

# DIFFUSION

METE 327, Fall 2008

# DIFFUSION

What do we mean by Diffusion? The movement of atoms in a solution. We will be concerned with solid solutions.

For Metals, we will first consider substitutional solid solutions.

Interstitial solid solutions will also be considered.

MOST CHANGES THAT OCCUR AT HIGH TEMPERATURE, OVER TIME, OCCUR BY DIFFUSION.

Kinetics—treat the metal as a continuum

Adolf Fick in 1855 posed two important equations

All of the subsequent knowledge in the Theory of Solids has not invalidated his approach!

First Law: The flux across a plane is proportional to the concentration gradient across the plane.

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

This satisfies requirement that Flux goes to zero as the specimen becomes homogeneous.

J is in units of (mass/length<sup>2</sup> time), flux

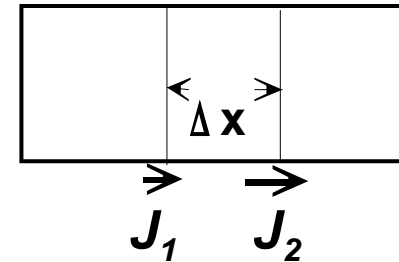
D is the diffusion coefficient, and has units of (length<sup>2</sup>/time)

c is concentration, (mass/volume) and x is (length)

diff1

Fick's Second Law: If a steady state does not exist, or the concentration at some point is changing with time, then

$$J_1 = J_2 - \Delta x \frac{\partial J}{\partial x}$$



$$J_1 - J_2 = \Delta x (\partial c / \partial t) = -\Delta x (\partial J / \partial x)$$

and inserting the first law into this we obtain:

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

Which is Fick's Second Law.

$$\frac{(\partial c)}{(\partial t)} = D \Delta^2 c$$

**At steady state, the change of concentration with time is zero. So the differential equation to solve is:**

$$D \Delta^2 c = 0$$

This is the mathematical foundation for diffusion equations. Note that we have not said anything about atomistics or mechanisms.

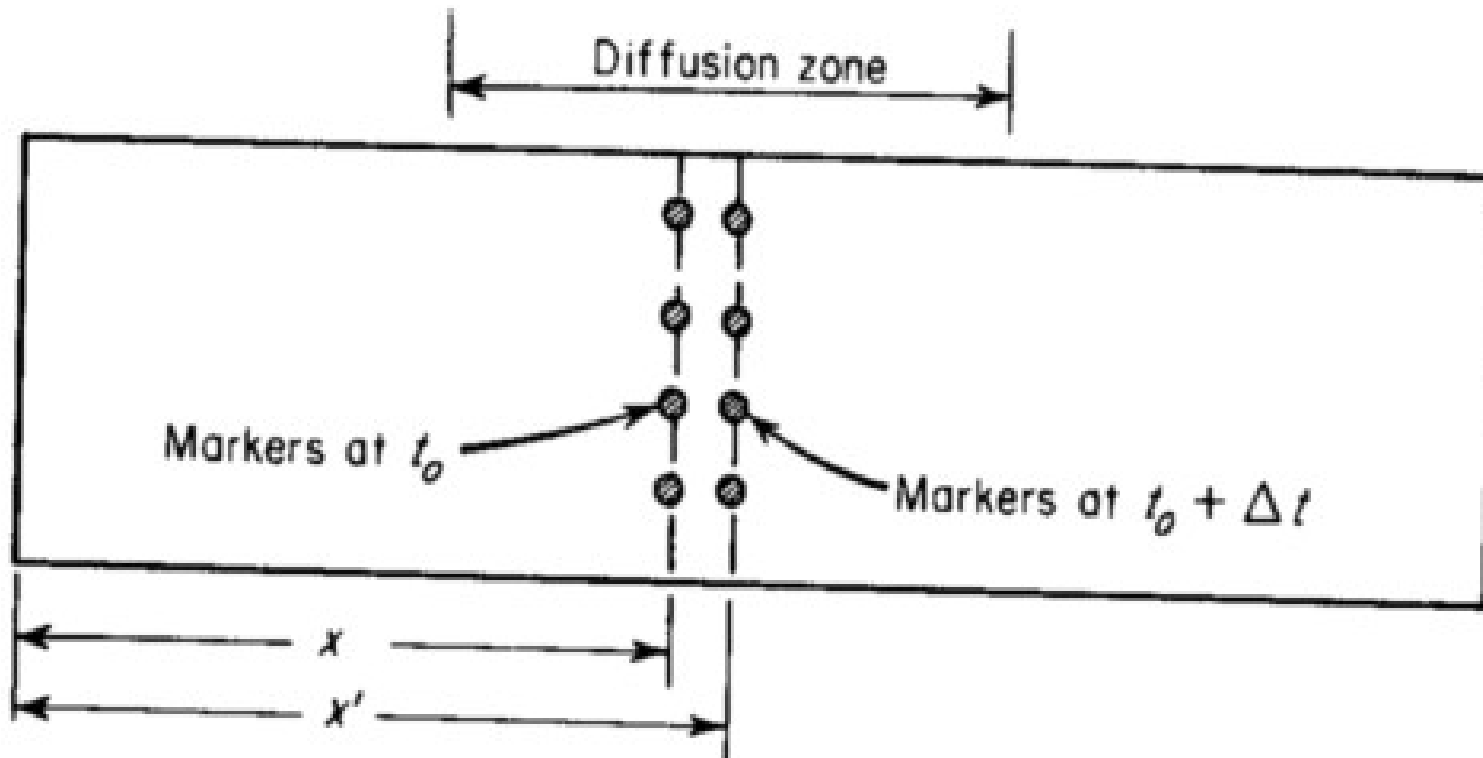
Next, we deal with more of the Historical Perspective.





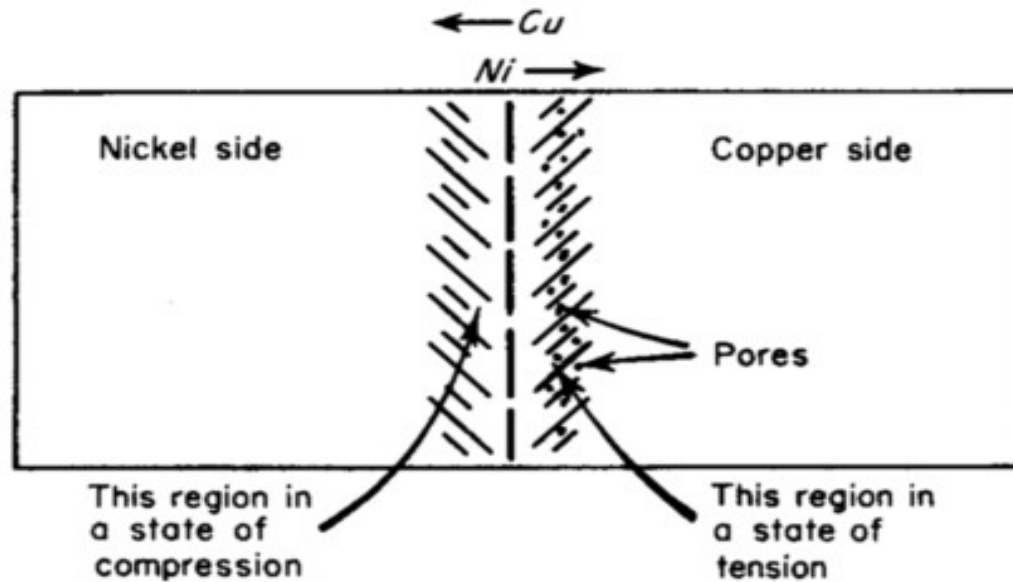
# The Smigelskas-Kirdendall Experiment

Marker movements, as measured from one end of a bar.



It must be noted that there are three fluxes to be considered: the flux of A atoms in one direction, the flux of B atoms in the other direction, and if they are not equal, the flux of vacancies that will balance these, and cause the markers to move.

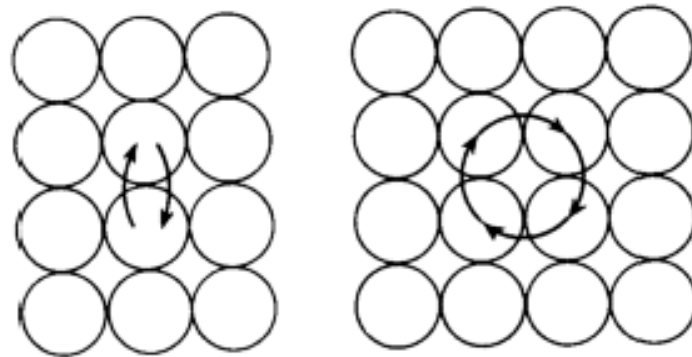
This can lead to porosity, as shown below:



## Mechanism:

Up to the S-K experimental result, it was thought that  $D$  was the same for both metals.

It was also assumed that some sort of ring or exchange mechanism was operating.



These mechanisms do not allow for different diffusion rates.

Discussion of the paper: Printed after the paper—not done today!

Smoluchowski—“The paper indicates in a most convincing manner that diffusion is not only a question of movement of two kinds of atoms, but that there is also a third “constituent”, the vacancies.”

Mehl—“Simple atom interchange is the most likely mechanism...” “If verified, this “Kirkendall effect” would greatly modify..the theory of the mechanism of diffusion.”

Darken—“ I should like to congratulate the authors for performing and reporting these highly significant experiments...it has been recognized for some time that in scale and tarnish the mobilities of different ions are not equal...” and, “The most likely mechanism of diffusion seems to involve the motion of dislocations...”

