

UNIVERSITY OF ESWATINI



MAIN EXAMINATION 2020/2021

TITLE OF PAPER:	ADVANCED PHYSICAL CHEMISTRY 1
COURSE NUMBER:	C402
TIME ALLOWED:	THREE (3) HOURS
INSTRUCTIONS:	THERE ARE SIX (6) QUESTIONS IN THIS PAPER. ANSWER QUESTION 1 AND ANY THREE OTHER QUESTIONS (EACH QUESTION IS 25 MARKS)

A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER

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QUESTION 1 (25 MARKS)

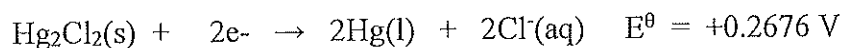
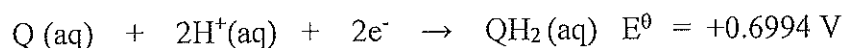
- a) Using diagrams, where necessary, in terms of relaxation effect and electrophoretic effect, explain the concentration dependence of molar conductivities shown by both strong and weak electrolytes. [5]
- b) Write short notes to define the nature and role of enzymes in reaction kinetics. Your notes should include examples to illustrate your answer. [5]
- c) Using an equation of your choice, briefly explain pre-equilibrium approach. [4]
- d) What approximations underlie the BET isotherms [4]
- e) Describe the formation of a hydrogen bond in terms of electrostatic interaction model and state its limitations [3]
- f) Define the mean free path (λ). How does it vary with the number density, particle diameter and particle mean speed. [4]

QUESTION 2 (25 MARKS)

- a) Given that $\Delta_r G^\ominus = -212.7$ kJ/mol for the reaction in a Daniel cell at 25 °C, and that $b(\text{CuSO}_4) = 1.0 \times 10^{-3}$ mol/kg and $b(\text{ZnSO}_4) = 3.0 \times 10^{-3}$ mol/kg, calculate the reaction quotient and the cell potential assuming that the activity coefficients of each ion is equal to the mean activity coefficient in the respective compartments [6]

Debye-Huckel constant A = 0.509

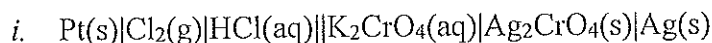
- b) A quinhydrone (quinhydrone, $\text{Q} \cdot \text{QH}_2$ is a complex of quinone, $\text{C}_6\text{H}_4\text{O}_2 = \text{Q}$ and hydroquinone, $\text{C}_6\text{H}_4\text{O}_2\text{H}_2 = \text{QH}_2$) electrode has the reduction half reaction;

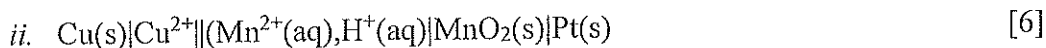


If the cell $\text{Hg} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{HCl}(\text{aq}) | \text{Q} \cdot \text{QH}_2 | \text{Au}$ is prepared and the measured cell potential was found to be +0.190V, calculate the pH of the HCl solution assuming that the Debye-Huckel limiting law holds.

$$\text{pH} = -\log[\text{H}^+] = -\log[a_{\text{H}^+}], \quad \ln x = \ln 10 \log x \quad [6]$$

- c) Write the electrode half reactions and the overall cell reactions for the following.





- d) For the liquid carbon tetrachloride, CCl_4 , at 20°C and 1 atm, the relative permittivity, ϵ_r , is 2.24 and the density is 1.59 g/cm^3 . Calculate the polarizability, α and the polarizability volume α' for CCl_4 . Given that vacuum permittivity, ϵ_0 , is $8.854 \times 10^{-12}\text{ C}^2\text{m}^{-1}\text{J}^{-1}$

[7]

QUESTION 3 (25 MARKS)

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

i. As the Ionic radius increases (r), the ion mobility (u), increases [2]

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

[1]

iii. The mobility of H^+ is 9.03 x higher than the mobility of Li^+ . [3]

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

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a (\Lambda_m^0)^2} \quad \text{Ostwald dilution law} \quad [4]$$

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

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

Show that these data is in accordance with the Ostwald dilution law. [5]

- 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,

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

that the rate of effusion, $Z_w A = \frac{p A N_A}{(2\pi M R T)^{\frac{1}{2}}}$ and $\int \frac{1}{x} = \ln x$

