

MODULE-2 & 3

Alloy Systems: Classification of Solid solutions, Hume- Rothery Rules

Diffusion: Diffusion Mechanisms: Vacancy Diffusion and Interstitial Diffusion, Fick's laws of diffusion, Factors affecting diffusion.

Phase Diagrams: Gibbs Phase Rule, Solubility limit, phase equilibrium and Phase Diagrams: Isomorphous systems, Invariant Binary Reactions: Eutectic reaction, Eutectoid reaction and Peritectic reaction, Lever Rule, Iron-Carbon Diagram. Effect of common alloying elements in steel.
Numerical on Lever rule.

Basics on Atoms and Molecules

Atom:

An atom is the smallest particle of an element that retains the chemical properties of that element. Atoms are electrically neutral, with a positively charged nucleus that binds one or more electrons in motion around it

Ions:

An ion is an atom or molecule that has acquired a charged by either gaining or losing electrons. An atom or molecule with missing electrons has a **net positive charge** and is **called a cation**. An atom or molecule with **extra electrons** has a **net negative charge** and is **called an anion**.

An Atom is the smallest particle of a chemical element that can exist. Electrons, protons and neutrons are its sub-atomic particles. While the protons and neutrons are in the nucleus, the electrons revolve around the nucleus in fixed orbits in their shells.

Example of atoms are: *O - atom of oxygen, H - atom of hydrogen etc.*

A molecule is the group of atoms bonded together for the existence of an element or compound which can take part in any chemical reaction.

For example: *O₂ is the molecule of oxygen gas containing two atoms of oxygen. H₂SO₄ is a molecule of sulphuric acid containing two atoms of hydrogen, one of sulphur and two atoms of oxygen.*

- ❖ An ion gets formed when an atom gains or loses electrons to obtain stable configuration. Atoms of metals lose electrons and form cations with positive charge whereas atoms of non-metals gain electrons and form anions with negative charge.
- ❖ Metalloids are those which can show both metallic and non-metallic properties.

❖ Molecules

The combination of atoms of same or different types of atoms in the fixed ratio by mass is known as molecule. The combination of same types of atoms is called molecule of element

What is the difference between an atom and an ion?

This is another great question!

Atoms are made up of 3 subatomic particles: protons, neutrons, and electrons.

Two of the subatomic particles carry an electric charge. Each proton is positively-charged, while each electron is negatively-charged.

Even though atoms are made up of charged particles, an atom as a whole carries no net charge. How is that possible?

In a neutral atom, the number of positively-charged protons and negatively-charged electrons is the same. A lithium atom has 3 protons contributing a charge of +3, but it also has 3 electrons contributing a charge of -3. The positive and negative charges cancel each other out.

So what is an ion? An ion is an atom that has gained a net charge.

Why?

Because it has either gained or lost electrons.

You see, while protons and neutrons are fixed within an atom, electrons are free to move. They can move both within an atom as well as from one atom to another. (The ability of electrons to move from atom to atom is the basis of electricity).

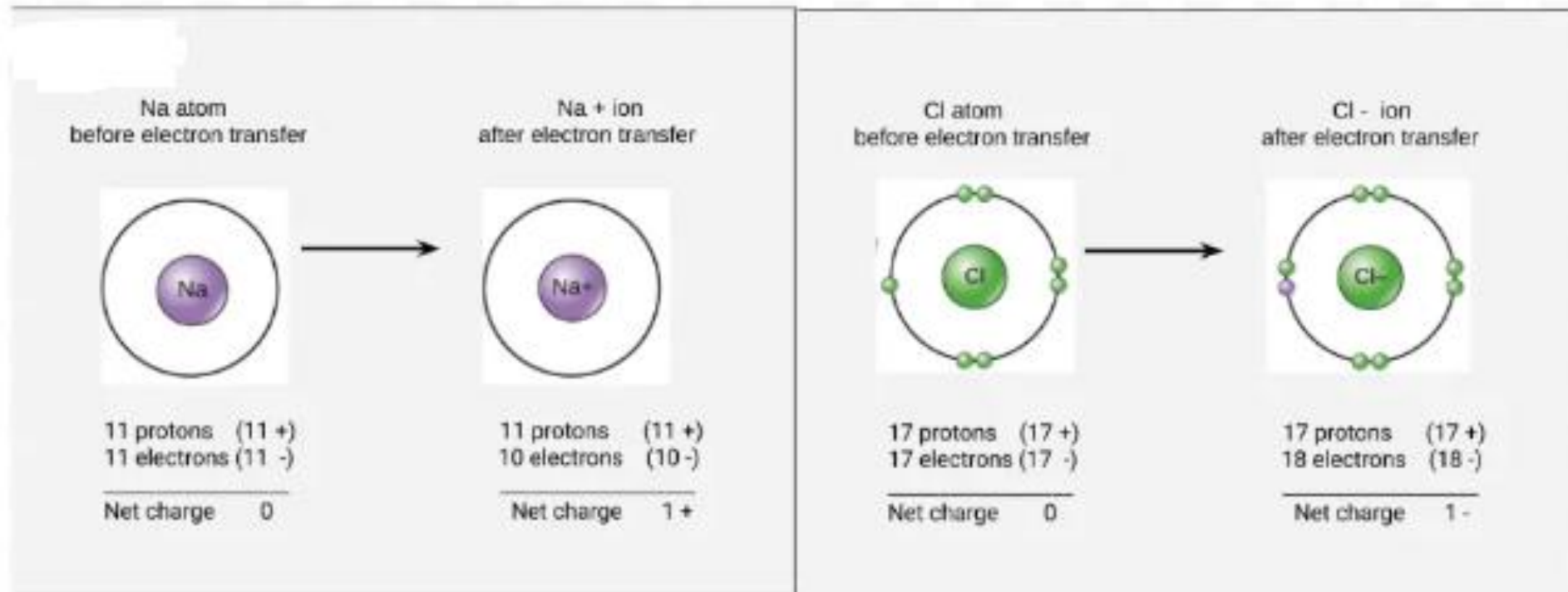
When an atom loses one or more electrons, it loses the negative charges associated with those electrons. Consequently, an atom that has lost electrons will have more positive charges than negative charges, since it will have more positively-charged protons than it has negatively-charged electrons. We see this happen often with metallic elements.

