

**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]

$$\text{Rate} = PA_0 / (2\pi mkT)^{1/2}$$

- 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 4.3×10^{-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]

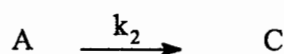
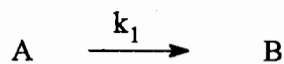
Question 2 [25 Marks]

- a) Write short notes on any Two the following pairs:
- half life and relaxation time [5]
 - pseudo first order rate constant [5]
 - 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:

- order of the reaction [5]
 - rate constant of the reaction [2]
 - 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:



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

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

Using Lineweaver-Burk plot determine [15]

- (a) The maximum attainable reaction rate.
(b) Strength of the Enzyme Substrate complex.
(c) Vibrational frequency of the Enzyme Substrate 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) isomorphous replacement and the phase problem
- b) Derive the Bragg's equation: [5]

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

- c) A powder diffraction photograph of KCl gave lines at the following distances from the center spot when Mo X-rays ($\lambda=10.8 \text{ pm}$) 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 1.0 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 $0.0242 \text{ JKm}^{-1}\text{s}^{-1}$. [4]

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

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

- (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 $1.2 \times 10^{-3} \text{ Pa s}$. 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

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

- (ii) The diffusion coefficient of a molecule MH_2Cl_2 in octane at 24.8°C is $5 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, 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 coefficients in chemistry [4]

Useful Relations			General Data		
$(RT)_{298.15K} = 2.4789 \text{ kJ/mol}$			speed of light	c	$2.997\ 925 \times 10^8 \text{ ms}^{-1}$
$(RT/F)_{298.15K} = 0.025\ 693 \text{ V}$			charge of proton	e	$1.602\ 19 \times 10^{-19} \text{ C}$
T/K: 100.15 298.15 500.15 1000.15			Faraday constant	$F = Le$	$9.648\ 46 \times 10^4 \text{ C mol}^{-1}$
T/Cm ⁻¹ : 69.61 207.22 347.62 695.13			Boltzmann constant	k	$1.380\ 66 \times 10^{-23} \text{ J K}^{-1}$
1mmHg = 133.222 N m ⁻²			Gas constant	$R = Lk$	$8.314\ 41 \text{ J K}^{-1} \text{ mol}^{-1}$
hc/k = 1.438 78 x 10 ⁻² mK					$8.205\ 75 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
1atm	1 cal	1 eV			
$1.01325 \times 10^5 \text{ Nm}^{-2}$	4.184 J	$1.602\ 189 \times 10^{-19} \text{ J}$	Planck constant	h	$6.626\ 18 \times 10^{-34} \text{ Js}$
760 torr	96.485 kJ/mol	$1.9864 \times 10^{-23} \text{ J}$		$\frac{h}{2\pi}$	$1.054\ 59 \times 10^{-34} \text{ Js}$
1 bar	8065.5 cm ⁻¹				
			Avogadro constant	$L \text{ or } N_{av}$	$6.022\ 14 \times 10^{23} \text{ mol}^{-1}$
SI-units:			Atomis mass unit	u	$1.660\ 54 \times 10^{-27} \text{ kg}$
$1 \text{ L} = 1000 \text{ ml} = 1000 \text{ cm}^3 = 1 \text{ dm}^3$			Electron mass	m_e	$9.109\ 39 \times 10^{-31} \text{ kg}$
1 dm = 0.1 m			Proton mass	m_p	$1.672\ 62 \times 10^{-27} \text{ kg}$
1 cal (thermochemical) = 4.184 J			Neutron mass	m_n	$1.674\ 93 \times 10^{-27} \text{ kg}$
dipole moment: 1 Debye = $3.335\ 64 \times 10^{-30} \text{ C m}$			Vacuum permittivity	$\epsilon_0 = \mu_0^{-1} \text{ c}^{-2}$	$8.854\ 188 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
force: $1 \text{ N} = 1 \text{ J m}^{-1} = 1 \text{ kgms}^{-2} = 10^5 \text{ dyne}$ pressure: $1 \text{ Pa} = 1 \text{ Nm}^{-2} = 1 \text{ Jm}^{-3}$			Vacuum permeability	μ_0	$4\pi \times 10^{-7} \text{ Js}^2 \text{ C}^{-2} \text{ m}^{-1}$
$IJ = 1 \text{ Nm}$			Bohr magneton	$\mu_B = \frac{e\hbar}{2m_p}$	$9.274\ 02 \times 10^{-24} \text{ JT}^{-1}$
power: $1 \text{ W} = 1 \text{ J s}^{-1}$			Nuclear magneton	$\mu_N = \frac{e\hbar}{2m_p}$	$5.05079 \times 10^{-27} \text{ JT}^{-1}$
magnetic flux: $1 \text{ T} = 1 \text{ Vsm}^{-2} = 1 \text{ JCs m}^{-2}$ current: $1 \text{ A} = 1 \text{ Cs}^{-1}$					
Prefixes:			Gravitational constant	G	$6.67259 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$
p nano	m micro	m milli	Gravitational acceleration	g	9.80665 ms^{-2}
c centi	d deci	k kilo	Bohr radius	a_0	$5.291\ 77 \times 10^{-11} \text{ m}$
M mega	G giga				
10 ⁻¹²	10 ⁻⁹	10 ⁻⁶			
10 ⁻³	10 ⁻²	10 ⁻¹			
10 ³	10 ⁶	10 ⁹			