UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2011/12

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 PERIODIÇ 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) The reaction rate as a function of initial reactant pressures was investigated for the reaction $2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$ and the following data were obtained:

Run	P_0 H_2/(kPa)	P_0 NO/(kPa)	Rate/(kPa s^{-1})
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

Determine the rate law including the value of the rate constant [5]

(b) In the stratosphere, the rate constant for the conversion of ozone to molecular oxygen by atomic chlorine, $Cl + O_3 \rightarrow ClO + O$, is $k = 1.7 \times 10^{10}\ M^{-1}s^{-1}e^{-260K/T}$.

(i) What is the rate of this reaction at 20 km where $[Cl] = 5 \times 10^{-17}$ M and $[O_3] = 8 \times 10^{-9}$ M and T = 220 K?

(ii) The concentrations at 45 km are $[Cl] = 3 \times 10^{-15}$ M and $[O_3] = 8 \times 10^{-11}$ M and T = 270 K, what is the reaction rate at this attitude? [6]

(c) The unimolecular decomposition of urea in aqueous solution is measured at two different temperatures and the following data are observed;

Trial no.	Temperature/ (°C)	Rate constant k/ (s^{-1})
1	60.0	1.20×10^{-7}
2	71.5	4.40×10^{-7}

Determine the Arrhenius parameters for this reaction. [5]

(d) The pK_a of NH_4^+ is 9.25 at 25 °C. The rate constant at 25 °C for the reaction of NH_4^+ and OH^- to form aqueous ammonia is $4.0 \times 10^{10}\ dm^3\ mol^{-1}s^{-1}$.

(i) Calculate the rate constant for proton transfer to NH_3.

(ii) What relaxation time would be observed if a temperature jump were applied to a solution of 0.15 M $NH_3(aq)$ at 25 °C.

Useful data: $Kw = 1.0 \times 10^{-14}$ and $Kw = K_a K_b$ [9]

Question 2(25 marks)

(a) Consider the following reaction:

$$H_2(g) + 2AgCl(s) \rightarrow 2HCl(aq) + 2\,Ag(s)$$

(i) Devise a cell in which the above reaction is the cell reaction [2]

(ii) Write the Nernst equation for the cell in (i) [2]

(iii) The emf for the above cell was 0.3524 V when the molality of HCl was 0.100 mol/kg and the hydrogen pressure was 1 bar. Calculate the activity and mean activity coefficient of the HCl assuming hydrogen is a perfect gas. [5]

(iv) Calculate the per cent error in the mean activity coefficient if the Debye-Huckel limiting is used to calculate it. ($\log \gamma_{\pm} = -|z_+z_-|AI^{1/2}$, A=0.509 at 25 °C) [4]

(b) For the cell: Pt| Ag(s)| AgCl(s)| HCl(aq)| $Hg_2Cl_2(s)$| Hg(l)| Pt;

$$\frac{dE^{\theta}}{dT} = 0.338 mV/K$$ at 25 °C and 1 bar.

(i) Write the cell reaction [2]

(ii) Calculate Δ_rG^{θ}, Δ_rH^{θ} and Δ_rS^{θ} for the cell reaction [10]

Table 1: Standard potentials at 298 K

Reduction half reaction	E^{θ}/V
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$2H^+(aq) + 2e^- \rightarrow H_2(aq)$	0, by definition
$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.27

Question 3(25 marks)

(a) When a mixture of H_2 and O_2 is irradiated with light of wavelength 253.7 nm no reaction is observed. When a small amount of mercury vapour is added to the mixture and the mixture irradiated with 253.7 nm light, a rapid formation of water is observed. Given that the bond dissociation energies for O_2 and H_2 are 498 and 436 kJ/mol, respectively, account for the above observations. [6]

(b) The quantum yield is 2 for the photolysis of gaseous HI to I_2 and H_2 by light of 253.7 nm wavelength. Calculate the number of moles HI that will be decomposed if 300 J of light of this wavelength is absorbed [5]

(c) An enzyme catalysed reaction conversion of a substrate at 25 °C has Michaelis constant of 0.042 mol L^{-1}. The rate of the reaction is 2.45 x 10^{-4} mol L^{-1} s^{-1} when the substrate concentration is 0.890 mol/L. What is the maximum velocity of this enzmolysis. [5]

(d) Consider the following reaction of methane with molecular chlorine:
$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$
for which the following mechanism has been proposed

$$Cl_2 \xrightarrow{k_1} 2Cl^{\bullet}$$

$$Cl^{\bullet} + CH_4 \xrightarrow{k_2} HCl + CH_3^{\bullet}$$

$$CH_3^{\bullet} + Cl_2 \xrightarrow{k_3} CH_3Cl + Cl^{\bullet}$$

$$Cl^{\bullet} + Cl^{\bullet} \xrightarrow{k_4} Cl_2$$

Show that the mechanism is consistent with the experimental rate law

$$\frac{d[HCl]}{dt} = k[CH_4][Cl_2]^{1/2}$$ [7]

