UNIVERSITY OF SWAZILAND

FINAL 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) 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 $\frac{d[P]}{dt} = \frac{k_2[S][E]_0}{K_M + [S]}$ where $K_M = \frac{k_1' + k_2}{k_1}$

The following data relate to such a reaction.

[S]/mol L^{-1}	0.00125	0.0025	0.0050	0.020
Rate/Mol $L^{-1}s^{-1}$	2.78×10^{-5}	5.00×10^{-5}	8.33×10^{-5}	1.67×10^{-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]

Question 2 (25 marks)

(a) Determine E° for the reaction $Cr^{2+} + 2e^- \rightarrow Cr$ from the reduction potentials of the redox couples Cr^{3+}/Cr and Cr^{3+}/Cr^{2+} which are given in the below:

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ E° = -0.744 V

$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$ E° = -0.407 [5]

(b) You are given the following half-cell reactions:

$Pd^{2+}(aq) + 2e^- \rightleftharpoons Pd(s)$ E° = 0.83 V

$PdCl_4^{2-}(aq) + 2e^- \rightleftharpoons Pd(s) + 4Cl^-(aq)$ E° = 0.64 V

(i) Calculate the equilibrium constant for the reaction

$Pd^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons PdCl_4^{2-}(aq)$

(ii) Calculate $\Delta_rG°$ for this reaction [5]

(c) Between 0 °C and 90 °C, the potential of the cell

$Pt(s)|H_2(g, p = 1\text{ atm})|HCl(aq, m = 0.100)|AgCl(s)|Ag(s)$

is described by the equation E(V) = 0.35510 – 0.3422 x 10^{-4}t -3.2347 x$10^{-6}t^2$ + 6.314 x $10^{-9}t^3$, where t is the temperature on the Celsius scale.

(i) Write the cell reaction

(ii) Calculate Δ_rG, Δ_rH, and Δ_rS for the cell reaction at 50 °C. [15]

Question 3 (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 $5 \times 10^{-6}\ m^2\ s^{-1}$. 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]

[Useful equations $\lambda = \frac{kT}{\sqrt{2}\sigma p}$ $\quad \bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2}$]

(c) The mobilities of H^+, Na^+ and Cl^- are given I 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 4 (25 marks)

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

(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) The gas phase reaction

$RI + HI \rightarrow RH + I_2$

is first order in each reactant or second order overall. The observed activation energy is 100 kJ/mol. A calculation using the kinetic molecular theory shows that if the concentration of each reactant is 1.0 M, the rate of the reaction at 300 K is 5.0×10^{10} mol dm^{-3} s^{-1} if every collision is effective.

(i) Calculate the predicted rate constant at 300 K using the collision theory.

(ii) The observed rate constant at 300 K is 3.0×10^{8} dm^3 mol^{-1} s^{-1}. What is the value of the steric factor and what does it mean? [8]

(b) One of the hazards of nuclear explosions is the generation of ^{90}Sr and its subsequent incorporation in bones in place of calcium. This isotope emits β-rays of energy 0.55 MeV and has a half-life of 28.1 years. Suppose 1.0 μg was absorbed by a newly born child, how much will remain after (i) 18 years and (ii) 70 years? [8]

(c) Nitrous oxide decomposes according to the reaction

$2\,N_2O(g) \rightarrow 2\,N_2(g) + O_2(g)$

The rate of the decomposition is quite small unless a halogen is present as a catalyst. Thus in the presence of Cl_2, the rate depends both on N_2O and Cl_2 pressure, i.e.

$$-\frac{dP_{N_2O}}{dt} = kP_{N_2O}^{a}P_{Cl_2}^{b}$$

The course of the reaction can be followed by measuring the increase in the total pressure at constant temperature. The following data were obtained in a series of experiments at 800 K.

Initial pressure /Torr		Initial rate/Torr min^{-1}
P_{N_2O}	P_{Cl_2}	Increase in total pressure
30	4.0	0.30
15	4.0	0.15
30	1.0	0.15

(i) From the given data determine the values of *a* and b in the rate law.

(ii) Calculate the rate constant at 800 K. [9]

Question 6 (25 marks)

(a) A first order decomposition reaction is observed to have the following rate constants at the indicated temperatures.

$k/10^{-3}\ s^{-1}$	2.46	45.1	576
$\theta/^{o}C$	0	20.0	40.0

Evaluate the Arrhenius parameters, E_a and A (Arrhenius equation; $k = Ae^{-E_a/RT}$). [8]

(b) Conductivities are often measured by comparing the resistance of a cell filled with the sample to its resistance when filled with a standard solution, such as aqueous potassium chloride. At 25 °C the conductivity of water is 76 mS m^{-1} and that of a 0.100 M KCl(aq) is 1.1639 S m^{-1}. A cell had a resistance of 33.21 Ω when filled with 0.100 M KCl(aq) and 300.0 Ω when filled with 0.100 M CH_3COOH(aq). What is the molar conductivity of acetic acid at that concentration and temperature? [8]

(c) Values of the molar polarization, P_m, of gaseous water at 100 kPa were determined and are given below as a function of temperature.

T/K	384.3	420.1	444.7	484.1	522.0
$P_m/(cm^3\ mol^{-1})$	57.4	53.5	50.1	46.8	43.1

Use this data to calculate the dipole moment of H_2O and its polarizability volume.

$$\left(\text{Useful equations:}\quad P_m = \frac{4\pi}{3}N_A\alpha' + \frac{N_A\mu^2}{9\varepsilon_0 kT} \qquad \text{with } \alpha = 4\pi\varepsilon_0\alpha'\right)$$ [9]

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}

PERIODIC TABLE OF ELEMENTS

GROUPS

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

TRANSITION ELEMENTS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	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											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											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.