UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2014/15

TITLE PAPER: PHYSICAL CHEMISTRY

COURSE NUMBER: C402

TIME: THREE (3) HOURS

INSTRUCTIONS:
There are **six (6)** questions. Each question is worth 25 marks. Answer **any four (4)** questions.

A data sheet and a periodic table are attached

Non-programmable electronic calculators may be used.

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Question 1 (25 marks)

(a) Tabulated values of standard entropies of some aqueous ions are negative. Why is this statement consistent with the third law of thermodynamics? [3]

(b) Calculate the ionic strength, I, the mean activity coefficient, $\gamma_{\pm}$, and the activity, a, of a 0.0250 mol/kg $AlCl_3$(aq) solution. [6]

(c) Consider the solubility equilibrium

$PbI_2(s) \rightarrow Pb^{2+}(aq) + 2I^-(aq)$ $K_{sp} = 7.1 \times 10^{-9}$ at 298 K.

(i) Write down the expression of the solubility equilibrium constant, K_{sp}, in terms of the mean activity coefficient and the solubility, s, of the salt.

(ii) Use the Debye-Huckel limiting law to explain how the solubility, s, will vary when the ionic strength of the solution is increased by adding an inert salt like KNO_3. [4]

(d) For the half cell reaction $AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$, $E^\theta = +0.0713$ V. Using this result and $\Delta_f G^\theta(AgBr,s) = -96.9$ kJ/mol, determine $\Delta_f G^\theta(Br^-,aq)$. [5]

(e) Consider the following reaction:

$$4\ NO_3^-(aq) + 4\ H^+(aq) \rightarrow 4\ NO(g) + 2\ H_2O(l) + 3\ O_2(g)$$

(i) Identify the two half reactions.

(ii) Using data from the table below calculate the standard cell potential and the equilibrium constant of the reaction. [7]

Question 2 (25 marks)

Consider the cell

$Zn|ZnCl_2(aq, 0.00500\ m)|Hg_2Cl_2(s)|\ Hg(l)$

given that the cell potential is +1.2272 V and redox potentials in the table below,

(a) Write the cell reaction and Nernst equation in terms of the mean activity coefficient and molality of the zinc chloride solution. [5]

(b) Determine the standard cell potential, $\Delta_r G$, $\Delta_r G^o$ and the equilibrium constant, K, for the cell reaction. [7]

(c) Determine the mean activity coefficient of $ZnCl_2$ from (1) the measured cell potential and (2) the Debye-Huckel limiting law. [8]

(d) Given that $\frac{dE}{dT} = -4.52x10^{-4} VK^{-1}$ calculate $\Delta_r S$ and $\Delta_r H$ [5]

Table 1: Standard potentials at 298 K

Reduction half reaction	E°/V
$AgBr + e^- \rightarrow Ag + Br^-$	+0.0713
$NO_3^- + 4 H^+ + 3e^- \rightarrow NO + 2 H_2O$	0.957
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$2H^+ + 2e^- \rightarrow H_2$	0, by definition
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2 Cl^-(aq)$	+0.2676
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.7628

Question 3 (25 marks)

(a) Provide a molecular explanation for the observation that the viscosity of a gas increases with temperature whereas the viscosity of a liquid decreases with increasing temperature.

[4]

(b) A Knudsen cell was used to determine the vapour pressure of germanium at 1000 °C. During an interval of 7200 s the mass loss through a small hole of radius 0.50 mm amounted to 43 μg. What is the vapour pressure of germanium at 1000 °C. Assume the gas is monatomic. [8]

(c) Show that the flux of particles is proportional to the concentration gradient, the proportionality constant being $D = \frac{1}{3}\lambda\bar{c}$. [6]

(d) Calculate (i) the diffusion constant of argon at 25 °C and 10^{-6} atm and (ii) the flow/flux of argon if a pressure gradient of 0.1 atm cm^{-1} is established in a pipe. (Hint express concentration gradient in terms of pressure gradient first)

(For argon σ =0.36 nm^2, and $\bar{c}$ = 397 m/s at 25 °C.) [7]

Question 4 (25 marks)

(a) Given the following data:

Salt	Λ_m^0 /S cm^2mol^{-1}
NaCl	126.4
KNO_3	144.9
KCl	149.8

And that t_+ for Na^+ in NaCl is 0.39, calculate

(i) Λ_m^0 for $NaNO_3$ [3]

(ii) t_+ for Na^+ in $NaNO_3$ [4]

(b) The conductance of KI has been measured in a binary solvent mixture of water and 1,3-dioxolan-2-one. The following data was obtained:

c/mmolL^{-1}	17.68	10.88	7.19	2.67	1.28	0.83	0.19
Λ_m /S cm^2mol^{-1}	42.45	45.91	47.53	51.81	54.09	55.78	57.42

(i) Show that the data follows Kohlrausch's law: $\Lambda_m = \Lambda_m^0 - \kappa c^{1/2}$.

(ii) Determine the value of Λ_m^0 of KI in this solvent system. [8]

(c) At 25 °C the molar ionic conductivity of Br^- is 7.82 mS m^2 mol^{-1}. Calculate

(i) its mobility (ii) its diffusion coefficient and (iii) estimate its effective radius in water. Viscosity of water is 1.00 cP. [10]

Question 5 (25 marks)

(a) The equilibrium $A \rightleftharpoons B + C$ at 25 °C is subjected to a temperature jump that slightly increases the concentrations of B and C. The measured relaxation time is 3.0 μs. The equilibrium constant for the system is 2.0 $\times 10^{-16}$ at 25 °C, and the equilibrium concentrations of B and C are both 2.0 $\times 10^{-4}$ M. Calculate the rate constants for he forward and reverse steps. [8]

(b) The rate constant for the decomposition of a certain substance is 1.70 x 10^{-2} $M^{-1}s^{-1}$ at 24 °C and 2.01 $\times 10^{-2}$ $M^{-1}s^{-1}$ at 37 °C. Determine the Arrhenius parameters for the reaction.

[6]

(c) The rate constant for the first order decomposition of a compound A in the reaction

$A \rightarrow P$ is k= 3.56 $\times 10^{-3}$ s^{-1} at 25 °C.

(i) What is the half-life of A?

(ii) What will be the pressure after 50 s of reaction if the initial pressure was 33.0 kPa.

[5]

(d) The following chain mechanism has been proposed for the reaction $H_2(g) + Cl_2(g) \rightarrow 2 HCl(g)$ which occurs when a gas mixture of hydrogen and Chlorine is exposed to light with wavelength < 480 nm.

Initiation $Cl_2 + h\nu \longrightarrow 2\,Cl\cdot$ $v = I_a$

Propagation: $Cl\cdot + H_2 \xrightarrow{k_1} HCl + H\cdot$

$H\cdot + Cl_2 \xrightarrow{k_2} HCl + Cl\cdot$

Termination $Cl\cdot \xrightarrow{k_3} \frac{1}{2}\,Cl_2$ (on wall)

Use the steady state approximation method to show that the rate law is independent of $[Cl_2]$, but is first order with respect $[H_2]$ and with respect to I_a. [6]

Question 6 (25 marks)

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

(b) In an experiment to measure the quantum yield of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from a 87.5 W source for 28.0 min. The intensity of the transmitted radiation was 0.257 that of the incident radiation. As a result of the irradiation, 0.324 mol of the absorbing substance decomposed. Calculate the quantum yield. [6]

(c) An enzyme catalysed reaction following the Michaelis-Menten mechanism

$$E + S \rightleftharpoons ES \rightarrow P + E \qquad \text{rate constants are } k_1, k_{-1}, k_2$$

has the rate law $\dfrac{d[P]}{dt} = \dfrac{k_2[S][E]_0}{K_M + [S]}$, *where* $K_M = \dfrac{k_1 + k_2}{k_{-1}}$

The following data relate to such a reaction.

[S]/mol L^{-1}	0.00125	0.0025	0.0050	0.020
Rate/Mol $L^{-1}s^{-1}$	2.78 x10^{-5}	5.00 x10^{-5}	8.33 x10^{-5}	1.67 x10^{-4}

The enzyme concentration is 2.3nM. Calculate (i) the maximum rate, v_{max} (ii) the Michaeli's constant K_M, (iii) k_2 and (iv) catalytic efficiency. [15]

General data and fundamental constants

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

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\ 2 \times 10^{-19}$ 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

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	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.