UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2009/10

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) Define the mean free path. How does this quantity vary with number density, particle diameter and the mean particle speed? [3]

(b) Calculate the mean free path of argon ($\sigma = 0.36\ nm^2$) at 298 K at (i) 0.3 atm and (ii) $5x10^{-6}$ atm. [6]

(c) A thermopane window consists of two sheets of glass separated by a volume filled with air (which we will model as N_2 where $\kappa = 0.0240\ J\ K^{-1}\ m^{-1}\ s^{-1}$). If the window is 1 m^2 in area with a separation between glass sheets of 3 cm, what is the loss of energy when:

(i) The exterior of the window is at a temperature of 10 °C and the interior of the window is a temperature of 22 °C?

(ii) The same temperature differential as in (i) is used, but now the window is filled with Ar ($\kappa = 0.0163\ J\ K^{-1}\ m^{-1}\ s^{-1}$) rather than N_2? [6]

(d) Gas cylinders of CO_2 are sold in terms of weight of CO_2. A cylinder contains 22.7 kg of CO_2. Use Poiseuille's formula $\left(\frac{dV}{dt} = \frac{(P_1^2 - P_2^2)\pi r^4}{16 l \eta p_0} \right)$ to determine for how long this cylinder can be used in an experiment that requires flowing CO_2 at 293 K (η = 146 μP) through a 1.00 m long tube (diameter 0.75 mm) with input pressure of 1.05 atm and output pressure of 1.00 atm. The flow is measured at the tube output. [6]

(e) A solid surface with dimensions 3.5 mm x 4.0 cm is exposed to helium gas at 111 Pa and 1500 K. How many collisions do the He atoms make with this surface in10s? [4]

Question 2(25 marks)

(a) Bearing in mind distinctions between the mechanism of stepwise and chain polymerization, describe ways in which it is possible to control the molar mass of a polymer by manipulating the kinetic parameters of the polymerization.[6]

(b) For the reaction 2 HI(g) $\rightarrow$ H_2(g) + I_2(g), the values of the rate constant are 1.2 x 10^{-3} L mol^{-1} s^{-1} at 700 K and 3.0 x 10^{-5} L mol^{-1} s^{-1} at 629 K. Estimate the Arrhenius parameters, E_a and A. [6]

(c) In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from a 87.5 W source for 28.0 minutes. The intensity of the transmitted light was 0.257 that of the incident light. As a result of irradiation 0.324 mol of the absorbing substance decomposed. Determine the quantum efficiency. [6]

(d) The mechanism of the reaction $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$ is

(1) $I_2 \rightleftharpoons 2\ I$

(2) $I + H_2 \rightarrow HI + H$

(3) $H + I_2 \rightarrow HI + I$

The rate constants are k_1 and k_{-1} for step (1) and k_2 and k_3 for steps (2) and (3), respectively. Find the rate law using the steady state approximation. [7]

Question 3(25marks)

(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

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

(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(25marks)

(a) The gas phase reaction

$RI + HI \rightarrow RH + I_2$

is first order in each reactant or second order overall. The observed activation energy is 100 kJ/mol. A calculation using the kinetic molecular theory shows that if the concentration of each reactant is 1.0 M, the rate of the reaction at 300 K is 5.0×10^{10} mol dm^{-3} s^{-1} if every collision is effective.

(i) Calculate the predicted rate constant at 300 K using the collision theory.

(ii) The observed rate constant at 300 K is 3.0×10^{8} dm^{3} mol^{-1} s^{-1}. What is the value of the steric factor and what does it mean? [8]

(b) One of the hazards of nuclear explosions is the generation of ^{90}Sr and its subsequent incorporation in bones in place of calcium. This isotope emits β-rays of energy 0.55 MeV and has a half life of 28.1 years. Suppose 1.0 μg was absorbed by a newly born child, how much will remain after (i) 18 years and (ii) 70 years? [8]

(c) Nitrous oxide decomposes according to the reaction

$2\,N_2O(g) \rightarrow 2\,N_2(g) + O_2(g)$

The rate of the of the decomposition is quite small unless a halogen is present as a catalyst. Thus in the presence of Cl_2, the rate depends both on N_2O and Cl_2 pressure., i.e.

$$-\frac{dP_{N_2O}}{dt} = kP_{N_2O}^{a}P_{Cl_2}^{b}$$

The course of the reaction can be followed by measuring the increase in the total pressure at constant temperature. The following data were obtained in a series of experiments at 800 K.

Initial pressure /Torr		Initial rate/Torr min^{-1}
P_{N_2O}	P_{Cl_2}	Increase in total pressure
30	4.0	0.30
15	4.0	0.15
30	1.0	0.15

(i) From the given data determine the values of *a* and b in the rate law.

(ii) Calculate the rate constant at 800 K. [9]

Question 5 (25 marks)

(a) What assumptions did Langmuir make when deriving his isotherm, $\theta = \frac{Kp}{1+Kp}$.

[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
$V/(cm^3/g)$	101	136	153	162	165	166

(i) Show that the data fits the Langmuir isotherm.
(ii) Determine the value of K.
(iii) Determine the volume of N_2 needed for monolayer coverage. [13]

(c) For H_2 adsorbed on W powder, the following data were found:

θ	0.005	0.005	0.10	0.10
p/Torr	0.0007	0.03	8	23
t/°C	500	600	500	600

where p is the H_2 pressure in equilibrium with tungsten at fractional coverage θ and temperature t. Calculate $\Delta_{ad}H^{\theta}$ at (i) $\theta = 0.005$ and (ii) $\theta = 0.10$. [8]

Question 6 (25 marks)

(a) Explain why the polarizability of a molecule decreases at high frequencies.

[8]

(b) Values of the molar polarization, P_m, of gaseous water at 100 kPa were determined and are given below as a function of temperature.

T/K	384.3	420.1	444.7	484.1	522.0
$P_m/(cm^3\ mol^{-1})$	57.4	53.5	50.1	46.8	43.1

Use this data to calculate the dipole moment of H_2O and its polarizability volume. $\left(\text{Useful equations: } P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\varepsilon_0 kT} \quad \text{with } \alpha = 4\pi\varepsilon_0 \alpha' \right)$

[9]

(c) A dilute solution of potassium permanganate in water at 25 °C was placed in a horizontal tube of length 10 cm. At first there was a linear gradation of intensity of the purple solution from the left where the concentration was 0.100 mol L^{-1} to the right where the concentration was 0.050 mol L^{-1}. What is the magnitude and sign of the thermodynamic force acting on the solute

(i) Close to the left face of the tube

(ii) Close to the right face of the tube.

In each case give the force per mole and per molecule. [8]

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}

PERIODIC TABLE OF ELEMENTS

GROUPS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	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.