

MERRYLAND HIGH SCHOOL - ENTEBBE
CHEMISTRY WORK
S.6
SET 2

PHYSICAL CHEMISTRY:

1. a) (i) State **Hess' law of constant heat summation**, clearly stating its significance in thermodynamics.
- (ii) You are provided with the following thermochemical data.
Molar heat of combustion of ethyne is **-1260kJmol⁻¹**
Molar heat combustion of ethanol is **-1160kJmol⁻¹**
Calculate the standard enthalpy change of hydrolysis of ethyne.
- b) (i) Define the term **standard molar enthalpy change of formation**.
- (ii) The equation below shows the reaction between ammonia and fluorine

$$\text{NH}_3(\text{g}) + 3\text{F}_2(\text{g}) \longrightarrow 3\text{HF}(\text{g}) + \text{NF}_3(\text{g})$$
Using the standard molar enthalpy of formation in the table below, calculate the molar enthalpy change of the reaction.

Compound	NH ₃	HF	NF ₃
Standard molar enthalpy change of formation (KJmol ⁻¹)	-46	-269	-114

- (ii) Using the average bond enthalpy in the table below, calculate the molar enthalpy change of the same reaction in (b) above.

Bond	N-H	F-F	H-F	N-F
Average bond enthalpy (KJmol ⁻¹)	388	158	562	272

- (iii) Explain why the answer you have calculated in b(ii) regarded as a more reliable value?
- c) Using the following thermochemical data,
Lattice energy of Rubidium chloride = -665kJmol⁻¹
Dissociation energy of chlorine = +226kJmol⁻¹
Heat of atomization of Rubidium metal = -439kJmol⁻¹
Standard heat of formation of solid Rubidium chloride = -439kJmol⁻¹
Ionization energy of Rubidium = +397kJmol⁻¹

- (i) Construct a Born Haber cycle for the formation of rubidium chloride from its elements.
 - (ii) Use your Born Haber cycle to calculate the electron affinity of chlorine.
- 2.
- a) What is meant by the following terms as used in colligative properties?
 - (i) Ebullioscopic constant
 - (ii) Osmotic pressure.
 - b)
 - (i) Describe an experiment that can be used to determine the relative molecular mass of neoprene rubber by Berkley and Hartly method.
 - (ii) The osmotic pressure of a solution containing 1.24% of a polymer is 3.1×10^{-3} atmosphere. Determine the relative molecular mass of the polymer.
 - (iii) Explain why the osmotic pressure method is more preferred over ebullioscopy and cryoscopy in determining the relative molecular mass of polymers.
 - c) The table below shows how the boiling point of a certain ketone changes with addition of different concentrations of non-volatile solution W at constant temperature.

Concentration (g l^{-1})	0.0	4.0	8.0	10.0	14.0	16.0
Boiling point ($^{\circ}\text{C}$)	80	80.06	80.15	80.18	80.21	80.24

- (i) Plot a graph of boiling point elevation against concentration.
 - (ii) Use your graph to determine the molecular mass of the W. (Boiling point elevation constant of the ketone is $2.28^{\circ}\text{C mol}^{-1} \text{ kg}^{-1}$)
- 3.
- a) Explain the following terms as used in kinetics.
 - (i) Elementary reaction
 - (ii) Molecularity
 - (iii) Initial rate
 - (iv) Order of reaction
 - (v) Activated complex.

- b) The initial rate of the reaction between substances **A** and **B** is given by

$$\text{Rate} = K[A][B]^2$$

(i) Complete the table below for reaction between **A** and **B**.

Expt no.	Initial [A] / moldm ⁻³	Initial [B] / moldm ⁻³	Initial rate (moldm ⁻³)
1	0.020	0.020	1.2×10^{-4}
2	0.040	0.040	
3		0.040	2.4×10^{-4}
4	0.060	0.030	
5	0.040		7.2×10^{-4}

- (ii) Using the data for experiment 1, calculate the value of the rate constant.
- (iii) State **three** methods which might have used to study the rate of the chemical reaction in the table above.
- c) (i) Describe an experiment to show that catalytic decomposition of hydrogen peroxide is a **first order** reaction.
- (ii) A certain volume of Hydrogen peroxide solution was decomposed in the presence of platinum. The amount of Hydrogen peroxide after time **t** was found by withdrawing a liquots of solution, adding dilute Sulphuric acid and titrating with Potassium manganate (VII) solution. The volume of Potassium manganate (VII) solution remaining, **Vt** were as follows:

T (min)	0	5	10	15	20	25	30	35	40	45
Vt (cm ³)	12.30	9.20	6.690	5.20	3.90	2.90	2.20	1.60	1.20	1.15

