UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE
SUPPLEMENTARY 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) i) Derive and calculate the root mean square speed of CO_2 molecules at 298 K. [5]

ii) Given the Maxwell Botzmann distribution of molecular speeds what is the probability that the CO_2 molecules travel within ± 1 m/s of its root mean square speed at 25°C. [4]

a) Write the general Ficks first law for flux, J_X, for the following transport phenomena in gases:

(i) thermal conductivity [3]
(ii) viscocity [3]
(ii) Diffusion [3]

b) The pressure gradient of Argon, Ar, at 25°C and 100 kPa is 0.1 atm cm^{-1}.
Assuming ideal gas behaviour,

i) Calculate the diffusion constant . [3]
ii) Calculate the flow of gas, Jx, due to diffusion. [4]

Useful equation: $D = \frac{1}{3}\lambda \bar{c}$

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 ϖ 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

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

Is given by: $[A]_t = [A]_o \left[\frac{k_{-1} + k_1 EXP[-(k_1 + k_{-1})]t}{k_1 + k_{-1}} \right]$ [5]

Question 3 [25 Marks]

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

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ES] \xrightarrow{k_2} P$$

a) i) Using the steady state approximation and the Lineweaver-Burk treatment show that Michaelis-Menten equation is: [6]

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

ii) 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 [3]

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

V_o/ 10^{-5}mol $dm^{-3}s^{-1}$	13	20	29	38
[S]/10^{-3} 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 g/mol
Calculate:

i) Michaelis constant, K_m [5]
ii) V_{max} [3]
iii) The number of substrate molecules converted into product per unit time, when the enzyme is fully saturated with substrate. [2]

Question 4 [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. [10]

Useful relations:

$$\eta = \tfrac{1}{3} m\lambda\bar{c}[A]; \eta = C\exp\left(\tfrac{\Delta E_{vis}}{RT}\right),\ \bar{c} = \sqrt{\frac{8RT}{\pi MW}},\ \lambda = {}^{kT}\!/\!_{\sqrt{2}}\sigma P \text{ and } 1\text{Poise}=1\text{P} = 0.1\ \text{Nm}^{-2}\text{s}$$

(b) Viscosity of gases flowing in tubes is given by Poiseuille's formula:

$$\eta = \frac{\pi R^4\left(P_1^2 - P_2^2\right)}{16 l P_o V} t$$

The viscosity of carbon dioxide was measured by comparing its rate of flow through a long narrow tube with that of argon. For the same pressure differential, the same volume of carbon dioxide passed through the tube in 55 s as that of argon in 83 s. The viscosity of argon at 25^{o}C is 208 μP;

i) what is the viscosity of carbon dioxide? [2]

ii) Estimate the molecular diameter of carbon dioxide. [2]

(c) 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 3-dimensions [4]

useful relation: $<r>^2 = <x>^2 + <y>^2 + <z>^2;\ <x>^2 = <y>^2 = <z>^2$

(ii) The diffusion coefficient of a molecule MH_2Cl_2 in octane at 24.8^{o}C is 5×10^{-10} m^2s^{-1}, estimate the 3-dimensional root mean square displacement, r_{rms}, for the molecule after 2500 seconds. [3]

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

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:

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

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 1.00×10^{-3} $kgm^{-1}s^{-1}$.

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^{-1} ions in solution.

Useful equations:

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

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

Question 6 [25 Marks]

a) Distinguish in some detail between physisorption and chemisorption [10]
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) The data below are for the chemisorption of hydrogen on copper powder at 25°C..

P/Torr	0.19	0.97	1.90	4.05	7.50	11.95
V_a/cm^3	0.042	0.163	0.221	0.321	0.411	0.471

i) Confirm that they fit the Langmuir isotherm at low coverages. [6]
ii) Find the value of K for the adsorption equilibrium and the adsorption volume corresponding to complete coverage.[4]

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

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 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

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	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	56 **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.*
SOURCE: International Union of Pure and Applied Chemistry, I mills, ed., Quantities, Units, and symbols in Physical Chemistry, Blackwell Scientific publications, Boston,