UNIVERSITY OF MOHAMED KHIDER-BISKRA

The faculty of Exact Sciences Natural and Life Sciences

Department of Material science

Analytical chemistry and thermodynamics -chemistry1-

Lessons and Exercises

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Chapter I: Generalities

I.1 Definitions

I.1.1 Atom

It is the smallest particle of an element or compound that can have a stable independent existence. That retains the properties of that element. An atom is an electrically neutral entity consisting of a central part, the nucleus (protons + neutrons), where practically all of its mass is concentrated, and around which electrons are located.

I.1.2 Nucleus

The nucleus contains two types of massive particles:

- **The proton,** which has a charge of ***+1.60 x*** 10^{-19} ***C*** (coulombs), corresponding to the elementary charge, with a mass of ***1.673 x*** 10^{-27} ***kg***.
- **The neutron** has a neutral charge and a mass of ***1.675 x*** 10^{-27} ***kg***. It's worth noting that protons and neutrons have similar masses but different charges. The nucleus, therefore, carries a positive charge. Neutrons and protons constitute nucleons, which are held together by strong nuclear interaction.

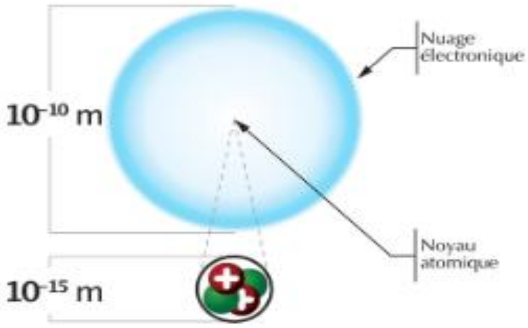


Figure I.1: atomic structure and size

I.1.3 the Electron Cloud

This corresponds to the collection of electrons. An electron has a charge of ***-1.60 x*** 10^{-19} ***C*** and a mass of ***0.911 x*** 10^{-30} ***kg***. Therefore, it is **1800** times lighter than a proton. Its charge is negative and exactly opposite to that of the proton. An atom contains an equal number of electrons and protons (resulting in a net charge of zero), All of the space in matter is made up of electrons, although the bulk of an atom's mass is found in its nucleus.

Table I.1: Mass and charge of subatomic particles

		Charge	
Particle	Mass (g)	Coulomb	Charge unit
Electron	9.10938×10^{-28}	-1.6022×10^{-19}	-1
Proton	1.67262×10^{-24}	$+1.6022 \times 10^{-19}$	+1
Neutron	1.67493×10^{-24}	0	0

I.2 Identification of Elements

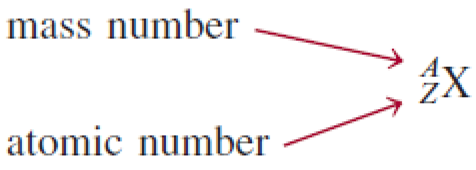
Representation each chemical element is associated with a symbol. The symbol is always written with an initial capital letter, possibly followed by a lowercase letter.

Z, which stands for the number of protons (and, for a neutral atom, the number of electrons), is also known as the atomic number or charge number.

For any given element, the charge of the nucleus (protons) is ***+Ze***. Similarly, the charge of the electrons will be ***-Ze***.

A is called the *mass number*, and it represents the number of nucleons (protons + neutrons). If **N** represents the number of neutrons, the relationship is expressed as:

$$\mathbf{A = Z + N}.$$

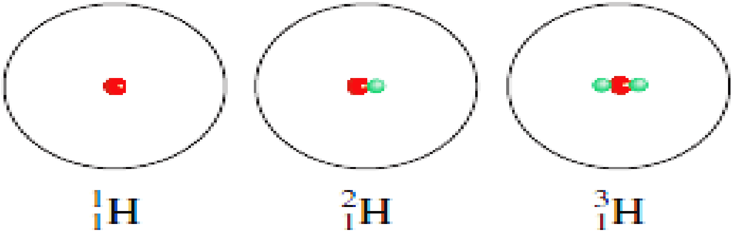


I.2.1 Isotopes

Isotopes are atoms of the same element with the same number of protons (Z) but different numbers of neutrons, resulting in different mass numbers (A). An element can have one or more isotopes.

It is not possible to separate them through chemical reactions; however, this can be achieved using physical techniques, especially mass spectrometry.

One, simply known as hydrogen, has one proton and no neutrons. The deuterium isotope has one proton and one neutron, and tritium has one proton and two neutrons. Thus, for the isotopes of hydrogen, we write hydrogen deuterium tritium



For a nucleus to be stable, the number of neutrons should be equal to or slightly greater than the number of protons. Nuclei that have too many of either kind of fundamental particle are unstable, and break down radioactively

I.3 Atomic Mass

The atomic mass is the total of the masses of an atom's components:

$$m_{atom} = Zm_e + Zm_p + Nm_N \ (kg)$$

Using this unit is not convenient, so more user-friendly chemical units have been chosen, with the reference term being **carbon 12**.

The atomic mass unit (uma) is a standard unit of measurement used to measure the mass of atoms. By convention, an atom of carbon 12, which contains six protons and six neutrons, has a mass of exactly 12 uma. An atomic mass unit is defined as 1/12 of the mass of this atom.

I.4 Mole and Molar Mass

I.4.1 Mole

The *mole* is the amount of substance that contains as many atoms as there are in 12 grams of ***carbon 12***. The number is called Avogadro's number (N): $N = 6.023 \times 10^{23}$.

By definition, one mole of carbon 12 atoms weighs 12 grams. The mass of one atom is 12 uma, so:

$$12g = N \times 12\ uma \text{ or } 1uma = 1/N = 1.66 \times 10^{-24}\ g = 1.66 \times 10^{-27}\ kg.$$

I.4.2 Molar Mass

The *mass* of one mole of atoms of an element is called the molar mass of the atom.

I.5 Relative Atomic Mass

In the general case, an element has one or more isotopes. Therefore, the atomic mass is the sum of the relative proportions of each isotope:

$$m = \frac{\Sigma(xi \times mi)}{100}\ uma \text{ Similarly, the molar mass is: } M = \frac{\Sigma(xi \times Mi)}{100}\ g/mol$$

- ***Example***

Boron exists in the form of two isotopes, 10B and 11B, with respective proportions of 19.91% and 80.09%. The molar mass given in the tables is 10.83 g. This value is the average of the molar masses of the two isotopes. The molar masses of one mole of atoms of these isotopes are 10.0129 g and 11.0093 g, respectively.

$$M(B) = 10.0129 \times (19.91 / 100) + 11.0093 \times (80.09 / 100) = 10.83\ g$$

I.6 Ions

An ***ion*** is *an atom or a group of atoms that has a net positive or negative charge.* The number of positively charged protons in the nucleus of an atom remains the same during ordinary chemical changes (called chemical reactions), but negatively charged electrons may be lost or gained. The loss of one or more electrons from a neutral atom result in a ***cation,*** *an ion with a net positive charge.*

For example, a sodium atom (Na) can readily lose an electron to become a sodium cation, which is represented by Na^{+1}:

Na Atom	**Na^+ Ion**
11 protons	**11 protons**
11 electrons	**10 electrons**

On the other hand, an ***anion*** is *an ion whose net charge is negative* due to an increase in the number of electrons. A chlorine atom (Cl), for instance, can gain an electron to become the chloride ion Cl^-:

Cl Atom	**Cl^- Ion**
17 protons	**17 protons**
17 electrons	**18 electrons**

Sodium chloride (NaCl), ordinary table salt, is called an ***ionic compound*** because it is *formed from cations and anions.* An atom can lose or gain more than one electron. Examples of ions formed by the loss or gain of more than one electron are Mg^{2+}, Fe^{3+}, S^{2+}, and N^{3+}.

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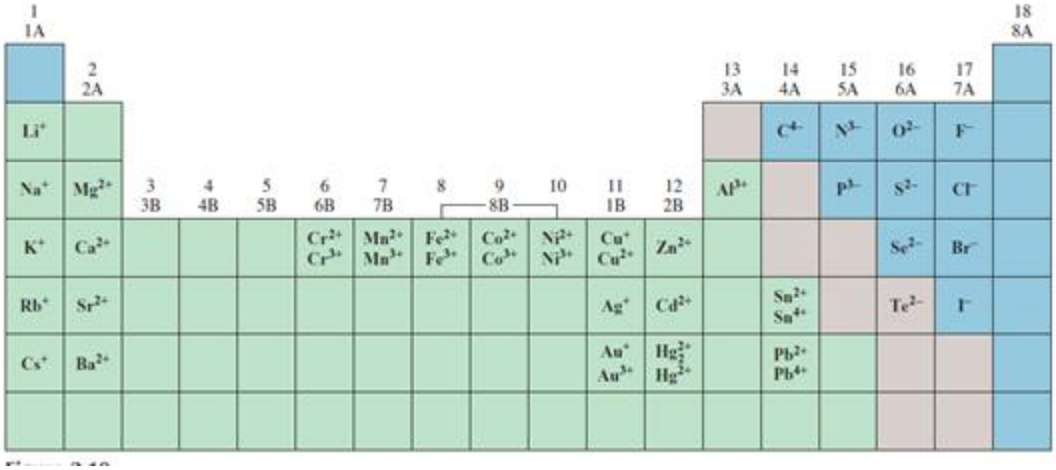


Figure I.2 : common monoatomic ions according to their position in the periodic table,

I.7 Mass energy and nuclear binding energy

I.7.1 Mass Energy

Albert Einstein revolutionized our understanding of energy and mass through his theory of special relativity. He demonstrated that mass is not just a physical quantity but a condensed form of energy. This groundbreaking insight is expressed in the famous equation:

$E = mc^2$

where:

E is the energy, measured in joules (J),

m is the mass, measured in kilograms (kg),

c is the speed of light in a vacuum (3×10^8 m s^{-1}).

This equation reveals that mass and energy are interchangeable; a small amount of mass can be converted into a vast amount of energy due to the large value of (c^2). This principle underpins many physical phenomena, including nuclear reactions, where mass is converted into energy.

- ***Example:***

Calculate the energy equivalent of 1 g of substance.

Solution:

$$\boldsymbol{E = 10^{-3} \times (3 \times 10^{8})^{2} J = 10^{-3} \times 9 \times 10^{16} = 9 \times 10^{13} J}$$

Thus, if one gram of matter is converted to energy, there is a release of enormous amount of energy.

To convert energy from joules (J) to megaelectronvolts (MeV), we use the relationship between joules and electronvolts:

$1\text{J}=\frac{1}{1.602\times10^{-19}\text{eV}}\approx6.242\times10^{18}\text{eV}$

$1\text{J}=\frac{1}{1.602\times10^{-13}}1\text{MeV}\approx6.242\times10^{12}\text{MeV}$.

In nuclear and particle physics, the mass-energy equivalence principle allows us to express the mass of 1uma≈931.494MeV/c^2

I.7.2 Nuclear binding energy

We have seen that the nucleus is made up of neutrons and protons. Therefore, it may be expected that the mass of the nucleus is equal to the total mass of its individual protons and neutrons. However, the nuclear mass M is found to be always less than this. For example, let us consider O_8^{16} ; a nucleus which has 8 neutrons and 8 protons. We have:

$$\boldsymbol{Mass\ of\ atom = 16,13184\ u}\begin{cases}\boldsymbol{Mass\ of\ 8\ neutrons = 8\ \times 1,00688\ uma}\\ \boldsymbol{Mass\ of\ 8\ protons = 8\ \times 1,00727\ uma}\\ \boldsymbol{Mass\ of\ 8\ electrons = 8\ \times 0,00055\ uma}\end{cases}$$

The atomic mass of O_8^{16} found from mass spectroscopy experiments is seen to be 15.99493 uma. Thus, we find that the mass of the nucleus $O_8^{16}$is less than the total mass of its constituents by 0.13691uma.

The difference in mass of a nucleus and its constituents, Δm, is called **the mass defect**, and is given by the relation between the theoretical mass (m_theoretical) and the experimental mass (m_experimental) of a nucleus can be expressed as follows:

$$\boldsymbol{\Delta m = m\_theoretical\ -\ m\_experimental}$$

In this equation:

Δm represents the mass defect, which is the difference in mass.

m_theoretical is the theoretically calculated mass of the nucleus based on the sum of the masses of its individual protons and neutrons.

m_experimental is the actual measured mass of the nucleus.

In other words, the mass defect represents the amount of mass that has been converted into energy, as described by Einstein's equation. If one were to break the oxygen nucleus into its constituent protons and neutrons (in an unbound state), an extra amount of energy (**ΔE**) equivalent to the mass defect (**Δm**) times the speed of light squared (**c^2**) would need to be supplied. This energy required (**E_b**) to disassemble the nucleus is related to the mass defect by the equation:

$$\boldsymbol{E_b = \Delta m\ \times\ c^2}$$

In this equation:

E_b is the energy required to break the nucleus into its individual constituents.

Δm is the mass defect.

c is the speed of light in a vacuum (approximately 3.00 x 10^8 meters per second).

- ***Example:***

Find the energy equivalent to one atomic mass unit. First in Jules then MeV. Using this, express the mass defect of O_8^{16}in MeV/c^2.

Solution:

$$\mathbf{1uma = 1.6605 \times 10^{-27}\ kg}$$

To convert it into energy units, we multiply it by c^2 and find that

$$\boldsymbol{Energy\ equivalent = 1,6605 \times 10^{-27} \times (2,9979 \times 10^{8})^{2}\ \frac{kg.m^{2}}{s^{2}}}$$

$$\boldsymbol{= 1,4924 \times 10^{-10} J}$$

$$= \boldsymbol{\frac{1,4924 \times 10^{-10}}{1,602 \times 10^{-19}} eV = 0,9315 \times 10^{9} eV = 931,5\ MeV\quad or\quad 1u = 931,5\ MeV/c^{2}}$$

For O_8^{16} :

$$\boldsymbol{\Delta m = 0,13691\ uma = 0,13691\ \times 931,5\ MeV/c^{2} = 127,5\ MeV/c^{2}}$$

The energy needed to separate O_8^{16} into its constituents is thus **127,5 MeV/c².**

A nucleus is more stable when this quantity ΔE is larger. This is why ΔE is called the binding energy (or cohesion energy) of the nucleus. To compare the stabilities of nuclei from various elements, we compare the binding energies per nucleon, expressed in ***MeV/nucleon²***. This energy is positive because it is absorbed by the system under consideration (the nucleus).

For example, let’s calculate the binding energy of a helium nucleus: First, we calculate its mass defect:

There are the masses of protons and neutrons, and $\mathbf{\Delta m_{He}}$ is the mass of a helium nucleus. We calculate this as:

Then, we calculate the binding energy:

$$\Delta m = 2 \times m_p + 2 \times m_n - m_{{}_2^4He}$$

$$= 2 \times 1{,}67262 * 10^{-27} + 2 \times 1{,}67493 * 10^{-27} - 6{,}644492 * 10^{-27}$$

$$= 5{,}061 * 10^{-29} kg$$

$$E_l = \Delta m \times c^2 = 5{,}061 * 10^{-29} \times (3{,}0 * 10^8)^2 = 4{,}6 * 10^{-12} J = 28\ MeV$$

I.7.3 Binding Energy per Nucleon

It is equal to the binding energy of the nucleus divided by the number of nucleons present in that nucleus: ***E_b/A***. It is generally expressed in ***MeV per nucleon***.

- ***Example:***

For example, if a nucleus has a total binding energy of 7.6 MeV and contains 8 nucleons, the binding energy per nucleon would be:

$E_{\text{binding per nucleon}} = \frac{7.6\ \text{MeV}}{8} = 0.95$ MeV/nucleon.

This value indicates the average energy required to remove each nucleon from the nucleus

Exercises

Exercise I

List the components of the following elements

$$^{112}_{48}Cd;\ ^{56}_{26}Fe;\ ^{32}_{16}S^{2-};\ ^{99}_{43}Tc;\ ^{24}_{12}Mg^{2+};\ ^{54}_{26}X;\ ^{210}_{84}Po^{2-};\ ^{40}_{20}Ca$$

Exercise II

The mass of lead (Z=82) is 207.2 g/mole. Calculate the ratio of the masses of electrons to that of the atom. Conclusion. Given: me = 9.11 x 10^{-31} kg and N = 6.023 x 10^{23}.

Exercise III

The nucleus of a lithium atom is composed of 4 neutrons and 3 protons. Let's calculate the theoretical mass of this nucleus in atomic mass units (u.m.a), compare it to its actual value of 7.01601 u.m.a, and then calculate the binding energy of this nucleus in joules (J) and mega-electronvolts (MeV).

Given data

mp =1,00727 u.m.a; mN =1,00866 u.m.a; c =3 10^8 m/s; N =6,023 10^{23}

Exercise IV

Natural copper is composed of two stable isotopes with respective molar masses of 62.929 and 64.927 g/mol. The atomic number of Copper is Z=29

a- Indicate the composition (p.n and electron) of the two stable isotopes

b- Knowing that the molar mass of the natural isotopic mixture is 63.54, calculate the abundance of the two isotopes.

Exercise V

The nucleus of the calcium (Ca) atom contains 20 positive charges:

a) Give the atomic number Z of the calcium atom.

b) Determine as a function of (e) and in coulombs, Qn the nucleus charge of this atom.

c) Determine as a function of (e) and in coulombs, Qe the charge of the electrons of this atom.

d) Calculate Qa the overall charge of the atom.

2- The calcium atom can lose two electrons to give the calcium ion.

a) Write the chemical formula of the calcium ion and give its type.

b) Determine the number of electrons in the calcium ion.

c) Determine according to (e), Qe the charge of the electrons of the calcium ion.

d) Calculate based on (e) the charge of the calcium ion.

Exercise VI

Calculate the average binding energy per nucleon for the following isotopes

$^{15}_{8}O$ (15.0030 uma); $^{16}_{8}O$ (15.99491 uma); $^{17}_{8}O$ (16.99913 uma); $^{18}_{8}O$ (17.99920 uma)

Before performing the calculations, which isotope do you estimate to be the most stable? Given: mp = 1.00728 u.m.a; mn = 1.00867 u.m.a.

Solutions

Exercise I:

List the components of the following elements:

Element	Protons	Neutrons	Electrons
Cd	48	64	48
Fe	26	30	26
S^{2-}	16	16	18
Tc	43	56	43
Mg^{2+}	12	12	10
Fe	26	28	26
Po^{2-}	84	126	86
Ca	20	20	20

Exercise II:

To calculate the ratio between the mass of the electrons in a lead atom and the mass of one lead atom, follow these steps:

1. **Mass of the electrons in a lead atom**: The number of electrons is 82, so:

   Mass of the electrons in one lead atom=$82\times me=82\times 9.11\times 10^{-31}=7.4702\times 10^{-29}$ kg

2. **Mass of one lead atom**: The mass of one lead atom is:

   Mass of a lead atom=M* NA=$0.2072\ 6.023\times 10^{23}=3.44\times 10^{-25}$ kg

   Calculate the ratio: The ratio between the mass of the electrons and the mass of the lead atom is:

   Mass of the electrons/Mass of the atom=$7.4702\times 10^{-29}/3.44\times 10^{-25}\approx 2.17\times 10-4$

Thus, the ratio between the mass of the electrons and the mass of one lead atom is approximately 2.17×10^{-4}.

***Exercise III** (Lithium Nucleus):*

The nucleus of lithium is composed of 3 protons and 4 neutrons. We are asked to calculate the **theoretical mass**, compare it with the actual mass, and determine the **binding energy**.

1. Theoretical mass:
Theoretical mass=3×1.00727+4×1.00866=7.05441 u

2. Mass defect:
Δm=7.05441−7.01601=0.0384 u

3. Binding energy:

Convert mass defect to energy using 1 u=931.5 MeV

E=0.0384 u×931.5 MeV/u=35.79 MeV

4. Binding energy per nucleon:

Lithium has 7 nucleons (3 protons and 4 neutrons), so the binding energy per nucleon is:

35.79/7=5.11 MeV/nucleon

Exercise IV:

- Composition of the isotopes:
    - Cu-63: 29 protons, 34 neutrons, 29 electrons.
    - Cu-65: 29 protons, 36 neutrons, 29 electrons.
- To calculate the abundance, solve the system of equations: 62.929x+64.927(1−x) =63.5462.929x + 64.927(1-x) = 63.5462.929x+64.927(1−x) =63.54
- The result gives the relative abundance of each isotope.
- - Cu-63: 69.15%
  - Cu-65: 30.85%

Exercise V:

- (a) Z for calcium is 20.
- (b) Qn=20e, where e=1.6×10−19 so Qn=3.2×10−18 C Qe=−20e=−3.2×10−18 C
- (d) Qa=0 C as the atom is neutral.

For the calcium ion:

- (a) The ion is Ca2+
- (b) The ion has 18 electrons.
- (c) Qe=−18e=−2.88×10−18

- (d) The charge of the ion is 2e=3.2×10−19 C

Exercise VI:

(Oxygen Isotopes) :

1. Oxygen $\boldsymbol{O_8^{15}}$

- Number of protons Z=8
- Number of neutrons N=7
- Actual mass: 15.0030 u

Theoretical mass:

Theoretical mass=8×1.00728+7×1.00867=15.11252 u

Mass defect:

Δm=15.11252−15.0030=0.10952 u

Binding energy:

E=0.10952 u×931.5 MeV/U= 102.05MeV

Binding energy per nucleon:

102.0/15=6.80 MeV/nucleon

2. Oxygen $\boldsymbol{O_8^{16}}$

- Number of protons Z=8
- Number of neutrons N=8
- Actual mass: 15.99491 u

Theoretical mass:

Theoretical mass=8×1.00728+8×1.00867=16.1196 u\

Mass defect:

Δm=16.1196−15.99491=0.12469 u

Binding energy:

E=0.12469 u×931.5 MeV/u=116.06 MeV

Binding energy per nucleon:

116.06/16=7.25 MeV/nucleon

3. Oxygen $\boldsymbol{O}_{\mathbf{8}}^{\mathbf{17}}$

- Number of protons Z=8
- Number of neutrons N=9
- Actual mass: 16.99913 u

Theoretical mass:

Theoretical mass=8×1.00728+9×1.00867=17.12827 u

Mass defect:

Δm=17.12827−16.99913=0.12914 u

Binding energy:

E=0.12914 u×931.5 MeV/u=120.26 MeV

Binding energy per nucleon:

120.26/17=7.07 MeV/nucleon

4. Oxygen $\boldsymbol{O}_{\mathbf{8}}^{\mathbf{18}}$

- Number of protons Z=8
- Number of neutrons N=10
- Actual mass: 17.99920 u

Theoretical mass:

Theoretical mass=8×1.00728+10×1.00867=18.13694 u

Mass defect:

Δm=18.13694−17.99920=0.13774 u

Binding energy:

E=0.13774 u×931.5 MeV/u=128.26 MeV

Binding energy per nucleon:

128.2618=7.13 MeV/nucleon

Applying Neutron-to-Proton Ratio (N/Z ratio): to the Oxygen Isotopes:

- $\boldsymbol{O_8^{15}}$: 7 neutrons, 8 protons. N/Z ratio = 7/8 = 0.875.
- $\boldsymbol{O_8^{16}}$: 8 neutrons, 8 protons. N/Z ratio = 8/8 = 1.0 (ideal for lighter elements).
- $\boldsymbol{O_8^{17}}$9 neutrons, 8 protons. N/Z ratio = 9/8 = 1.125.
- $\boldsymbol{O_8^{18}}$: 10 neutrons, 8 protons. N/Z ratio = 10/8 = 1.25.

Before performing the calculations, the isotope $\boldsymbol{O_8^{16}}$is likely to be the **most stable** because: It has an N/Z ratio of 1.0, which is optimal for light elements like oxygen.

