{ of } O_2}{RFM \text{ of Y}}}$$

$$\frac{\frac{V}{38}}{\frac{V}{28}} = \sqrt{\frac{32}{RFM \ of \ Y}}$$

$$(C_3H_9N)n = 59$$

n = 1

therefore molecular formula of Y = C<sub>3</sub>H<sub>9</sub>N

(c) Y reacts with a mixture of concentrated hydrochloric acid and aqueous sodium nitrite to form a yellow oily liquid.

Ethylmethylamine; CH<sub>3</sub>CH<sub>2</sub>NHCH<sub>3</sub>

(ii) Write equation of reaction that takes place. (01 mark)

$$CH_3CH_2NHCH_3 + NaNO_2 + HCI \rightarrow CH_3CH_2N-NO + NaCI + H_2O$$

$$CH_3CH_2NHCH_3 + NaNO_2 + HCI \rightarrow CH_3CH_2N-NO + NaCI + H_2O$$

12. Name the reagents that can be used to distinguish between the following pairs of compounds.

In each case state what would be observed if each member of the pair is separately treated with the reagent.

(03 marks each)

Name of reagent (s): hot sodium hydroxide followed by lead iodide

#### Observation(s)

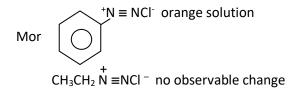
Yellow precipitate

no observable change

(b) 
$$\stackrel{+}{N} \equiv NCI^-$$
 and  $CH_3CH_2 N \equiv NCI^-$ 

Name of reagent: phenol

#### Observation(s)



2

|                                     | Observation          |                      |
|-------------------------------------|----------------------|----------------------|
| Name of reagent;                    | CH₂CH0               | C − CH <sub>3</sub>  |
| Fehling's solution                  | Red ppt              | No observable change |
| Ammoniacal silver nitrate           | Silver mirror        | No observable change |
| lodine in sodium hydroxide solution | No observable change | Yellow ppt           |

13. (a) (i) Compare the reactivity of hydrides of group (VII) elements with concentrated sulphuric acid.

(Write equation(s) for the reaction(s) which take place if any) (04)

HF and HCl do not react

HBr and HI are oxidized to element

2HX (X = Br or I) + 
$$SO_4^{2-}(aq) + 2H^+(aq) \rightarrow X_2 + SO_2(g) + 2H_2O(I)$$

(ii) Give a reason for the difference in reactivity shown by the hydrides in a(i) above. (01)

Br and I are strong reducing agents while F and Cl are not

(b) The bond lengths of the hydrides of group (VII) elements are given in the table below

| Hydride          | HF   | HCl  | HBr  | HI   |
|------------------|------|------|------|------|
| Bond length (A°) | 0.86 | 1.28 | 1.42 | 1.60 |

(i) State the trend in variation of bond length of the hydrides. (01)

H-X bond length increases from HF to HI

(ii) Explain your answer in b (i) above. (03)

Electronegativity decreases from F to I reducing electron attraction between H and X

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14. (a) Nitrogen reacts with hydrogen in a mole ratio of 1:3 to form ammonia.

Write;

(i) Equation for the reaction that takes place.

(01%)

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$$

(ii) the expression for the equilibrium constant (Kc) (0 ½)

$$Kc = \frac{[NH_3]}{[N_2][H_2]^3}^2$$

(b) State the conditions used to obtain maximum yield of ammonia during it manufacture by the Habers process. (01½)

Temperature: 400-500°

Pressure: 200 atmosphere

Catalyst: iron

(c) The percentage of ammonia in the equilibrium mixture of gases was found to be 15% at 600°C. Calculate the equilibrium constant (Kc) for the reaction at 600°C. (04)

