UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2012/13

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.

Question1(25 marks)

(a) What is a half-life? Briefly explain how you can use the half-life of a reaction to distinguish between a first order and second order reaction. [4]

(b) You are given the following data for the decomposition of acetaldehyde

Initial concentration (M)	9.72×10^{-3}	4.56×10^{-3}
Half-life (s)	328	692

(i) Determine the order of the reaction
(ii) Calculate the rate constant for the reaction [6]

(c) Consider the schematic reaction $A \xrightarrow{k} B$
(i) If the reaction is one-half order with respect to A, what is the integrated rate law expression for this reaction?
(ii) What plot would you construct to determine the rate constant *k* for the reaction?
(iii) What would be the half-life? Will it depend on the initial concentration of the reactant? [6]

(d) The rate constant for the reaction of hydrogen with iodine is 2.45×10^{-4} $M^{-1}s^{-1}$ at 302 °C and 0.950 $M^{-1}s^{-1}$ at 508 °C.
(i) Calculate the Arrhenius parameters, i.e. the activation energy and pre-exponential factor, for this reaction.
(ii) What is the value of the rate constant at 400 °C? [9]

Question 2 (25 marks)

(a) The quantum yield for the production of CO in the photolysis of gaseous acetone is unity for wavelengths between 250 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
(ii) the intensity absorbed in J s^{-1}. [7]

(b) The following reaction occurs in aqueous solution:

$I^-(aq) + OCl^-(aq) \rightarrow OI^-(aq) + Cl^-(aq)$

The initial rate was studied as a function of concentration and the following date were obtained:

Expt	$[I^-]_0$ (M)	$[OCl^-]_0$ (M)	$[OH^-]_0$ (M)	Initial rate (M s^{-1})
1	2.0×10^{-3}	1.5×10^{-3}	1.00	1.8×10^{-4}
2	4.0×10^{-3}	1.5×10^{-3}	1.00	3.6×10^{-4}
3	2.0×10^{-3}	3.0×10^{-3}	2.00	1.8×10^{-4}
4	4.0×10^{-3}	3.0×10^{-3}	1.00	7.2×10^{-4}

(i) Determine the rate law and the value of the rate constant.

(ii) The following mechanism has been proposed for this reaction

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \text{ (rate constants } k_1 \text{ and } k_{-1})$$
$$I^- + HOCl \xrightarrow{k_2} HOI + Cl^-$$
$$HOI + OH^- \xrightarrow{k_3} H_2O + OI^-$$

Derive the rate law for the formation of Cl^- based on this mechanism (*hint*: [OH] should appear in rate law). Is the rate law in agreement with the experimental rate law in determined in (i)? [12]

(c) A likely mechanism for the photolysis of acetaldehyde is

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

Use steady state approximation to derive the rate law for the formation of CO based on this mechanism. [6]

Question 3(25 marks)

(a) Define the ionic strength of a solution. What is the molality of $Al_2(SO_4)_3$ that has the same ionic strength as 0.500 mol kg^{-1} $Ca(NO_3)_2$? [6]

(b) Devise cells in which the following are the reactions:

(i) $H_2(g) + I_2(g) \rightarrow 2HI(aq)$

(ii) $Sn(s) + 2AgCl(s) \rightarrow SnCl_2(aq) + 2Ag(s)$ [4]

(c) Derive an expression for the potential of an electrode for which the half-reaction is the reduction of MnO_4^- ions to Mn^{2+}ions in acidic solution. [3]

(d) For the cell $Pt|Fe(s)|Fe^{2+}(aq)|Fe^{2+}(aq),Fe^{3+}(aq)|Pt$, it was found that

$$\frac{dE^\circ}{dT} = 1.14 \text{ mV at } 25\ ^\circ C.$$

(i) Write the cell reaction using the smallest whole numbers as the stoichiometric coefficients.

(ii) Given that $E^\circ(Fe^{2+},Fe) = -0.44$ V and $E^\circ(Fe^{3+},Fe^{2+}) = +0.771$ V, calculate $\Delta_r G^\circ$, $\Delta_r S^\circ$, $\Delta_r H^\circ$ for the cell reaction at 25 °C. [12]

Question 4 (25 marks)

(a) What is the difference between a strong and a weak electrolyte? How can you distinguish them experimentally? [6]

(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. [8]

(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? [7]

Question 5(25 marks)

(a) Discuss the unique physical and chemical properties of zeolites that make them useful heterogeneous catalysts. [6]

(b) The data for the adsorption of ammonia on barium fluoride at 273 K are given below:

p/kPa	14.0	37.6	65.6	79.2	82.7	100.7	106.4
V/cm^3	11.1	13.5	14.9	16.0	15.5	17.3	16.5

At 273 K, the vapour pressure of ammonia p^* is 429.6 kPa.

(i) Confirm that the data fits the BET isotherm:

$$\frac{V}{V_{mon}} = \frac{cz}{(1-z)(1-(1-c)z)} \quad with \quad z = \frac{p}{p^*}$$ [7]

(ii) Determine the values of c and V_{mon}. [4]

(c) A solid in contact with a gas at 12 kPa and 25 °C adsorbs 2.5 mg of the gas and obeys the Langmuir isotherm, $\theta = \frac{Kp}{1+Kp}$. The enthalpy change when 1.0 mmol of the adsorbed gas is desorbed is +10.2 J. What is the equilibrium pressure at 40 °C? [8]

Question 6 (25 marks)

(a) In the kinetic theory of gases, define the mean free path. Explain how the mean free path varies with (i) number density (ii) particle diameter and (iii) average speed of the molecule. [6]

(b) Compute the root mean square speed, c, the mean speed, $\bar{c}$, and the most probable speed, c*, for O_2 at 300K. How much faster will the corresponding values for H_2 be? [8]

(c) At what temperature is the mean speed, $\bar{c}$, for H_2 equal to that of O_2 at 300 K. [4]

(d) The thermal conductivity of Kr is about one half that of Ar under identical pressure and temperature conditions. Both gases are monatomic such that $C_{V,m} = \frac{3}{2}R$.

(i) Why would one expect the thermal conductivity of Kr to be less that that of Ar?

(ii) Determine the ratio of the collisional cross-sections of Ar relative to Kr assuming identical pressure and temperature conditions.

(iii) For Kr at 273 K and 1 atm, $\kappa = 8.7 \times 10^{-3}$ J $K^{-1}m^{-1}s^{-1}$. Determine the collision cross-section of Kr. [7]

USEFUL DATA

$$\int x^n dx = \frac{x^{n+1}}{n+1} + constant$$

Arrhenius equation: $k = Ae^{-E_a/RT}$

Coefficient of thermal conductivity $\kappa = \frac{1}{3}\frac{\lambda \bar{c} C_{V,m} N}{V} = \frac{\bar{c} C_{V,m}}{3\sqrt{2} N_A \sigma}$

$$\bar{c} = \left[\frac{8RT}{\pi M}\right]^{1/2} \qquad c = \left[\frac{3RT}{M}\right] \qquad c^* = \left[\frac{2RT}{M}\right]$$

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										Atomic mass → Symbol → Atomic No. →	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				TRANSITION ELEMENTS							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								

*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.