

## 6. Interdiffusion

During our previous classes, we learned about point defects, now it's time to see how they affect the mass transport phenomena. Any theory of atom diffusion must answer the question: "How this atom moved from here to there?". In crystalline solids, presence of the crystal lattice restricts the possible atom motions, what allows simple descriptions of the processes. Of course, even in crystals, multiple mechanisms are possible. The most important are:

- Exchange mechanism
- Ring mechanism
- Interstitial mechanism
- Interstitialcy mechanism
- Crowdion mechanism
- Vacancy mechanism
- Divacancy mechanism
- Relaxion mechanism
- Dislocation pipe diffusion mechanisms
- Grain boundary diffusion mechanisms
- Surface diffusion mechanisms

The most common of them are vacancy and interstitial mechanisms, but historically they were the last to be observed. We will use a "Tracer atom" an atom usually of the same kind as the matrix atoms, but somehow distinguishable for us (during real experiments this role is fulfilled by isotopes).

### 6.1. Diffusion mechanisms

#### Exchange and ring mechanism

Exchange mechanism is possibly the simplest mechanism we can think of - during this process, two atoms are exchanging their positions. This mechanism is the most probable in loosely packed crystal, because neighbors of the moving atoms have to compress, to allow them to squeeze past one another and interchange positions. **Such mechanism has also another, very important consequence - both atoms are moving at the same rate, so diffusion coefficients must be the same.**

Ring mechanism is similar, but here a number of atoms placed in "a ring" move together. As a result the ring rotates by one atom distance. Here on the one hand, the neighboring atoms do not have to compress as much as in exchange mechanism, but on the other the mechanism is much more complex, what makes it less likely to occur.

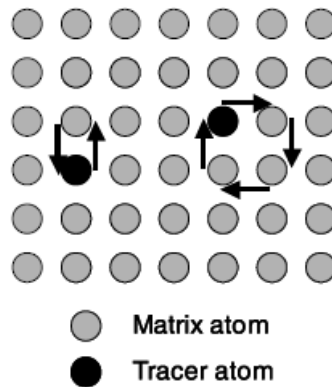


Fig.6.1. Exchange and ring mechanisms

### Interstitial mechanism (Direct interstitial mechanism)

In this mechanism (discovered in 1933) , atom moves directly between one interstitial site to another. This mechanism is especially important, when migrating atom is much smaller the atoms of the matrix (for example hydrogen, carbon), because jumping process of such small atoms do not greatly displace the atoms of the matrix from their normal lattice sites.

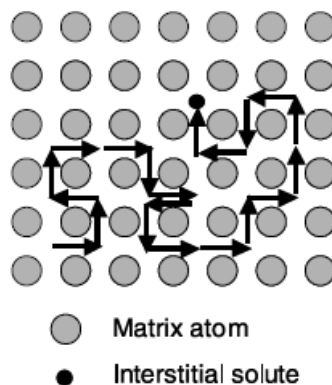


Fig.6.2. Interstitial mechanism

### Interstitialcy mechanism (Indirect interstitial mechanism)

In this case the interstitial atom does not move from one interstitial site to the other, but it pushes atom from the lattice site into interstitial position and takes its place in the lattice. As it can be seen it the Fig.6.3., two jumps are needed to move the atom from one lattice site to the next one. There is much more to tell about this mechanism, but maybe another time..

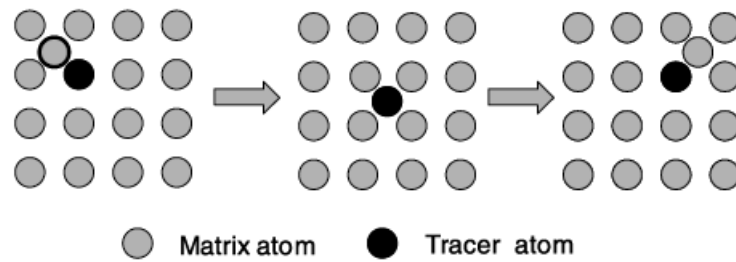


Fig.6.3. Interstitialcy mechanisms

### Vacancy mechanism

As we already know, any crystal in temperature above 0[K], contains a certain number of vacancies. These vacancies provide an easy path for diffusion - atom can jump into neighboring vacancy. As a result the atom moved, while a new vacancy was created (because atom and vacancy exchanged positions). Each atom moves through the crystal by making a series of exchanges with the various vacancies which from time to time are in its vicinity. **In this mechanisms, because of the presence of vacancies, atoms of different components can move at different speed, what was shown for the first time, by Kirkendall in 1947.**

