UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2008/09

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(25marks)

a. Consider the following cell at 25 °C:

$Cu(s)|CuCl_2(aq,m)|AgCl(s)|Ag(s)$

The cell potential is 0.191 V when the copper(II) chloride concentration is 1.0 x 10^{-4} mol kg^{-1} and is -0.074V when the concentration is 0.20 mol kg^{-1}.

(i) Write the individual electrode reactions and the overall cell reaction. [3]

(ii) Write the expression for the cell potential, E, in terms of the concentration of $CuCl_2$ and the mean activity coefficient. [3]

(iii) Calculate the standard cell potential, E^{θ}, by assuming that the mean activity coefficient, $\gamma_{\pm}$, is approximately unity in the more dilute solution. [3]

(iv) Use the results of (ii) and (iii) to estimate the mean activity coefficient in the 0.20 mol kg^{-1} solution. [4]

b. Discuss the factors responsible for the magnitude of the Gibbs energy of formation of an ion in solution. [6]

c. The standard potential of the AgCl/Ag,Cl^- couple is 0.2224 V at 25 °C and the Standard Gibbs energy of formation of solid silver chloride, $\Delta_f G^{\theta}$(AgCl,s), is -109.79 kJ/mol. Calculate the standard Gibbs energy of formation of Cl^-(aq) 25 °C. [6]

Question 2 (25 marks)

a. The resistances of a series of aqueous NaCl solutions, formed by successive dilution of a sample, were measured in a cell with cell constant 0.2063 cm^{-1}. The following data was obtained:

c/(mol L^{-1})	0.00050	0.0010	0.0050	0.010	0.020	0.050
R/Ω	3314	1669	342.1	174.1	89.08	37.14

(i) Show that that these data do follow Kohlrausch's law, $\Lambda_m = \Lambda_m^0 - \kappa\sqrt{c}$. [4]

(ii) Determine the value of the coefficient κ and the limiting molar conductivity, Λ_m^0. [4]

(iii) Use the value of κ and the information that $\lambda(Na^+) = 5.01 \times 10^{-3}$ Sm^2 mol^{-1} and $\lambda(I^-) = 7.68 \times 10^{-3}$ Sm^2 mol^{-1} to predict the molar conductivity and resistance it would show in the cell, of 0.010 mol L^{-1} NaI(aq) at 25 °C. [5]

b. Explain why Li^+ has a lower ionic conductivity than Na^+ and why the value for H^+ is so much higher than the values for both these ions. [6]

c. The transport numbers and molar conductivity for HCl at infinite dilution are estimated to be $t_+^0 = 0.821$, $t_-^0 = 0.179$ and $\Lambda_m^0 = 426.16 Scm^2 mol^{-1}$. Calculate the mobilities of the hydrogen and chloride ions at infinite dilution. [6]

Question 3 (25 marks)

a. The concentration of $(CH_3)_3CBr$ was measured as a function of time as the reaction $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$ progressed.

Time/h	0	3.13	6.20	10.00	18.30	30.80
$[(CH_3)_3CBr]$ mol/L	0.1039	0.0896	0.0776	0.0639	0.0353	0.0207

(i) Show that the reaction follows first order kinetics. [4]

(ii) Determine the rate constant and the molar concentration of $(CH_3)_3CBr$ after 43.8 h. [4]

(iii) What is the half-life of this reaction? [2]

(iv) Suggest a reason why the concentration of water does not appear in the rate law. [1]

b. The rate constant for the decomposition of a certain substance is 2.80×10^{-3} dm^3 mol^{-1} s^{-1} at 30 °C and 1.38×10^{-2} dm^3 mol^{-1} s^{-1} at 50 °C. Evaluate the Arrhenius parameters, A and E_a, of the reaction. [7]

c. Find the relaxation time for the reaction $A \rightleftharpoons 2X$, when the system is subjected to a small perturbation. Assume the forward reaction to be first order and the reverse reaction to be second order. [7]

Question 4 (25 marks)

a. Bearing in mind distinctions between the mechanisms 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 polymerization. [8]

b. In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100 W source for 45 minutes. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of irradiation. 0.344 mol of the absorbing substance decomposed. Determine the quantum efficiency. [7]

c. The following is a famous gas-phase reaction, with the following proposed mechanism:

Stoichiometry: $2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$

Mechanism:

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$
$$NO_2 + NO_3 \xrightarrow{k_1'} N_2O_5$$
$$NO_2 + NO_3 \xrightarrow{k_2} NO + O_2 + NO_2$$
$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

Determine the rate law using the steady state approximation. [10]

Question 5 (25 marks)

a. A certain solid sample adsorbs 0.44 mg of CO when the pressure of the gas is 26.0 kPa and the temperature is 300 K. The amount adsorbed when the pressure is 3.0 kPa and temperature 300 K is 0.19 mg. The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage at the surface at the two pressures. [10]

b. Hydrogen iodide is very strongly adsorbed on gold but only slightly adsorbed on platinum. If the adsorption follows the Langmuir isotherm on both surfaces, predict the order of the HI decomposition on each of the two surfaces. [6]

c. In an experiment on the adsorption of ethene on iron it was found that the same volume of gas desorbed in 1856 s at 873 K and 8.44 s at 1012 K. What is the activation energy desorption? How long would it take for the same amount of ethene to desorb at (i) 298 K, (ii) 1500 K? [9]

Question 6 (25 marks)

a. Explain how the permanent dipole moment and polarizability of a molecule arise. [6]

b. The relative permittivity of camphor (molar mass M = 152.3 g/mol and melting point 175 °C) was measured over a range of temperatures. Use the data that was obtained and is given in the table below to calculate the dipole moment and polalarizabilty of camphor. [12]

Temperature θ, °C	Relative permittivity, ε_r	Density, ρ g cm^{-3}
0	12.5	0.99
20	11.4	0.99
40	10.8	0.99
60	10.0	0.99
80	9.50	0.99
100	8.90	0.99
120	8.10	0.97
140	7.60	0.96
160	7.11	0.95
200	6.21	0.91

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

c. The refractive index of CH_2I_2 is 1.732 for 656 nm light. Its density at 20 °C is 3.32 g cm^{-3}. Calculate the polarizability of the molecule at this wavelength. [7]

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

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

TRANSITION ELEMENTS

PERIODS	GROUPS 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.