UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2015/2016

TITLE OF PAPER: **PHYSICAL CHEMISTRY**

COURSE NUMBER: **C402**

TIME: **THREE (3) HOURS**

INSTRUCTIONS:

There are **six (6)** questions. Each question carries 25 marks. Answer **Question one (1) and any three (3)** other 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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QUESTION 1 (25 MARKS)

a) Explain how the permanent dipole moment and the polarizability of a molecule arise [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 the steady state approach. [4]

d) What approximations underlie the Langmuir and BET isotherms [4]

e) Why is the stoichiometry of a reaction generally not sufficient to determine the reaction order? When is it possible to infer the reaction order from stoichiometry? [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) The standard potential of the cell Pt(s) | H_2(g) | HBr(aq) | AgBr(s) | Ag(s) was measured over a range of temperatures, and the data was found to fit the following polynomial.

$$E^{\ominus}_{cell}/V = 0.07131 - 4.99\times10^{-4}(T/K - 298) - 3.45\times10^{-6}(T/K - 298)^2$$

i. Evaluate the standard **Gibbs** energy, **enthalpy** and **entropy** at 25 °C. [9]

b) Using the Nernst equation and the Debye-Huckel limiting law for a NaCl-electrolyte, derive the equation used to measure the standard potential when the molality approaches zero.

NB: $2\ln x = \ln x^2$, $\ln 10 \log x = \ln x$

$$E_{cell} + \frac{2RT}{F}\ln b = E^{\ominus} + Cb^{1/2}$$ [8]

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) [8]

QUESTION 3 (25 MARKS)

a) Define or briefly explain what the following terms mean in chemical kinetics

i. Collision cross section

ii. Cage effect

iii. Diffusion controlled reaction

iv. Activation energy

v. Kinetic salt effect [10]

b) The diffusion coefficient of I in CCl_4 is estimated to be 4.2 x 10^{-5} cm^2s^{-1} at 25 °C. Given that the radius of I is about 200pm, calculate the rate constant k_d for

$I + I \rightarrow I_2$ at 25 °C. [5]

c) For the gas phase reaction $A + A \rightarrow A_2$, the experimental rate constant has been fitted to the Arrhenius equation with pre exponential factor A = 4.07 x 10^5 $Lmol^{-1}s^{-1}$ at 300K and the activation energy of 65.43 kJ/mol. Calculate the $\Delta^{\dagger}S$, $\Delta^{\dagger}H$ and $\Delta^{\dagger}G$ for the reaction. [10]

QUESTION 4 (25 MARKS)

a) When a mixture of H_2 and O_2 is irradiated with light of wavelength 253.7nm, no reaction is observed. When a small amount of mercury vapour is added to the mixture and then irradiated with 253.7 nm light, a rapid formation of water is observed. Given that the bond dissociation energies for O_2 and H_2 are 498 and 436 kJ/mol respectively, account for the above observation. [6]

b) The quantum yield is 2 for the photolysis of gaseous HI to I_2 and H_2 by light of 253 nm wavelength. Calculate the number of moles of HI that will be decomposed if 300 J of light of this wavelength is absorbed. [5]

c) An enzyme calalysed reaction conversion of substrate at 25 °C has Michaelis constant of 0.042 mol/L. the rate of reaction is 2.45 x 10-4 molL-1s-1 when the substrate concentration is 0.890 mol/L. What is the maximum velocity of this enzymolysis?

[5]

d) A possible mechanism for the reaction, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ in the presence of mercury vapour is

$$Hg + H_2 \xrightarrow{k1} Hg + 2H\bullet$$
$$H\bullet + C_2H_4 \xrightarrow{k2} \bullet C_2H_5$$
$$\bullet C_2H_5 + H_2 \xrightarrow{k3} C_2H_6 + H\bullet$$
$$H\bullet + H\bullet \xrightarrow{k4} H_2$$

Determine the expression for the rate of formation of C_2H_6 in terms of the rate constants and cconcentrations of Hg, H_2 and C_2H_4 using the steady state approximation

[9]

QUESTION 5 (25 MARKS)

a) Discuss the advantages of photochemical activation over thermal activation in chemical kinetics. [6]

b) The mechanism of the decomposition of $2O_3(g) \rightarrow 3O_2(g)$ is

(1) $O_3 \leftrightarrow O2 + O$ k_1 and $k_1^{'}$

(2) $O + O_3 \rightarrow 2O_2$ k_2

Find the expression of the rate law for the decomposition of ozone (O_3) using the pre-equilibrium Approach. [5]

c) An enzyme catalysed reaction, following the Michelis-Menten mechanism

$E + S \leftrightarrow P + E$ with rate constants k_1, $k_1^{'}$ and k_2,

has the rate law $\frac{d[P]}{dt} = \frac{k_2[S][E]_o}{K_M + [S]}$,where $K_M = \frac{k_1^{'} + k_2}{k_1}$.

The following data relate to such a reaction

[S]/mol L-1	0.00125	0.0025	0.0050	0.020
Rate/mol L^{-1} s^{-1}	2.78×10^{-5}	5.00×10^{-5}	8.33×10^{-5}	1.67×10^{-4}

Given that the enzyme concentration is 2.3 nM, calculate

i. The maximum rate, v_{max}

ii. The Michaeli's constant K_M

iii. k_2

iv. The catalytic efficiency [14]

QUESTION 6 (25 MARKS)

a) Distinguish between physisorption and chemisorption [8]

b) A surface is half covered by a gas when the pressure is 1.0 atm. If the Langmuir isotherm is followed:

i. What is the value of the adsorption coefficient, α? [4]

ii. What pressure would give 90% coverage? [2]

iii. What coverage is given by a pressure of 0.10 atm? [2]

c) 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. [9]

THE END **/100/**

Useful information

Standard potentials at 25 °C

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
$Hg_2Cl_2 + 2e \rightarrow 2Hg + 2\,Cl^{-}$	+0.2676
$Hg^{2+} + 2e^{-} \rightarrow Hg$	+0.86

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	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ 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	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^2$	$1.097\,37 \times 10^7$ 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											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.