UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE
FINAL EXAMINATION 2007

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) Using diagrams and equations write short notes to describe the process of effusion. [6]

b) Derive the expression for rate of effusion. [8]

$$Rate = PA_o/(2\pi mkT)^{1/2}$$

c) Germanium was introduced into a container and heated to 1000° C . When a hole of radius 0.5 mm was opened for 7200 s, a mass loss of $4.3\text{x}10^{-5}$ g was measured. AW(Ge)=72.61 g/mol.

(i) Derive an expression that shows how pressure varies with time [6]
(ii) Calculate the vapour pressure of germanium at 1000°C, assuming it to be monoatomic. [5]

Question 2 [25 Marks]

a) Write short notes on <u>any Two</u> 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 it 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] Your notes should include examples to illustrate your points.

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

(i) Using the pre-equilibrium approach 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]

a) Write short notes on any Two of the following: [10]
 i) single crystal X-ray diffraction
 ii) powder X-ray diffraction
 iii) isormorphous replacement and the phase problem

b) Derive the Bragg's equation: [5]

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2 + k^2 + l^2\right)$$

c) A powder diffraction photograph of KCl gave lines at the following distances from the center spot when Mo X-rays (λ=10.8 pm) were used in a camera with radius 5.74 cm:
13.2, 18.4, 22.8, 26.2, 29.4, 32.2, 37.2, 39.6, 41.8, 43.8 and 46.0 mm
 (i) index the lines [2]
 (ii) identify the kind of unit cell [2]
 (iii) determine the size of the unit cell [4]
 (iv) Determine the packing efficiency of the unit cell [2]

Question 5 [25 Marks]

a) i) Write an expression for flux of heat according to Ficks Law. [2]

ii) Evaluate the rate of heat conduction through a window of 1.o cm^2 from two surfaces separated by 0.50 cm of air such that the temperature difference is 2.5°C. The thermal conductivity coefficient of air is 0.0242 $JKm^{-1}s^{-1}$. [4]

(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:

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

(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]

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