

22

UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2005

TITLE OF PAPER: **INTRODUCTORY INORGANIC CHEMISTR**

COURSE NUMBER: **C201**

TIME: **THREE (3) HOURS**

INSTRUCTIONS: **There are six (6) questions each worth 25 marks.
Answer any four (4) questions.
A data sheet and periodic table are attached.
Non-programmable calculators may be used.**

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

Question 1

- (a) On the same diagram, sketch the radial distribution for the 1s, 2s and 2p orbitals. Mention two differences between the 2s and 2p orbitals. [5]
- (b) Explain the following terms, giving examples where possible to clarify your answers. [8]
- (i) Lattice Energy
 - (ii) Three centre-two electron bond
 - (iii) Inert pair effect
 - (iv) Diagonal relationship
- (c) The Li^{2+} ion is a one electron system similar to hydrogen. Calculate the frequency of the radiation involved if the electron undergoes a transition from $n=3$ to $n=1$ energy levels. Is the radiation absorbed or emitted? [3]
- (d) (i) Write the electronic configuration of the Cr atom.
- (ii) Using Slater's rules, calculate the effective nuclear charges on an electron in the 4s and the 3s orbital of the Cr atom.
- (iii) From which orbital would an electron be removed to form the Cr^+ ion? [1,3,2]
- (e) Explain why the 1st I.E. of Mg is higher than that of Na, but the 2nd I.E. of Na is higher than that of Mg. [3]

Question 2

- (a) (i) Draw a clear well labelled molecular orbital diagram of the CN molecule. [4]
- (ii) How does this molecule differ from the CN^- molecule in bond length, bond strength and magnetic properties. [4]
- (b) Consider the following molecules
- XeF_4 , ClF_3 and IF_4^+
- (i) Determine the hybridization of the central atom.
- (ii) Draw the Lewis structure and predict the shape. [6]
- (c) Account for the following observations
- (i) SF_6 is known but OF_6 does not exist
- (ii) CCl_4 is completely inert towards water whereas SiCl_4 is immediately hydrolysed on contact with water.
- (iii) Boron halides are Lewis acids only, but trivalent phosphorus compounds can serve as both Lewis acids and Lewis bases. [6]
- (d) Explain, with examples, the following terms
- (i) n-type semi-conductor
- (ii) hydrogen bonding [5]

Question 3

- (a) The distance between the centres of the positive and negative ions in NaF is 321 pm. Determine:
- (i) The ionic radii of Na^+ and F^-
 - (ii) The coordination number and shape of the NaF crystal lattice.
- [5]
- (b) The crystal lattice is usually far from being perfect and different defects may be found in a crystal. Discuss the following defects and state how they help in improving the conductivity of the ionic solid.
- (i) Metal excess
 - (ii) Frenkel defects
 - (iii) Schottky defects
- [9]
- (c) Explain the meaning and differences between a metallic conductor, a semiconductor and an insulator
- [6]
- (d) Arrange the following compounds in order of increase in lattice energy
- $\text{Mg}(\text{OH})_2$, MgO , Al_2O_3 , NaOH and $\text{Al}(\text{OH})_3$
- Justify your order.
- [5]

Question 4

- (a) (i) Give the names and symbols (A_ZX) of the three isotopes of hydrogen. [1½]
- (ii) Describe one method for the industrial production of hydrogen. [3]
- (iii) Mention one use of hydrogen gas. [2½]
- (iv) Discuss the similarities and differences between the bonding in B_2H_6 and B_2Cl_6 . [4]
- (b) When a white substance (A), was treated with dilute $HCl(aq)$ a colourless gas, B, was evolved which turned moist litmus paper red. On bubbling the gas B through lime water, a white precipitate was formed which dissolved to give a clear solution D. On strong heating, A decomposed to give a white precipitate E which turned litmus paper blue. When 1.9735 g of A was heated, it gave 1.5334 g of E. A 25.00 mL portion of the resulting solution required 20.30 mL of a 0.0985 M $HCl(aq)$ for titration to the end point.
- (i) Identify, with explanations, the compound A to E by name and chemical formulae.
- (ii) Write balanced equations for all the reactions mentioned.
- (iii) From the titration data, calculate the molar mass of A. [14]

Question 5

- (a) Define the following terms
- (i) Isotope
 - (ii) β decay
 - (iii) Nuclear fusion.
- [6]
- (b) Write equation showing how ${}_{92}^{238}\text{U}$ and ${}_{7}^{13}\text{N}$ under α decay and β^+ emission respectively.
- [4]
- (c) Explain or account for the following:
- (i) The variation in boiling points of the Group VI hydrides whose values are 100, -60, -42 and -2.3°C for H_2O , H_2S , H_2Se and H_2Te respectively.
- [6]
- (ii) The difference in bond angles of H_2O (105°) and F_2O (102°)
- [5]
- (d) In each of the following pairs, which is the larger radius
- (i) S^{2-} , Br^-
 - (ii) Fe^{2+} , Co^{3+}
- [4]

QUESTION 6

- (a) Draw Lewis structures to show the arrangement of valence electrons in boric acid and in its conjugate base. Write an equation to show how boric acid ionises in water. [4]
- (b) (i) Suggest the reasons why Be^{2+} ion is less than half the size of Mg^{2+} .
(ii) Why does Be have the same properties as Al?
(iii) What do you understand by the term hydrolyse?
(iv) Explain why Be salts (e.g. the chloride) readily hydrolyse whereas strontium salts do not.
(v) BeH_2 and AlCl_3 are both polymers. Explain why the two compounds polymerise and describe the bonding in both. [10]
- (c) Write balanced equations to show how water reacts with
(i) sodium
(ii) sodium oxide
(iii) sodium hydride [6]
- (d) The hardness of water may be 'temporary' or 'permanent'. What causes each of these conditions and how is each treated? [5]

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	VIIIB	VIIIB			IB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H																	4.003 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
3	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																		
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 Rc 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) Uue 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 $\hbar = h/2\pi$	$6.626\,08 \times 10^{-34} \text{ J s}$ $1.054\,57 \times 10^{-34} \text{ J s}$
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	$\epsilon_0 = 1/c^2 \mu_0$ $4\pi\epsilon_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
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

UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION 2005

TITLE OF PAPER: **INTRODUCTORY INORGANIC CHEMISTR**

COURSE NUMBER: **C201**

TIME: **THREE (3) HOURS**

INSTRUCTIONS: There are six (6) questions each worth 25 marks.
 Answer any four (4) questions.
 A data sheet and periodic table are attached.
 Non-programmable calculators may be used.

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

QUESTION 1

- a) Various quantum numbers are needed to describe the state of an electron in an atom.
- what are the quantum numbers? *(1 mark)*
 - what properties of the electrons or atomic orbitals are determined or described by these quantum numbers? *(4 marks)*
 - give all the quantum numbers of each of the valence electrons in chlorine. *(3 marks)*

- b) Using the data below, predict the crystal structure of MgS.

ion	ionic radius (pm)	
Mg	86	
S	170	<i>(2 marks)</i>

- c) Describe the type of defects that can occur in the solid state. In each case give at least one example and indicate if any electrical conduction is possible and by what mechanism. *(15 marks)*

QUESTION 2

- a) What postulates did Bohr advance in explaining how electrons are confined to orbitals instead of slowing down or being attracted towards the nucleus? (5 marks)
- b) The transition from the $n = 7$ to the $n = 2$ level of hydrogen atom is accompanied by the emission of light slightly beyond the range of human perception. Determine the energy and the wavelength of this light. (5 marks)
- c) Draw a clear well-labelled molecular orbital diagram of O_2 . Using the diagram, deduce:
- the bond orders of O_2 , O_2^- , O_2^{2-} and O_2^+
 - for each of the above species discuss the magnetic properties. (10 marks)
- d) Arrange the following compounds in order of increase in lattice energy:
 $Mg(OH)_2$, MgO , Al_2O_3 , Na_2O , $NaOH$, $Al(OH)_3$
Justify your order. (5 marks)

QUESTION 3

a) Use Slater's rules to calculate the effective nuclear charge experienced by

- i. the valence electron in the atom N
- ii. the valence 4s electron in the atom Zn
- iii. a 3d electron in Zn

(2 each = 6 marks)

b) i. Define the terms 'ionization energy' and 'electronegativity'

(1 mark)

Account for the following observations:

ii. variation in electronegativity

F	Cl	Br	I
4.10	2.83	2.74	2.21

(3 marks)

iii. variation in first ionization energies of Group II metal (kJ mol^{-1})

Be	Mg	Ca	Sr
899	737	590	549

(3 marks)

c) Define the following terms:

- i. α -decay
- ii. γ -radiation
- iii. nuclear fission

(6 marks)

d) If X, Y and Z represent elements of atomic number 9, 17 and 55 respectively, predict

the type of bonding you would expect to occur between

- i. X and Y
- ii. X and Z
- iii. Y and Z

(6 marks)

QUESTION 4

a) Account for the following observations:

- i. There is no reaction between NCl_3 and Cl_2 whereas PCl_3 reacts with Cl_2 to give PCl_5 .
- ii. Ionic compounds usually react rapidly whilst covalent compounds usually react slowly.
- iii. Methanol CH_3OH has a much higher boiling point than methyl mercaptan, CH_3SH .

(6 marks)

b) Write equations for each of the following reactions:

- i. Hydrolysis of diborane
- ii. Hydrolysis of SiCl_4
- iii. Reduction of BF_3 with NaH

(6 marks)

c) The hardness of water may be 'temporary' or 'permanent'. What causes each of these conditions and how is each treated?

(8 marks)

d) On treatment with cold water, an element (A) reacted quickly liberating a colourless odourless gas (B) and a solution (C). When carbon dioxide was bubbled through solution (C) an initial white precipitate (D) was formed, but this re-dissolved forming solution (E) when more carbon dioxide was added. Name the substances (A) to (E).

(5 marks)

QUESTION 6

- a) Orthoboric acid may be written as H_3BO_3 or $\text{B}(\text{OH})_3$. Is it a strong or a weak acid? How does it ionize in water? [1, 2 marks]
- b) Draw a simple well-labeled molecular orbital diagram of CO (carbon monoxide).
- determine the bond order of CO.
 - is it paramagnetic or diamagnetic?
 - how would you prepare CO in the laboratory?
 - give two uses of CO
 - explain how CO is quantitatively determined [3, 1, 1, 2, 2, 2 marks]
- c) Boron halides are Lewis acids only but trivalent phosphorus compounds can serve as both Lewis acids and Lewis bases. Explain this observation. [6 marks]
- d) Explain what is meant by 'inert pair effect'. [3 marks]
- e) The ionization energy of Pb is unexpectedly higher than that of Sn. Why? [2 marks]

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 1.008	IIA	IIIB	IVB	VB	VIB	VIIA	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	H 1	He 4.003																He 4.003
2	Li 6.941	Be 9.012																F 18.998
3	Na 22.990	Mg 24.305																Ne 20.180
4	K 39.098	Ca 40.078	Sc 44.956	Ti 47.88	V 50.942	Cr 51.996	Mn 54.938	Fe 55.847	Co 58.933	Ni 58.69	Cu 63.546	Zn 65.39	Ga 69.723	Ge 72.61	As 74.922	Se 78.96	Br 79.904	Ar 39.948
5	Rb 85.468	Sr 87.62	Y 88.906	Zr 91.224	Nb 92.906	Mo 95.94	Tc 98.907	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.71	Sb 121.75	Te 127.60	I 126.90	Xe 131.29
6	Cs 132.91	Ba 137.33	*La 138.91	Hf 178.49	Ta 180.95	W 183.85	Rc 186.21	Os 190.2	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	(209)	At (210)	Rn (222)
7	Fr 223	Ra 226.03	**Ac (227)	Rf (261)	Rf (262)	Uuh (263)	Uns (262)	Uno (265)	Uue (266)	Uun (267)								

TRANSITION ELEMENTS

Atomic mass	Symbol	Atomic No.
10.811	B	5
26.982	Al	13
28.086	Si	14
30.974	P	15
32.06	S	16
35.453	Cl	17
39.948	Ar	18

*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 kJ mol ⁻¹

Prefixes	f	p	n	μ	m	c	d	k	M	G
	fermto	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

UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE

EXAMINATION 2005

TITLE OF PAPER : PHYSICAL CHEMISTRY

COURSE NUMBER : C202

TIME : 3 HOURS

INSTRUCTIONS : THERE ARE SIX QUESTIONS

: ANSWER ANY FOUR QUESTIONS

: BEGIN THE ANSWER TO EACH QUESTION ON
A SEPARATE SHEET OF PAPER

: DATA SHEETS ARE PROVIDED WITH THIS
EXAMINATION PAPER

DO NOT OPEN THIS PAPER UNTIL THE INVIGILATOR INSTRUCTS YOU TO DO
SO.

Question 1 [25 Marks]

- a) Define the variable, compressibility factor, z . With the aid of Lennard-Jones potential plot and compressibility plots, compare and contrast real and ideal gases.

Your account should make mention of interactions, equations and any necessary theories to help clarify your discussion. [10]

- b) A mixture of butane (C_4H_{10}) and propene (C_3H_6) occupied 35.5 L at 1.000 bar and 405 K. This mixture reacted completely with 220.6 g of O_2 to produce CO_2 and H_2O .
- What was the composition of the original mixture? Assume ideal gas behaviour. MW (O_2)=32 g/mol [9]
 - Calculate the partial pressure, mole fraction of each gas and the total pressure of the final mixture. [6]

Question 2 [25 Marks]

- a) Write short notes on any One of the following: [10]
- Virial equation
 - van der waal's equation

Use diagrams, equations or plots to clarify your notes where necessary.

- b) A real gas equation of state for a gas is given by:

$$P = RT(V_m - 3b)^{-1} - (2a/T)V_m^{-2} \quad (1)$$

- Derive an expression for $V_{m,c}$, T_c and P_c . [6]
- Find an expression for the Boyle's temperature, T_B . [4]
- Estimate the temperature at which oxygen behaves as an ideal gas, T_B given the constants: $a=1.748 \text{ L}^2\text{atm mol}^{-2}\text{K}$ and $b=0.0345 \text{ L mol}^{-1}$. [2]
- Estimate the radii of real gas molecules using equation (1) given that the critical molar volume is $250 \text{ cm}^3\text{mol}^{-1}$ [3]

Question 3 [25 MARKS]

- a) Using examples and/or diagrams compare and contrast Any Two of the following terms
- reversible and irreversible expansion [5]
 - path and state functions [5]
 - work and heat [5]
 - change in internal energy and change in enthalpy [5]
- b) 2 moles of methane occupies 12 L at 310 K.
- Derive an expression for reversible isothermal expansion. [5]
 - Calculate the work done when the gas expands isothermally against a constant external pressure of 200 torr until its volume has tripled. [5]
 - Calculate the work that would be done if the same expansion in b(ii) occurred in a series of equilibrium steps. [5]

Question 4 [25 Marks]

- a) Write short notes on **Any Two** of the following concepts:
- Statistical view of entropy [5]
 - Clausius inequality [5]
 - Second law of thermodynamics [5]
 - Third law of thermodynamics [5]

For each concept include the origin or a short derivation showing its origin, an example where applicable and the role or implication of each of the concepts in thermodynamics.

- b) (i) Using an illustration of your choice define fugacity [5]
 (ii) Using the following chemical potential expression for ideal and real gases

$$\mu_2 = \mu_1^\ominus + RT \ln \left(\frac{p_2}{p_1^\ominus} \right) \text{ and } \mu_2 = \mu_1^\ominus + RT \ln \left(\frac{f_2}{f_1^\ominus} \right), \text{ respectively.}$$

Derive the fugacity expression

$$f = p \exp \int_{p_1}^{p_2} \left\{ \frac{Z(p, T) - 1}{p} \right\} dp \quad [5]$$

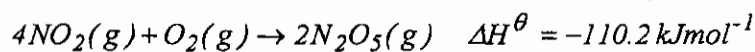
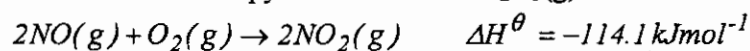
- (iii) Given that fugacity is given by the expression: [5]

$$f = p \exp \int_{p_1}^{p_2} \left\{ \frac{Z(p, T) - 1}{p} \right\} dp$$

Evaluate fugacity of O₂ at 200 K given that the compression factor of O₂ is 0.98796 at 4.00000 atm.

Question 5 [25 Marks]

- a) (i) Calculate the enthalpy of formation of N₂O₅(g) from the following data: [9]

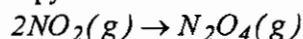


- (ii) Using the enthalpy of formation of N₂O₅(g) obtained from a(i) calculate the change in internal energy for the formation of N₂O₅(g) [6]

- b) (i) Derive Kirrchoff's equation: [4]

$$\Delta H_r(T_2) = \Delta H_r(T_1) + \Delta_r C_p \Delta T$$

- (ii) Predict the standard enthalpy of reaction at 100°C for the reaction: [6]



Refer to table and the data below:

	C _p J mol ⁻¹ K ⁻¹
N ₂ O ₄ (g)	77.28
NO ₂ (g)	37.20

Question 6 [25 Marks]

- a) Calculate the change in entropies of the system, ΔS_{sys} , the surroundings, ΔS_{surr} , and the total change in entropy, ΔS_{tot} , when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in:
- an isothermal reversible expansion [6]
 - an irreversible isothermal expansion against an external pressure of 0.5 bar. [4]
- b) What would the change in entropy be if the gas in (a) was compressed to half its volume and simultaneously heated to twice its initial temperature? [5]
- c) If 50g water at 80°C is poured into 100g water at 10°C in an insulated vessel given that $C_{p,m}=75.5 \text{ JK}^{-1}\text{mol}^{-1}$: Calculate:
- final temperature of the mixture [4]
 - the entropy change [6]

THE PERIODIC TABLE OF ELEMENTS

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
	IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIIIB	VIIIB	VIIIB	IB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
Period 1	1 H 1.008																	2 He 4.003	
2	3 Li 6.94	4 Be 9.01																	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31																	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.9	26 Fe 55.85	27 Co 58.71	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.7	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80	
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 91.22	42 Mo 95.94	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3	
6	55 Cs 132.9	56 Ba 137.3	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 210	85 At 210	86 Rn 222	
7	87 Fr 223	88 Ra 226.0	103 Lr 257	104 Unq	105 Unp	106 Uhh	107 Uns	108 Uno	109 Une										

METALS

METALLOIDS

NON-METALS

Lanthanides						
57	58	59	60	61	62	63
La	Ce	Pr	Nd	Pm	Sm	Eu
138.9	140.1	140.9	144.2	146.9	150.9	151.3
89	90	91	92	93	94	95
Ac	Th	Pa	U	Np	Pu	Am
227.0	232.0	231.0	238.0	237.1	239.1	241.1
64	65	66	67	68	69	70
Gd	Tb	Dy	Ho	Er	Tm	Yb
157.3	158.9	162.5	164.9	167.3	168.9	173.0
96	97	98	99	100	101	102
Cm	Bk	Cf	Es	Fm	Md	No
247.1	249.1	251.1	254.1	257.1	258.1	255

Numbers below the symbol indicates the atomic masses, and the numbers above the symbol indicates the atomic numbers.

F

Standard molar enthalpies of formation at 298.15 K

Temperature dependence of heat capacities, $C_{p,m} = a + bT + cT^{-2}$

M ₁		M ₂		M ₃		M ₄		M ₅	
ΔH _f ⁰ /kJ/mol		ΔH _f ⁰ /kJ/mol		ΔH _f ⁰ /kJ/mol		ΔH _f ⁰ /kJ/mol		ΔH _f ⁰ /kJ/mol	
T/K		T/K		T/K		T/K		T/K	
Fusion ^a		Evaporation ^b		Fusion ^a		Evaporation ^b		Fusion ^a	
H ₂ O(g)	18.015	-241.8	O ₂ (g)	47.998	+142.7	He, Ne, Ar, Kr, Xe	20.78	0	0
H ₂ O(l)	18.015	-285.8	NO(g)	30.006	+90.2	H ₂	27.28	3.26	0.50
H ₂ O(s)	34.015	-187.8	NO ₂ (g)	46.006	+33.2	O ₂	29.96	4.18	-1.67
NH ₃ (g)	17.031	-46.1	N ₂ O(g)	92.012	+9.2	N ₂	28.96	3.77	-0.50
NH ₃ (l)	32.045	+50.6	SO ₂ (g)	64.063	-296.8	CH ₄	37.03	0.67	-2.85
NH ₃ (s)	43.028	+264.1	H ₂ S(g)	34.080	-20.6	CO ₂	44.23	8.19	-6.62
NH ₄ (g)	43.028	+294.1	SF ₆ (g)	146.054	-1209	H ₂ O	30.54	10.29	0
HNO ₂ (l)	63.013	-174.1	HF(g)	20.006	-271.1	NH ₃	29.75	25.10	-1.55
NH ₄ OH(s)	33.030	-114.2	HCl(g)	36.461	-92.3	CH ₄	23.64	47.86	-1.92
NH ₄ Cl(s)	53.492	-314.4	HCl(aq)	36.461	-167.2	C(s)	16.86	4.77	-8.54
HgCl ₂ (s)	271.50	-224.3	HBr(g)	80.917	+36.4				
H ₂ SO ₄ (l)	98.078	-814.0	HI(g)	127.912	+26.5				
H ₂ SO ₄ (aq)	98.078	-909.3	CO ₂ (g)	44.010	-393.5				
NaCl(s)	58.443	-411.0	CO(g)	28.011	-110.5				
NaOH(s)	38.997	-426.7	Al ₂ O ₃ (s)	101.945	-1675.7				
KCl(s)	74.555	-435.9	SiO ₂ (s)	60.085	-910.9	Standard molar enthalpies of formation and combustion at 298.15 K			
KBr(s)	119.011	-392.2	FeS(s)	87.91	-1020	C ₂ H ₂ (g)	26.039	+226.8	-1300
KI(s)	166.006	-327.6	FeS ₂ (s)	119.975	-178.2	C ₂ H ₄ (g)	28.054	+52.30	-1411
DIATOMICS	Eq. N ₂ , O ₂ , H ₂	0	AgCl(s)	143.323	-127.1	C ₂ H ₆ (g)	30.070	-84.64	-1560
						C ₂ H ₆ (l)	42.081	53.35	-2091
						C ₂ H ₆ (propene)(g)	42.081	20.5	-2058
						C ₂ H ₁₀ n-butane (g)	58.124	-126.11	-2877
						C ₂ H ₁₂ n-pentane(g)	72.151	-146.4	-3536
						C ₂ H ₁₂ cyclohexane (l)	84.163	-156.2	-3920
						C ₂ H ₁₄ n-hexane (l)	86.178	-198.7	-4163
						C ₂ H ₆ benzene (l)	78.115	+48.98	-3268
						C ₂ H ₁₈ n-octane (l)	114.233	-249.8	-5471
						C ₂ H ₁₆ naphthalene (l)	128.175	+78.53	-5157
						CH ₃ OH (l)	32.042	-239.0	-726.1
						CH ₃ CHO (g)	44.054	-166.0	-1193
						CH ₃ CH ₂ OH (l)	46.070	-277.0	-1366
						CH ₃ COOH (l)	60.053	-464.2	-874.5
						CH ₃ COOC ₂ H ₅ (l)	88.107	-486.6	-2231
						CH ₃ COOC ₂ H ₅ (s)	94.114	-165.0	-3054
						C ₂ H ₅ OH (s)	93.129	-31.1	-3393
						C ₂ H ₅ NH ₂ (l)	90.056	-333.0	-632.2
						NH ₂ CO.NH ₂ , urea(s)	75.088	-537.2	-964.4
						CH ₂ (NH ₂)CO ₂ H, glycine (s)	180.159	-1274	-2802
						C ₆ H ₁₂ O ₆ , α-D-glucose (s)	180.159	-1268	-2808
						C ₆ H ₁₂ O ₆ , β-D-glucose (s)	342.303	-2222	-5645
						C ₁₂ H ₂₂ O ₁₁ , sucrose (s)	90.079	-694.0	-1344
						CH ₃ CH(OH)COOH			
						lactic acid (s)			

^a Sublimation; ^b various pressures; ^c at 1 atm

Source: American Institute of Physics handbook, McGraw-Hill.

5

Heat capacities at 25°C

	$C_{v,m}$	$C_{p,m}$
	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$
He, Ne, Ar, Kr, Xe	12.47	20.78
H ₂	20.50	28.81
O ₂	21.01	29.33
N ₂	20.83	29.14
CO ₂	28.83	37.14
NH ₃	27.17	35.48
CH ₄	27.43	35.74
N ₂ O ₄		77.28
NO ₂		37.20

F.P. Depression, B.P. Elevation

Solvent	F.P. °C	K _f °C kg mol ⁻¹	B.P. (°C, 101kNm ⁻²)	K _b °C kg mol ⁻¹
Water	0	1.86	100.0	0.52
Benzene	5.51	5.10	80.1	2.60
Acetic Acid	16.6	3.90	118.1	3.10
Cyclohexane	6.5	20.2	81.4	2.79
Camphor	177.7	40.0	205	-
Nitrobenzene	5.7	6.9	210.9	5.24
Ethanol	-177		78.5	1.22
Chloroform	-64		61.3	3.63

Third Law entropies at 25°C, $\text{Sm}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$

Solids		Liquids		Gases	
Ag	42.68	Hg	76.02	H ₂	130.6
C(gr)	5.77	Br ₂	152.3	N ₂	192.1
C(d)	2.44			O ₂	205.1
Cu	33.4			Cl ₂	223.0
Zn	41.6	H ₂ O	70.0		
I ₂	116.7			CO ₂	213.7
S(Rh)	31.9	HNO ₃	155.6	HCl	186.8
				H ₂ S	205.6
AgCl	96.2	C ₂ H ₅ OH	161.0	NH ₃	192.5
AgBr	104.6	CH ₃ OH	126.7	CH ₄	186.1
CuSO ₄ ·5H ₂ O	305.4	C ₆ H ₆	49.03	C ₂ H ₆	229.4
HgCl ₂	144	CH ₃ COOH	159.8	CH ₃ CHO	265.7
Sucrose	360.2	C ₆ H ₁₂	298.2		