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

QUESTION 4 (25 MARKS)

a) The reaction rate (v) in the reaction $2A + B \rightarrow 2C + 3D$ is $1.0 \text{ mol L}^{-1}\text{s}^{-1}$. State the rate of formation or consumption of A, B, C and D. [4]

b)

i. What is a half life?

ii. Derive the expression that relates the half life to the rate constant and initial concentration for a zero order reaction. [4]

c) For the decomposition of N_2O_5 , the following data was obtained:

$\theta/^\circ\text{C}$	25	35	45	55	65
$k/\text{S}^{-1}(\times 10^{-5})$	1.72	6.55	24.95	75	240

Calculate the activation energy and the pre exponential factor for this reaction

[10]

d) For the reaction, $\text{H}_3\text{O}^+ + \text{OH}^- \leftrightarrow 2\text{H}_2\text{O}$,

i. Show that for a small perturbation, the relaxation time expression for the reaction (with k_f and k_r being the constants for the forward and reverse reactions) is given

by $\frac{1}{\tau} = k_f([H_3O^+] + [OH^-])$ assuming that the concentration of water remains

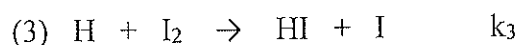
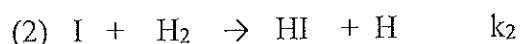
constant even after the perturbation [4]

ii. Hence calculate the equilibrium concentrations of the hydronium and hydroxyl ions which are assumed to be equal at 25°C , given that $\tau = 3.7 \times 10^{-5}\text{s}$ and $k_f = 1.35 \times 10^8 \text{ m}^3 \text{ mole}^{-1}\text{s}^{-1}$. [3]

QUESTION 5 (25 MARKS)

a) Discuss the advantages of photochemical activation over thermal activation in chemical kinetics. [4]

b) The mechanism of a reaction $\text{H}_2(\text{g}) + \text{I}_2 \rightarrow 2\text{HI}(\text{g})$ is



Find the expression of the rate law for the formation of HI using the steady state approximation. [7]

- c) The molar polarization, P_m , is defined as $P_m = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right)$. 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
$P_m/(\text{cm}^3/\text{mol})$	57.4	53.5	50.1	46.8	43.1

Calculate:

- i. The dipole moment
- ii. Polarizability and
- iii. The polarizability volume of water. [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 $A_{\text{des}} = 2.4 \times 10^{14}/\text{s}$ and $E_{\text{a,des}} = 151\text{kJ/mol}$. 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, $\theta = kp^n$. 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]

THE END

/100/

PERIODIC TABLE OF THE ELEMENTS

PERIOD	GROUP	GROUP NUMBERS IUPAC RECOMMENDATION (1985)		GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)		ATOMIC NUMBER		SYMBOL		RELATIVE ATOMIC MASS (1)		ELEMENT NAME																										
		1	2	13	14	15	16	17	18	1	2	3	4																									
1	1	1.008											He HELIUM																									
2	1	6.94	4	9.0122									Ne NEON																									
3	1	39.098	20	40.078									Ar ARGON																									
4	1	39.098	20	40.078									K POTASSIUM																									
4	2	6.94	4	9.0122									Ca CALCIUM																									
5	1	39.098	20	40.078									Rb RUBIDIUM																									
5	2	6.94	4	9.0122									Sr STRONTIUM																									
6	1	132.91	56	137.33									Ba CAESIUM																									
6	2	6.94	4	9.0122									Fr FRANCIUM																									
7	1	223.018	88	226									Ra RADIUM																									
7	2	6.94	4	9.0122									Ac ACTINIUM																									
8	3	21	44	95.96	23	50.942	24	51.996	25	54.938	26	55.845	27	58.933	28	58.933	29	63.546	30	65.38	31	69.723	32	72.64	33	74.922	34	78.971	35	79.904	36	83.798						
8	4	39	88	90.06	40	91.224	41	92.906	42	95.95	43	99	44	101.07	45	102.91	46	108.42	47	107.87	48	112.41	49	114.82	50	118.71	51	121.76	52	127.60	53	126.90	54	131.29				
8	5	37	85	468	38	87.62	39	88.906	40	91.224	41	92.906	42	95.95	43	99	44	101.07	45	102.91	46	108.42	47	107.87	48	112.41	49	114.82	50	118.71	51	121.76	52	127.60	53	126.90	54	131.29
8	6	55	132.91	56	137.33	57	71	72	178.49	73	180.95	74	183.84	75	186.21	76	190.23	77	192.22	78	195.08	79	196.97	80	200.59	81	204.38	82	207.2	83	208.98	84	209	85	210	86	222	
8	7	87	223	226	88	226	89	103	104	267	105	268	106	271	107	272	108	276	109	277	110	281	111	280	112	285	113	285	114	287	115	289	116	294	117	294	118	294
8	8	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262	105	262		
8	9	57	138.91	58	140.12	59	140.91	60	144.24	61	145	62	150.36	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.05	71	174.97							
8	10	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	11	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	12	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	13	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	14	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	15	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	16	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	17	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				
8	18	89	227	232	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262				