- Tabulate values of log Vt
- Plot a graph of log Vt against time
- State order of reaction with respect to Hydrogen peroxide. Give reason for your answer.
- Determine the rate constant for the reaction
- Calculate the half-life for the reaction

- d) The rate of a certain reaction is $\text{Rate} = k[A][B]^2[C]$ where $[C]$ is the concentration moles per litre and k is the rate constant. State how the rate of the reaction will change if;
- Concentration of B and C is doubled and A is kept constant.
 - Concentration of A and C were kept constant and concentration of B is halved
 - $[A]$ and $[C]$ were kept constant and $[B]$ was doubled.
 - Concentration of A, B and C were doubled.
4. Propanoic acid is a weak acid with K_a of $1.32 \times 10^{-5} \text{ mol dm}^{-3}$ at 20°C .
- What is meant by the term **weak acid**?
 - Both propanoic acid and aniline dissociates in water. Write down the expressions of their dissociation constants.
 - Calculate the pH of propanoic when its concentration is 0.05M and that of aniline is 0.025M. (K_b of aniline is $2.94 \times 10^{-5}\text{M}$)
 - Explain why the solution of methyl ammonia chloride is acidic
 - Calculate the hydrolysis constant of a solution of 6.7g of methyl ammonium chloride in 500cm^3 of water when its pH is 2.33.
 - Calculate the volume of the above solution that would react completely with 10cm^3 of 0.25M sodium hydroxide solution.
 - Describe an experiment to determine the solubility product of calcium iodate.
 - If the solubility product of calcium iodate $1.9 \times 10^{-4} \text{ M}$ at 25°C . Calculate the solubility of calcium iodate in;
 - Water
 - 0.1M sodium iodate.
 - Comment on your answer in (ii) above.
 - With an example in each case, clearly distinguish between acidic buffers and basic buffers.
 - Calculate the pH of the solution obtained 20cm^3 of 0.1M sodium hydroxide is added to 100cm^3 of 0.1M ethanoic acid. (K_a of ethanoic acid is $1.8 \times 10^{-3}\text{M}$).
 - Sketch a graph showing pH changes when small amounts of ethanoic acid is added to sodium hydroxide from the burette. Account for the shape of your graph.

5. a) During the extraction of aluminium, a current of 0.2 ampere was passed for one hour through aluminium sulphate solution.
- Write an equation for the reaction that took place at each electrode.
 - Calculate the mass of aluminium produced.
- b) (i) What is meant by the following terms:
- Cell constant
 - Resistivity
 - Molar conductivity.
- (ii) Using the same conductivity cell, resistance of 0.1M KCL solution and 0.1M Bromoethanoic acid solution were found to be 24.96Ω and 66.5Ω respectively at 25°C when determined using the same conductivity cell (conductivity of KCl at 25°C = $0.01164\Omega^{-1}\text{cm}^{-1}$ molar conductivity of Bromoethanoic acid at infinite dilution is $389\Omega^{-1}\text{cm}^2\text{mol}^{-1}$).
- Calculate the cell constant
 - Calculate the molar conductivity of the 0.1M Bromoethanoic acid.
- c) (i) The molar conductivity of HNO_3 , KNO_3 and KF are 421, 145 and $129\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively at infinite dilution, calculate the molar conductivity of HF acid at infinite dilution.
- (ii) The electrolytic conductivity of a saturated solution of AgCl at 291K after deducting the electrolytic conductivity of water is $1.22 \times 10^{-4}\text{Sm}^{-1}$.
- The molar conductivity of the Ag^+ and Cl^- at infinite dilution at 291K are 0540×10^{-2} and $0.652 \times 10^{-2}\text{Sm}^2\text{mol}^{-1}$ respectively. Calculate the solubility of AgCl at 291K in gmol^{-1} ($\text{Ag} = 108$, $\text{Cl} = 35.5$)
- d) (i) What is **standard electrode potential**?
- (ii) Explain why it's not possible to measure standard electrode potential absolutely.

- (iii) The standard electrode potential of some systems are given below:

Electrode	E^\ominus (V)
$\text{Cr}^{3+}(\text{aq}) / \text{Cr}^{2+}(\text{aq})$	-0.402
$\text{MnO}_4^-(\text{aq}) / \text{Mn}^{2+}(\text{aq})$	+1.52

- Write the convention of the cell formed when the electrodes are coupled.
- Write an equation for the cell reaction.
- Determine the standard cell potential of the cell.
- Giving a reason, state whether the reaction is feasible or not.

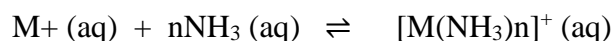
6. a) (i) State **Raoult's law**.
- (ii) Calculate the composition of benzene – toluene mixture which at 760mmHg boil at 88°C if the saturated vapour pressure of benzene and Toluene at this temperature are 957mmHg and 378mmHg respectively.
- (iii) Calculate the composition of the vapour obtained when the liquid mixture in (a) boils.
- (iv) Which of the two liquids is more volatile? Give a reason for your answer.