No matter how obvious this might seem today, it was not fully accepted for some time thereafter. In the discussion of Darken's paper some of the main researchers at the time said:

“The lack of consideration of the mechanism of the diffusion process is a major weakness....” and “Another major difficulty is that it is based on one experiment of questionable validity.” “If a chip is thrown into a stream, be it of mercury, water or brass, the chip will respond immediately to acceleration of the surrounding stream only if the chip surface is wetted by the stream.” “Nor is it easy to visualize the movement of a massive wire by a series of processes, the units of which involve not more than a few dozen atoms.” And on for about four pages.

Another discussor said, “ I believe that Darken’s analysis of the two component diffusion case is excellent....Dr. Darken does not really have anything to say about mechanism at all....If there are two diffusivities, then the markers must move. If the markers move, and if there are two diffusivities, the Dr. Darken’s paper tells us how to treat the problem. Detailed discussions of the ‘truth’ of the Smigelskas-Kirkendall experiments do not mitigate against the validity of Darken’s analysis based on his assumptions.”

So, in 1948, it was still quite difficult to accept the idea that vacancies had a major role to play in the diffusion process, and even the correct mathematical formulation, that did not speak of mechanism, aroused controversy, because it was not easy to accept that different metal atoms would diffuse at different rates.

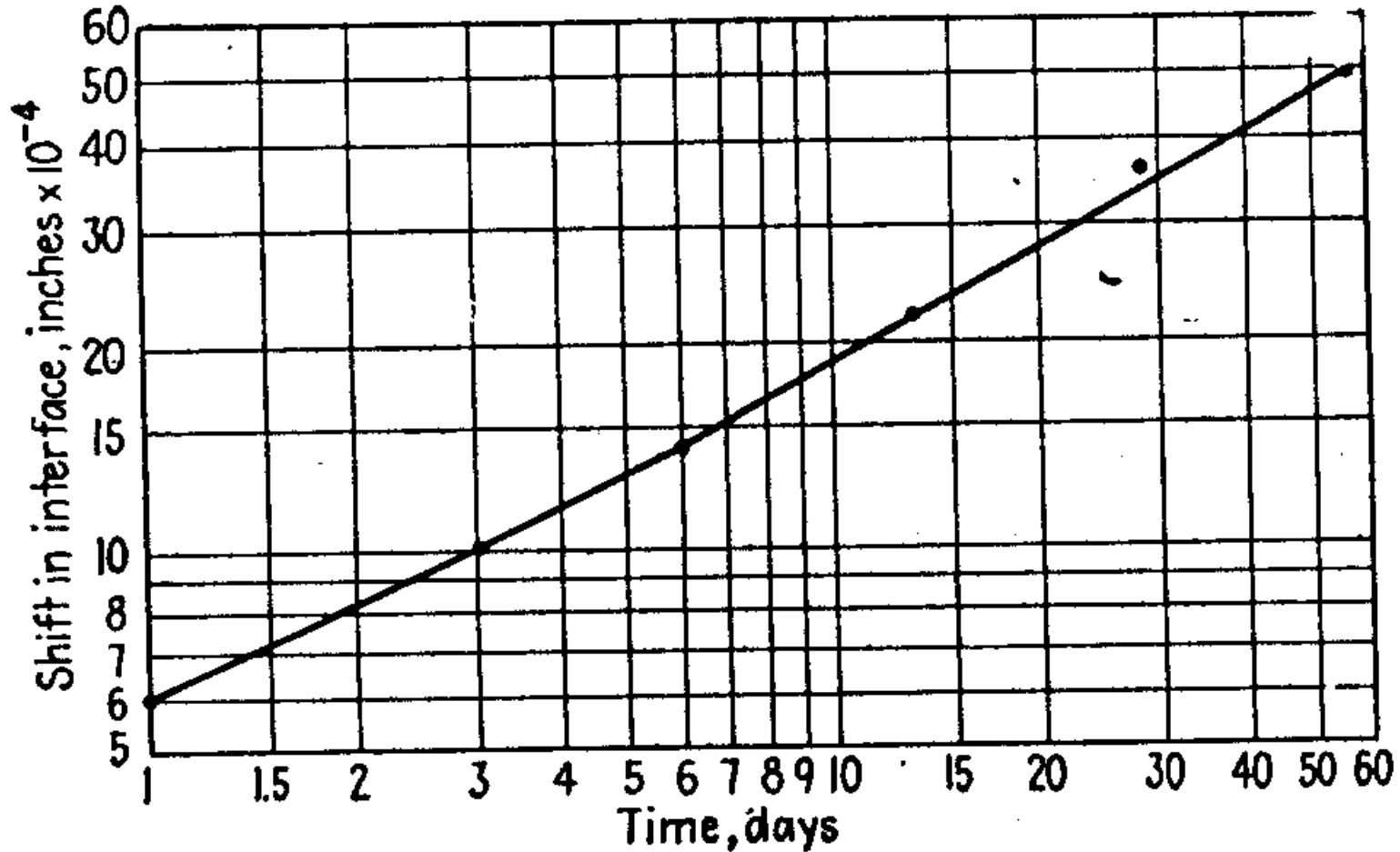


FIG. 2—EFFECT OF AMOUNT OF DIFFUSION ON LOCATION OF INTERFACE.

... of the 26 day ... and no correction had to be made

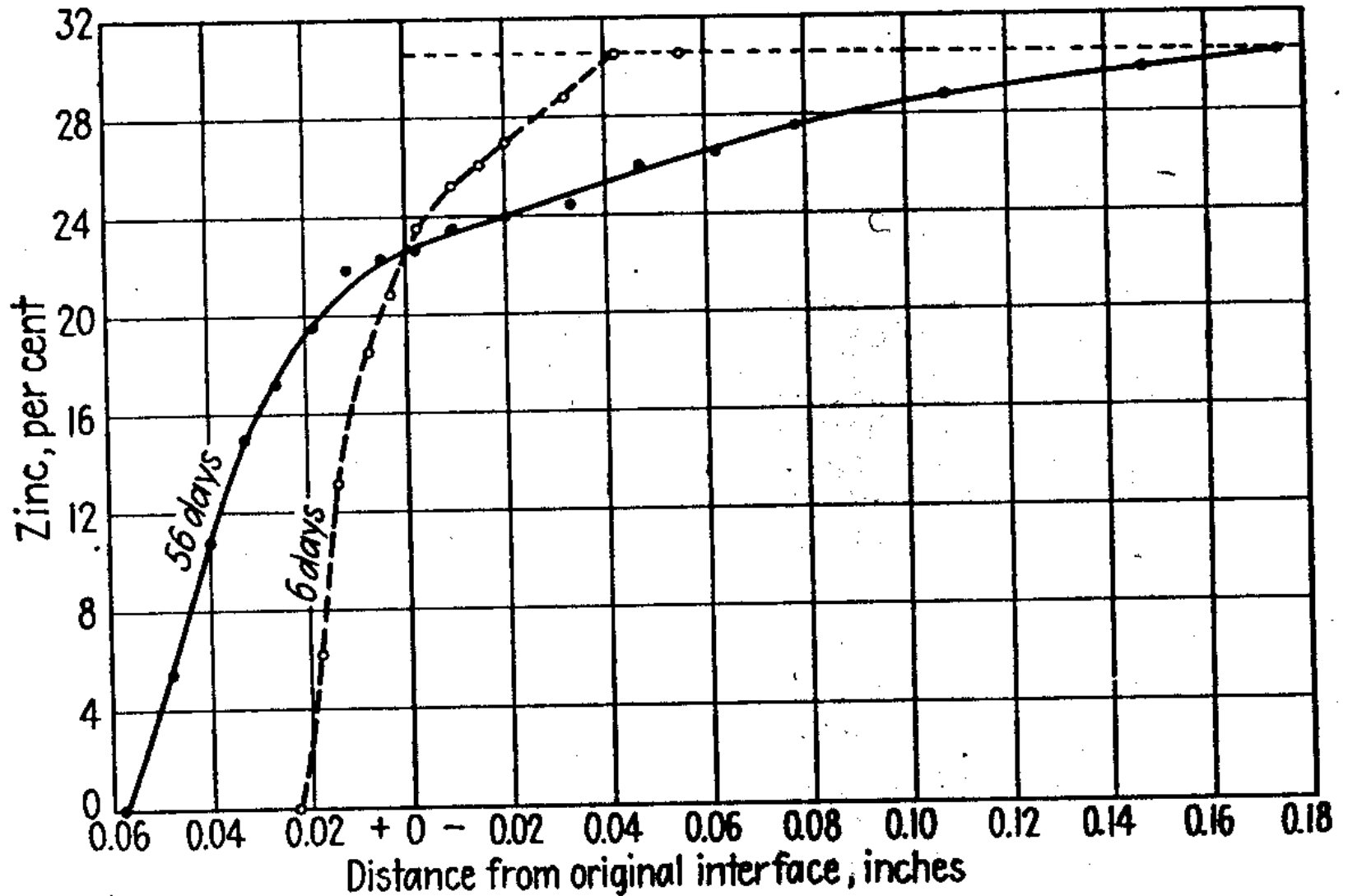


FIG 3.—DIFFUSION PENETRATION CURVES FOR 6-DAY AND 56-DAY SAMPLES.  
The interface is a moving plane identified by molybdenum wires.

