

**UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE
FINAL 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 function of velocities in three dimensions x, y and z, between $v \rightarrow v+dv$ is given by:

$$F(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2kT} \right)$$

- (i) Derive an equation for the average velocity, \bar{v} . [5]
- (ii) Find an expression for the most probable velocity, v^* . [5]
- b) i) Calculate the number of collisions made by a single N_2 molecule per sec given that the collision diameter is 373 nm. [3]
- ii) What is the total number of collisions made by N_2 if the oven volume is 50.0 cm^3 and the vapour pressure of N_2 at $300 \text{ }^\circ\text{C}$ is 50 torr. [2]

useful equations:

$$Z_A = \frac{\sqrt{2}\sigma\bar{c}p}{kT}; Z_{AA} = \frac{1}{2}z_A \frac{N}{V}; \bar{c} = \sqrt{\frac{8RT}{\pi MW (\text{kg/Mol})}}$$

- iii) Calculate the mean free path of N_2 using the parameters for N_2 above [5]
- iv) Calculate the time intervals between collisions [3]
- v) Does the gas, N_2 , obey the kinetic theory of gases: Verify and give reasons. [2]

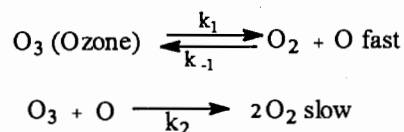
Useful equation: $\lambda = \frac{kT}{\sqrt{2}\sigma p}$

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



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

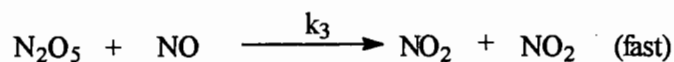
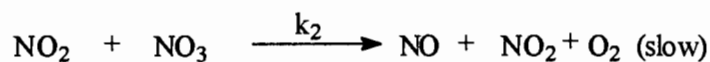
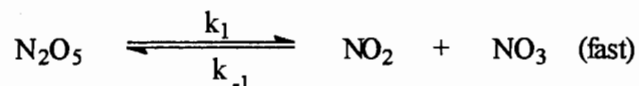
After making all necessary assumptions where $K = k_1/k_{-1}$. [5]

c) The experimental rate law for the reaction:



$$\text{is } \nu = k[\text{N}_2\text{O}_5],$$

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



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

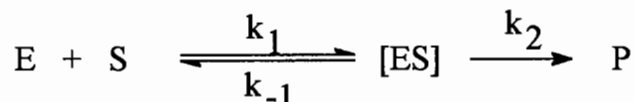
d) Thermal decomposition of a compound has been studied using optical absorption at 350 nm. The following data was obtained:

<i>t</i> (s)	0	600	1200	∞
<i>A</i> /absorbance	1.50	0.92	0.65	0.40

Given the rate law: $\ln \frac{A-A_\infty}{A_0-A_\infty} = \ln \frac{[A]}{[A]_0} = -kt$ determine the rate constant 'k'. [5]

Question 3 [25]

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



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

$$\frac{1}{V_0} = \frac{K_m}{V_{max}} \frac{1}{S} + \frac{1}{V_{max}}$$

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

a) V_{max} [3]

b) Michaelis constant, K_m [3]

c) k_2 [2]

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

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

The enzyme concentration is 2.0 g/dm^3 and the molecular weight is $50\,000 \text{ g/mol}$

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. [4]

Question 4 [50]

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

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

Briefly outline the kinetic arguments made in deriving the above equation. Using Arrhenius equation also explain its significance in reaction kinetics. [5]

Useful relations:

$$Z_{AB} = \sigma \bar{c}_{rel} L^2 [A][B]$$

$$\text{and } \bar{c}_{rel} = \sqrt{\frac{8kT}{\pi\mu}}$$

b) The Arrhenius parameters for some gas-phase reactions are:

	$A/M^1 S^{-1}$		P
	Experiment	Theory	
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24×10^6	7.3×10^{11}	-
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.1×10^{11}	4.8

i) Using the Simple Collision theory estimate the P-factor for the hydrogenation of ethane at 628 K. [5]

$$\sigma(H_2) = 0.27 \text{ nm}^2, \quad \sigma(C_2H_4) = 0.64 \text{ nm}^2 \quad \text{and} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

ii) Account for any discrepancies in the results above (including your calculated P-value. [5]

c) The activated complex theory states:

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

- i) Define an activated complex and Give a thermodynamic formulation of the activated complex theory (ACT). [8]
- ii) Derive an expression for activation energy for a bimolecular gas phase reaction using the ACT. [2]