- b) The following data was obtained for a mixture of aniline and hydrochloric acid.

Mole fraction of aniline	0.0	0.2	0.4	0.6	0.8	1.0
Partial pressure of aniline (mmHg)	0	35	82	142	219	293
Partial pressure of hydrochloric acid (mmHg)	347	270	185	102	37	0

- (i) Plot a graph of vapour pressure of mixture against fraction of hydrochloric acid.
- (ii) Draw the boiling point composition diagram for the mixture of aniline and hydrochloric acid and on it indicate a tie line.
- (iii) Describe what would happen if a liquid mixture containing 20% aniline was fractionally distilled.

- d) (i) State the distribution law.
- (ii) An aqueous solution contains 10g of **z** in a litre of solution. 100cm³ of this solution was shaken with 20cm³ of an ether and the ether extracted 0.8g of **z**. Calculate the volume of the ether that is required to extract 80% of **z** from 500cm³ of the aqueous solution.
- (iii) What assumptions are used in your calculation in d(ii) above?
- e) Ions of metal **M** react with excess ammonia to form a complex according to the following equation.



25cm³ of ammonia solution was added to 25cm³ of a 0.1M aqueous solution of a metal **M**⁺ ions, followed by 50cm³ of trichloromethane. The mixture was shaken and allowed to reach equilibrium at 20°C. The aqueous layer required 27.5cm³ of 1.0M nitric acid and the trichloromethane layer required 18.0cm³ of 0.05M nitric acid for complete neutralization. Calculate the:

- (i) Concentration of ammonia in trichloromethane layer.
- (ii) Concentration of ammonia that formed the complex **M**⁺ ions. (distribution coefficient of ammonia between water and trichloromethane is 25 at 20°C)
- (iii) Determine the value of **n** in the complex.

7. a) State the **equilibrium law**.

- b) (i) Describe an experiment to determine the equilibrium constant for the decomposition of hydrogen iodide.
- (ii) 1.54g of hydrogen iodide was heated in 0.6dm³ bulb at 530°C. When equilibrium was attained, the bulb was rapidly cooled to room temperature and broken under potassium iodide solution. The iodine formed from the decomposition of hydrogen iodide required 67.0cm³ of 0.1M sodium thiosulphate solution for complete reaction. Calculate;
- Number of moles of hydrogen iodide in 1.54g.
 - Number of moles of iodine formed.
 - Value of **K_c** at 530°C

- c) The reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, $\Delta H = -92\text{KJmol}^{-1}$, illustrate synthesis of ammonia.
- (i) Give one source of hydrogen and nitrogen for this process.
- (ii) Stoichiometric amounts of nitrogen and hydrogen were reacted at 50 atmospheres. At equilibrium, 0.8 moles of ammonia was formed. Calculate the;
- Amount of nitrogen and hydrogen present at equilibrium
 - Value of the equilibrium constant for the reaction
- (iii) State and explain the effect on the above equilibrium if;
- Pressure is increased
 - Ammonia is removed from the mixture of gases
 - Operating temperature is increased
- d) Write equations to show nitric acid is synthesized from ammonia.
- e) Outline three uses of ammonia

INORGANIC CHEMISTRY:

8. The elements beryllium, magnesium and barium belong to group II of the periodic table.
- a) State three chemical properties shown by the elements. For each property write an equation to illustrate the answer.
- b) Beryllium differs in some of its properties from the rest of the members of the group.
- (i) State two properties in which beryllium differs from the rest of the members of the group.
- (ii) Give reasons why beryllium shows different properties from the rest of the elements in the group.

- c) Explain:
- (i) The trend in the solubilities of the hydroxides of group (II) elements in water
 - (ii) The trend in the solubilities of the sulphates of group (II) elements in water
 - (iv) Why beryllium carbonate is less thermally stable than barium carbonate.
 - (v) Why beryllium ion has a smaller electrical conductivity than the barium ion when both ions are in aqueous solution.

9. a) The first electron affinity of elements Na to Cl in period 3 are given below:

Element	Na	Mg	Al	Si	P	S	Cl
First electron affinity / kJmol^{-1}	-20	+67	-30	-135	-60	-200	-364

- (i) Describe and explain the general trend in the electron affinities from Na to Cl
 - (ii) Why is the first electron affinity of Mg more positive than one might expect from the general trend in the values above?
 - (iii) Why is the electron affinity of silicon more exothermic than that of phosphorus?
- b) Explain the expected difference between second and first electron affinity of oxygen.
- c) State and explain how the value of first ionization energy of magnesium would compare with the corresponding value of calcium.
10. a) In the complex $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$.
- (i) State the oxidation state of cobalt in the complex and name the complex.
 - (ii) State **three** factors that affect complex formation.
- b) Chromium and belong to d-block elements in the periodic table and are true transition elements.