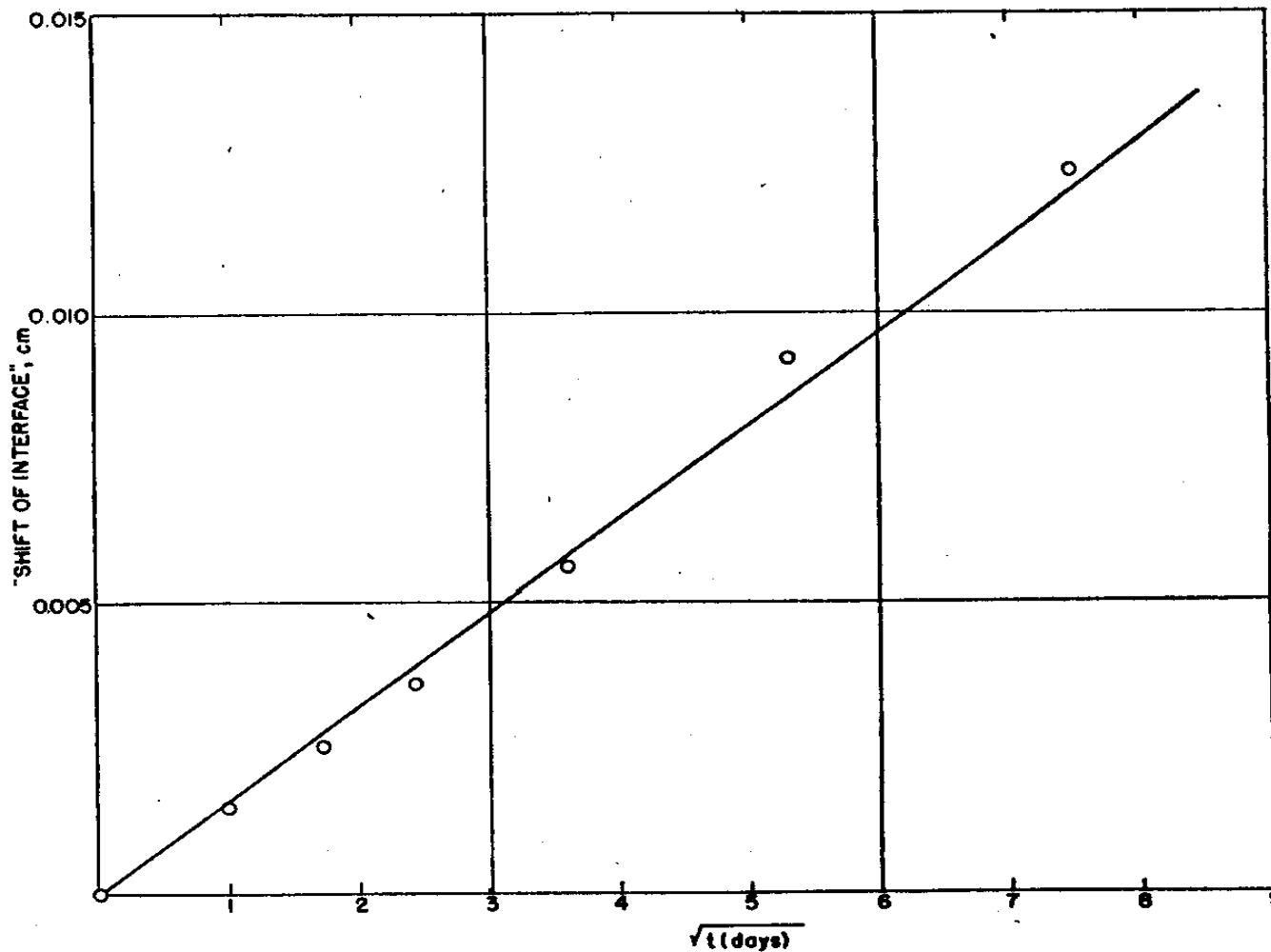


FIG 1—DATA OF SMIGELSKAS AND KIRKENDALL FOR DIFFUSION IN BRASS PLOTTED TO SHOW LINEAR VARIATION OF SHIFT IN POSITION OF INERT MARKERS WITH SQUARE ROOT OF TIME OF DIFFUSION IN ACCORDANCE WITH EQ 9.

Darken's Analogy: Consider a flowing stream. Suppose that some ink were introduced into the stream. How should one measure the diffusion of the ink, without complication of the moving stream? Consider some chips floating in the stream. These move at the same velocity as the stream, and so it is possible to establish a coordinate system for the diffusion process that is fixed on the chips.

Darken proposed that the velocity of the chips or markers could

be written:  $v = (D_A - D_B) \frac{\partial N_A}{\partial x}$

or:  $v = (D_B - D_A) \frac{\partial N_B}{\partial x}$

$N_A = f(\lambda)$  where  $\lambda = \frac{x}{\sqrt{t}}$

Darken's Second Equation:

$$\tilde{D} = N_B D_A + N_A D_B$$

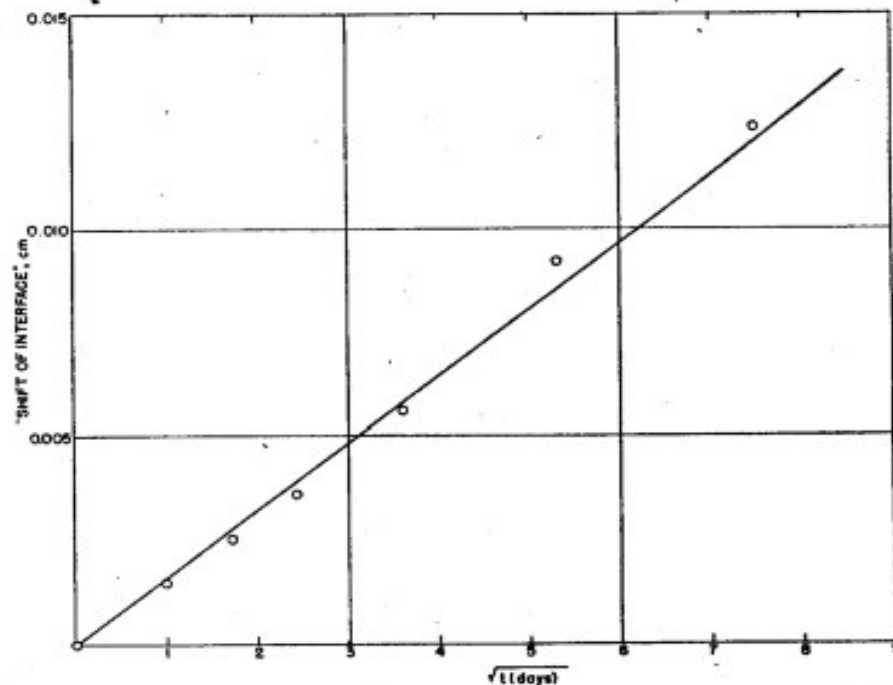


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The solution for a diffusion couple of two alloys of elements A and B with one composition  $N_{A1}$  and the other composition  $N_{A2}$  is at the start of the diffusion process:

$$N_A = N_{A1} + \frac{(N_{A2} - N_{A1})}{2} \left[ 1 + \operatorname{erf} \frac{x}{2\sqrt{\tilde{D}t}} \right]$$

where  $N_A$  is the composition or atom fraction at

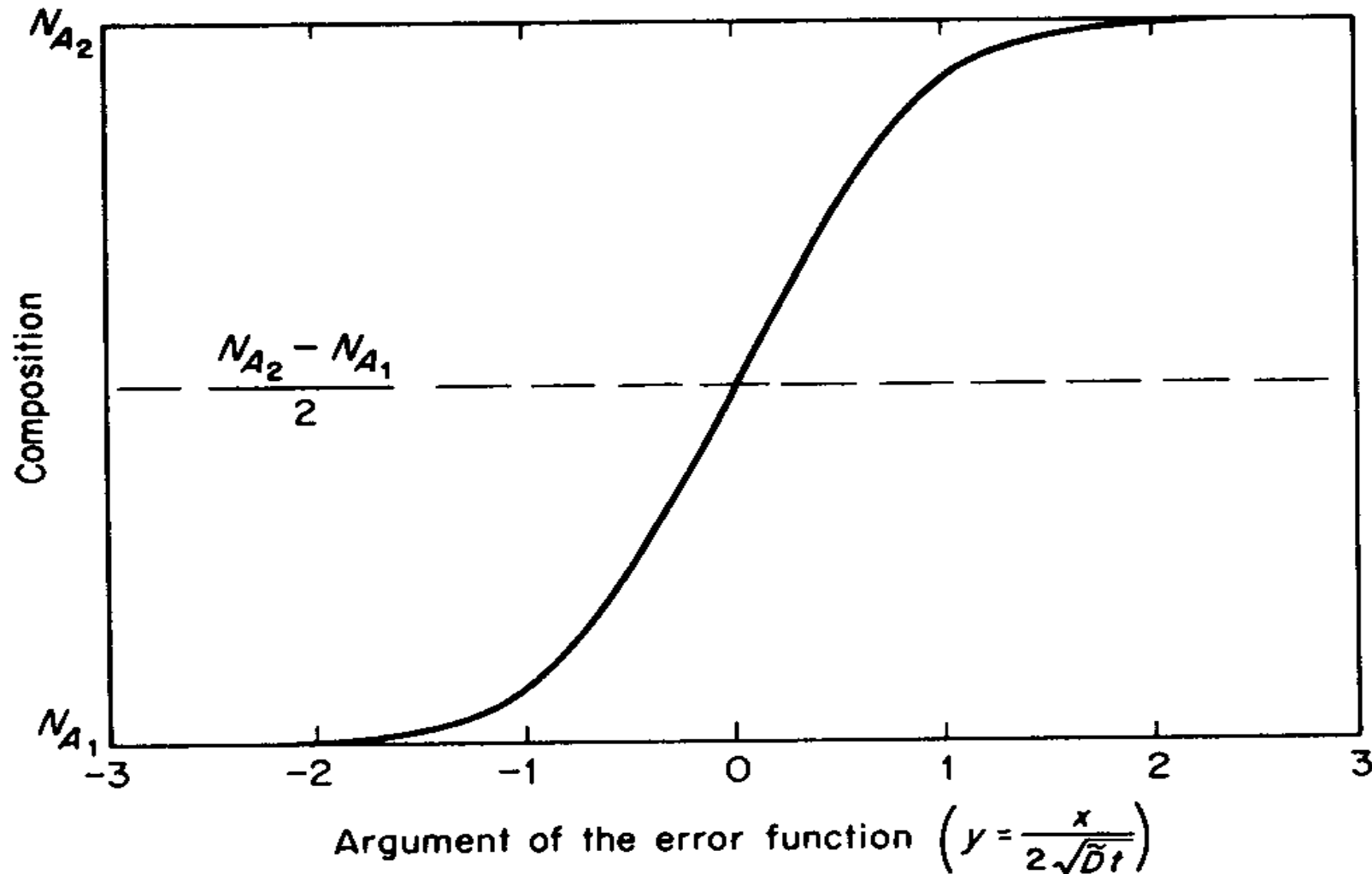
a distance  $x$  from the weld interface,  $t$  is the time in seconds, and  $\tilde{D}$  is the diffusivity. The symbol  $\operatorname{erf}$  represents the error function of ( $y$ ) where  $y = x/2(\tilde{D}t)^{1/2}$

