

**UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE
SUPPLEMENTARY EXAMINATION 2008**

- 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]

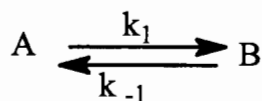
- a) The kinetic theory is a link between macroscopic gas behaviour with microscopic studies of physical chemistry. Using examples of your choice discuss the meaning of this statement in the context of molecular behaviour and reaction studies. [15]
- b) (i) Write the general Ficks first law for flux, J_x , for the following transport phenomena:
- (a) thermal conductivity [3]
 - (b) viscosity [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 $5.4 \times 10^{-3} \text{JK}^{-1}\text{m}^{-1}\text{s}^{-1}$. Calculate:
- (a) the flux of energy between the two surfaces [3]
 - (b) rate of heat conduction through a window of 1.0 m^2 . [2]

Question 2 [25 Marks]

- a) Write short notes on any Two the following terms:
- i) half life [5]
 - ii) relaxation time [5]
 - iii) pseudo first order rate constant [5]
- b) The composition of a liquid phase reaction $A \rightarrow B$ was followed as a function of time by a spectroscopic method with the following results:

T/min	0	10	20	30	40	00
[B]/mol dm ⁻³	0	0.089	0.153	0.200	0.230	0.312

- i) What is the order of the reaction? [5]
 - ii) What is the value of the rate constant? [3]
 - iii) What is the half life of the reaction? [2]
- c) Show that the rate law for the reaction



Is given by: $[A]_t = [A]_0 \left[\frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{k_1 + k_{-1}} \right]$ [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) derive the Briggs – Haldane equation: [5]
- (ii) The hydrolysis of N-glutaryl-L-phenylalanine – p – nitroanalide (GPNA) to p-nitro-aniline 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]

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 $5 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, estimate the 3-dimensional root mean square displacement, r_{rms} , for the molecule after 2500 seconds. [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 $2.5 \times 10^{-2} \text{ Moles L}^{-1} \text{ m}^{-1}$ 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) viscosity [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 $5.4 \times 10^{-3} \text{ JK}^{-1} \text{ m}^{-1} \text{ s}^{-1}$. 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 5 [25 Marks]

- a) 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:

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

Using diagrams, where necessary, explain the concentration dependence of molar conductivities shown by strong and weak electrolytes. [10]

- b) The resistances of a series of aqueous NaCl solutions, formed by successive dilution of a sample, were measured in a cell with a cell constant 0.2063 cm^{-1} . The following values were found:

C/mol L ⁻¹	0.0050	0.0010	0.0050	0.010	0.020	0.050
R/Ω	3314	1669	342.1	174.1	89.08	37.14

The viscosity of water is $1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$.

- i) Verify that the molar conductivity follows Kohlrausch's law and [3]
 ii) find the limiting molar conductivity, Λ_m^o . [2]
 iii) Determine the Kohlrausch coefficient κ . [2]
- c) Given the transport number of Na^+ ion in 0.005 M solution is 0.3930 and using the information calculated in 'd' above, calculate:
- i) the molar conductivities [2]
 ii) mobilities [2]
 iii) diffusion coefficients [2]
 iv) hydrodynamic radii [2]
- of Na^+ and Cl^- ions in solution.

Useful equations:

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

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

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 above isotherm. [10]

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

$V \times 10^6 / \text{m}^3$	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.

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]

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

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

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		c	2.997 925 × 10 ⁸ ms ⁻¹
(RT/F) _{298.15K} = 0.025 693 V		e	1.602 19 × 10 ⁻¹⁹ C
T/K:	100.15 298.15 500.15 1000.15	F = Le	9.648 46 × 10 ⁴ C mol ⁻¹
T/Cm ⁻¹ :	69.61 207.22 347.62 695.13	k	1.380 66 × 10 ⁻²³ J K ⁻¹
1 mmHg =	133.222 N m ⁻²	R = Lk	8.314 41 J K ⁻¹ mol ⁻¹
hc/k =	1.438 78 × 10 ⁻² m K		8.205 75 × 10 ⁻² dm ³ atm K ⁻¹ mol ⁻¹
1 atm	1 cal	1 eV	1 cm⁻¹
-1.01325 × 10 ⁵ Nm ⁻²	-4.184 J	-1.602 189 × 10 ⁻¹⁹ J	-0.124 × 10 ⁻³ eV
-760 torr	-96.485 kJ/mol	-96.485 kJ/mol	-1.9864 × 10 ⁻²³ J
-1 bar	= 8065.5 cm ⁻¹		
SI-units:			
1 L = 1000 ml = 1000 cm³ = 1 dm³			
1 dm = 0.1 m			
1 cal (thermochemical) = 4.184 J			
dipole moment: 1 Debye = 3.335 64 × 10 ⁻³⁰ C m			
force: 1 N = 1 J m ⁻¹ = 1 kg ms ⁻² = 10 ⁵ dyne pressure: 1 Pa = 1 Nm ⁻² = 1 Jm ⁻³			
1 J = 1 Nm			
power: 1 W = 1 J s ⁻¹		potential: 1 V = 1 J C ⁻¹	
magnetic flux: 1 T = 1 V sm ⁻² = 1 J Csm ⁻²		current: 1 A = 1 Cs ⁻¹	
Prefixes:			
p	n	m	m
pico	nano	micro	milli
10 ⁻¹²	10 ⁻⁹	10 ⁻⁶	10 ⁻³
		10 ⁻²	10 ⁻¹
		10 ¹	10 ²
		10 ³	10 ⁶
		10 ⁹	10 ¹²
		10 ¹⁵	10 ¹⁸
		10 ²¹	10 ²⁴
		10 ²⁷	10 ³⁰
		10 ³³	10 ³⁶
		10 ³⁹	10 ⁴²
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		10 ¹²⁹³	10 ¹²⁹⁶
		10 ¹³⁰⁰	10 ¹³⁰²
		10 ¹³⁰⁶	10 ¹

THE PERIODIC TABLE OF ELEMENTS

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	VII B	VIII B	IIIB	IB	II B	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
Period 1	1 H 1.008																		
2	3 Li 6.94	4 Be 9.01												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												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 79.9	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			

NON-METALS

METALLOIDS

METALS

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.