

**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

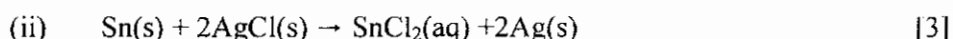
NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED.

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**Question 1(25marks)**

- a. Define the ionic strength of a solution. What is the molality of  $\text{Al}_2(\text{SO}_4)_3$  that has the same ionic strength as  $0.500 \text{ mol kg}^{-1} \text{ Ca}(\text{NO}_3)_2$ ?  
[6]

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



- c. Derive an expression for the potential of an electrode for which the half-reaction is the reduction of  $\text{MnO}_4^-$  ions to  $\text{Mn}^{2+}$  ions in acidic solution. [6]

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

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

Calculate the standard Gibbs energy of formation of  $\text{Cl}^-(\text{aq})$  at  $25^\circ\text{C}$ .

$[\Delta_f G^\ominus(\text{AgCl}, \text{s}) = -109.79 \text{ kJ/mol}]$  [7]

**Question 2 (25 marks)**

- a. Starting with  $dw = d\mu$  and  $\mu = \mu^\ominus + RT \ln a$ , 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  $25^\circ\text{C}$  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  $0.100 \text{ mol L}^{-1}$  to the right where the concentration was  $0.050 \text{ mol L}^{-1}$ . 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  $\text{KCl}$  the apparatus consisted of a tube of internal diameter 4.146 mm, and it contained an aqueous  $\text{KCl}$  at a concentration of  $0.021 \text{ mol L}^{-1}$ . A steady current of 18.2 mA was passed, and the boundary advanced as follows:

$\Delta t/\text{s}$	200	400	600	800	1000
$x/\text{mm}$	64	128	192	254	318

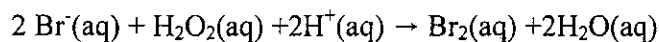
Find the transport number of  $\text{K}^+$ , its mobility and its ionic conductivity.

$[\Lambda_m^\ominus(\text{KCl}) = 149.9 \text{ Scm}^2 \text{mol}^{-1}]$  [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



follows the rate law

$$v = k[\text{H}_2\text{O}_2][\text{H}^+][\text{Br}^-]$$

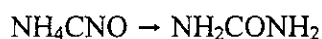
(i) If the concentration of  $\text{H}_2\text{O}_2$  is increased by a factor of 3, by what factor is the rate of consumption of  $\text{Br}^-$  ions increased? [3]

(ii) If, under certain conditions, the rate of consumption of  $\text{Br}^-$  ions is  $7.2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ , what is the rate of consumption of  $\text{H}_2\text{O}_2$ ? [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  $\text{Br}^-$ ? 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



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

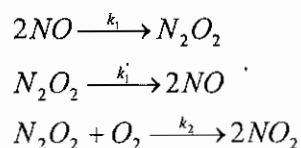
(i) Show that the reaction follows a second order rate law. [5]

(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  $\mu\text{g}$  of HI is decomposed. How many molecules of HI are decomposed by one photon of radiation of this wavelength? [8]
- c. At 25 °C,  $k = 1.55 \text{ L}^2\text{mol}^{-3}\text{min}^{-1}$  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  $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$  is believed to occur by the following mechanism:



Assume  $\text{N}_2\text{O}_2$  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  $\text{O}_2$ ? [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 <sup>3</sup>	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:

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

- (ii) Determine the values of  $c$  and  $V_{\text{mon}}$ . [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<sup>-1</sup>. 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,  $\epsilon_r$  of chlorobenzene is:

$\theta / ^\circ\text{C}$	-50	-20	20
$\epsilon_r$	7.28	6.30	5.71

- Assuming that the density, which is 1.11 g cm<sup>-3</sup>, 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<sub>4</sub> has the dimensions  $a = 634$  pm,  $b = 784$  pm and  $c = 516$  pm, and the density of the solid is 3.9 g cm<sup>-3</sup>. 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	$c$	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$
Elementary charge	$e$	$1.602\,177 \times 10^{-19} \text{ C}$
Faraday constant	$F = N_A e$	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Boltzmann constant	$k$	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = N_A k$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $6.2364 \times 10 \text{ L Torr K}^{-1} \text{ mol}^{-1}$
Planck constant	$h$	$6.626\,08 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$
Avogadro constant	$N_A$	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	$u$	$1.660\,54 \times 10^{-27} \text{ Kg}$
Mass		
electron	$m_e$	$9.109\,39 \times 10^{-31} \text{ Kg}$
proton	$m_p$	$1.672\,62 \times 10^{-27} \text{ Kg}$
neutron	$m_n$	$1.674\,93 \times 10^{-27} \text{ Kg}$
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
	$4\pi\epsilon_0$	$1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability	$\mu_0$	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3$
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$
g value	$g_e$	2.002 32
Bohr radius	$a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$
Fine-structure constant	$\alpha = \mu_0 e^2 c / 2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4 / 8h^3 c \epsilon_0^2$	$1.097\,37 \times 10^7 \text{ m}^{-1}$
Standard acceleration of free fall	$g$	$9.806\,65 \text{ m s}^{-2}$
Gravitational constant	$G$	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ Kg}^{-2}$

## Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	$1 \times 10^{-7} \text{ J}$
1 eV	=	$1.602\,2 \times 10^{-19} \text{ J}$	1 eV/molecule	=	$96\,485 \text{ kJ mol}^{-1}$

Prefixes	f	p	n	$\mu$	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	GROUPS																		
	I	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
	IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII B	IX	X	IB	II B	IIIA	IVA	VA	VIA	VIIA	VIIIA	
1	H 1.008 1																	He 4.003 2	
2	Li 6.941 3	Be 9.012 4											B 10.811 5	C 12.011 6	N 14.007 7	O 15.999 8	F 18.998 9	Ne 20.180 10	
3	Na 22.990 11	Mg 24.305 12											Al 26.982 13	Si 28.086 14	P 30.974 15	S 32.06 16	Cl 35.453 17	Ar 39.948 18	
4	K 39.098 19	Ca 40.078 20	Sc 44.956 21	Ti 47.88 22	V 50.942 23	Cr 51.996 24	Mn 54.938 25	Fe 55.847 26	Co 58.933 27	Ni 58.69 28	Cu 63.546 29	Zn 65.39 30	Ga 69.723 31	Ge 72.61 32	As 74.922 33	Se 78.96 34	Br 79.904 35	Kr 83.80 36	
5	Rb 85.468 37	Sr 87.62 38	Y 88.906 39	Zr 91.224 40	Nb 92.906 41	Mo 95.94 42	Tc 98.907 43	Ru 101.07 44	Rh 102.91 45	Pd 106.42 46	Ag 107.87 47	Cd 112.41 48	In 114.82 49	Sn 118.71 50	Sb 121.75 51	Te 127.60 52	I 126.90 53	Xe 131.29 54	
6	Cs 132.91 55	Ba 137.33 56	*La 138.91 57	Hf 178.49 72	Ta 180.95 73	W 183.85 74	Re 186.21 75	Os 190.2 76	Ir 192.22 77	Pt 195.08 78	Au 196.97 79	Hg 200.59 80	Tl 204.38 81	Pb 207.2 82	Bi 208.98 83	Po (209) 84	At (210) 85	Rn (222) 86	
7	Fr 223 87	Ra 226.03 88	**Ac (227) 89	Rf (261) 104	Ha (262) 105	Unh (263) 106	Uns (262) 107	Uno (265) 108	Une (266) 109	Uun (267) 110									

Atomic mass →  
Symbol →  
Atomic No. →

### TRANSITION ELEMENTS

140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

\*Lanthanide Series

\*\*Actinide Series

( ) indicates the mass number of the isotope with the longest half-life.