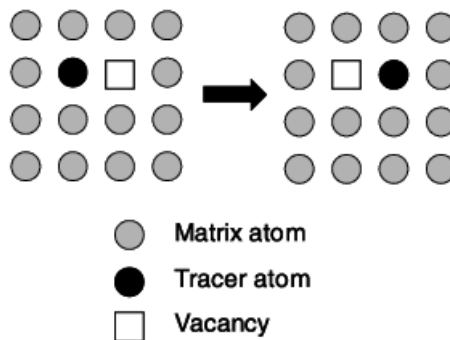


Fig.6.4.Vacancy mechanism

### 6.2. Kirkendall's experiment

In 1947, Ernest Kirkendall and his student Alice Smigelskas, conducted the first marker experiment. In this experiment, on a polished bar made out of brass 70-30 (70% wt. Cu i 30% wt. Zn) , thin Mo wires were stretched (there were acting as a markers). Such system was then covered with pure copper. Obtained **diffusion couple**, was then annealed in 1058K for extended period of time. Every few days, the distance between two opposite rows of Mo wires were measured. **As a result, the movement of the markers was observed.** To be more precise - the distance between markers was shrinking. Such effect could be explained only in one way - zinc from the brass core was escaping on a faster rate, than the copper from the outside was replacing it. This difference of fluxes, resulted in a macroscopic move of the material. This effect is now known as a **Kirkendall effect**.

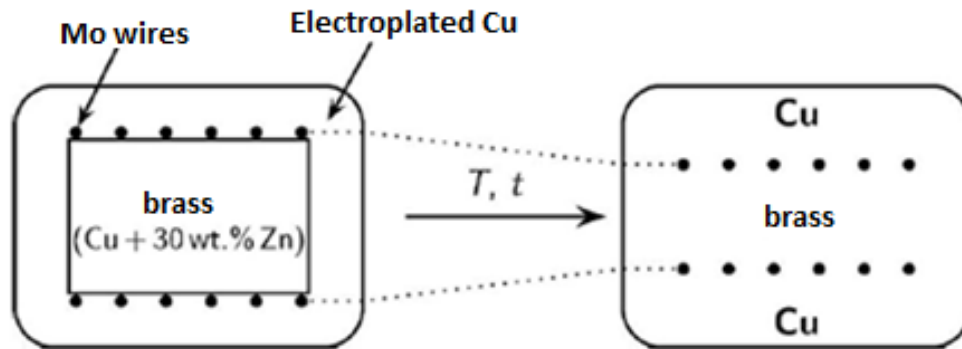


Fig. 6.5. Kirkendall's experiment.

### 6.3. Darken's equations

In 1948, Darken proposed the first mathematical description of Kirkendall's effect (or so called interdiffusion). This description is in fact valid up to this day. Now let's imagine an ink droplet which is diffusing in the river. It can be shown, that if we were moving at the river's speed, the diffusion flux of ink would be indistinguishable from the one observed in for example glass of water. On the other hand, someone standing on the river's bank would be observing something totally different - a mass flux of ink would for him consist of both diffusion flux and advection flux created by the river. Darken's approach is completely analogous to this situation - our river is the material itself (which according to Kirkendall's experiment is moving), while the "pure" diffusion flux can be described by a standard Fick's equation. The form of a total mass flux will strictly depend on the reference frame - if we were moving with the same speed as the material (so called lattice reference frame), we will observe normal Fick's fluxes, but if we were looking at the sample from outside (laboratory reference frame) our observation will be the flux, which is a sum of diffusion flux and advection flux.

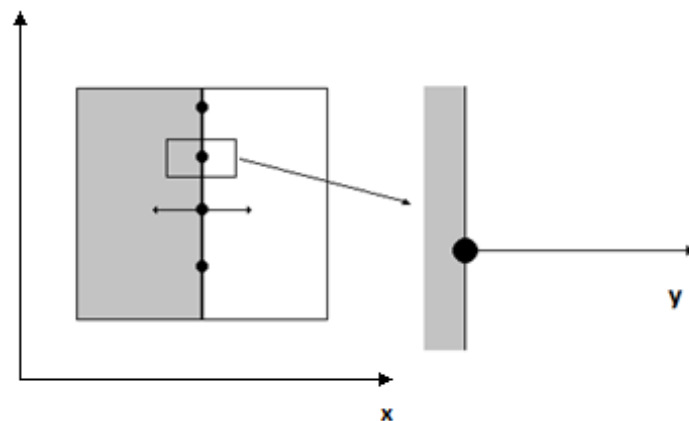


Fig.6.6. Reference frames: "x"- laboratory reference frame, "y" -lattice reference frame, which is moving with the same speed as the marker. .