When an atom gains one or more electrons, it gains a net negative charge since it has more negatively-charged electrons than it has positively-charged protons. This happens commonly with atoms of nonmetal elements.

Positively-charged ions are called cations and negatively-charged ions are called anions.

A special type of chemical bond called an ionic bond often forms between a cation and an anion. Ionic bonds are formed by the opposite electrical charges of the positively-charged cation and the negatively-charged anion.

Sodium chloride (NaCl), commonly known as table salt, is held together by ionic bonds between sodium (Na) cations and chlorine (Cl) anions.



Na atom
before electron transfer



11 protons (11 +)
11 electrons (11 -)

Net charge 0



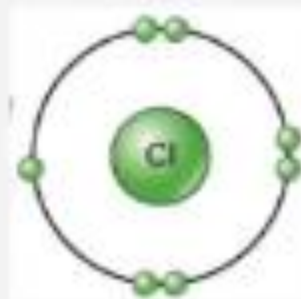
Na⁺ ion
after electron transfer



11 protons (11 +)
10 electrons (10 -)

Net charge 1 +

Cl atom
before electron transfer

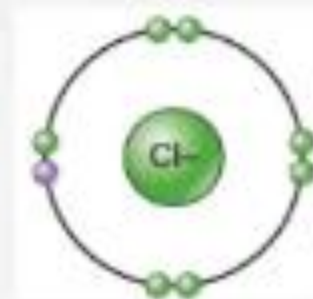


17 protons (17 +)
17 electrons (17 -)

Net charge 0

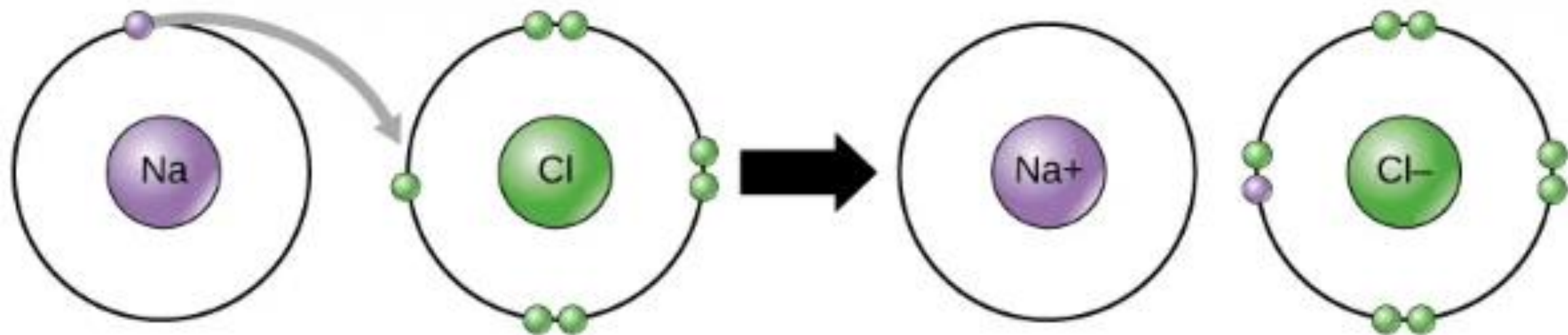


Cl⁻ ion
after electron transfer



17 protons (17 +)
18 electrons (18 -)

Net charge 1 -



What Is an Atom?

An atom is the smallest possible unit of an element. Atoms are considered to be the basic building blocks of matter because they cannot be divided into smaller particles by any chemical process.

An atom consists of three types of subatomic particles: neutrons, protons, and electrons. Neutrons and protons are both located in the nucleus of the atom; neutrons are neutrally charged particles, and protons are positively charged particles. Electrons are negatively charged particles which orbit the nucleus of the atom. Their arrangement and movement are the basis for many of the chemical properties of the element.

