UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE
FINAL EXAMINATION 2008

TITLE OF PAPER	:	**PHYSICAL CHEMISTRY**
COURSE CODE	:	**C402**
TIME	:	**3 HOURS**
TOTAL MARKS	:	**100 MARKS**
INSTRUCTIONS	:	**THERE ARE SEVEN 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]

The Maxwell Boltzmann distribution function of kinetic energies along the x-direction between $\varepsilon_{trans,x} \rightarrow \varepsilon_{trans,x} d\varepsilon_{trans,x}$ is given by:

$$F(\varepsilon) = \left(\sqrt{\frac{1}{\pi\, k\, T\, \varepsilon_{trans,x}}}\right) \exp\left(\frac{-\varepsilon_{trans,x}}{kT}\right)$$

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.[6]

b) i) Derive an equation for the average translational kinetic energy in one dimension. [5]

ii) Find an expression for the most probable kinetic energy. [5]

iii) The root mean square kinetic energy. [5]

c) Using the Maxwell Boltzmann distribution calculate probability that the CO_2 molecules travel within $\pm$ 5.0x10^{-9} kJ/mol of its root mean square kinetic energy at +25^{0}C at 1 atmospheric pressure confined within a 24 L container.

[4]

Question 2 [25 Marks]

a) Derive an expression for the collisional frequency for single particles, Z_A in a container. [6]

$$z_A = \frac{\sqrt{2}\sigma \bar{c}\, p}{kT}$$

where means speed $\bar{c} = \sqrt{8RT/\pi M}$ and mean free path $\lambda = \frac{kT}{\sqrt{2}\sigma P}$.

b) i) Calculate the number of collisions made by a single Cs atom per sec given that the collision diameter is 40 pm. [4]

ii) What is the total number of collisions made by Cs if the oven volume is 50.0 cm^3 and the vapour pressure of Cs(1) at 500^{0}C is 80 torr. [4]

iii) Calculate the time between collisions for the Cs atoms in (ii) above. [4]

iv) Calculate mean free path of Cs above. [4]

c) Does the Cs atoms in (b) above obey the kinetic theory ? Give reasons. [3]

Question 3 [25]

a) Briefly explain each of the following:
i) the pre-equilibrium approach [5]
ii) the steady state approximation [5]

Use any reaction equation of your choice to illustrate your point.

b) Lindemann's mechanism for the dissociation of ozone in the stratosphere $2O_3 \rightarrow 3O_2$ is:

$$O_3\ (\text{Ozone}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O \quad \text{fast}$$

$$O_3 + O \xrightarrow{k_2} 2O_2 \quad \text{slow}$$

Using the steady state approximation show that the rate law is $\upsilon = \dfrac{k_2 K [O_3]^2}{O_2}$

After making all necessary assumptions where $K = k_1/k_{-1}$. [5]

c) The experimental rate law for the reaction:

$$2N_2O_5\ (g) \longrightarrow 4NO_2\ (g) + O_2(g)$$

is $\upsilon = k[N_2O_5]$,

The proposed mechanism for the reaction has the following elementary single step processes:

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3\,(fast)$$

$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2\,(slow)$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

Using the pre-equilibrium approach verify whether the proposed mechanism is right. [5]

d) Thermal decomposition of a compound has been studied using optical absorption at 350 nm. The following data was obtained:

t (s)	*0*	*600*	*1200*	∞
A/absorbance	***1.50***	***0.92***	***0.65***	***0.40***

Given the rate law: $ln\,\dfrac{A - A_\infty}{A_o - A_\infty} = ln\,\dfrac{[A]}{[A]_o} = -kt$ determine the rate constant 'k'. [5]

Question 4 [25]

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) The mechanism for enzyme catalysed reactions as proposed by V. Henri (1903) is:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ES] \rightarrow P + E$$

c) i) Using the steady state approximation and the Lineweaver-Burk treatment show that Michaelis-Menten equation is: [5]

$$\frac{1}{V_o} = \frac{K_m}{V_{max}}\frac{1}{S} + \frac{1}{V_{max}}$$

ii) Briefly explain and define the role of the following in enzyme kinetics:

a) V_{max} [3]
b) Michaelis constant, K_m [2]
c) k_2 [2]

d) The following data refer to an enzyme catalysed reaction:

V_o/ 10^{-5}mol dm^{-3}s^{-1}	13	20	29	38
[S]/10^{-3} mol dm^{-3}	2.0	4.0	8.0	20

The enzyme concentration is 2.0 g/dm^3 and the molecular weight is 50 000 g/mol
Calculate:

i) Michaelis constant, K_m [3]
ii) V_{max} [3]
iii) The number of substrate molecules converted into product per unit time, when the enzyme is fully saturated with substrate. [2]

Question 5 [25]

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^{2}s^{-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 $2.5x10^{-2}$ 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 6 [25]

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:

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

a) Using diagrams, where necessary, explain in terms of the relaxation effect and the electrophoretic effect, the concentration dependence of molar conductivities shown by strong and weak electrolytes. [4]

b) Derive Ostwald's dilution law and express it in its linearised form. [3]