From the calculations, we find that the binding energy per nucleon for the isotope $\boldsymbol{O_8^{16}}$ is 7.25 MeV/nucleon, which is higher than that of the other isotopes. This higher value indicates that the isotope $\boldsymbol{O_8^{16}}$ is the most stable among the four isotopes.

Chapter II: The Electronic Structure of Atoms

Introduction

In quantum mechanics, the behavior of electrons in atoms is described by Schrödinger's equation, which is a fundamental equation for the wave function ψ of a quantum system:

$H\ \psi = E\psi$

Here:

- H is the Hamiltonian operator representing the total energy of the system.
- E is the energy eigenvalue.
- Ψ is the wave function, which provides the probability distribution of the electron's position.

When solving Schrödinger's equation for the hydrogen atom, the wavefunction $\psi(r,\theta,\phi)$ is obtained as a solution that describes the probability distribution of the electron's position in three-dimensional space. The equation is separated into radial and angular components, leading to specific solutions that depend on quantum numbers.

II.1 Quantum Numbers for Atoms

A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom.

The first three (n, l, ml) specify the particular orbital of interest, and the fourth (ms) specifies how many electrons can occupy that orbital.

- **Principal Quantum Number (n): n = 1, 2, 3 ,….**

Specifies the energy of an electron and the size of the orbital. It takes positive integer values (n=1,2, 3,…) and determines the electron's distance from the nucleus.

All orbitals that have the same value of n are said to be in the same shell (level).

For a hydrogen atom with n=1, the electron is in its ground state; if the electron is in the n=2 orbital, it is in an excited state.

The total number of orbitals for a given n value is $\mathbf{n^2}$.

- **Secondary Quantum Number (l): l = 0,., n-1.**

Specifies **the shape** of an orbital with a particular principal quantum number.

The secondary quantum number divides the shells into smaller groups of orbitals called subshells (sublevels).

Usually, a letter code is used to identify l to avoid confusion with n:

l	0	1	2	3	4	5	...
Letter	*s*	*p*	*d*	*f*	*g*	*h*	...

The subshell with *n*=2 and *l*=1 is the 2*p*

subshell; if *n*=3 and *l*=0, it is the 3*s* subshell, a so on.

The value of *l* also has a slight effect on the energy of the subshell; the energy of the subshell increases with *l* (*s* < *p* < *d* < *f*).

- **Magnetic Quantum Number (ml): ml = -l, ..., 0, ..., +l.**

The **Magnetic Quantum Number (ml)** specifies the orientation of an orbital in three-dimensional space for a given energy level (n) and shape (l).

This quantum number divides a subshell into individual orbitals, each capable of holding up to two electrons.

The values of ml range from −l to +l, including zero, resulting in a total of 2l+1 possible orbitals within a subshell. For example:

- **s subshell (l=0)**:
  ml=0, so there is **1 orbital**.

- **p subshell (l=1)**:

  ml=−1,0, +1 so there are **3 orbitals**.

- **d subshell (l=2l)**:

  ml=−2, −1,0, +1, +2, so there are **5 orbitals**.

- **f subshell (l=3l)**:

  ml=−3, −2, −1,0, +1, +2, +3, so there are **7 orbitals**.

Each orbital represents a specific orientation of the electron cloud within the subshell, and the total number of orbitals within a subshell corresponds to the number of unique ml values.

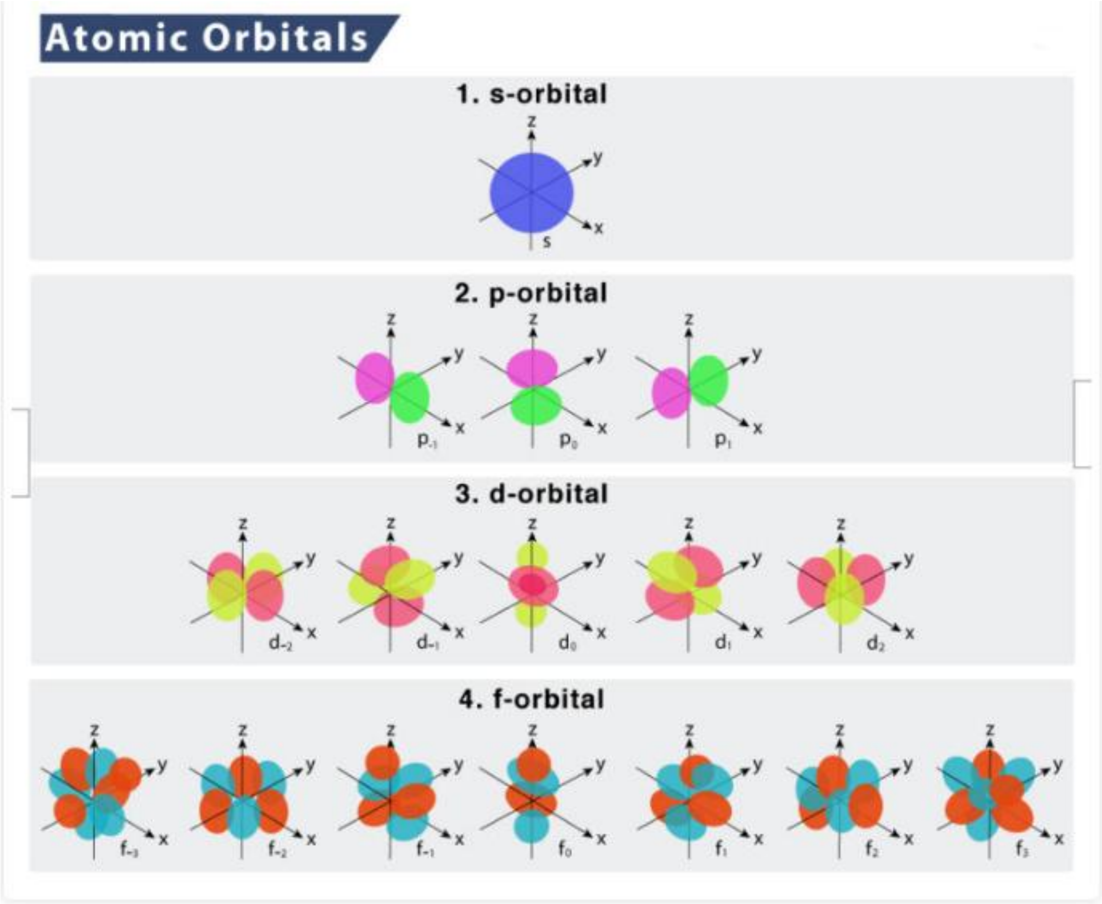


Figure 1 **: Atomic orbitals**

- **Spin Quantum Number (ms): ms = +½ or -½.**

Specifies **the orientation** of the spin axis of an electron. An electron can spin in only one of two directions (sometimes called up and down). Because an electron spins, it creates a magnetic field, which can be oriented in one of two directions. For two electrons in the same orbital, the spins must be opposite to each other.

The spins are said to be paired. These substances are not attracted to magnets and are said to be *diamagnetic*.

Atoms with more electrons that spin in one direction than another contain unpaired electrons. These substances are weakly attracted to magnets and are said to be *paramagnetic.*

II.2 Atomic orbitals

Table 1 shows the relation between quantum numbers and atomic orbitals. We see that when, l=0 (2l+1) =1 and there is only one value of m_l thus, we have an *s* orbital. When, l= 1, (2l+ 1) = 3, so there are three values of *m*l or three *p* orbitals, labeled *px*, *py*, and *pz.* When, l=2, (2l+1) = 5 and there are five values of m_l, and the corresponding five *d* orbitals are labeled with more elaborate subscripts.

Table 1 Relation between Quantum Numbers and Atomic orbital

n	*l*	*ml*	*Number of orbitals*	*Atomic orbital designation*
1	***0***	***0***	***1***	***1s***
2	***0***	***0***	***1***	***2s***
	1	***-1, 0, 1***	***3***	***2px, 2py, 2pz***
3	***0***	***0***	***1***	***3s***
	1	***-1, 0, 1***	***3***	***3px, 3py, 3pz***
	2	***-2, -1, 0, 1, 2***	***5***	***3dxy, 3dyz, 3dxz***
				$3d_{x^2-y^2}$, $3d_{z^2}$

II.3 Electron Configuration

The four quantum numbers *n*, l, *m* and *ms* enable us to label completely an electron in any orbital in any atom. In a sense, we can regard the set of four quantum numbers as the "address" of an electron in an atom, somewhat in the same way that a street address, city, state, and postal ZIP code specify the address of an individual.

For example, the four quantum numbers for a 2*s* orbital electron are *n* = 2, l= 0, *m*, = 0, and *ms* = +1/2 or -1/2. It is inconvenient to write out all the individual quantum numbers, and so we use the simplified notation (*n*, l, *m*, *ms*). For the preceding example, the quantum numbers are either (2, 0, 0, +1/2) or (2, 0, 0, -1/2). The value of *ms* has no effect on the energy, size, shape, or orientation of an orbital, but it determines how electrons are arranged in an orbital.

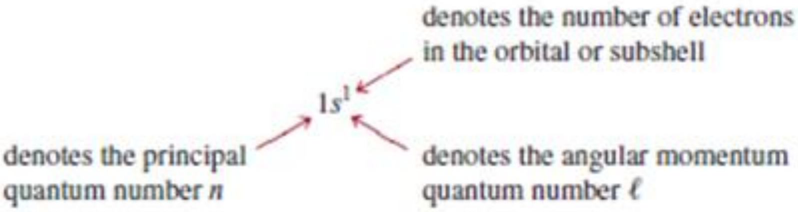
- ***Example*:**

Write the four quantum numbers for an electron in a 3*p* orbital. What do the "3" and "*p*" designate in 3*p*? How many orbitals (values of *m*,) are there in a 3*p* subshell? What are the possible values of electron spin quantum number?

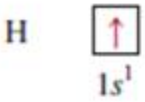
Solution

To start with, we know that the principal quantum number *n* is 3 and the angular momentum quantum number, must be 1 (because we are dealing with a *p* orbital).

For, l = 1, there are three values of *m*, given by, -1, 0, and +1. Because the electrons spin quantum number *ms* can be either (+1/2 or -1/2) in the 1*s* orbital, so its electron configuration is $1s^1$



The electron configuration can also be represented by an *orbital diagram* that shows the spin of the electron



II.4 The electronic structure of poly-electronic atoms

The distribution of electrons in different orbitals of atom is known as electronic configuration of the atoms. Filling up of orbitals in the ground state of atom is governed by the following rules:

The Building-Up Principle (KLECHKOWSKI)

- According to this principle, "In the ground state, the atomic orbitals are filled in order of increasing energies i.e. in the ground state the electrons first occupy the lowest energy orbitals available".
- According to this rule

(a) Lower the value of $n + l$, lower is the energy of the orbital and such an orbital will be filled up first.

(b) When two orbitals have same value of $(n+l)$, the orbital having lower value of "n" has lower energy and such an orbital will be filled up first. Thus, order of filling up of orbitals is as follows: 1s < 2s < 2p < 3s < 3p < 4s < 4 p < 5s < 4d < 5 p < 6s < 6 f < 5d

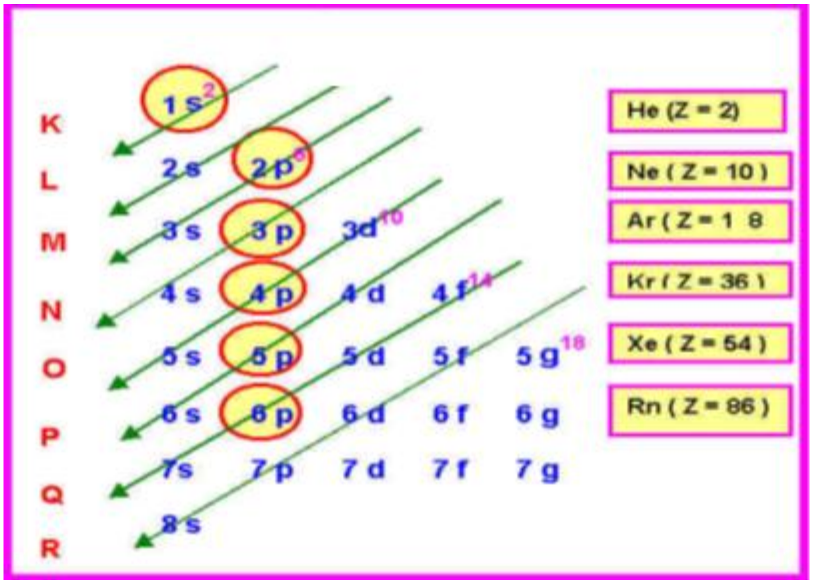


Figure 2: Klechkowski Rule

Pauli Exclusion Principle

In 1926, Wolfgang Pauli discovered that a set of quantum numbers is specific to a certain electron. That is, no two electrons can have the same values for n, l, ml, and ms. Although the first three quantum numbers identify a specific orbital and may have the same values, the fourth is significant and must have opposite spins.

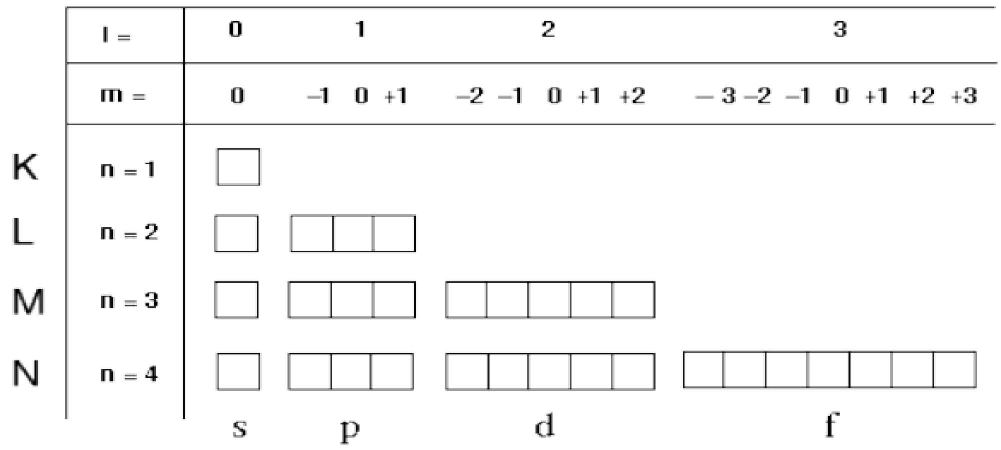


Figure 3: Quantum box

- A quantum box can contain a maximum of two electrons with opposite spins.
- For a shell with principal quantum number n, the number of quantum boxes is $\mathbf{n^2}$, and the number of electrons is $\mathbf{2n^2}$.

Hund’s Rule

Orbitals may have identical energy levels when they are of the same principal shell. These orbitals are called degenerate, or "equal energy." According to Hund's Rule, electrons fill orbitals one at a time. This means that when drawing electron configurations using the model with the arrows, you must fill each shell with one electron each before starting to pair them up. Remember that the charge of an electron is negative and electrons repel each other. Electrons will try to create distance between it and other electrons by staying unpaired. This further explains why the spins of electrons in an orbital are opposite (i.e. +1/2 and -1/2).

II.5 Electronic configuration

- **Core Electrons**

Core electrons are the electrons in an atom that occupy the inner energy levels or orbitals, closer to the nucleus. They are tightly bound to the nucleus and do not usually participate in chemical bonding or reactions.

Characteristics of Core Electrons:

1. **Location**: They reside in lower energy levels (closer to the nucleus) than the valence electrons.

2. **Stability**: Core electrons are more stable and less reactive compared to valence electrons due to their lower energy and stronger attraction to the nucleus.
3. **Involvement in Reactions**: Core electrons rarely take part in chemical reactions or bonding, as these processes primarily involve valence electrons.
4. **Configuration**: In electron configurations, core electrons are represented by the noble gas configuration in shorthand notation. For example:

For sodium (Z=11): [Ne]3s1 (10 core electrons from Ne).

- ***Example:***

In the atom of oxygen (Z=8):

- The electron configuration is $1s^2 2s^2 2p^4$.
- The **core electrons** are the $1s^2$ electrons (2 electrons in the first energy level).
- The remaining $2s^2 2p^4$ electrons are valence electrons.

❖ Valence Electrons

Valence electrons are the electrons in the outermost energy level (or shell) of an atom. These electrons are involved in chemical bonding and determine the chemical reactivity and properties of an element. Unlike core electrons, valence electrons have higher energy and are less tightly bound to the nucleus.

Characteristics of Valence Electrons:

1. **Location**: Found in the outermost shell, which corresponds to the highest principal quantum number (n) in the atom's electron configuration.
2. **Role in Bonding**: Valence electrons are responsible for forming chemical bonds, including covalent, ionic, and metallic bonds.
3. **Determination of Reactivity**: The number of valence electrons influences an element's ability to gain, lose, or share electrons, determining its reactivity and position in the periodic table.
4. **Periodic Trends**: Elements in the same group (vertical column) of the periodic table have the same number of valence electrons, which gives them similar chemical properties.

Determining Valence Electrons:

- For **main group elements (Groups 1-2 and 13-18)**, the number of valence electrons corresponds to the group number.

Group 1 (e.g., Na): 1 valence electron.

Group 16 (e.g., O): 6 valence electrons.

- For **transition metals (Groups 3-12)**, valence electrons include the d-electrons in addition to the s-electrons of the outermost shell, depending on the element's oxidation state.

➢ ***Example:***

1. **Oxygen (Z=8)**:

Electron configuration: $1s^2 2s^2 2p^4$.

Valence electrons: $2s^2 2p^4$ (6 electrons in the second energy level).

2. **Sodium (Z=11)**:

Electron configuration: $1s^2 2s^2 2p^6 3s^1$.

Valence electrons: 3s1 (1 electron in the third energy level).

Electron configurations can be shortened in notation by using the noble gas that precedes the element and only indicating the part that differs from it.

This notation is often referred to as:

Atom	Electronic configuration	Abbreviated writing
$_{11}$Na	**$1s^2\ 2s^2\ 2p^6\ 3s^1$**	**$_{10}$[Ne] $3s^1$**
$_{21}$Sc	**$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$**	**$_{18}$[Ar] $3d^1\ 4s^2$**
$_{30}$Zn	**$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$**	**$_{18}$[Ar] $3d^{10}\ 4s^2$**

II.6 Extra stability of half-filled and completely filled orbitals

The **extra stability of half-filled and completely filled orbitals** arises from their unique electronic configurations, which result in lower energy states due to symmetrical distribution and exchange energy.

Reasons for Extra Stability:

1. **Symmetrical Distribution**:
   Half-filled and fully filled orbitals have a more symmetric distribution of electrons. Symmetry leads to a balanced electrostatic repulsion among electrons, reducing the overall energy of the atom or ion.
2. **Exchange Energy**:
   Electrons with parallel spins in degenerate orbitals (orbitals of the same energy) can exchange their positions, resulting in stabilization known as **exchange energy**. The number of possible exchanges is maximized in half-filled and fully filled orbitals, leading to extra stability.
3. **Hund's Rule of Maximum Multiplicity**:
   In half-filled orbitals, electrons occupy separate orbitals with parallel spins, minimizing electron repulsion. Similarly, completely filled orbitals maximize pairing within the lowest energy state, which also contributes to stability.

➢ ***Examples of Extra Stability:***

- **Chromium (Z=24)**:

Expected configuration: $[Ar]3d^4 4s^2$.

Actual configuration: $[Ar]3d^5 4s^1$.

The half-filled $3d^5$ configuration provides extra stability.

- **Copper (Z=29)**:

Expected configuration: $[Ar]3d^9 4s^2$.

Actual configuration: $[Ar]3d^{10} 4s^1$.

The fully filled $3d^{10}$ orbital is more stable than $3d^9$.

Exercises

Exercise 1

What is the maximum number of electrons described by the following quantum numbers if they exist:

- $n = 3$, $l = 2$
- $n = 2$, $l = 1$, and $m = -1$
- $n = 1$, $l = 0$, and $m = 0$
- $n = 3$, $l = 2$, and $m = -2$

Exercise 2

Provide the quantum numbers for the following electrons:

$4S^2$, $3d^1$, $2p^3$, $4d^4$

Based on the quantum numbers of the last electron, find the corresponding Z value.

(1, 0, 0, -1/2), (3, 1, 1, +1/2), (4, 1, 0, -1/2), (4, 2, 1, +1/2)

Exercise 3

Are the following statements true or false? Why?

a) If l=1, the electron is in a d subshell.

b) If n=4, the electron is in the O shell.

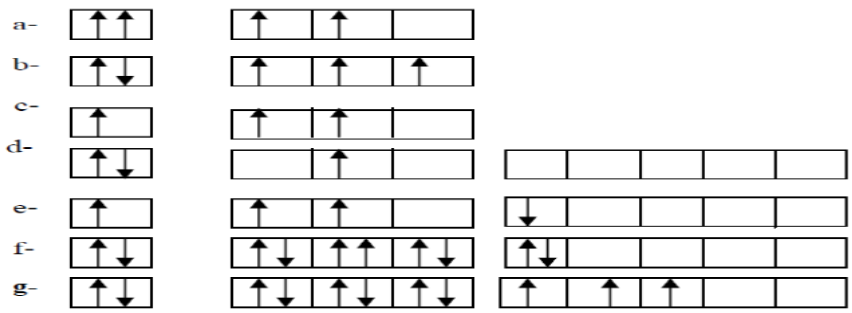
c) For an electron in a d subshell, m can be equal to 3.

d) If l=2, the corresponding subshell can hold a maximum of 6 electrons.

e) The value of n for an electron in an f subshell can be 3.

Exercise 4

Among the following electron configurations, which ones do not follow the rules for electron filling? Explain.



Exercise 5

An element from the periodic table has 28 electrons, with two electrons in an **s** subshell and eight in a **d** subshell.

1. Write its complete electron configuration using quantum notation.
2. What type of ion can it form by losing or gaining electrons?

Solutions

Exercise 1

The maximum number of electrons described by the following quantum numbers

- $n = 3, l = 2$:

The possible values for m are: $m = -2, -1, 0, 1, 2$.

Each m value can hold 2 electrons (one with spin $+\frac{1}{2}$ and one with spin $-\frac{1}{2}$).

Therefore, the maximum number of electrons is:

$5 \times 2 = 10$ electrons.

- $n = 2, l = 1, m = -1$:

This corresponds to a p orbital, where only one m value is specified.

Therefore, the maximum number of electrons is: 2 electrons.

- $n = 1, l = 0, m = 0$:

This corresponds to an s orbital, where $m = 0$.

Therefore, the maximum number of electrons is: 2 electrons.

- $n = 3, l = 2, m = -2$:

Only one m value is specified, so it can hold 2 electrons.

Exercise 2

1- The quantum numbers for the following electrons are as follows:

- $4S^2$:
  Quantum numbers:
  $n = 4, l = 0, m = 0, s = +\frac{1}{2}$
  $n = 4, l = 0, m = 0, s = -\frac{1}{2}$

- $3d^1$:

  Quantum numbers:

  n = 3, l = 2, m = 0, s = +½
- $2p^3$:

  Quantum numbers:

  n = 2, l = 1, m = -1, s = +½

  n = 2, l = 1, m = 0, s = +½

  n = 2, l = 1, m = +1, s = +½
- $4d^4$:

  Quantum numbers:

  n = 4, l = 2, m = 0, s = +½

  n = 4, l = 2, m = 1, s = +½

2- Let's break down each set of quantum numbers to identify the element and its corresponding atomic number (Z value) for each electron.

