Diffusion in Solids -

There are two main reasons for studying diffusion in solids.

First, a knowledge of diffusion is basic to an understanding of the changes that occur in solids at high~~t~~ temperatures.

Thus it is essential that the person interested in the kinetics of precipitation, oxidation, creep, annealing, etc, be acquainted with the fundamentals of diffusion.
familiar

Also, it is often the case that a more detailed study of these processes requires the use of the more advanced concepts of diffusion in solids.

The second reason for studying diffusion is to learn more about how atoms move in solids.

This is intimately connected with the study of point defects in solids & their movement.

Point defects are the simplest type of defect in a solid, yet their concentration & movement can not be observed directly.

Since the number of such defects & their movement can be theoretically related to the diffusion coefficient, diffusion experiments have come to be the most frequently used means of studying point defects in solids.

References -

Diffusion in Solids
Paul G. Shewmon
McGraw-Hill Book Company

Diffusion refers to the movement of atoms in solids.

Structural control in a solid to achieve the optimum properties is dependent on the rate of diffusion.

The carburization of a steel or the oxidation of a metal is controlled by the diffusion rate of atoms (or ions) through the surface layer.

The introduction of a very small concentration of an impurity in a solid state device requires knowledge of the diffusion phenomenon.

Diffusion in Solids - 'Diffusion Equations'

Changes in the structure of metals & their relation to physical & mechnanical properdies are the primary interest of the physical metallurgist.

Since most changes in structure occurs by diffusion, any real understanding of phase changes, homogenization, spheroidization*, etc, must be based on a knowledge of diffusion.

These kinetic processes can be treated by assuming that the metal is a continuum, that is, by ignoring the atomic structure of the solid. The problem then becomes one of obtaining & solving an appropirate differential equation.

Now we will discuss basic differential equations for diffusion, along with their solutions for the simpler boundary conditions, diffusion coefficient & its experimental determination.

At no point in Diffusion equation does the atomic nature of the material enter the problem.

This is not meant to detract from the importance of the study of atomic mechanisms in diffusion, since the most interesting & most active areas of study in diffusion are, & will continue to be, concerned with the information that diffusion studies can contribute to the atomic models of solids.

We initially omit models of diffusion to emphasize the types of problems that can be treated in this manner.

In any theoretical development there are certain advantages & disadvantages to making the fewest possible assumptions.

One advantage is that the results are quite generally applicable; a disadvantage is that the results are devoid of information about the atomic mechanism of the process. (Thermodynamics is an excellent example of this type of approach)

The assumption we make here, were first applied to the problem in 1855 by Adolf Fick.

It is indicative of the power of this approach that all the subsequent developments in the theory of solids have in no way affected the validity of the approach.

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Spheroidization
heat ~~tratme~~ treatment for iron based alloys
commonly carbon steel,
in order to convert them into
Ductile & machinable alloys.

It is conducted at temperatures that are slightly below the eutectoid temperature (temperature at which the solution is a solid solution rather than liquid), followed by a slow cooling process.

Diffusion –

is a mass flow process by which atoms (or molecules) change their positions relative to their neighbours in a given phase under the influence of thermal energy and a gradient.

The gradient can be a concentration gradient, an electric or magnetic field gradient or a stress gradient.

We shall consider mass flow under concentration gradients only.

Fick's macroscopic laws of diffusion

Consider unidirectional flow of matter in a binary system of A & B atoms.

The two types of atoms will move in opposite directions under the influence of a concentration gradient.

Let us assume that B is the only moving species.

Fick's first law states that

$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

$\frac{dn}{dt}$ → no. of moles of B atoms crossing per unit time a cross-sectional plane of area A, perpendicular to the diffusion direction x.

$$J = \frac{1}{A}\frac{dn}{dt} = -D\frac{dc}{dx}$$

Steady state Diffusion -

Diffusion is a time - dependent process
i.e. in a macroscopic sense, the quantity of an element that is transported within another is a function of time.

often it is necessary to know how fast diffusion occurs, or the rate of mass transfer. This rate is frequently expressed as diffusion flux (J), defined as the mass (or, equivalently, the number of atoms) M diffusing through and ~~a~~ perpendicular to a unit cross - sectional area of solid per unit time.

$$J = \frac{M}{At}$$

A → area across which diffusion is occurring
t → elapsed diffusion time

In differential form $$J = \frac{1}{A} \frac{dM}{dt}$$

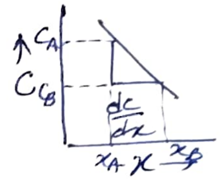
Unit of J → kg/m^2-s or $atoms/m^2-s$

If the diffusion flux does not change with time, a steady state condition exists.

