

**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**

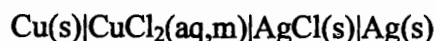
**GRAPH PAPER IS PROVIDED**

**NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED.**

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### Question 1(25marks)

- a. Consider the following cell at 25 °C:



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

- (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  $\text{CuCl}_2$  and the mean activity coefficient. [3]
  - (iii) Calculate the standard cell potential,  $E^\ominus$ , 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  $0.20 \text{ mol kg}^{-1}$  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  $\text{AgCl}/\text{Ag}, \text{Cl}^-$  couple is 0.2224 V at 25 °C and the Standard Gibbs energy of formation of solid silver chloride,  $\Delta_f G^\ominus(\text{AgCl,s})$ , is -109.79 kJ/mol. Calculate the standard Gibbs energy of formation of  $\text{Cl}^-(\text{aq})$  at 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  $0.2063 \text{ cm}^{-1}$ . The following data was obtained:

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

- (i) Show that that these data do follow Kohlrausch's law,  $\Lambda_m = \Lambda_m^\ominus - \kappa\sqrt{c}$ . [4]
- (ii) Determine the value of the coefficient  $\kappa$  and the limiting molar conductivity,  $\Lambda_m^\ominus$ . [4]
- (iii) Use the value of  $\kappa$  and the information that  $\lambda(\text{Na}^+) = 5.01 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$  and  $\lambda(\text{I}^-) = 7.68 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$  to predict the molar conductivity and resistance it would show in the cell, of  $0.010 \text{ mol L}^{-1} \text{ NaI}(\text{aq})$  at 25 °C. [5]

- b. Explain why  $\text{Li}^+$  has a lower ionic conductivity than  $\text{Na}^+$  and why the value for  $\text{H}^+$  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  $\Lambda_m^0 = 426.16 \text{ Scm}^2 \text{ mol}^{-1}$ . Calculate the mobilities of the hydrogen and chloride ions at infinite dilution. [6]

**Question 3 (25 marks)**

- a. The concentration of  $(\text{CH}_3)_3\text{CBr}$  was measured as a function of time as the reaction  $(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HBr}$  progressed.

Time/h	0	3.13	6.20	10.00	18.30	30.80
$[(\text{CH}_3)_3\text{CBr}]$ mol/L	0.1039	0.0896	0.0776	0.0639	0.0353	0.0207

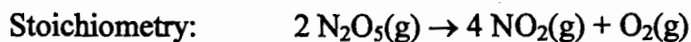
- (i) Show that the reaction follows first order kinetics. [4]
- (ii) Determine the rate constant and the molar concentration of  $(\text{CH}_3)_3\text{CBr}$  after 43.8 h. [4]
- (iii) What is the half-life of this reaction? [2]
- (iv) Suggest a reason why the concentration of water does not appear in the rate law. [1]
- b. The rate constant for the decomposition of a certain substance is  $2.80 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $30^\circ\text{C}$  and  $1.38 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $50^\circ\text{C}$ . Evaluate the Arrhenius parameters,  $A$  and  $E_a$ , of the reaction. [7]
- c. Find the relaxation time for the reaction  $\text{A} \rightleftharpoons 2\text{X}$ , 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)**

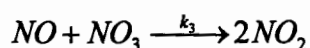
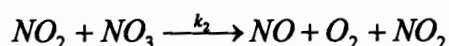
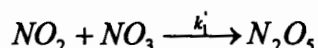
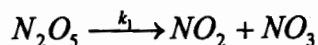
- a. Bearing in mind distinctions between the mechanisms of stepwise and chain polymerization, describe ways in which it is possible to control the molar mass of a polymer by manipulating the kinetic parameters of polymerization. [8]
- b. In an experiment to measure the quantum efficiency of a photochemical 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:



Mechanism:



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  $M = 152.3 \text{ g/mol}$  and melting point  $175 \text{ }^\circ\text{C}$ ) 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 polarizability of camphor. [12]

Temperature $\theta, ^\circ\text{C}$	Relative permittivity, $\epsilon_r$	Density, $\rho$ $\text{g cm}^{-3}$
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

$$\left[ \text{Useful equation } P_m = \frac{N_A}{3\epsilon_0} \left( \alpha + \frac{\mu^2}{3kT} \right) \quad \text{where } P_m = \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \frac{M}{\rho} \right]$$

- c. The refractive index of  $\text{CH}_2\text{I}_2$  is 1.732 for 656 nm light. Its density at  $20^\circ\text{C}$  is  $3.32 \text{ g cm}^{-3}$ . Calculate the polarizability of the molecule at this wavelength.

[7]

## General data and fundamental constants

Quantity	Symbol	Value
Speed of light	$c$	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$
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	$h$ $\hbar = h/2\pi$	$6.626\,08 \times 10^{-34} \text{ J s}$ $1.054\,57 \times 10^{-34} \text{ J s}$
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	$\epsilon_0 = 1/c^2 \mu_0$ $4\pi\epsilon_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
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 kJ mol <sup>-1</sup>

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	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
	IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IX	X	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 →  
Symbol →  
Atomic No. →

### TRANSITION ELEMENTS

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
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

\*Lanthanide Series

\*\*Actinide Series

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