

Solution for variable D:

All of the solutions discussed so far have been valid only for constant D.

In real experiments the diffusion coefficient can, and will vary. The diffusion coefficient for a given composition can vary with time, owing to changes in temperature. It can also change with composition, and since there is concentration gradient, this means that D changes with position along the sample. In this latter case $D = D(x)$, & Fick's second law must be written as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) = \frac{\partial D}{\partial x} \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} \quad \text{--- (1)}$$

The term $\partial D / \partial x$ makes the eqⁿ inhomogeneous, and the solution in closed form then ranges from difficult (for special cases) to impossible.

We will first discuss the solution for $D = D(c)$ which is most frequently used in solids & then show how to treat the case in which $D = D(t)$.

Boltzmann - Matano Analysis -

This is the solution for $D = D(c)$ most commonly referred to in metallurgical diffusion studies. It will serve as an example of the different line of attack required.

It does not give a solution $c(x, t)$, as obtained before, but allows $D(c)$ to be calculated from an experimental $c(x)$ plot. If the initial conditions can be described in terms of the one variable $\eta \equiv x/t^{1/2}$, c is a function only of η , & eqⁿ (1) can be transformed into an ordinary homogeneous differential equation. Using the definition of η , we have

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \eta} \frac{\partial \eta}{\partial t} = -\frac{1}{2} \frac{x}{t^{3/2}} \frac{dc}{d\eta} \quad \eta^2 = \frac{x}{t^{1/2}}$$

$$\& \quad \frac{\partial c}{\partial x} = \frac{\partial c}{\partial \eta} \frac{\partial \eta}{\partial x} = \frac{1}{t^{1/2}} \frac{dc}{d\eta}$$

Substituting in the first part of eqⁿ (1), we obtain

(16)

$$-\frac{x}{2t^{3/2}} \frac{dc}{d\eta} = \frac{\partial}{\partial x} \left(\frac{D}{t^{1/2}} \frac{dc}{d\eta} \right) = \frac{1}{t} \frac{d}{d\eta} \left(D \frac{dc}{d\eta} \right)$$

$$-\frac{\eta}{2} \frac{dc}{d\eta} = \frac{d}{d\eta} \left(D \frac{dc}{d\eta} \right) \quad \text{--- (2)}$$

This transformation of eqⁿ (1) into eqⁿ (2) is due to Boltzmann. The method was first used to determine $D(c)$ by Matano.

Consider the infinite diffusion couple which is described by the following initial conditions:

$$c = c_0 \quad \text{for } x < 0, \quad \text{at } t = 0$$

$$c = 0 \quad \text{for } x > 0, \quad \text{at } t = 0$$

Since $x=0$ is excluded at $t=0$ and the original concentration is not a function of distance aside from the discontinuity at $x=0$, the initial conditions can be expressed in terms of η only as

$$c = c_0 \quad \text{at } \eta = -\infty$$

$$c = 0 \quad \text{at } \eta = \infty$$

Since eqⁿ (2) contains only total differentials, we can "cancel" $1/d\eta$ from each side & integrate b/w $c=0$ & $c=c'$, where c' is any concentration $0 < c' < c_0$.

$$-\frac{1}{2} \int_{c=0}^{c=c'} \eta dc = \left[D \frac{dc}{d\eta} \right]_{c=0}^{c=c'}$$

The data on $c(x)$ are always at some fixed time so that substituting for η gives

$$-\frac{1}{2} \int_0^{c'} x dc = \int_0^{c'} Dt \left[\frac{dc}{dx} \right]_{c=0}^{c=c'} = Dt \left(\frac{\partial c}{\partial x} \right)_{c=c'} \quad \text{--- (3)}$$

The last quantity in eqⁿ (3), comes from the fact that in this infinite system $dc/dx = 0$ at $c = 0$. From the additional fact that $dc/dx = 0$ at $c = c_0$, we have the condition

$$\int_0^{c_0} x \, dc = 0 \quad \text{--- (4)}$$

so that eqⁿ (4) defines the plane at which $x = 0$. with this definition of x , $D(c')$ can be obtained from the graphical integration & determination of $c(x)$ using the eqⁿ

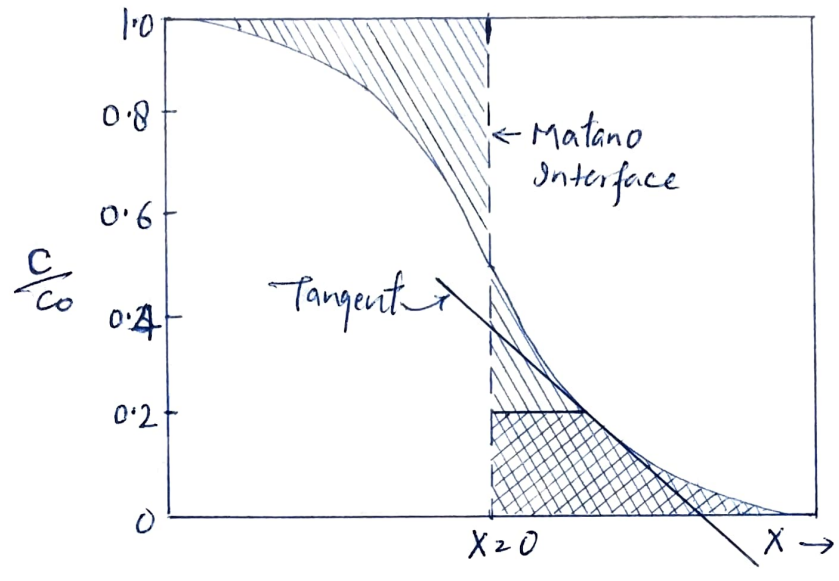
$$\cancel{D(c')} \quad D(c') = -\frac{1}{2t} \left(\frac{dx}{dc} \right)_c \int_0^{c'} x \, dc \quad \text{--- (5)}$$

