Solution for a pair of semi-infinite solids:

Consider the initial distribution ~~x~~ which results if a piece of pure A is joined to pure B without interdiffusion. This distribution is shown graphically in fig (4) the boundary conditions are given by

$C = 0$ for $x < 0$, at $t = 0$

$C = C'$ for $x > 0$, at $t = 0$

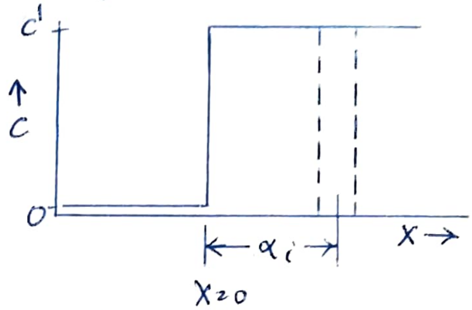


Fig (4)

A solution to the diffusion eq^n for this case can be obtained in the following manner:

Imagine that the region of $x > 0$ consists of n slices, each of thickness $\Delta\alpha$ x unit cross sectional area.

Consider one particular slice. It initially contains $c'\Delta\alpha$ of solute, and if the surrounding regions were initially solute free, the distribution after some diffusion would be that given by the thin film solution ie by eq^n

$$C = \frac{\alpha}{2\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \quad \text{———} \quad (14)$$

The fact that there is solute in the adjacent slices does not in any way affect this result, and the actual solution is thus given by a superposition of the distributions from the individual slabs.

If α_i is the distance from the center of the ith slice to $x = 0$, the Conc^n at any given value of x after time t will be

$$C(x,t) \simeq \frac{c'}{2\sqrt{\pi D t}} \sum_{i=1}^{n} \Delta\alpha_i \exp\left[-\frac{(x-\alpha_i)^2}{4Dt}\right] \quad \text{——} (15)$$

Fig (5), shows how these various exponentials superimpose to give the actual distribution for the case of rather thick slices. In the limit of n going to infinity, $\Delta\alpha_i$ goes to zero, and from the definition of an integral

$$C(x,t) = \frac{c'}{2\sqrt{\pi D t}} \int_0^{\infty} \exp\left[-\frac{(x-\alpha)^2}{4Dt}\right] d\alpha_i \quad \text{——} (16)$$

Substituding $(x-\alpha)/2\sqrt{Dt} = \eta$

$$c(x,t) = \frac{c'}{\sqrt{\pi}} \int_{-\infty}^{x/2\sqrt{Dt}} \exp(-\eta^2)\, d\eta \qquad —(17)$$

This type of integral appears quite generally in the solutions of problems where the initial source of solute is an extended one and the diffusion distance $2\sqrt{Dt}$ is small relative to the length of the system.

The integral can not be evaluated in any simple manner, but because of its frequent apperance in diffusion & heat flow problems, its values are available in tabular form, in the name of error function.

The error function is defined by the equation

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^{z} \exp(-\eta^2)\, d\eta \qquad —(18)$$