- **Quantum numbers (1, 0, 0, -½):**
  a. n = 1 l=0, m = 0, s=−½
  b. This corresponds to the 1s orbital. The electron described here is one of the two electrons in the 1s subshell.
  c. This suggests the element is **Hydrogen** (Z = 1), or it could be a heavier element that also has electrons in the 1s orbital.
- **Quantum numbers (3, 1, 1, +½):**
  a. n = 3 l = 1, m=1, s=+½
  b. This corresponds to the 3p orbital. The electron described is in the 3p subshell.
  c. An element with electrons in the 3p subshell could be **Phosphorus** (Z = 15), where the 3p subshell starts filling.
- **Quantum numbers (4, 1, 0, -½):**
  a. n=4, l=1, m=0, s=−½
  b. This corresponds to the 4p orbital. The electron described is in the 4p subshell.
  c. Z=35 the element is **Bromine.**
- **Quantum Numbers (4, 2, 1, +½)** can be interpreted as follows:

- n=4: The electron is in the 4th energy level.
- l=2: This corresponds to a **d subshell**.
- m=1: The magnetic quantum number indicates the specific orbital within the d subshell.
- s=+½: The electron has a positive spin.

This describes an electron in the **4d** orbital.

The element with an electron configuration that reaches the 4d subshell is **Molybdenum (Mo)**, which has the atomic number Z=42.

Therefore, the corresponding Z value for the quantum numbers (4, 2, 1, +½) is **42**.

Exercise 3

Are the following statements true or false? Why?

a) False – If l = 1, the electron is in a p subshell, not a d subshell.

b) True – For n = 4, the electron is in the O shell (4th shell).

c) False – For a d subshell, m values range from -2 to +2, so m cannot be 3.

d) False – A subshell with l = 2 (d subshell) can hold a maximum of 10 electrons.

e) True – The value of n for an f subshell can be 3, as in the case of 4f orbitals.

Exercise 4

Among the given electron configurations, the ones that do not follow the correct electron filling rules are:

a. The configuration is incorrect. It does not follow the Pauli Exclusion Principle, where two electrons in the same orbital have opposite spins.

c. The distribution is incorrect because it is not allowed to move to the next orbital unless the previous one is fully occupied.

d. The distribution is incorrect because it is not allowed to move to the next orbital unless the previous one is fully occupied.

e. The distribution is incorrect because it is not allowed to move to the next orbital unless the previous one is fully occupied.

f. This configuration is incorrect. Electrons are paired in the same orbital, but there are still empty orbitals available, which violates Hund's rule.

Exercise 5

For an element with 28 electrons:

1. Electron configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2 3d^8$

2. This element is Nickel (Ni), and it can form the following ion:
By losing 2 electrons: Ni^{2+} (common oxidation state).
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^0$

Nickel loses electrons from the 4s orbital first because, although the 4s orbital is filled before the 3d orbital when nickel is in its neutral state, the 4s electrons are at a higher energy level once the atom is ionized. In transition metals like nickel, the 3d electrons are more tightly bound to the nucleus, so the 4s electrons are lost more easily during ionization.

Chapter III: Periodic classification of the elements

III.1 Mendeleev’s periodic table

Dmitri Mendeleev, a Russian scientist, created one of the first practical periodic tables in the 19th century, laying the foundation for the modern periodic table. His innovative approach organized elements based on patterns in their properties and atomic masses, allowing him to predict the existence of undiscovered elements.

The modern periodic table builds on Mendeleev’s principles with some modifications. Key ideas from Mendeleev's work include:

- **Order of Atomic Mass**: Elements were arranged by increasing atomic mass, highlighting periodic trends.
- **Periods**: The horizontal rows in the table, now known as periods, represent elements with the same principal energy level.
- **Groups**: The vertical columns, called groups, consist of elements with similar chemical and physical properties due to their valence electron configurations.
- **Similarity within Groups**: Elements within the same group exhibit similar chemical behaviors, such as forming similar compounds.

Although Mendeleev's table was later revised to arrange elements by increasing atomic number rather than atomic mass, his groundbreaking ideas remain fundamental to the structure and utility of the modern periodic table.

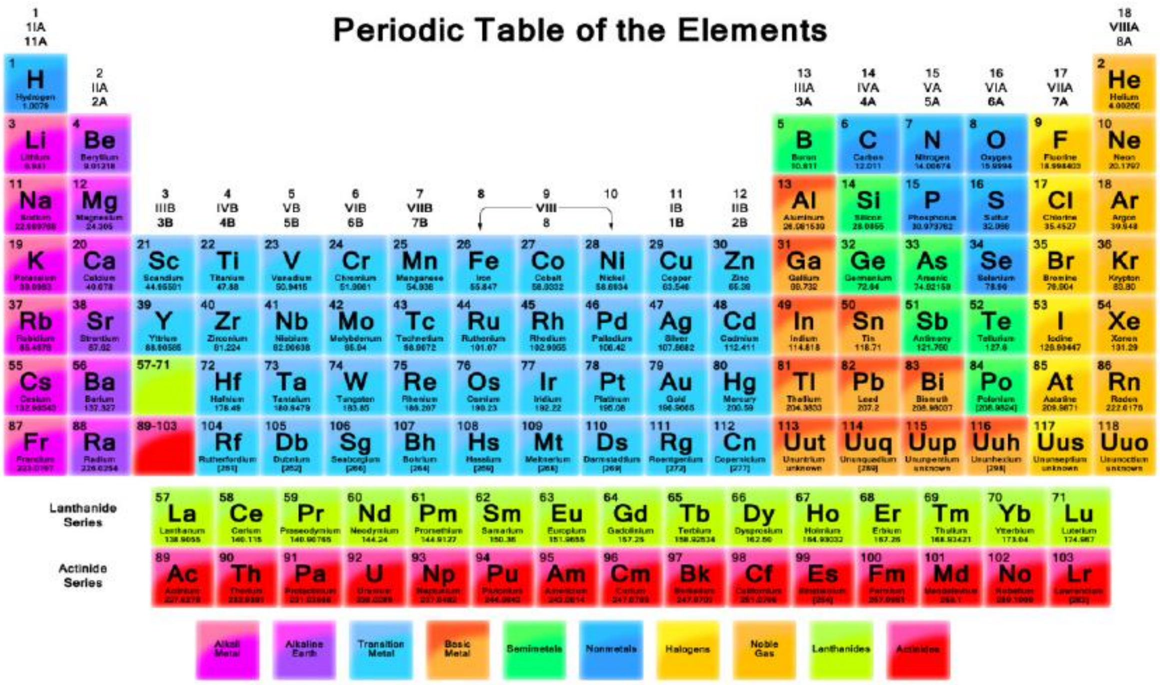


Figure 4: priodic table of element

III.2 Description of the periodic table: Groups and periods

The periodic table is a consequence of electron configurations. Periodic classification is based on the formation of groups consisting of elements with similar chemical properties. Elements with the same value of the principal quantum number n (representing the outermost electron shell, such as K, L, M, N, etc.) are grouped in the same row (period), and elements with similar electron configurations in the outermost shell are grouped in the same column (family or group). Elements in the same family have the same number of valence electrons.

1. Periods

A horizontal row in the periodic table forms a period. There are 7 periods, each with varying lengths. The period number corresponds to the principal quantum number (n) of the outermost electron shell.

2. Groups

The periodic table consists of 18 columns divided into 9 groups (I to VII and 0), which include subgroups (A and B).

Subgroup A: Contains elements with an outermost subshell of ns or np

-The S block consists of groups 1 (IA) and 2 (IIA) and includes elements with valence electrons in the outermost S orbital.

-The P block includes groups 13 (IIIA) to 18 (VIIIA) and contains elements with valence electrons in the outermost P orbitals.

Subgroup B: Subgroup B includes the families located between (IIA) and (IIIA) and is represented by the d-block, often referred to as the transition elements.

Remark

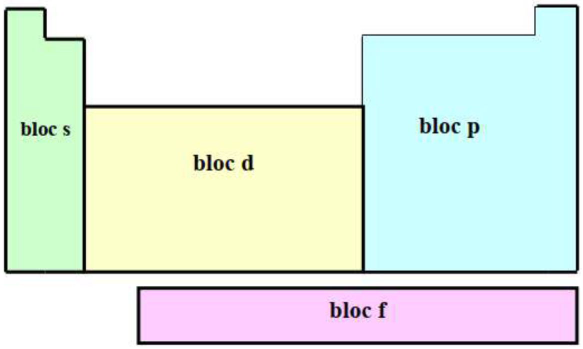
The group corresponding to the noble gases, which should be in Group VIIIA, is labeled as Group 0. This is because the outermost shell of these elements (ns2 np6) is fully saturated, providing them with great stability. They are characterized by a valency of 0, which explains their lack of chemical reactivity (inert gases)

For Subgroup B, the group number corresponds to the number of electrons in the outermost shell (ns + (n-1) d), except when the total is 8, 9, or 10 (in which case Group VIIIB), or when the total is 11 or 12 (in which case it is labeled as IB or IIB).

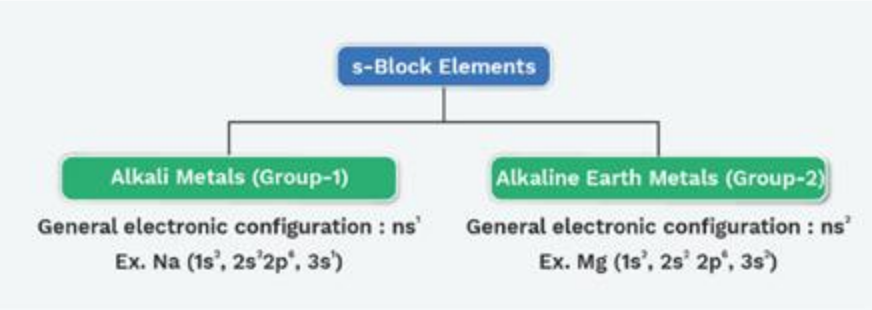
The Roman numerals (I, II, III, etc.) indicate the number of electrons in the outermost shell.

III.3 Different Blocks of the Periodic Table

The periodic classification of elements consists of several sets or blocks of elements:



s-Block: It corresponds to the elements in column 1 (ns1, Group (IA)), known as alkali metals, which are monovalent, and in column 2 (ns2, Group (IIA)), known as alkaline earth metals, which are divalent.



p-Block:

(1) p-block elements are present in right part of the periodic table.

(2) These constituted the groups IIIA to VIIIA, groups 13 to 18 of the periodic table.

(3) Most of p-block elements are metalloids and non-metals but some of them are metals also.

(4) The last electron fills in p-orbital of valence shell.

Group or family	I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A	$VIII_A$
Valance layer configuration	ns^1	ns^2	$ns^2\ np^1$	$ns^2\ np^2$	$ns^2\ np^3$	$ns^2\ np^4$	$ns^2\ np^5$	$ns^2\ np^6$
Valance electrons number	1	2	3	4	5	6	7	8

Element	$_3$Li	$_{12}$Mg	$_{13}$Al	$_6$C	$_7$N	$_8$O	$_9$F	$_{10}$Ne

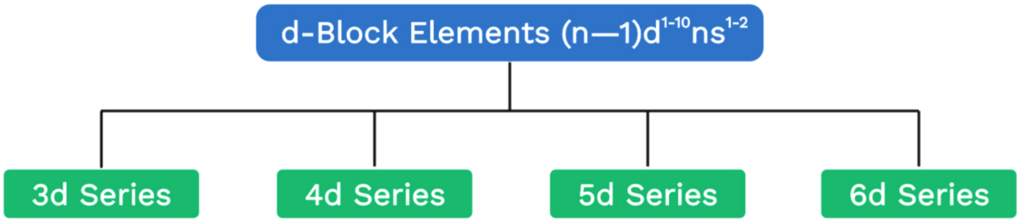
Exception: Helium shows the $1s^2$ electronic configuration

d-Block:

(1) These are present in the middle part of the periodic table (between s and p block elements)

(2)These constitute IIIB to VIIIB, IB and IIB i.e., 3 to 12 groups of the periodic table .

(3) Filling of electrons takes places in penultimate shell. i.e., (n – 1) shell.



3d Series: Also known as first transition series having 10 elements starting from "Scandium" (Z = 21) to "Zinc" (Z = 30). **Ex :** Fe : [Ar] $3d^6 4s^2$

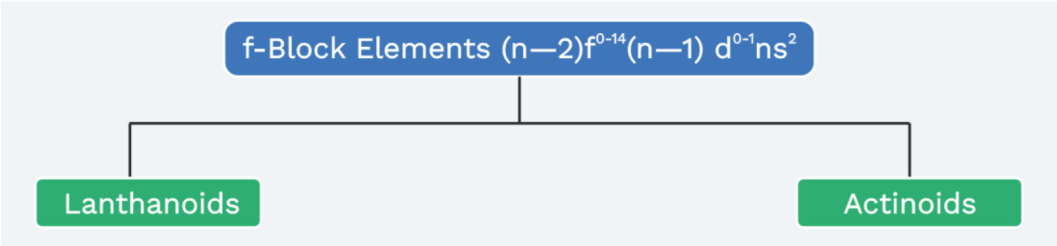
4d Series: Also known as second transition series having 10 elements starting from "Yttrium" (Z = 39) to "Cadmium" (Z = 48). **Ex :** Pd : [Kr] $4d^{10} 5s^0$

5d Series: Also known as third transition series having 10 elements starting from "Lanthanum" (Z = 57) to "Mercury" (Z = 80). **Ex :** Au : [Xe] $5d^{10} 6s^1$

6d Series: Also known as fourth transition series having 10 elements starting from "Actinium" (Z = 89) to "Copernicium" (Z = 112). **Ex**: Rf : [Rn] $6d^2 7s^2$

f-Block:

It corresponds to the Lanthanides and Actinides, known as rare earth elements. When the 6s orbital is saturated with 6s2 electrons, the 4f orbitals appear, and they fill before the 5d orbitals (according to Hund's Rule).



(1) All are metals.

(2) They are paramagnetic in nature.

(3) They form colored compounds.

(4) They have tendency to form complexes.

(5) Filling of electrons takes place in anti-penultimate shell. i.e. (n – 2) shell.

(6) Chemically, lanthanides are very similar. It is difficult to separate them form a mixture by application of a chemical property. Similarly, actinides have similar chemical properties. The members of actinides show the phenomenon of radioactivity.

Lanthanides: (Atomic number 58–71)

Lanthanides belongs to 3rd group (III B group) and VI period having $(n–2)\ f^{1–14}\ (n–1)\ d^{0-10}\ ns^2$ electronic configuration.

Actinides: (Atomic number 90–103)

Actinides belongs to 3rd group (III B group) and VII period $(n–2)\ f^{0–14}\ (n–1)d^{0-10}ns^2$ electronic configuration

column1	Alkali metals
column 2	Alkaline earth metals
column 3 to 12	Transition metals
column13	Boron family
column 14	Carbon family
column15	Nitrogen family

column16	Oxygen family (Chalcogen family)
column17	Halogens
column 18	Noble gases

III.4 Position of the element in the periodic table

The positioning of the element is done from the configuration of the outermost electron shell

- Period: The period corresponds to the number of the outermost shell (n).

- Group: The group number is related to the number of valence electrons.

- Subgroup A: Elements in this subgroup have valence electrons in the ns or ns and np orbitals.

- Subgroup B: Elements in this subgroup have valence electrons in the ns and (n-1) d orbitals.

For elements in Subgroup B (d-block), the valence shell will have the form nsx(n-1) dy. The sum of (x + y) of the electrons informs us about the group of the element:

- When $3 \leq (x + y) \leq 7$, the corresponding elements belong to groups IIIB, IVB, VB, VIB, and VIIB.

- When $8 \leq (x + y) \leq 10$, the corresponding elements belong to Group VIIIB.

- When $(x + y) > 10$:

  - (n-1)d10 ns1: The elements belong to Subgroup IB.

  - (n-1)d10 ns2: The elements belong to Subgroup IIB.

- ***Examples:***

- 37Rb: 36[Kr] $5s^1$, 1 valence electron, so Rb belongs to Group I and Subgroup A.

- 33As: 18[Ar] $3d^{10}$ $4s^2$ $4p^3$, 5 valence electrons, so As belongs to Group V and Subgroup A.

III.5 Evolution and periodicity of the physicochemical properties of the elements

III.5.1 Atomic size (The atomic radius):

Atomic size refers to radius of an atom. It is a distance between the center of the nucleus and the outermost shell of an isolated atom.

In Period : On moving from left to right in a period, atomic size decreases because nuclear charge increases.

Example: Size of second period elements: Li > Be > B > C > N > O > F

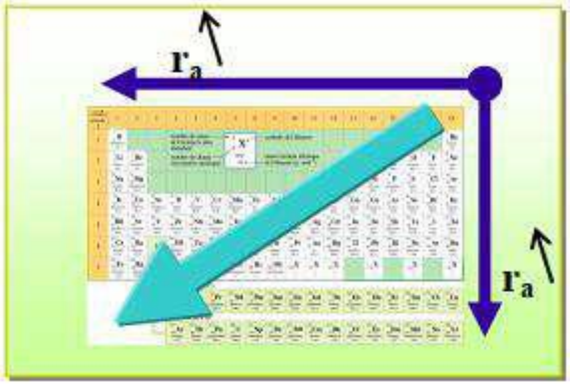
Point to know: The atomic size of noble gases in corresponding period is largest
due to presence of fully filled electronic configuration (i.e. complete octet).

In Group: Atomic size increases down the group because new shells are being added in spite of the increase in nuclear charge.

- ***Example:*** Atomic size of first group element: Li < Na < K < Rb < Cs < Fr Atomic size of 17th group elements: F < Cl < Br < I

The size or radius of ions and atoms is influenced by the number of electrons and the effective nuclear charge. When an atom loses one or more electrons to become a cation (positively charged ion), it loses electrons from its outer electron shell. This result in an increased attraction of the nucleus for the remaining electrons, causing the electron cloud to be drawn closer to the nucleus and, thus, reducing the ionic radius compared to the neutral atom.

On the other hand, when an atom gains one or more electrons to become an anion (negatively charged ion), it adds electrons to its outer electron shell. This increases the electron-electron repulsion, causing the electron cloud to expand, resulting in a larger ionic radius compared to the neutral atom.



III.5.2 Ionization Energy (E.I)

The ionization energy of an atom is the energy required to remove an electron from an atom or ion in the gaseous state.

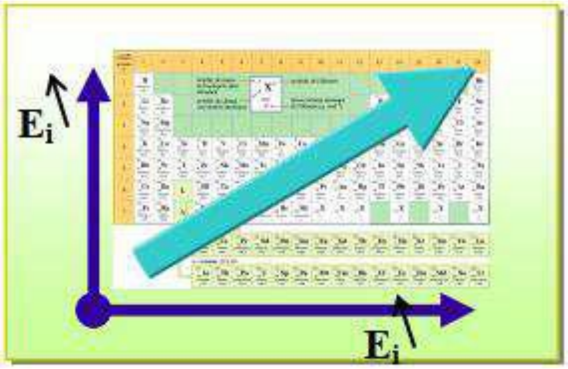
$$X(gas) \rightarrow X^{+}(gas) + 1e^{-}$$

For example:

$$Be \rightarrow Be^{+} + 1e^{-} \qquad E.I1 = +899\ kJ\ mol^{-1}$$

In a period, ionization energy increases across a period from left to right. This is because the electron is more tightly bound to the nucleus as the attractive force exerted by the nucleus is greater.

In a group, ionization energy decreases from top to bottom with the increase in atomic number Z and the principal quantum number n. The outermost electron moves farther away from the nucleus, making it less tightly bound.

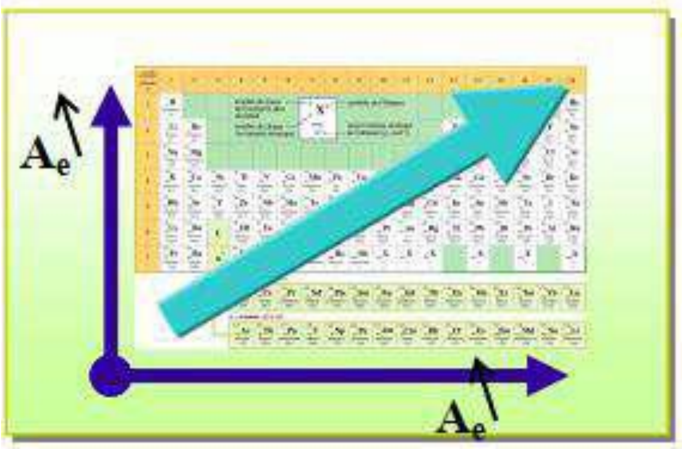


III.5.3 Electron Affinity (A.E)

The electron affinity of an atom X is the energy released when that atom captures an electron.

$$X_{(gas)} + 1e- \rightarrow X^{-}_{(gas)}$$

In comparison to ionization energy, electron affinity is its equivalent in absolute value. This implies that electron affinity varies in the same direction as ionization energy in the periodic table.

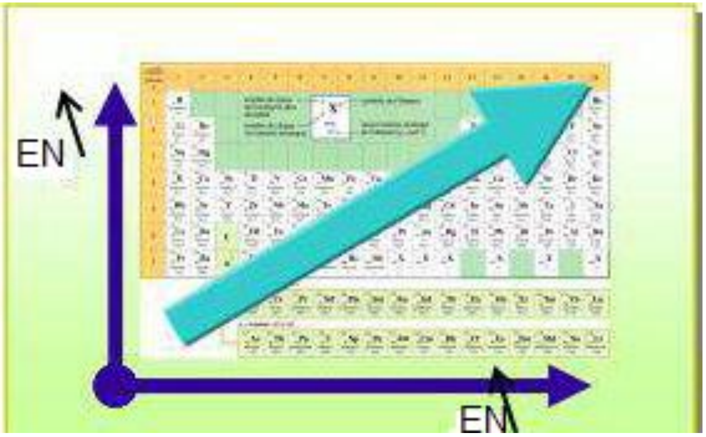


III.5.4 Electronegativity (χ)

Electronegativity (E.N) of an atom becomes apparent when it is in the presence of another atom. It represents an atom's ability to attract an electron from another atom into its electron cloud. Electronegativity takes into account both the ionization potential (PI) and electron affinity (AE).

In a row of the periodic table, the electronegativity of elements increases from left to right.

In a column, it increases from bottom to top



Exercises

Exercise 1

Provide the electron configuration for the following elements:

2He, 4B, 8O, 11Na, 15P, 19K, 26Fe, 29Cu, 31Ga, 40Zr, 45Rh, 52Te, 78Pt, 82Pb

Indicate the period, group, subgroup, and block for each element.

Exercise 2

Consider the following atoms and ions:

7N, 7N^{-3}, 15P, 15P^{+3},

1. Provide the electronic configuration of the atoms and ions and represent the valence shell using quantum boxes.

2. Provide the four quantum numbers of the penultimate electron.

Exercise 3

Consider one of the electrons in the valence subshell of the Arsenic atom (33As) characterized by the quantum number n = 4.

1/What are the possible values of the other quantum numbers for this electron?

2/ an element belongs to the period of Krypton (36Kr) and the group of Nitrogen (7N). What is its atomic number?

Exercise 4

Arrange the following atoms in ascending order of atomic radius, and ionization energy:

5B, 6C, 7N, 8O, 9F.

9F, 17Cl, 35Br, 53I.

Exercise 5

Write the ground-state electron configuration for the following elements: 80Hg and 84Po. Which ions are they likely to form, and why? Compare the atomic radius of each element with its ionic radius.

Exercise 6

Assign the corresponding electronegativity to each element from the following: 37Rb, 11Na, 9F, 8O, 3Li, with electronegativity values of 0.9, 4, 0.8, 1.0, 3.5. Justify your answer.

Solutions

Exercise 1

Provide the electron configuration for the following elements:
2He, 4B, 8O, 11Na, 15P, 19K, 26Fe, 29Cu, 31Ga, 40Zr, 45Rh, 52Te, 78Pt, 82Pb.
Indicate the period, group, subgroup, and block for each element.