Each type of atom is assigned an atomic number which tells the number of protons in the atom. Normally, an atom has the same number of positive particles (protons) and negative particles (electrons). So the number of protons is identical to the number of electrons, and both are identical to the atomic number.

What Is an Ion?

Ions are atoms with extra electrons or missing electrons. When an atom's outermost orbital gains or loses electrons (also known as valence electrons), the atom forms an ion. ***An ion with more protons than electrons carries a net positive charge and is called a cation. An ion with more electrons than protons carries a net negative charge and is called an anion.***

The number of neutrons doesn't come into play since they are electrically neutral. Changing the number of neutrons determines the isotope.

Ions are often formed in nature when static electricity draws electrons away from atoms. When you experience an electrical shock after touching a doorknob, you have released a stream of electrons, thus creating ions.

What Are the Properties of Ions?

In addition to being positively or negatively charged, ions can quickly bond with ions with the opposite charge. Some common compounds are made up almost entirely of chemically bonded ions.

For example, salt is made up of a repeating series of chloride anions and sodium cations.

Other examples of important ions include electrolytes, such as chloride, potassium, magnesium, and calcium ions which are essential to health. Electrolytes in sports beverages help to hydrate the body.

Potassium ions help to regulate heart and muscle functions. Calcium is critical for bone growth and repair, and it also plays a role in supporting nerve impulses and blood clotting.

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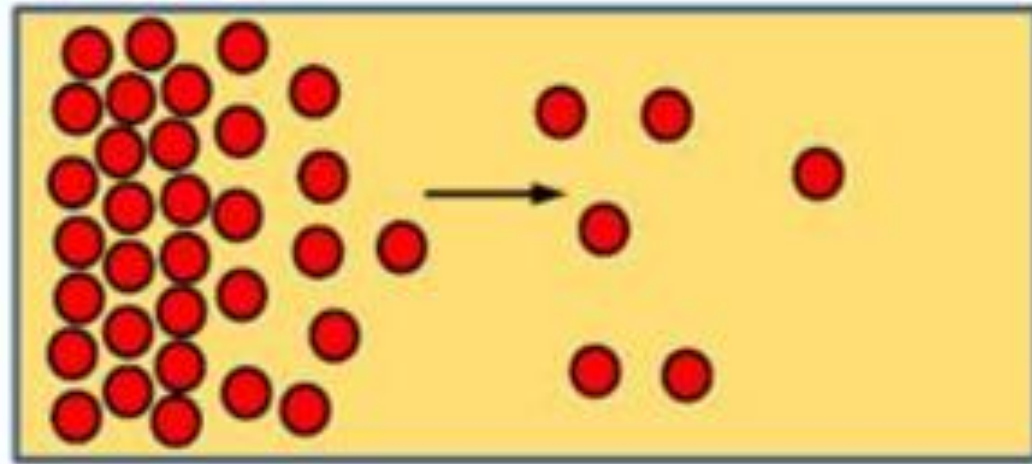
Atomic Diffusion

Diffusional phenomenon

- The migration of atoms from their original lattice sites in a structure to other sites is known as diffusion. Diffusion involves the movement of atoms, ions or molecules from one position to another position and occurs mainly due to thermal agitation or the presence of concentration gradients.
- Diffusion in gaseous state is very rapid because there is hardly any obstruction from other atoms or molecules. Diffusion takes place in liquids also, where the atoms are more closely spaced.

- But in solids, although diffusion is present, the rate of diffusion is very slow. This is because the atoms in solids are closely packed and occupy definite equilibrium positions whose displacement is difficult when compared to gases and liquids.
- However, imperfections normally present in all solids make diffusion possible. Since these imperfections increase with thermal agitation, diffusion becomes more and more pronounced at higher temperatures.
- The basic mathematical expressions governing atomic diffusion are known as Fick's laws of diffusion.

- Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient.
- Atoms move from higher to lower concentration region.
- If this movement is from one element to another e.g. Cu to Ni, then it is termed *inter-diffusion*. If the movement is within similar atoms as in pure metals, it is termed *self-diffusion*.



