

UNIVERSITY OF SWAZILAND
FINAL EXAMINATION: 2009/2010

TITLE OF PAPER : **Introductory Chemistry II**

COURSE CODE : **C112**

TIME : **THREE (3) HOURS**

INSTRUCTIONS : **There are Six Questions. Answer ANY FOUR Questions. Each question carries 25 marks.**

**Use of Non Programmable Electronic Calculators
is allowed.**

You must not open this examination paper until the chief invigilator has granted permission to do so.

SECTION A

Question 1 (25 marks)

- (a) State the conditions under which gases (real), deviate from ideal behaviour. Explain how these conditions cause deviations from ideality. [5]
- (b) (i) State the ideal gas law and the Van der Waals' equation for real gases. [2]
(ii) For the Van der Waals equation, interpret the constants 'a' and 'b' in the expression and discuss the factors that influence each of them. [4]
- © A 10.0 mol sample of ammonia gas is contained in a 60.0 L container at 100.0°C.
(i) Calculate the pressure exerted by the gas assuming ideal behaviour. [4]
(ii) Calculate the pressure exerted by the gas assuming real behaviour. [6]
(iii) By what percentage do the two pressures obtained in (i) differ? [4]

(For $\text{NH}_3(\text{g})$: a = 4.17 L²-atm/mol², and
b = 0.0371 L/mol
Use : R = 0.0821 L.atm.mol⁻¹K⁻¹)

Question 2 (25 marks)

- (a) State the Arrhenius equation relating the specific rate constant and the activation energy of a reaction at a given temperature. Define the parameter 'A', in this equation and discuss its units and significance. [6]
- (b) From the Arrhenius equation, discuss:
(i) The variation of the specific rate constant, k, with temperature
(ii) The variation of the activation energy, E_a , with the specific rate constant
(iii) The variation of the activation energy with temperature. [3]
- (a) The data obtained during the reaction between aqueous hydrochloric acid and aqueous sodium thiosulphate to precipitate sulphur are tabulated below:

T(°C)	25	35	45	55	65
t(s)	25.3	17.9	12.5	9.0	6.0
k(s ⁻¹)	0.040	0.056	0.080	0.111	0.152

- (i) Using the Arrhenius plot, evaluate the activation energy, E_a , for this reaction. [10]
- (ii) Calculate the 'A' factor for this reaction at 25°C. [3]
- (iii) If the precipitation of the sulphur follows a first order rate law, estimate its half life at a temperature of 45°C. [3]

Question 3 (25 marks)

- (a) Define or explain the following terms:
(i) Calorimeter constant
(ii) Enthalpy change of combustion, ΔH°_c
(iii) Enthalpy change of vapourization, $\Delta H^\circ_{\text{vap}}$ [3]
- (b) Differentiate between the terms: 'specific enthalpy' and 'enthalpy density' with respect to fuels and food. Give the S.I. units of each of them. [3]
- (c) When a reaction that was known to release 35.10 KJ of heat was carried out in a bomb calorimeter containing 100 mL of water, a 7.3°C rise in temperature was observed. A small amount of a salt was placed in the same calorimeter and 100.0 mL of dilute $\text{HCl}_{(\text{aq})}$ was added to it. The temperature then rose by 3.25°C. Calculate the heat released during this reaction. [6]
- (d) The 50.0L tank of an automobile engine using hydrogen gas as fuel was filled with hydrogen gas at 15.0 atm and 298K. After running the engine for some period of time, the pressure dropped to 3.0 atm, while the temperature was maintained at 298K
(i) Calculate the number of moles of hydrogen burned while the engine was running. [5]
(ii) What quantity of heat was given off by the combustion of that amount of hydrogen? [4]

$$(\Delta H^\circ_c = -286 \text{ KJ/mol, for } \text{H}_{2(\text{g})})$$

- (e) Given the data in the table below, calculate the $\Delta H^\circ_{\text{rxn}}$ for the reaction:



