FICK'S FIRST LAW :-

If an inhomogeneous single-phase alloy is annealed, matter will flow in a manner which will decrease the concentration gradients.

If the specimen is annealed long enough, it will become homogeneous & the net flow of matter will cease.

Given the problem of obtaing a flux equation for this kind of a system, it would be reasonable to take the flux across a given plane to be proportional to the concentration gradient across that plane.

For example, if the x-axis is taken parallel to the concentration gradient of component 1 the flux of component 1 (J_1) along the gradient can be given by the equation

$$J_1 = -D_1 \left(\frac{\partial c_1}{\partial x}\right)_t \qquad -①$$

where D_1 is called the diffusion coefficient.
This equation is called Fick's first law & fits the empirical fact that the flux goes to zero as the specimen becomes homogeneous.

Although it need not have been the case, experiment shows that D_1, or equivalently the ratio of $-J_1$ to $\partial c_1 / dx$, is independent of the magnitude of $\partial c_1 / dx$.

In this respect eq^n (1) is similar to Ohm's law, where the resistance is independent of the voltage drop, or to the basic heat-flow equations in which the conductivity is independent of the magnitude of the temperature gradient.

To emphasize the dimensions of the terms, eq^n (1) is written again below with the dimensions of each term given in parentheses.

$$J\left(\frac{mass}{L^2 t}\right) = -D\left(\frac{L^2}{t}\right)\frac{\partial c}{\partial x}\left(\frac{mass/L^3}{L}\right)$$

The concentration can be given in a variety of units, but the flux must be put in consistent units.

The diffusion coefficient is almost always given in terms of square centimeters per seconds.

The units of concentration vary with the experiment & experimenter.

In a lattice with cubic symmetry, D has the same value in all directions, that is, the alloy is said to be isotropic in D.

If there are other types of gradients in the system, other terms are added to the flux equation. These effects are ~~interested~~ interesting but complicated. They will be considered later.

As an example of the application of eqⁿ (1), consider the following experiment performed by Smith.

A hollow cylinder of iron is held in the isothermal part of a furnace.

A carburizing gas is passed through the inside of the cylinder, & a decarburizing gas over the outside.

When the carbon concentration at each point in the cylinder no longer changes with time, that is,

$$\left(\frac{\partial c}{\partial t}\right)_x = 0,$$

& the quantity of carbon passing through the cylinder per unit time (q/t) is a constant.

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However, since J is the flow per unit area, it is a function of the radius r and is given by the equation

$$J = \frac{q}{At} = \frac{q}{2\pi r l t} \qquad \text{— (2)}$$

where l is the length of the cylinder through which carbon diffusion occurs.

Combining eq^n's (1) & (2) gives an equation for q, the total amount of carbon which passed through the cylinder during the time t:

$$q = -D\,(2\pi l t)\,\frac{dc}{d\ln r}$$

For a given run, q, l, and t can be measured.

If the carbon concentration through the cylinder ~~wall~~ wall is determined by chemical analysis, D can be determined from a plot of c versus $\ln r$. Such a plot will be a straight line if the diffusion coefficient does not vary with composition.

However, for carbon in γ-iron Smith found that the slope of this plot ($dc/d\ln r$) became smaller in passing from the low-carbon side of the tube to the high-carbon side.

An example of his result for 1000°C is shown in fig(1).
At this temperature the diffusion coefficient varies from 2.5×10^{-7} cm^2/sec at 0.15 weight percent carbon to 7.7×10^{-7} cm^2/sec at 1.4 wt. percent carbon.

Similar experiments have frequently been performed by passing a gas through a metal membrane.

Often the membranes are so thin, it is impossible to determine the concentration as a function of distance in the membrane by means of chemical analysis.

The experimental results therefore consist of a measured steady-state flux, the pressure drop across the membrane, and the thickness of the

