

Question one

Which of the two electronic configurations has a lower energy: (i) $[\text{Ar}]3d^44s^2$ (ii) $[\text{Ar}]3d^54s^1$? Identify this element and discuss Hund's rule as it applies to this case.

[4 marks]

- b) When the 116th element is discovered, what would be its probable electronic configuration? Which group would it belong to?

[4 marks]

- c) The radial function $R(r)$ for a 2p orbital in a hydrogen atom is $K r \exp(-r/2a_0)$, where K is a constant and a_0 is the Bohr radius.

- i) Give the expression for the radial distribution function?
ii) What is the most probable radius, r_p ? Express r_p in terms of the Bohr radius a_0 .

[6 marks]

- d) Estimate the energy of radiation emitted from a one-electron cation with $Z=74$ when the electron drops from the N shell to the M shell

[4 marks]

- e) Give limits of values of each of the polar coordinates r , θ , ϕ in three-dimensional space around the nucleus of an atom.

[3 marks]

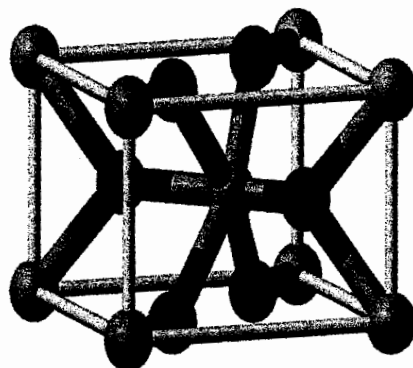
- f) For the $4dx^2-y^2$ atomic orbital, sketch:

- i) the radial distribution function, $P(r)$
ii) the angular part, $A(\theta, \phi)$, of the orbital

[4 marks]

Question Two

- a) Determine the number of formula units per unit cell of a titanium oxide whose unit cell has a rutile structure which is sketched below. [Note: oxide ions are represented by black spheres] **[5 marks]**



- b) Outline the Born-Haber cycle and calculate the lattice energy of RbF(s) given the following data:

Sublimation of Rb(s)	+86 kJmol ⁻¹
Ionization energy of Rb(g)	+402 kJmol ⁻¹
Dissociation energy of F ₂ (g)	+155 kJmol ⁻¹
Electron affinity of F(g)	-346 kJmol ⁻¹
Enthalpy of formation of RbF(s)	- 548 kJmol ⁻¹

[10 marks]

- c) Gold crystallizes in the fcc system, which has 4 lattice points per unit cell. The radius of the atom is 1.44 Å. Calculate the

- i) length of one side of the unit cell
- ii) volume of the unit cell
- iii) mass of the unit cell
- iv) density of gold

[10 marks]

Question Three

- a) Assuming the internuclear axis coincides with the z axis, sketch molecular orbitals arising from the following combinations of atomic orbitals:

- i) d_{z²} with d_{z²} (both bonding and antibonding)
- ii) p_y with d_{yz} (both bonding and antibonding)

[4 marks]

- b) Consider the diatomic molecule C_2 :
- Prepare a molecular orbital energy level diagram for this molecule
 - Use the diagram in i) above to give electron configurations for the ions C_2^{2-} , C_2^{4-} and C_2^{6-}
 - Calculate the bond order for each of the ions
 - List the ions in order of expected bond length, starting with the smallest.
- [12 marks]**
- c) (i) Write three **non-equivalent** Lewis structures of SO_3F^- , where sulphur is the central atom. Use formal charges to determine the best Lewis structure.
- (ii) Determine the hybridization of the S atom and the average S-O bond order in the best Lewis structure.
- [9 marks]**

Question Four

- a) On the basis of electron configuration, explain why:
- Sulphur has a lower electron affinity than chlorine
 - Iodine has a lower electron affinity than bromine
 - Sulphur has a lower ionization energy than phosphorus
- [6 marks]**
- b) Electron configurations for Ce, Pr, and Nd are, respectively, $[Xe]4f^15d^16s^2$, $[Xe]4f^36s^2$, $[Xe]4f^46s^2$.
- Use Slater's rules to calculate the effective nuclear charge, Z^* , for a 4f electron in Ce, Pr and Nd.
 - Are your calculated values consistent with the expected trend? Explain your answer.
- [12marks]**
- c) Explain the fact that SF_6 is known but OF_6 is not. Your answer should include hybridization scheme of SF_6 .
- [7 marks]**

Question Five

- a) How do anhydrous CaCl_2 and CaH_2 function as drying agents? [3 marks]
- b) Give a balanced chemical equation depicting reaction between:
- i) Strontium peroxide and hydrochloric acid
 - ii) Aluminium hydroxide and potassium hydroxide
 - iii) Potassium superoxide and water
 - v) BCl_3 and $\text{CH}_3\text{CH}_2\text{OH}$
 - v) B_2H_6 and O_2
- [8 marks]
- c) The values of the lattice energies of MgO , CaO and SrO are -3795 , -3414 and $-3220 \text{ kJ mol}^{-1}$ respectively. Show that this trend in values is consistent with the Kapustinski equation. [8 marks]
- d) Consider the salts Na_2CO_3 , Cs_2CO_3 , Na_2SO_4 , Li_2CO_3 , Li_2Cl and LiF .
- (i) Which ones are readily soluble in water?
 - (ii) Using LiCl and LiF as examples, discuss factors that contribute to the solubility of a salt.

