UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE
SUPPLEMENTARY EXAMINATION 2008

TITLE OF PAPER	:	**PHYSICAL CHEMISTRY**
COURSE CODE	:	**C402**
TIME	:	**3 HOURS**
TOTAL MARKS	:	**100 MARKS**
INSTRUCTIONS	:	**THERE ARE SIX QUESTIONS**
	:	**ANSWER FOUR QUESTIONS ONLY**
	:	**EACH QUESTION IS 25 WORTH MARKS**
	:	**A PERIODIC TABLE AND DATA SHEETS ARE PROVIDED WITH THIS EXAMINATION PAPER**
	:	**NO FORM OF ANY PAPER SHOULD BE BROUGHT INTO NOR TAKEN OUT OF THE EXAMINATION ROOM**
	:	**BEGIN THE ANSWER TO EACH QUESTION ON A SEPARATE SHEET OF PAPER**
	:	**ALL CALCULATIONS/WORKOUT DETAILS SHOULD BE SUBMITTED WITH YOUR ANSWER SHEET(S)**

DO NOT OPEN THIS EXAMINATION PAPER UNTIL PERMISSION HAS BEEN GRANTED BY THE INVIGILATOR.

Question 1 [25 Marks]

a) The kinetic theory is a link between macroscopic gas behaviour with microscopic studies of physical chemistry. Using examples of your choice discuss the meaning of this statement in the context of molecular behaviour and reaction studies.[15]

b) (i) Write the general Ficks first law for flux, J_X, for the following transport phenomena:
(a) thermal conductivity [3]
(b) viscocity [2]

(ii) Argon is confined in a cubic vessel of side 10 cm, one wall at 300 K and the one opposite at 295 K. The thermal conductivity of argon is $5.4 \times 10^{-3} JK^{-1}m^{-1}s^{-1}$. Calculate:
(a) the flux of energy between the two surfaces [3]
(b) rate of heat conduction through a window of $1.0\ m^2$. [2]

Question 2 [25 Marks]

a) Write short notes on any Two the following terms:
i) half life [5]
ii) relaxation time [5]
iii) pseudo first order rate constant [5]

b) The composition of a liquid phase reaction A → B was followed as a function of time by a spectroscopic method with the following results:

T/min	0	10	20	30	40	00
[B]/mol dm^{-3}	0	0.089	0.153	0.200	0.230	0.312

i) What is the order of the reaction? [5]
ii) What is the value of the rate constant? [3]
iii) What is the half life of the reaction? [2]

c) Show that the rate law for the reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

Is given by: $[A]_t = [A]_o \left[\frac{k_{-1} + k_1 exp[-(k_1 + k_{-1})]t}{k_1 + k_{-1}} \right]$ [5]

Question 3 [25 Marks]

(a) Write short notes to define the nature and role of enzymes in reaction kinetics. [5] Your notes should include examples to illustrate your points.

(b) Briggs-Haldane equation states $V_0 = \dfrac{V_m[s]}{K_m + [s]}$ *where* $V_m = K_2[E]$

(i) derive the Briggs – Haldane equation: [5]

(ii) The hydrolysis of N-glutaryl-L-phenylalanine – p – nitroanalide (GPNA) to p-nitro-analine and N-glutaryl-L-phenylalanine is catalysed by α-chymotrypsin

$[S]/10^{-4}$ M	2.6	5.1	11	14.9
$Vo/10^{-6}$M min^{-1}	2.1	4.0	6.1	6.9

$[E]_0 = 4.0 \times 10^{-6}$ M

Using Lineweaver-Burk plot determine [15]

(a) The maximum attainable reaction rate.
(b) Strength of the Enzyme Subtrate complex.
(c) Vibrational frequency of the Enzyme Subtrate complex.

Question 4 [25 marks]

Given the distribution function for the flow of particles in liquids:

$$F(x) = \frac{exp\left(-x^2/_{4Dt}\right)}{\sqrt{\pi Dt}}$$

a) Find expressions for:

(i) root mean square distance in one dimension $\langle x^2 \rangle^{1/2} = \sqrt{2Dt}$ [5]

(ii) The diffusion coefficient of a molecule MH_2Cl_2 in octane at 24.8°C is 5×10^{-10} m^2s^{-1}, estimate the 3-dimensional root mean square displacement, r_{rms}, for the molecule after 2500 seconds. [5]