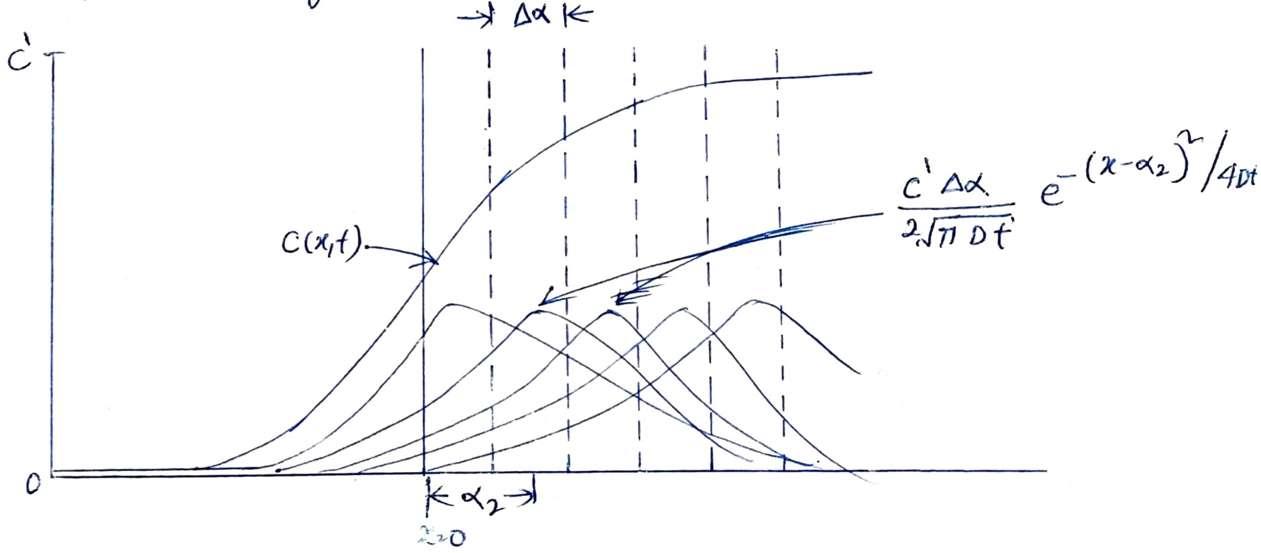
It can be shown that $\mathrm{erf}(\infty) = 1$, & it is evident that

$$\mathrm{erf}(-z) = -\mathrm{erf}(z)$$

eq^n (17) can thus be written as

$$c(x,t) = \frac{c'}{2}\left[1 + \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad —(19)$$

this is plotted in fig (5).



Fig(5): c(x,t) is the sum of the exponential curves which represent the solute diffusing out of each slab $\Delta\alpha$ thick.

It should be noted that each value of the ratio c/c' is associated with a particular value of $z \equiv x/2\sqrt{Dt}$. Thus $z=1$ is always associated with $c/c' = 0.92$, the position of the plane whose composition is $0.92c'$ is given by the equation $x = 2\sqrt{Dt}$.

Further inspection shows that each composition moves away from the plane of $x=0$ at a rate proportional to $\sqrt{Dt}$, with the exception of $c = c'/2$, which corresponds to $z=0$ & thus remains at $x=0$.

'Infinite' system - Surface composition constant -

It has already been pointed out that the composition at the plane $x=0$ in eq^n (19) does not change with time. Thus eq^n (19) in the region $x>0$ can be used for the case in which an initially homogeneous alloy of solute c' is held in an atmosphere which reduces the surface concentration to $c'/2$ and keeps it there for all $t>0$. The boundary conditions are

$$c = \frac{c'}{2} \quad \text{for} \quad x=0, \quad \text{at } t>0$$

$$c = c' \quad \text{for} \quad x>0, \quad \text{at } t=0$$

and the solution is still eq^n (19). If the surface concentration is held at $c=0$ instead of $c'/2$ for all $t>0$, the solution becomes

$$c(x,t) = c' \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \text{——(20)}$$

If the surface concentration of an initially solute-free specimen is maintained at some composition c'' for all $t>0$, solute is added to the specimen, and the solution is equivalent to eq^n (19) in the region $x<0$. Since $\operatorname{erf}(-z) = -\operatorname{erf}(z)$, the solution for this case (in the region $x>0$) is

$$c(x,t) = c''\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad \text{——(21)}$$

Inspection of this eq^n shows that it fits the situation, since for $x=0$, $c=c''$ and at $x \gg 2\sqrt{Dt}$, $c \simeq 0$.

It should be pointed out that in any of the solutions, given by eq's (14) & (19) to (21) the zero of concentration can be shifted to fit the case where the initial or surface concentration is not zero, but some other constant value, say C_0. As an example, if the boundary conditions are

$$C = C_0 \quad \text{for} \quad x > 0 \, , \quad \text{at} \quad t = 0$$

$$C = C' \quad \text{for} \quad x < 0 \, , \quad \text{at} \quad t = 0$$

the solution is simply changed to

$$C(x,t) - C_0 = \frac{C' - C_0}{2} \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}} \right) \right] \qquad \text{— (22)}$$

Application of Error-Function solution-

The assumption of a constant D independent of position in the couple places a severe restriction on the use of this type of solution in making accurate determinations of D.