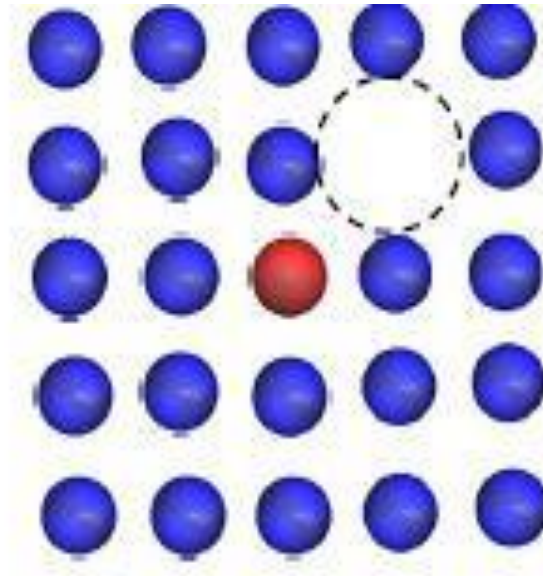
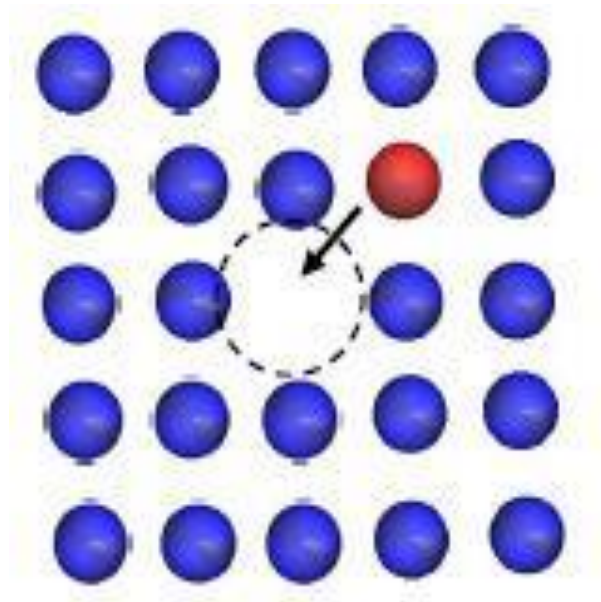
Diffusion Mechanisms

- ❖ Atomic diffusion by vacancy migration.
- ❖ Atomic diffusion by interstitialcy migration.
- ❖ Diffusion by interchange of atoms.

1. Atomic diffusion by vacancy migration:

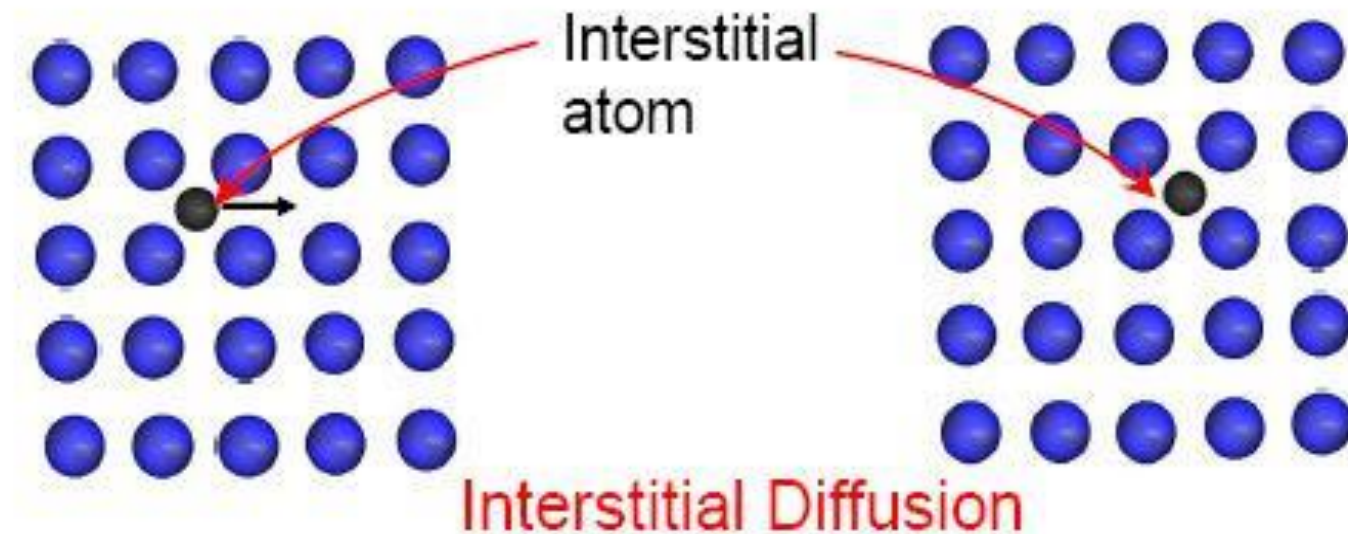
- This mechanism involves movement of atoms from a regular lattice site to an adjacent vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.
- Vacancies move through the lattice and produce random shifts of atoms from one lattice position to another as a result of atom jumping. Concentration changes takes place due to diffusion over a period of time.

- Generally vacancies are continually being created and destroyed at the surface, grain boundaries and suitable interior positions, e.g. dislocations. Obviously, the rate of diffusion increases rapidly with increasing temperature.



2. Atomic diffusion by Interstitial migration

- This mechanism involves migration of atoms from one interstitial site to a neighboring empty interstitial site.
- This mechanism is more prevalent for impurity atoms such as hydrogen, carbon, nitrogen, oxygen which are small enough to fit in to an interstitial position.



