

UNIVERSITY OF ESWATINI

SUPPLEMENTARY EXAMINATION 2018/2019

TITLE OF PAPER: **ADVANCED PHYSICAL CHEMISTRY**

COURSE NUMBER: **C402**

TIME: **THREE (3) HOURS**

INSTRUCTIONS:

There are **six (6)** questions. Each question carries 25 marks. Answer **any four (4)** questions.

NB: Each question should start on a new page.

A data sheet and a periodic table are attached

A non-programmable electronic calculator may be used

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Question 1 [25 Marks]

- a) The Maxwell Boltzmann distribution function of velocities in three dimensions between $v \rightarrow v + dv$ is

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

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

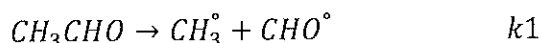
Useful equations

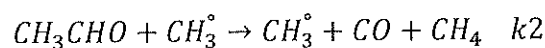
$$Z_A = \frac{\sqrt{2}\sigma\bar{v}p}{kT}; \quad Z_{AA} = \frac{1}{2}Z_A \frac{N}{V}; \quad \bar{v} = \left(\frac{8RT}{\mu M}\right)^{\frac{1}{2}}; \quad \lambda = \frac{kT}{\sigma p\sqrt{2}}$$

- iii. Calculate the mean free path of nitrogen gas using the parameters above [5]
- iv. Calculate the time intervals between collisions [3]
- v. Does the nitrogen gas obey the kinetic theory of gasses? Verify and give reasons for your answer. [2]

Question 2 [25 Marks]

- a) In an experiment to measure quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100W source for 45 minutes. The intensity of the transmitted light was 40% of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Calculate the quantum efficiency. [6]
- b) The rate constant for the bimolecular elementary gaseous reaction $CO + O_2 \rightarrow CO_2 + O$ is 1.22×10^5 M/s at 2500K and 3.66×10^5 M/s at 2800K.
- i. Calculate the activation energy and pre exponential factor. [7]
 - ii. Assuming a hard sphere with a diameter of 350pm for O_2 and of 360 pm for CO, calculate the steric factor in the collision theory. [6]
- c) A proposed free radical chain mechanism for the decomposition of acetaldehyde consists of the following steps:



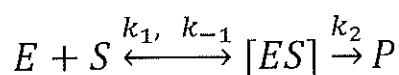


Show that the rate of formation of methane is

$$\frac{d[CH_4]}{dt} = k_2 \left(\frac{k_1}{2k_3} \right)^{1/2} [CH_3CHO]^{3/2} \quad [6]$$

Question 3 [25 Marks]

- a) The mechanism for enzyme catalyzed reactions as proposed by V. Henri (1903) is



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

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

- 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 catalyzed reaction:

$V_o/10^{-3}M/s$	13	20	29	38
$[S]/10^{-3}M$	2.0	4.0	8.0	20

Given that the enzyme concentration is 2.0 g/dm^3 and the molar weight is 50 000g/mol, using an appropriate plot, calculate

- i. K_m [6]
 ii. V_{max} [2]
 iii. The number of substrate molecules converted into products per unit time when the enzyme is fully saturated with substrate. [3]

Question 4 [25 Marks]

The Kohlrausch equation for strong electrolytes is

$$\Lambda_m(c) = \Lambda_m^0 - K\sqrt{c}$$

And the Ostwald dilution law for weak electrolytes states;

$$K_{eq} = \left(\frac{\left(\frac{\Lambda'_m}{\Lambda_m^0} \right)}{\left(\frac{\Lambda'_m}{\Lambda_m^0} \right)} \right) c$$

- a) Using diagrams where necessary, explain in terms of the relaxation effect and the electrophoretic effect, the concentration dependence of molar conductivities shown by both strong and weak electrolytes. [4]
- b) Derive the Ostwald dilution law and express it in its linearized form [3]
- c) The following conductivity data are for a weak acid, $\text{MH}_3\text{CO}_2\text{H}$ in aqueous solution at 25 °C.

$c/10^{-3} \text{ M}$	6.25	3.13	1.56	0.781	0.391	0.195	0.0977
$\Lambda_m/\text{Scm}^2/\text{mol}$	53.1	72.4	96.8	127.7	164.0	205.8	249.2

And the viscosity of water is given by $\eta = 1.00 \times 10^{-3} \text{ kg}/(\text{ms})$

Determine

- The limiting conductivity [2]
- pKa value [2]
- the transport number of the MH_3COO^- and the H^+ ions given that the limiting conductivity of MH_3COO^- to be $40.9 \text{ Scm}^2/\text{mol}$ [2]
- mobility of MH_3COO^- in units of $\text{m}^2/(\text{Vs})$ [2]
- diffusion coefficient of MH_3COO^- in units of m^2/s [2]
- hydrodynamic radius of MH_3COO^- [2]

Useful information

$$K = \left(\frac{1}{R} \right) \frac{1}{A}; t_{\pm} = \frac{\lambda_{\pm}}{\lambda_{-} + \lambda_{+}} = \frac{\lambda_{\pm}}{\Lambda_m^0} = \frac{u_{\pm}}{u_{-} + u_{+}}; \Lambda_m^0 = v_{+}\lambda_{+} + v_{-}\lambda_{-}; \lambda_{\pm} = zu_{\pm}F; t_{+} + t_{-} = 1$$