Substance	$\text{H}_2\text{O}_{(\text{l})}$	$\text{NO}_{(\text{g})}$	$\text{NO}_{2(\text{g})}$	$\text{HNO}_{3(\text{aq})}$	$\text{NH}_3(\text{g})$
$\Delta H^\circ_f(\text{KJ/mol})$	-286	90	34	-207	-46

[4]

SECTION B**STRUCTURE AND PROPERTIES OF ORGANIC COMPOUNDS****Question 4 (25 marks)**

- (a) Use the principles and rules that govern the distribution of electrons in atomic orbitals to write the correct ground state electron configuration of any five elements in the periodic table which are most commonly associated with the majority of organic compounds. (8 marks)

- (b) Using suitable examples, explain how the ground state electron configuration of an element determines the ability of that element to form bonds to other elements. (9 marks)
- (c) Nitrite ion $[\text{NO}_2]$ has the connectivity ONO .
- (i) Write Lewis structures for nitrite ion that obey the octet rule (4 marks)
- (ii) Do the two Lewis structures contribute equally to the resonance hybrid? (4 marks)

Question 5 (25 marks)

- (a) (i) Describe the bonding in ammonia assuming sp^3 hybridization of nitrogen. (3 marks)
- (ii) In what kind of orbital is the unshared pair of electrons? (2 marks)
- (iii) What orbital overlaps are involved in the $\text{N} - \text{H}$ bonds? (2 marks)
- (iv) Explain how the trigonal pyramidal structure of ammonia molecule determines its properties. (2 marks)
- (b) Explain the following terms as completely as possible. In each case, use suitable examples and illustrations to support the explanations. (8 marks)
- (i) Covalent bond
- (ii) An Orbital
- (iii) Formal Charge
- (iv) Resonance
- (c) Write the structural formulas for all the constitutional isomers that have the following molecular formula. (8 marks)
- (i) $\text{C}_2\text{H}_7\text{N}$.
- (ii) $\text{C}_3\text{H}_7\text{Cl}$
- (iii) $\text{C}_3\text{H}_8\text{O}$

Question 6 (25 marks)

- (a) Hypochlorous and hypobromous acid (HOCl and HOBr) are weak acids.
- (i) Write chemical equations for the ionization of each in water. (4 marks)

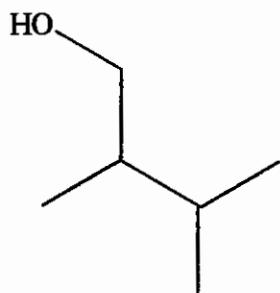
(ii) Predict which one is the stronger acid. Support your predictions with sound reasons. (4 marks)

(b) Expand the following bond line representations to show all the atoms including carbon and hydrogen. (8 marks)

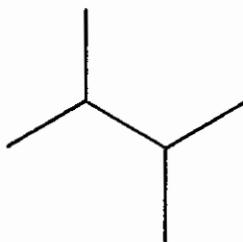
(i)



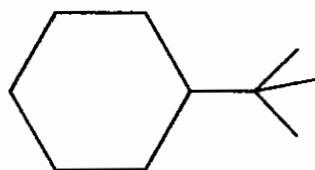
(ii)



(iii)



(iv)



(c) Borontrifluoride (BF_3) reacts readily with ammonia to form a compound $\text{BF}_3 \cdot \text{NH}_3$.

(i) What factors account for the reaction taking place so readily? (3 marks)

(ii) Specify the formal charge present on (a) boron, (b) nitrogen atoms in the product $\text{BF}_3 \cdot \text{NH}_3$. (3 marks)

(iii) What hybridization state would one expect for boron and nitrogen atoms in the product? (3 marks)

PERIODIC TABLE OF ELEMENTS

GROUPS

DPS		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18					
		IA	IIA	IIIB	IVB	VB	VIB	VII	VIII		IB		IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA					
	H 1																			He 2				
	6.941 Li 3	9.012 Be 4																	10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
	22.990 Na 11	24.305 Mg 12																	26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
TRANSITION ELEMENTS																								
	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						
	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						
	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						
	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														

Atomic mass →
Symbol ←→
Atomic No. ←

*Lanthanide Series		**Actinide 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
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.

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