If D is to be measured with a tracer in a chemically homogeneous alloy, it is usually easier to use the thin film solution discussed earlier.

On the otherhand, if D is to be determined in a couple which has a range of chemical compositions in it, D will usually vary with position, ie., composition, and the Matano-Boltzmann solution will be required.

In spite of these restrictions on the use of error-function solutions, eqⁿ (19) has been used by Johnson to accurately determine D for radioactive gold in a 50 : 50 Au-Ag alloy and to determine the chemical D in the range 45 to 55% Au.

The most frequent use of the error-function solutions arises when it is ~~determined~~ desired to estimate the amount of diffusion that will occur in a system where D is known to vary across the diffusion zone.

A complete solution of the problem with a variable D is quite time-consuming, and essentially the same answer can be obtained by using an ~~va~~ average value of D. This problem is found in the carburizing or decarburizing of steel, for which eq's (20) & (21) will often give adequate answers.

Another case, in which these same equations would not give as accurate an answer, is in the dezincing of a Cu-Zn alloy. Here, as the zinc is removed, the sample shrinks, thus moving the original interface relative to the interior of the sample. No shrinkage was allowed for in the derivations of eqn's (19) to (21), this further detracts from the accuracy of the answers obtained with these equations.

Separation of Variables -

The above solutions have dealt with infinite systems. We now turn briefly to the type of solution which is simplest for "small systems", that is, for those which approach complete homogenization.

It is first assumed that there exist solutions which are the product of a function only of time T(t) and a function of distance X(x). That is, we assume that

$$C(x,t) = X(x)\,T(t) \qquad — (23)$$

It may be noted that the solutions discussed up to this point are excluded from this family since they are of the form $c(x,t) = f(x/\sqrt{Dt})$.

If we differentiate eqn (23) in the prescribed manner & substitute ~~it~~ in Fick's second law, the result is

Ficks II law

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

$$X\frac{dT}{dt} = DT\frac{d^2X}{dx^2}$$

or

$$\frac{1}{DT}\frac{dT}{dt} = \frac{1}{X}\frac{d^2X}{dx^2} \qquad —— (24)$$

The equation now contains only total differentials. The left side is a function only of time, and the right side ~~is~~ a function only of distance.

But since x & t can be varied independently eqⁿ (24) can be satisfied only if both sides of the equation are equal to a constant. This constant will be designated as $-\lambda^2$, where λ is a real number.

The differential equation in time then is

$$\frac{1}{T}\frac{dT}{dt} = -\lambda^2 D$$

which integrates to

$$T = T_0 \exp(-\lambda^2 D t) \quad \text{--- (25)}$$

Where T_0 is a constant.

The reason for requiring that the quantity $-\lambda^2$ have only −ve values stems from our desire to deal only with systems in which any inhomogenities disappear as time passes, ie, that T approaches zero as t- increases.

The equation in X is
$$\frac{d^2X}{dx^2} + \lambda^2 X = 0$$

Since λ^2 is alway +ve, the solution to this eqⁿ is of the form

$$X(x) = A' \sin \lambda x + B' \cos \lambda x \quad \text{--- (26)}$$

where A' & B' are constants.

Combining eqⁿ (25) & (26) gives

$$C(x,t) = (A \sin \lambda x + B \cos \lambda x) \exp(-\lambda^2 \cancel{t} D t)$$

But if this solution holds for any real value of λ, then a sum of solutions with different values of λ is also a solution. Thus in its most general form the product solution will be an infinite series of the form

$$C(x,t) = \sum_{n=1}^{\infty} (A_n \sin \lambda_n x + B_n \cos \lambda_n x) \exp(-\lambda_n^2 D t) \quad \text{--- (27)}$$