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

- d) Describe any one method of determining transport numbers. [3]

- e) In a moving boundary experiment on KCl, the aqueous consisted of a tube of internal diameter 4.146 mm, and it contained aqueous KCl at concentration of 0.021 M. 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 $149.9 \text{ Scm}^2/\text{mol}$ [3]

Useful information

$$t = \frac{zcVF}{I\Delta t}$$

Question 5 [25 Marks]

- a) Distinguish between physisorption and chemisorption [5]
 b) The Langmuir adsorption isotherm for non-dissociative adsorption of a single species is given by;

$$\theta = \frac{kP}{1 + kP}$$

Outline the kinetic argument used to derive the adsorption isotherm for two molecules A and B as given by [5]

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}, \quad \theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B}$$

- c) An adsorption isotherm for nitrogen adsorbed on a sample of colloidal silica was measured at -19°C and the following data was obtained:

$V/ \times 10^6/\text{m}^3$	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 P_0 is the measured saturated vapour pressure of nitrogen at the given temperature.

- 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 molecule occupies 0.162 nm^2 in a monolayer. [10]

Useful equation

$$\text{BET isotherm is given by: } \frac{P}{V(P_0 - P)} = \frac{1}{CV_m} + \frac{C-1}{CV_m} \frac{P}{P_0}$$

where P_0 is the bulk vapour pressure is the equilibrium vapour pressure, V_m is the monolayer volume capacity and V the total volume of material adsorbed

Question 6 [25 Marks]

- a) Explain why the polarizability of a molecule decreases at high frequencies [5]
 b) The polarizability volume of NH_3 is $2.22 \times 10^{-24} \text{ cm}^3$. Calculate the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength 15.0 kV/m . [5]
 c) The molar polarization, P_m , is defined as $P_m = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right)$. The molar

polarization of gaseous water at 100 kPa , is given in the table below.

T/K	384.3	420.1	444.7	484.1	522.0
$P_m/(\text{cm}^3/\text{mol})$	57.4	53.5	50.1	46.8	43.1

Calculate:

- i. The polarizability volume of water. [15]

Total /100/

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$
Elementary charge	e	$1.602\,177 \times 10^{-19} \text{ C}$
Faraday constant	$F = N_A e$	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = N_A k$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$
		$8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
		$6.2364 \times 10 \text{ L Torr K}^{-1} \text{ mol}^{-1}$
Planck constant	h	$6.626\,08 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$
Avogadro constant	N_A	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	u	$1.660\,54 \times 10^{-27} \text{ Kg}$
Mass		
electron	m_e	$9.109\,39 \times 10^{-31} \text{ Kg}$
proton	m_p	$1.672\,62 \times 10^{-27} \text{ Kg}$
neutron	m_n	$1.674\,93 \times 10^{-27} \text{ Kg}$
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
	$4\pi\epsilon_0$	$1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability	μ_0	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$
		$4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3$
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$
g value	g_e	2.002 32
Bohr radius	$a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$
Fine-structure constant	$\alpha = \mu_0 e^2 c / 2\hbar$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4 / 8\hbar^3 c \epsilon_0^2$	$1.097\,37 \times 10^7 \text{ m}^{-1}$
Standard acceleration of free fall	g	$9.806\,65 \text{ m s}^{-2}$
Gravitational constant	G	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ Kg}^{-2}$

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	$1 \times 10^{-7} \text{ J}$
1 eV	=	$1.602\,2 \times 10^{-19} \text{ J}$	1 eV/molecule	=	$96\,485 \text{ kJ mol}^{-1}$

Prefixes	f	p	n	μ	m	c	d	k	M	G
	femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	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			IB	IIB	IIIA	IVA	V A	VI A	VII A	VIIIA	VIIIA
1	H 1.008																		He 4.003
2	Li 6.941	Be 9.012																	Ne 20.180
3	Na 22.990	Mg 24.305																	Ar 39.948
TRANSITION ELEMENTS																			
4	K 39.098	Ca 40.078	Sc 44.956	Ti 47.88	V 50.942	Cr 51.996	Mn 54.938	Fe 55.847	Co 58.933	Ni 58.69	Cu 63.546	Zn 65.39	Ga 69.723	Ge 72.61	As 74.922	Se 78.96	Br 79.904	Kr 83.80	
5	Rb 85.468	Sr 87.62	Y 88.906	Zr 91.224	Nb 92.906	Mo 95.94	Tc 98.907	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.71	Sb 121.75	Tc 127.60	I 126.90	Xe 131.29	
6	Cs 132.91	Ba 137.33	*La 138.91	Hf 178.49	Ta 180.95	W 183.85	Re 186.21	Os 190.2	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	Po (209)	At (210)	Rn (222)	
7	Fr 223	Ra 226.03	**Ac (227)	Rf (261)	Rn (262)	Uuh (263)	Uus (262)	Uuo (265)	Uue (266)	Uun (267)									

Atomic mass →
Symbol →
Atomic No. →

140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Du 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

() indicates the mass number of the isotope with the longest half-life.

*Lanthanide Series

**Actinide Series