[6 marks]

Question Six

- a) Consider the molecules BF_3 , B_2H_6 and Al_2Cl_6 .
- i) BF_3 has triangular planar geometry and has a p_π orbital that does not participate in σ -bonding. Use suitable diagrams to illustrate how this orbital gives rise to delocalized pi bonding in BF_3 . [5 marks]
 - ii) Draw the structure of B_2H_6 and indicate the two types of bonding present. [3 marks]
 - iii) Draw the structure of Al_2Cl_6 and indicate the two types of bonds present [2 marks]

b) Y is an element that belongs to group 2 and reacts with hot water to form A and a gas B, but the element does not react with cold water. Y reacts with hot air to form compounds C and D. Compound C is commonly used as a refractory material. Y is a strongly electropositive metal such that it reacts with AgNO_3 to form Ag and compound E. The oxide of Y reacts with hydrogen peroxide, H_2O_2 , to form peroxide, F.

i) Identify the element Y and the compounds A, B, C, D, E, and F.

ii) Give the reaction equations that lead to the formation of A, B, C, D, F and E. [It is not necessary to balance the equations].

[15 marks]

~~~~~**END OF EXAM**~~~~~

# 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                 | VIIIB                | VIII                |                      | IB                  | IIIB                 | IIIB                | IIIA                 | IVA                  | VA                   | VIA                 | VIIA                | VIIIA               |
| 1       | 1.008<br><b>H</b>    |                      |                       |                     |                      |                     |                      |                     |                      |                     |                      |                     |                      |                      |                      |                     |                     | 4.003<br><b>He</b>  |
| 2       | 6.941<br><b>Li</b>   | 9.012<br><b>Be</b>   |                       |                     |                      |                     |                      |                     |                      |                     |                      |                     | 10.811<br><b>B</b>   | 12.011<br><b>C</b>   | 14.007<br><b>N</b>   | 15.999<br><b>O</b>  | 18.998<br><b>F</b>  | 20.180<br><b>Ne</b> |
| 3       | 22.990<br><b>Na</b>  | 24.305<br><b>Mg</b>  |                       |                     |                      |                     |                      |                     |                      |                     |                      |                     | 26.982<br><b>Al</b>  | 28.0855<br><b>Si</b> | 30.9738<br><b>P</b>  | 32.06<br><b>S</b>   | 35.453<br><b>Cl</b> | 39.948<br><b>Ar</b> |
| 4       | 39.0983<br><b>K</b>  | 40.078<br><b>Ca</b>  | 44.956<br><b>Sc</b>   | 47.88<br><b>Ti</b>  | 50.9415<br><b>V</b>  | 51.996<br><b>Cr</b> | 54.938<br><b>Mn</b>  | 55.847<br><b>Fe</b> | 58.933<br><b>Co</b>  | 58.69<br><b>Ni</b>  | 63.546<br><b>Cu</b>  | 65.39<br><b>Zn</b>  | 69.723<br><b>Ga</b>  | 72.61<br><b>Ge</b>   | 74.922<br><b>As</b>  | 78.96<br><b>Se</b>  | 79.904<br><b>Br</b> | 83.80<br><b>Kr</b>  |
| 5       | 85.468<br><b>Rb</b>  | 87.62<br><b>Sr</b>   | 88.906<br><b>Y</b>    | 91.224<br><b>Zr</b> | 92.9064<br><b>Nb</b> | 95.94<br><b>Mo</b>  | 98.907<br><b>Tc</b>  | 101.07<br><b>Ru</b> | 102.906<br><b>Rh</b> | 106.42<br><b>Pd</b> | 107.868<br><b>Ag</b> | 112.41<br><b>Cd</b> | 114.82<br><b>In</b>  | 118.71<br><b>Sn</b>  | 121.75<br><b>Sb</b>  | 127.60<br><b>Te</b> | 126.904<br><b>I</b> | 131.29<br><b>Xe</b> |
| 6       | 132.905<br><b>Cs</b> | 137.33<br><b>Ba</b>  | 138.906<br><b>*La</b> | 178.49<br><b>Hf</b> | 180.948<br><b>Ta</b> | 183.85<br><b>W</b>  | 186.207<br><b>Re</b> | 190.2<br><b>Os</b>  | 192.22<br><b>Ir</b>  | 195.08<br><b>Pt</b> | 196.967<br><b>Au</b> | 200.59<br><b>Hg</b> | 204.383<br><b>Tl</b> | 207.2<br><b>Pb</b>   | 208.980<br><b>Bi</b> | (209)<br><b>Po</b>  | (210)<br><b>At</b>  | (222)<br><b>Rn</b>  |
| 7       | (223)<br><b>Fr</b>   | 226.025<br><b>Ra</b> | (227)<br><b>**Ac</b>  | (261)<br><b>Rf</b>  | (262)<br><b>Ha</b>   | (263)<br><b>Unh</b> | (262)<br><b>Uns</b>  | (265)<br><b>Uno</b> | (266)<br><b>Une</b>  |                     |                      |                     |                      |                      |                      |                     |                     |                     |

