UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2012/13

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.

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Question 1(25 marks)

(a) Bearing in mind distinctions between the mechanism of stepwise and chain polymerization, describe ways in which it is possible to control the molar mass of a polymer by manipulating the kinetic parameters of the polymerization [6]

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

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

(1) $I_2 \rightleftharpoons 2\ I$
(2) $I + H_2 \rightarrow HI + H$
(3) $H + I_2 \rightarrow HI + I$

The rate constants are k_1 and k_{-1} for step (1) and k_2 and k_3 for steps (2) and (3), respectively. Find the rate law using the steady state approximation. [7]

(d) The equilibrium $A \rightleftharpoons B + C$ (k_f and k_r are the rate constants for the forward and reverse reactions respectively) is subjected to a temperature jump that slightly decreases the concentrations of B and C. The measured relaxation time is 3.0 μs and the equilibrium constant for the system is 2.0×10^{-16} at 25°C.

(i) Show that the expression for the relaxation time is $\tau^{-1} = k_f + k_r\{[B]_{eq} + [C]_{eq}\}$.
(ii) Calculate the rate constants k_f and k_r when the equilibrium concentrations of B and C are both 2.0×10^{-4} M at 25 °C. [6]

Question 2(25 marks)

(a) Explain why the reaction rate of two ions with the same charge increases with increasing ionic strength where as that of ions of opposite charges decreases with increasing ionic strength. [5]

(b) The rate of dimerizarion in aqueous solution of a cationic protein with charge z+ has been studied a function of ionic strength, I. The data below was obtained at 25 °C.

k/k^o	8.10	13.30	20.50	27.80	38.10	52.00
I	0.0100	0.0150	0.0200	0.0250	0.030	0.0350

Where k is the rate constant at ionic strength I and k^o the rate constant at zero ionic strength. Deduce the charge on the protein. [7]

(c) The second order rate constant for the reaction for the reaction of oxygen atoms with benzene are given in the table below:

Temperature, K	300.3	392.2
Rate constant, $dm^3\ mol^{-1}\ s^{-1}$	1.44×10^7	6.9×10^7

(i) Determine the Arrhenius parameters (E_a and A) for the reaction

(ii) Determine the Eyring parameters $\Delta^{\ddagger}H$, $\Delta^{\ddagger}S$ and $\Delta^{\ddagger}G$ for this reaction at 298 K.

[13]

Question 3(25 marks)

(a). Use the Debye-Huckel limiting law to estimate the mean activity coefficient of $La_2(SO_4)_3$ in a solution that is 3.00×10^{-4} mol/kg in $La_2(SO_4)_3$ and 2.00×10^{-3} mol/kg in K_2SO_4. [5]

(b) Use the standard potentials of the couples Au^+/Au (+1.69 V), Au^{3+}/Au (+1.40 V), and Fe^{3+}/Fe^{2+} (+0.77 V) to calculate E^{θ} and the equilibrium constant for the reaction

$$2\ Fe^{2+}(aq) + Au^{3+}(aq) \rightarrow 2Fe^{3+}(aq) + Au^+(aq)$$ [10]

(c). The standard cell potential of the cell $Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag$ is 0.223 V and $\left(\dfrac{\partial E^{\theta}}{\partial T}\right)_p = -6.5x10^{-4}VK^{-1}$. The standard enthalpy of formation of HCl(g) and AgCl(s) are-92.30 KJ/mol and -127.03 kJ/mol, respectively. Calculate the standard enthalpy of transfer of HCl from the gas phase to the aqueous solution:

$HCl(g) \rightarrow HCl(aq)$ $\Delta H^{\theta} = $? [10]

Question 4(25 marks)

(a) Suggest explanations for the following observations, in each case write an appropriate rate equation based on the Langmuir isotherm . $\theta = \dfrac{Kp}{1+Kp}$

    (i) The decomposition of phosphine on tungsten is first order at low pressures and zero order higher pressures, the activation energy being higher at the higher pressure. [3]

    (ii) On certain surfaces (e.g. Au) the hydrogen-oxygen reaction is first order in hydrogen and zero order in oxygen, with no decrease in the rate as the oxygen pressure is greatly increased. [3]]

(b) The volume of gas at 20°C and 1.00 bar adsorbed on the surface of 1.50 g of a sample of silica at 0 °C was 1.60 mL at 52.4 kPa and 2.73 mL at 104 kPa. What is the value of V_{mon}? [8]

(c) The adsorption of a gas is described by the Langmuir isotherm with $K = 0.777$ kPa^{-1} at 25 °C. Calculate the pressure at which the fractional surface coverage is
(i) 0.20   (ii) 0.75. [6]

(d) The chemisorption of hydrogen on manganese is activated but only weakly so. Careful measurements have shown that it proceeds 35% faster at 1000 K than at 600 K. What is the activation energy for chemisorption? [5]

Question 5 (25 marks)

(a) Use the kinetic theory of gases to explain the following:

    (i) The thermal conductivity of a perfect gas is expected to be independent of pressure.

    (ii) The thermal conductivity of a perfect gas increases as $T^{1/2}$ [6]

(b) (i) The diffusion coefficient for Xe at 273 K and 1 atm is 5×10^{-6} m^2 s^{-1}. What is the collisional cross section of Xe?

    (ii) The diffusion coefficient of N_2 is threefold greater than that of Xe under the same pressure and temperature conditions. What is the collisional cross section of N_2?
(Atomic masses: Xe = 131.29 u and of N_2 = 28.02 u) [10]

(c) The mobilities of H^+, Na^+ and Cl^- are given in the table below:

Ion	Mobility, m^2 s^{-1} V^{-1}
H^+	3.623×10^{-7}
Na^+	0.519×10^{-7}
Cl^-	0.791×10^{-7}

(i) What proportion of the current is carried by the protons in a 1.00×10^{-3} M HCl(aq)?
(ii) What fraction do they carry when NaCl is added to the acid so that the solution is 1.0 M in the salt? [9]

Question 6 (25 marks)

(a) (i) State Kohlrausch's law of independent migration of ions.

(ii) The limiting molar conductivities of NaI, NaCH$_3$CO$_2$, and Mg(CH$_3$CO$_2$)$_2$ are 12.69 mS m^2 mol^{-1}, 9.10 mS m^2 mol^{-1} and 18.78 mS m^2 mol^{-1}, respectively (all at 25 °C). What is the limiting molar conductivity of MgI$_2$ at this temperature? [5]

(b) Given that the chemical potential of a solution of activity a is $\mu = \mu^o + RT \ln a$, and that the work required to move an object through a distance dx against a force F is dw = -Fdx, show that the thermodynamic force acting on solute particles in the solution is

$$F = -\frac{RT}{c}\frac{dc}{dx}$$ where c is the concentration of the solution. [6]

(c) A dilute solution of potassium permanganate in water at 25 °C was prepared. The solution was in a horizontal tube of length 10 cm, and at first there was a linear gradation of intensity of the purple solution from left (where the concentration was 0.100 M) to the right (where the concentration was 0.05 M). What is the magnitude of the thermodynamic force acting on the solute (i) close to the left face of the container, (ii) in the middle and (iii) close to the right face? Give the force per mol in each case. [8]

(d) A solution of LiCl (molar mass 42.39 g/mol) was electrolyzed in a Hittorf cell. After a current of 0.77 A had been passed for two hours, the mass of LiCl in the anode compartment had decreased by 0.793 g. Calculate the transport numbers of the Li$^+$ and Cl$^-$ ions. [6]

5

USEFUL DATA

$\text{Log } k = \log k^0 + 2AZ_AZ_B \sqrt{I}$ with A= 0.509 for aqueous solutions at 25 °C.

Arrhenius equation : $k = Ae^{-E_a/RT}$

Mean free path $\lambda = \dfrac{kT}{\sqrt{2}\sigma p}$

Diffusion coefficient $\qquad D = \dfrac{1}{3}\lambda \bar{c}$

$t_+^0 = \dfrac{I_+}{I}$

$$\bar{c} = \left[\frac{8RT}{\pi M}\right]^{1/2} \qquad c = \left[\frac{3RT}{M}\right] \qquad c^* = \left[\frac{2RT}{M}\right] \qquad \kappa = \frac{\bar{c}C_{V,m}}{3N_A \sqrt{2}.\sigma}$$

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	ge	$2.002\ 32$
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}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4							Atomic mass → 10.811 Symbol → B 5 Atomic No. →	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
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

**Actinide Series

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