- When a solid is composed of two or more elements whose atomic radii differ significantly, interstitial solutions may occur. The large size atoms occupy lattice sites whereas the smaller size atoms fit into the voids (called as interstices) created by the large atoms.
- The diffusion mechanism in this case is similar to vacancy diffusion except that the interstitial atoms stay on interstitial sites.
- An activation energy is associated with interstitial diffusion because, to arrive at the vacant site, it must squeeze past neighbouring atoms with energy supplied by the vibrational energy of the moving atoms.
- Obviously, interstitial diffusion is a thermally activated process. The interstitial mechanism process is simpler since the presence of vacancies is not required for the solute atom to move.

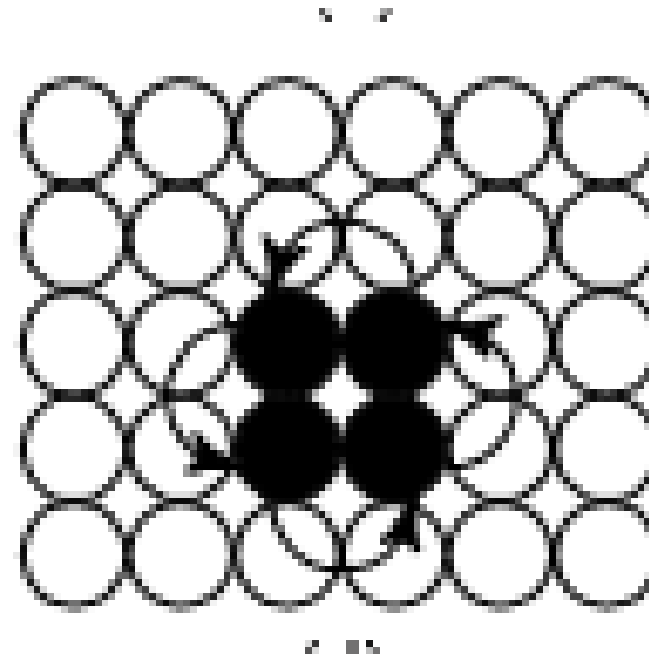
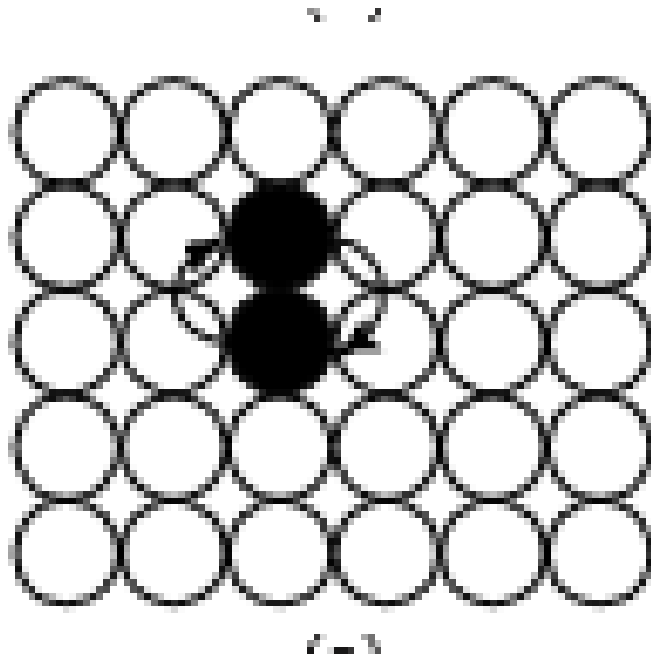
This mechanism is vital for the following cases:

- (a) The presence of very small atoms in the interstices of the lattice affect to a great extent the mechanical properties of metals.
- (b) At low temperatures, oxygen, hydrogen and nitrogen can be diffused in metals easily.

3. Atomic diffusion by Interchange of atoms:

- In this type of mechanism, the atoms exchange places through rotation about a midpoint. The activation energy for the process is very high and hence this mechanism is highly unlikely in most systems.
- Two or more adjacent atoms jump past each other and exchange positions, but the number of sites remains constant.
- This interchange may be two-atom or four-atom (Zenner ring) for BCC. Due to the displacement of atoms surrounding the jumping pairs, interchange mechanism results in severe local distortion.

