UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2015/2016

TITLE OF PAPER: PHYSICAL CHEMISTRY

COURSE NUMBER: C402

TIME: THREE (3) HOURS

INSTRUCTIONS:

There are **six (6)** questions. Each question carries 25 marks. Answer **Question one (1) and any three (3)** other questions.

NB: Each question should start on a new page.

A data sheet and a periodic table are attached

A non-programmable electronic calculator may be used

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QUESTION 1 (25 MARKS)

a) Using diagrams, where necessary, in terms of relaxation effect and eletrophoretic effect, explain the concentration dependence of molar conductivities shown by both strong and weak electrolytes. [5]

b) Write short notes to define the nature and role of enzymes in reaction kinetics. Your notes should include examples to illustrate your answer. [5]

c) Using an equation of your choice, briefly explain pre-equilibrium approach. [4]

d) What approximations underlie the BET isotherms [4]

e) Describe the formation of a hydrogen bond in terms of electrostatic interaction model and state its limitations [3]

f) Define the mean free path (λ). How does it vary with the number density, particle diameter and particle mean speed. [4]

QUESTION 2 (25 MARKS)

a) Given that $\Delta rG^{\ominus}$ = -212.7 kJ/mol for the reaction in a Daniel cell at 25 °C, and that $b(CuSO_4) = 1.\ 0 \times 10^{-3}$ mol/kg and $b(ZnSO_4) = 3.0 \times 10^{-3}$ mol/kg, calculate the reaction quotient and the cell potential assuming that the activity coefficients of each ion is equal to the mean activity coefficient in the respective compartments [6]

Debye-Huckel constant A = 0.509

b) A quinehydrone (quinehydrone, $Q{\cdot}QH_2$ is a complex of quinine, $C_6H_4O_2$=Q and hydroquinone , $C_6H_4O_2H_2$=QH_2) electrode has the reduction half reaction;

$$Q(aq) + 2H^+(aq) + 2e^- \rightarrow QH_2(aq) \quad E^{\theta} = +0.6994\ V$$

$$Hg_2Cl_2(s) + 2e- \rightarrow 2Hg(l) + 2Cl^-(aq) \quad E^{\theta} = +0.2676\ V$$

If the cell **$Hg\,|\,Hg_2Cl_2(s)\,|\,HCl\ (aq)\,|\,Q{\cdot}QH_2\,|\,Au$** is prepared and the measured cell potential was found to be +0.190V, calculate the pH of the HCl solution assuming that the Debye-Huckel limiting law holds.

pH =-log[H+]=-log[a_{H+}], lnx=ln10logx [6]

c) Write the electrode half reactions and the overall cell reactions for the following.

i. $Pt(s)|Cl_2(g)|HCl(aq)||K_2CrO_4(aq)|Ag_2CrO_4(s)|Ag(s)$

ii. $Cu(s)|Cu^{2+}||(Mn^{2+}(aq),H^{+}(aq)|MnO_2(s)|Pt(s)$ [6]

d) For the liquid carbon tetrachloride, CCl_4, at 20 °C and 1 atm, the relative permittivity, ε_r, is 2.24 and the density is 1.59 g/cm^3. Calculate the polarizability, α and the polarizability volume α' for CCl_4. Given that vacuum permittivity, ε_0, is 8.854 x 10^{-12} $C^2m^{-1}J^{-1}$

[7]

QUESTION 3 (25 MARKS)

a) With the aid of an equation or any other information explain the following observations

i. As the Ionic radius increases (r), the ion mobility (u), increases [2]

ii. Ionic hydrodynamic radius (a) decreases with an increase of ionic radius (r).

[1]

iii. The mobility of H^+ is 9.03 x higher than the mobility of Li^+. [3]

b) Derive the linearised Ostwald dilution law for a weak electrolyte. (clearly show all steps)

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a(\Lambda_m^0)^2}$$ Ostwald dilution law [4]

c) The following data were obtained for a weak electrolyte, HA in ethanol at 25 °C

Concentration c/10^{-4} mol/dm^3	1.566	2.600	6.219	10.441
Conductivity K/10^{-6} Scm^{-1}	1.788	2.418	4.009	5.336

Show that these data is in accordance with the Ostwald dilution law. [5]

d) Derive an expression that shows how the pressure of a gas inside an effusing oven varies with time if the oven is not replenished as the gas escapes,

$$p = p_0 e^{-\frac{t}{\tau}}, \tau = \left(\frac{2\pi M}{RT}\right)^{\frac{1}{2}} \frac{V}{A}$$ where A is the area of the effusing hole and given

that the rate of effusion, $Z_w A = \frac{pAN_A}{(2\pi MRT)^{\frac{1}{2}}}$ and $\int \frac{1}{x} = \ln x$

Then show that the half life ($t_{\frac{1}{2}}$) is independent of the initial pressure. [10]

QUESTION 4 (25 MARKS)

a) The reaction rate (υ) in the reaction $2A + B \rightarrow 2C + 3D$ is 1.0 mol $L^{-1}s^{-1}$. State the rate of formation or consumption of A, B, C and D. [4]

b)

- *i.* What is a half life?
- *ii.* Derive the expression that relates the half life to the rate constant and initial concentration for a zero order reaction. [4]

c) For the decomposition of N_2O_5, the following data was obtained:

θ/°C	25	35	45	55	65
k/S^{-1}(x 10^{-5})	1.72	6.55	24.95	75	240

Calculate the activation energy and the pre exponential factor for this reaction

[10]

d) For the reaction, $H_3O^+ + OH^- \leftrightarrow 2H_2O$,

- *i.* Show that for a small perturbation, the relaxation time expression for the reaction (with k_f and k_r being the constants for the forward and reverse reactions) is given by $\frac{1}{\tau} = k_f([H_3O^+]+[OH^-])$ assuming that the concentration of water remains constant even after the perturbation [4]
- *ii.* Hence calculate the equilibrium concentrations of the hydronium and hydroxyl ions which are assumed to be equal at 25 °C, given that τ=3.7 x 10^{-5}s and k_f=1.35 x 10^8 m^3 $mole^{-1}s^{-1}$. [3]

QUESTION 5 (25 MARKS)

a) Discuss the advantages of photochemical activation over thermal activation in chemical kinetics. [4]

b) The mechanism of a reaction $H_2(g) + I_2 \rightarrow 2HI(g)$ is

(1) $I_2 \leftrightarrow 2I$ k_1 and k_1'

(2) $I + H_2 \rightarrow HI + H$ k_2

(3) $H + I_2 \rightarrow HI + I$ k_3

Find the expression of the rate law for the formation of HI using the steady state approximation. [7]

c) The molar polarization, P_m, is defined as $P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$. The molar polarization of gaseous water at 100 kPa , is given in the table below.

T/K	384.3	420.1	444.7	454.1	522.0
$P_m/(cm^3/mol)$	57.4	53.5	50.1	46.8	43.1

Calculate:

i. The dipole moment

ii. Polarizability and

iii. The polarizability volume of water. [14]

QUESTION 6 (25 MARKS)

a) What assumptions did Langmuir make when deriving his isotherm $\theta = \frac{\alpha p}{1+\alpha p}$

[4]

b) For N_2 adsorbed on a certain sample of charcoal at -77 °C, the volume of adsorbed N_2 (measured at 0 °C and 1 atm) per gram of charcoal varied with N_2 pressure as given below:

P/atm	3.5	10.0	16.7	25.7	33.5	39.2
$V/(cm^3/g)$	101	136	153	162	165	166

i. Show that the data fits the Langmuir isotherm.

ii. Determine the value of α

iii. Determine the volume of N_2 needed for monolayer coverage. [10]

c) CO adsorbs non-dissociatively on the (111) plane of Ir with A_{des} = 2.4 x 1014/s and $E_{a,des}$ = 151kJ/mol. Find the half life of CO chemisorbed on Ir (111) at 300K [3]

d) The adsorption of solutes on solids from liquids often follows a Freundlich isotherm, $\theta = kp^{\frac{1}{n}}$. Adapt the equation to apply to a solution and check its applicability to the following data for the adsorption of acetic acid on charcoal and determine the constants ***k*** and **n**.

[acid]mol/L	0.05	0.10	0.50	1.0	1.5
W_a/g	0.04	0.06	0.12	0.16	0.18

Wa is the mass adsorbed per unit mass of charcoal. [8]

THE END **/100/**

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\ 924\ 58 \text{ X } 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\ 177 \text{ X } 10^{-19}$ C
Faraday constant	$F = N_A e$	$9.6485 \text{ X } 10^{4}$ C mol^{-1}
Boltzmann constant	k	$1.380\ 66 \text{ X } 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\ 51$ J K^{-1} mol^{-1} $8.205\ 78 \text{ X } 10^{-2}$ dm^{3} atm K^{-1} mol^{-1} $6.2364 \text{ X } 10$ L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\ 08 \text{ X } 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\ 57 \text{ X } 10^{-34}$ J s
Avogadro constant	N_A	$6.022\ 14 \text{ X } 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\ 54 \text{ X } 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\ 39 \text{ X } 10^{-31}$ Kg
proton	m_p	$1.672\ 62 \text{ X } 10^{-27}$ Kg
neutron	m_n	$1.674\ 93 \text{ X } 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\ 19 \text{ X } 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	$1.112\ 65 \text{ X } 10^{-10}$ J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_0	$4\pi \text{ X } 10^{-7}$ J s^{2} C^{-2} m^{-1} $4\pi \text{ X } 10^{-7}$ T^{2} J^{-1} m^{3}
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\ 02 \text{ X } 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\ 79 \text{ X } 10^{-27}$ J T^{-1}
g value	g_e	2.002 32
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\ 77 \text{ X } 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\ 35 \text{ X } 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^{\ 2}$	$1.097\ 37 \text{ X } 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\ 65$ m s^{-2}
Gravitational constant	G	$6.672\ 59 \text{ X } 10^{-11}$ N m^{2} Kg^{-2}

Conversion factors

1 cal = 4.184 joules (J)

1 eV = $1.602\ 2 \text{ X } 10^{-19}$ J

1 erg = $1 \text{ X } 10^{-7}$ J

1 eV/molecule = 96 485 kJ mol^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4										Atomic mass → Symbol → Atomic No. →	10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12					TRANSITION ELEMENTS						26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.