UNIVERSITY OF SWAZILAND

FINAL 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.

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Question 1 (25marks)

(a) What is the role of defects in adsorption on surfaces? [3]

(b) The volume of methane, measured at STP (0°C, 1 atm), adsorbed on 1g of charcoal at 0 °C and several different pressures is

P/ cm Hg	10	20	30	40
V/cm^3	9.75	14.5	18.2	21.4

Show that the data follows the Freundlich isotherm, $\theta = c_1 P^{1/c_2}$, and determine the constants c_1 and c_2 [8]

(c) In an experiment on the adsorption of ethene on iron it was found that the same volume of gas was desorbed in 1856 s at 873 K and 8.44 s at 1012 K.

(i) What is the activation energy of desorption? [6]

(ii) How long would it take the same amount of ethene to desorb at 298 K? at 2000 K? [8]

Question 2 (25marks)

(a) Estimate the mean activity coefficient of $CaCl_2$ in a solution that is 0.020 mol kg^{-1} NaCl(aq) and 0.035 mol kg^{-1} $CaCl_2$(aq) [5]

(b) Given that $Hg_2Cl_2(s) + 2e^- \rightarrow 2\,Hg(l) + 2Cl^-(aq)$ $E^o = +0.27$ V and that $\Delta_f G^o(Hg_2Cl_2,s) = -210.7$ $kJmol^{-1}$, determine $\Delta_f G^o(Cl^-,aq)$. [6]

(c) Write the appropriate half-cell reactions for the following reactions. Identify which is the cathode reaction.

(i) $2\,Cd(OH)_2(s) \rightarrow Cd(s) + O_2(g) + 2H_2O(l)$ [2]

(ii) $Sn(s) + Sn^{4+}(aq) \rightarrow 2\,Sn^{2+}(aq)$ [2]

(d) Consider the cell $Hg(l)|Hg_2SO_4(s)|FeSO_4(aq, a = 0.0100)|Fe(s)$
$[E^o(Fe^{2+},Fe) = -0.447$ V and $E^o(Hg_2SO_4,Hg, SO_4^{2-}) = 0.6125$ V]

(i) Write the cell reaction [2]

(ii) Calculate the cell potential at 25°C [5]

(iii) Calculate the equilibrium constant for the cell reaction [3]

Question 3 (25marks)

(a) Use the kinetic theory of gases to explain the following:

(i) The thermal conductivity of a perfect gas is expected to be independent of pressure.

(ii) The thermal conductivity of a perfect gas increases as $T^{1/2}$ [6]

(b) (i) The diffusion coefficient for Xe at 273 K and 1 atm is 5×10^{-6} m^2 s^{-1}. What is the collisional cross section of Xe?

(ii) The diffusion coefficient of N_2 is threefold greater than that of Xe under the same pressure and temperature conditions. What is the collisional cross section of N_2? (Atomic masses: Xe = 131.29 u and of N_2 = 28.02 u) [10]

(c) The mobilities of H^+, Na^+ and Cl^- are given I table below:

Ion	Mobility, m^2 s^{-1} V^{-1}
H^+	3.623×10^{-7}
Na^+	0.519×10^{-7}
Cl^-	0.791×10^{-7}

(i) What proportion of the current is carried by the protons in a 1.00×10^{-3} M HCl(aq)?

(ii) What fraction do they carry when NaCl is added to the acid so that the solution is 1.0 M in the salt? [9]

Question 4 (25marks)

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

(i) collision cross-section

(ii) cage effect

(iii) diffusion controlled reaction

(iv) activation energy

(v) kinetic salt effect [5]

(b) The diffusion coefficient of I in CCl_4 is estimated to be 4.2×10^{-5} cm^2 s^{-1} at 25 °C. Given that the radius of I is about 200 pm, calculate the rate constant k_d for $I + I \rightarrow I_2$ in CCl_4 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 the pre-exponential factor A = 4.07 x 10^5 L mol^{-1} s^{-1} at 300 K and an activation energy of 65.43 $kJmol^{-1}$. Calculate $\Delta^{+}S$, $\Delta^{+}H$, and $\Delta^{+}G$ for the reaction. [10]

(d) At 25 °C, $k = 1.55\ L^2mol^{-2}min^{-1}$ at an ionic strength of 0.0241 for a reaction in which the rate determining step involves the encounter of two singly charged cations. Use the Debye-Huckel limiting law to estimate the rate constant at zero ionic strength. [5]

Question 5 (25 marks)

(a) The rate of formation of C in the reaction $2A + B \rightarrow 2C + 3D$ is 1.0 mol $L^{-1}s^{-1}$. State the reaction rate, and the rates of formation or consumption of A, B, 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) Methane is a by-product of a number of natural and industrial processes. Reaction with the hydroxyl radical, OH, is the main path by which CH_4 is removed from the lower atmosphere. The rate constants for this bimolecular gas-phase reaction have been measured over a range of temperatures of interest in atmospheric chemistry. Deduce the Arrhenius parameters, E_a and A, from the following data. [10]

T/K	295	223	218	213	206	200	195
$k/10^6 Lmol^{-1}s^{-1}$	3.55	0.494	0.452	0.379	0.295	0.241	0.217

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

(ii) The measured relaxation time for a small temperature jump is 3.0 μs. If at 25 °C the equilibrium constant for the system is 2.0×10^{-16}, and the equilibrium concentrations of B and C are both 2.0×10^{-4} M, calculate the rate constants, k_f and k_r. [3]

Question 6 (25 marks)

(a) Explain how the permanent dipole moment and polarizability of a molecule arise. [6]

(b) The relative permittivity of camphor (molar mass M = 152.3 g/mol and melting point 175 °C) was measured over a range of temperatures. Use the data that was obtained and is given in the table below to calculate the dipole moment and polalarizabilty of camphor. [12]

Temperature θ, °C	Relative permittivity, ε_r	Density, ρ g cm^{-3}
0	12.5	0.99
20	11.4	0.99
40	10.8	0.99
60	10.0	0.99
80	9.50	0.99
100	8.90	0.99
120	8.10	0.97
140	7.60	0.96
160	7.11	0.95
200	6.21	0.91

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

(c) The refractive index of CH_2I_2 is 1.732 for 656 nm light. Its density at 20 °C is 3.32 g cm^{-3}. Calculate the polarizability of the molecule at this wavelength. [7]

THE PERIODIC TABLE OF ELEMENTS

NON-METALS (shaded)

METALLOIDS (bold-outlined)

METALS (plain boxes)

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																	He
2	3 Li 6.94	4 Be 9.01											5 B 10.81	C	N	O	[illegible]	Ne
3	11 Na 22.99	12 Mg 24.31											13 Al 26.9	14 Si 28.09	[illegible]	S	[illegible]	[illegible]
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	Se	Br	Kr
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	I	Xe
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	Rn 222
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	$F = N_A e$	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}