(iii) Define the general equation for flux for molecules in solution with a concentration gradient and calculate flux arising from a concentration gradient of 2.5×10^{-2} Moles L^{-1} m^{-1} for the MH_2Cl_2 in octane at 24.8°C in a(iii). [3]

b) (i) Write the general Ficks first law for flux, J_x, for the following transport phenomena:

(a) thermal conductivity [2]
(b) viscocity [2]

(ii) Argon is confined in a cubic vessel of side 10 cm, one wall at 300 K and the one opposite at 295 K. The thermal conductivity of argon is $5.4x10^{-3} JK^{-1}m^{-1}s^{-1}$. Calculate:
(a) the flux of energy between the two surfaces [5]
(b) rate of heat conduction through a window of 1.0 m^2. [3]

Question 5 [25 Marks]

a) The Kohlrausch equation for strong electrolytes states:

$$\Lambda_m(c) = \Lambda_m^o - K\sqrt{c}$$

and the Ostwald dilution law for weak electrolytes states:

$$K_{eq} = \left(\frac{\left(\Lambda_m' / \Lambda_m^o \right)^2}{1 - \left(\Lambda_m' / \Lambda_m^o \right)} \right) c \text{ where } \Lambda_m^o = \nu_+ \lambda_+^o + \nu_- \lambda_-^o$$

Using diagrams, where necessary, explain the concentration dependence of molar conductivities shown by strong and weak electrolytes. [10]

b) The resistances of a series of aqueous NaCl solutions, formed by successive dilution of a sample, were measured in a cell with a cell constant 0.2063 cm^{-1}. The following values were found:

C/mol L^{-1}	0.0050	0.0010	0.0050	0.010	0.020	0.050
R/Ω	3314	1669	342.1	174.1	89.08	37.14

The viscosity of water is $1.00x10^{-3}$ $kgm^{-1}s^{-1}$.

i) Verify that the molar conductivity follows Kohlrausch's law and [3]
ii) find the limiting molar conductivity, Λ_m^o. [2]
iii) Determine the Kohlrausch coefficient κ. [2]

c) Given the transport number of Na^+ ion in 0.005 M solution is 0.3930 and using the information calculated in 'd' above, calculate:

i) the molar conductivities [2]
ii) mobilities [2]
iii) diffusion coefficients [2]
iv) hydrodynamic radii [2]

of Na^+ and Cl^{-1} ions in solution.

Useful equations:

$$\kappa = \left(\frac{1}{R}\right)\frac{l}{A};\ t_{\pm} = \frac{\lambda_{\pm}}{\lambda_{+}+\lambda_{-}} = \frac{\lambda_{\pm}}{\Lambda_m^o} = \frac{u_{\pm}}{u_{+}+u_{-}};\ \Lambda_m^o = \nu_{+}\lambda_{+} + \nu_{-}\lambda_{-};\ \lambda_{\pm} = zu_{\pm}F,\ t_{+} + t_{-} = 1,$$

$$D = \frac{kT}{6\pi\eta a} \text{ and } D = \frac{ukT}{ze} = \frac{uRT}{zF}.$$

Question 6 [25 Marks]

a) Distinguish in some detail between physisorption and chemisorption [5]

b) The Langmuir adsorption isotherm for non-dissociative adsorption of single species is given by:

$$\theta = \frac{kP}{1 + kP}$$

Outline the kinetic arguments used to derive above isotherm. [10]

c) An adsorption isotherm for nitrogen adsorbed on a sample of colloidal silica was measured at -196°C and gave the following data:

$V \times 10^6$ / m^3	P/P_o
44	0.008
61	0.067
68	0.125
80	0.250
90	0.333

Where V is the volume adsorbed (corrected to STP) and P_o is the saturated vapour pressure of nitrogen at -196°C.

Determine the monolayer volume capacity and the surface area of the sample given that one adsorbed nitrogen molecules occupies 0.162 nm^2 in a monolayer. [10]

C402 EXAMINATION SUPPLEMENTARY INFORMATION

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Useful standard integrals:

$$I_n = \int_0^\infty x^n e^{-ax^2} dx$$

n	0	1	2	3	4
In	$\frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$	$\frac{1}{2a}$	$\frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$	$\frac{1}{2a^2}$	$\frac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2}$

$$i_n = \int_0^\infty x^{\frac{n}{2}} e^{-ax} dx$$

n	1	2	3	4	5
i_n	$\frac{(\pi/a)^{1/2}}{2a}$	$\frac{1}{a^2}$	$\frac{3(\pi/a)^{1/2}}{4a^2}$	$\frac{2}{a^3}$	$\frac{15(\pi/a)^{1/2}}{8a^3}$

