CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF

CHEM 120: PHYSICAL CHEMISTRY I

STREAMS: **TIME: 2 HOURS**

DAY/DATE: TUESDAY 16/04/2019 **2.30 P.M. – 4.30 P.M.**

INSTRUCTIONS:

- **Answer question ONE and any other TWO questions**

QUESTION ONE (30 MARKS)

1. (a) (i) State Faraday's first and second law of electrolysis. (1 mark)

(ii) Explain the significance of Faraday's second law of electrolysis. (2 marks)

(iii) Three cells, containing respectively solutions of silver nitrate, copper (II) sulphate and dilute sulphuric acid, are fitted with platinum electrodes and placed in series. When an electric current of 2.5 amperes is passed through the cells, 0.4g of silver was deposited in the first cell. Calculate:

(I) The weight of copper deposited in the second cell. (1 mark)

(II) The period of time the current was passed.

{H=1, Cu=63.6, Ag = 108, IF = 96,500 coulombs} (1 mark)

(III) The volume of hydrogen liberated at $17^0 C$ and 770 mmHg in the third cell. (3 marks)

(b) (i) Selenium in a 10.0 g soil sample is distilled as the tetra-bromide, which is collected in aqueous solution where it is hydrolyzed to $Se0_3^{2-}$.

The $Se0_3^{2-}$ is determined iodometrically requiring 4.5 ml of standard thiosulphate solution for the titration. If the thiosulphate titer is 0.049 mg $K_2Cr_20_7/$ ml, calculate the concentration of selenium in the soil in ppm.

{Se=78.96, 0=15.9994, K=39.098, Cr=51.996, I=126.9045} (6 marks)

(ii) Distinguish between reversible cell and irreversible cell. (4 marks)

(iii) Briefly explain the metal-metal ion reversible electrode with suitable example. (2 marks)

(iv) Explain why the standard hydrogen electrode is assigned zero electrode potential. (2 marks)

(c) (i) Calculate the EMF of a decimolar Daniell's cell at 25^0C given that E^0 values for zinc and copper electrodes are -0.7623V and +0.337V at 25^0 C. (1 mark)

(ii) Calculate the cell EMF if concentration of $ZnSO_4$ solution is 0.1 M and that of $CuSO_4$ solution is 0.01 M. {R=8.314J $JK^{-1}MOL^{-1}, F=96500\,C\,MOL^{-1}$}

(1 marks)

(d) Distinguish the terms in the following pairs:

(i) Enthalpy of a reaction at constant volume from that at constant pressure. (2 marks)

(ii) Bond enthalpy from bond dissociation enthalpy. (1 mark)

(iii) Integral enthalpy of dilution from differential enthalpy of dilution. (1 mark)

QUESTION TWO (20 MARKS)

2. (a) (i) State Hess's law ($\frac{1}{2}$ marks)

(ii) Use Hess's law to calculate the following enthalpy of reaction of the major process of steam reforming:

$$CH_4(g)+H_20(g)\rightleftharpoons CO(g)+3H_2(g)$$

Given that the separate reactions of carbon dioxide and hydrogen gas and methane decomposition are (2 $\frac{1}{2}$ marks)

$$CO(g)+H_2(g)\longrightarrow C(graphite)+H_20(g)\Delta H^0_{\square}=-131.3KJ$$

$$C(graphite)+2H_2(g)\longrightarrow CH_4(g)\Delta H^0_{\square}=-74.8KJ$$

(iii) From the following information on bond enthalpy data, calculate the enthalpy of formation of gaseous isoprene

$$CH_2{=}\underset{\Big|}{C}-CH=CH_2$$
$$\quad\ CH_2$$

Bond enthalpies of $H-H, C-H, C-C$ and $C=C$ are 435.94 $KJ\,MOL^{-1}, 415.8\,KJ\,MOL^{-1}, 347.7\,KJ\,MOL^{-1} \wedge 600.7\,KJMOL^{-1}$, respectively. The enthalpy of sublimation of carbon is $716.68\,KJ\,MOL^{-1}$. If the enthalpy of formation of gaseous isoprene obtained from the combustion data is $8.79\,KJMOL^{-1}$, how would you account in the two values? (2 marks)

(iv) From the measured enthalpy of the reaction:

C (graphite)+ $\frac{1}{2}Cl_2(g)+\frac{3}{2}H_2(g)\longrightarrow CH_3CI(g)\Delta H^0=-82.01\,KJ\,MOL^{-1}$

Calculate the enthalpy of the reaction

$$C(g)+CI(g)+3H(g)\rightarrow CH_3CI(g)$$

Given that

C(graphite) $\rightarrow C(g)\Delta H^0 = 716.68\ KJ\ MOL^{-1}$

$H_2(g) \rightarrow 2H(g)\Delta H^0 = 435.94\ KJ\ MOL^{-1}$

$CI(g)\Delta H^0 = 242.15\ KJ\ MOL^{-1}$

$CI_2(g) \rightarrow 2¿$ (3 marks)

(b) (i) Discuss the useful information that is obtained from equilibrium constant. (3 marks0

(ii) State Le Chatelier's principle. (1 mark)

(iii) Explain how equilibrium will vary with changes in volume and pressure of gases. (1 mark)

(c) (i) For the reaction

$CO(g)+H_20(g) \rightleftharpoons CO_2(g)+H_2(g)$

KC at 800K is 4.24

Calculate the equilibrium concentrations of CO_2, H_2, CO and H_20 at 800K, if only CO and H_20 are present initially at concentrations of 0.10M each. (2 $\frac{1}{2}$ marks)

(ii) For the equilibrium

$2NOCI(g) \rightleftharpoons 2NO(g)+CI_2(g)$

the value of the equilibrium constant, $Kc\ is 3.75 \times 10^{-6}$ at 1069k.