## TRANSITION ELEMENTS

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

\* 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 <sup>12</sup>C = 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 CONSTANTS

|                                |                  |                                                                          |
|--------------------------------|------------------|--------------------------------------------------------------------------|
| Speed of light in a vacuum     | $c_0$            | $2.99792458 \times 10^8 \text{ m s}^{-1}$                                |
| Permittivity of a vacuum       | $\epsilon_0$     | $8.854187816 \times 10^{-12} \text{ F m}^{-1}$                           |
|                                | $4\pi\epsilon_0$ | $1.11264 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$      |
| Planck constant                | $h$              | $6.6260755(40) \times 10^{-34} \text{ J s}$                              |
| Elementary charge              | $e$              | $1.60217733(49) \times 10^{-19} \text{ C}$                               |
| Avogadro constant              | $N_A$            | $6.0221367(36) \times 10^{23} \text{ mol}^{-1}$                          |
| Boltzmann constant             | $k$              | $1.380658(12) \times 10^{-23} \text{ J K}^{-1}$                          |
| Gas constant                   | $R$              | $8.314510(70) \text{ J K}^{-1} \text{ mol}^{-1}$                         |
| Bohr radius                    | $a_0$            | $5.29177249(24) \times 10^{-11} \text{ m}$                               |
| Rydberg constant               | $R_\infty$       | $1.0973731534(13) \times 10^7 \text{ m}^{-1}$<br>(infinite nuclear mass) |
|                                | $R_H$            | $1.09677759(50) \times 10^7 \text{ m}^{-1}$<br>(proton nuclear mass)     |
| Bohr magneton                  | $\mu_B$          | $9.2740154(31) \times 10^{-24} \text{ J T}^{-1}$                         |
|                                | $\pi$            | 3.14159265359                                                            |
| Faraday constant               | $F$              | $9.6485309(29) \times 10^4 \text{ C mol}^{-1}$                           |
| Atomic mass unit               | $m_u$            | $1.6605402(10) \times 10^{-27} \text{ kg}$                               |
| Mass of the electron           | $m_e$            | $9.1093897(54) \times 10^{-31} \text{ kg}$                               |
|                                |                  | or<br>$5.48579903(13) \times 10^{-4} m_u$                                |
| Mass of the proton             | $m_p$            | $1.007276470(12) m_u$                                                    |
| Mass of the neutron            | $m_n$            | $1.008664904(14) m_u$                                                    |
| Mass of the deuteron           | $m_d$            | $2.013553214(24) m_u$                                                    |
| Mass of the triton             | $m_t$            | $3.01550071(4) m_u$                                                      |
| Mass of the $\alpha$ -particle | $m_\alpha$       | $4.001506170(50) m_u$                                                    |

## CONVERSION FACTORS

To convert from units in the first column to units in columns 2 through 4, multiply by the factor given. For example,  $1 \text{ eV} = 96.4853 \text{ kJ/mol}$ .

|                  | $\text{cm}^{-1}$ | eV                        | kJ/mol                    | kcal/mol                 |
|------------------|------------------|---------------------------|---------------------------|--------------------------|
| $\text{cm}^{-1}$ | 1                | $1.239842 \times 10^{-4}$ | $11.96266 \times 10^{-3}$ | $2.85914 \times 10^{-3}$ |
| eV               | 8065.54          | 1                         | 96.4853                   | 23.0605                  |
| kJ/mol           | 83.5935          | $1.036427 \times 10^{-2}$ | 1                         | 0.239006                 |
| kcal/mol         | 349.755          | $4.336411 \times 10^{-2}$ | 4.184                     | 1                        |

SOURCE: International Union of Pure and Applied Chemistry, I. Mills, ed., *Quantities, Units, and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Boston, 1988, pp. 81-2, 85, inside back cover.