

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.

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

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 ($\sigma = 0.36 \text{ nm}^2$) at 298 K at (i) 0.3 atm and (ii) 5×10^{-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 $\mathcal{K} = 0.0240 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$). 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 ($\mathcal{K} = 0.0163 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$) 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 $\left(\frac{dV}{dt} = \frac{(P_1^2 - P_2^2)\pi r^4}{16l\eta p_0} \right)$ to determine for how long this cylinder can be used in an experiment that requires flowing CO_2 at 293 K ($\eta = 146 \mu\text{P}$) 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 in 10s? [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 $2 \text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, the values of the rate constant are $1.2 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 700 K and $3.0 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ 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 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g})$ is

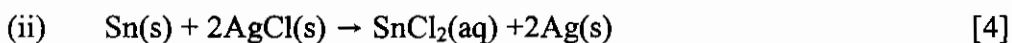
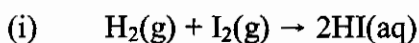
- (1) $\text{I}_2 \rightleftharpoons 2 \text{I}$
- (2) $\text{I} + \text{H}_2 \rightarrow \text{HI} + \text{H}$
- (3) $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$

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 $\text{Al}_2(\text{SO}_4)_3$ that has the same ionic strength as $0.500 \text{ mol kg}^{-1} \text{ Ca}(\text{NO}_3)_2$? [6]

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



(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 $\text{Pt}|\text{Fe}(\text{s})|\text{Fe}^{2+}(\text{aq})|\text{Fe}^{2+}(\text{aq}),\text{Fe}^{3+}(\text{aq})|\text{Pt}$, it was found that

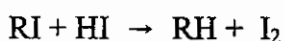
$$\frac{dE^\circ}{dT} = 1.14 \text{ mV at } 25^\circ\text{C}.$$

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

(ii) Given that $E^\circ(\text{Fe}^{2+},\text{Fe}) = -0.44 \text{ V}$ and $E^\circ(\text{Fe}^{3+},\text{Fe}^{2+}) = +0.771 \text{ V}$, 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

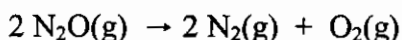


is first order in each reactant or second order overall. The observed activation energy is 100 kJ/mol. A calculation using the kinetic molecular theory shows that if the concentration of each reactant is 1.0 M, the rate of the reaction at 300 K is $5.0 \times 10^{10} \text{ mol dm}^{-3} \text{ s}^{-1}$ 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 $3.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. 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



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.

$$-\frac{dP_{\text{N}_2\text{O}}}{dt} = kP_{\text{N}_2\text{O}}^a P_{\text{Cl}_2}^b$$

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
$P_{\text{N}_2\text{O}}$	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 N₂ needed for monolayer coverage. [13]
- (c) For H₂ 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 H₂ pressure in equilibrium with tungsten at fractional coverage θ and temperature t. Calculate Δ_{ad}H^θ at (i) θ = 0.005 and (ii) θ = 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 H₂O and its polarizability

volume. (Useful equations: $P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\epsilon_0 kT}$ with $\alpha = 4\pi\epsilon_0 \alpha'$) [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
- Close to the left face of the tube
 - 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	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$
Elementary charge	e	$1.602\,177 \times 10^{-19} \text{ C}$
Faraday constant	$F = N_A e$	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = N_A k$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $6.2364 \times 10 \text{ L Torr K}^{-1} \text{ mol}^{-1}$
Planck constant	h	$6.626\,08 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$
Avogadro constant	N_A	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	u	$1.660\,54 \times 10^{-27} \text{ Kg}$
Mass		
electron	m_e	$9.109\,39 \times 10^{-31} \text{ Kg}$
proton	m_p	$1.672\,62 \times 10^{-27} \text{ Kg}$
neutron	m_n	$1.674\,93 \times 10^{-27} \text{ Kg}$
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
	$4\pi\epsilon_0$	$1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability	μ_0	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3$
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$
g value	g_e	2.002 32
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c \epsilon_0^2$	$1.097\,37 \times 10^7 \text{ m}^{-1}$
Standard acceleration of free fall	g	$9.806\,65 \text{ m s}^{-2}$
Gravitational constant	G	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ Kg}^{-2}$

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	$1 \times 10^{-7} \text{ J}$
1 eV	=	$1.602\,2 \times 10^{-19} \text{ J}$	1 eV/molecule	=	$96\,485 \text{ kJ mol}^{-1}$

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