Calculate the Kp for the reaction at this temperature

(1 mark)

(d) (i) 25 ml of H_2 and 18ml of I_2 vapour were heated in a sealed glass bulb at $465^0 C$ when at equilibrium 30.8 ml of HI was formed. Calculate the degree of pure HI at 4.65^0 C.

(3 marks)

(ii) When PCI_5 is heated at gasifies and dissociates into $PCI_3 \wedge CI_2$. The density of the gas mixture at $200^0 C$ is 70.2. Calculate the degree of dissociation of PI_5 at $200^0 C$. (1 mark)

QUESTION THREE (20 MARKS)

3. (a) (i) Explain how you can characterize the deviation from ideality of a real gas.

(ii) Two separate bulbs are filled with an ideal gas A and a non-ideal gas B respectively in such a way that PV remains the same and B is below it's Boyle temperature. Show mathematically that, B has greater temperature than A. (2 marks)

(iii) 0.540 gm of an organic liquid displaces $71.52\,cm^3$ of dry air $99.80^0 C$. The barometer pressure was 691.4 mm of Hg. The compound is saturated and contains only carbon, fluorine and chlorine. There is 57% CI_2 by weight. Determine its molecular formula. {CI=35.5, C=12, F=19)

(iv) A gaseous compound x contained 44.4% carbon, 51.9% nitrogen and 3.7% hydrogen. Under the same conditions $50\,cm^3$ of is x diffused through a porous plug in 25 seconds while hydrogen gas having the same volume as x diffused in 6.8 second. Deduce the molecular formula of x

{Vapour density of H_2 =1 g/c m^3, C=12, N=14, H=1} (3 marks)

(b) (i) For a reaction:

$$+¿ \rightarrow 33\,Br_2 + 3\,H_2 0$$
$$-¿ + 6\,H^{¿}$$
$$-¿ + 5\,Br^{¿}$$
$$BrO_3^{¿}$$

A set of experiments were performed to investigate the concentration effect of one of the reactants while keeping others constant, with different initial conditions as shown in the table below.

Experiment	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Initial rate
1	0.10	0.10	**0**.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Determine the rate law and rate constant. (2 marks)

(ii) State Arrhenius equation and explain the terms involved. (2 marks)

(iii) Biologists carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature T.

(I) Use the data in the table below, along with the suitable graph to calculate activation energy (Ea) for the biochemical reaction that controls cricket chirping

F	200	179	158	141	126	112	100	89	79
T	299	298	296	294	293	292	290	289	287

(2 $\frac{1}{2}$ *marks*¿

(II) Predict the chirping rate on a very hot evening, when the temperature is $308\,K\left(35^0\,C \vee 95^0\,F\right)$ (Assume the initial temperature was 296K) (1 mark)

(III) Determine the value of frequency factor ($\frac{1}{2}$ mark)

QUESTION FOUR (20 MARKS)

4. (a) Calculate the volume of 85% (wt/wt) $H_3PO_4(SP.gr\,1.69)$ and the weight of KH_2PO_4 required to prepare 200 ml of a buffer of pH 3.0 that has an ionic strength of 0.20

$$-¿\,Ka_1 = 1.1 \times 10^{-2}$$
$$+¿ + H_2PO_4^{¿}$$
$$H_3PO_4 \rightleftharpoons H^{¿}$$

$$Ka = 39.098, H = 1.00794, O = 15.9994$$ (6 marks)

(b) (i) Write short notes on buffer capacity. (5 marks)

(ii) A buffer solution contains $0.1\,M\ Na\,H_2PO_4$ and 0.070 Na_2HPO_4. Calculate its buffer intensity in moles/liter per pH. By how much would the pH change if 0.01 ml of 1.0 M HCI OR 0.01 ml 1.0 M NaOH were added to 10 ml of the buffer. (2 marks)

(c) A 100 ml aliquot of a solution containing HCI and H_3PO_4 is titrated with 0.2 M NaOH. The methyl red end point occurs at 25.0 ml and the bromothymol blue end point occurs at 10.0 ml later (Total 35.0 ml). Calculate the concentrations of HCI and H_3PO_4 in the solution. (2 marks)

(d) A sample containing the amino acid alanine, $CH_3CH(N\,H_2)COOH$, plus inert matter is analyzed by the KJeldahl method. A 2.00g. Sample is digested, then NH_3 is distilled and collected in 50.0 ml of 0.150 M H_2SO_4 and a volume of 9.0 ml of 0.100 m NaOH is required for back titration. Calculate the percent alanine in the sample. {N=14.0067, C=12.0011, H=1.00794, 0=15.9994} (5 marks)