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LANTHANIDE

57	138.91	58	140.12	59	140.91	60	144.24	61	145	62	150.36	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.05	71	174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu															
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	Ytterbium	LUTETIUM															

ACTINIDE

89	227	90	232	91	231	92	238	93	237	94	244	95	243	96	247	97	247	98	251	99	252	100	257	101	257	102	258	103	259	104	262
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																	
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	EINSTEINIUM	FERMIUM	MENDELEVIUM	NOBELIUM	LAWRENCIUM																	

(1) Atomic weights of the elements 2013. Pure Appl. Chem., 88, 2463-291 (2016)

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TABLE I An abbreviated list of the CODATA recommended values of the fundamental constants of physics and chemistry based on the 2014 adjustment.

Quantity	Symbol	Numerical value	Unit	Relative std. uncert. u_r
speed of light in vacuum	c, c_0	299 792 458	m s^{-1}	exact
magnetic constant	μ_0	$4\pi \times 10^{-7}$ $= 12.566 370 614... \times 10^{-7}$	N A^{-2}	exact
electric constant $1/\mu_0 c^2$	ϵ_0	$8.854 187 817... \times 10^{-12}$	N A^{-2}	exact
Newtonian constant of gravitation	G	$6.674 08(31) \times 10^{-11}$	F m^{-1}	exact
Planck constant	h	$6.626 070 040(81) \times 10^{-34}$	$\text{m}^3 \text{kg}^{-1} \text{s}^{-2}$	4.7×10^{-5}
$h/2\pi$	\hbar	$1.054 571 800(13) \times 10^{-34}$	J s	1.2×10^{-8}
elementary charge	e	$1.602 176 6208(98) \times 10^{-19}$	J s	1.2×10^{-8}
magnetic flux quantum $h/2e$	Φ_0	$2.067 833 831(13) \times 10^{-15}$	Wb	6.1×10^{-9}
conductance quantum $2e^2/h$	G_0	$7.748 091 7310(18) \times 10^{-5}$	S	6.1×10^{-9}
electron mass	m_e	$9.109 383 56(11) \times 10^{-31}$	kg	2.3×10^{-10}
proton mass	m_p	$1.672 621 898(21) \times 10^{-27}$	kg	1.2×10^{-8}
proton-electron mass ratio	m_p/m_e	$1836.152 673 89(17)$		1.2×10^{-8}
fine-structure constant $e^2/4\pi\epsilon_0\hbar c$	α	$7.297 352 5664(17) \times 10^{-3}$		9.5×10^{-11}
inverse fine-structure constant	α^{-1}	$137.035 999 139(31)$		2.3×10^{-10}
Rydberg constant $\alpha^2 m_e c/2h$	R_∞	$10 973 731.568 508(65)$	m^{-1}	2.3×10^{-10}
Avogadro constant	N_A, L	$6.022 140 857(74) \times 10^{23}$	mol^{-1}	5.9×10^{-12}
Faraday constant $N_A e$	F	$96 485.332 89(59)$	C mol^{-1}	1.2×10^{-8}
molar gas constant	R	$8.314 4598(48)$	$\text{J mol}^{-1} \text{K}^{-1}$	6.2×10^{-9}
Boltzmann constant R/N_A	k	$1.380 648 52(79) \times 10^{-23}$	J K^{-1}	5.7×10^{-7}
Stefan-Boltzmann constant $(\pi^2/60)k^4/\hbar^3 c^2$	σ	$5.670 367(13) \times 10^{-8}$	$\text{W m}^{-2} \text{K}^{-4}$	5.7×10^{-7}
electron volt (e/C) J	eV	Non-SI units accepted for use with the SI		2.3×10^{-6}
(unified) atomic mass unit $\frac{1}{12} m(^{12}\text{C})$	u	$1.602 176 6208(98) \times 10^{-19}$	J	6.1×10^{-9}
		$1.660 539 040(20) \times 10^{-27}$	kg	1.2×10^{-8}