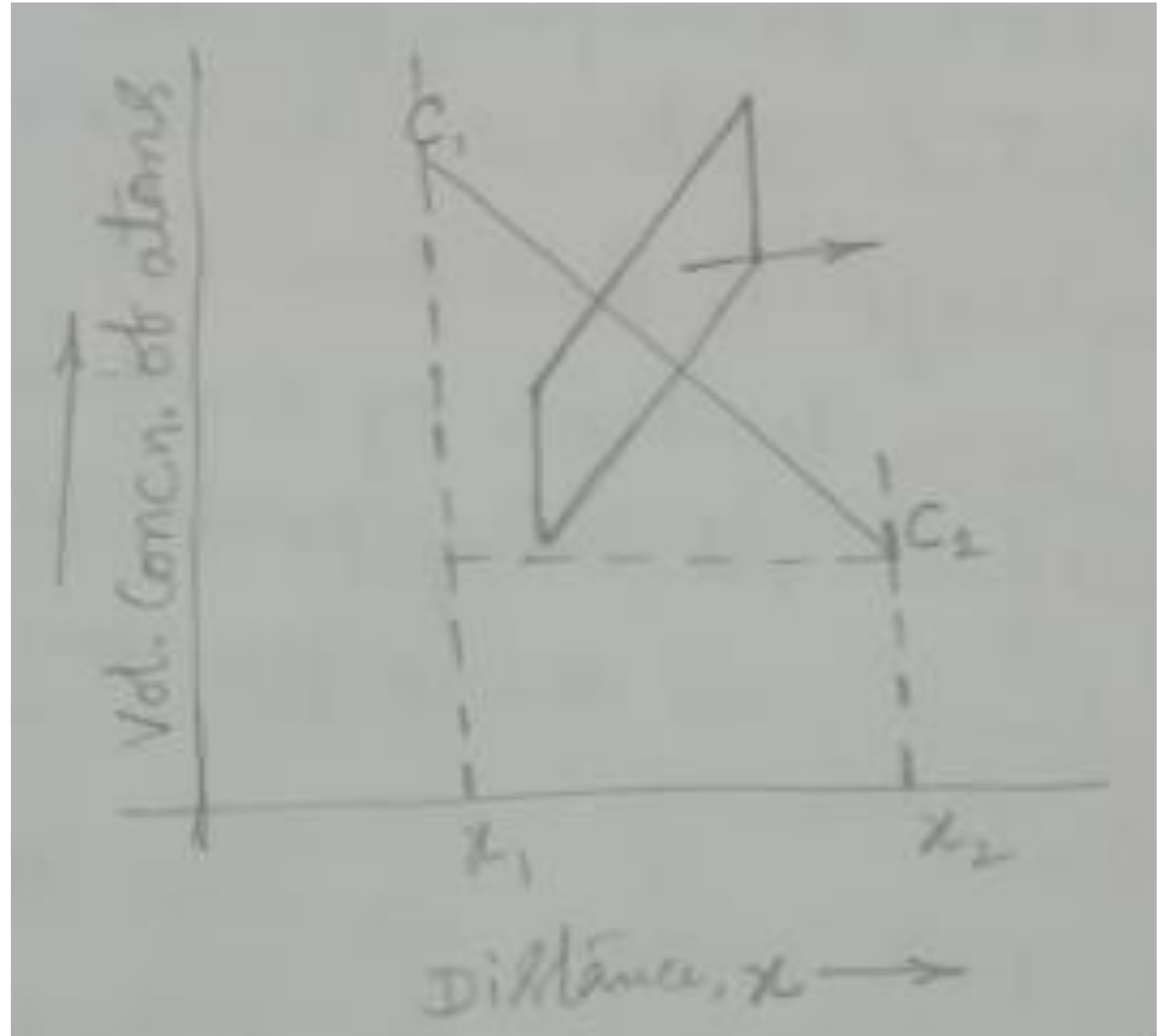
For substitutional diffusion atoms exchange their places directly or along a ring (ring diffusion mechanism)



Fick's Ist Law of diffusion:

(Steady state diffusion)

- Consider the diffusion of solute atoms in the x-direction between two parallel atomic planes (perpendicular to the paper) separated by a distance 'x'.
- Assuming that over a period of time the concentration of atoms at plane 1 is C_1 and that of plane 2 is C_2 . That is, there is no change in the concentration of solute atoms at these planes for the system with time. Such diffusion conditions are said to be steady state condition.



The flux or flow of atoms in this type is proportional to the concentration gradient.

$$J \propto \frac{dC}{dx}$$

It states that, “the flux of atoms J moving across a unit surface area in unit time is proportional to the concentration gradient dc/dx .”

i. e,

$$J \propto \frac{dC}{dx}$$

Under steady state flow,

$$J = -D \frac{dC}{dx}$$

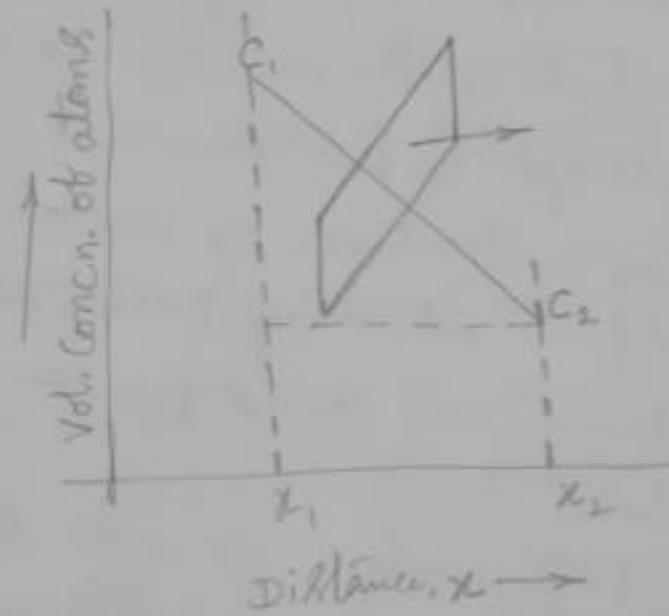
Where, J= number of atoms/ unit area of diffusion per unit time. (atoms/mt²sec)

C= volume concentration of atoms (atoms/m³)

X= distance between the planes in the direction of flow of atoms (in m)

D= diffusion coefficient or diffusivity (m²/sec)

-ve sign= indication that flux of atoms moves from higher to lower concentration.