$$\operatorname{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy$$

This function is tabulated, or can be calculated using most spreadsheets.

A theoretical penetration curve can be calculated (distance vs. composition), when the solution to Fick's equation is plotted

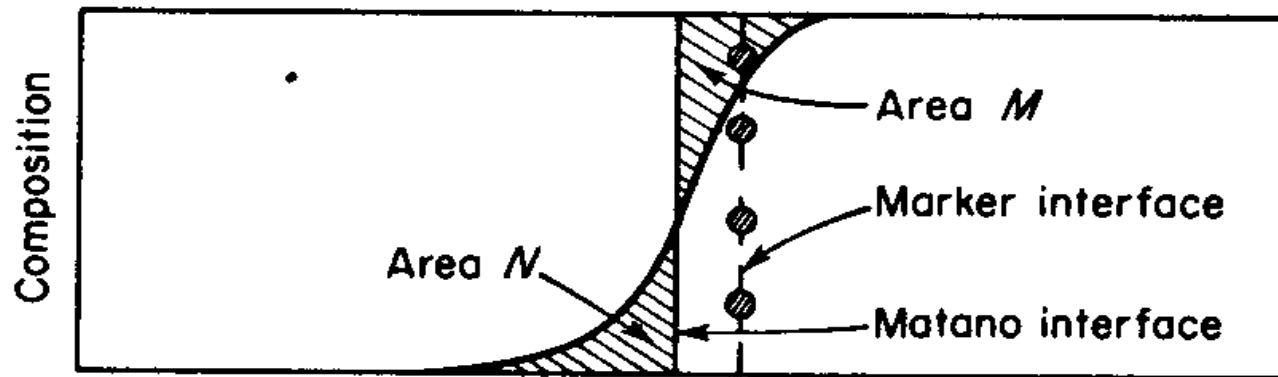
## 12.5 Fick's Second Law



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## The Matano Method:

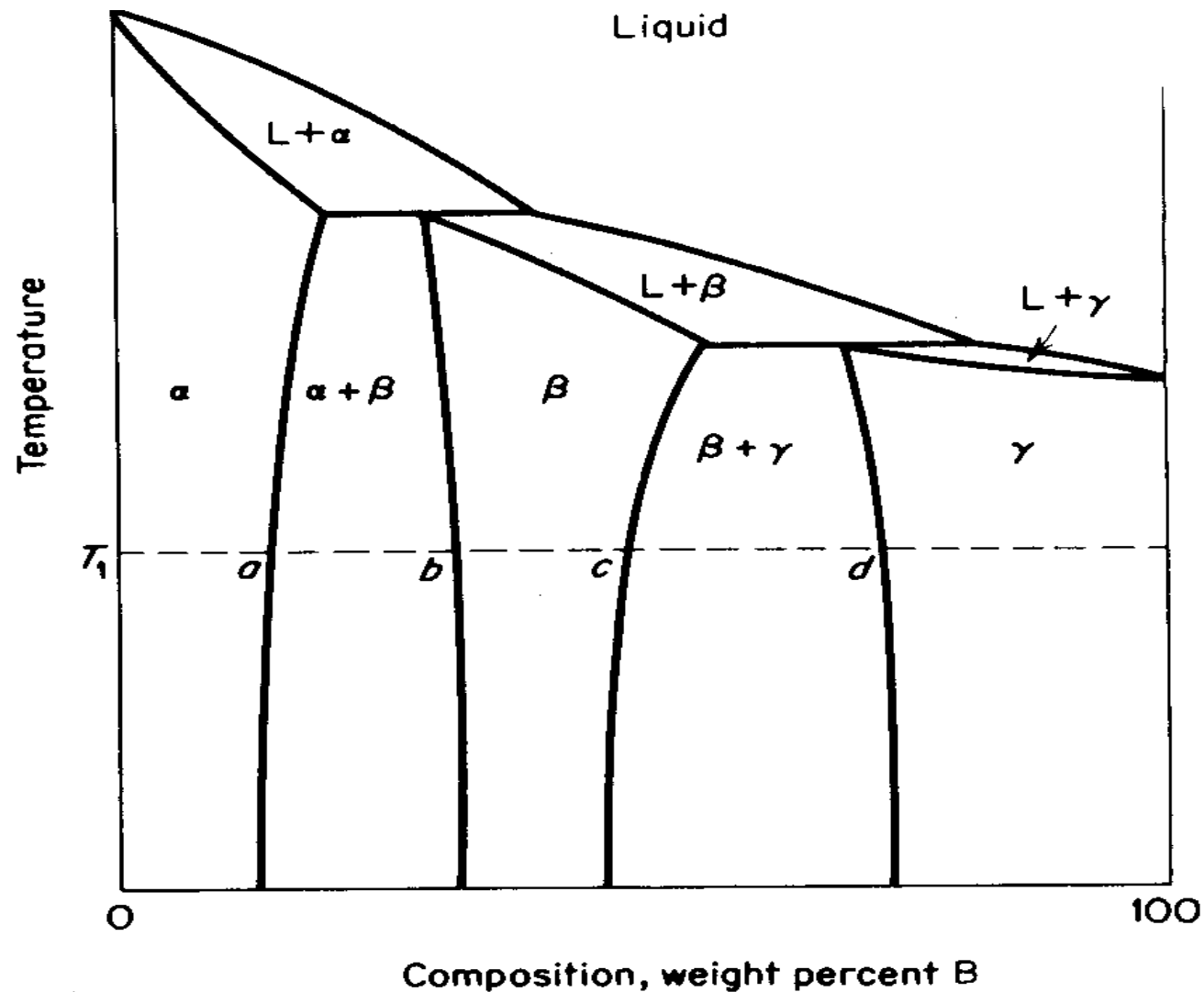
First proposed in 1933, based on a solution of Fick's Second Law, first proposed by Boltzmann in 1894. In this method,  $\tilde{D}$  is assumed to be a function of concentration.



The Matano interface is determined by graphical integration, such that Area M = Area N, and is usually at the original weld position.

This is then the origin of the x coordinate, right is positive.