Useful Relations

$(RT)_{298.15K}$=2.4789 kJ/mol				
$(RT/F)_{298.15K}$=0.025 693 V				
T/K:	100.15	298.15	500.15	1000.15
T/Cm^{-1}:	69.61	207.22	347.62	695.13
1mmHg=133.222 $N\ m^{-2}$				
hc/k=1.438 78×10^{-2} m K				

1atm	1 cal	1 eV	$1cm^{-1}$
=1.01325x10^5 Nm^{-2}	=4.184 J	=1.602 189x10^{-19} J	=0.124x10^{-3} eV
=760torr **=1 bar**		=96.485 kJ/mol = 8065.5 cm^{-1}	=1.9864x10^{-23}J

SI-units:

1 L = 1000 ml = 1000cm³ = 1 dm³

1 dm = 0.1 m

1 cal (thermochemical) = 4.184 J

dipole moment: 1 Debye = 3.335 64x10^{-30} C m

force: ***1N=1J m⁻¹= 1kgms⁻²***=10^5 dyne   pressure: ***1Pa=1Nm⁻²***=$1Jm^{-3}$

1J = 1 Nm

power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}

magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}

Prefixes:

p	n	m	m	c	d	k	M	G
pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

General Data

speed of light	c	**2.997 925x10^{8} ms^{-1}**
charge of proton	e	1.602 19x10^{-19} C
Faraday constant	F=Le	9.648 46x10^{4} C mol^{-1}
Boltzmann constant	**k**	**1.380 66x10^{-23} J K^{-1}**
Gas constant	**R=Lk**	**8.314 41 J K^{-1} mol^{-1}**
		8.205 75x10^{-2} dm^3 atm K^{-1} m
Planck constant	**h**	**6.626 18x10^{-34} Js**
	$\hbar = \frac{h}{2\pi}$	1.054 59x10^{-34} Js
Avogadro constant	**L or N_{av}**	**6.022 14x10^{23} mol^{-1}**
Atonis mass unit	u	1.660 54x10^{-27} kg
Electron mass	m_e	**9.109 39x10^{-31} kg**
Proton mass	m_p	1.672 62x10^{-27} kg
Neutron mass	m_n	1.674 93x10^{-27} kg
Vacuum permittivity	$\varepsilon_o = \mu_o^{-1}c^{-2}$	8.854 188x10^{-12} J^{-1} C^2 m^{-1}
Vacuum permeability	μ_o	4πx10^{-7} Js^2C^{-2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 02x10^{-24} JT^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.05079x10^{-27} JT^{-1}
Gravitational constant	G	6.67259x10^{-11} Nm^2kg^{-2}
Gravitational acceleration	**g**	**9.80665 ms^{-2}**
Bohr radius	a_o	5.291 77x10^{-11} m

THE PERIODIC TABLE OF ELEMENTS

NON-METALS

METALLOIDS

METALS

Group	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
Period 1	1 **H** 1.008																	2 **He** 4.003
2	3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.9	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.9	26 **Fe** 55.85	27 **Co** 58.71	28 **Ni** 58.71	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.7	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
5	37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 91.22	42 **Mo** 95.94	43 **Tc** 98.9	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
6	55 **Cs** 132.9	56 **Ba** 137.3	71 **Lu** 174.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 196.9	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 208.9	84 **Po** 210	85 **At** 210	86 **Rn** 222
7	87 **Fr** 223	88 **Ra** 226.0	103 **Lr** 257	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Uno**	109 **Une**									

Lanthanides	57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** 146.9	62 **Sm** 150.9	63 **Eu** 151.3	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0
Actinides	89 **Ac** 227.0	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.1	94 **Pu** 239.1	95 **Am** 241.1	96 **Cm** 247.1	97 **Bk** 249.1	98 **Cf** 251.1	99 **Es** 254.1	100 **Fm** 257.1	101 **Md** 258.1	102 **No** 255

*Numbers **below** the symbol indicates the **atomic masses**; and the numbers above the symbol indicates the atomic numbers.*

SOURCE: International Union of Pure and Applied Chemistry, I mills, ed., Quantities, Units, and symbols in Physical Chemistry, Blackwell Scientific publications, Boston, 1988, pp 86-98.