UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2017/2018

TITLE OF PAPER: **ADVANCED PHYSICAL CHEMISTRY**

COURSE NUMBER: **C402**

TIME: **THREE (3) HOURS**

INSTRUCTIONS:

There are **seven (7)** questions in **four** sections. Each question carries 25 marks. **Answer at least one question from each section (four Questions in total)**

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

QUESTION1. [25 Marks]

a) Explain why each of the formulas for the transport coefficients in the kinetic theory of gases is proportional to the mean free path (λ) and the mean speed (υ_{mean}) [4]

b) Explain why you would expect the viscosity of nitrogen gas to increase with an increase in temperature whilst the viscosity of nitrogen liquid is expected to decreases with an increase in temperature. [4]

c) The viscosity of CO_2 at 1atm and 0^oC is 139 μP. Calculate the collision cross section of CO_2 at this temperature. [4]

d) A solid surface with dimensions 3.5 mm x 4 cm is exposed to helium gas at 111 Pa and 1500 K. How many collisions do the He atoms make with the surface in 100s. 4]

e) The diffusion coefficient of glucose in water is 6.81 x 10^{-10} m^2s^{-1} at 25^oC. The viscosity of water at the same temperature is 8.937 x 10^{-4} $kgm^{-1}s^{-1}$ and the density of glucose is 1.55g/cm^{-3}. Assuming that Stokes law applies and that the molecule is spherical, estimate

i. The radius of the glucose molecule. [4]

ii. The molar mass of glucose [5]

Question 2. [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 s 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]

SECTION B

Question 3 [25 Marks]

a) Discuss the main features of the isolation method used in the determination of rate laws. [5]

b) The following data were obtained for the decomposition of dinitrogen trioxide.

Time/s	0	184	526	867	1877
$[N_2O_3]$/M	2.33	2.08	1.67	1.36	0.72

i. Show that the decomposition follows the first order kinetics [6]

ii. Determine the value of the rate constant and the half-life of the reaction [4]

c) For the reaction at 298K, $CH_3COO^- + H^+ \leftrightarrow CH_3COOH$, $k_f = 4.5 \times 10^{10}$ M/s and $k_r = 8.0 \times 10^5$ M/s. A solution is made from 0.100 mol acetic acid and enough water to make 1.00L. Find the relaxation time, τ, if a small perturbation is imposed on the solution such that the final temperature is 298.5K. [10]

Question 4 [25 Marks]

a) Briefly explain each of the following by using any equation or diagram of your choice to illustrate your point:

i. The pre-equilibrium approach [5]

ii. The steady state approximation [5]

b) Lundeman's mechanism for the dissociation of ozone in the stratosphere\ $2O_3 \rightarrow 3O_2$ is

$$O_3(ozone) \leftrightarrow O_2 + O \quad k_1, k_{-1}$$
$$O_3 + O \rightarrow 2O_2 \quad k_2$$

Using the steady state approximation, show that the rate law is $v = \frac{k_2 K_{eq}[O_3]^2}{[O_2]}$ [5]

c) The experimental rate law for the reaction:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

$is\ v = k[N_2O_5]$,

The proposed mechanism for the reaction has the following elementary single step processes

$$N_2O_5 \overset{k_1,k_{-1}}{\longleftrightarrow} NO_2 + NO_3\ fast$$

$$NO_2 + NO_3 \overset{k_2}{\rightarrow} NO + NO_2 + O_2\ Slow$$

$$N_2O_5 + NO \overset{k_3}{\rightarrow} NO_2 + NO_2$$

Using the pre equilibrium approach verify whether the proposed mechanism is correct or not [5]

d) Thermal decomposition of a compound has been studied using optical absorption at 350nm. The following data was obtained:

Time/s	0	600	1200	∞
A/absorbance	1.50	0.92	0.65	0.40

Given that the rate law: $ln\frac{A-A_{\infty}}{A_0-A_{\infty}} = ln\frac{[A]}{[A]_o} = -kt$ determine the rate constant, k [5]

SECTION C

Question 5 [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 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) 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 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) 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]

SECTION D

QUESTION 7. [25 marks]

a) With the aid of an equation/diagram or any other information explain the following observations

i. As the Ionic radius increases (r), the limiting molar conductivity (Λ^0_m) and the ion mobility (u), increases [2]

ii. Ionic hydrodynamic radius (a) decreases with an increase of ionic radius (r). [2]

iii. The mobility of H^+ is 9.03 x higher than the mobility of Li^+. [2]

b) Derive the linearised Ostwald dilution law for a weak electrolyte. (clearly show all steps) [4]

c) The following data were obtained for a weak electrolyte, HA in ethanol at 25°C

Concentration, $c/10^{-4}$ mol/dm^{-3}	1.566	2.600	6.219	10.441
Conductivity, $K/10^{-6}$ Scm^{-1}	1.788	2.418	4.009	5.336

i. Show that these data is in accordance with the Ostwald dilution law. [4

ii. Calculate the dissociation constant for this electrolyte. [1]

d) Derive an expression that shows how the pressure of a gas inside an effusing oven varies with time if the oven is not replenished as the gas escapes,

$p = p_0 e^{-\frac{t}{\tau}}, \tau = \left(\frac{2\pi M}{RT}\right)^{\frac{1}{2}} \frac{V}{A}$ where A is the area of the effusing hole and

given that the rate of effusion, $Z_w A = \frac{pAN_A}{(2\pi MRT)^{\frac{1}{2}}}$ and $\int \frac{1}{x} = \ln x$

Then show that the half life ($t_{\frac{1}{2}}$) is independent of the initial pressure. [10]

TOTAL **/100 Marks/**

Useful Information

Debye-Huckel constant A=0.509

Diffusion coefficient $D = \frac{\lambda \upsilon_{mean}}{3}$, Coefficient of thermal conductivity, $K = \frac{1}{3}\frac{\lambda \upsilon_{mean} C_{v,m} N}{V}$,

Coefficient of viscosity $\eta = \frac{m\lambda \upsilon_{mean} N}{3}$, volume of a sphere $V = \frac{4}{3}\pi r^3$,

mass of CO_2=7.306 x 10^{-26} kg. $Z_w = \frac{p}{(2\pi kmT)^{\frac{1}{2}}}$, $\lambda_i = z_i u_i F$, $s = uE$, $D = \frac{kT}{f} = \frac{kT}{6\pi\eta a}$,

$$c = \frac{n_0}{A(\pi Dt)^{\frac{1}{2}}} e^{-x^2/4Dt}$$

Reduction half reaction	$E^{\ominus}$**/V**
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$AgBr + e^- \rightarrow Ag + Br^-$	+0.0713
$Hg_2Cl_2 + 2e \rightarrow 2Hg + 2Cl^-$	+0.2676
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.86
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Co^{2+} + 2e^- \rightarrow Co$	-0.28

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	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	=	1×10^{-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

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										Atomic mass → Symbol → Atomic No. →	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					TRANSITION ELEMENTS						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.