# Diffusion in Alloy Systems



Hypothetical Phase Diagram, Components A and B

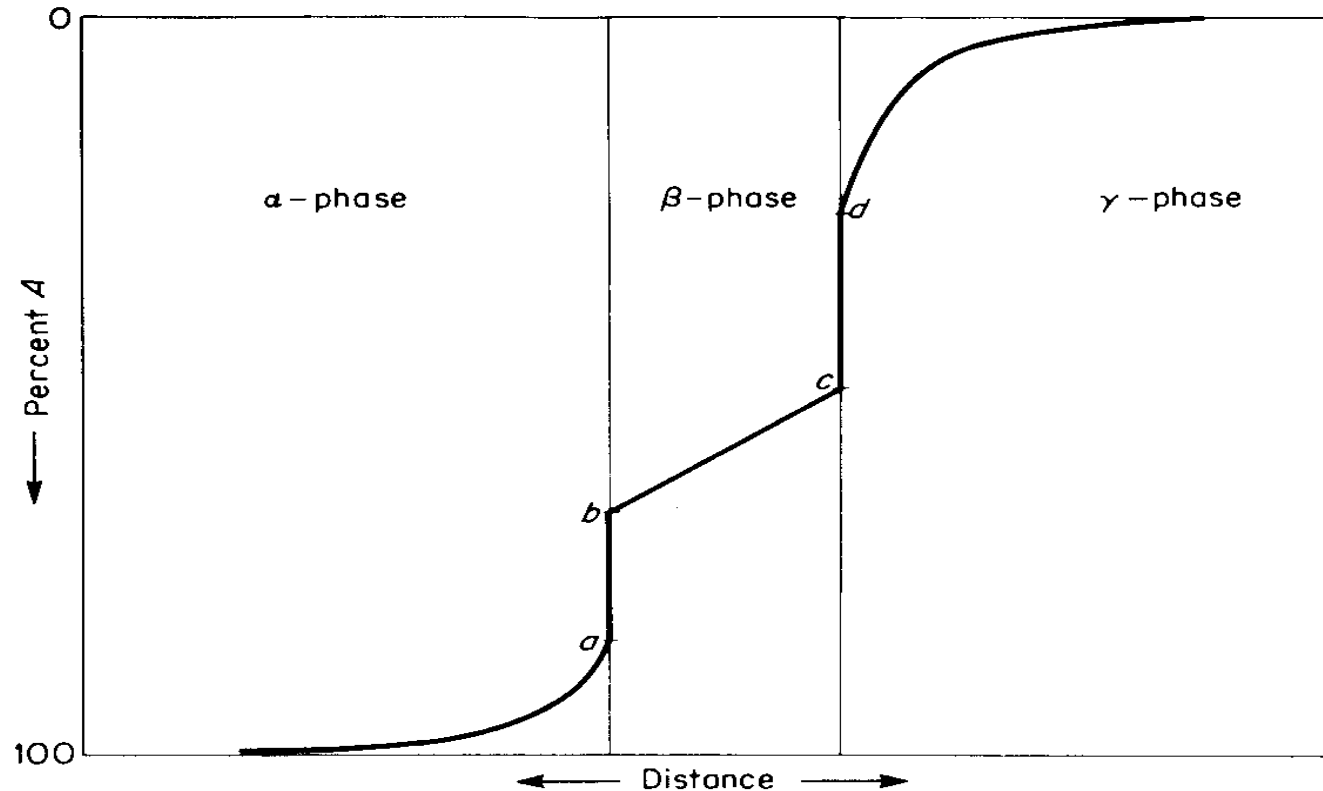
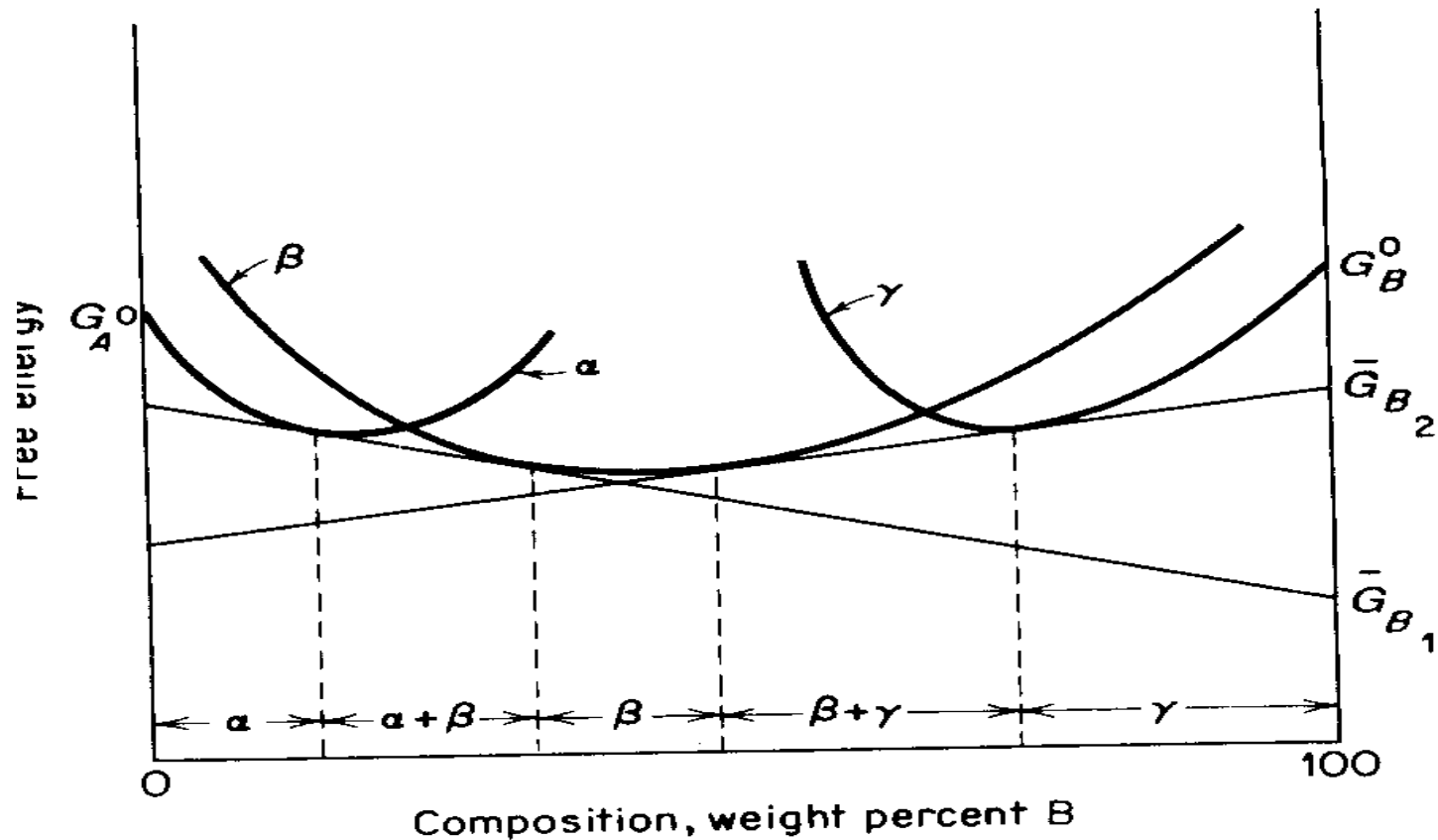


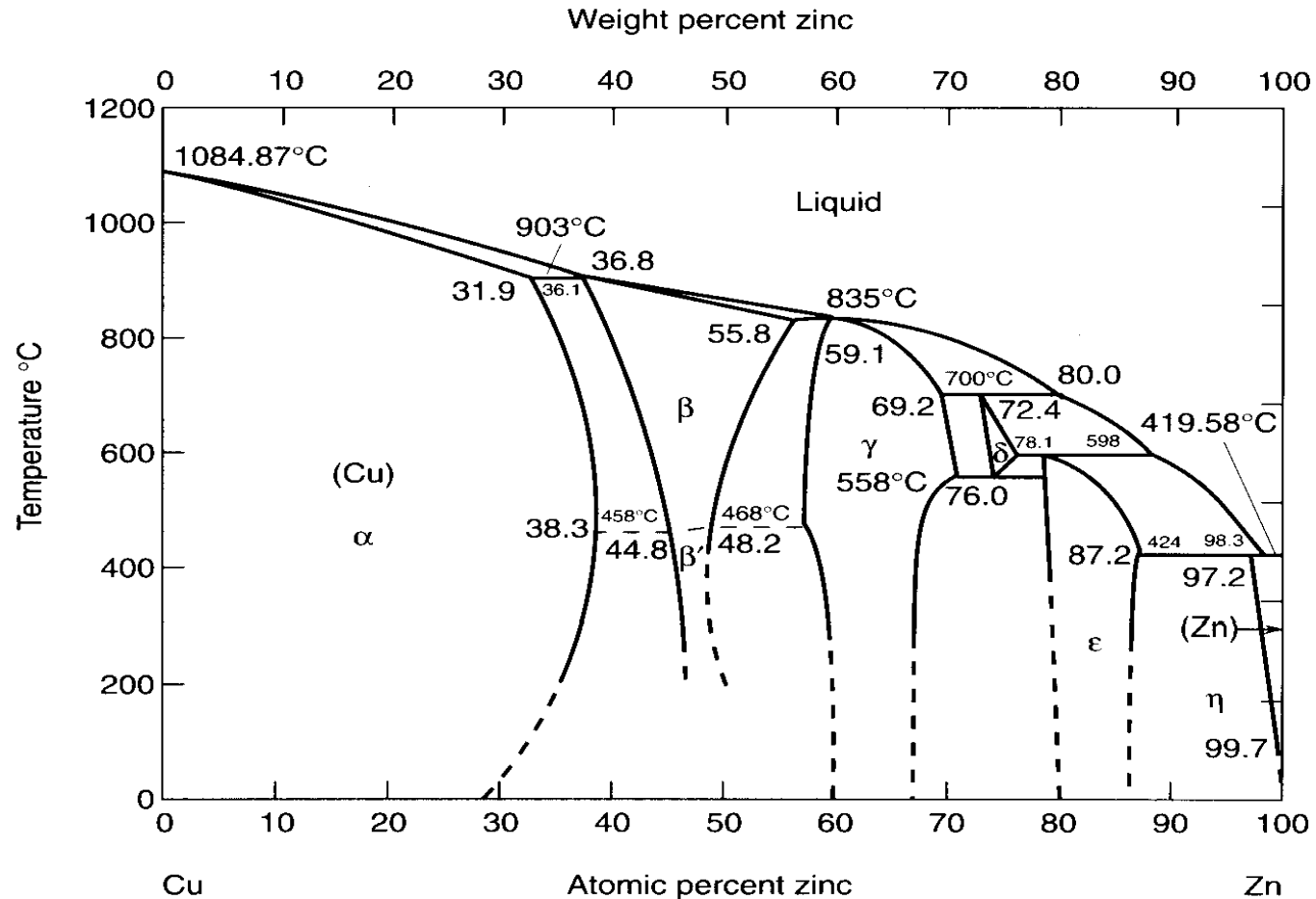
Fig. 12.25 A diffusion couple formed by welding a layer of

The Diffusion Couple formed from welding pure A and pure B together, and annealing for a long time at high temperature. The curve shows how composition varies (B component) across the couple.

