CHUKA  UNIVERSITY

UNIVERSITY EXAMINATIONS

FIRST YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION (SCIENCE)

CHEM 120: PHYSICAL CHEMISTRY I

STREAMS: BSC (CHEM, MATHS, BIOL, BIOCHEM, INDUSTRIAL. CHEM, BIOMED) **TIME: 2 HOURS**

DAY/DATE: FRIDAY 18/12/2020 **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS: Answer question ONE and any other TWO questions

QUESTION ONE (30 MARKS)

(a) (i) State the Avogadro's law (1 mark)

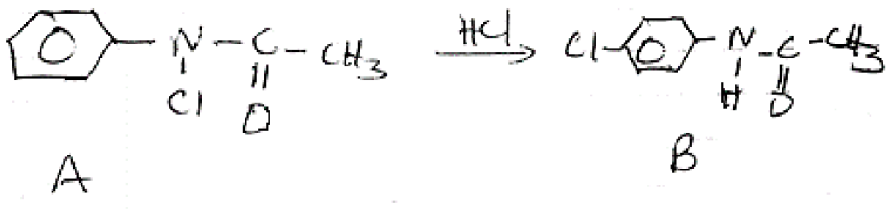
(ii) State what can you deduce from the fact that at STP 22.4 dm^3 of carbon dioxide contain morethan 6.02 $x10^{23}$ molecules (2 marks)

(iii) On reacting potassium chromate (VII) (potassium chlorate), $KClO_4$, with fluorosulphonic acid FSO_3H a gas X is evolved. A 0.245 g of X are found to occupy 112cm^3 at 293 k and at pressure of 5.20 x 10^4 Pa. Calculate the relative molecular mass of X. {(K = 39.098, Cl = 34.45, O = 15.999 g/mol) R =8.314 $JK^{-1}mol^{-1}$} (2 marks)

(iv) Describe how the syringe method can be used to determine the relative molecular mass of a gas and vapour (volatile liquids) (5 marks)

(b) (i) Write short notes on the order of reaction and rate constants (3 marks)

(ii) The progress of the reaction below can be followed by using the fact that compound Areacts with acidified potassium iodide, liberating iodine whereas compound B does not.



A series of experiments was carried out to determine the initial rate of reaction for various concentrations of compound A. The following data were obtained.

Concentration of compound A (mol dm^{-3})	Initial rate (mol $dm^{-3}s^{-1}$)
0.060	3.12×10^{-4}
0.120	6.23×10^{-4}
0.180	9.38×10^{-4}
0.240	12.5×10^{-4}

From the data in the table, deduce the order of reaction with respect to compound A. Explain your reasoning (1 mark)

(iii) In an investigation of the recombination of X atoms to give X_2 molecules in the gas phase in the presence of argon, that is the reaction $X + X + Ar \rightarrow X_2 + Ar$ the following data were obtained.

With the concentration of argon fixed at 1.0×10^{-3}mol dm^{-3}

Concentration [X] (mol dm^{-3})	Initial rate $\frac{d[X_2]}{dt}$ (mol $dm^{-3}s^{-1}$)
1.0×10^{-5}	8.70×10^{-4}
2.0×10^{-5}	3.48×10^{-3}
4.0×10^{-5}	1.39×10^{-2}

With the concentration of X fixed at 1.0×10^{-5} mol dm^{-3}

Initial concentration [Ar] (mol dm^{-3})	Initial rate $\frac{d[X_2]}{dt}$ (mol $dm^{-3}s^{-1}$)
1.0×10^{-3}	8.70×10^{-4}
5.0×10^{-3}	4.35×10^{-3}
1.0×10^{-2}	8.69×10^{-3}

Find the order of reaction with respect to [X] and [Ar], hence determine the overall velocity constant for the formation of X_2 molecules (3 marks)

(c) Draw the various types of curves showing variation of the rate with temperature (5 marks)

(d) At certain temperature, equilibrium constant for the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ is 5.0. If the reaction started with initial partial pressures of CO and steam as 1 atmosphere and 10 atmospheres, calculate the partial pressure of all the gases when the equilibrium state is reached. (5 marks)

(e) A 2.5 M solution of a weak monobasic acid has the same pH as 0.017M HCl. Assuming that the HCl is completely ionized;

(i) calculate the pH of these solutions (1 mark)

(ii) determine the degree of ionization of the weak acid in its 2.5M solution (2 marks)

QUESTION TWO (20 MARKS)

a) The rate constant for the reaction $H_2\ (g) + I_2\ (g) \rightarrow 2HI\ (g)$ is $5.4 \times 10^{-4}\ m^{-1}s^{-1}$ at 326°C. At 410°C the rate constant was found to be $2.8 \times 10^{-2}\ m^{-1}s^{-1}$ calculate the

