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UNIVERSITY OF SWAZILAND

SUPPLEMENTARY 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. Define the ionic strength of a solution. What is the molality of $Al_2(SO_4)_3$ that has the same ionic strength as 0.500 mol kg^{-1} $Ca(NO_3)_2$?
[6]

b. Devise cells in which the following are the reactions:

(i) $H_2(g) + I_2(g) \rightarrow 2HI(aq)$ [3]

(ii) $Sn(s) + 2AgCl(s) \rightarrow SnCl_2(aq) + 2Ag(s)$ [3]

c. Derive an expression for the potential of an electrode for which the half-reaction is the reduction of MnO_4^- ions to Mn^{2+}ions in acidic solution. [6]

d. The standard potential of the AgCl/Ag, Cl^- couple has been measured over a range of temperature and the results were found to fit the expression

$E^\theta/V = 0.23659 - 4.8564 \times 10^{-4}(\theta/°C) - 3.4205 \times 10^{-6}(\theta/°C)^2 + 5.869 \times 10^{-9}(\theta/°C)^3$

Calculate the standard Gibbs energy of formation of $Cl^-(aq)$ at 25 °C.
[$\Delta_f G^\theta(AgCl,s) = -109.79$ kJ/mol] [7]

Question 2 (25 marks)

a. Starting with $dw = d\mu$ and $\mu = \mu^\theta + RT\ln a$, show that the thermodynamic force is given by

$$\mathcal{F} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T}$$ [7]

b. A dilute solution of potassium permanganate in water 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 the left where the concentration was 0.100 mol L^{-1} to the right where the concentration was 0.050 mol L^{-1}. What is the magnitude and sign of 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? [8]

c. In a moving boundary experiment on KCl the apparatus consisted of a tube of internal diameter 4.146 mm, and it contained an aqueous KCl at a concentration of 0.021 mol L^{-1}. A steady current of 18.2 mA was passed, and the boundary advanced as follows:

Δt/s	200	400	600	800	1000
x/mm	64	128	192	254	318

Find the transport number of K^+, its mobility and its ionic conductivity.
[$\Lambda_m^o(KCl) = 149.9\ \mathrm{S cm^2} mol^{-1}$] [10]

Question 3 (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 4 (25 marks)

a. Explain the essential features of a chain reaction. [4]

b. Hydrogen iodide undergoes decomposition into $H_2 + I_2$ when irradiated with radiation having a wavelength of 207 nm. It is found that when 1 J of energy is absorbed, 440 μg of HI is decomposed. How many molecules of HI are decomposed by one photon of radiation of this wavelength? [8]

c. At 25 °C, k = 1.55 $L^2 mol^{-3} min^{-1}$ 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]

d. The reaction $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ is believed to occur by the following mechanism:

$$2NO \xrightarrow{k_1} N_2O_2$$
$$N_2O_2 \xrightarrow{k_1'} 2NO$$
$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$

Assume N_2O_2 to be in a steady state and derive the rate equation. Under what conditions does the rate equation reduce to second order kinetics in NO and first-order kinetics in O_2? [8]

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. Explain the origin of the London (dispersion) interaction. [5]

b. The relative permittivity, ε_r of chlorobenzene is:

θ /°C	-50	-20	20
ε_r	7.28	6.30	5.71

Assuming that the density, which is 1.11 g cm^{-3}, does not change with temperature, estimate the dipole moment of this compound. [Molar mass = 112.45 g/mol]. [8]

c. The orthorhombic unit cell of $NiSO_4$ has the dimensions a =634 pm, b= 784 pm and c = 516 pm, and the density of the solid is 3.9 g cm^{-3}. Determine the number of formula units per unit cell and calculate a more precise density. [8]

d. The glancing angle of a Bragg reflection from a set of crystal planes separated by 99.3 pm is 20.85°. Calculate the wavelength of the x-rays. [4]

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	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										Atomic mass → Symbol → Atomic No. →	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				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
**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.