[Take the fraction dissociated for weak electrolytes as: $\alpha = \Lambda_m' / \Lambda_m^o$]

c) The following conductivity data are for a weak acid, MH_3CO_2H in aqueous solution at 25°C:

$c/10^{-2}$ mol L^{-1}	6.25	3.13	1.56	0.781	0.391	0.195	0.0977
Λ_m/ S cm^2mol^{-1}	53.1	72.4	96.8	127.7	164	205.8	249.2

and the viscosity of water is given by $\eta_{water} = 1.00 \times 10^{-3}\ kgm^{-1}s^{-1}$

Determine the

(i) limiting conductivity, Λ_m^o [2]
(ii) pK_a value [2]

(iii) the transport numbers of the $MH_3CO_2^-$ and H^+ ions given the limiting conductivity of $MH_3CO_2^-$ to be 40.9 S cm^2 mol^{-1} [2]
(iv) mobility of $MH_3CO_2^-$ in units of $m^2S^{-1}V^{-1}$ [2]
(v) diffusion coefficient of $MH_3CO_2^-$ in units of m^2S^{-1} [2]
(vi) hydrodynamic radius of $MH_3CO_2^-$ [2]

Useful equations:

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

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

d) i) Describe any one method of determining transport numbers. (3)
ii) In a moving boundary experiment on KCl the apparatus consisted of a tube of internal diameter 4.146 mm, and it contained aqueous KCl at 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
x/mm	64

Find the transport number of K^+, its mobility, and its ionic conductivity given the limiting conductivity to be 149.9 S cm^{2}mol^{-1}. (3)

Useful information:

$$t = zcVF/I\Delta t$$

Question 7 [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. [5]

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

$V\times10^6$ / 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.

(i) Verify whether or not these results conform to the Langmuir or BET adsorption isotherm. [5]

(ii) 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]

Useful equation:

B.E.T isotherm is given by: $\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\frac{P}{P_o}$ where P_o is the bulk vapour pressure, P is the equilibrium vapour pressure, V_m is the monolayer volume capacity and V the total volume of material adsorbed.

C402 EXAMINATION SUPPLEMENTARY INFORMATION

DR J. M. THWALA

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	General Data		
$(RT)_{298.15K}$=2.4789 kJ/mol	**speed of light**	**c**	**2.997 925x10^{8} ms^{-1}**
$(RT/F)_{298.15K}$=0.025 693 V	charge of proton	*e*	1.602 19x10^{-19} C
T/K: 100.15 298.15 500.15 1000.15	Faraday constant	F=L*e*	9.648 46x10^{4} C mol^{-1}
T/Cm^{-1}: 69.61 207.22 347.62 695.13	**Boltzmann constant**	**k**	**1.380 66x10^{-23} J K^{-1}**
1mmHg=133.222 N m^{-2}	**Gas constant**	R=Lk	**8.314 41 J K^{-1} mol^{-1}**
hc/k=1.438 78x10^{-2} m K			**8.205 75x10^{-2} dm^{3} atm K^{-1} mol^{-1}**
1atm 1 cal 1 eV 1cm^{-1}			
1.01325x10^{5} Nm^{-2} 4.184 J 1.602 189x10^{-19} J 0.124x10^{-3} eV	**Planck constant**	**h**	**6.626 18x10^{-34} Js**
760torr 96.485 kJ/mol 1.9864x10^{-23}J **1 bar** 8065.5 cm^{-1}		$\hbar = \frac{h}{2\pi}$	1.054 59x10^{-34} Js
	Avogadro constant	**L or N_{av}**	**6.022 14x10^{23} mol^{-1}**
SI-units:	Atomis mass unit	u	1.660 54x10^{-27} kg
1 L = 1000 ml = 1000cm^{3} = 1 dm^{3}	**Electron mass**	**m_e**	**9.109 39x10^{-31} kg**
1 dm = 0.1 m	Proton mass	m_p	1.672 62x10^{-27} kg
1 cal (thermochemical) = 4.184 J	Neutron mass	m_n	1.674 93x10^{-27} kg
dipole moment: 1 Debye = 3.335 64x10^{-30} C m	Vacuum permittivity	$\varepsilon_o = \mu_o^{-1}c^{-2}$	8.854 188x10^{-12} J^{-1} C^{2} m^{-1}
force: ***1N=1J m^{-1}= 1$kgms^{-2}$***=10^{5} dyne pressure: ***1Pa=1Nm^{-2}***=1Jm^{-3}	Vacuum permeability	μ_o	4πx10^{-7} $Js^{2}C^{-2}$ m^{-1}
1J = 1 Nm power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}	Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 02x10^{-24} JT^{-1}
magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}	Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.05079x10^{-27} JT^{-1}
Prefixes:	Gravitational constant	G	6.67259x10^{-11} $Nm^{2}kg^{-2}$
p n m m c d k M G	**Gravitational**	**g**	**9.80665 ms^{-2}**
pico nano micro milli centi deci kilo mega giga	**acceleration**		
10^{-12} 10^{-9} 10^{-6} 10^{-3} 10^{-2} 10^{-1} 10^{3} 10^{6} 10^{9}	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.

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