Diffusion in solids

The movement or jumping of atoms, within the solid is called diffusion. As the temperature is increased, the increased energy permits the atoms to vibrate into greater or shorter interatomic distances.

The activation energy for diffusion (Q) (cal /mole, J/atom or ev/ atom) depends upon the following factor:-

1- Atomic size → Greater the atomic size →higher Q
2- Bond strength → Greater the bond strength of solid → higher Q
3- Diffusion mechanism→ Vacancy diffusion mechanism needs higher Q than that for interstitial diffusion mechanism.

Classification of diffusion

1- Self diffusion:- The movement of atoms through their own structure is called self diffusion. This type studied experimentally by adding a trace of radioactive isotopes of Ni, into a normal Ni.

2- Inter diffusion:- The movement of atoms in two different metas from both sides into each other is called inter diffusion. The inter diffusion is observed in binary metal alloys such as Cu- Ni system.

3- Grain boundary diffusion:- The movement of atoms along the grain boundaries of a material is called grain boundary diffusion.

4- Surface diffusion:- The movement of atoms along the surface of material is called surface diffusion.

The diffusion process is governed by two laws derived by Fick in 1880.

Fick's first law gives the relation between the flux (the amount of substance flowing in unite time through unite surface area perpendicular to the flux, and the concentration gradient of the diffusing substance.

$$J= - D (\partial C/\partial X)$$

where:- J= the flux

C= concentration perpendicular to the direction of flow.

$(\partial C/\partial X)$= concentration gradient.

D= diffusion coefficient and it is a measure of the rate at which the system tends to eliminate the concentration difference (cm^2/sec).

Fick's second law gives the relation between the concentration gradient and the rate of change of concentration caused by:- diffusion at a point in the system:-

$$\partial C/\partial t = D\partial^2 C/\partial X^2$$

The relationship between (D) and temperature:-

$$D = D_0 \exp -Q/ RT$$

Where :- D_0 = frequency factor (cm^2/sec).

Q= activation energy of diffusion.

R = gas constant (1.987 cal. mol/ °K) or (8. 314 J/ mol. °K)

T = absolute temperature. (°K)

Factors affecting coefficients of diffusion:-

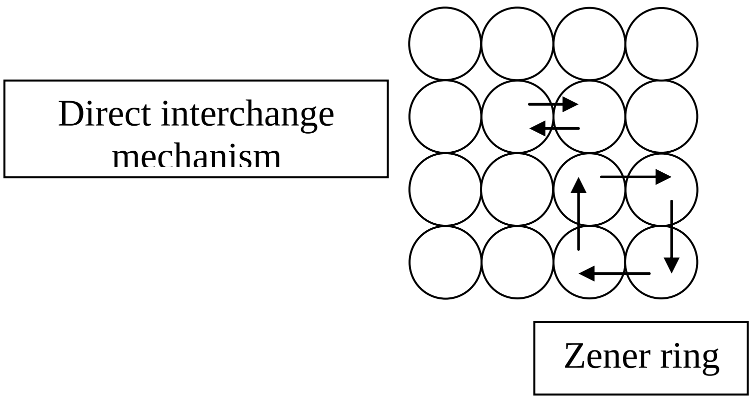
1- Temperature:- (D) increases exponentially with the increase in temperature.

2- Crystal structure:- (D) is higher for those crystal structures which have low packing density.

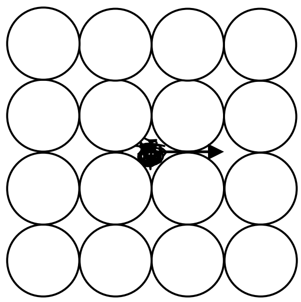
3- Atomic radius:- (D) in a binary solution is higher if the atomic radii of the solute and solvent different.
4- Melting temperature:- (D) is higher for the solids having lower melting temperatures.
5- Grain size:- (D) is higher for fine grain size materials than coarse grain size materials.

<u>Diffusion Mechanisms:-</u>

1- Direct Interchange Mechanism.
Two atoms interchange their positions; this process requires a large amount of energy in distorting the crystal as the atoms pass.
The Zener Ring mechanism of diffusion avoids the problem of having the atoms squeeze past one another, its proposes that a ring of atoms (may be 3 or 4) engages in a cooperative shift.



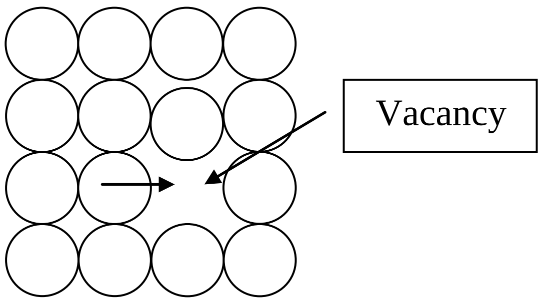
2- Interstitial Mechanism.
This type of mechanism occurs in those binary metallic alloys whose atomic radii differ in size significantly, for example the diffusion of carbon atoms in FCC or BCC iron takes place by interstitial mechanism.(atomic radius of C atom is 0.77 nm while that of FCC iron is 0.127 nm).



Interstitial Mechanism

3- Vacancy Mechanism.

The diffusion occurs because of the atoms jumping into the vacant sites, it may be noted that as the atoms move in one direction through vacancy mechanism the vacancies move in the opposite direction.



Vacancy Mechanism

Example:- Diffusion coefficient of Cu in Al needs to activation energy equal to $136 * 10^3$ J/ mol, while the frequency factor is $0.84 * 10^{-5}$ m^2 / sec.

Determine :- 1- Diffusion coefficient at 130 °C.

2- Distance which Cu atoms can be diffused through one day according to the relation:- $X^2 = 4Dt$,Take R = 8.314 J/ mol.°K.

Solution:-

$$T = 130 + 273 = 403 \text{ °K}$$

1- $D = D_0 \exp -Q/ RT$

$$D = 0.854 * 10^{-5} \exp (- 136 * 10^3 /8.314 * 403)$$

$$= 1.97 * 10^{-23} \text{ m}^2\text{/ sec.}$$

2- $X^2 = 4Dt$

$X^2 = 4 (1.97 * 10^{-23}$ m^2/ sec) (24 * 60 * 60) sec

$X^2 = 6.83 * 10^{-18}$ m^2

$X = 2.61 * 10^{-9}$ m = 26.1 A°.