UNIVERSITY OF ESWATINI

FINAL EXAMINATION 2018/2019

TITLE OF PAPER: **APPLIED PHYSICAL CHEMISTRY**

COURSE NUMBER: **CHE442**

TIME: **THREE (3) HOURS**

INSTRUCTIONS:

There are **2 sections in this paper. Answer Section A and any three other questions in section B.**

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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SECTION A. [15 Marks]

a) At 25 °C, k= 1.55 $L^2Mol^{-2}min^{-1}$ at an ionic strength of 0.0241 for a reaction in which the rate determining step involves an encounter of two single charged cations. Use the Debye-Huckel limiting law to estimate the rate constant at zero ionic strength **[5]**

b) Nitrogen gas adsorbed on a surface to the extent of 1.242 cm^3/g at 350 kPa ad 180 K, but at 240K the same amount of adsorption was achieved only when the pressure was increased to 1.02 MPa. What is the enthalpy of adsorption of nitrogen on the surface? **[5]**

c) The magnitude of the electric field at a distance r from the point charge Q is equal to $Q/4\pi\varepsilon_o r^2$. How close to a water molecule (of polarizability volume 1.48 x $10^{-30}m^3$) must a proton approach before the dipole moment it induces has a magnitude equal to that of the permanent dipole moment of the molecule (1.85D). **[5]**

SECTION B [75 Marks]

Question 1. [25 Marks]

a) Explain why the polarizability of a molecule decreases at high frequencies **[6]**

b) Suppose you are told that Ozone adsorbs on a particular surface in accordance with a Langmuir isotherm. How would you use the pressure dependence of the fractional coverage to distinguish between adsorption without dissociation and with dissociation? **[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 using a graphical method. **[14]**

Question 2 [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:

$V / \times 10^6/m^3$	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 3 [25 Marks]

a) A solid in contact with a gas at 12 kPa and 25 °C adsorbs 2.5 mg of the gas and obeys Langmuir isotherm. The enthalpy change when 1.0 mmol of the adsorbed gas is desorbed is +10.2 kJ/mol. What is the equilibrium pressure at 40°C? **[8]**

b) Explain the origin of the London (dispersion) interaction **[5]**

c) The relative permittivity of chlorobenzene was measure at different temperatures:

$\theta/^{o}C$	-50	-20	20
ε_r	7.28	6.3	5.71

Assuming that the density, which is 1.11 g/cm^3, does not change with temperature, estimate the dipole moment of this compound [molar mass = 112.45 g/mol] **[8]**

d) The glacial angle of a Bragg reflection from a set of crystal planes separated by 99.3 pm is 20.85°. Calculate the wavelength of the x-rays. **[4]**

Question 4 [25 Marks]

a) Consider the following reaction:

$H_{2(g)}$ + 2AgCl(s) → 2HCl (aq) + 2Ag(s)

i. Devise a cell in which the above reaction is the cell reaction **[2]**

ii. Write the Nernst equation for the cell in (i) above. **[1]**

b) The Zero-current potential for the above cell was 0.3524 V when the molality of HCl was 0.100 mol/kg and the hydrogen pressure was 1 bar. Calculate the activity and mean activity coefficient of the HCl assuming hydrogen is a perfect gas. **[4]**

c) Calculate the percent error in the mean activity coefficient if the Debye-Huckel limiting law is used to calculate it. **[2]**

d) Using the standard potentials of the couples Co^{3+}/Co^{2+}, Co^{2+}/Co and $AgCl/Cl^{-},Ag$ calculate the standard potential and equilibrium constant of the following reaction. **[12]**

$$Co^{3+}(aq)+3Cl^{-}+3Ag(s)\rightarrow 3AgCl(s)+Co(s)$$

e) Calculate the masses (separately) of

i. KNO_{3}(aq) and

ii. $Ba(NO_3)_2$ (aq) to add to a 0.110 mol/kg solution of KNO_3(aq) containing 500g of solvent to raise its ionic strength to 1.00. **[4]**

TOTAL **/90 Marks/**

General data and fundamental constants

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

Conversion factors

1 cal = 4.184 joules (J)

1 eV = $1.602\ 2 \text{ X } 10^{-19}$ J

1 erg = $1 \text{ X } 10^{-7}$ 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

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

TRANSITION ELEMENTS

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	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	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.