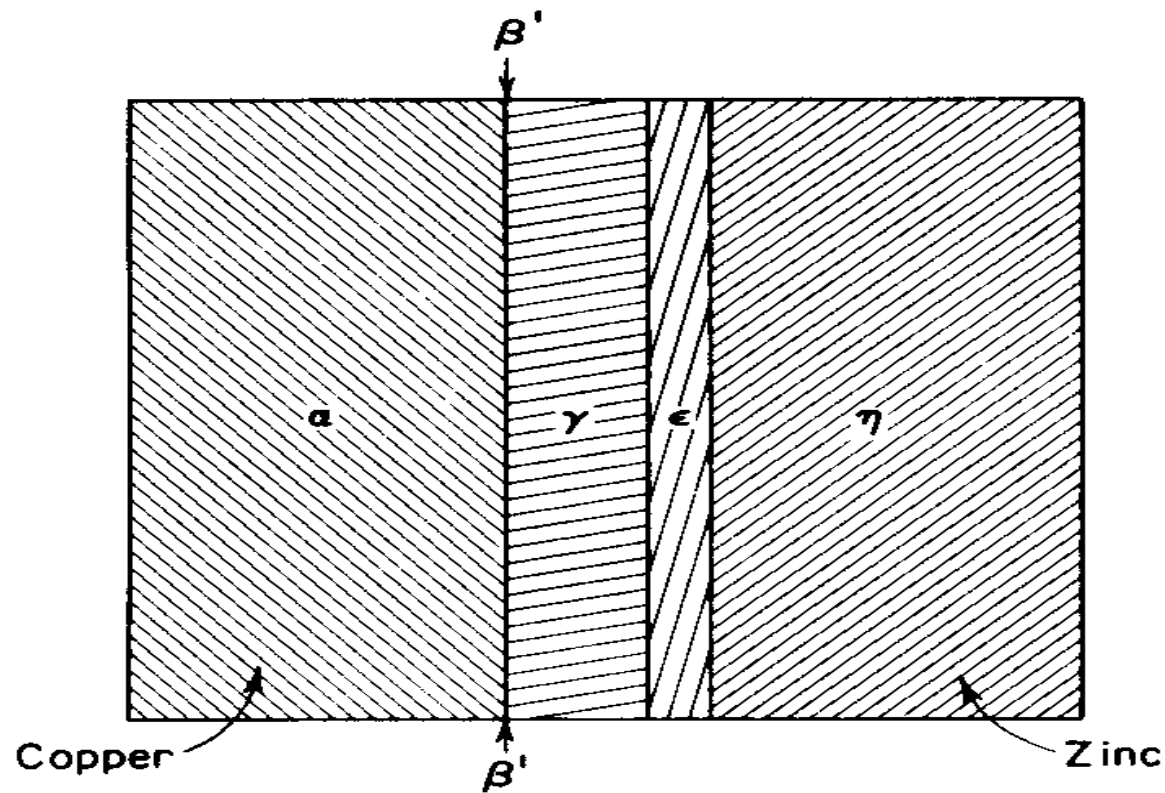


Free Energy vs. Composition curves for all 3 phases  
at Temperature  $T_1$

# Diffusion in the Copper-Zinc System



**Fig. 11.23** Copper-zinc phase diagram. (From *Binary Alloy Phase Diagrams*, Massalski, T. B., Editor-in-Chief, ASM International, 1986, p. 981. Used by permission.)



A Cu-Zn Diffusion Couple annealed for a short time at 380C does not show a visible layer of the beta prime phase.

Experiment: Reaction of Liquid Rare-Earth Metals with Beryllium.

All have similar phase diagrams—simple eutectics, one high melting point compound,  $MBe_{13}$ . Be-Y is shown below:

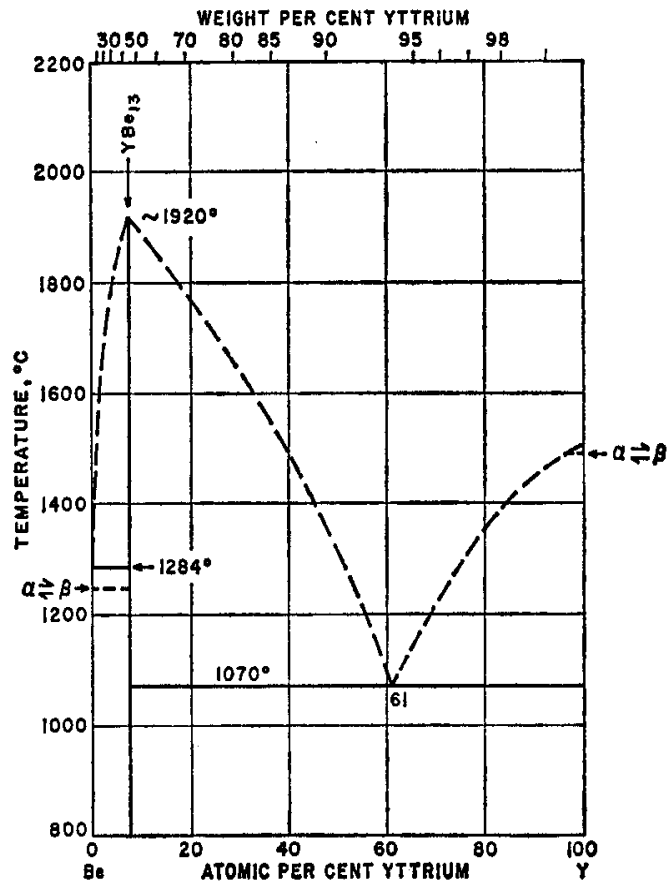
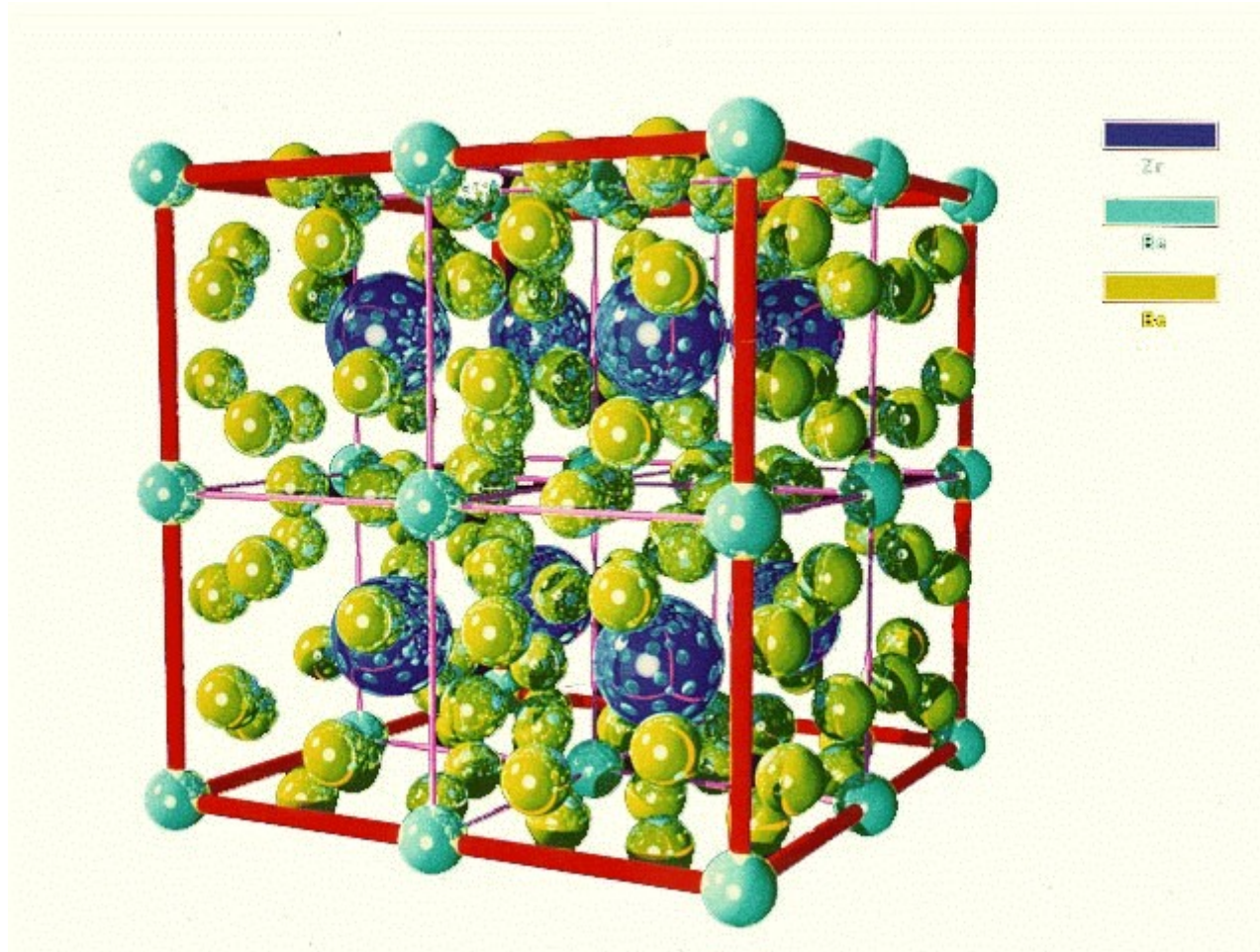
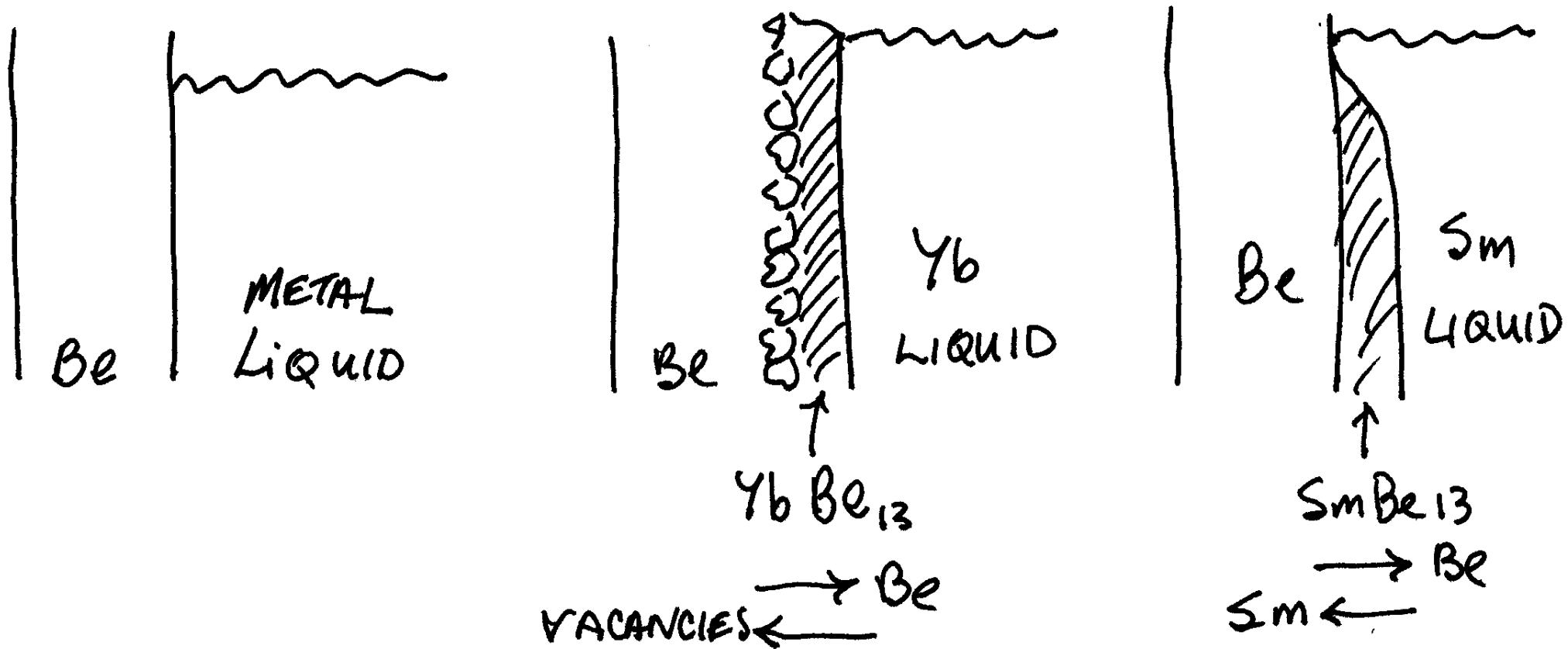