Element	Electron Configuration (Noble Gas)	Period	Group	Block
2He	$1s^2$	1	IIA	s
4B	$[He]\ 2s^2\ 2p^1$	2	IIIA	p
8O	$[He]\ 2s^2\ 2p^4$	2	VIA	p
11Na	$[Ne]\ 3s^1$	3	IA	s
15P	$[Ne]\ 3s^2\ 3p^3$	3	VA	p
19K	$[Ar]\ 4s^1$	4	IA	s
26Fe	$[Ar]\ 4s^2\ 3d^6$	4	VIIIB	d
29Cu	$[Ar]\ 4s^1 3d^{10}$	4	IB	d
31Ga	$[Ar]\ 4s^2\ 3d^{10}\ 4p^1$	4	IIIB	p

40Zr	$[Kr]\ 5s^2 4d^2$	5	IVB	d
45Rh	$[Kr]\ 5s^2 4d^7$	5	VIIIB	d
52Te	$[Kr]\ 5s^2\ 4d^{10}\ 5p^4$	5	VIA	p
78Pt	$[Xe]\ 6s^1 4f^{14}\ 5d^9$	6	IB	d
82Pb	$[Xe]\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^2$	6	IVA	p

Exercise 2

Consider the following atoms and ions: 7N, $7N^{-3}$, 15P, $15P^{+3}$.

1. Provide the electronic configuration of the atoms and ions and represent the valence shell using quantum boxes.

2. Provide the four quantum numbers of the penultimate electron.

Electronic Configurations and Quantum Boxes:

Species	Configuration	Valence Shell (Boxes)
7N	$[He]\ 2s^2\ 2p^3$	↑↓ ↑ ↑ ↑
$7N^{-3}$	$[He]\ 2s^2\ 2p^6$	↑↓ ↑↓ ↑↓ ↑↓
15P	$[Ne]\ 3s^2\ 3p^3$	↑↓ ↑ ↑ ↑
$15P^{+3}$	$[Ne]\ 3s^2$	↑↓

2. Four Quantum Numbers for the Penultimate Electron:

For 15P:

- Principal quantum number (n): 3
- Azimuthal quantum number (l): 1 (p-orbital)
- Magnetic quantum number (m): 0 (one of the 3p orbitals)
- Spin quantum number (s): +½

Exercise 3

1. For an electron in the valence subshell of Arsenic (33As) with n = 4, the possible quantum numbers are:
   - Azimuthal quantum number (l): 0 (s), 1 (p), 2 (d), 3 (f).
   - Magnetic quantum number (m):
     - $l = 0 \rightarrow m = 0$
     - $l = 1 \rightarrow m = -1, 0, +1$
     - $l = 2 \rightarrow m = -2, -1, 0, +1, +2$
   - Spin quantum number (s): +½ or -½.

2. An element belongs to the period of Krypton (36Kr) and the group of Nitrogen (7N). What is its atomic number?

   Step 1: Identify the Element's Position in the Periodic Table

   - The element is said to belong to the same period as Krypton (Kr). This places the element in period 4 because Krypton is in the 4th period.
   - The element is also in the same group as Nitrogen (N). Nitrogen belongs to group VA (also known as group V).

   Step 2: Determine the General Electron Configuration for Group 15

   - Elements in group VA share a similar valence shell configuration: $ns^2\ np^3$
   - Since the element is in period 4, the principal quantum number is 4.

   Thus, the valence shell configuration becomes: $4s^2\ 4p^3$

   Step 3: Build the Complete Electron Configuration

   - The closest noble gas before period 4 is Argon (Ar), with an electron configuration of:

   $[Ar] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

   - To reach group 15 in period 4, we add the following electrons after Argon:
     - Filling the 3d subshell.
     - Filling the 4s orbital.
     - Partially filling the 4p orbitals.
   - The full electron configuration is: $[Ar]\ 3d^{10}\ 4s^2\ 4p^3$

   Step 4: Calculate the Atomic Number

   $18 + 10 + 2 + 3 = 33$

   Step 5: Identify the Element

   the atomic number 33 corresponds to the element Arsenic (As).

-Period: 4

- Group: 15
- Electron Configuration: [Ar] $4s^2\ 3d^{10}\ 4p^3$

Exercise 4

1. Atomic radius (ascending order):

- Trend: Decreases across a period.
- Order: $_9F < {}_8O < {}_7N < {}_6C < {}_5B$.

Ionization energy (ascending order):

- Trend: Increases across a period.
- Order: $_5B < {}_6C < {}_7N < {}_8O < {}_9F$.

2. Atomic radius (ascending order):

- Trend: Increases down a group.
- Order: $_9F < {}_{17}Cl < {}_{35}Br < {}_{53}I$.

Ionization energy (ascending order):

- Trend: Decreases down a group.
- Order: $_{53}I < {}_{35}Br < {}_{17}Cl < {}_9F$.

Exercise 5

1. Electron Configurations:

- $_{80}Hg$: [Xe] $4f^{14}\ 5d^{10}\ 6s^2$.
- $_{84}Po$: [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$.

2. Likely Ions:

- Hg → Hg^{2+} (loses 2 electrons from 6s).
- Po → Po^{2-} (gains 2 electrons to complete the p orbital).

3. Atomic Radius vs Ionic Radius:

- Hg^{2+}: Ionic radius < atomic radius (loss of electrons).
- Po^{2-}: Ionic radius > atomic radius (gain of electrons).

Exercise 6

Electronegativity values and justification:

- 37Rb: 0.8 (low, Group 1, large atomic radius).
- 11Na: 0.9 (low, Group 1, smaller than Rb).
- 3Li: 1.0 (higher than Na and Rb, smaller radius).
- 8O: 3.5 (high, strong nuclear attraction).
- 9F: 4.0 (highest, strongest pull-on electrons in Group 17).

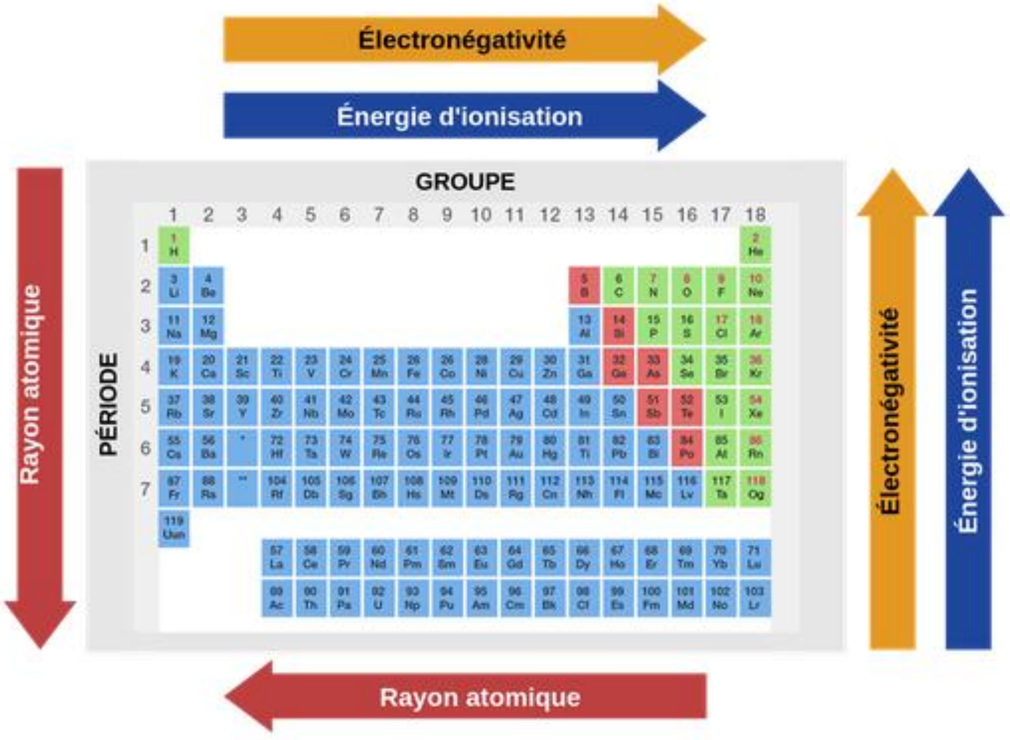


Figure 1 : Les tendances dans le tableau périodique

Chapter IV: Chemical bonds

IV.1 Introduction

Chemical Bonding it is attractive force holding atoms together, can be broadly categorized into two main types: strong and weak chemical bonds

IV.1.1 Strong Chemical Bonds

Strong chemical bonds are characterized by the sharing or transfer of electrons between atoms, resulting in the formation of stable compounds. These bonds are typically classified into two subtypes: covalent and ionic bonds. We will delve into them in detail in this chapter.

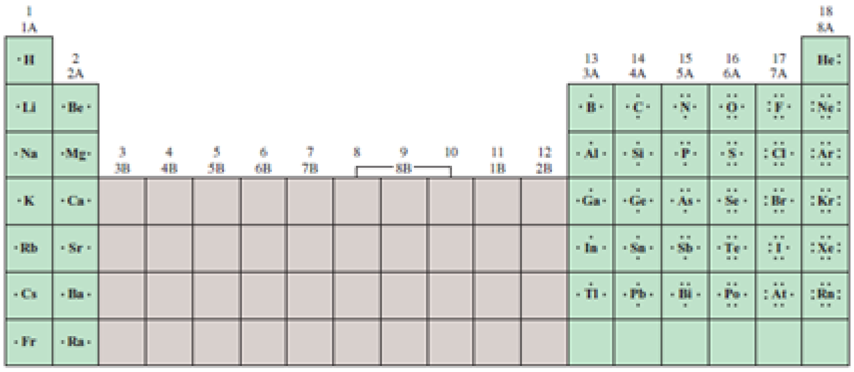
IV.1.2 Weak Chemical Bonds

Weak chemical bonds are interactions between molecules or within a molecule that are relatively weaker than strong chemical bonds. These bonds are crucial in various biological and chemical processes. Two significant types of weak chemical bonds are hydrogen bonds and van der Waals forces.

IV.2 Representation of Chemical Bonding Using the Lewis Model

Gilbert Lewis (1916) proposed the first real model for chemical bonding, which allows for the prediction of the number of bonds each atom forms and explains molecular configurations using simple and effective rules. This model is established based on the electron configuration of atoms. For this purpose:

- Each electron is represented by a dot (.) and each electron pair (whether bonding or non-bonding) is represented by a line (doublet).
- The total number of valence electrons (ev) is calculated, which is the number of electrons present in the outermost shell of the atom.
- The total number of pairs (whether bonding or non-bonding) to be placed in the structure is inferred using the octet (or duet) rule when possible.



IV.2.1 Construction of the Molecular Lewis Structure

Octet rule in a molecule, atoms exchange as many electron pairs as necessary to achieve their octet (an electron configuration of $ns^2\ np^2$).

The maximum number of bonds an atom can form is x = 8 - Nv, where Nv represents the number of valence electrons. This rule is applicable to the second and third periods of the periodic table.

Exceptions:

Hydrogen: (x = 2 - 1 = 1 maximum bond)

General Method for Writing a Lewis Formula

We are considering a molecule with a central atom bonded to all the other atoms. For example: $COCl_2$.

First Step: We calculate all available electrons (Ne) and the number of possible electron pairs (Nd): Nd = Ne / 2.

Ne = Total valence electrons - z, where z is the number of elementary charges carried by the atom.

Nd = Ne / 2.

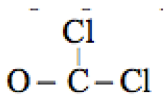
For example, for COCl2: Ne = 4 + 6 + 2 × 7 - 0 = 24.

Number of possible electron pairs: Nd = Ne / 2.

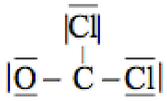
If Ne is even, (Ne - 1) / 2 (indicating the presence of an unpaired electron).

In this case, Nd = 12 electron pairs.

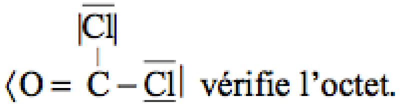
Second Step: We form single covalent bonds between the central atom and the peripheral atoms.



Third Step: We complete the octet for the peripheral atoms by assigning non-bonding electron pairs to them.



Fourth Step: We assign all remaining electron pairs and electrons to the central atom and check if it satisfies the octet rule. (If not, proceed to step 5). In this case, no changes; C does not satisfy the octet.



Fifth Step: We start over by considering multiple bonds between the central atom and the peripheral atoms.

Sixth Step: We assign a formal charge to each atom

Sixth Step: We assign a formal charge to each atom

IV.2.2 Concept of Formal Charges

To complete a Lewis diagram, we calculate the formal charges (Cf) for each atom. The sum of the formal charges always equals the overall charge (q) of the molecule.

A simple rule allows us to calculate formal charges in advance:

Haut du formulaire

$$Cf = Nv - N_b - 2 \times N_l$$

Where:

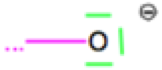
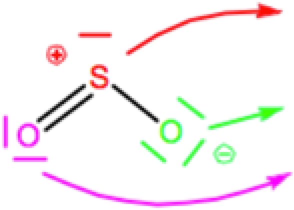
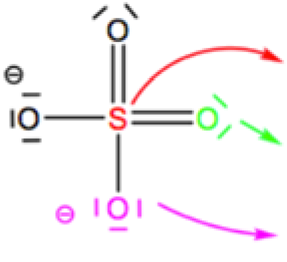
Nv = Number of valence electrons of the atom under consideration in its isolated ground state.

Nb = Number of bonds formed by the atom in the molecule being studied.

Nl = Number of lone pairs of electrons on the atom in the molecule being studied.

This formula allows us to calculate the formal charge (Cf) for each atom in a molecule, which helps in understanding the distribution of charges within the molecule and its overall charge.

Exemples

	**O**:$1s^2$ $2s^2$ $2p^4$; 6 $Cf = 6 - 2 - 2 \times 2 = 0$;
	**O**: $1s^2$ $2s^2$ $2p^4$; $Cf = 6 - 1 - 2 \times 3 = -1$;
	**S**: $1s^2$ $2s^2$ $2p^6 3s^2 3p^4$; $Cf = 6 - 3 - 2 \times 1 = +1$ **O**: $1s^2$ $2s^2$ $2p^4$; $Cf = 6 - 1 - 2 \times 3 = -1$ **O**: $1s^2$ $2s^2$ $2p^4$; $Cf = 6 - 2 - 2 \times 2 = 0$
	**S**: $1s^2$ $2s^2$ $2p^6 3s^2 3p^4$; $Cf = 6 - 6 - 2 \times 0 = 0$ **O**: $1s^2$ $2s^2$ $2p^4$; $Cf = 6 - 2 - 2 \times 2 = 0$ **O**: $1s^2$ $2s^2$ $2p^4$; $Cf = 6 - 1 - 2 \times 3 = -1$

Rule: The sum of the formal charges is always equal to the overall charge of the molecule.

IV.2.3 Type of bonds

In chemistry, there are primarily two types of chemical bonds: covalent bonds and ionic bonds.

Ionic Bond

As the name suggests, ionic bonds are a result of the attraction between ions. Ions are formed when an atom loses or gains an electron. These types of bonds are commonly formed between a metal and a nonmetal

Characterized by the complete transfer of electrons from one atom to another, are influenced by the electronegativity disparity, determining the strength of the resulting electrostatic attraction between ions.$\boldsymbol{\Delta x} > \mathbf{1.9}$ Understanding these electronegativity-related phenomena is vital for predicting the behavior and properties of substances in various chemical contexts.

Covalent Bond

In the case of a covalent bond, an atom shares one or more pairs of electrons with another atom and forms a bond. This sharing of electrons happens because the atoms must satisfy the octet (noble gas configuration) rule while bonding. Such a type of bonding is common between two nonmetals. The covalent bond is the strongest and most common form of chemical bond in living organisms. Together with the ionic bond, they form the two most important chemical bonds.

A covalent bond can be divided into a nonpolar covalent bond and a polar covalent bond.

Pure Covalent Bond (Nonpolar Bond)

This type of bond forms between two atoms that are very similar or have closely matched electronegativities. In a pure covalent bond, the electron cloud is evenly distributed between the two atoms. Nonpolar covalent bonds:

formed between atoms with similar electronegativities, $\boldsymbol{\Delta x} = \mathbf{0}$ rely on balanced electron sharing, affecting properties such as boiling points and melting points

Polar Covalent Bond

Electronegativity plays a crucial role in determining the nature of chemical bonds.

where atoms with different electronegativities are involved, $\mathbf{0.5 < \Delta x < 1.9}$ the magnitude of the electronegativity difference dictates the degree of polarity and influences properties like solubility and reactivity.

IV.3 Dipole Moment in Polar Covalent Bonds

A polar covalent bond represents an intermediate state between ionic and pure covalent bonding, where it exhibits both partial ionic and partial covalent character. This occurs when two atoms have significantly different electronegativities. $\mathbf{0.5 < \Delta x < 1.9}$

The electron pair forming the bond tends to be closer to the more electronegative atom, resulting in an uneven distribution of charge. As a consequence, a small partial charge, denoted as δ (δ < 1), appears on each atom.

The more electronegative atom tends to have a partially negative charge (-δ) due to the electron density it attracts, while the less electronegative atom, which loses some of its electrons, carries a partially positive charge (+δ). This creates an electric dipole within the molecule.

The molecule then becomes a polar molecule with a dipole moment symbolized by μ.

The dipole moment indicates the magnitude and direction of the charge separation within the molecule. It is a measure of the molecule's overall polarity and is often expressed in Debye units (D). (The first letter of the scientist's name Debye)

The dipole moment is an important concept in understanding molecular interactions and properties.

$$\chi_H = 2.1 < \chi_{Cl} = 3.0$$

By definition, the dipole moment (μ) is a vector that arises between two separated charges at a distance "d." The direction of the dipole moment is determined from the negative pole to the positive pole, meaning from the more electronegative atom to the less electronegative one.

$$\mathbf{1D = 3{,}33.10^{-30}\ C.m} \qquad \vec{\mu} = \delta.\vec{d} \qquad \boxed{\vec{\mu} = q.\ d = \delta e.\ \vec{d}}$$

The ionic (or ion) character of a bond is represented by the value of δ:

When $\delta = 0$, the bond is purely covalent (100% nonpolar).

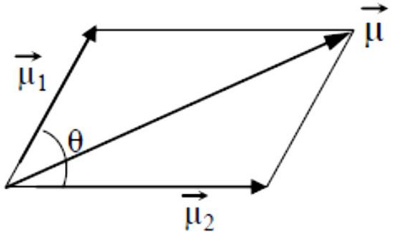
When $\delta = 1$, the bond is purely ionic (100% polar).

When $0 < \delta < 1$, the bond is partially ionic, and the percentage of ionic character is $\delta\%$, with the remaining percentage being covalent ($100 - \delta\%$).

In the case of molecules with multiple atoms, the global dipole moment equals the vector sum of individual dipole moments, either through its coefficient (as per equation 1) or through the triangular relationship.

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2\cos\theta} \qquad \text{(équation 1)}$$

$$\mu = 2\mu_1 \cos\frac{\mu_1\mu_2}{2} \qquad \text{(équation 2)}$$



The ionic character (IC) of a bond is generally a middle ground between purely covalent and purely ionic bonds. In this case, we say that the covalent bond has a certain degree of ionic character, denoted as IC. Its determination often relies on the dipole moment.

It can be expressed using the following relationship:

$$C_i(\%) = \frac{\mu_{exp}}{\mu_{théo}} \times 100$$

$$\left.\begin{matrix} \mu_{exp} = \delta.d \\ \\ \mu_{théo} = e.d \end{matrix}\right. \Longrightarrow C_i(\%) = \frac{\delta.d}{e.d} \times 100 = \frac{\delta}{e} \times 100$$

Example: We have a molecule of hydrochloric acid with μ exp = 1.08 D and a bond length of H - Cl = 0.128 nanometers.

We can use the provided information to calculate the ionic character (IC) of the bond between hydrogen and chlorine in hydrochloric acid using the given relationship. The relationship between IC, dipole moment (μ), and bond length (d) is as follows:

$$\%C.I = \frac{1{,}08 \times 3{,}33.10^{-30}}{1{,}6.10^{-19} \times 0{,}128.10^{-9}} \times 100 \quad \Rightarrow \quad \%C.I = 17\%$$

So, the bond in a molecule of hydrochloric acid is approximately 17% ionic and 83% covalent in character.

IV.4 The Gillespie theory

Also known as the Valence Shell Electron Pair Repulsion (VSEPR) theory is based on the principle that the electron pairs or electron doublets in the outermost valence shell of a central atom (A) repel each other. The VSEPR theory is used to predict the three-dimensional molecular geometry of a molecule based on the arrangement of valence electron pairs around the central atom.

The method involves determining the following from the Lewis structure of a molecule:

1. The number (m) of bonding pairs between the central atom (A) and the surrounding bonded atoms (X).
2. The number (n) of non-bonding pairs (E) on the central atom.
3. The compound's formula is then represented as **AXmEn**, and its geometry will depend on the total number of (m + n) electron pairs.

IV.4.1 Gillespie's rules

1. All electron pairs (both bonding and non-bonding) in the valence shell of the central atom A are placed on the surface of a sphere centered on the nucleus.
2. Electron pairs are positioned in a way that minimizes electronic repulsions (the electron pairs are located as far away from each other as possible.

IV.4.2 How to determine the hybridization of an atom

Determine the number and type of atomic orbitals used by the atom; include all the electrons in the valence shell. For example, boron, with three valence electrons, uses one s and two p orbitals; nitrogen, with five valence electrons, uses one s and three p orbitals .

If there are π bonds present, determined by the Lewis structure, discount one partially filled p orbital for every π bond to the atom of interest. Remember a double bond ≡ 1σ + 1π bond and a triple bond ≡ 1σ + 2π bonds .

“Mix” the remaining orbitals to form hybrid orbitals

One s + one p ⇒ two sp hybrid orbitals

One s + two p ⇒ three sp2 hybrid orbitals

One s + three p ⇒ four sp3 hybrid orbitals

One s + three p + one d ⇒ five sp3 d hybrid orbitals

One s + three p + two d ⇒ six sp3 d 2 hybrid orbitals

Alternatively…A quick way of determining the hybridization of an atom is to count the σ bonds and lone pairs around that atom and assign one hybrid orbital to each.

2 electron pairs ⇒ sp hybrids, 3 electron pairs ⇒ sp2 hybrids, 4 electron pairs ⇒ sp3 hybrids.

Exercises

EXERCISE 01:

Given the electronegativity of the atoms:

H(2.2), F(4), Cl(3.1), K(0.8),

predict the primary character (ionic, polar, covalent) of the bonds in the following molecules: K-F, H-F, K-Cl, H-Cl, and H-H.

EXERCISE 02:

Provide the Lewis notation for the following molecules and ions

NO_2^- .ClO_2^- . SO_2, HCN, PCl_3.

Use VSEPR theory predict the geometry of these molecules.

EXERCISE 03

Calculate the dipole moment of the hydrogen fluoride (HF) molecule in Cm units and Debyes, knowing that the partial ionic character of the bond is 42%, and the distance between H and F in the molecule is 0.92 Å.

Given:

1 Debye = 3.336×10^{-30} C.m units

Elementary charge (e) = 1.6×10^{-19} C

EXERCISE 04:

The dipole moment (μ) of the CsCl molecule is 3.473×10^{-29} C·m, and the bond length (d) of Cs-Cl is 0.35 nm.

Calculate the partial ionic character of the bond.

EXERCISE 05:

We consider the bonds in the molecules HBr, HCl, HI, and HF to be purely ionic.

1. Calculate the dipole moment in Debyes (D) for each molecule:

The dipole moment (μ) in Debyes can be calculated using the following formula:

$\mu \text{ (in D)} = \mu \text{ (in C·m)} / 3.336 \times 10^{-30} \text{ C·m/C)}$

Given the bond lengths for each molecule: HBr (1.40 Å), HCl (1.27 Å), HI (1.61 Å), and HF (0.92 Å).

