UNIVERSITY OF SWAZILAND

FINAL SUPPLEMENTARY EXAMINATION 2013/14

TITLE OF PAPER: ADVANCED PHYSICAL CHEMISTRY

COURSE NUMBER: C402

TIME: THREE (3) HOURS

INSTRUCTIONS:

THERE ARE **SIX** QUESTIONS. EACH QUESTION IS WORTH 25 MARKS. ANSWER **ANY FOUR** QUESTIONS.

A DATA SHEET AND A PERIODIC TABLE ARE ATTACHED

GRAPH PAPER IS PROVIDED

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED.

DO NOT OPEN THIS PAPER UNTIL PERMISSION TO DO SO IS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1 (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 x10^{-16} at 25 °C, and the equilibrium concentrations of B and C are both 2.0 x10^{-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 x10^{-2} $M^{-1}s^{-1}$ at 37 °C. Determine the Arrhenius parameters for the reaction. (Arrhenius equation; $k = Ae^{-E_a/RT}$). [6]

(c) The rate constant for the first order decomposition of a compound A in the reaction A $\rightarrow$ P is k= 3.56 x10^{-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 $Cl_2 + h\nu \longrightarrow 2\,Cl\cdot$ $\quad v = I_a$

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

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

Termination $Cl\cdot \xrightarrow{k_3} \tfrac{1}{2} Cl_2$ (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 2 (25 marks)

(a) Why is it not possible to measure γ_+ for Na^+? [2]

(b) Express $\gamma_\pm$ in terms of γ_+ and γ_- for K_3PO_4 [3]

(c) Use the Debye-Huckel limiting law to calculate the mean activity coefficient, $\gamma_\pm$, for a 0.0250 mol kg^{-1} solution of $AlCl_3$. [5]

(d) Devise a cell in which the following reaction occurs:

$Pb(s) + Hg_2SO_4(s) \rightarrow PbSO_4(s) + 2\,Hg(l)$

What is its potential when the electrolyte is saturated with both salts at 25 °C? [5]

(e) Consider the following cell at 298 K:

$$Pt(s)|Mn^{2+}(aq, a = 0.0150), Mn^{3+}(aq, a = 0.200)||Zn^{2+}(aq, a = 0.100)|Zn(s)$$

(i) write the half reactions and the cell reaction

(ii) Calculate the cell potential, E.

(iii) Calculate the equilibrium constant of the cell reaction at 298 K. [10]

Question 3 (25 marks)

(a) Distinguish between physisorption and chemisorption [8]

(b) A surface is half covered by a gas when the pressure is 1.0 atm. If the Langmuir isotherm, $\theta = \frac{Kp}{1+Kp}$, is followed:

(i) What is the value of the adsorption coefficient, K? [4]

(ii) What pressure would give 90% coverage? [2]

(iii) What coverage is given by a pressure of 0.10 atm? [2]

(c) The adsorption of solutes on solids from liquids often follows a Freundlich isotherm, $\theta = kp^{1/n}$. 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

W_a is the mass adsorbed per unit mass of charcoal. [9]

Question 4 (25 marks)

(a) Estimate the magnitude of the diffusion controlled rate constant at 298 K for a species in concentrated sulphuric acid which has a viscosity of 2.7×10^{-2} kg m^{-1} s^{-1}. [5]

(b) The reaction $A^- + H^+ \rightarrow P$ has a rate constant given by the empirical expression $k_2 = 8.72 \times 10^{12})e^{-6134K/T}$ L $mol^{-1}s^{-1}$. Evaluate (i) $\Delta^{\ddagger}H$, (ii) $\Delta^{\ddagger}S$ and (iii) $\Delta^{\ddagger}G$. [15]

(c) At 25 °C, k = 1.55 dm^6 mol^{-2} min^{-1} at an ionic strength of 0.0241 for a reaction in which the rate determining step involves the encounter of two singly charged cations. Use the Debye –Huckel limiting law to estimate the rate constant at zero ionic strength. [5]

Question 5 (25 marks)

(a) The charge of Mg^{2+} is twice that of Na^+, and from the equation

$$u = \frac{ze}{6\pi\eta a}$$

one might therefore expect Mg^{2+}(aq) to have a much greater mobility than Na^+(aq). Actually, these ions have similar mobilities. Explain why? [3]

(b) Derive the Ostwald dilution law for a weak electrolyte (all steps must be clearly shown).

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

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

Concentration c/ mol dm^{-3}	1.566 x 10^{-4}	2.600 x 10^{-4}	6.219 x 10^{-4}	10.441 x 10^{-4}
Conductivity κ/ S cm^{-1}	1.788 x 10^{-6}	2.418 x 10^{-6}	4.009 x 10^{-6}	5.336 x 10^{-6}

(i) Confirm that these values are in accordance with the Ostwald dilution law.
(ii) Calculate the dissociation constant for this electrolyte. [8]

(d) For the perchlorate ion, ClO_4^-, in water at 25 °C, $\lambda_m^0 = 67.2 Scm^2 mol^{-1}$.

(i) Calculate the mobility, **u**, of ClO_4^- in water
(ii) Calculate the drift speed, **s**, of ClO_4^- in water in a field of 24 V/cm.
(iii) Calculate the diffusion coefficient of ClO_4^- in water
(iv) Estimate the radius of the hydrated perchlorate ion given that the viscosity of water is 8.91 x 10^{-4} kg m^{-1} s^{-1}. [10]

Question 6 (25 marks)

(a) The standard cell potential of the cell, Pt|H_2(g)|HBr(aq)|AgBr(s)|Ag(s), was measured over a range of temperatures and the data were found to fit the following polynomial, E^{θ}_{cell}/K = 0.07131-4.99 x 10^{-4}(T/K -298) – 3.45 x10^{-6}(T/K -298)^2.

(i) Write the cell reaction
(ii) Evaluate $\Delta_r G^{\theta}$, $\Delta_r S^{\theta}$ and $\Delta_r H^{\theta}$ for the cell reaction at 298 K. [10]

(b) The relative permittivity of methanol corrected for density variation is given below. Calculate the dipole moment and polarizability volume of the molecule. Take $\rho = 0.791$ g cm^{-3} at 20 °C.

θ/ °C	-80	-50	-20	0	20
ε_r	57	49	42	38	34

[Useful equation $P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$ where $P_m = \left(\frac{\varepsilon_r - 1}{\varepsilon + 2}\right)\frac{M}{\rho}$] [10]

(c) Provide a molecular interpretation for the observation that the viscosity of a gas increases with temperature whereas the viscosity of a liquid decreases with increasing temperature. [5]

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	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ 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	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^2$	$1.097\,37 \times 10^7$ 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

7

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.