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 →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 x 10^5 M/s at 2500K and 3.66 x 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:

$$CH_3CHO \rightarrow CH_3^{\circ} + CHO^{\circ} \qquad k1$$

$$CH_3CHO + CH_3^{\circ} \rightarrow CH_3^{\circ} + CO + CH_4 \quad k2$$

$$2CH_3^{\circ} \rightarrow C_2H_6 \quad k3$$

Show that the rate of formation of methane is

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

Question 3 [25 Marks]

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

$$E + S \overset{k_1,\ k_{-1}}{\longleftrightarrow} [ES] \overset{k_2}{\rightarrow} P$$

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:

$Vo/10^{-3}M/s$	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. Km **[6]**

ii. Vmax **[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

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

And the Ostwald dilution law for weak electrolytes states;

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

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, MH_3CO_2H in aqueous solution at 25 °C.

$c/10^{-3}$ M	6.25	3.13	1.56	0.781	0.391	0.195	0.0977
Λ_m/Scm²/mol	53.1	72.4	96.8	127.7	164.0	205.8	249.2

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

Determine

i. The limiting conductivity **[2]**

ii. pKa value **[2]**

iii. the transport number of the MH_3COO^- and the H+ ions given that the limiting conductivity of MH_3COO^- to be 40.9 Scm²/mol **[2]**

iv. mobility of MH_3COO^- in units of $m^2/(Vs)$ **[2]**

v. diffusion coefficient of MH_3COO^- in units of m^2/s **[2]**

vi. hydrodynamic radius of MH_3COO^- **[2]**

Useful information

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

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

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:

Δt/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 Scm^2/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]**

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

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/ x 10^6/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 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

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

where P_o 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 x 10^{-24} 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 $P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$. 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
$P_m/(cm^3/mol)$	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	$2.997\,924\,58 \times 10^{8}\ m\ s^{-1}$
Elementary charge	e	$1.602\,177 \times 10^{-19}\ C$
Faraday constant	$F = N_A e$	$9.6485 \times 10^{4}\ C\ mol^{-1}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23}\ J\ K^{-1}$
Gas constant	$R = N_A k$	$8.314\,51\ J\ K^{-1}\ mol^{-1}$
		$8.205\,78 \times 10^{-2}\ dm^{3}\ atm\ K^{-1}\ mol^{-1}$
		$6.2364 \times 10\ L\ Torr\ K^{-1}\ mol^{-1}$
Planck constant	h	$6.626\,08 \times 10^{-34}\ J\ s$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}\ J\ s$
Avogadro constant	N_A	$6.022\,14 \times 10^{23}\ mol^{-1}$
Atomic mass unit	u	$1.660\,54 \times 10^{-27}\ Kg$
Mass		
electron	m_e	$9.109\,39 \times 10^{-31}\ Kg$
proton	m_p	$1.672\,62 \times 10^{-27}\ Kg$
neutron	m_n	$1.674\,93 \times 10^{-27}\ Kg$
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}\ J^{-1}\ C^{2}\ m^{-1}$
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}\ J^{-1}\ C^{2}\ m^{-1}$
Vacuum permeability	μ_0	$4\pi \times 10^{-7}\ J\ s^{2}\ C^{-2}\ m^{-1}$
		$4\pi \times 10^{-7}\ T^{2}\ J^{-1}\ m^{3}$
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}\ J\ T^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}\ J\ T^{-1}$
g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}\ m$
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^{\,2}$	$1.097\,37 \times 10^{7}\ m^{-1}$
Standard acceleration of free fall	g	$9.806\,65\ m\ s^{-2}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}\ N\ m^{2}\ Kg^{-2}$

Conversion factors

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

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

TRANSITION ELEMENTS

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

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

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