(i) Activation energy ($R = 8.314\ JK^{-1}mol^{-1}$) (3 marks)

(ii) High temperature limiting rate constant for this reaction. (2 marks)

b) Briefly explain why the study of the effect of temperature on rates is important(3 marks)

c) The table below gives values for the velocity constant k, of the reaction between potassium hydroxide and bromoethane in ethanol at a series of temperature, T

K ($dm^3mol^{-1}s^{-1}$)	T (k)
0.182	305.0
0.466	313.0
1.35	323.1
3.31	332.7
10.2	343.6
22.6	353.0

Calculate the value for the activation energy of the reaction ($R = 8.31\ JK^{-1}mol^{-1}$) (5 marks)

d) The following data are for the reaction

A + B ⇌ Products

[A]	[B]	Initial rate (mol litre^{-1} sec^{-1})
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

(i) Determine the order with respect to A and B (4 marks)

(ii) Calculate the rate constant (2 marks)

(iii) Determine the reaction rate when the concentrations of A and B are 0.2M and 0.35M respectively. (1 mark)

QUESTION THREE (20 MARKS)

a) This question concerns the following reversible process

$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)\ \Delta H^o = -98\ KJ\ mol^{-1}$

Explain the effect on the position of equilibrium on;

(i) Increasing the pressure at constant temperature (1 marks)

(ii) Increasing the temperature at constant pressure ($1^1/_2$ mark)

(iii) Bearing in mind your answer for part (i), how do your account for the fact that industrially a temperature of about 800K, a pressure of 1 or 2 atm and a catalyst are used. (2 marks)

(iv) At 800K, the equilibrium partial pressures in atmospheres are; $P_{SO2} = 0.1$, $P_{O2} = 0.7$ and $P_{SO2} = 0.8$. Calculate K_P ($1^1/_2$ mark)

b) Consider the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$. For such a system of total volume, dm^3 and a total pressure of 202.6 kPa, at equilibrium the percentage dissociation of PCl_5 (g) at temperatures of 200^{o}C and 300^{o}C are 48.5 and 97.0 respectively.

(i) Calculate the value for Kp at 200^{o}C (4 marks)

(ii) Calculate the percentage dissociation of PCl_5that would result if the pressure of the system was reduced to 135.1 kPa. {Temperature remains constant} (2 marks)

(iii) How is the value obtained in (ii) explained in terms of Le chatelier's principle? (1 mark)

c) State the law of Gay-Lussac and show how it is related to Avogadro's principle (3 marks)

d) The reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, is forming NO_2 at the rate of 0.0076 mol/L/sec at some time. Calculate;

(i) The rate of appearance of O_2 at this time (2 marks)

(ii) The rate of disappearance of N_2O_5 at this time (2 marks)

QUESTION FOUR (20 MARKS)

a) Distinguish between electrolytic cell and electrochemical cell with aid of suitable diagrams (4 marks)

b) Will Ce^{3+} (a=1) ions reduce chlorine to Cl^- (a=1) ions at 298 K according to the reaction

$Ce^{3+}(a=1) + \frac{1}{2}Cl_2$ (p = 1 atm) $\rightleftharpoons Ce^{4+}(a=1) + Cl^-(a=1)$

Given that

$E^o_{ce^{4+}}/Ce^{3+}/Pt = 1.82$ V

$E^o_{Cl^-}/Cl_2/Pt = 1.3595$ V (4 marks)

c) Using the thermochemical data given below at 298 K,

$2OF_2\ (g) \rightarrow O_2\ (g) + 2F_2\ (g)$ $\Delta H^o = -49.4$ KJ

$2ClF\ (g) + O_2\ (g) \rightarrow Cl_2O\ (g) + OF_2\ (g)$ $\Delta H^o = +205.6$ KJ

$ClF_3\ (g) + O_2\ (g) \rightarrow \frac{1}{2}Cl_2O\ (g) + \frac{3}{2}OF_2\ (g)$ $\Delta H^o = +266.7$ KJ

Calculate the change in enthalpy (ΔH^o) for the following reaction

$ClF\ (g) + F_2\ (g) \rightarrow ClF_3\ (g)$ $\Delta H^o = ?$ (3 marks)

d) The first proton of sulphuric acid is completely ionized but the second proton is only partially dissociated with an acidity constant Ka_2 of 1.2×10^{-2}. Calculate the pH of the solution. (4 marks)

e) The hydrogen sulphate ion, HSO_4^-, is a moderately strong Bronsted acid with a Ka of 1.0×10^{-2}

i. Write the equilibrium expression for this acid (1 mark)

ii. Calculate the value of $\{H^+\}$ in 0.010M HSO_4^- (Furnished by the salt, $NaHSO_4$). (3 marks)

iii. Calculate the percentage ionization of HSO_4^- into H^+ and SO_4^{2-} in 0.010M HSO_4^- (1 mark)