Fig. 87. Be-Y



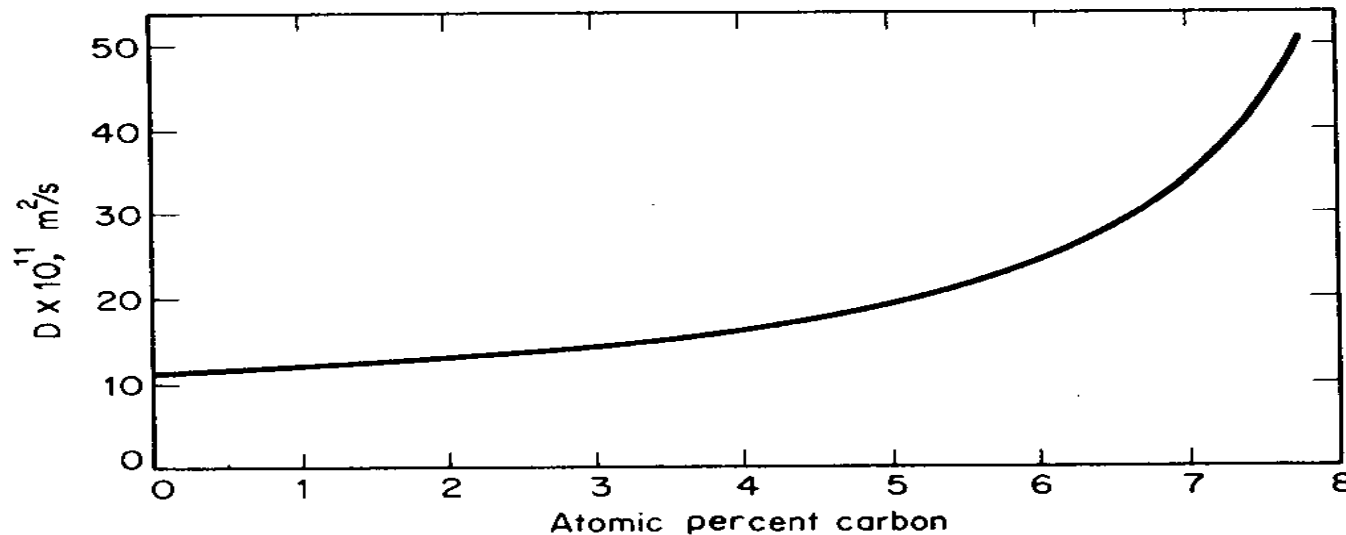
Results of different experiments, using Ytterbium,  $Z = 70$ , and  
Samarium,  $Z = 62$ :



# Interstitial Diffusion

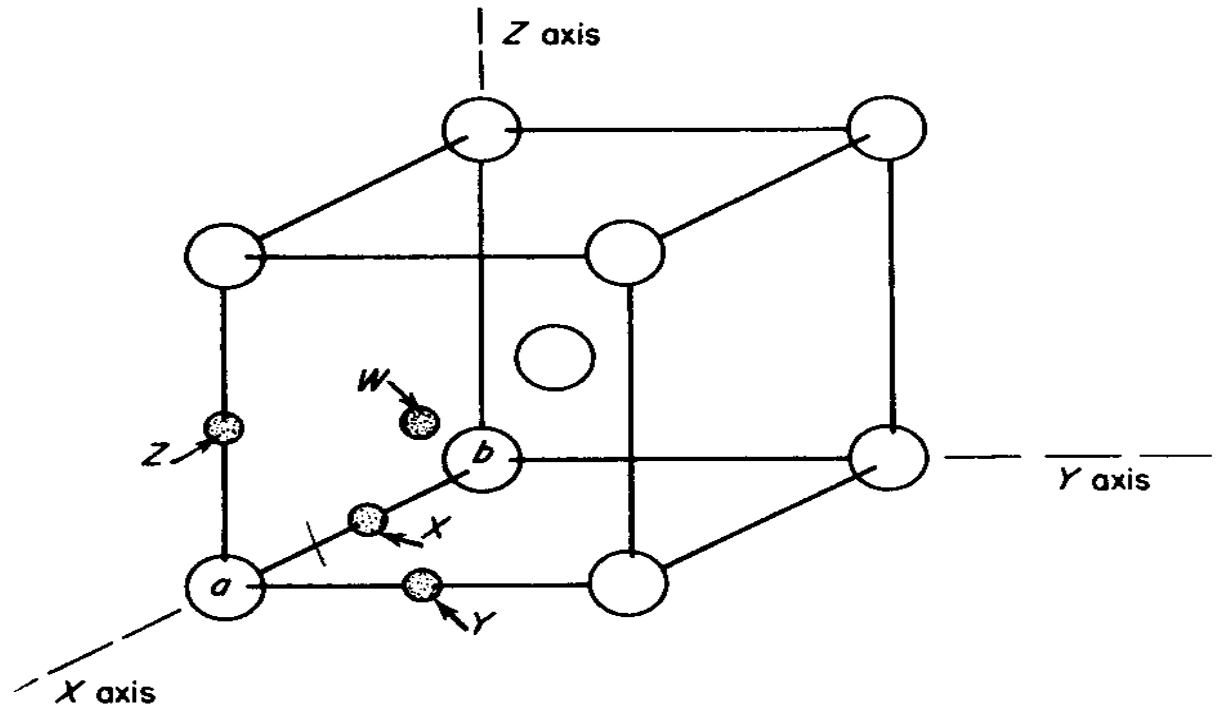
Differs from substitutional case where atoms jump into vacancies since interstitial atoms move by jumping from one interstitial site to a neighboring one.

Diffusivities can be measured by the same methods as before (Grube or Matano) and they are also functions of composition as shown in the plot below for carbon in gamma iron at 1127C.



# The Snoek Effect:

The figure shows the interstitial sites in a BCC lattice. At zero stress, all are equally occupied. Applied stress causes some sites to be favored.