J = flux of atoms across plane with unit area.

$$J = -D \left(\frac{dc}{dx} \right) = -D \left[\frac{C_2 - C_1}{x_2 - x_1} \right]$$

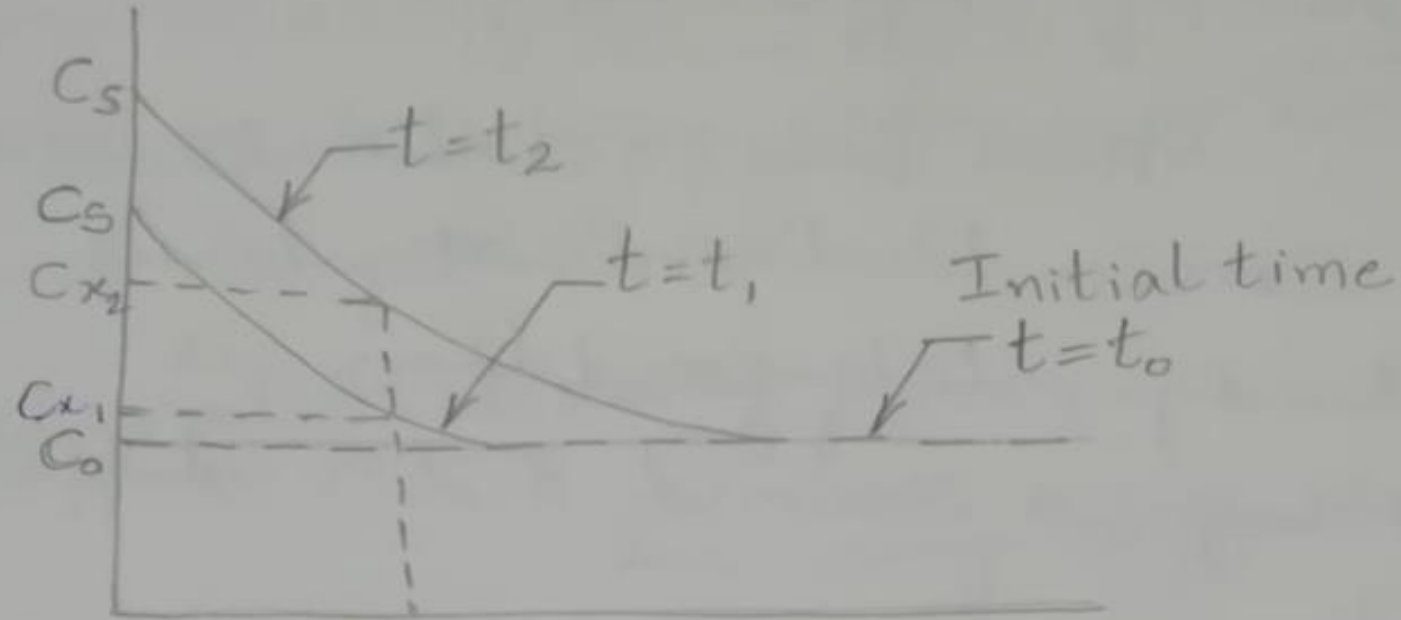
$$J \left(\frac{\text{atoms}}{\text{m}^2 \text{ sec}} \right) = D \left(\frac{\text{m}^2}{\text{sec}} \right) \left(\frac{\text{atoms}}{\text{m}^3} \times \frac{1}{\text{m}} \right) \frac{dc}{dx}$$

$$\frac{dc}{dx} = \text{Concentration gradient}$$

Fick's 2nd Law of diffusion: (Non-steady state diffusion)

- Concentration of solute atoms at any point in the material changes with time takes place.
- **For example**, if carbon is being diffused into the surface of a steel camshaft to harden its surface, the concentration of carbon under the surface at any point will change with time, as the diffusion process progresses.
- For cases of non-steady state diffusion in which the diffusivity is independent of time, Fick's 2nd law of diffusion states that *“the rate of compositional change is equal to the diffusivity times the rate of change of concentration gradient”*.

↑
volume concn. of atoms



Distance, $x \rightarrow$
Concn. of diffusing atoms at distance ' x ' is C_x .

FICK'S II law of diffusion:

This law relates to the change in concentration with time. This non-steady state condition is represented by a second order differential equation.

