

Question one

- a) Give the Rydberg equation and define all the parameters in it. **[6 marks]**
- b) Give three quantum numbers that are obtained from solving the Schrodinger equation. For each quantum number, state possible values that are allowed. **[4.5 marks]**
- c) Give the quantum number that determines the
- shape of an orbital
 - energy of an orbital
 - orientation of an orbital
- [1.5 marks]**
- d) Consider three one-electron species N^{6+} , B^{4+} and C^{5+} . With the help a brief explanation, answer the following questions:
- Which one of the species has the smallest and which one has the largest most probable radius of the 1s orbital? **[4 marks]**
 - Which one of the species is expected to have the smallest energy gap and which one is expected to have the largest energy gap between any two shells? **[4 marks]**
- e) Sketch the angular part and the radial distribution function of the $5d_{zx}$ orbital **[5 marks]**

Question Two

- a) Consider the two atoms Ca and K.
- Calculate the effective nuclear charge (Z_{eff}) for an electron in the 4s orbital of each of the atoms (K and Ca) [6 marks]
 - The first ionization energies, IE_1 , of K and Ca are 418.8 and 589.8 kJmol^{-1} respectively. Is the trend in these values consistent with the values of Z_{eff} you calculated in i) above? Explain your answer. [2 marks]
- b) Consider the molecule XeO_2Cl_2 .
- Write three non-equivalent Lewis structures for the molecule
 - Out of the structures in i) above, use formal charges to determine the most reasonable one
 - Write the formula of the molecule in the form AB_xE_y and then determine, for the molecule, the
 - ❖ overall geometry
 - ❖ molecular geometry (or shape)
 - ❖ hybridization of the Xe atom
- [17 marks]

Question Three

- a) One member of each of the following sets is not isoelectronic with the others. Which one in each set is not isoelectronic with the others?
- $[\text{NO}_2]^+$, CO_2 , $[\text{NO}_2]^-$ and $[\text{N}_3]^-$
 - CO , NO^+ , CN^- and NO
- [4 marks]
- b) Each of the following is a radical. For which does a Lewis structure incorrectly predict this property? Your answer should include Lewis structures of the molecules.
- i) NO ii) O_2 iii) NF_2
- [3 marks]
- c) Draw two equivalent Lewis structures for the O_3 molecule and calculate the average bond order.
- [3 marks]

- d) Using **valence orbitals only**, prepare a molecular orbital energy level diagram for C_2 , showing clearly how the atomic orbitals interact to form molecular orbitals. Use the diagram you have drawn to answer the following questions.
- Write electron configurations for each of the species C_2 , C_2^{2-} and C_2^{4+} .
 - For each of the species in i) above, predict the bond order and the number of unpaired electrons
 - Which of the species in i) above would you expect to have the shortest bond, and why?

[15 marks]

Question Four

- a) For each of the following, give one example and a complex derived from it:
- Group 13 halide
 - Group 15 halide
- [4 marks]
- b) With the help of a balanced reaction equation, illustrate the synthesis of each of the following:
- $EtMgCl$
 - CaH_2
- [4 marks]
- c) Briefly describe the difference between saline and molecular hydrides with respect to the following:
- Nature of bonding
 - Reaction with protic solvents
 - Melting and boiling points
- [6 marks]
- d) What explanation can you give for the decrease in solubility of the alkaline earth metal sulphates in the sequence $CaSO_4 > SrSO_4 > BaSO_4$?
- [4 marks]
- e) Explain the fact that the maximum coordination number of Li^+ complexes is 4 whereas that of other group 1 ions, such as Na^+ , can have coordination numbers as high as six. [Hint: Use hybridization schemes to illustrate your answer].
- [7 marks]

Question Five

- a) Sketch the Born-Haber cycle for the formation of LiH(s) from Li(s) and H₂(g). Then calculate the electron affinity of the gaseous hydrogen atom from the following data:

Sublimation of Li(s)	+155 kJmol ⁻¹
Ionization of Li(g)	+518 kJmol ⁻¹
Dissociation of H ₂ (g)	+432 kJmol ⁻¹
Enthalpy of formation of LiH(s)	-90 kJmol ⁻¹
Lattice energy of LiH(s).....	-906 kJ mol ⁻¹

[9 marks]

- b) Cs metal crystallizes in a bcc lattice and has density of 1.873g.cm⁻³. Calculate the radius of a cesium atom.

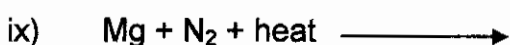
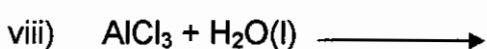
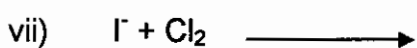
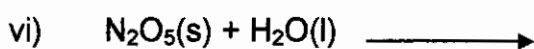
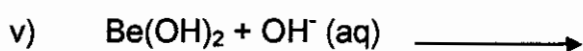
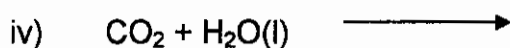
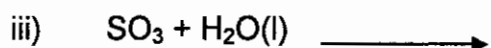
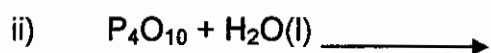
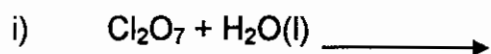
[13 marks]

- c) Explain the fact that of all group 1 halides, lithium halides are the most soluble in organic solvents.

[3 marks]

Question Six

- a) Complete and balance the following reactions:



[18 marks]

b) For each of the following species, sketch the structure and indicate the coordination number around the central atom.

- i) Ga_2H_6
- ii) IF_7
- iii) $[\text{SiF}_6]^{2-}$
- iv) H_3BNH_3

[7 marks]

PERIODIC TABLE OF THE 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	VIIA	VIII	IB	IIA	IIIB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
1	1.008 H																		4.003 He
2	6.941 Li	9.012 Be																	20.180 Ne
3	22.990 Na	24.305 Mg																	39.948 Ar
4	39.0983 K	40.078 Ca	44.956 Sc	47.88 Ti	50.9415 V	51.996 Cr	54.938 Mn	55.847 Fe	58.933 Co	58.69 Ni	63.546 Cu	65.39 Zn	69.723 Ga	72.61 Ge	74.922 As	78.96 Se	79.904 Br	83.80 Kr	
5	85.468 Rb	87.62 Sr	88.906 Y	91.224 Zr	92.9064 Nb	95.94 Mo	98.907 Tc	101.07 Ru	102.906 Rh	106.42 Pd	107.868 Ag	112.41 Cd	114.82 In	118.71 Sn	121.75 Sb	127.60 Te	126.904 I	131.29 Xe	
6	132.905 Cs	137.33 Ba	138.906 *La	178.49 Hf	180.948 Ta	183.85 W	186.207 Re	190.2 Os	192.22 Ir	195.08 Pt	196.967 Au	200.59 Hg	204.383 Tl	207.2 Pb	208.980 Bi	(209) Po	(210) At	(222) Rn	
7	(223) Fr	226.025 Ra	(227) **Ac	(261) Rf	(262) Ha	(263) Unh	(262) Uns	(265) Uno	(266) Une										

TRANSITION ELEMENTS

140.115 Ce	140.908 Pr	144.24 Nd	(145) Pm	150.36 Sm	151.96 Eu	157.25 Gd	158.925 Tb	162.50 Dy	164.930 Ho	167.26 Er	168.934 Tm	173.04 Yb	174.967 Lu
232.038 Th	231.036 Pa	238.029 U	237.048 Np	(244) Pu	(243) Am	(247) Cm	(247) Bk	(251) Cf	(252) Es	(257) Fm	(258) Md	(259) No	(260) Lr

* Lanthanide series

** Actinide series

Numbers below the symbol of the element indicates the atomic numbers. Atomic masses, above the symbol of the element, are based on the assigned relative atomic mass of ¹²C = exactly 12; () indicates the mass number of the isotope with the longest half-life.

SOURCE: International Union of Pure and Applied Chemistry, I. Mills, ed., *Quantities, Units, and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Boston, 1988, pp 86-98.

PHYSICAL AND CHEMICAL CONSTANTS

Avogadro's number	$N_A = 6.022045 \times 10^{23} \text{ mol}^{-1}$
Electron charge	$e = 4.8030 \times 10^{-10} \text{ abs esu}$ $= 1.6021892 \times 10^{-19} \text{ C}$
Electron mass	$m_e = 9.1091 \times 10^{-31} \text{ kg}$ $= 5.4860 \times 10^{-4} \text{ amu}$ $= 0.5110 \text{ MeV}$
Proton mass	$m_p = 1.6726485 \times 10^{-27} \text{ kg}$ $= 1.007276470 \text{ amu}$
Gas constant	$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$ $= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$
Ice point	$= 273.15 \text{ K}$
Molar volume	$= 22.414 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ $= 2.2414 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$
Planck's constant	$h = 6.626176 \times 10^{-34} \text{ J s}$ $= 6.626176 \times 10^{-27} \text{ erg s}$
Boltzmann's constant	$k = 1.380662 \times 10^{-23} \text{ J K}^{-1}$
Rydberg constant	$R = 1.097373177 \times 10^{-7} \text{ m}^{-1}$
Faraday's constant	$F = 9.648670 \times 10^4 \text{ C mol}^{-1}$
Speed of light	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$
Bohr radius	$a_0 = 0.52917706 \times 10^{-10} \text{ m}$
Other numbers	$\pi = 3.14159$ $e = 2.7183$ $\ln 10 = 2.3026$

CONVERSION FACTORS

1 cal	$= 4.184 \text{ joules (J)}$
1 eV/molecule	$= 96.485 \text{ kJ mol}^{-1}$ $= 23.061 \text{ kcal mol}^{-1}$
1 kcal mol ⁻¹	$= 349.76 \text{ cm}^{-1}$ $= 0.0433 \text{ eV}$
1 kJ mol ⁻¹	$= 83.54 \text{ cm}^{-1}$
1 wave number (cm ⁻¹)	$= 2.8591 \times 10^{-5} \text{ kcal mol}^{-1}$
1 erg	$= 2.390 \times 10^{-11} \text{ kcal}$
1 centimeter (cm)	$= 10^8 \text{ \AA}$ $= 10^7 \text{ nm}$
1 picometer (pm)	$= 10^{-2} \text{ \AA}$
1 nanometer (nm)	$= 10 \text{ \AA}$