The experimentally obtained dipole moments are HBr (0.79 D), HCl (1.07 D), HI (0.38 D), and HF (1.82 D).

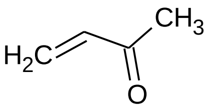
2. Calculate the values of δ for each molecule.

EXERCISE 06:

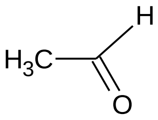
Consider the following molecules, hybridization states of the carbon atoms.

$H_2C{=}CH_2$

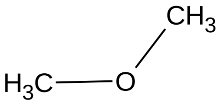
$HC{\equiv}CH$

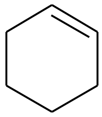


$H_3C{-}OH$

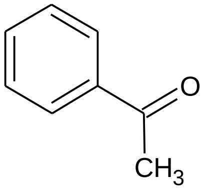


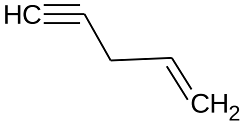
$H_3C{-}NH_2$

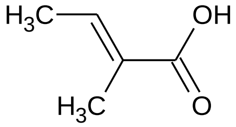




$H_3C{-}OH$





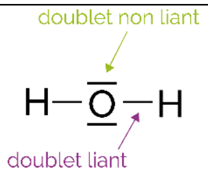
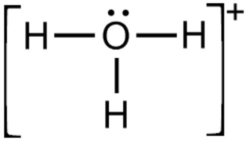
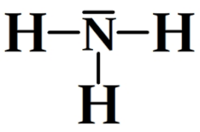
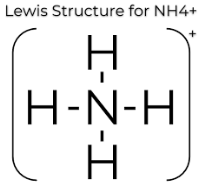
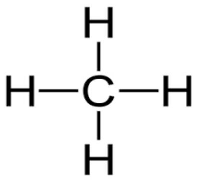


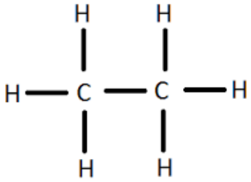
Solutions

EXERCISE 01: Predict Bond Character

Molecule	Electronegativity Difference (Δχ)	Bond Type
K-F	Δχ = 4.0 - 0.8 = 3.2	Ionic
H-F	Δχ = 4.0 - 2.2 = 1.8	Polar Covalent
K-Cl	Δχ = 3.1 - 0.8 = 2.3	Ionic
H-Cl	Δχ = 3.1 - 2.2 = 0.9	Polar Covalent
H-H	Δχ = 2.2 - 2.2 = 0.0	Nonpolar Covalent

EXERCISE 02: Lewis Structures and Geometry

Molecule/Ion		Lewis Structure Description	VSEPR Geometry
H_2O	$\frac{2*1+6}{2}=4$		AX_2E_2
H_3O^+	$\frac{3*1+6-1}{2}=4$		AX_3E_1
NH_3	$\frac{3*1+5}{2}=4$		AX_3E_1
NH_4^+	$\frac{4*1+5-1}{2}=4$		AX_4
CH_4	$\frac{4*1+4}{2}=4$		AX_4

C_2H_6	$\frac{6*1+2*4}{2}=7$		AX_4

EXERCISE 03: Calculate Dipole Moment of HF

Given Data:

Bond Length (d): 0.92 Å = 0.92×10^{-10} m

Partial Ionic Character: 42%

Elementary Charge (e): 1.6×10^{-19} C

1 Debye = 3.336×10^{-30} C·m

Calculation:

1. Calculate the dipole moment (μ) in C·m:

$\mu = 0.42 \times e \times d = 0.42 \times 1.6 \times 10^{-19} \times (0.92 \times 10^{-10}) = 6.18 \times 10^{-30}$ C·m

2. Convert to Debyes:

$\mu (D) = \mu (C\cdot m) / (3.336 \times 10^{-30}) = 6.18 \times 10^{-30} / 3.336 \times 10^{-30} \approx 1.85$ D

EXERCISE 04: Partial Ionic Character in CsCl

Formula: Partial Ionic Character = $(\mu / (e \times d)) \times 100$

Given:

$\mu = 3.473 \times 10^{-29}$ C·m

$d = 0.35$ nm $= 0.35 \times 10^{-9}$ m

$e = 1.6 \times 10^{-19}$ C

Calculation:

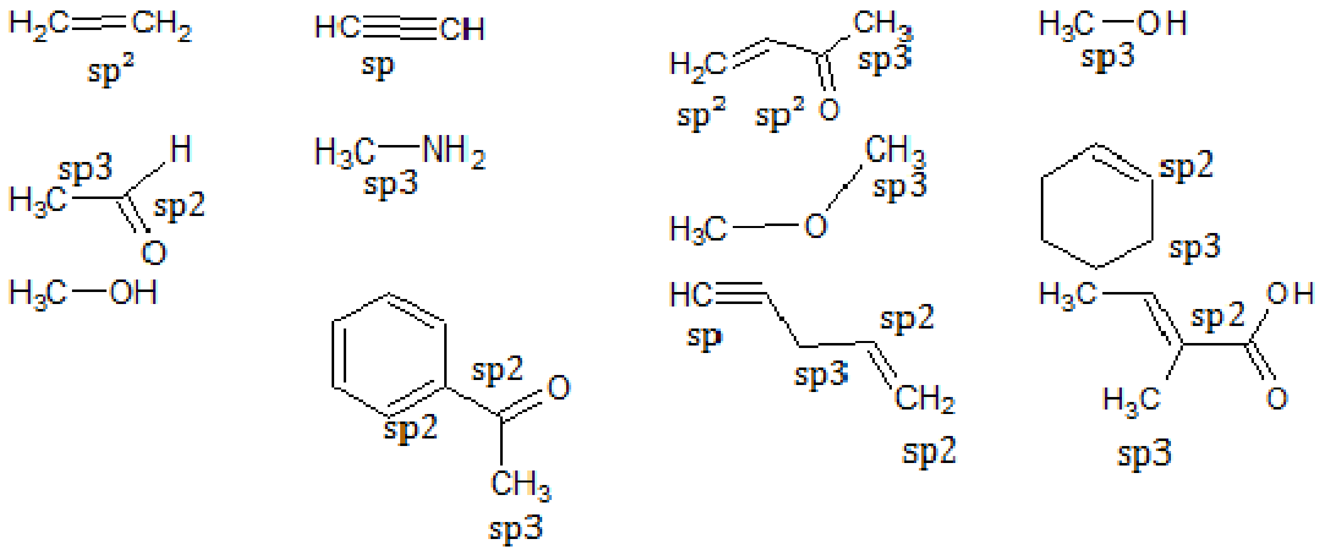
Partial Ionic Character = $(3.473 \times 10^{-29}) / ((1.6 \times 10^{-19}) \times (0.35 \times 10^{-9})) \times 100$

EXERCISE 05: Dipole Moments and Partial Charges

Molecule	Bond Length (Å)	Dipole Moment (Calculated, D) $\mu = 4.8 \times d$	Dipole Moment (Experimental, D)	Partial Charge $\delta = \mu_{exp} / \mu_{theo}$
HBr	1.40	6.72	0.79	0.117
HCl	1.27	6.10	1.07	0.175
HI	1.61	7.72	0.38	0.049
HF	0.92	4.416	1.82	0.412

EXERCISE 06: Carbon Hybridization

Determine the hybridization of carbon atoms in the following molecules:



Chapter V: Chemical Equilibrium

V.1 Acide- Base System

Chemical equilibrium in acid-base systems is a fundamental concept in chemistry that governs the behavior of acids and bases when they react with each other. It is a dynamic state in which the forward and reverse reactions proceed at equal rates, resulting in no net change in the concentrations of reactants and products over time. Understanding chemical equilibrium in acid-base reactions is crucial for various fields including chemistry, biology, and environmental science, as it helps explain phenomena such as buffering capacity, pH regulation in biological systems, and the behavior of acid rain. Acids and bases are two classes of compounds that play essential roles in numerous chemical processes.

V.2 BRONSTED Definition

Among the various theories of acids and bases, the theory proposed by BRONSTED in 1923 is still the most widely used today.

✓ An acid: is a chemical species, ion, or molecule capable of donating a proton H^+. An acid must necessarily contain the hydrogen element, but not every hydrogen-containing compound is necessarily an acid:

$$AH \leftrightarrow A^- + H^+$$

✓ A base: is a chemical species, ion, or molecule capable of accepting a proton H+.

$$B + H^+ \leftrightarrow BH^+$$

It should be noted that compounds such as NaOH, KOH, ... in water dissociate to give OH- ions, which are bases since they can accept a proton:

$$OH^- + H^+ \leftrightarrow H_2O$$

V.3 Conjugate Acid-Base Pairs

Consider the reaction: $AH \leftrightarrow A^- + H^+$

The species A^- and the proton formed can recombine to give AH; therefore, A^- is a base.

The combination of both species involved in the same equilibrium constitutes a conjugate acid-base pair.

The acid and base within the same pair are called *conjugates*. We denote the conjugate acid-base pair as HA/A^-.

V.4 Strength of Acids and Bases

There are two types of acids and bases based on their dissociation:

V.4.1 Strong Acids and Bases

These are strong electrolytes, and the dissociation reaction is complete:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

$$NaOH \rightarrow Na^+ + OH^-$$

V.4.2 Weak Acids and Bases

These are weak electrolytes. There is equilibrium of dissociation that significantly favors the reverse reaction:

$$HCN + H_2O \leftrightarrow H_3O^+ + CN\text{-} \text{ (HCN is a weak acid)}$$

$$F^- + H_2O \leftrightarrow HF + OH^- \text{ (}F^-\text{ is a weak base)}$$

V.5 Acid and Base Constants

Let HA is a weak acid:

$$HA + H_2O \rightleftharpoons H_3O+ + A^-$$

The law of mass action allows us to write: $Kc = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}][\mathrm{H_2O}]}$

So, $Kc\times[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$ We define Ka (the acid dissociation constant) as:

$$Ka = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

This constant, Ka, is a measure of the strength of the acid.

Acids are stronger when their Ka (acid dissociation constant) is larger and their pKa (negative logarithm of Ka) is smaller.

It's worth noting that strong acids are completely dissociated in solution and do not possess a Ka value.

Similarly, we can define the strength of bases based on the equilibrium established in aqueous solutions, using the base dissociation constant Kb. For example, for the conjugate acid-base pair AH/A-:

$A^- + H_2O \rightleftharpoons HA + OH^-$ $\quad Kb = \frac{[OH^-][HA]/}{[A^-]} = \frac{[OH^-][conjugate\ acid]}{[base]}$

However, it can be observed that for conjugate acid-base pairs, Ka and Kb are related:

$Ka \times Kb = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[OH^-][HA]}{[A^-]} = [H_3O^+][OH^-]$

This product is called the ion product of water, K$_w$, and its value depends only on the temperature.

$$K_w = [H_3O^+][OH^-] = 10^{-14} \text{ at } 25°C.$$

This relationship is general and applies to any aqueous solution, regardless of the source of H_3O^+ and OH^- ions and other species present in the solution. In all cases:

$$Ka \times Kb = 10^{-14} \text{ and } pKa + pKb = 14.$$

Therefore, it is not necessary to establish a scale of basicity for bases. It is sufficient to know the Ka values of their conjugate acids.

For example, consider two acid-base pairs:

HF/F- ($pKa_1 = 3.2$) and CH3COOH/CH3COO$^-$ ($pKa_2 = 4.8$)

pKb1 = 14 - 3.2 = 10.8 and pKb2 = 14 - 4.8 = 9.2

pKa1 < pKa2, so the acid HF is stronger than CH3COOH.

pKb2 < pKb1, so the base CH3COO$^-$ is stronger than F$^-$.

In summary, the stronger the acid, the weaker its conjugate base, and vice versa.

V.6 Calculation of pH in aqueous solutions

The measurement of the pH of an aqueous solution allows it to be classified as acidic or basic.

By definition: $pH = -\log [H_3O^+]$

✓ Neutral solution $[H3O+] = [OH^-] \rightarrow [H_3O^+]^2 = 10^{-14}$, $[H_3O^+] = 10^{-7}$ *mol/L, and* $pH=7$

✓ *Acidic solution* $[H3O+] > [OH^-] \rightarrow pH<7$

✓ *Basic solution* $[H3O+] < [OH^-] \rightarrow pH>7$

V.6.1 Case of a Strong Acid

Main Chemical Reactions

1. Ionization of Acid (AH):

$$AH^+ + H_2O \rightarrow A^- + H_3O^+$$

2. Water Self-Ionization:

$$2H_2O \rightleftharpoons OH^- + H_3O^+$$

Key Chemical Species in Solution

- Water molecules (H_2O)
- Conjugate base (A^-)
- Hydronium ions (H_3O^+)
- Hydroxide ions (OH^-)

Note: The acid AH is completely ionized in the solution, so it is not present.

Relationships Between Concentrations

1. Ion Product Constant for Water: $Kw = [H_3O^+][OH^-]$
2. Conservation of Matter: $[A^-] = C$ (where C is the initial concentration of the acid)

3. Electrical Neutrality: $[OH^-] + [A^-] = [H_3O^+]$

Simplified pH Calculations

1. Moderately Concentrated Solutions ($C > 10^{-65}$ M):

In this case, the hydronium ion concentration from the acid is significantly higher than that from water dissociation.

- Approximation:

$[OH^-] \ll [H_3O^+]$

The contribution of water dissociation is negligible, and the solution is sufficiently acidic.

- Result:

$[A^-] = [H_3O^+] = C$

pH = -log C

2. Highly Dilute Solutions ($C < 10^{-65}$ M):

In this case, the contribution of hydronium ions from water dissociation is not negligible compared to the acid's ionization.
No approximations are made, and the concentrations must be determined by solving a quadratic equation.

- Key Equations:
  1. $Kw = [H_3O^+][OH^-]$
  2. $[A^-] = C$
  3. $[OH^-] + [A^-] = [H_3O^+]$

- Substituting $[OH^-] = Kw / [H_3O^+]$:

$Kw / [H_3O^+] + C = [H_3O^+]$

Simplifies to:

$[H_3O^+]^2 - [H_3O^+]C - Kw = 0$

- Solving this quadratic equation gives:

$[H_3O^+] = (-b \pm \sqrt{(b^2 - 4ac)}) / 2a$

where $a = 1, b = -C, c = -Kw$.

Only the positive root is physically meaningful.

$$[H_3O^+] = \frac{C + \sqrt{C^2 + 4K_W}}{2}$$

$$pH = -\log[H_3O^+] = -\log\left(\frac{C+\sqrt{C^2+4K_W}}{2}\right)$$

Interpretation of Results

1. If C is much smaller than Kw, the hydronium ion concentration is approximately $\sqrt{Kw}$, indicating water's ionization dominates.
2. If C is slightly larger, the hydronium concentration results from both the acid and water's ionization.

V.6.2 Case of a Weak Acid

Chemical Reactions

1. Weak Acid Ionization:

$$AH + H_2O \rightleftharpoons A^- + H_3O^+$$

2. Water Self-Ionization:

$$2H_2O \rightleftharpoons OH^- + H_3O^+$$

Chemical Species in Solution

- Weak acid molecules (AH)
- Conjugate base (A^-)
- Water (H_2O)

- Hydronium ions (H_3O^+)
- Hydroxide ions (OH^-)

Relationships between Concentrations

1. Ion Product Constant for Water:

$Kw = [H_3O^+][OH^-]$

2. Acid Dissociation Constant:

$Ka = [H_3O^+][A^-]/[AH]$

3. Conservation of Matter:

$[AH] + [A^-] = C_a$ (where C_a is the initial concentration of the weak acid)

4. Electrical Neutrality:

$[OH^-] + [A^-] = [H_3O^+]$

Approximations for Simplification

1. Approximation 1:

If the solution is sufficiently acidic, the self-ionization of water can be neglected:

$$[OH^-] \ll [H_3O^+]$$

2. Approximation 2:

If the acid is weakly ionized, the concentration of the conjugate base is much smaller than the concentration of the un-ionized acid:

$$[A^-] \ll [AH]$$

this is valid if:

$$Ka \,/\, C_a \leq 10^{-2}\, M^{-1}$$

Simplified Calculations

1. Using Both Approximations

$[A^-] \approx [H_3O^+]$

$[AH] \approx C_a$

Substituting these into the acid dissociation constant equation:

$Ka = [H_3O^+]/C_a$

$$[H_3O^+] = \sqrt{}(Ka \times C_a)$$

$$pH = ½(pKa - log\, C_a)$$

2. When Approximation 2 is Not Valid

If $Ka / C_a > 10^{-2}\, M^{-1}$, approximation 2 cannot be applied. In this case:

$$[A^-] \approx [H_3O^+]$$

$$[AH] = C_a - [H_3O^+]$$

Substituting into the acid dissociation constant:

$$Ka = [H_3O^+]^2 / C_a$$

Rearranging:

$[H_3O^+]^2 + Ka \times [H_3O^+] - Ka \times C_a = 0$

Solving this equation gives us the expression for the concentration of [H3O+]:

$$[H_3O^+] = \frac{-K_a + \sqrt{{K_a}^2 + 4K_aC}}{2}$$

$$\text{pH} = -\log\left(\frac{-K_a + \sqrt{{K_a}^2 + 4K_aC}}{2}\right)$$

Interpretation of Results

1. Weak Acids with Small Ka:

Approximations simplify the calculations significantly, especially for weak acids in dilute solutions.

2. Stronger Weak Acids or Higher Concentrations:

The full quadratic solution is required to accurately determine the hydronium ion concentration.

V.6.3 Case of a Strong Base

Chemical Reactions

1. Base Ionization:

$B + H_2O \rightarrow BH^+ + OH^-$

(where $[B]_0 = C$, the initial concentration of the base)

2. Water Self-Ionization:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Key Relationships

1. Ion Product Constant for Water:

$Kw = [H_3O^+][OH^-]$

2. Electroneutrality Condition:

$[H_3O^+] + [BH^+] = [OH^-]$

3. Mass Conservation:

$C = [BH^+]$

General Equation

Combining the above relationships:

$$Kw + C[OH^-] = [OH^-]^2$$

Rearranging gives a quadratic equation:

$$[OH^-]^2 - C[OH^-] - Kw = 0$$

Approximations

1. If $C > 10^{-65}$ M (Moderate or High Concentration):

The self-ionization of water (Kw) is negligible, leading to:

$[OH^-] \approx C$

Substituting into the pOH calculation:

$$pOH = -log\,[OH^-] = -log\,C$$

Using the relationship between pH and pOH:

$$pH = 14 - pOH$$

Therefore:

$$pH = 14 + log\,C$$

2. If C < 10^{-65} M (Very Low Concentration):

The contribution of water’s self-ionization cannot be ignored. You must solve the quadratic equation:

$$[OH^-]^2 - C[OH^-] - Kw = 0$$

Solve using the quadratic formula:

$$[OH^-] = (-b \pm \surd(b^2 - 4ac))\;/\;2a$$

where:

$$a = 1, b = -C, c = -Kw$$

$$[OH^-] = \frac{C + \sqrt{C^2 + 4K_w}}{2}$$

$$pH = 14 - pOH \text{ , pH= 14+log} \left(\frac{C+\sqrt{C^2+4K_w}}{2}\right)$$

Interpretation of Results

1. High Base Concentration (C > 10^{-65}):
The solution is strongly basic, and the pH is dominated by the base concentration.

2. Low Base Concentration (C < 10^{-65}):
The contributions of both the base and water self-ionization must be considered, and a more detailed calculation is needed.

V.6.4 Case of a Weak Base

Let's explore the behavior of weak bases in water in a structured way, maintaining clarity and essential details.

Chemical Reactions

1. Weak Base Ionization:
$B + H_2O \rightleftharpoons BH^+ + OH^-$

2. Water Self-Ionization:
$2H_2O \rightleftharpoons H_3O^+ + OH^-$ (negligible contribution in basic solutions).

Chemical Species in Solution

- Weak base molecules (B)
- Conjugate acid (BH^+)
- Water (H_2O)
- Hydroxide ions (OH^-)

Relationships Between Concentrations

1. Ion Product Constant for Water:
$Kw = [H_3O^+][OH^-]$

2. Base Dissociation Constant:
$Kb = [OH^-][BH^+] / [B]$

3. Mass Conservation:
$C = [B] + [BH^+]$ (where C is the initial concentration of the weak base).

4. Electrical Neutrality:

$$[OH^-] = [BH^+]$$

Approximations for Simplification

1. Approximation 1:

If the base is weakly ionized, the concentration of the conjugate acid is much smaller than the concentration of the un-ionized base:

$$[BH^+] \ll [B].$$

This is valid if:

$Kb / C \leq 10^{-2}$

2. Approximation 2:

If the base is highly dissociated, the concentration of $[BH^+]$ cannot be neglected compared to [B]:

$$[B] = C - [OH^-]$$

Simplified Calculations

1. Using Approximation 1 (Weakly Ionized Base)

$$[BH^+] \approx [OH^-]$$

$$[B] \approx C$$

Substituting these into the base dissociation constant equation:

$$Kb = [OH^-]^2 / C$$

$$[OH^-] = \sqrt{(Kb \times C)}$$

$$pOH = ½(pKb - \log C)$$

2. When Approximation 2 is Not Valid (Highly Dissociated Base)

$$[\mathrm{BH}^+] \approx [\mathrm{OH}^-]$$

$$[\mathrm{B}] = \mathrm{C} - [\mathrm{OH}^-]$$

Substituting into the base dissociation constant:

$$\mathrm{Kb} = \frac{[\mathrm{OH}^-]^2}{\mathrm{C} - [\mathrm{OH}^-]}$$

Rearranging:

$$[\mathrm{OH^-}]^2 + \mathrm{Kb}[\mathrm{OH^-}] - \mathrm{KbC} = 0$$

This quadratic equation can be solved for [OH⁻].

$$[OH-] = \left(\frac{-K_b + \sqrt{(K_b{}^2 + 4K_bC)}}{2}\right)$$

$$pOH = -log\left(\frac{-K_b + \sqrt{(K_b{}^2 + 4K_bC)}}{2}\right)$$

$$\boldsymbol{pH = 14 + log}\left(\frac{-K_b + \sqrt{(K_b{}^2 + 4K_bC)}}{2}\right)$$

Interpretation of Results

1. Weak Bases with Small Kb:

Approximations simplify the calculations significantly, especially for weak bases in dilute solutions.

2. Stronger Weak Bases or Higher Concentrations:

The full quadratic solution is required to accurately determine the hydroxide ion concentration.

1. pH of a Polyacid Solution

Dissociation of a Diacid (H_2A):

A diacid dissociates in water according to two equilibria:

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$$

$$HA^- + H_2O \rightleftharpoons A^{-2} + H_3O^+$$

Dependence on Dissociation Constants (Ka):

- **Strong Acids or Bases:** The pH is similar to that of a strong monoprotic acid or base at the same concentration.
- **Weak Acids or Bases:**
    - If the acid dissociation steps are distant (e.g., ΔpKa ≥ 4), the pH resembles that of a single strong monoprotic acid, neglecting subsequent steps.

- If the acid dissociation steps are close ($\Delta pKa \leq 4$), the pH is influenced by the mixture of acids or bases.