One common example of Steady State diffusion -
the diffusion of atoms of a gas through a plate of metal for which the concentrations of the diffusing species on both surfaces of the plate are held constant.

When concentration C is plotted versus position (or distance) with in the solid x, the resulting curve is termed the concentration profile, the slope at a particular point on the curve is the concentration gradient :

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



$$= \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

unit of concentration
= mass of diffusing species per unit vol. of solid

= kg/m^3 or g/cm^3

Mathematically,

Steady state diffusion in a single (x) direction

$$J = -D\frac{\partial c}{\partial x} \qquad \text{①}$$

J → flux ⇒ flow per unit cross - sectional area per unit time

D → Diffusion coefficient (or diffusivity)
→ It is a constant characteristic of the system
→ It depends on the
- Nature of the diffusing species
- The matrix in which it is diffusing
- The temperature at which diffusion occurs

$\frac{\partial c}{\partial x}$ → concentration gradient in the x - direction

-ve sign → Indicates that the flow of matter occurs down the concentration gradient, from a high to a low concentration.

Equation ① is also called Fick's First law.

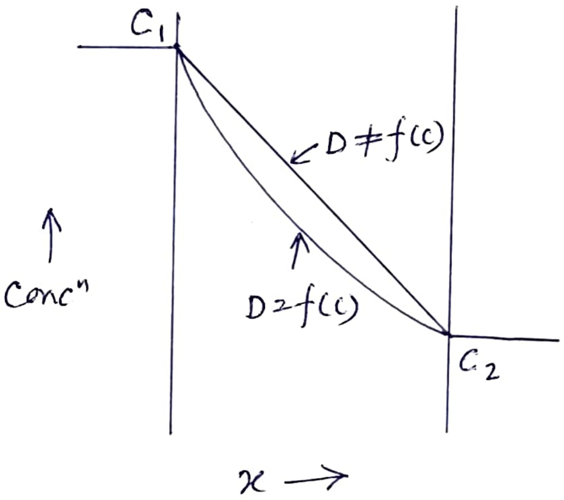
One practical example of steady state diffusion -

Purification of Hydrogen gas

One side of a thin sheet of palladium metal is exposed to the impure gas composed of hydrogen and other gaseous species such as nitrogen, oxygen and water vapor. The hydrogen selectively diffuses through the sheet to the opposite side, which is maintained at a constant and lower hydrogen pressure.

Fick's first law can be used to describe flow under steady state conditions. Under this condition, the flux is independent of time and remains the same at any cross sectional plane along the diffusion direction: $J \neq f(x,t)$

Concⁿ - distance profile under steady state flow



(i) if D is independent of concⁿ

$D \neq f(c)$

Profile is a straight line.

(ii) if D depends on concⁿ

$D = f(c)$

the profile will be such that the product $D\left(\frac{dc}{dx}\right)$ is a constant.

In neither case, the profile changes with time, under conditions of steady state flow.

Ex - A plate of iron is exposed to a carburizing (Carbon - rich) atmosphere on one side and a decarburizing (Carbon-deficient) atmosphere on the other side at 700°C. If a ~~st~~ condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 & 10 mm beneath the carburizing surface are 1.2 & 0.8 kg/m³, respectively. Assume a diffusion coefficient of 3×10^{-11} m²/s at this temperature.

$$J = -D \frac{\partial c}{\partial x}$$

$$J = -D \frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11} \, m^2/s) \frac{(1.2 - 0.8) \, kg/m^3}{(5 \times 10^{-3} - 10^{-2}) \, m}$$

$$= 2.4 \times 10^{-9} \, kg/m^2\text{-}s$$

Ex - A steel tank contains hydrogen at a constant pressure of 10 atm, with a vacuum outside. The hydrogen concentration at the inner surface of the tank is equal to 10 kg m^{-3}. The diffusion coefficient of hydrogen in steel at room temp is $10^{-9} \, m^2 s^{-1}$. Calculate the rate at which hydrogen escapes through the wall of the tank, which has a thickness of 5 mm.

As soon as steady state flow is established, a constant flux of hydrogen will escape through the tank wall, as the pressure drop inside is negligible.

There is vacuum on the outside. So, the concentration of hydrogen on the outer surface of the wall is zero.

$$J = -D \frac{\partial c}{\partial x} = 10^{-9} \times \frac{10}{5 \times 10^{-3}}$$

$$= 2 \times 10^{-6} \, kg \, m^{-2} s^{-1}$$