UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2005

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(25marks)

a. Distinguish between galvanic and electrolytic cells [4]

b. Use the Debye-Huckel limiting law to estimate the mean activity coefficient and activity of $CaCl_2$ in a solution that is 0.010 mol kg^{-1} $CaCl_2(aq)$ and 0.030 mol kg^{-1} NaF(aq). [6]

c. Consider the cell below at 25 °C:

$Hg(l)|\ Hg_2Cl_2(s)|\ HCl(aq,m)|\ H_2(g,P^\theta)|\ Pt$

$E^\theta(Hg_2Cl_2, Cl^-, Hg) = 0.27\ V$

(i) Write the reaction occurring in the cell. [2]

(ii) Calculate the cell potential when the activity of HCl is 0.100. [5]

(iii) Calculate the value of $\Delta_r G^\theta$ for the cell reaction. [3]

(iv) Calculate the value of the equilibrium constant for the cell reaction. [3]

(v) Which is the positive electrode and in which direction do electrons tend to flow? [2]

Question 2 (25 marks)

a. 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. [6]

b. The molar conductivities of NaI and KI have been measured in a solvent that is 80% ethylene carbonate and 20 % water. The results are given in the table below:

NaI		KI	
c/mmol L^{-1}	Λ_m/Scm^{2}mol^{-1}	c/mmol L^{-1}	Λ_m/Scm^{2}mol^{-1}
32.02	50.26	17.68	42.54
20.28	51.99	10.88	45.91
12.06	54.01	8.719	47.53
8.64	55.75	2.67	51.81
2.85	57.99	1.28	54.09
1.24	58.44	0.83	55.78
0.83	58.67	0.19	57.42

(i) Verify Kolhrausch's law, $\Lambda_m = \Lambda_m^0 - \kappa c^{1/2}$ for both salts. [5]

(ii) Calculate Λ_m^0 for NaI and KI in this solvent. [2]

(iii) Calculate $\lambda^0(Na^+) - \lambda^0(K^+)$ [2]

(iv) Compare your results in (ii) and (iii) with the analogous quantities in aqueous solution where $\lambda^0(Na^+) = 50.1$ Scm^2 mol^{-1}, $\lambda^0(K^+) = 73.50$ S cm^2 mol^{-1} and $\lambda^0(I^-) = 76.8$ Scm^2 mol^{-1}. [4]

c. Estimate the effective radius of a sugar molecule in water at 25 °C given that its diffusion coefficient is 5.2×10^{-6} cm^2 s^{-1} and the viscosity of water is 1.0×10^{-3} kg m^{-1} s^{-1}. [6]

Question 3 (25 marks)

a. Discuss the main features of the isolation method as used in the determination of rate laws. [5]

b. The following date were obtained for the decomposition of dinitrogen trioxide:

Time/s	0	184	526	867	1877
$[N_2O_3]$/mol L^{-1}	2.33	2.08	1.67	1.36	0.72

(i) Show that the decomposition follows first order kinetics. [6]

(ii) Determine the value of the rate constant and half-life of the reaction. [4]

c. For the reaction at 298 K,

$CH_3CO_2^- + H^+ \rightleftharpoons CH_3CO_2H$

$k_f = 4.5 \times 10^{10}$ L mol^{-1} s^{-1} and $k_r = 8.0 \times 10^5$ s^{-1}. A solution is made from 0.100 mol acetic acid and enough water to make 1.00 L. Find the relaxation time, τ, if a small perturbation is imposed on the solution such that the final temperature is 298 K. [10]

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Question 4 (25 marks)

a. 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 incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Find the quantum efficiency. [6]

b. The rate constant for the bimolecular elementary gaseous reaction

$CO + O_2 \rightarrow CO_2 + O$

Is 1.22×10^5 L mol^{-1} s^{-1} at 2500 K and 3.66×10^5 L mol^{-1} s^{-1} at 2800 K.

(i) Find the activation energy and pre-exponential factor. [7]

(ii) Assuming a hard sphere diameter of 350 pm for O_2 and of 360 pm for CO, calculate the value of the steric factor in the collision theory. [6]

c. A proposed free radical chain mechanism for the decomposition of acetaldehyde consists of the following steps:

$$CH_3CHO \xrightarrow{k_1} CH_3^{\bullet} + CHO^{\bullet}$$
$$CH_3^{\bullet} + CH_3CHO \xrightarrow{k_2} CH_4 + CO + CH_3^{\bullet}$$
$$2CH_3^{\bullet} \xrightarrow{k_3} C_2H_6$$

Show that the rate of formation of methane is

$$\frac{d[CH_4]}{dt} = k_2\left(\frac{k_1}{2k_3}\right)^{1/2}[CH_3CHO]^{3/2}$$ [6]

Question 5 (25 marks)

a. What is the role of defects in adsorption on surfaces? [5]

b. The volume of methane, measured at STP (0°C, 1 atm), adsorbed on 1g of charcoal at 0 °C and several different pressures is

P/ cm Hg	10	20	30	40
V/cm^3	9.75	14.5	18.2	21.4

Show that the data follows the Freundlich isotherm, $\theta = c_1 P^{1/c_2}$, and determine the constants c_1 and c_2 [8]

c. In an experiment on the adsorption of ethene on iron it was found that the same volume of gas was desorbed in 1856 s at 873 K and 8.44 s at 1012 K.

(i) What is the activation energy of desorption? [6]

(ii) How long would it take the same amount of ethene to desorb at 298 K? [6]

Question 6 (25 marks)

a. Explain why the polarizability of a molecule decreases at high frequencies. [5]

b. The polarizability volume of NH_3 is 2.22×10^{-24} cm^3. Calculate the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength 15.0 kV m^{-1}. [5]

c. Find the Miller indices of the planes that intersect the crystallographic axes at the distances (2*a*, 3b,2c) and (2*a*, 2b,∞c) [4]

d. Potassium nitrate crystals have orthorhombic unit cells of dimensions a = 542 pm, b = 917 pm, and c = 645 pm. Calculate the glancing angles for the (100), (010) and (111) reflections using Cu K_α radiation (154 pm). [11]

The End

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

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											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								

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

TRANSITION ELEMENTS

*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.