UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2010-11

TITLE OF PAPER: ADVANCED PHYSICAL CHEMISTRY

COURSE NUMBER: C402

TIME: THREE (3) HOURS

INSTRUCTIONS:

THERE ARE **SIX** QUESTIONS. EACH QUESTION IS WORTH 25 MARKS. ANSWER **ANY FOUR** QUESTIONS.

A DATA SHEET AND A PERIODIC TABLE ARE ATTACHED

GRAPH PAPER IS PROVIDED

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED.

DO NOT OPEN THIS PAPER UNTIL PERMISSION TO DO SO IS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1 (25marks)

a. A certain solid sample adsorbs 0.44 mg of CO when the pressure of the gas is 26.0 kPa and the temperature is 300 K. The amount adsorbed when the pressure is 3.0 kPa and temperature 300 K is 0.19 mg. The Langmuir isotherm $\left(\theta = \frac{Kp}{1+Kp}\right)$ is known to describe the adsorption. Find the fractional coverage at the surface at the two pressures. [10]

b. Hydrogen iodide is very strongly adsorbed on gold but only slightly adsorbed on platinum. If the adsorption follows the Langmuir isotherm on both surfaces, predict the order of the HI decomposition on each of the two surfaces. [6]

c. Nitrogen gas was adsorbed on charcoal to the extent of 0.921 cm^3g^{-1} at 4.8 atm and 190 K, but at 250 K the same amount of adsorption was achieved only when the pressure was increased to 32 atm. What is the molar enthalpy of adsorption on charcoal? [9]

Question 2 (25marks)

Consider the cell

$Zn|ZnCl_2(0.0050\ mol\ kg^{-1})|Hg_2Cl_2(s)|\ Hg(l)$

Given that at 298 K, E° (Zn^{2+},Zn) = -0.7628 V, E° (Hg_2Cl_2, Hg) = +0.2676 V , E = + 1. 2272 V and $\frac{dE}{dT} = -4.52x10^{-4}VK^{-1}$,

a. Write the cell reaction and Nernst equation in terms of the mean activity coefficient and molality of the zinc chloride solution. [5]

b. Calculate Δ_rG, Δ_rG^o, and K for the cell reaction [8]

c. The mean activity coefficient from the measured cell potential [4]

d. The mean activity coefficient from the Debye-Huckel limiting law (A=0.509) [4]

e. Calculate Δ_rS Δ_rH for the cell reaction. [4]

Question 3 (25marks)

a. What is the difference between a strong and a weak electrolyte? How can you distinguish them experimentally? [5]

b. The following molar conductivity data were obtained for an electrolyte.

Concentration/M	Λ_m^0 / S m^2 mol^{-1}
0.0005	0.01245
0.001	0.01237
0.005	0.01207
0.01	0.01185
0.02	0.01158
0.05	0.01111
0.1	0.01067

(i) Determine if the electrolyte is strong or weak.
(ii) Determine the molar conductivity of the electrolyte at infinite dilution. [5]

c. Use the following data to determine the molar conductivity of $NaNO_3$ at infinite dilution :

Λ_m^0 (KCl) $= 0.0149$ S m^2 mol^{-1}
Λ_m^0 (NaCl) $= 0.0127$ S m^2 mol^{-1}
Λ_m^0 (KNO_3) $= 0.0145$ S m^2 mol^{-1} [4]

d. A standard solution of KCl of conductivity $\kappa = 1.06296 \times 10^{-6}$ S m^{-1} was used to calibrate a conductivity cell and the measured resistance was 4.2156 Ω. The same cell when filled with HCl (aq) the resistance was 1.0326 Ω.
(i) Calculate the cell constant
(ii) What is the conductivity of the HCl solution? [6]

e. The diffusion coefficient of glycine in water is 1.055×10^{-9} m^2 s^{-1}. Given that the viscosity of water at 25 °C is 1.00 cP, estimate the effective radius of a glycine molecule. (1 P = 0.1 kg m^{-1} s^{-1}). [5]

Question 4 (25marks)

a. The quantum yield for CO production in the photolysis of gaseous acetone is one for wavelengths between 250 nm and 320 nm. After 20 minutes of irradiation at 313 nm, 18.4 cm^3 of CO (measured at 1008 Pa and 22 °C) is produced. Calculate (i) the number of photons absorbed and (ii) the absorbed intensity in J s^{-1}. [8]

b. A likely mechanism for the photolysis of acetaldehyde is

$$CH_3CHO + h\nu \longrightarrow CH_3\cdot + CHO\cdot$$
$$CH_3\cdot + CH_3CHO \xrightarrow{k_1} CH_4 + CH_3CO\cdot$$
$$CH_3CO\cdot \xrightarrow{k_2} CO + CH_3\cdot$$
$$CH_3\cdot + CH_3\cdot \xrightarrow{k_3} C_2H_6$$