- (i) Distinguish between a transition element and a d-block element.
 - (ii) Write the electronic configuration of chromium and copper
 - (iii) With examples state three properties of chromium and copper that make them different from S-block elements.
 - c) Give **two** chemical properties in each case in which manganese and chromium are similar and different.
 - d) To an aqueous solution containing chromium (III) ions was added sodium hydroxide solution drop wise until in excess and to the resultant mixture, hydrogen peroxide solution was added and warmed.
 - (i) State the observations made.
 - (ii) Write equations for the reactions that took place.
 - e) Determine the oxidation state of manganese in MnO_4^- , MnO_4^{2-} and MnO_2
 - f) Write an equation and explain what would be observed if;
 - (i) Water is added to potassium manganate (VI)
 - (ii) Carbon dioxide is bubbled through manganate (VI) solution
 - (iii) Aqueous sodium hydroxide solution was added to a solution containing manganese (II) ions drop wise until in excess.
11. The elements C, Si, Ge, Sn and Pb belong to group (IV) of the periodic table.
- a)
 - (i) Write down the general outer configuration of group (IV) elements.
 - (ii) Explain the variation in the stability of the oxidation states shown by group (IV) elements.
 - b)
 - (i) Sketch a graph to show the variation of melting points with atomic number for group (IV) elements.

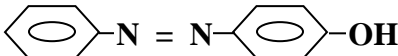
- (ii) Explain the shape of the graph drawn in (i) above.
- c) Although the bonding in carbon dioxide and silicon dioxide is covalent, carbon dioxide is a gas whereas silicon dioxide is a solid with a high melting point.
 - (i) Draw the structure and name the shapes adopted by the two oxides.
 - (ii) Explain the difference in melting points.
- d) Whereas carbon forms limitless number of stable hydrides, this tendency decreases rapidly down the group with increasing atomic number.
 - (i) Explain why it is so.
 - (ii) Write equations for the formation of the tetrahydrides and dihydrides of group (VI) elements.
 - (iii) Describe the reactions of the hydrides of group (VI) elements with water.
- e) Describe how ions of tin and lead behave when treated with common laboratory reagents. **Accompany your answers with equations.**

ORGANIC CHEMISTRY:

12. When 3.7g of an organic compound **Q** was exploded with excess oxygen, 4.5g of water and 6.48dm³ of a gaseous mixture were formed. On bubbling the gaseous mixture into a wash bottle containing concentrated potassium hydroxide solution, the volume of the gaseous mixture reduced to 2.0dm³. All volume measured at stp.
- a) Calculate the empirical formula of **Q**.
 - b) When **Q** was steam distilled at normal atmospheric pressure of 760mmHg, the distillate was found to contain 43.6% by composition of **Q** at this temperature; the vapour pressure of water is 640mmHg.
 - (i) Calculate the relative molecular mass of **Q**
 - (ii) Determine the molecular formula of **Q**.
 - c) **Q** evolves a colourless gas when reacted with sodium metal. Write the structural formulae of all possible isomers of **Q**.

- d) When Lucas' reagent was added to a test tube containing a solution of **Q**, a cloudy solution was formed immediately. Identify **Q**.
- e) Using equations show how;
- (i) **Q** can be converted to 2-methylpropan-1,2-ol
- (ii) **Q** can be synthesized from propan-1-ol
13. Name a reagent that can be used to distinguish the following pair of compounds. In each case state what is observed and write the equation for the reaction(s) if any that take place when each member is treated with the reagent stated.
- a) But-2-yne and But-1-yne
- b) Cyclohexane and phenol
- c) Ethanol and propan-1-ol
- d) Phenyldehyde and methanol
- e) iodocyclohexane and iodo benzene
- f) methanoic acid and ethanoic acid.
14. Write equations to show how the following compounds react and in each case outline the mechanism leading to the formation of the major product.
- a) Phenol with warm fuming sulphuric acid
- b) Phenylethanone with hydroxylamine
- c) 1-methylcyclohex-1-ene with hydrogen chloride gas
- d) Methanol with benzoic acid in hot concentrated sulphuric acid
- e) Propanone with sodium cyanide in presence of dilute sulphuric acid
- f) Ethanoyl chloride with hydroxyl benzene in sodium hydroxide solution

15. Using equations while writing conditions necessary show how the following compounds can be synthesized.

- a) 1-chloro propane to phenol
- b) Propan-2-ol to ethanol
- c) Propene to 2,2-dimethylpropan-1,3-dioic acid
- d) Methanol to 2-methylpropene
- e) Ethyne to cyclohexan-1,2-diol
- f) Benzene to 

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