Let's start with the lattice reference frame „y“. The flux of a component A is given by expression:

$$J_A = -D_A \frac{\partial c_A}{\partial y} \quad (6.1)$$

Now, let's move to the laboratory reference frame „y“ $\Rightarrow$ „x“, in which the lattice reference frame is moving with a drift velocity (Darken's velocity)  $v^d = v^d(x, t)$ . As a result:

$$\tilde{J}_A = -\left(D_A \frac{\partial c_A}{\partial x} - c_A v^d\right) \quad (6.2)$$

The Fick's 2nd law for such flux looks as follow:

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x} \left( D_A \frac{\partial c_A}{\partial x} - c_A v^d \right) \quad (6.3)$$

And for the B component:

$$\frac{\partial c_B}{\partial t} = \frac{\partial}{\partial x} \left( D_B \frac{\partial c_B}{\partial x} - c_B v^d \right) \quad (6.4)$$

Assuming that:

$$const = c = c_A + c_B \quad (6.5)$$

we can write down a mass conservation law for the whole system (sum of fluxes):

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_A \frac{\partial c_A}{\partial x} + D_B \frac{\partial c_B}{\partial x} - c v^d \right) \quad (6.6)$$

Now we can see, that we are missing value of  $v^d$ . Let's assume, that our system is closed (because no additional mass is coming from outside):

$$\sum_{i=1}^2 \tilde{J}_i = 0 \quad (6.7)$$

so:

$$\sum_{i=1}^2 \tilde{J}_i = \sum_{i=1}^2 (J_i + c_i v^d) = 0 \Rightarrow \sum_{i=1}^2 J_i = -v^d \sum_{i=1}^2 c_i \Rightarrow v^d = -\frac{1}{c} \sum_{i=1}^2 J_i \quad (6.8)$$

Substituting (6.8) to equation (6.3), we will obtain a mass conservation law for the A component (for B it would be a total analogy):

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x} \left( D_A \frac{\partial c_A}{\partial x} - \frac{c_A}{c} \left( D_A \frac{\partial c_A}{\partial x} + D_B \frac{\partial c_B}{\partial x} \right) \right) \quad (6.9)$$

Now, let's use a molar fractions instead of concentration

$$N_A = \frac{c_A}{c}, N_B = \frac{c_B}{c} \quad \text{and} \quad N_A + N_B = 1 \quad (6.10)$$

On the basis of (6.5) we can write:

$$const = c_A + c_B \Rightarrow \frac{\partial c_A}{\partial x} + \frac{\partial c_B}{\partial x} = 0 \Rightarrow \frac{\partial c_A}{\partial x} = -\frac{\partial c_B}{\partial x} \quad (6.11)$$

From (6.10):

$$N_i = \frac{c_i}{c} \Rightarrow \frac{\partial N_i}{\partial x} = \frac{1}{c} \frac{\partial c_i}{\partial x} \quad (6.12)$$

Putting equations (6.10)-(6.12) together, we can rewrite (6.9) in a form:

$$c \frac{\partial N_A}{\partial t} = \frac{\partial}{\partial x} \left( c D_A \frac{\partial N_A}{\partial x} - N_A \left( c D_A \frac{\partial N_A}{\partial x} - c D_B \frac{\partial N_A}{\partial x} \right) \right) \quad (6.13)$$

and next:

$$\frac{\partial N_A}{\partial t} = \frac{\partial}{\partial x} \left( D_A \frac{\partial N_A}{\partial x} - (1 - N_B) D_A \frac{\partial N_A}{\partial x} + N_A D_B \frac{\partial N_A}{\partial x} \right) \quad (6.14)$$

Finally we will obtain:

$$\frac{\partial N_A}{\partial t} = \frac{\partial}{\partial x} \left[ (N_B D_A + N_A D_B) \frac{\partial N_A}{\partial x} \right] \quad (6.15)$$

Now we can see, that our result is looking like 2nd Fick's law, but the diffusion coefficient has a different form:

$$\tilde{D} = N_B D_A + N_A D_B \quad (6.16)$$

After substituting (6.16) into (6.15) we will get:

$$\frac{\partial N_A}{\partial t} = \tilde{D} \frac{\partial^2 N_A}{\partial x^2} \quad (6.17)$$

**where  $\tilde{D}$  is a interdiffusion coefficient.**