Use the steady state approximation to derive the rate law for the formation of CO based on the above mechanism. [8]

c. An enzyme catalysed reaction following the Michaelis-Menten mechanism

$E + S \rightleftharpoons ES \rightarrow P + E$ rate constants are k_1, k_1', k_2

has the rate law $\frac{d[P]}{dt} = \frac{k_2[S][E]_0}{K_M + [S]}$ 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 $\times10^{-5}$	5.00 $\times10^{-5}$	8.33 $\times10^{-5}$	1.67 $\times10^{-4}$

The enzyme concentration is 2.3nM. Calculate (i) the maximum rate, v_{max} (ii) the Michaeli's constant K_M, and (iii) k_2. [9]

Question 5 (25marks)

a. The rate law of the reaction A + 2 B → 3 C + D was reported as d[C]/dt = k[A][B]$[C]^{-1}$.
   (i) What are the units of k?
   (ii) Express the rate law in terms of the reaction rate. [3]

b. The half-life for the radioactive decay of ^{14}C is 5730 y. An archaeological sample contained wood that had only 72% of the ^{14}C found in living trees. What is its age? [5]

c. For the decomposition of N_2O_5, the following data has been obtained:

$\theta/^{o}C$	25	35	45	55	65
k/s^{-1}	1.72×10^{-5}	6.55×10^{-5}	24.95×10^{-5}	75×10^{-5}	240×10^{-5}

Calculate the activation energy and pre-exponential factor for this reaction. [10]

d. (i) Show that for a small perturbation the relaxation time for the reaction $H_3O^+ + OH^- \rightleftharpoons 2\,H_2O$ (k_f and k_r are the rate constants for the forward and reverse reactions) is given by $\tau = \{k_f[H_3O^+]_{eq} + k_f[OH^-]_{eq}\}^{-1}$. [4]

(ii) Hence calculate the equilibrium concentrations of the hydronium and hydroxyl ions assumed to be equal at 298 K given that $\tau = 3.7 \times 10^{-5}$ s and $k_f = 1.35 \times 10^{8}\ m^3\ mol^{-1}\ s^{-1}$. [3]

Question 6 (25marks)

a. The dipole moment of toluene, $C_6H_5CH_3$, is 0.4 D. Estimate the dipole moments of the three xylenes, $C_6H_4(CH_3)_2$. Which of the three results can you be sure about? [6]

b. Define or briefly explain the following terms
(i) Polarization (ii) Orientation polarization (iii) refractive index
(iv) dipole-dipole interactions (v) magnetization [10]

c. Given that the polarizability of methanol is $3.23 \times 10^{-40}\ J^{-1}\ C^2\ m^2$ and its dipole moment and density at 20°C are 5.70×10^{-30} C m and 0.7914 g cm^{-3}, respectively calculate:
(i) its molar polarization
(ii) relative permittivity and
(iii) refractive index [9]

[Useful equation $P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$ where $P_m = \left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\right)\frac{M}{\rho}$]

THE PERIODIC TABLE OF ELEMENTS

NON-METALS (shaded)
METALLOIDS (boxed)
METALS (unboxed)

Group	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
Period 1	1 H 1.008																	
2	3 Li 6.94	4 Be 9.01											5 B 10.81					
3	11 Na 22.99	12 Mg 24.31											13 Al 26.9	14 Si 28.09				
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.9	26 Fe 55.85	27 Co 58.71	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.7	32 Ge 72.59	33 As 74.92			
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 91.22	42 Mo 95.94	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6		
6	55 Cs 132.9	56 Ba 137.3	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 210	85 At 210	
7	87 Fr 223	88 Ra 226.0	103 Lr 257	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.9	63 Eu 151.3	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.1	94 Pu 239.1	95 Am 241.1	96 Cm 247.1	97 Bk 249.1	98 Cf 251.1	99 Es 254.1	100 Fm 257.1	101 Md 258.1	102 No 255

Numbers below the symbol indicates the atomic masses; and the numbers above the symbol indicates the atomic numbers.

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	$F = N_Ae$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\ 66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_Ak$	$8.314\ 51$ 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	$a_o = 4\pi\varepsilon_o\hbar/m_ee^2$	$5.291\ 77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_oe^2c/2h$	$7.297\ 35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_ee^4/8h^3c\varepsilon_o^2$	$1.097\ 37 \times 10^{7}$ 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}