UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE
SUPPLEMENTARY EXAMINATION 2006

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 Maxwell Boltzmann distribution functions of kinetic energy in one dimension and in three dimensions are given by:

$$F(\varepsilon) = 2\pi\sqrt{\varepsilon}\left(\frac{1}{\pi kT}\right)^{3/2} exp\left(\frac{-\varepsilon}{kT}\right) \text{ and } F(\varepsilon_x) = \left(\frac{1}{\pi kT\varepsilon_x}\right)^{1/2} exp\left(\frac{-\varepsilon_x}{kT}\right)$$

i) Derive an expression for the mean kinetic energy between the limits $0 \rightarrow \infty$ [5]

ii) Calculate the mean kinetic energy for N_2 at 298 K. [5]

c)

i) Derive an expression for the most probable kinetic energy. [5]

ii) Calculate the most probable kinetic energy for nitrogen gas at 298 K [5]

d) Write brief notes on methods of determining mean velocities for gaseous molecules [5]

Question 2 [25 Marks]

a) Write short notes on any Two the following pairs:

- i) half life and relaxation time [5]
- ii) pseudo first order rate constant [5]
- iii) Stopped flow technique [5]

use any diagram and/or equation of your choice to illustrate your answer

b) The alkaline hydrolysis of ethyl benzoate at various time gave the following results:

t/ sec	0	100	300	400	500	600	700	800
[A]/moles dm^{-3}	0.05	0.0275	0.0225	0.0185	0.0160	0.0148	0.0148	0.0138

Determine:

- i) order of the reaction [5]
- ii) rate constant of the reaction [2]
- iii) half life, $t_{1/2}$. If $t_{1/2}$ is concentration dependent evaluate at 0.05 M [3]

c) Show that the integrated rate law for the concurrent reaction:

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

where $k_2 \neq k_1$

is given by:

$$[A]_t = [A]_0 e^{-(k_1+k_2)t} \quad [5]$$

Question 3 [25 Marks]

(a) Write short notes to define the nature and role of enzymes in reaction kinetics. [5]

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

(i) Using Briggs – Haldane n derive

$$\upsilon_0 = \frac{-V_0}{[S]} K_m + V_m \quad Eodie\text{-}Hofstee\ n \quad [5]$$

(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	2.5	5.0	10.0	15.0
$Vo/10^{-6}$M min^{-1}	2.2	3.8	5.9	7.1

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

Using Lineweaver-Burk plot determine [15]

(a) V_m
(b) K_m
(c) K_2

Question 4 [25 Marks]

a) The rate constant for de-similar molecules as obtained from the Simple Collision Theory for bimolecular reactions states:

$$k_2 = \sigma P L \sqrt{\frac{8kT}{\pi\mu}}\, exp\left(\frac{-E_a}{RT}\right)$$

Briefly outline the kinetic arguments made in deriving the above equation. Using Arrhenius equation also explain its significance in reaction kinetics. [10]

Useful relations:

$$Z_{AB} = \sigma \bar{c}_{rel} L^2 [A][B]$$
$$and\ \bar{c}_{rel} = \sqrt{\frac{8kT}{\pi\mu}}$$

b) The activated complex theory states:

$$k_2 = \frac{kT}{h} exp\left(\frac{\Delta S^{\#}}{R}\right) exp\left(\frac{-\Delta H}{RT}\right)$$

i) Define an activated complex and Give a thermodynamic formulation of the activated complex theory (ACT). [10]

ii) Derive an expression for activation energy for a bimolecular gas phase reaction using the ACT. [5]

Question 5 [25 Marks]

a) Sketch the appropriate viscosity plots showing its change with temperature for both gases and liquids. Give an account of the differences between the two plots. [6]

Useful relations:

$$\eta = \frac{1}{3} m\lambda\bar{c}[A]; \eta = C\, exp\left(\frac{\Delta E_{vis}}{RT}\right)$$

(b) Viscosity of liquids flowing in a Ostwald viscometer is given by:

$$\eta = \frac{\pi R^4 \Delta P t}{8Vl}$$

(i) Sketch the Ostwald and Ubbelodhe viscometers. Comment on the use of these viscometers in viscosity measurements. [4]

(ii) The time required for water and methanol to drain were 42.6 s and 64.5 and that their densities are 0.9982 g/ml (water) and 0.789 g/ml (methanol), respectively. The viscosity of methanol is 1.2×10^{-3} Pa s. Determine the viscosity of water. [5]

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

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

(i) Find expressions for root mean square distance in one dimension

$$\langle x^2 \rangle^{1/2} = \sqrt{2Dt} \qquad [4]$$

(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. [2]

(iii) Give an account on the use of diffusion coefficents in chemistry [4]

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 the adsorption isotherm above [5]

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

$V \times 10^6$ / 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.

(i) Verify whether or not these results conform to the 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

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

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.*

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}= 1kgms^{-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