Question 5 [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:

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

- 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: $\alpha = \frac{\Lambda'_m}{\Lambda_m^o}$]
- c) The following conductivity data are for a weak acid, $\text{MH}_3\text{CO}_2\text{H}$ in aqueous solution at 25°C :

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

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

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 $40.9 \text{ S cm}^2 \text{mol}^{-1}$ [2]
- (iv) mobility of MH_3CO_2^- in units of $\text{m}^2 \text{S}^{-1} \text{V}^{-1}$ [2]
- (v) diffusion coefficient of MH_3CO_2^- in units of $\text{m}^2 \text{S}^{-1}$ [2]
- (vi) hydrodynamic radius of MH_3CO_2^- [2]

Useful equations:

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

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

- 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:

$\Delta t/s$	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 cm²mol⁻¹. (3)

Useful information:

$$t = zcVF/IA\Delta t$$

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 for two molecules 'A' and 'B' as given by

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} ; \quad \theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \quad [5]$$

- 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_0
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 P₀ 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 nm² 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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3/01/2006

Useful standard integrals:

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

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

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

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		
$(RT)_{298.15K}=2.4789 \text{ kJ/mol}$		speed of light	c	$2.997925 \times 10^8 \text{ ms}^{-1}$
$(RT/F)_{298.15K}=0.025693 \text{ V}$		charge of proton	e	$1.60219 \times 10^{-19} \text{ C}$
T/K: 100.15 298.15 500.15 1000.15		Faraday constant	$F=Le$	$9.64846 \times 10^4 \text{ C mol}^{-1}$
T/Cm ⁻¹ : 69.61 207.22 347.62 695.13		Boltzmann constant	k	$1.38066 \times 10^{-23} \text{ J K}^{-1}$
1mmHg=133.222 N m ⁻²		Gas constant	$R=Lk$	$8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$
hc/k=1.43878 × 10 ⁻² m K				$8.20575 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
1atm	1 cal 1 eV 1cm ⁻¹			
$1.01325 \times 10^5 \text{ Nm}^{-2}$	4.184 J 1.602189 × 10 ⁻¹⁹ J 0.124 × 10 ⁻³ eV	Planck constant	h	$6.62618 \times 10^{-34} \text{ Js}$
760 torr	96.485 kJ/mol 1.9864 × 10 ⁻²³ J		$\frac{h}{2\pi}$	$1.05459 \times 10^{-34} \text{ Js}$
1 bar	8065.5 cm ⁻¹			
SI-units:		Avogadro constant	$L \text{ or } N_{av}$	$6.02214 \times 10^{23} \text{ mol}^{-1}$
$1 L = 1000 \text{ ml} = 1000 \text{ cm}^3 = 1 \text{ dm}^3$		Atomis mass unit	u	$1.66054 \times 10^{-27} \text{ kg}$
1 dm = 0.1 m		Electron mass	m_e	$9.10939 \times 10^{-31} \text{ kg}$
1 cal (thermochemical) = 4.184 J		Proton mass	m_p	$1.67262 \times 10^{-27} \text{ kg}$
dipole moment: 1 Debye = 3.33564 × 10 ⁻³⁰ C m		Neutron mass	m_n	$1.67493 \times 10^{-27} \text{ kg}$
force: $1N=1Jm^{-1} = 1kgms^{-2} = 10^5 \text{ dyne}$ pressure: $1Pa=1Nm^{-2} = 1Jm^{-3}$		Vacuum permittivity	$\epsilon_0 = \mu_0^{-1}c^{-2}$	$8.854188 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
$1J = 1Nm$		Vacuum permeability	μ_0	$4\pi \times 10^{-7} \text{ Js}^2 \text{ C}^{-2} \text{ m}^{-1}$
power: $1W = 1Js^{-1}$		Bohr magneton	$\mu_B = \frac{e\hbar}{2m_e}$	$9.27402 \times 10^{-24} \text{ JT}^{-1}$
magnetic flux: $1T=1Vsm^{-2}=1JCs^{-2}$ current: $1A=1Cs^{-1}$		Nuclear magneton	$\mu_N = \frac{e\hbar}{2m_p}$	$5.05079 \times 10^{-27} \text{ JT}^{-1}$
Prefixes:		Gravitational constant	G	$6.67259 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$
p nano	n micro	acceleration	g	9.80665 ms^{-2}
10^{-12}	10^{-9}	Bohr radius	a_0	$5.29177 \times 10^{-11} \text{ m}$