2. pH of Ampholytic Solutions

An ampholyte is a substance that can act as both an acid and a base. Examples include:

- **Anions of polyacids:** HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}
- **Metallic hydroxides:** $Zn(OH)_2$, $Al(OH)_3$
- **Organic molecules:** COOH, SO_3H, phenols, amines, α-amino acids

Calculation Formula:

For an ampholyte solution:

$$pH = \frac{1}{2}(pKa_1 + pKa_2)$$

3. Mixture of a Strong Acid and a Weak Acid

Definitions:

- **HA_1:** Strong acid, concentration C_1, volume V_1
- **HA_2:** Weak acid, concentration C_2, volume V_2
- Acid dissociation constant (Ka) for HA_2

After Mixing:

Account for dilution effects:

$$C_1' = (C_1 \times V_1) / (V_1 + V_2)$$

$$C_2' = (C_2 \times V_2) / (V_1 + V_2)$$

Scenarios:

1. **If $C_1' \gg C_2'$:** The strong acid dominates:

$$HA_1 + H_2O \rightarrow A^- + H_3O^+$$

$$pH = -\log(C_1')$$

2. **If $C_1' \ll C_2'$:** Both acids contribute:

$$HA_1 + H_2O \rightarrow A_1^- + H_3O^+$$

$$HA_2 + H_2O \rightleftharpoons A_2^- + H_3O^+$$

Use:

$$Ka = [H_3O^+][A_2^-] / [HA_2]$$

And:

- **Electroneutrality:** $[H_3O^+] = [A_1^-] + [A_2^-]$
- **Mass conservation:** $C_1' = [A_1^-]$

If HA_2 is weakly dissociated:

$$[A_2^-] = \frac{Ka \times C_2'}{[H_3O^+]}$$

Result: $[H_3O^+] = \frac{C_1' + \sqrt{C_1'^2 + 4KaC_2'}}{2}$

4. Mixture of Two Weak Acids

Definitions:

HA_1: Weak acid, concentration C_1, volume V_1, dissociation constant Ka_1

HA_2: Weak acid, concentration C_2, volume V_2, dissociation constant Ka_2

Cases:

1. **If $pKa_2 - pKa_1 \geq 4$:** HA_1 dominates:

$HA_1 + H_2O \rightleftharpoons A_1^- + H_3O^+$

After dilution: $C_1' = \frac{(C_1 \times V_1)}{(V_1 + V_2)}$

$$pH = ½(pKa_1 - \log C_1') \text{ if } Ka_1C_1' \leq 10^{-2}$$

Or solve: $pH = -\log(\frac{(-Ka_1 + \sqrt{(Ka_1^2 + 4Ka_1C_1')}}{2})$

2. **If $pKa_2 - pKa_1 < 4$:**

Both acids contribute

$HA_1 + H_2O \rightleftharpoons A_1^- + H_3O^+$

$HA_2 + H_2O \rightleftharpoons A_2^- + H_3O^+$

After mixing:

$C_1' = (C_1 \times V_1) / (V_1 + V_2)$

$C_2' = (C_2 \times V_2) / (V_1 + V_2)$

Relationships:

$Ka_1 = [H_3O^+][A_1^-] / [HA_1]$

$Ka_2 = [H_3O^+][A_2^-] / [HA_2]$

If both acids are weakly dissociated:

$[A_1^-] = Ka_1 \times C_1' / [H_3O^+]$

$[A_2^-] = Ka_2 \times C_2' / [H_3O^+]$

Electroneutrality:

$[H_3O^+] = [A_1^-] + [A_2^-]$

Result: $[H_3O^+]^2 = Ka_1C_1' + Ka_2C_2'$

$$pH = -\frac{1}{2}(Ka_1C_1' + Ka_2C_2')$$

V.7.Buffer Solutions

V.7.1 Definition of a Buffer Solution.

A buffer solution is a solution composed of an "equimolecular" mixture of a weak acid HA and its conjugate base A-.

V.7.2 Properties of Buffer Solutions.

A buffer solution is characterized by a constant pH.

It allows for the maintenance of a specific pH in a reaction medium.

V.7.3 Preparation of Buffer Solutions.

- By mixing solutions with similar concentrations of a weak acid (e.g., CH_3COOH) and a salt of its conjugate base (e.g., CH_3COONa).

- By mixing solutions with similar concentrations of a weak base (e.g., NH_3) and a salt of its conjugate acid (e.g., NH_4Cl).

V.7.4 Calculation of the pH of a Buffer Solution.

The species HA and A^- is in equilibrium:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$Ka = [H_3O^+][A^-]/[HA]$$

$$So, \qquad [H_3O^+] = \frac{Ka[HA]}{[A-]}$$

$$pH = pKa + log(\frac{[A-]}{[HA]})$$

$$pH = pKa + log([Base]/[Acid])$$

$$If\ [HA] = [A-], then\ pH = pKa$$

VI.1 Classical concepts of oxidation reduction

Oxidant: An oxidant is a chemical substance with the ability to capture electrons from another substance during a chemical reaction. Oxidants are often chemical species that are themselves reduced during the reaction because they gain electrons.

Reductant: A reductant is a chemical substance with the ability to donate electrons to another substance during a chemical reaction. Reductants are often chemical species that are oxidized them during the reaction because they lose electrons.

Oxidation: Oxidation is the process by which a substance loses electrons. This generally leads to an increase in the oxidation number of the atom or ion. In your example, Cu (copper) undergoes oxidation by changing from Cu to Cu^{2+} and losing two electrons.

Reduction: Reduction is the process by which a substance gains electrons. This generally leads to a reduction in the oxidation number of the atom or ion. In your example, Cu^{2+} undergoes reduction by changing from Cu^{2+} to Cu and gaining two electrons.

Redox Couple (Oxidation-Reduction Couple): A redox couple is composed of two chemical species, one being the oxidant and the other the reductant, involved in an oxidation-reduction reaction. The redox couple is characterized by the transfer of electrons between the two species. For example, $Cu^{2+/}$Cu represent a redox couple for copper, where Cu^{2+} is the oxidized form, and Cu is the reduced form.

$$Cu^{+2} + 2e^{-} \leftrightarrow Cu$$

RULES FOR ASSIGNING OXIDATION NUMBERS

These rules govern the assignment of oxidation numbers in chemical compounds:

1. Elemental form: The oxidation number of an element in its elemental form is always 0 (zero).

2. Simple ions: The oxidation number of a simple ion is equal to the charge on the ion. The sign (+ or -) and magnitude of the charge are both part of the oxidation number. For example, an ion might have an oxidation number of +2 or -2.

3. Group 1A and 2A elements: The oxidation numbers of Group 1A and 2A elements are +1 and +2, respectively.

4. Hydrogen: In compounds, the oxidation number of hydrogen is typically +1. However, an exception occurs when hydrogen combines with metals; in such cases, the oxidation number of hydrogen is usually -1.

5. Oxygen: In compounds, the oxidation number of oxygen is typically -2. Peroxides are exceptions where the oxidation number of oxygen is -1. For instance, hydrogen peroxide (H_2O_2) showcases this exception where each oxygen atom has an oxidation number of -1.

6. Fluorine: In compounds, the oxidation number of fluorine is always -1. Other halogens (Cl, Br, I) also typically have an oxidation number of -1, except when combined with oxygen. When combined with oxygen, the oxidation number of halides (except for fluorine) is typically positive.

7. Complex ions: For a complex ion, the sum of the positive and negative oxidation numbers of all elements in the ion equals the charge on the ion.

8. Electrically neutral compounds: For an electrically neutral compound, the sum of the positive and negative oxidation numbers of all elements in the compound equals zero.

VI.2 Balancing Redox Equation

Every chemical reaction must be balanced according to the "Law of conservation of mass". The chemical equations which involve oxidation and reduction can also be balanced with the help of the following methods

- Oxidation number method.
- Ion electron method (or half reaction method)

Oxidation number method:

The various steps involved in balancing a redox equation by oxidation method are discussed here through an example.

- ***Example:*** Balance the chemical equation by the oxidation number method

$$CuO + NH_3 \rightarrow Cu + N_2 + H_2O$$

Solution:

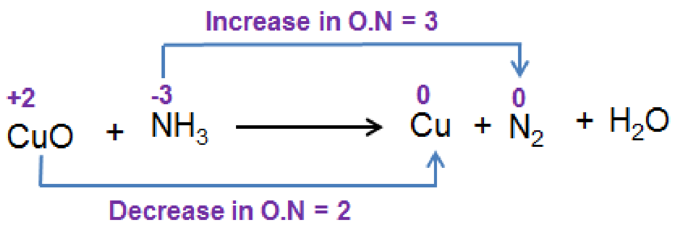
Step-1: Write the oxidation number of each atom in the skeleton equation

$$\overset{+2}{Cu}\,\overset{-2}{O} + \overset{-3}{N}\,\overset{+1}{H_3} \longrightarrow \overset{0}{Cu} + \overset{0}{N_2} + \overset{+1}{H_2}\overset{-2}{O}$$

Step-2: Identify the atoms which undergo change in oxidation number.

$$\overset{+2}{CuO} + \overset{-3}{NH_3} \longrightarrow \overset{0}{Cu} + \overset{0}{N_2} + H_2O$$

Step-3 : Calculate the increase and decrease in oxidation number w.r.t reactant atoms.



Step-4 : Equate the increase and decrease in oxidation number on the reactant side.

$$3CuO + 2NH_3 \longrightarrow Cu + N_2 + H_2O$$

Step-5 : Balance the number of Cu and N atoms on both sides of the equation.

$$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + H_2O$$

Step-6 : Now balance H and O atoms by hit and trial method.

$$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$$

Note:

(i) In the reactions taking place in acidic medium, balance the O atom by adding the required number of H_2O molecules to the side deficient in O atoms. Then balance the H atoms by adding H^+ to the side deficient in H atoms.

(ii) In the basic medium, first balance the number of negative charges by adding the required number of OH^- ions to the side deficient in the magnitude of the charges. Then add H_2O molecules on the other side in order to balance the OH^- ions added.

Ion electron method (or half reaction method):

It is based on the principle that the electrons lost during oxidation half reaction in a particular redox reaction is equal to the electrons gained in the reduction half reaction. The method is called half reaction method. The balancing is completed in the following steps:

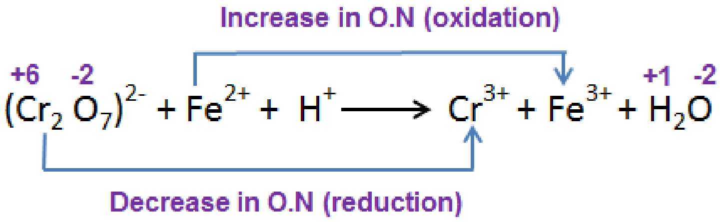
- **Example:** Balance the chemical equation by ion-electron method:

$$\boldsymbol{Cr2O72-\ \ +\ Fe2+\ \ +\ \ H+\ \ \rightarrow\ \ Cr3+\ \ +\ Fe3+\ \ +\ H2O}$$

Step-1: Write the oxidation number of each atom in the skeleton equation:

$$(\overset{+6}{Cr_2}\ \overset{-2}{O_7})^{2-} + Fe^{2+} + H^{+} \longrightarrow Cr^{3+} + Fe^{3+} + \overset{+1}{H_2}\overset{-2}{O}$$

Step-2: Find out the species involved in the oxidation and reduction half reactions:



Step-3: Balancing oxidation half reaction:

As oxidation number increases 1, add one e^- on the product side to balance change in O.N.

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

Step-4: Balancing reduction half reaction:

The decrease in oxidation number per Cr atom is 3 and the total decrease in O.N for two Cr atoms is 6. Therefore, add 6e⁻ on the reactant side. In order to balance O atoms add 7 H_2O molecules on the product side then balance H atoms by adding 14 H^+ on reactant side.

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Step-5 : Adding the two half reactions:

$$\begin{array}{c}
[\,Fe^{2+} \longrightarrow Fe^{3+} + e\,] \times 6 \\
Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \\
\hline
Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O
\end{array}$$

VI.3 Redox Potentials: NERNST EQUATION

VI.3.1 Standard Potential

The oxidizing or reducing power of a chemical species is characterized by its redox potential, denoted as E°.

E° is measured under standard conditions of temperature and pressure (P = 1 atm, T = 25°C). It is written as E° (Ox/Red). By convention: E° (H+/H2) = 0 V. All E° values are then referenced with respect to E° (H+/H2).

VI.3.2 Nernst Equation

The oxidizing or reducing power of a species depends not only on E° (standard potential) but also on the concentrations in solution.

$$a\ Ox + ne^- \leftrightarrow b\ red$$

$$E_{ox/red} = E^{\circ}_{ox/red} + \frac{RT}{nF} \ln \frac{[ox]^a}{[red]^b}$$ Equation of Nernst

$$E_{\frac{ox}{red}} = E^{\circ}_{\frac{ox}{red}} + \frac{0.06}{n} \log \frac{[ox]^a}{[red]^b}$$

n is the number of electrons involved in the reaction.

- R is the ideal gas constant.

- T is the temperature in Kelvin.

- F is the Faraday constant.

$$Fe^{3+}/Fe^{2+}$$

$$Fe^{3+} + 1\ e- \leftrightarrows Fe^{2+}$$

$$E_{Fe^{3+}/Fe^{2+}} = E°_{Fe^{3+}/Fe^{2+}} + 0{,}06\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$I_2/I^-$$

$$I_2 + 2e \leftrightarrows 2I^-$$

$$E_{I_2/I^-} = E°_{I_2/I^-} + 0{,}03\log(\frac{[I_2]}{[I^-]^2})$$

$$MnO_4^-/Mn^{2+}$$

$$MnO_4^- + 8H^+ + 5e- \leftrightarrows Mn^{2+} + 4H_2O$$

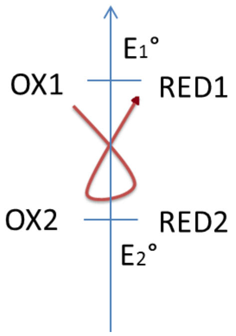
$$E_{MnO_4^-/Mn^{2+}} = E°_{MnO_4^-/Mn^{2+}} + \frac{0{,}06}{5}\log(\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]})$$

VI.4 Redox reaction

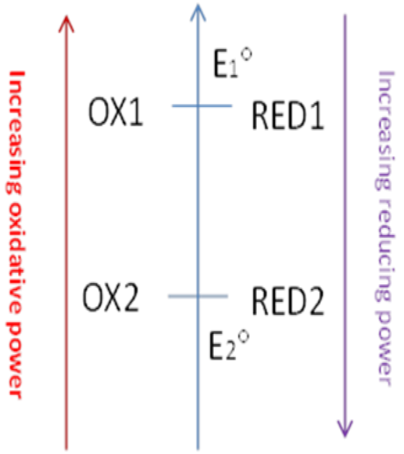
VI.4.1 Definition:

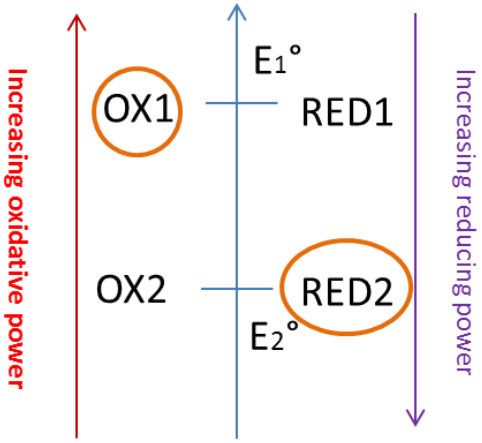
A redox reaction is a reaction involving the exchange of electrons between an oxidant Ox1 (ox1/red1) and a reductant red2 (ox2/red2):

$$Ox1 + red2 \rightleftharpoons red1 + Ox2$$



For this reaction to proceed in the forward direction, it is necessary that E°(Ox1/Red1) > E°(Ox2/Red2) (a thermodynamic condition). In other words, such a reaction evolves in a direction that transforms the strongest oxidant and reductant into the weakest oxidant and reductant.





1. Position the two couples on a potential scale
2. Circle the strongest oxidant and strongest reductant that correspond to the reaction reactants.
3. Identify the products of the reaction.

VI.4.2 Writing Redox Reactions

The rules for balancing redox reactions are based on:

1. Conservation of electrons.

2. Conservation of atoms.

3. Electrical neutrality of solutions.

- **Example:**

1. Consider the redox couples: E°(Fe3+/Fe2+) = 0.77 V/ENH and E°(MnO4-/Mn2+) = 1.51 V/ENH.

Since E°(MnO4-/Mn2+) > E°(Fe3+/Fe2+), the possible half-reactions from a thermodynamic perspective are:

Oxidation: $Fe^{2+} \rightleftharpoons Fe^{3+} + 1\ e^-$ (multiplied by 5)

Reduction: MnO4- + $8H^+ + 5e^- \rightleftharpoons$ Mn2+ + 4H2O

The overall reaction is: $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

2. E°(Fe3+/Fe2+) = 0.77 V/ENH and E°(Sn4+/Sn2+) = 0.15 V/ENH.

Since E°(Fe3+/Fe2+) = 0.77 V/ENH > E°(Sn4+/Sn2+) = 0.15 V/ENH, the possible half-reactions are:

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ (multiplied by 2, reduction)

$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$ (oxidation)

The overall reaction is: $2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}$

VI.4.3 The Nernst equation for a redox system

is used to calculate the potential of a redox couple in a chemical reaction. It's expressed as:

$$E = E^{\circ} + \frac{0.06}{n}\log\frac{[Ox_1]^a[Red_2]^b}{[Red_1]^c[Ox_2]^d}$$

Here's what each symbol represents:

- E: potential of the redox system

- E°: standard potential of the redox couple

- [cRed1], [dOx2], [aOx1], [bRed2]: activities (or concentrations in dilute cases) of the corresponding chemical species in the redox reaction.

VI.5 Calculating the equilibrium constant (K_C):

After a while of a reversible reaction being underway, a state of equilibrium is reached, with the concentrations of reactants (A and B) and products (C and D) changing not much thereafter. These concentrations are called the **equilibrium concentrations**.

We can calculate the equilibrium concentration by finding the **equilibrium constant**, which is the ratio of the concentration of products to the concentration of reactants.

The **equilibrium constant, Kc** can be deduced for a reversible reaction by using the following expression:

$aA + bB \rightarrow cC + dD$

$$\mathrm{K_c} = \frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$$

The magnitude of Kc can be used to estimate the position of equilibrium in a reaction:

$\boldsymbol{K_C\,Value}$	**Position of equilibrium**
$K_C = 1$	Same concentration of reactants and products
$K_C > 1$	Position of equilibrium shifted to the left (more products)
$K_C < 1$	Position of equilibrium shifted to the right (more reactants)

- **Exemple** Consider the redox couples (Ce^{4+}/Ce^{3+}) and (Fe^{3+}/Fe^{2+}):

E°(Ce4+/Ce3+) = 1.44 V/ENH and E°($Fe^{3+/}Fe^{2+}$) = 0.77 V/ENH.

Since E°($Ce^{4+/}Ce^{3+}$) > E°($Fe^{3+/}Fe^{2+}$), the possible half-reactions from a thermodynamic perspective are:

Reduction half-reaction: $Ce^{4+} + e^{-} \rightleftharpoons Ce^{3+}$

Oxidation half-reaction: $Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-}$

The overall reaction is: $Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$

Now, to determine if the reaction is complete, calculate the equilibrium constant (Kc) at the end of the reaction:

Kc = $[Ce^{3+}][Fe^{3+}] / [Ce^{4+}][Fe^{2+}]$

Using the Nernst equations for the two redox couples:

E(Fe^{3+}/Fe^{2}+) = E°(Fe^{3+}/Fe^{2+}) + 0.06 log [Fe^{2}+]/[Fe3+]

E(Ce^{4+}/Ce^{3+}) = E°(Ce^{4+}/Ce^{3+}) + 0.06 log $[Ce^{4+}]/[Ce^{3+}]$

When the reaction is complete, ΔE = 0, so E(Ce^{4+}/Ce^{3+}) = E(Fe^{3+}/Fe^{2+}), which implies:

ΔE° = E(Ce^{4+}/Ce^{3+}) - E(Fe^{3+}/Fe^{2+}) = 0.06 log Kc

Kc = 10^(ΔE°/0.06) = 1.47 x 10^11

Since Kc is very large, the reaction is total in the forward direction (1).

VII. Solubility Equilibria

1. Solubility

« S » is the maximum concentration of solute (a substance that dissolves in a solvent) that can be dissolved in the solvent (dissolver).

When this normal quantity is reached, the solution is saturated, and when this quantity is exceeded, it is said that there is precipitation of the solute

This solubility can be expressed in mol/L or in mass units such as *g/L*

2. Different categories of a compound:

In particular, salts are soluble in solvents like water. However, the solubility of salts in water is extremely variable

-Soluble compounds

-Insoluble compounds

-Poorly soluble compounds

- **The solubility product:**

$[M_nX_m]$ can dissolve or form: $[M_nX_m] \leftrightarrow nM^{m+} + mX^{n-}$

Note:

- To the right: dissolution

- To the left: precipitation

When the equilibrium state is reached, a relationship links the concentrations of different species. This is expressed by the solubility constant:

$\mathbf{Ks = [M^{m+}]^{n} . [X^{n-}]^{m}}$

Note: **Ks** depends solely on temperature.

The expression is only applicable if the equilibrium exists; meaning if and only if there is solid present in the solution (even a grain...). We define:

$$pK_S = -logK_S \qquad K_S = 10^{-pK_S}$$

Ks represents the value corresponding to the saturated solution; thus, it is the maximum ionic product compatible with the absence of precipitation. For this reason, it's termed the solubility product.

The larger the pK_s the more insoluble the salt

If: $[M^{m+}]^n * [X^{n-}]^m < Ks$ ⟶ the compound remains dissolved

If: $[M^{m+}]^n * [X^{n-}]^m > Ks$ ⟶ solid precipitation occurs

If: $[M^{m+}]^n * [X^{n-}] m = Ks$ ⟶ The solution is saturated

- **Relationship between solubility and solubility product:**

For a salt A_XB_Y, the equilibrium of dissolution in water is expressed as:

$$A_XB_y(s) \Leftrightarrow x\,A^{y+}(aq) + yB^{x-}(aq)$$

$$s = \left[A_XB_y)\right]_{dissou}$$

The solubility of this salt is:

And we can write:

$$A_XB_y(s) \Leftrightarrow A_XB_y(dissous) \Leftrightarrow x\,A^{y+}(aq) + yB^{x-}(aq)$$

EI	0	0	0
Eq	s	x.s	y.s

$$\left[A^{y+}\right] = x.s \quad \text{et} \quad \left[B^{x-}\right] = y.s$$

$$K_S = \left[A^{y+}\right]^x . \left[B^{x-}\right]^y$$

And can write KS:

$$K_S = (x.s)^X . (y.s)^Y$$

$$K_s = x^X . y^Y . S^{(x+y)} \qquad S = \sqrt[(x+y)]{\frac{K_S}{x^X . y^Y}}$$

Examples

a) Let us study the solubility of silver chloride AgCl ($Ks = 2.\ 10^{-10}$) and silver chromate Ag2CrO4 ($K's = 10^{-12}$)

- Consider the dissolution of silver chloride AgCl in pure water according to the equation reaction:

$AgCl\ (s) = Ag^{+}(aq) + Cl^{-}\ (aq)$

When the solution is saturated (see Progress table below):

$$[Ag^{+}] = s \text{ and } [Cl^{-}] = s$$

hence: $Ks = [Ag+].[Cl-] = s2 = 2.10-10$

$$or: s = Ks = 1.4.10-5\ mole.L-1$$

For the dissolution of silver chromate Ag2CrO4 in pure water according to the reaction

equation: $Ag_2CrO_4\ (s) \leftrightarrow 2Ag^{+}\ (aq) + CrO_4^{2-}\ (aq)$

At saturation (see progress table below): $[Ag^{+}] = 2\ s'$ and $[CrO_4{}^{2-}] = s'$

hence: $Ks' = [Ag+]^{2}. [CrO_4^{2-}] = 4s'^{3} = 10^{-12}$

or: $s' = \frac{\sqrt[3]{Ks}}{4} = 6.3.\ 10^{-5}$ mole. L^{-1}

We note that $s(AgCl) < s(Ag2CrO4)$ *while* $Ks(AgCl) > Ks(Ag2CrO4)$.

b) Mix 10 mL of sodium sulfate solution and 10 mL of silver nitrate solution,
   both at the concentration $c = 8.10^{-2}$ mol. L^{-1}.
   Is a precipitate of silver sulfate observed?
   Data: $Ks\ (Ag_2SO_4) = 1.5.10^{-5}$.
   Corrected:
   The concentrations provided or introduced of the silver (I) and sulfate ions, taking into account the dilution, but before any possible reaction, are worth:

$$[Ag^{+}] = [SO_4^{2-}] = cv/20 = 4.10-2\ mol.L^{-1}$$

If there is precipitation, the system is the seat of balance:

$$Ag_2SO_4\ (s) \leftrightarrow 2\ Ag^{+}\ (aq) + SO_4^{2-}\ (aq)$$

of constant $Ks = 1.5.\ 10^{-5}$.