Application of Boltzmann - Matano Solution -

The quantities needed to calculate ^a value of D are shown in fig1. The Matano interface is the plane at which $x = 0$ in eqⁿ (4). Graphically, it is the line that makes the two hatched areas of fig1, equal. The values of D at $c = 0.2c_0$ would be calculated by measuring the cross-hatched area of the figure, and the reciprocal of the slope.

The errors in the calculated values of $D(c)$ are largest at $\frac{c}{c_0} \approx 1$ and $\frac{c}{c_0} \approx 0$, since in these regions the integral is very small and dx/dc very large. In an effort to minimize these errors, the original concentration vs distance data are usually plotted on probability paper, and the best line through the points used to make a plot is similar to fig1.

This solution, which is quite useful for obtaining a composite value of D over a range of compositions, has been used during the last 25 years for what are now considered survey studies. For studies of the atoms in binary alloy, this technique has been largely superseded by tracer techniques.



Fig(1) The Matano interface is positioned to make the hatched areas on either side of it equal. The cross-hatched area & tangent show the quantities involved in calculating D at $c = 0.2c_0$.

Solutions for D a function of time :

If D is a function of time but not of position, inspection of eqⁿ ①

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

shows that the eqⁿ reduces to $\frac{\partial c}{\partial t} = D(t) \frac{\partial^2 c}{\partial x^2}$

What this means is that all of the solutions which were used for constant D can be used, but the product Dt must be replaced by an averaged product designated \overline{Dt} & given by the eqⁿ

$$\overline{Dt} = \int_0^t D(t) dt \quad \text{--- (6)}$$

The most common application of this eqⁿ is to correct for the diffusion that occurs during the heating & cooling of a diffusion couple which has been annealed at some fixed temp, although it can also be used to calculate the degree of homogenization achieved during a complicated annealing cycle.

the application of

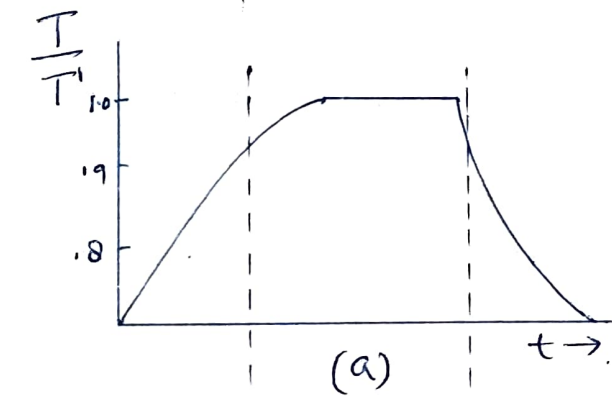
As an example of $\int_n \exp^n(t)$, consider a diffusion couple that has the temperature time history shown in fig 2(a).

The problem is to determine the time t' at temperature T' which would have produced the same amount of diffusion as actually occurred during the heating, annealing, and cooling.

This can be determined graphically once the T versus t data are transformed into a plot of D versus t . This has been done in fig 2(b).

It is seen that time spent in heating up to $0.8T'$ contributes nothing to the total amount of diffusion. This stems from the fact that $D(T)$ is given by an \exp^n of the form

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



For many cases Q is such that near the melting point of the metal D increases by a factor of 10 for each increase of 10% in the absolute temp. Fig (ab) was obtained by using this relationship.

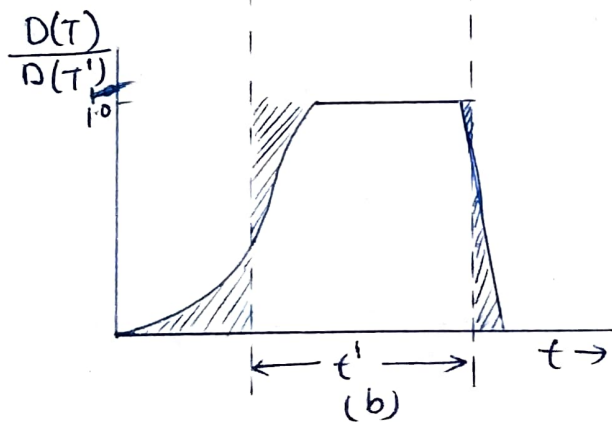


Fig 2. (a) Temperature versus time record of diffusion sample.
(b) D versus time for same sample

t' is the time at T' which would give the same amount of diffusion as actually occurred in the cycle.