UNIVERSITY OF ESWATINI

RE-SIT 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) In the dimerization of methyl radicals at 25 °C, the pre exponential factor is 2.4 x 10^{10} $dm^3mol^{-1}s^{-1}$. What are the reactive cross section and the p-factor for the reaction if the C-H bong length is 154 pm? **[5]**

b) Suppose you are told that Ozone adsorbs on a particular surface in accord 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) Account for the dependence of catalytic activity of the surface on the strength of chemisorption. **[5]**

SECTION B [75 Marks]

Question 1. [25 Marks]

a) Explain why the reaction of two ions with the same charge increases with increasing ionic strength where as that of ions of opposite charges decreases with increasing ionic strength. **[5]**

b) Define or briefly explain what the following terms mean in kinetics
   - *i.* Collision cross section
   - *ii.* Cage effect
   - *iii.* Diffusion controlled reactions **[6]**

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 graphical method. **[14]**

Question 2 [25 Marks]

a) What assumptions did Langmuir make when deriving his isotherm $\theta = \frac{\alpha p}{1+\alpha p}$ [4]

b) For N_2 adsorbed on a certain sample of charcoal at -77 °C, the volume of adsorbed N_2 (measured at 0 °C and 1 atm) per gram of charcoal varied with N_2 pressure as given below:

P/atm	3.5	10.0	16.7	25.7	33.5	39.2
V/(cm^3/g)	101	136	153	162	165	166

i. Show that the data fits the Langmuir isotherm.

ii. Determine the value of α

iii. Determine the volume of N_2 needed for monolayer coverage. **[10]**

c) CO adsorbs non-dissociatively on the (111) plane of Ir with A_{des} = 2.4 x 10^{14}/s and $E_{a,des}$ = 151kJ/mol. Find the half life of CO chemisorbed on Ir (111) at 300K **[3]**

d) The adsorption of solutes on solids from liquids often follows a Freundlich isotherm, $\theta = kp^{\frac{1}{n}}$. Adapt the equation to apply to a solution and check its applicability to the following data for the adsorption of acetic acid on charcoal and determine the constants ***k*** and **n**.

[acid]mol/L	0.05	0.10	0.50	1.0	1.5
W_a/g	0.04	0.06	0.12	0.16	0.18

W_a is the mass adsorbed per unit mass of charcoal. **[8]**

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:

$\theta/^oC$	-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) Define the ionic strength of a solution. What is the molality of $Al_2(SO_4)_3$ that has the same ionic strength as 0.500 mol/kg $Ca(NO_3)_2$ **[6]**

b) Devise cells in which the following are the reactions

i. $H_2(g) + I_2(g) \rightarrow 2HI(aq)$ **[3]**

ii. $Sn(s) + 2AgCl(s) \rightarrow SnCl_2(aq) + 2Ag(s)$ **[3]**

c) Derive an expression for the potential of an electrode for which the half reaction is the reduction of MnO_4^- ions and Mn^{2+} ions in acidic solution **[6]**

d) The standard potential of the AgCl/Ag, Cl^- couple has been measured over a range of temperatures and the results were found to fit the expression

$E^\theta/V = 0.23659 - 4.8564 \times 10^{-4} (\theta/^oC) - 3.4205 \times 10^{-6} (\theta/^oC)^2 + 5.869 \times 10^{-9} (\theta/^oC)^3$

Calculate the standard Gibbs energy of formation of $Cl^-(aq)$ at 25°C

[$\Delta_f G^\theta(AgCl,s) = -109.79$ kJ/mol **[7]**

TOTAL **/90 Marks/**

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	$F = N_A e$	9.6485×10^{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}
		6.2364×10 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	ge	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	=	1×10^{-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

PERIODS	GROUPS 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	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								

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

TRANSITION ELEMENTS

*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.