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

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

QUESTION 1 (25 MARKS)

a) Using diagrams, where necessary, in terms of relaxation effect and eletrophoretic 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 $\Delta rG^{\ominus}$ = -212.7 kJ/mol for the reaction in a Daniel cell at 25 °C, and that b($CuSO_4$) = 1. 0 x 10^{-3} mol/kg and b($ZnSO_4$) = 3.0 x 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 quinehydrone (quinehydrone, $Q{\cdot}QH_2$ is a complex of quinine, $C_6H_4O_2$=Q and hydroquinone , $C_6H_4O_2H_2$=QH_2) electrode has the reduction half reaction;

$$Q\,(aq) + 2H^{+}(aq) + 2e^{-} \rightarrow QH_2\,(aq) \quad E^{\theta} = +0.6994\ V$$

$$Hg_2Cl_2(s) + 2e- \rightarrow 2Hg(l) + 2Cl^{-}(aq) \quad E^{\theta} = +0.2676\ V$$

If the cell **Hg | $Hg_2Cl_2(s)$ | HCl (aq) | $Q{\cdot}QH_2$ | 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.

pH =-log[H+]=-log[a_{H+}], lnx=ln10logx [6]

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

i. $Pt(s)|Cl_2(g)|HCl(aq)||K_2CrO_4(aq)|Ag_2CrO_4(s)|Ag(s)$

ii. $Cu(s)|Cu^{2+}||(Mn^{2+}(aq),H^{+}(aq)|MnO_2(s)|Pt(s)$ [6]

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 8.854×10^{-12} $C^2m^{-1}J^{-1}$

[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)

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a(\Lambda_m^0)^2}$$

Ostwald dilution law [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

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,

$$p = p_0 e^{-\frac{t}{\tau}}, \tau = \left(\frac{2\pi M}{RT}\right)^{\frac{1}{2}} \frac{V}{A}$$

where A is the area of the effusing hole and given

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

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

QUESTION 4 (25 MARKS)

a) The reaction rate (υ) in the reaction $2A + B \rightarrow 2C + 3D$ is 1.0 mol $L^{-1}s^{-1}$. 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:

θ/°C	25	35	45	55	65
$k/S^{-1}(\times 10^{-5})$	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, $H_3O^+ + OH^- \leftrightarrow 2H_2O$,

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 τ=3.7 x 10^{-5}s and k_f=1.35 x 10^8 m^3 $mole^{-1}s^{-1}$. [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 $H_2(g) + I_2 \rightarrow 2HI(g)$ is

(1) $I_2 \leftrightarrow 2I$	k_1 and k_1'
(2) $I + H_2 \rightarrow HI + H$	k_2
(3) $H + I_2 \rightarrow HI + I$	k_3

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 $P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$. 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
$P_m/(\mathrm{cm^3/mol})$	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
$V/(\mathrm{cm^3/g})$	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 1014/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

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

THE END **/100/**

PERIODIC TABLE OF THE ELEMENTS

GROUP NUMBERS
IUPAC RECOMMENDATION
(1985)

GROUP NUMBERS
CHEMICAL ABSTRACT SERVICE
(1986)

13 IIIA

ATOMIC NUMBER — 5

10.811 — RELATIVE ATOMIC MASS (1)

SYMBOL — B

BORON — ELEMENT NAME

GROUP

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.008 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.94 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.81 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.085 Si SILICON	15 30.974 P PHOSPHORUS	16 32.06 S SULPHUR	17 35.45 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.971 Se SELENIUM	35 79.904 Br BROMINE	36 83.798 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.95 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (285) Nh NIHONIUM	114 (287) Fl FLEROVIUM	115 (289) Mc MOSCOVIUM	116 (291) Lv LIVERMORIUM	117 (294) Ts TENNESSINE	118 (294) Og OGANESSON

LANTHANIDE

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

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

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(1) Atomic weights of the elements 2013, Pure Appl. Chem., 88, 265-291 (2016)

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	$4\pi \times 10^{-7}$	N A^{-2}	
		$= 12.566\,370\,614... \times 10^{-7}$	N A^{-2}	exact
electric constant $1/\mu_0 c^2$	ϵ_0	$8.854\,187\,817... \times 10^{-12}$	F m^{-1}	exact
Newtonian constant of gravitation	G	$6.674\,08(31) \times 10^{-11}$	m^3 kg^{-1} s^{-2}	4.7×10^{-5}
Planck constant	h	$6.626\,070\,040(81) \times 10^{-34}$	J s	1.2×10^{-8}
$h/2\pi$	$\hbar$	$1.054\,571\,800(13) \times 10^{-34}$	J s	1.2×10^{-8}
elementary charge	e	$1.602\,176\,6208(98) \times 10^{-19}$	C	6.1×10^{-9}
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	2.3×10^{-10}
electron mass	m_e	$9.109\,383\,56(11) \times 10^{-31}$	kg	1.2×10^{-8}
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)		9.5×10^{-11}
fine-structure constant $e^2/4\pi\epsilon_0\hbar c$	α	$7.297\,352\,5664(17) \times 10^{-3}$		2.3×10^{-10}
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}	5.9×10^{-12}
Avogadro constant	N_A, L	$6.022\,140\,857(74) \times 10^{23}$	mol^{-1}	1.2×10^{-8}
Faraday constant $N_A e$	F	96 485.332 89(59)	C mol^{-1}	6.2×10^{-9}
molar gas constant	R	8.314 4598(48)	J mol^{-1} K^{-1}	5.7×10^{-7}
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	$5.670\,367(13) \times 10^{-8}$	W m^{-2} K^{-4}	2.3×10^{-6}
	Non-SI units accepted for use with the SI			
electron volt (e/C) J	eV	$1.602\,176\,6208(98) \times 10^{-19}$	J	6.1×10^{-9}
(unified) atomic mass unit $\frac{1}{12}m(^{12}\mathrm{C})$	u	$1.660\,539\,040(20) \times 10^{-27}$	kg	1.2×10^{-8}