UNIVERSITY OF ESWATINI

FINAL EXAMINATION 2018/2019

TITLE OF PAPER: ADVANCED PHYSICAL CHEMISTRY

COURSE NUMBER: C402

TIME: THREE (3) HOURS

INSTRUCTIONS:

There are **six (6)** questions and 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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QUESTION1. [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) Starting with dw = dμ and that $\mu = \mu^\theta + RT\ln a$, show that the thermodynamic force is given by

$$F = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T}$$ **[7]**

e) 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]**

Question 2. [25 Marks]

a) 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]**

b) In a moving boundary experiment on KCl the apparatus consisted of a tube of internal diameter of 4.146 mm and it contained an aqueous KCl at a concentration of 0.021 mol/L. A steady current of 18.2 mA was passed and the boundary advanced as follows:

Δt/s	200	400	600	800	1000
x/mm	64	128	192	254	318

Find the transport number of K^+, its mobility and its ionic conductivity

$[\Lambda_m^o(KCl) = 149.9 Scm^2 mol^{-1}]$ **[10]**

c) 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]**

Question 3 [25 Marks]

a) Distinguish between reaction order and molecularity **[5]**

b) The oxidation of bromine ions by hydrogen peroxide in acidic solution

$2Br^-(aq) + H_2O_2 + 2H^+ \rightarrow Br_2(aq) + 2H_2O(l)$

Follows the rate law

$v = k[H_2O_2][H^+][Br^-]$

i. If the concentration of hydrogen peroxide is increased by a factor of 3, by what factor is the rate of consumption of Br- ions increased? **[3]**

ii. If under certain conditions, the rate of consumption of Br- ions is 7.2×10^{-3} mol/Ls, what is the rate of consumption of hydrogen peroxide **[2]**

iii. What is the effect on the rate constant k of increasing the concentration of the bromine ions? **[2]**

iv. If by the addition of water to the reaction mixture the total volume was doubled, what would be the effect on the rate of change of Br-? What would be the effect on the rate constant k? **[3]**

c) The data below apply to the formation of urea from ammonium cyanate according to the reaction

$NH_4CNO \rightarrow NH_2CONH_2$

Initially, 22.9g of ammonium cyanate was dissolved in enough water to prepare 1L of solution.

Time/s	0	20	50	65	150
Mass urea/g	0	7	12.1	13.8	17.7

i. Show that the reaction follows second order rate law **[5]**

ii. Determine the rate constant [2]

iii. Determine the mass of ammonium cynate left after 300 minutes [3]

Question 4 [25 Marks]

a) Explain the essential features of a chain reaction [4]

b) Hydrogen iodide undergoes decomposition into H_2 + I_2 when irradiated radiation having a wavelength of 207nm. It is fund that when 1J of energy is absorbed, 440 µg of HI is decomposed. How many molecules of HI are decomposed by the photon of radiation of this wavelength [8]

c) At 25°C. K= $1.55L^2Mol^{-3}$ min^{-1} at an ionic strength of 0.0241 for a reaction in which the rate determining step involves the encounter two singly charged cations. Use the Debye-Huckel limiting law to estimate the rate constant at zero ionic strength. [5]

d) 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]

e) The reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is believed to follow the following mechanism:

$$2NO \xrightarrow{k1} N_2O_2$$

$$N_2O_2 \xrightarrow{k-1} 2NO$$

$$N_2O_2 + O2 \xrightarrow{k2} 2NO_2$$

i. Assume N_2O_2 to be in a steady state and derive the rate equation. [4]

ii. Under what conditions the rate equation does reduces to second order kinetics in NO and first order kinetics in O_2? [4]

Question 5 [25 Marks]

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

b) The reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is believed to follow the following mechanism:

$$2NO \xrightarrow{k1} N_2O_2$$
$$N_2O_2 \xrightarrow{k-1} 2NO$$
$$N_2O_2 + O2 \xrightarrow{k2} 2NO_2$$

iii. Assume N_2O_2 to be in a steady state and derive the rate equation. **[4]**

iv. Under what conditions the rate equation does reduces to second order kinetics in NO and first order kinetics in O_2? **[4]**

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

θ/°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 6 [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) A solution of potassium permanganate in water at 25 °C was prepared. A solution was in a horizontal tube of length 10 cm, and at first there was a linear gradation of intensity of purple solution from left where the concentration was 0.100mol/L to the right where the concentration was 0.050 mol/L. what is the magnitude and sign of the thermodynamic force acting on the solute

i. Close to the left face of the container

ii. In the middle

iii. Close to the right face **[8]**

TOTAL **/100 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

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
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

*Lanthanide Series

**Actinide Series

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