UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2009/10

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) 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}	1.566×10^{-4}	2.600×10^{-4}	6.219×10^{-4}	10.441×10^{-4}
Conductivity κ/ S cm^{-1}	1.788×10^{-6}	2.418×10^{-6}	4.009×10^{-6}	5.336×10^{-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 8.91×10^{-4} kg m^{-1} s^{-1}. [10]

Question 2(25 marks)

(a) Define or briefly explain what the following terms mean in kinetics

(i) collision cross-section

(ii) cage effect

(iii) diffusion controlled reaction

(iv) activation energy

(v) kinetic salt effect [5]

(b) The diffusion coefficient of I in CCl_4 is estimated to be 4.2×10^{-5} cm^2 s^{-1} at 25 °C. Given that the radius of I is about 200 pm, calculate the rate constant k_d for $I + I \rightarrow I_2$ in CCl_4 at 25 °C. [5]

(c) For the gas phase reaction $A + A \rightarrow A_2$, the experimental rate constant has been fitted to the Arrhenius equation with the pre-exponential factor A = 4.07×10^5 L $mol^{-1}\ s^{-1}$ at 300 K and an activation energy of 65.43 $kJmol^{-1}$. Calculate $\Delta^{\ddagger}S$, $\Delta^{\ddagger}H$, and $\Delta^{\ddagger}G$ for the reaction. [10]

(d) At 25 °C, k = 1.55 $L^2mol^{-2}min^{-1}$ 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 3(25marks)

(a) Devise a cell in which the following reaction is the cell reaction:

$H_2(g) + 2AgCl(s) \rightarrow 2HCl(aq) + Ag(s)$ [2]

(b) Write the Nernst equation for the cell in (a) [2]

(c) The emf for the above cell at 25 °C was 0.3524 V when the molality of HCl was 0.100 mol/kg and the hydrogen pressure was 1 bar. Calculate the activity and mean activity coefficient of the HCl assuming hydrogen is a perfect gas. [6]

(d) Calculate the per cent error in the mean activity coefficient if the Debye-Huckel limiting law is used to calculate it. [3]

(e) For the cell: Pt| Ag(s)| AgCl(s)| HCl(aq)| Hg_2Cl_2(s)| Hg(l)| Pt;

$$\frac{dE}{dT} = 0.338 mV/K$$ at 25 °C and 1 bar.

(i) Write the cell reaction [2]

(ii) Calculate Δ_rG^{θ}, Δ_rH^{θ} and Δ_rS^{θ} for the cell reaction [10]

Reduction half reaction	E^{θ} /V
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Hg_2Cl(s) + 2e^- \rightarrow 2\ Hg(l) + 2\ Cl^-(aq)$	+0.27

Question 4 (25 marks)

(a) Distinguish between reaction order and molecularity. [5]

(b) The oxidation of bromide ions by hydrogen peroxide in acidic solution

$$2\,Br^{-}(aq) + H_2O_2(aq) + 2H^{+}(aq) \rightarrow Br_2(aq) + 2H_2O(aq)$$

follows the rate law

$$v = k[H_2O_2][H^{+}][Br^{-}]$$

(i) If the concentration of H_2O_2 is increased by a factor of 3, by what factor is the rate of consumption of Br^{-} ions increased? [3]

(ii) If, under certain conditions, the rate of consumption of Br^{-} ions is 7.2×10^{-3} mol L^{-1} s^{-1}, what is the rate of consumption of H_2O_2? [2]

(iii) What is the effect on the rate constant *k* of increasing the concentration of bromide ions? [2]

(iv) If by the addition water to the reaction mixture the total volume were doubled, what would be the effect on the rate of change of Br^{-}? What would be the effect on the rate constant *k*? [3]

(c) The data below apply to the formation of urea from ammonium cyanate according to the reaction

$$NH_4CNO \rightarrow NH_2CONH_2$$

Initially 22.9 g of ammonium cyanate was dissolved in enough water to prepare 1.00 L of solution.

Time /min	0	20.0	50.0	65.0	150
Mass of urea/g	0	7.0	12.1	13.8	17.7

(i) Show that the reaction follows a second order rate law. [5]
(ii) Determine the rate constant [2]
(iii) Determine the mass of ammonium cyanate left after 300 minutes. [3]

Question 5(25 marks)

(a) Discuss the unique physical and chemical properties of zeolites that make them useful heterogeneous catalysts. [6]

(b) The data for the adsorption of ammonia on barium fluoride at 273 K are given below:

p/kPa	14.0	37.6	65.6	79.2	82.7	100.7	106.4
V/cm^3	11.1	13.5	14.9	16.0	15.5	17.3	16.5

At 273 K, the vapour pressure of ammonia p^* is 429.6 kPa.

(i) Confirm that the data fits the BET isotherm:

$$\frac{V}{V_{mon}} = \frac{cz}{(1-z)(1-(1-c)z)} \quad with \quad z = \frac{p}{p^*}$$ [7]

(ii) Determine the values of c and V_{mon}. [4]

(c) A solid in contact with a gas at 12 kPa and 25 °C adsorbs 2.5 mg of the gas and obeys the Langmuir isotherm. The enthalpy change when 1.0 mmol of the adsorbed gas is desorbed is +10.2 kJ mol^{-1}. What is the equilibrium pressure at 40 °C? [8]

Question 6 (25 marks)

(a) Describe the formation of a hydrogen bond in terms of in terms of molecular orbitals. [7]

(b) The polarizability of NH_3 is 2.22 x 10^{-30} m^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}. [6]

(c) The relative permittivity of methanol corrected for density variation is given below. Calculate the dipole moment and polarizability volume of the molecule. Take ρ = 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 $P_m = \left(\frac{\varepsilon_r - 1}{\varepsilon + 2}\right)\frac{M}{\rho}$] [12]

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	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											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.