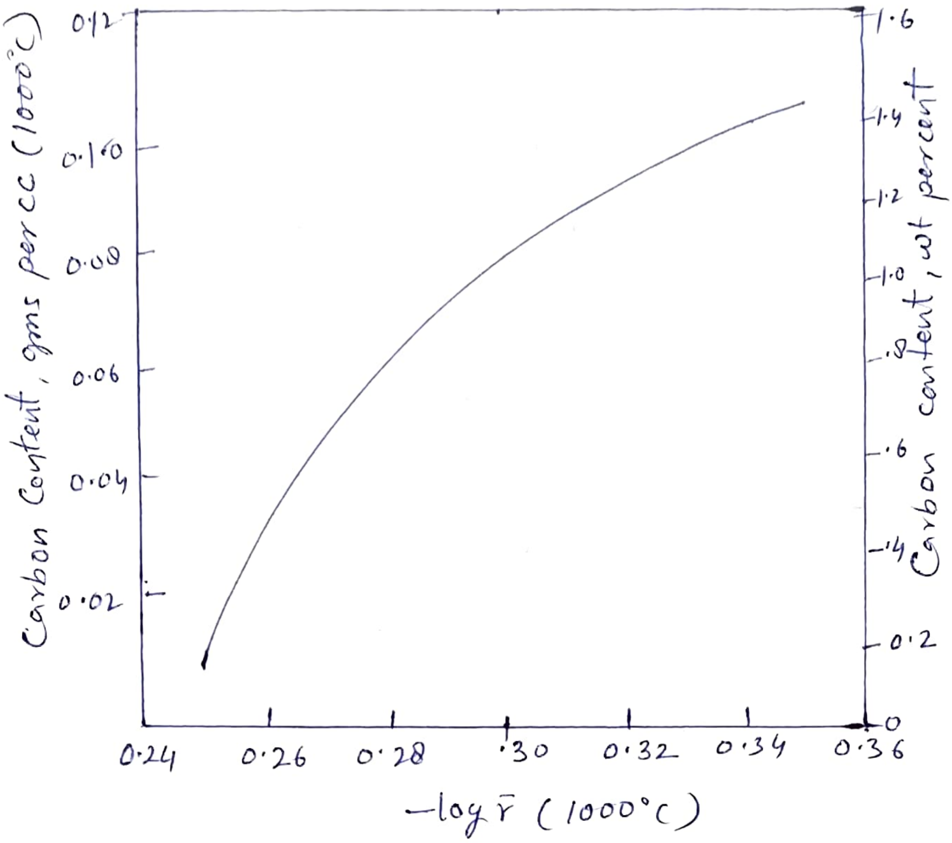

Fig 1: $\bar{c}$ versus log $\bar{r}$ for a hollow cylinder of iron which attained a steady state with a ~~de~~carburizing gas passing through the inside and a decarburizing gas passing over the outside.

membrane (Δy).

This flux, for a given pressure drop, is called the permeability.

To obtain a value of D from these data, the value of $\partial c / \partial y$ inside the membrane must be determined.

One way to do this is to assume that the value of c in the metal at each gas-metal interface is the value that would exist in equilibrium with the gas if there were no net flux.

This would be true if the solution of gas in the surface ~~in the surface~~ of the metal occured much more rapidly than the diffusion out of the surface region into the rest of the metal.

Experimentally, this assumption is checked by determining the fluxes for two thicknesses of membrane under the same pressure differential & at the same temperature.

If equilibrium does exist at the gas-metal interface, then ΔC is the same for both cases, & eqn (1) gives

$$J = -D\frac{\Delta C}{\Delta y}$$

That is, J will be inversely proportional to Δy.

At the other extreme, if the rate of solution of gas at the interface is what determines the flux, the flux will be the same for both values of membrane thickness, and no value of D can be obtained from the flux.

Fick's Second Law

is an extension of the first law to non-steady state flow.

Here, at any given instant,

the flux is not the same at different coss-sectional planes along the diffusion direction x.

Also, at the same cross-section, the flux is not the same at different times.

Consequently, the concentration distance profile changes with time.

Non-steady state flow is frequently met with in practical applications of the diffusion laws.

Consider an elemental slab of thickness Δx along the diffusion distance x.

Let the slab cross-section be perpendicular to x and its area be unity. The volume of the slab is then Δx.

Under non-steady state conditions, the flux into the slab J_x is not equal to the flux out of the slab, $J_{x+\Delta x}$.

The rate of accumulation (or depletion) of the diffusing atoms within this elemental volume is $\left(\frac{\partial c}{\partial t}\right)\Delta x$. It can be expressed as the difference of fluxes in and out of the slab

$$\frac{\partial c}{\partial t} \cdot \Delta x = J_x - J_{x+\Delta x}$$

$$= J_x - \left(J_x + \frac{\partial J}{\partial x} \Delta x \right)$$

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

$$= - \frac{\partial}{\partial x} \left(-D \frac{\partial c}{\partial x} \right)$$

$$\boxed{\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right)}$$

This is fick's second law for unidirectional flow under non steady state conditions.

If D is independent of concentration

$$\boxed{\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}}$$