The reaction quotient Qa when mixing the two solutions is:

Qa = $[Ag^{+}]^2 . [SO_4^{2-}]$

= $(4.10^{-2})^2 . (4.10^{-2}) = 6.4 . 10^{-5}$

During mixing, Qa > Ks: silver sulfate precipitates. The quantity of precipitate formed is such that at the end of precipitation, the new equilibrium reaction quotient, Qeq, is equal to Ks.

3. Influence of the environment on solubility

4. Influence common ion

If a salt A_XB_Y is dissolved in a solvent already containing a common ion B^{X-} from another soluble salt C_XB_Z, the solubility product of the salt A_XB_Y, which is a constant, is written as:$\boldsymbol{[A^{y+}]^x \ [B^{x-}]^y = Ks}$

In this case, **$[B^{x-}] > y.s$** where ***s*** is the solubility of A_XB_Y before the introduction of the common ion. Indeed, the ions B^{X-} come partly from the solute A_XB_Y and partly from the other soluble salt C_XB_Z.

The dissolution of A_XB_Y is then altered. Let's call it **s'** here the ions B^{x-} from C_XB_E are at the concentration C and can be written as:

$$[A^{y+}] = [A^{y+}]_{A_xB_y} = x.s'$$

$[A^{y+}]_{A_xB_y}$This means the concentration of $[A^{y+}]$from A_XB_Y.

$$\left[B^{x-}\right] = \left[B^{x-}\right]_{A_XB_y} + \left[B^{x-}\right]_{C_XB_z} = yS' + c$$

Therefore, the expression for the solubility product is: $K_s = (x.s')^x . (y.s' + c)^y$

ConsideringA_XB_Y as a sparingly soluble salt, we can neglect the quantity ***y.s'*** compared to C, since C_XB_Z is a soluble salt.

$$K_S = (x^x . s')^x . c^y$$

$$s' = \sqrt[x]{\frac{K_s}{x^x . c^y}}$$

Note:

- The presence of common ions results in a decrease in the solubility of the sparingly soluble salt.

- The introduction of common ions causes a shift in the solubility equilibrium towards reducing the common ions, thus favoring precipitation (Le Chatelier's principle).

$$A_X B_Y(s) \underset{1}{\overset{2}{\Leftrightarrow}} xA^{y+}(aq) + yB^{x-}(aq)$$

(Equilibrium shifted in direction 2)

This is referred to as a decrease in solubility due to the common ion effect.

Exemple: Calculate the solubility s and s' of silver chloride AgCl respectively in pure water and in a solution already containing chloride ions Cl^- the concentration c = 10^{-1} mol. L-1

. Data at 25°C: KS(AgCl) = $10^{-9.8}$

. Solubility of AgCl

To calculate the solubility (s) of AgCl in pure water and in a solution already containing chloride ions (Cl^-) at a concentration of c = 10^{-1} mol/L, we use the solubility product constant (K_s) at 25°C: K_s(AgCl) = $10^{-9}.{}^{8}$.

Solubility in Pure Water (s):

The dissociation of AgCl in pure water is: AgCl(s) ⇌ $Ag^+ + Cl^-$.
Let the solubility of AgCl in water be s. Since $[Ag^+] = [Cl^-] = s$, we have:
$K_s = [Ag^+]\,[Cl^-] = s^2$.
Thus, s = √K = √($10^{-9.8}$) = $10^{-4}.{}^{9}$ mol/L.

Solubility in Solution Containing Cl^- (s'):

In a solution already containing Cl^-, let $[Cl^-]$ = c = 10^{-1} mol/L. The dissociation of AgCl is:
AgCl(s) ⇌ $Ag^+ + Cl^-$.

Here, $[Ag^+] = s'$ and $[Cl^-] \approx c$ (since $s' \ll c$). Therefore:
$Ks = [Ag^+][Cl^-] \approx s' \cdot c$.
Solving for s': $s' = Ks / c = 10^{-9.8} / 10^{-1} = 10^{-8.8}$ mol/L.

Final Results:

- Solubility in pure water: $s = 10^{-4.9}$ mol/L.

- Solubility in solution with $[Cl^-] = 10^{-1}$ mol/L: $s' = 10^{-8.8}$ mol/L.

- **Influence of pH:**

The solubility of a solid depends on the pH in the case where the ions which come from the dissolution of this solid have significant acid-basic properties. This is generally the case where the anions are hydroxyl groups (OH^-) or conjugate bases (A-) of weak acids (HA).

Example

Calculate the solubility s, and the pH of a saturated solution of Mg(OH)2. $Ks(Mg(OH)_2,s)=1.2.10^{-11}$

Solubility of $Mg(OH)_2$

To calculate the solubility (s) and the pH of a saturated solution of Mg $(OH)_2$, we use its solubility product constant (Ks): $Ks(Mg(OH)_2) = 1.2 \times 10^{-11}$.

Solubility (s):

The dissociation of Mg $(OH)_2$ in water is: $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$.
Let the solubility of $Mg(OH)_2$ be s. Then, $[Mg^{2+}] = s$ and $[OH^-] = 2s$.
$K_s = [Mg^{2+}][OH^-]^2 = s \cdot (2s)^2 = 4s^3$.
Solving for s: $s = \sqrt[3]{(K_s / 4)} = \sqrt[3]{(1.2 \times 10^{-11} / 4)} = 1.44 \times 10^{-4}$ mol/L.

$[OH^-]$ and pH:

From the dissociation, $[OH^-] = 2s = 2 \times 1.44 \times 10^{-4} = 2.88 \times 10^{-4}$ mol/L.
The pOH is calculated as: $pOH = -\log [OH^-] = -\log (2.88 \times 10^{-4}) \approx 3.54$.
The pH is: $pH = 14 - pOH = 14 - 3.54 = 10.46$.

Final Results:

- Solubility: $s = 1.44 \times 10^{-4}$ mol/L.

- pH of the saturated solution: pH = 10.46.

At constant temperature, Ks= Cte.

• When $[OH^-]$ increases (pH increases), $[Mg^{2+}]$ decreases and **s** also decreases.

• When the pH decreases ($[OH^-]$ decreases), $[Mg^{2+}]$ increases and also **s** increases.

Exercices of Acid- Base

Exercise 1 :

1. Give the conjugate acid of each base: NH_3, HSO_4^-, $C_2O_4^{2-}$

2. Provide the conjugate base of each acid: HNO_2, $CH_2ClCOOH$, H_3PO4, $H_2PO_4^-$

3. State the equations for the reactions of acids with the base H_2O: HI, HNO_3, HF.

4. State the equations for the reactions of bases with the acid H2O: HS^-, PH_2^-, F^-.

Exercise 2:

1. What particles are present in an aqueous solution of sulfuric acid H_2SO_4?

2. What is the pH of a solution in which $C_{OH-} = 0.01$ mol/L?

3. A certain vinegar has a pH of 2.8. What are the values of C_{H3O+} and C_{OH-}

Exercise 3:

What are the concentrations (initial, before dissociation or reaction) c_0

1. of acetic acid (CH_3COOH) in a mixture of 50 ml of 1 M acetic acid with 150 ml of water?
2. of ammonia (NH_4^+) in a mixture of 50 ml of 0.100 M ammonia with 150 ml of 0.200 M ammonia?

3. of 2-chloro-2-methylpropanoic acid ($CH_3CCl(CH_3)COOH$) in a mixture of 10.0 ml at 0.123 g/l with 5 ml of 0.0030 M of the same acid.

Exercise 4

Calculate the pH of an aqueous solution of hydrofluoric acid with a concentration of:

.C1 = 10^{-1} M

.C2 = 10^{-3} M.

Given at 25°C, pKa(HF/F-) = 3.18, pKe = 14.

Exercise 05:

1. Calculate the pH of a decimolar solution of nitric acid at 25°C.
2. Calculate the pH of a solution of nitric acid with a concentration of 10^{-8} M at 25°C.

Exercise 06:

Calculate the pH of the following solutions:

1. Hydrochloric acid HCl with a concentration of 10^{-2} M.
2. 10 mL of 10^{-5} M HCl + 990 mL of water.
3. Sodium hydroxide NaOH with a concentration of 10^{-2} M.
4. Ammonium chloride NH4Cl with a concentration of 0.2 M, pKa(NH4+/NH3) = 9.25.
5. Sodium formate HCOONa with a concentration of 0.1 M, pKa = 3.8.
6. Sodium bicarbonate NaHCO3 with a concentration of 0.2 M, (H2CO3: pKa2 = 6.4, pKa1 = 10.3

Solutions

Exercise 1:

Conjugate Acids, Bases, and Reactions

1. Conjugate Acids of the Bases

- NH_3: Conjugate acid: NH_4^+

- HSO_4^-: Conjugate acid: H_2SO_4
- $C_2O_4^{2-}$: Conjugate acid: $HC_2O_4^-$

2. Conjugate Bases of the Acids

- HNO_2: Conjugate base: NO_2^-
- $CH_2ClCOOH$: Conjugate base: CH_2ClCOO^-
- H_3PO_4: Conjugate base: $H_2PO_4^-$
- $H_2PO_4^-$: Conjugate base: HPO_4^{2-}

3. Reactions of Acids with Water

HI: $HI + H_2O \rightarrow H_3O^+ + I^-$

HNO_3: $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

HF: $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

4. Reactions of Bases with Water

HS^-: $HS^- + H_2O \rightleftharpoons H_2S + OH^-$

PH_2^-: $PH_2^- + H_2O \rightleftharpoons PH_3 + OH^-$

F^-: $F^- + H_2O \rightleftharpoons HF + OH^-$

Exercise 2:

Acidic and Basic Solutions

1. Particles in Aqueous Sulfuric Acid: H_3O^+, HSO_4^-, SO_4^{2-}

2. pH Calculation for $[OH^-] = 0.01$ M: pOH = 2, pH = 12

3. Vinegar pH = 2.8:

$[H_3O^+] \approx 1.58 \times 10^{-3}$ M, $[OH^-] \approx 6.31 \times 10^{-12}$ M

Exercise 3:

Initial Concentrations

1. Acetic Acid: $c_0 = 0.25$ M

2. Ammonia: $c_0 = 0.175$ M

3. 2-Chloro-2-Methylpropanoic Acid:

Solution 1: $c_0 \approx 0.082$ g/L

Solution 2: $c_0 = 0.001$ M

Exercise 4:

Hydrofluoric Acid (HF)

Dissociation: $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

Charge Conservation: $[H_3O^+] = [F^-]$

Mass Conservation: C_HF = [HF] + $[F^-]$

Ka Equation: $Ka = [H_3O^+][F^-] / [HF]$

For C_HF = 0.1 M: pH ≈ 2.09

For C_HF = 0.001 M: pH ≈ 3.09

Exercise 5:

Nitric Acid (HNO_3)

Dissociation: $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

Charge Conservation: $[H_3O^+] = [NO_3^-]$

Mass Conservation: C_HNO_3 = $[NO_3^-]$

For C = 0.1 M: pH = 1

For C = 10^{-8} M: pH ≈ 7 (Water Autoionization Dominates)

Exercise 6:

Hydrochloric Acid (HCl)

Dissociation: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

Charge Conservation: $[H_3O^+] = [Cl^-]$

Mass Conservation: C_HCl = $[Cl^-]$

For C = 0.01 M: pH = 2

For C = 10^{-5} M diluted: pH ≈ 6.7

Exercise 6:

Sodium Hydroxide (NaOH)

Dissociation: $NaOH \rightarrow Na^+ + OH^-$

Charge Conservation: $[Na^+] = [OH^-]$

Mass Conservation: C_NaOH = $[OH^-]$

For C = 0.01 M: pH = 12

Additional Details for Exercise 4

For Hydrofluoric Acid (HF):

Case 1: For initial concentration C_HF = 0.1 M:

Using Ka = 10^(-3.18), the dissociation equilibrium gives pH ≈ 2.09.

Case 2: For initial concentration C_HF = 0.001 M:

The calculation shows that the pH ≈ 3.09 due to reduced initial acid concentration.

Additional Details for Exercise 5

Nitric Acid (HNO3) Dissociation:

For C = 10^(-8) M: The autoionization of water contributes significantly. Total [H3O+] = 10^-7 + 10^-8 ≈ 10^-7. Thus, pH ≈ 7.

For C = 0.1 M: Being a strong acid, HNO3 fully dissociates, giving pH = 1.

Additional Details for Exercise 6

Hydrochloric Acid (HCl)

Case 1: For C = 0.01 M:

pH = -log(0.01) = 2, as HCl fully dissociates in water.

Case 2: For diluted C = 10^(-5) M HCl in 990 mL of water:

Adding water reduces the concentration to ~10^-7 M. Combining with water ionization, total [H3O+] ≈ 2 x 10^-7 M, giving pH ≈ 6.7.

Sodium Hydroxide (NaOH)

Case 1: For C = 0.01 M:

pOH = -log(0.01) = 2. pH = 14 - 2 = 12, since NaOH is a strong base and fully dissociates.

Additional Calculations for Buffer Solutions

Exercise 6 also includes calculations for buffering effects with compounds like NH4Cl and NaHCO3. For example:

1. Ammonium chloride (NH4Cl) with pKa = 9.25 and 0.2 M concentration: pH ≈ 5.
2. Sodium bicarbonate (NaHCO3) with pKa = 6.4 at 0.2 M concentration: pH ≈ 8.3.

Exercises of redox balance and solubility

Exercise 1:

Calculate the oxidation number of the element Sulfur in the following compounds: ; H_2SO_4 ; HS^- ; $S_2O_3^{2-}$; HSO_3^-

2. Arrange the following in order of decreasing oxidation number of the nitrogen atom**: N_2, NH_3, N_2O_4, N_2O, N_2H_4, and NO_3^-**

Exercise 2:

Balance the following equations using oxidation numbers and indicate: oxidation, reduction, oxidizing agent, and reducing agent.

. in acidic solution:

$As + NO_3- = As_2O_5 + NO$

$Cr_2O_7^{-2} + HNO_2 \rightarrow Cr^{+3} + NO_3^-$

$As+ClO3^- \rightarrow H3AsO3+HClO$

in basic solution:

$Al(s) + NO_3^- = Al(OH)_4^- + NH_3(g)$

$NO_3^- + Zn = NH_3 + ZnO_2^{2-}$

$N_2H_4 + ClO_3 \rightarrow NO+Cl^-$

Exercise 3:

For each of the following couples: $Zn^{2+/}Zn(s)$; $HgCl_2(s)/Hg(l)$; O2 (g)/H_2O_2; ClO^{-4} /Cl_2 (g):

1. Write electronic half-equations.

2. Deduce the corresponding Nernst relations.

Exercise 4:

write the half-equations, then calculate the potentials E, at 25°C, for the following systems:

1. Dihydrogen at a pressure p = 1 bar and an acidic solution at pH = 3.
   Couple H+ aq / H2. E o = 0,00 V

2. Iron plate immersed in a solution of iron (II) sulfate with concentrations Couple Fe2+/Fe. E o = – 0,44 V, c = 0.1 mol.L-1

Exercise 5:

A zinc rod is placed in a lead nitrate solution (0.1 mol.L^{-1}) at 25°C, and after some time, a dark deposit forms on the surface of the zinc. We aim to explain this phenomenon using a redox transformation.

1. What are the two redox couples involved in this transformation? Indicate the associated redox equilibria.

2. Provide the expression for the equilibrium potential associated with each couple.

4. Provide the overall balanced equation for the considered transformation and calculate its equilibrium constant. Conclude.

E° (Zn2+/ Zn) = -0.76 V   E° (Pb2+/ Pb) = 0. 13 V

Exercice 6:

What is the solubility of silver chromate Ag_2Cro4 in:

a) pure water.

b) a 0.1 mol/L potassium chromate K_2Cro4 solution.

K_S (Ag_2 Cro4) $=10^{-11.95}$

Exercise 7:

For what pH value is the formation of zinc hydroxide of formula $Zn(OH)_2(s)$ observed in a zinc nitrate $Zn(NO_3)_2$ solution of initial concentration $C = 10^{-3}$ $mol.L^{-1}$?

We place ourselves at pH = 4.

a) What is the concentration of hydroxide ions (OH-)in the solution?

b) Calculate the product $Q= [Zn^{2+}] [OH^{-}]^{2}$.

c) Compare this to the solubility product of zinc hydroxide. The condition of no precipitation is it respected?

pK s (Zn(OH) 2(s)) = 17 à 298 K

Solutions

Exercise 1

1. Calculate the oxidation number of Sulfur (S) in the following compounds:
a) H2SO4:
  - Hydrogen (H) has an oxidation number of +1.
  - Oxygen (O) has an oxidation number of -2.
  - The compound is neutral, so the total is 0.
  Equation: 2(+1) + S + 4(-2) = 0, S = +6.

b) HS-:

- Hydrogen (H): +1.
- Total charge: -1. Equation: +1 + S = -1, S = -2.

c) $S_2O_3^{2-}$:

- Oxygen (O): -2.
- Total charge: -2. Equation: 2(S) + 3(-2) = -2, S = +2.

d) HSO_3^-:

- Hydrogen (H): +1, Oxygen (O): -2.
- Total charge: -1. Equation: +1 + S + 3(-2) = -1, S = +4.

2. Arrange the following in decreasing oxidation number of nitrogen:

N_2: 0, NH_3: -3, N_2O_4: +4, N_2O: +1, N_2H_4: -2, NO_3^-: +5.

Order: $NO_3^- > N_2O_4 > N_2O > N_2 > N_2H_4 > NH_3$.

Exercise 2

a) In acidic solution: $As + NO_3^- \rightarrow As_2O_5 + NO$

- Oxidation: As (0) -> As (+5).
- Reduction: N (+5) -> N (+2).

Balanced Equation: $3As + 5NO_3^- + 20H^+ \rightarrow As_2O_5 + 5NO + 10H_2O$.

b) In basic solution: $Cr_2O_7^{2-} + HNO_2 \rightarrow Cr^{3+} + NO_3^-$

- Oxidation: N (+3) -> N (+5).
- Reduction: Cr (+6) -> Cr (+3).

Balanced Equation: $Cr_2O_7^{2-} + 3HNO_2 + 8H^+ \rightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$.

Exercise 3:

a) $Zn^{2+}/Zn(s)$:

1. Half-reaction: $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$

2. Nernst Equation:

$E = E° - (0.059/2) \log([Zn^{2+}]/1)$

- Where E° = -0.76 V (standard reduction potential).
- Zn(s) is a solid, so its activity is considered 1.

b) HgCl2(s)/Hg(l):

1. Half-reaction: $HgCl_2(s) + 2e^- \rightleftharpoons Hg(l) + 2Cl^-$

2. Nernst Equation:

$E = E° - (0.059/2) \log([Cl^-]^2)$

- Where E° = 0.85 V (standard reduction potential).

c) O2(g)/H_2O_2:

1. Half-reaction: $O_2(g) + 2H^+ + 2e- \rightleftharpoons H_2O_2(aq)$

2. Nernst Equation:

$E = E° - (0.059/2) \log(P(O_2)/[H_2O_2])$

- Where E° = 0.68 V.

d) $ClO_4^-/Cl_2(g)$:

1. Half-reaction: $ClO4^- + 8H^+ + 8e^- \rightleftharpoons Cl_2(g) + 4H_2O$

2. Nernst Equation:

$E = E° - (0.059/8) * \log([ClO_4^-][H^+]\text{^}8/P(Cl_2))$

- Where E° = 1.39 V.

<u>Exercise 4:</u>

1. Hydrogen at p = 1 bar, pH = 3:

- Couple: H+/H2, E° = 0.00 V.
- Nernst Equation: $E = E° - (0.059/2) * \log([H^+]^2)$
- At pH = 3, $[H+] = 10^{-3}$.
- $E = 0.00 - 0.059 * \log(10^{-3}) = 0.00 + 0.177 = +0.177$ V.

2. Iron plate in $FeSO_4$ (c = 0.1 mol/L):

- Couple: Fe^{2+}/Fe, E° = -0.44 V.
- Nernst Equation: E = E° - (0.059/2) * log([Fe^{2+}]/1)
- Substituting [Fe^2+] = 0.1 mol/L:

E = -0.44 - 0.059 * log(0.1) = -0.44 - (-0.059) = -0.381 V.

<u>Exercise 5:</u>

1. Redox couples:

- Zn^{2+}/Zn, E° = -0.76 V.
- Pb^{2+}/Pb, E° = 0.13 V.

2. Reaction:

$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$.

3. Calculate standard cell potential (E°cell):

E°cell = E°(cathode) - E°(anode)

E°cell = 0.13 - (-0.76) = +0.89 V.

4. Equilibrium constant (K):

Using $\Delta G° = -nFE°_{cell}$ and $\Delta G° = -RT\ln(K)$:

$\ln(K) = nFE°_{cell} / RT$

Substituting n = 2, F = 96485 C/mol, R = 8.314 J/mol·K, T = 298 K:

ln(K) = (2 * 96485 * 0.89) / (8.314 * 298)

ln(K) ≈ 69.8, K ≈ e^69.8 (very large, reaction favors Zn oxidation).

Exercise 6:

a) In Pure Water:

1. Dissociation Reaction:

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

2. Solubility Product Expression:

$Ks = [Ag^+]^2 [CrO_4^{2-}]$

3. Defining Solubility:

Let S be the molar solubility of Ag_2CrO_4:

$[Ag^+] = 2S$, $[CrO_4^{2-}] = S$

4. Substitute into Ks:

$Ks = (2S)^2(S) = 4S^3$

5. Given $Ks = 10^{-11.95}$:

$4S^3 = 10^{-11.95} \rightarrow S = (10^{-11.95} / 4)^{(1/3)}$. $S=6.55\times10^{-5}$ mol/l

b) In 0.1 mol/L K_2CrO_4 Solution:

1. Fixed Concentration of CrO_4^{2-}:

$[CrO_4^{2-}] = 0.1$ mol/L

2. Solubility Product Expression:

$Ks = [Ag^+]^2 [CrO_4^{2-}]$

3. Solve for $[Ag^+]$:

$[Ag^+] = \sqrt{(Ks / [CrO_4^{2-}])}$

$[Ag+]=3.35\times10-6$ mol/L

cHAPTER VI: General notions of thermodynamics

I. Introduction

Thermodynamics is the science of energy transformations. It studies the energetic characteristics related to the transformation of matter, whether it's physical or chemical. It focuses more specifically on the transformation of a material system. Thermodynamic study essentially concerns the characteristics of the initial state (IS) and the final state (FS) of the evolving system. This study does not consider the time parameter (t) or the path followed during a given transformation. The rate of evolution, the transformation mechanism, and the intermediate steps through which the system passes to reach the final state are the subject of another branch of chemistry: chemical kinetics.