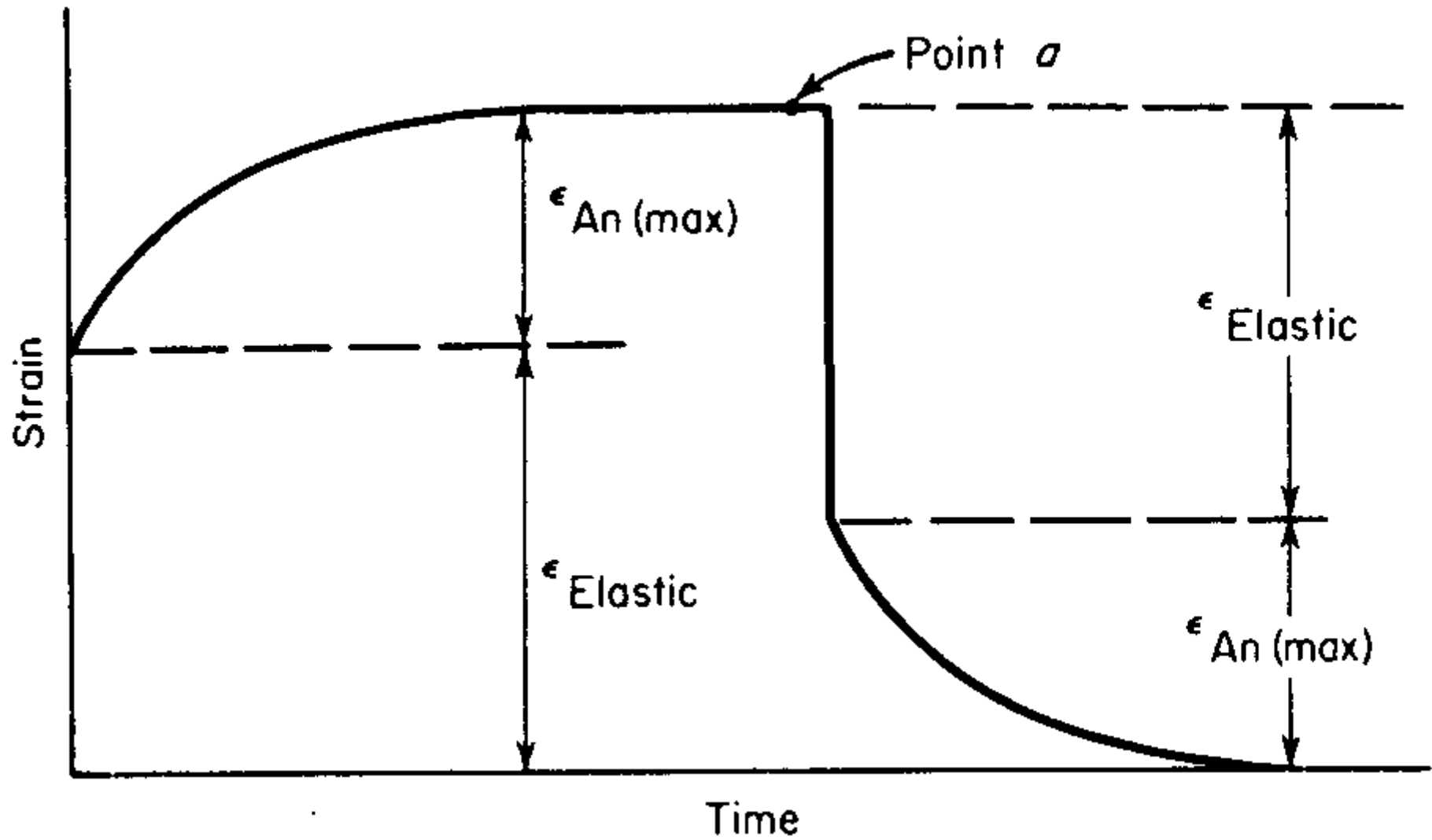
# Elastic and Anelastic Strain Measurement:

Relevant equations for this technique: the excess of solute atoms that occupy interstitial positions with axes parallel to applied tensile stress

$\Delta n_p = K s_n$  where  $s_n$  is the applied tensile stress.

The total strain is made up of two parts, the normal elastic strain and the anelastic strain,  $\varepsilon = \varepsilon_{el} + \varepsilon_{an}$ .

The time dependence is exponential:  $\Delta n_p = \Delta n_{p(max)} [1 - \exp(-t/\tau\sigma)]$ , where  $t$  is the time and  $\tau\sigma$  is a constant, the relaxation time at constant stress. After much computation, it can be shown that the mean time of stay of a solute atom in an interstitial position is:  $\tau = 3 \tau\sigma / 2$ .



And the diffusion coefficient can be calculated from the relation:

$$D = \alpha a^2/\tau$$

where  $a$  is the lattice constant and  $\alpha$  is a geometrical factor which for BCC = 1/24.

Substitution of the experimentally determined relaxation time gives the diffusivity directly.<sup>diff16</sup>

## Relaxation time—Experimental Determination:

If the relaxation time is short—seconds instead of minutes, use the torsion pendulum method.

The damped vibration is due to internal friction in the metal. Among the many sources of such internal friction is the movement of interstitial solute atoms.

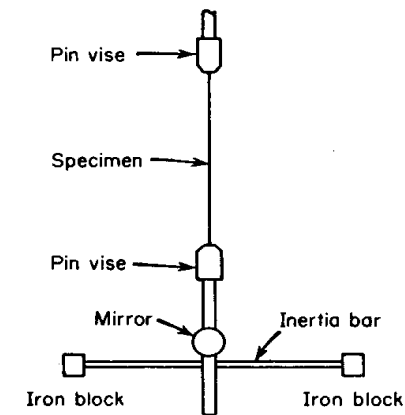
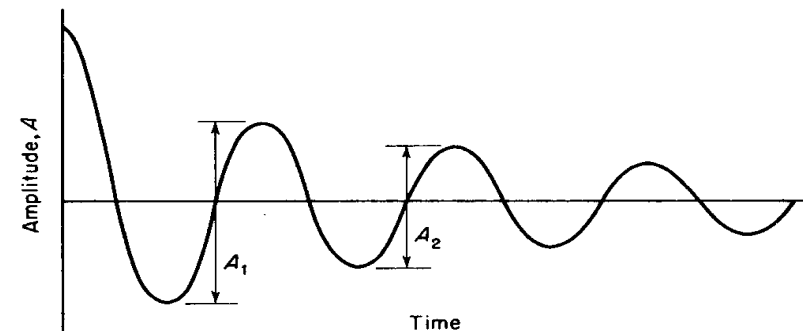


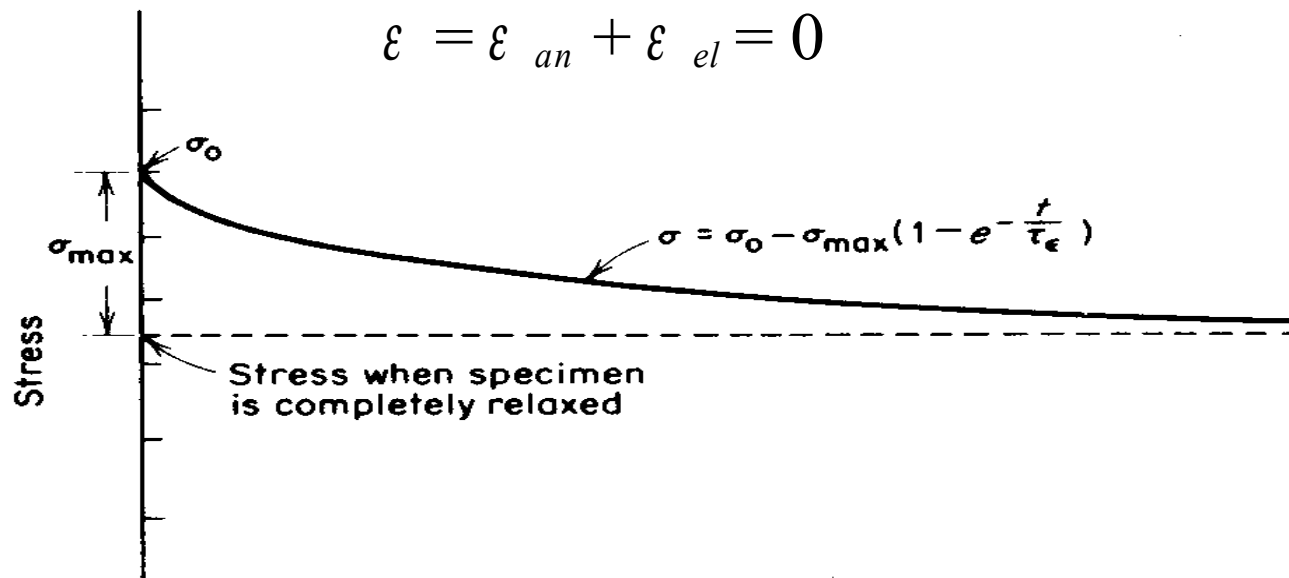
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## Anelastic Measurements at Constant Strain

Assume that a specimen is loaded to a given stress level, and then the test is stopped so that the grips remain fixed. The specimen will continue to deform anelastically, as shown below:

The stress will drop, but the strain will not change:



It is possible to measure a relaxation time at constant strain,  $\tau_\epsilon$ , which is not the same as  $\tau_\sigma$ , the relaxation time at constant stress.

Both of these times are related to the relaxation time for a torsion pendulum as follows:

$$\tau_R = (\tau_\sigma \tau_\epsilon)^{(1/2)}$$

so the  $\tau_R$  is the geometric mean of the other two relaxation times.