Percentage of  $H_2$  and  $N_2 = 100 - 15 = 85$ 

Percentage of 
$$H_2 = \frac{3}{4} \times 85 = 63.75$$

Percentage of 
$$N_2 = \frac{1}{4} \times 85 = 21.25$$

$$Kc = \frac{15^2}{21.25 \times 63.75^3} = 4 \times 10^{-5} \text{mol-1dm}^6$$

(d) State what would happen to the equilibrium position of the reaction in a(i) above when hydrogen chloride gas is added to the equilibrium mixture. Give a reason for your answer. (01½)

Equilibrium shift to right to replace ammonia removed by HCl

- 15. Write equations to show how the following conversions can be effected. (03 marks each)
- (a) Ethanol to benzene

$$CH_{3}CH_{2}OH \ \underline{Conc.\ H_{2}SO_{4},\ heat\ CH_{2}=CH_{2}\ \underline{Br_{2}/CCl_{4}} \ CH_{2}-CH_{2}\ \underline{EtOH/EtO-,\ heat}}$$
 Br Br

(b) 1, 2 – dibromo ethane to ethanol.

$$CH_2 - CH_2$$
 EtOH/EtO- reflux HC=CH lindlar catalyst  $CH_2 = CH_2$  dil H2SO4, warm  $CH_3CH_2OH$  Br Br

(c) 2-Phenyl propane to phenol.

16. (a) (i) State three characteristic properties exhibited by cobalt as a transition element. (01  $\frac{1}{2}$ )

Forms colored cations, e.g. Co<sup>2+</sup> is pink

Has variable oxidation states i.e. +2 and +3

Forms complexes

(ii) Explain why zinc is not considered to be a transition element.

(02)

It ions has full d-orbital

Forms colorless compound

- (b) Cobalt (II) nitrate decomposes on heating in the absence of air forming are green solid and dissolves in water forming a pink solution.
  - (i) Write equation for decomposition of cobalt (II) nitrate. (01 ½)

 $2Co(NO_3)_2(s)$  heat  $2CoO(s) + 4NO_2(g) + O_2$ 

- (ii) Name the species responsible for the pink color of solution. (01)  $Co(H_2O)_6^{2^+}$
- (c) To the aqueous solution in (b) was added concentrated hydrochloric acid dropwise until in excess. State what is observed and write equation for the reaction that takes place. (03)

(i) Observation

Solution turns blue

(ii) Equation;

$$Co(H_2O)_6^{2+} + 4Cl^-(aq) \rightarrow CoCl_4^{2-}(aq)$$

17. (a) Explain what is meant by the term partition coefficient.

(02)

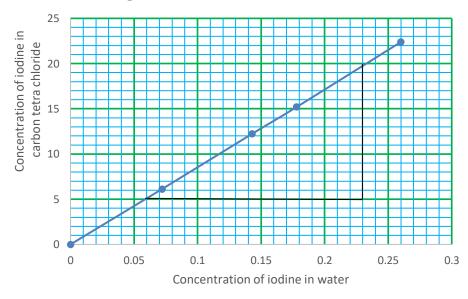
Partition coefficient is a ration of solute concentration in two immiscible liquids at equilibrium

(b) The table below shows the concentrations of iodine in the two layers when shaken with a mixture of carbon tetrachloride and water at 25°C.

| Concentration of I <sub>2</sub> in CCl <sub>4</sub> /moldm <sup>-3</sup> | 6.12  | 12.24 | 15.20 | 22.38 |
|--|-------|-------|-------|-------|
| Concentration of I <sub>2</sub> in water/ moldm <sup>-3</sup>            | 0.072 | 0.143 | 0.178 | 0.260 |

(i) Plot a graph of concentration of iodine in carbon tetra chloride against concentration of iodine in water

A graph of concentration of iodine in carbon tetra chloride against concentration of iodine in water



(ii) From the graph determine the partition coefficient for iodine distributed between carbon tetra chloride and water. (02)

$$K_D = \frac{20 - 5}{0.23 - 0.06} = 88.2$$

(c) State two applications of the partition coefficient. (02)

**Solvent extraction** 

Study of complexes

**END**