Question 4 (25 marks)

(a) The charge of Mg^{2+} is twice that of Na^{+}, and from the equation

$$u = \frac{ze}{6\pi\eta a}$$

one might therefore expect Mg^{2+}(aq) to have a much greater mobility than Na^{+}(aq). Actually, these ions have similar mobilities. Explain why? [3]

(b) Derive the Ostwald dilution law for a weak electrolyte (all steps must be clearly shown).

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a(\Lambda_m^0)^2}$$ Ostwald dilution law [4]

(c) The following data were obtained for a weak electrolyte HA in ethanol at 25°C:

Concentration c/ mol dm^{-3}	1.566 x 10^{-4}	2.600 x 10^{-4}	6.219 x 10^{-4}	10.441 x 10^{-4}
Conductivity κ/ S cm^{-1}	1.788 x 10^{-6}	2.418 x 10^{-6}	4.009 x 10^{-6}	5.336 x 10^{-6}

(i) Confirm that these values are in accordance with the Ostwald dilution law.
(ii) Calculate the dissociation constant for this electrolyte. [8]

(d) For the perchlorate ion, ClO_4^-, in water at 25 °C, $\lambda_m^0 = 67.2 Scm^2 mol^{-1}$.

(i) Calculate the mobility, **u**, of ClO_4^- in water

(ii) Calculate the drift speed, **s**, of ClO_4^- in water in a field of 24 V/cm.

(iii) Calculate the diffusion coefficient of ClO_4^- in water

(iv) Estimate the radius of the hydrated perchlorate ion given that the viscosity of water is 8.91 x 10^{-4} kg m^{-1} s^{-1}. [10]

(Useful data: $\lambda_i = z_i u_i F$ $\quad D = \frac{uRT}{zF} = \frac{kT}{6\pi\eta a}$)

Question 5 (25 marks)

(a) Distinguish between physisorption and chemisorption [8]

(b) A surface is half covered by a gas when the pressure is 1.0 atm. If the Langmuir isotherm, $\theta = \frac{Kp}{1+Kp}$, is followed:

(i) What is the value of the adsorption coefficient, K?

(ii) What pressure would give 90% coverage?

(iii) What coverage is given by a pressure of 0.10 atm? [8]

(c) The adsorption of solutes on solids from liquids often follows a Freundlich isotherm, $\theta = kp^{1/n}$. Adapt the equation to apply to a solution and check its applicability to the following data for the adsorption of acetic acid on charcoal and determine the constants *k* and n.

[acid] mol/L	0.05	0.10	0.50	1.0	1.5
W_a/g	0.04	0.06	0.12	0.16	0.18

W_a is the mass adsorbed per unit mass of charcoal. [9]

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Question 6 (25 marks)

(a) Give brief verbal explanations for each of the following

(i) Each of the formulas for the transport coefficients in the kinetic theory of gases is proportional to the mean free path, λ, and the mean speed. $\bar{c}$. [3]

(ii) The thermal conductivity and viscosity of a gas are independent of the number density, *N*. [3]

(b) The viscosity of CO_2 at 1 atm and 0 °C is 139 μP. Calculate the collision cross-section of CO_2 at this temperature. [5]

(c) Two sheets of copper of area 1.5 m^2 are separated by 10.0 cm. What is the rate of transfer of heat by conduction from the warm sheet at 50 °C to the cold sheet at -10 °C. [5]

(d) The diffusion coefficient of glucose in water is 6.81×10^{-10} m^2s^{-1} at 25 °C. The viscosity of water at 25 °C is 8.937×10^{-4} kg $m^{-1}s^{-1}$ and the density of glucose is 1.55 g cm^{-3}. Assuming Stoke's law applies and that the molecule is spherical estimate

(i) The radius of a glucose molecule.

(ii) The molar mass of glucose. [9]

Useful data

Coefficient of thermal conductivity for air $\kappa = 0.0241$ J K^{-1} m^{-1} s^{-1}

1 P = 0.1 kg m^{-1} s^{-1}

Diffusion coefficient $D = \frac{1}{3}\lambda\bar{c}$

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

Coefficient of viscosity $\eta = \frac{1}{3}m\lambda\bar{c}N = \frac{m\bar{c}}{3\sqrt{2}\sigma}$

Volume of a sphere $V = \frac{4}{3}\pi r^3$

Mass of CO_2 molecule $m = 7.306 \times 10^{-26}$ kg

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

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.