II. The system

The system is a portion of space under study. It is limited by a real or fictitious (arbitrary) surface through which exchanges of energy and/or matter occur with the external environment. The combination of the system and the external environment constitutes the universe. The distinctions are as follows:

-An open system can exchange both energy and matter with the external environment.

An example of an open system is a pot of boiling water on a stove. In this system, both energy (heat) and matter (water vapor) can freely exchange with the surroundings. Heat energy is transferred from the stove to the water, causing it to boil and release water vapor into the air

-A closed system can exchange energy but not matter with the external environment. A good example of a closed system is a thermos flask containing hot coffee. In this system, energy (heat) can be exchanged with the surroundings (like when the coffee cools down), but matter (the coffee itself) is confined within the flask and cannot escape. The coffee can lose heat to the environment, but it won't spill out.

-An isolated system cannot exchange either energy or matter with the external environment. In practice, perfect isolation is also impossible here. An example of an isolated system is a perfectly insulated container holding a certain amount of gas.

III. The state variables

These are the set of values taken by thermodynamic quantities related to the macroscopic state called "state variables" or "state parameters," such as mass (m), pressure (P), volume (V), concentration (C), density (d), temperature of phase change (Tce), etc. These variables allow the definition of the system's state

III.1 Intensive and Extensive Parameters:

-**An extensive parameter** is proportional to the quantity of matter. It is defined for the entire system.

Examples: Volume, mass, quantity of matter.

-**An intensive parameter** is defined at each point within a system and is independent of the quantity of matter.

Examples: Density, pressure, concentration, temperature.

III.2. Gibbs Variables (T, P, ..., n):

These are physico-chemical variables (or parameters) that define the state of the system. They consist, on one hand, of physical variables defining the thermodynamic state of the studied system:

T: Thermodynamic temperature in Kelvin (K)

P: Pressure in Pascal (Pa) or bar

V: Volume in cubic meters or liters (L)

III.3. Standard State of a Pure Substance

The Standard State of a Pure Substance is a reference condition used in thermodynamics to define the properties of a substance under specific, standardized conditions. It represents the most stable form of a substance at a given temperature and a reference pressure of P° = 1 bar =

10^5 Pa. The standard state must specify the physical state of the substance (solid, liquid, or gas) because its properties differ significantly depending on the state. For example, the standard state of water at 25°C is liquid, while the standard state of oxygen at the same temperature is a diatomic gas (O_2).

This concept is important because it provides a baseline for calculating thermodynamic quantities like enthalpy, entropy, and Gibbs free energy. It ensures consistency and comparability across different substances and conditions.

For gases, the standard state assumes ideal behavior at 1 bar pressure.

For liquids and solids, the standard state refers to the pure substance at 1 bar pressure and the specified temperature.

In the case of elements, the standard state refers to the most stable allotrope under the specified conditions, such as (O_2) for oxygen or graphite for carbon.

By establishing these reference conditions, the standard state simplifies the study and comparison of thermodynamic properties.

IV. Transformation of systems state:

A system undergoes a transformation when it moves from an initial state to a final state. The different types of transformations are:

- Isobaric transformations: At constant pressure, initial pressure equals final pressure (P initial = P final).

- Isothermal transformations: At constant temperature, initial temperature equals final temperature (T initial = T final).

- Isochoric transformations: At constant volume, initial volume equals final volume (V initial = V final).

- Adiabatic transformations: $Q = 0$, no heat exchange with the external environment.

- Reversible transformations: A theoretical transformation composed of a series of equilibrium states in such a way that if it were done in the opposite direction, the system would pass through the same equilibrium states as in the forward direction. This is a model (does not exist in reality) and is the limiting case where the transformation always remains close to the equilibrium state, that is, an infinitely slow transformation. Not to be confused with equilibrium.

- Irreversible transformations: Every real transformation is irreversible; these are fast and abrupt transformations. The intermediate state variables are not known at every instant except for the initial and final states.

V. Ideal Gas Equation:

The simplest and best-known equation of state for substances in the gas phase is the

Ideal-gas equation of state. It is experimentally observed that at a low pressure the volume of a gas is proportional to its temperature:

$$PV = nRT$$

P: Pressure inside the system in pascal (Pa)

V: Volume of the system in cubic meters (m^3)

n: Number of moles of gas in the system in moles (mol)

R: Ideal gas constant ($J.mol^{-1}K^{-1}$)

T: Temperature of the system in Kelvin (K)

The value of the ideal gas constant is R = 8.314 $J.mol^{-1}K^{-1}$.

Note:

- Standard temperature and pressure conditions (STP): P = $1.013 * 10^5$ Pa at 0°C, and one can calculate Molar Volume = 22.4 L/mol.

1 bar = 1 atm = $1.013 * 10^5$ Pa = 760 mmHg

0°C = 273.15 K

VI. Laws of perfect gases:

- Boyle's Law:

At constant temperature, the pressure of a mass of a perfect gas is inversely proportional to its volume.

$PV = \text{constant}$

Another formulation of this law can be useful:

$Pi * Vi = Pf * Vf$

- Gay-Lussac's Law:

Heating (or cooling) at constant pressure of a fixed quantity of a perfect gas allows writing:

$(P/T) = \text{constant} = (P_f/T_f)$

Another expression:

$(V/T) = \text{constant} = (V_f/T_f)$

At constant pressure, the volume of a mass of a perfect gas is proportional to its temperature.

- Charles's Law:

At constant volume, the pressure of a mass of a perfect gas is proportional to its temperature.

$(P/V) = \text{constant} = (P_f/V_f)$

Another expression:

$(V/T) = \text{constant} = (V_f/T_f)$

VII. Mixtures of ideal gases:

- Definition of an Ideal Mixture:

A mixture of perfect gases is considered ideal when all particles (whether identical or not) experience only elastic collisions and no other interactions. The total pressure of a mixture then depends not on the nature of the gases present but solely on the total quantity of material.

Molar Fraction of a Mixture's Component: $x_i = \frac{n_i}{n_{total}}$

Total quantity of material in the mixture: $n_{total} = \sum_i n_i$

- Dalton's Law, Partial Pressures:

The partial pressure Pi of a gas in a gas mixture refers to the pressure that the gas would exert on the walls of the container if it occupied the same volume alone at the same temperature.

The relationship between the total pressure P_{total} and the partial pressure Pi is given by:
$p_t = \sum_{i=1}^{n} p_i = p_1 + p_2 + p_3 + \cdots$

Partial pressure of each component in the mixture: $p_i = x_i * p_{total}$

VIII. Energy exchange

1. Notions of Heat or Quantity of Heat (Q)

Heat is a form of energy that appears during the transfer of energy between bodies or systems that are not at the same temperature.

Example:

Body A: T_A

Body B: T_B

$T_A \neq T_B$ ➡ Heat exchange

$T_A = T_B$ ➡ No heat exchange between A and B

This appears to be a formula describing the relationship between heat (Q), heat capacity (C), and temperature change (dT):

$$Q = \int_{T_i}^{T_f} C\, dT$$

Where:

Q : represents the amount of heat transferred

dT: represents the change in temperature

C: is the heat capacity or specific heat capacity expressed in J/K or cal/K.

The heat capacity, denoted as C, The energy needed to raise the temperature of a body by one degree (or one Kelvin).

There are different types of heat capacities: $C = nc_n = mc_m$

Explanation of heat capacity (C) in different forms:

- C n: molar heat capacity; expressed in J/mol.K or cal/mol.K
- Cm: mass heat capacity; expressed in J/g.K or cal/g.K
- Cp: heat capacity at constant pressure; can be molar or mass

Cv: heat capacity at constant volume; can be molar or mass.

For monatomic gases: $c_v = \frac{3}{2}R \quad c_p = \frac{5}{2}R$

For diatomic gases: $c_v = \frac{5}{2}R \ \ c_v = \frac{7}{2}R$

For ideal gases: $cp - cv = R$

Where R is the gas constant. This is known as Mayer's relation.

2. The latent heats of physical state changes:

This is the amount of heat, denoted as **L**, required to perform, at constant temperature and pressure, the physical state change of one mole or one gram (1g) of the considered pure substance. The pressure remains constant and equal to the equilibrium pressure between the two states.

Liquification Heat (fusion): The amount of heat required to convert a substance from a solid to a liquid phase at constant temperature and pressure.

Vaporization Heat: The amount of heat required to convert a substance from a liquid to a vapor phase at constant temperature and pressure.

Solidification Heat (freezing): The amount of heat required to convert a substance from a liquid to a solid phase at constant temperature and pressure.

Expressed in: J/mol; cal/mol; J/g; cal/g.

The amount of heat exchanged at constant T and P for any quantity of matter is written as:

$$Heat\ of\ Fusion\ Q\ =\ L\_fusion\ \times\ n$$

$$Heat\ of\ Solidification\,Q\ =\ L\_solidification\ \times\ n$$

$$Heat\ of\ Vaporization\,Q\ =\ L\_vaporization\ *\ n$$

The sign of Q:

Q < 0: The system releases heat, the reaction is called exothermic.

Example: Sodium hydroxide (NaOH) in water.

Q > 0: The system gains heat, the reaction is called endothermic.

Example: Potassium nitrate (KNO_3) in water.

Q = 0: No exchange with the surroundings, the reaction is called a thermal.

Example: Esterification equilibrium.

Clapeyron Diagram

A **Clapeyron Diagram** is a graphical representation of the thermodynamic transformations of a system, typically plotted on a P−V (Pressure-Volume) diagram. It illustrates how pressure and volume change during different thermodynamic processes, such as isothermal, adiabatic, isobaric, or isochoric transformations.

Key Features of a Clapeyron Diagram:

1. **Axes**:
   - The x-axis represents the **Volume (V)**.
   - The y-axis represents the **Pressure (P)**.
2. **Thermodynamic Processes**:

  - **Isothermal Process**: Represented by a hyperbolic curve (Boyle's Law).
  - **Adiabatic Process**: Typically, steeper than the isothermal curve.
  - **Isobaric Process**: A horizontal line, as pressure remains constant.
  - **Isochoric Process**: A vertical line, as volume remains constant.

3. **Areas Under Curves**:
   - The area under a curve in the Clapeyron diagram corresponds to the **work done by or on the system** during a process. For example, during an expansion or compression, the work is $W=-\int P\,dV$

First Law of Thermodynamics

The First Law of Thermodynamics is a statement of energy conservation applied to thermodynamic systems. It states:

$\Delta U=Q+W$

- ΔU: Change in internal energy of the system.
- Q: Heat exchanged between the system and its surroundings.
- W: Work done by or on the system.

The first law essentially explains that the total energy of an isolated system is constant, and energy can neither be created nor destroyed but only transformed from one form to another.

4.4.1. Work and Heat Expressions

Heat (Q)

The quantity of heat depends on the path followed (it is not a state function). To calculate the quantity of heat, it is necessary to determine the path followed.

At constant volume transformation:

$$\partial Q = \partial Q_v = C_v dT$$

$$Q = Q_v = \int_{T_i}^{T_f} C_v\, dT$$

At constant pressure transformation: $\partial Q = \partial Q_p = C_p dT$

$$Q = Q_p = \int_{T_i}^{T_f} C_p \, dT$$

Adiabatic transformation: Q = 0 .No exchange of heat with the surroundings

3. Work

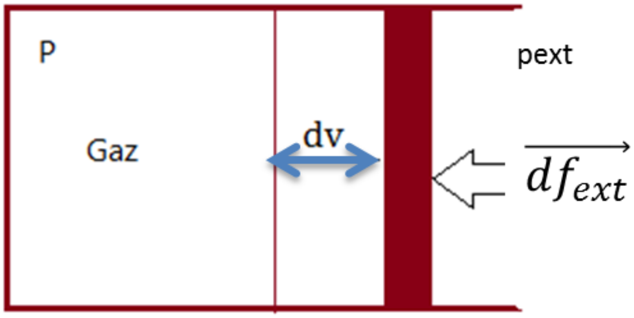
Is another form of energy (mechanical energy):

- It's an energy expressed in [J] or [cal].

- On a microscopic scale, its energy exchanged in an organized manner (for instance, through the displacement of a piston that gives a certain direction to the atoms).

- It is not a function of state.

Work often results from a change in volume of a deformable (non-rigid) system, for example, in the case of piston movement. This is called work done by Work resulting from piston displacement:



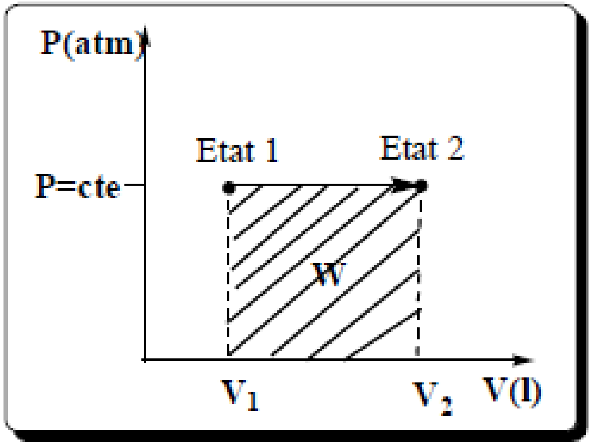
We define the pressure exerted by a force (F) on the surface (S) of the piston by:

The elemental work exchanged is then written as: $\delta W = -P_{ext} dV$

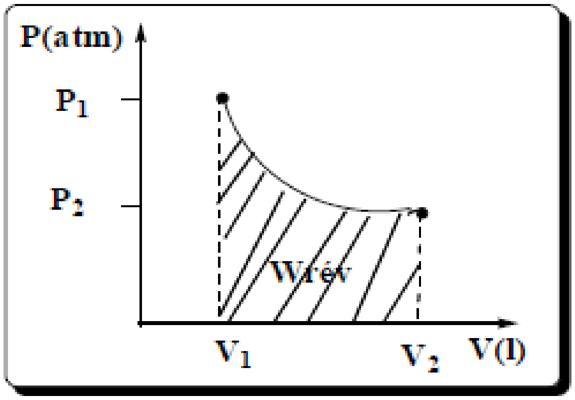
Calcul du travail pour les différentes transformations :

Transformation isochore : $\Delta V = 0 \Rightarrow W = 0$

Transformation isobare : $W = -P \int_{V_{initial}}^{V_{final}} dV = -P(V_{final} - V_{initial})$



Transformation isotherme:



$$p_{ext} = p_{int} = p_{gaz\,parfait} = \frac{nRT}{V}$$

$$w_{rev} = -\int_i^f p_{int}\,dv = -nRT\int_i^f \frac{1}{v}\,dv$$

$$w_{rev} = -nRT\ln\frac{v_f}{v_i} = -nRTln\frac{p_{int}}{p_{ext}}$$

4. Internal Energy (U) and Enthalpy (H)

Internal Energy (U)

The internal energy (ΔU) of a system is indeed a state function, meaning it depends only on the current state of the system, not on how that state was achieved. The change in internal energy (ΔU) during a transformation is indeed equal to the heat (ΔQ) added to the system minus the work (Δw) done by the system on its surroundings. Mathematically, this is expressed as $\Delta U = W + Q$

Enthalpy (H)

Enthalpy is a thermodynamic quantity defined as:

H=U+PV

- U: Internal energy.
- P: Pressure.

- V: Volume.

At constant pressure, the change in enthalpy (ΔH) equals the heat exchanged:

$\Delta H = Q_P$

- **Endothermic process**: $\Delta H > 0$.
- **Exothermic process**: $\Delta H < 0$

Enthalpy is particularly useful for describing processes such as chemical reactions, phase transitions, and heating/cooling.

Exercises

Exercise I.

Give the dimensions of the ideal gas constant (R) and determine its value when expressed:

1. in L. atm.mol-1. K-1

2. in J. mol-1. K-1

3. in cal. mol-.K

Exercise II.

A gas mixture consists of 0.2 g of H_2; 0.21g of N_2 and 0.51g of NH_3 under the pressure of one atmosphere and at a temperature of 27°C.

Calculate:

1. mole fractions.

2. the partial pressure of each gas.

3. the total volume.

Data: M(H) = 1g mol-1 and M(N) = 14g mol-1

Exercise III.

One mole of monatomic ideal gas undergoes a transformation from state (1) to state (2) following three different paths (a, b and c) with:

The 1st transformation is isochoric then isobaric (path a), the 2nd is isobaric then isochoric (path b) and the 3rd is such that PV=cste (path c).

State (1): P1 = 1 bar; V1= 3 l

State (2): P1 = 3 bar; V1= 1 l

1. Represent the three transformations in Clapeyron coordinates.
2. Calculate ΔU (internal energy variation between states 1 and 2).
3. Calculate the work in the three cases and deduce the heat exchanged; are they received or transferred by the system?

Exercise IV.

In the mountains, we need 5 liters of hot water at 40°C from ice taken on site. There ice temperature is -18°C. 5 kilograms of ice are melted in a kettle on a gas stove.

Calculate the amount of heat:

- Q1 to raise the ice temperature from -18°C to 0°C;

- Q2 to melt the ice at 0°C;

- Q3 to raise the water temperature from 0°C to 40°C.

Which of these three steps requires the most heat? Specific heats: Ceau =4180 J/[kg.°C]; Cice=2100 J/[kg.°C];

- for latent heat: 335kJ must be provided to melt a kilogram of ice at 0°C

Solutions

Exercise I:

1. Dimensions of the ideal gas constant (R):

- From the ideal gas law, PV = nRT, where:
  - P (Pressure) Atmosphere =$10^5 Pa$
  - V (Volume) l= 10^{-3}m³.
  - n (Moles) .
  - T (Temperature) is in Kelvin. 0C°=273K°
  -

2. Value of R in different units:

(a) in $L \cdot atm \cdot mol^{-1} \cdot K^{-1}$: R = 0.0821 $L \cdot atm \cdot mol^{-1} \cdot K^{-1}$.

(b) in $J \cdot mol^{-1} \cdot K^{-1}$: J= Pa*$m^3$: R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$.

(c) in $cal \cdot mol^{-1} \cdot K^{-1}$: R = 1.987 $cal \cdot mol^{-1} \cdot K^{-1}$.

Exercise II:

Given data:

- Mass of H_2 = 0.2 g, N_2 = 0.21 g, NH_3 = 0.51 g.
- Molar masses: M(H_2) = 2 g/mol, M(N_2) = 28 g/mol, M(NH_3) = 17 g/mol.
- Total pressure = 1 atm, Temperature = 27°C = 300 K.

1. Mole fractions:

- Moles of H_2: n(H_2) = 0.2 / 2 = 0.1 mol.
- Moles of N_2: n(N_2) = 0.21 / 28 = 0.0075 mol.
- Moles of NH_3: n(NH_3) = 0.51 / 17 = 0.03 mol.
- Total moles: n(total) = 0.1 + 0.0075 + 0.03 = 0.1375 mol.
- Mole fractions: $\chi(H_2)=\frac{n_{H2}}{n_t}=\frac{0.1}{0.1375}=0.727$ $\chi(N_2)=\frac{0.0075}{0.1375}=0.054$, and $\chi(NH_3)=\frac{0.03}{0.1375}=$ 0.218.

2. Partial pressures:

- Use P(gas) = χ(gas) × P(total) for pH_2=0.727atm, pN_2=0.054atm, and pNH_3=0.218atm.

3. Total volume:

- Use the ideal gas law: V = nRT / P. $p = \frac{1*0.082*300}{1} = 24.6l$

Exercise III:

Given data:

- State (1): P_1 = 1 bar, V_1 = 3 L.
- State (2): P_2 = 3 bar, V_2 = 1 L.

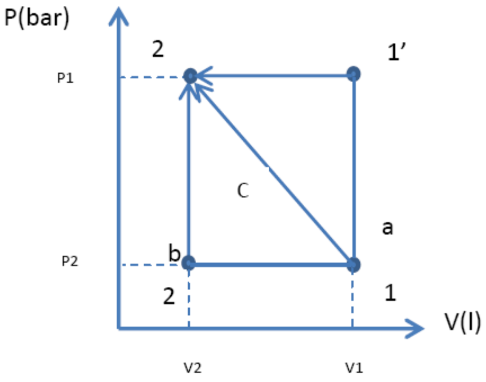
Using the ideal gas law:

PV=nRT

	P atm	V l	T k°
1	1	3	36.58
a	3	3	109.75
b	1	1	12.19
2	3	1	36.58

$$C_V = \frac{3}{2}R, \qquad C_P = \frac{5}{2}R$$

1. Representation in Clapeyron coordinates:



- Plot P vs. V for the three paths.

2

		W	Q	ΔU
a	V=cst	W1a = 0	ncv(Ta-T$_1$)	nc$_v$(Ta-T1)
	P=cst	Wa2 = -P$_2$(V$_2$ - Va)	ncp(T$_2$-Ta)	nc$_v$(T$_2$-Ta)
b	P=cst	Wa2 = -P2(V$_b$ – V$_1$)	ncp(T$_b$-T$_1$)	nc$_v$(Tb-T1)
	V=cst	Wb2 = 0 J	ncv(T$_2$-T$_b$)	nc$_v$(T$_2$-Tb)
c	T=cst	-nRT Ln(V2/V1)	nRTLn(V$_2$/V$_1$)	0

Exercise IV:

Given data:

- Ice mass = 5 kg, Temperature of ice = -18°C, Desired water = 5 L at 40°C.

1. Heat required to raise ice temperature (Q_1):

- Q_1 = m C(ice) ΔT = 5 × 2100 × (0 - (-18))=198000J= 198kJ

2. Heat required to melt the ice (Q_2):

- Q_2 = m L(fusion) = 5 × 335000=1675000J= 1675kJ

3. Heat required to raise water temperature (Q_3):

- Q_3 = m C(water) ΔT = 5 × 4180 × (40 - 0)=24050J= 240.5kJ

4. Comparison:

- Q_2 requires the most heat.

References:

1. Brown, T. E., LeMay, H. E., Bursten, B. E., Murphy, C. J., & Woodward, P. M. (2017). *Chemistry: The Central Science* (14th ed.). Pearson Education.
   ISBN: 978-0134414232

2. Petrucci, R. H., Herring, F. G., Madura, J. D., & Bissonnette, C. (2017). *General Chemistry: Principles and Modern Applications* (11th ed.). Pearson.
   ISBN: 978-0132931281

3. Silberberg, M. S., & Amateis, P. (2018). *Principles of General Chemistry* (4th ed.). McGraw-Hill Education.
   ISBN: 978-1259638138

4. Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. (2013). *Fundamentals of Analytical Chemistry* (9th ed.). Cengage Learning.
   ISBN: 978-0495558286

5. Harvey, D. (2000). *Modern Analytical Chemistry*. McGraw-Hill Education.
   ISBN: 978-0072375473

6. Harris, D. C. (2020). *Quantitative Chemical Analysis* (10th ed.). W. H. Freeman.
   ISBN: 978-1319254188

7. McQuarrie, D. A., & Simon, J. D. (1997). *Physical Chemistry: A Molecular Approach*. University Science Books.
   ISBN: 978-0935702996

8. Çengel, Y. A., & Boles, M. A. (2014). *Thermodynamics: An Engineering Approach* (8th ed.). McGraw-Hill Education.
   ISBN: 978-0073398174

9. Smith, J. M., Van Ness, H. C., & Abbott, M. M. (2005). *Introduction to Chemical Engineering Thermodynamics* (7th ed.). McGraw-Hill Education.
   ISBN: 978-0073104454

10. DeVoe, H. (2019). *Thermodynamics and Chemistry* (2nd ed.). Howard DeVoe Publications.
ISBN: 978-1732752408

11. واثق، محمد مجدي. *أساسيات الكيمياء العامة*. 2010، دار المريخ للنشر.

12. سامي، فؤاد. *الكيمياء التحليلية: النظرية والتطبيق*. 2012، دار الفكر العربي.

13. الشربيني، يوسف أحمد. *الديناميكا الحرارية الكيميائية*. 2015، دار النهضة العربية.