It states that,

$$\frac{dc}{dt} = D \frac{d}{dx} \left(\frac{dc}{dx} \right)$$

$$\boxed{\frac{dc}{dt} = D \frac{d^2c}{dx^2}}$$

where,

$\frac{dc}{dx}$ = Concentration gradient

D = diffusion co-efficient
(diffusivity)

② Rate of compositional change

$\frac{dc}{dt}$ = The rate of accumulation of diffusing atoms at a point where the concn. gradient is $\frac{dc}{dx}$

Diffusivity:

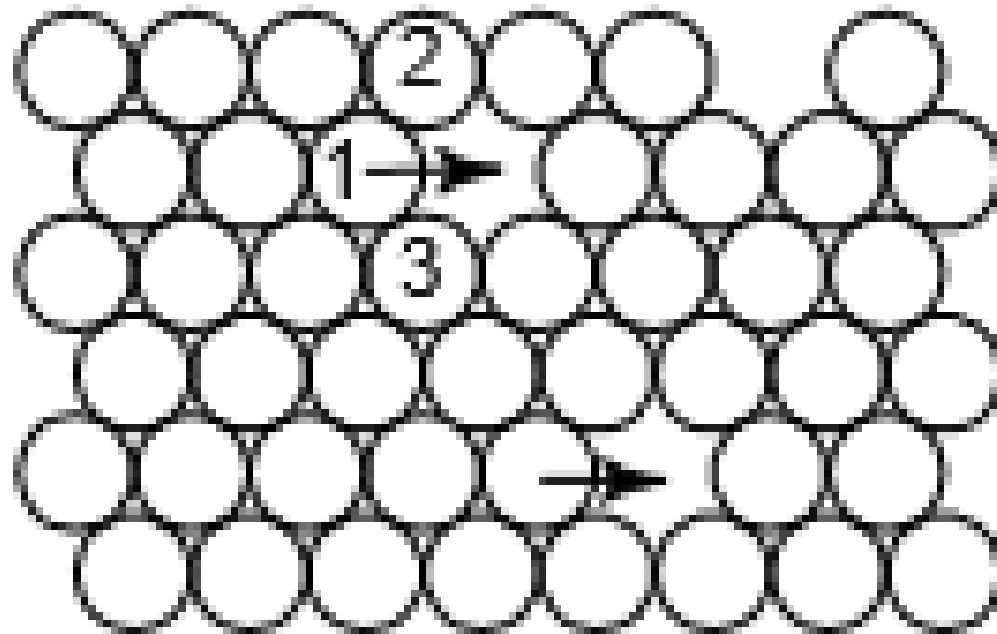
- Diffusivity or coefficient of diffusion (D) is defined as the amount of substance diffusing in unit time across a unit area through a unit concentration gradient and its unit is m^2/sec .
- The coefficient of diffusion (diffusivity) of various materials vary with crystal structure and temperature.
- Diffusivity is influenced by both types of diffusion: Interstitial and Substitutional
 - Small atoms of carbon diffuse interstitially in iron (Fe).
 - Cu atoms diffuse substitutionally in aluminum (Al)
 - Diffusivity is affected by the temperature.
 - If temperature is increases, diffusivity also increases.
 - Diffusivity affected by the type of crystal structure.
- BCC has APF of 0.68 (68%) and FCC has APF of 0.74 (74%).
- More open structure in BCC hence diffusivity is more in BCC.

Activation Energy:

In any diffusion mechanism, work must be done if the atoms are to move from one location to another. To do this work, an energy barrier must be overcome for the atoms to begin a jump from one site to another site.

The minimum energy required by the atoms to overcome this energy barrier is called the *activation energy of diffusion*.

- In vacancy mechanism, energy is required to pull the atoms from their positions to vacant atomic sites.
- In the interstitialcy mechanism, energy required to force the atoms between other atoms to different interstitial positions.



Activation energy depends on the number of factors, they are,

1. A small atom has a lower activation energy than a large atom or molecule.
2. Interstitial movements require more energy than vacancy movements.
3. High activation energies are required for atomic diffusion for those materials which are strongly bonded and have higher melting points.

Example: Tungsten, boron carbide, SiC.

Factors affecting atomic diffusion:

- Temperature: high temperature provides the necessary activation energy to the atoms to begin diffusion , so a higher temperature initiates diffusion faster.
- Crystal structure: if a crystal structure is distorted i.e **if there** are more imperfections, the rate of diffusion is increased.
- Atomic packing factor: if APF is high, the rate of diffusion will be decreased. Diffusion is much slower in FCC-iron than in BCC-iron.

- **Grain boundaries**: The diffusion process proceeds more rapidly along the grain boundaries since it is a zone of crystal imperfections
- **Grain size**: since diffusion through grain boundaries is faster than through the grains themselves, a material with finer grains will have a faster rate of diffusion.
- **Atomic size**: Diffusion occurs more readily when the size of the diffusing atom is less. Example: Carbon in iron.
- **Concentration gradient**: higher the concentration gradient higher will be the rate of diffusion.



Thank You

Factors affecting atomic diffusion:

Temperature: Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighbouring atoms those need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion. Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature.

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

where D_0 is a pre-exponential (factor) constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature. From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient.