

## Point defects

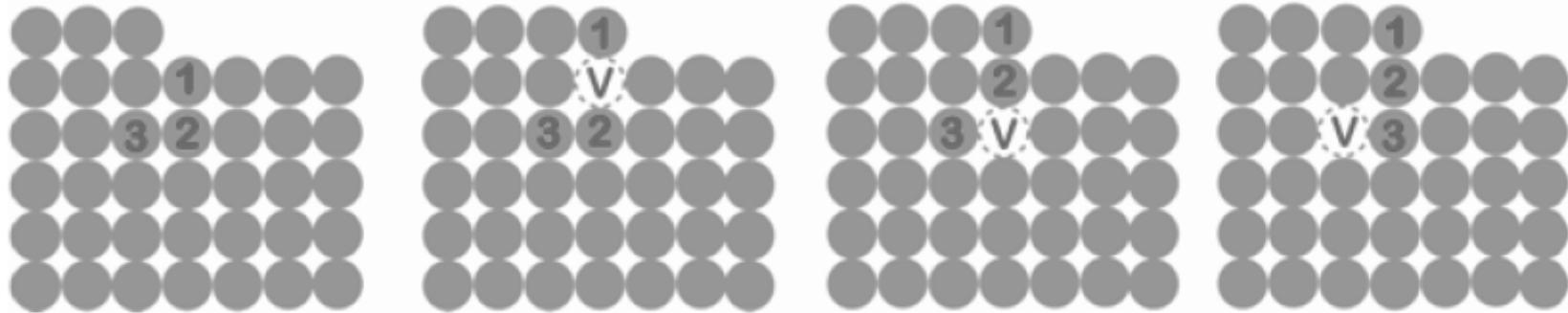
- Diffusion of elements is possible because of the presence of defects. For example, substitutional diffusion occurs because of exchange of an atom with vacancies. Further, impurities are present at the interstitial positions, which could diffuse to any neighboring vacant interstitial sites. This is called interstitial diffusion.
- Certain concentration of these impurities are always present in the pure elements in equilibrium condition, which will be discussed here.
- Further in the intermetallic compounds (ordered phases), antisites defects also could be present along with vacancies. Moreover, different sublattices could have different concentration of defects, which makes the diffusion process complicated.
- Now we shall discuss on defects, which will help to understand the atomic mechanism of diffusion.

## Equilibrium point defect calculations

- Let us not get confused with the structural defects present in pure elements.
- To understand simple atomic mechanism of diffusion at this point, we shall calculate the equilibrium concentration of point defects that is the equilibrium concentration of vacancies and interstitial atoms in pure elements
- Interesting point to be mentioned here that unlike dislocations, grain boundary or interfaces, point defects are equilibrium defects. It means that the system will try to have certain concentration of defects to decrease the free energy.

Let us first calculate the equilibrium concentration of vacancies, because of which lattice substitutional diffusion is possible

## Equilibrium vacancy concentration in a pure element



- Pure elements A and vacancies (V) can be considered as a mixture of two entities and follow the similar treatment as we did to calculate the total free energy after mixing of elements A and B.
- It can be easily visualized how the movement of atoms can create vacancies in the material in few steps.
- Equilibrium number of vacancies is so small that we can neglect the interaction between them.
- This means that we are neglecting V-V interactions. This also means that we are, at this point, neglecting the presence of divacancies, which are actually present in the material.

➤ If we consider that the number of vacancies is very small then the increase of enthalpy because of formation of vacancies can be written as

$$\Delta H \approx X_v \Delta H_v$$

$\Delta X_v$  is the mole fraction of vacancy and  
 $\Delta H_v$  is the increase in enthalpy because of one mole of vacancies

➤ There will be the change in the pattern of vibration of atoms next to vacancies because of extra free space. The increase in (thermal) entropy because of the extra freedom of vibration can be written as

$$\Delta S_{\text{thermal}} = X_v \Delta S_v$$

$\Delta S_v$  is the increase in entropy for one mole of vacancies

➤ In both the cases, we are actually assuming linear relationship because of very small concentration of vacancies.

**Note:** In the case of entropy change of A-B mixture, we did not consider the thermal entropy change, since we are considering the change at a particular temperature. However, in this case, although we are considering again at a particular temperature, we still need to consider the contribution because of the change in vibration pattern of atoms next to vacancies.

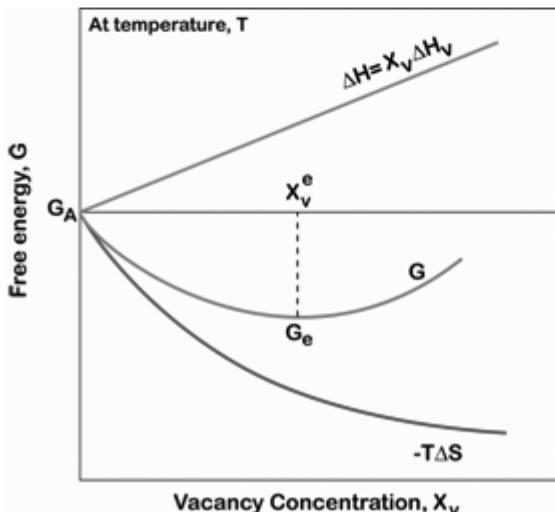
- Further there will be change in configurational entropy considering the mixing of A and V and can be expressed as (Note that we are considering  $X_A + X_v = 1$  )

$$\Delta S_{config} = -R[X_v \ln X_v + X_A \ln X_A] = -R[X_v \ln X_v + (1-X_v) \ln(1-X_v)]$$

- Total entropy of mixing  $\Delta S_{mix} = \Delta S_v X_v - R[X_v \ln X_v + (1-X_v) \ln(1-X_v)]$   
(Total contribution from thermal and configurational entropy)

- Total free energy in the presence of vacancies

$$\begin{aligned} G &= G_A + \Delta G \\ &= G_A + \Delta H - T\Delta S \\ &= G_A + X_v \Delta H_v - T\{\Delta S_v - R[X_v \ln X_v + (1-X_v) \ln(1-X_v)]\} \end{aligned}$$



Note here that G of element A when vacancies are present decreases. So always there will be vacancies present in materials. Further G decreases to a minimum value and then increases with the further increase in vacancy concentration. So, in equilibrium condition, certain concentration of vacancies will be present, which corresponds to  $G_e$ .

Since the slope is zero at the minima, we can find the equilibrium vacancy concentration from

$$\frac{dG}{dX_v} = 0$$

$$\Delta H_v - T\Delta S_v + RT \left[ \ln X_v + X_v \cdot \frac{1}{X_v} - \ln(1-X_v) - (1-X_v) \cdot \frac{1}{(1-X_v)} \right] = 0$$

Since the number of vacancies that can be present in the system is very small

$$1 - X_v \approx 1$$

$$\Delta H_v - T\Delta S_v + RT \ln X_v = 0$$

The relation for equilibrium concentration of vacancies can be written as

$$X_v^e = X_v = \exp \left( -\frac{\Delta H_v - T\Delta S_v}{RT} \right) = \exp \left( -\frac{\Delta G_v}{RT} \right)$$

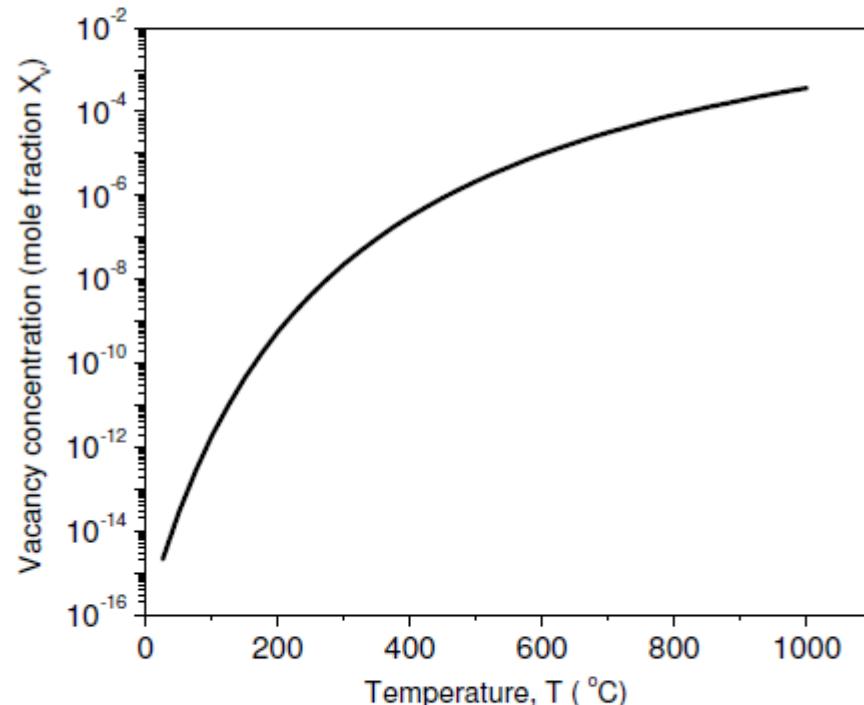
- Although there is increase in configurational entropy because of the presence of vacancies, it is not included in the activation energy barrier,  $\Delta G_v$
- Although there is activation energy barrier present because of formation, vacancies will still be present because of overall decrease in free energy of the materials.

From the equation in the previous slide, we can also write

$$X_v^e = X_v^0 \exp\left(-\frac{\Delta H_v}{RT}\right)$$

$\Delta H_v$  is the activation enthalpy for the formation of vacancies and

$X_v^0 = \exp\left(\frac{\Delta S_v}{R}\right)$  is the pre-exponential factor.



➤ The change in concentration of vacancies in pure Cu is shown in the graph, considering activation energy for vacancy formation to be 83.7 kJ/mole.

➤ The concentration of vacancies in mole fraction at 1000 °C is  $3.68 \times 10^{-4}$ . That means in a cube of  $10^4$  atoms in each direction, only one vacancy will be present in Cu at this temperature!!!

## Experimental determination of vacancy concentrations

- There are few techniques available following which one can measure the concentration of vacancies at certain temperature to determine the activation energy for vacancy formation
- In practice, mainly three techniques are followed: by thermal expansion measurements, by measuring resistivity after quenching and using positron annihilation technique.
- We shall consider these techniques in our discussion one by one.

### From thermal expansion experiments

- Expansion of volume of a metal because of increasing temperature happens mainly because of two reasons: (i) expansion in lattice parameter and (ii) creation of more vacancies.
- Volume expansion means the increase in lattice sites.
- Fraction of volume change is actually equal to the fraction of change in lattice sites,  $\Delta n/l n$ .
- The fraction of change in linear dimension is  $\Delta l/l$  and the fraction of change in lattice parameter is  $\Delta a/a$ .
- So the linear change because of creation of extra sites/vacancies is  $(\Delta l/l - \Delta a/a)$ .

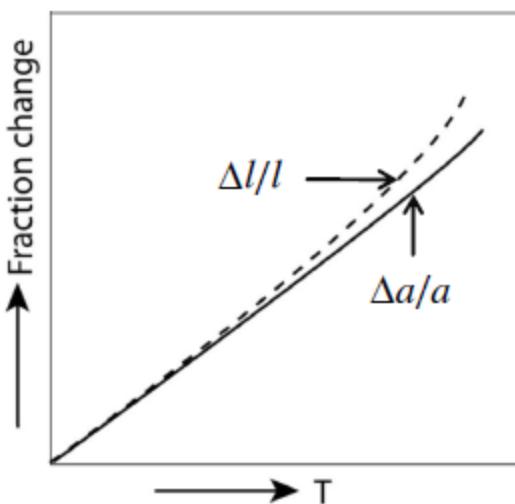
- In an isotropic structure, the change in volume is three times to the linear change and we can write

$$\Delta n \ln = 3(\Delta l/l - \Delta a/a)$$

We are just adding from every linear change. If vacancies are added in x direction only, there will be no change in other directions. So if we add the changes from every direction it will give total number of change in the sites.

- Although it seems very straightforward equation, it is very difficult to determine experimentally .

- We have previously explained that the concentration of vacancies even near the melting point is in the order of  $10^{-4}$ . So even if we show higher tolerance and ready to accept 5% (0.05 fraction) error, we need to be able to measure the length of the material and lattice parameter change in the range of  $5 \times 10^{-6}$ !
- Further, the change in length and lattice parameter should be measured simultaneously at a particular temperature.



- Typical deviation is seen as shown in the figure.
- In aluminium it was measured and the relation was found

$$\Delta n \ln = \exp(2.4) \exp(-0.76/kT)$$

It can be seen as  $X_v = \exp\left(-\frac{\Delta G_v}{RT}\right) = \exp\left(\frac{\Delta S_v}{R}\right) \exp\left(-\frac{\Delta H_v}{RT}\right)$  per mol  
 or  $\exp\left(\frac{\Delta S_v}{k}\right) \exp\left(-\frac{\Delta H_v}{kT}\right)$  per atom

- So enthalpy of vacancy formation is 0.76 eV/atom equivalent to 73 kJ/mol.

- The relation described above can be used in polycrystalline material with random orientation of grains or single crystals with cubic lattice.
- In a polycrystal it can give some error, because we neglect the presence of grain boundaries and grain growth.
- This relation should be modified to use in non cubic single crystals.
- For example Sn has tetragonal structure and the relations used should be

$$X_V = \frac{\Delta n}{n} = 2 \left[ \left( \frac{\Delta L}{L} \right)_a - \frac{\Delta a}{a} \right] + \left( \frac{\Delta L}{L} \right)_c - \frac{\Delta c}{c}$$

where a and c are the lattice parameters.

## From resistivity measurements

- Equilibrium concentration of vacancies depend on temperature. Higher the temperature higher the concentration of vacancies.
- Similarly resistance of a material is also a function of temperature.
- Resistance comes mainly from two contributions: lattice vibrations and defects.
- If we are able to control other defects like impurities, dislocation, grain boundaries etc., we can write

$$\Delta\rho = \Delta\rho_T + \Delta\rho_V$$

- where  $\Delta\rho$  is the change in total resistivity,  $\Delta\rho_T$  is the change in resistivity because of lattice vibration with increasing temperature and  $\Delta\rho_V$  is the change in resistivity because of the change in vacancy concentrations.
- When the temperature is increased at higher temperature, material will have higher equilibrium concentration of vacancies.
- Vacancies are originated from dislocations of grain boundaries, which act as source.
- Vacancies get dispersed by the diffusion process.

- When temperature is decreased the equilibrium concentration decreases and vacancies are absorbed by the dislocations or the grain boundaries. These then act as sink.
- If the metal is suddenly quenched (for example in liquid nitrogen at 77 K) from high temperature to a lower temperature, vacancies will not be able to diffuse to sinks. Even at low temperature diffusion rate is much lower.
- So the metal will have extra vacancies.
- So when resistivity is measured in a metal first at low temperature, it will have resistance from lattice vibration and equilibrium concentration of vacancies.
- Further when resistance is measured on the same metal at the same temperature but after quenching from a high temperature, resistance from lattice vibration will be the same but the resistance from the vacancies will be higher.
- So the difference in resistance will be proportional to the difference in vacancy concentration.

$$\Delta N_v = \alpha \Delta \rho_v \quad \alpha \text{ is the proportionality constant}$$

- Since the difference in vacancy concentration at these two different temperatures will be in many orders of magnitude we can write

$$\alpha \Delta \rho_v = \Delta N_v \approx N_v = \exp\left(\frac{\Delta S_v}{R}\right) \exp\left(-\frac{\Delta H_v}{RT}\right) \quad \text{➤ A is a constant}$$

$$\Delta \rho_v = A \exp\left(-\frac{\Delta H_v}{RT}\right)$$

- So measurements after quenching from different temperature will give the value for activation enthalpy for vacancy formation.

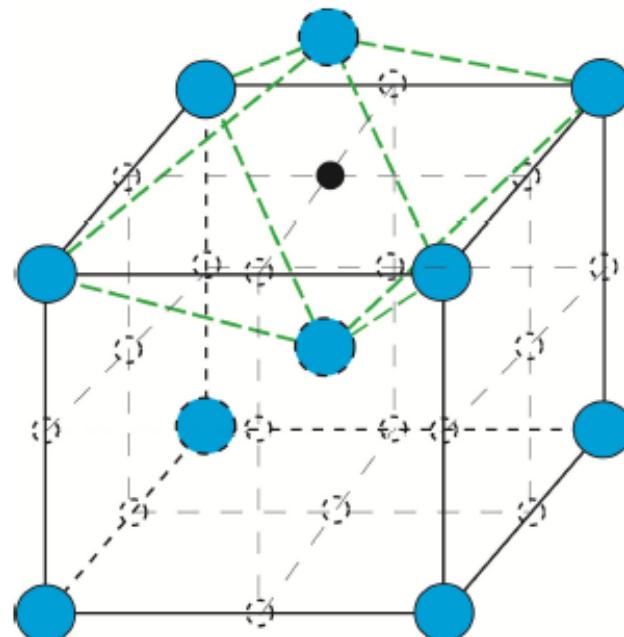
## Positron annihilation measurements

- Because of decay of a radioactive isotope, positrons with equal mass but opposite sign to electron emit.
- These positrons combine with electron to produce gamma rays with particular energies.
- When these positrons are bombarded on a solid material it may travel for some time in the range of pico seconds before it combines with electrons.
- Positrons have a tendency to get trapped in a bound state in a vacancy.
- Since vacancies do not have core electrons compared to other atoms, it takes longer time for annihilation in a vacancy.
- So higher the concentration of vacancies, higher the half life time for annihilation.
- If at a particular temperature half life does not increase beyond a certain point, it indicates the equilibrium concentration of vacancies.
- Based on this half life time one can calculate the equilibrium concentration of vacancies.
- Since the relations are bit complex, we shall not discuss it here.
- It is found that the positron annihilation technique is one of the most accurate techniques to measure the concentration of vacancies.
- Thermal expansion technique is rather least reliable.

## Equilibrium concentration of interstitial atoms

- In many metals, especially in transition metals, interstitial atoms such as carbon, nitrogen, oxygen, hydrogen can be present up to a certain extent depending on the metal.
- There are mainly two types of interstitial voids present in the structure, where these atoms can sit: tetrahedral (surrounded by four solvent atoms) and octahedral (surrounded by six solvent atoms).
- However, since impurities prefer to occupy octahedral interstices, we shall mainly consider this type of voids only.

Let us first consider a BCC crystal



- In general the size of the interstitial atoms is much larger than the interstitial void and lattice surrounding the interstitial will be strained. That means enthalpy of the system will be increased.
- Consider the increase in enthalpy because of addition of one mole of interstitial atoms is  $\Delta H_I$
- The enthalpy increment of the system because of addition of  $X_I$  is expressed by

$$\Delta H = X_I \Delta H_I$$

Where  $X_I = \frac{n_I}{N_0}$  Number of interstitial atom is  $n_I$

- Further, there will be **two different types** of contribution on entropy
- Vibration of atoms A, next to interstitial atoms will change from normal mode of vibration and will be more random and irregular because of distortion of the lattice

$$\Delta S_{thermal} = X_I \Delta S_I$$

$\Delta S_I$  is the change of the entropy of one mole of atoms because of change in vibration pattern

➤ From the crystal structure, we can say that for 2 solvent atoms there are 6 sites for interstitial atoms. So if we consider that there are  $N_0$  numbers of A atoms then there will be  $3N_0$  numbers of sites available for interstitial atoms.

➤ In other sense, we can say that  $n_I$  atoms will randomly occupy in  $3N_0$  sites available. So the configurational entropy can be written as

$$\Delta S_{config} = k \ln w = k \ln \frac{3N_0!}{n_I!(3N_0 - n_I)!} \quad \text{Following Stirling's approximation } \ln N! = N \ln N - N$$

$$\Delta S_{config} = k [3N_0 \ln 3N_0 - n_I \ln n_I - (3N_0 - n_I) \ln (3N_0 - n_I)]$$

$$\Delta S_{config} = R \left[ 3 \ln 3N_0 - \frac{n_I}{N_0} \ln n_I - \frac{3N_0 - n_I}{N_0} \ln (3N_0 - n_I) \right]$$

$$= R \left[ 3 \ln \frac{3N_0}{3N_0 - n_I} - \frac{n_I}{N_0} \ln \frac{n_I}{3N_0 - n_I} \right]$$

$$\Delta S_{config} = R \left[ 3 \ln \frac{3}{3 - X_I} - X_I \ln \frac{X_I}{3 - X_I} \right]$$

➤ So the total entropy change  $\Delta S = X_I \Delta S_I + R \left[ 3 \ln \frac{3}{3 - X_I} - X_I \ln \frac{X_I}{3 - X_I} \right]$

➤ Free energy in presence of interstitial impurities

$$G = G_A + \Delta G = G_A + \Delta H - T\Delta S_I$$

$$G = G_A + X_I \Delta H_I - T X_I \Delta S_I - RT \left[ 3 \ln \frac{3}{3 - X_I} - X_I \ln \frac{X_I}{3 - X_I} \right]$$

➤ To find the equilibrium concentration, we need to take

$$\frac{dG}{dX_I} = 0$$

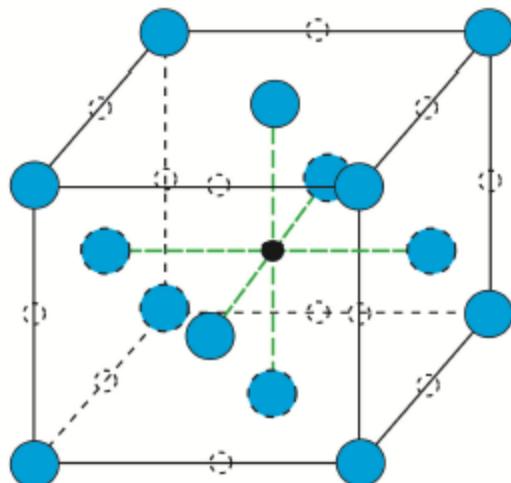
$$\Delta H_I - T\Delta S_I - RT \left[ -\frac{3}{3 - X_I} - \frac{X_I}{X_I} - \ln X_I + \ln(3 - X_I) - \frac{X_I}{3 - X_I} \right] = 0$$

$$\Delta H_I - T\Delta S_I + RT \ln \frac{X_I}{3 - X_I} = 0 \quad \text{since} \quad X_I \approx 0$$

$$X_I = 3 \exp \left( -\frac{\Delta H_I - T\Delta S_I}{RT} \right) = 3 \exp \left( -\frac{\Delta G_I}{RT} \right)$$

$G_I$  is the activation energy barrier

## Let us now consider the FCC crystal



- If we consider FCC crystal, then the number of sites available for interstitial atoms are 4. Further in a FCC unit cell, total 4 solvent atoms are accommodated. So we can say that for  $N_0$  solvent atoms there will be  $N_0$  sites available for interstitial atoms. Like previous example, we consider  $n_1$  interstitial atoms which will occupy randomly.
- Then following similar procedure, we can show the equilibrium concentration of interstitial atoms present in a metal with FCC crystal as

$$X_I = \exp\left(-\frac{\Delta G_I}{RT}\right)$$

➤ So in general, we can write that the equilibrium concentration of interstitial impurities present is

$$X_I = B \exp\left(-\frac{\Delta G_I}{RT}\right)$$

B depends on the crystal structure

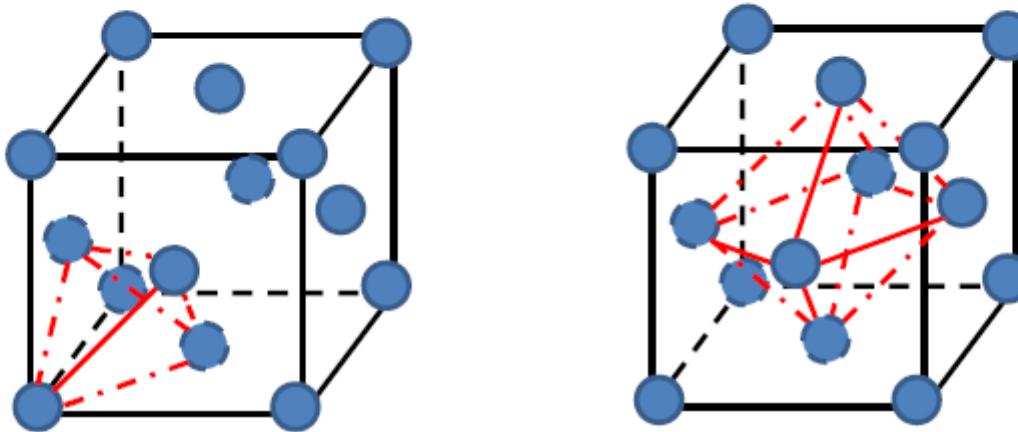
$$X_I = X_I^0 \exp\left(-\frac{\Delta H_I}{RT}\right)$$

$\Delta H_I$  is the activation enthalpy for interstitial impurities

$$X_I^0 = B \exp\left(\frac{\Delta S}{R}\right) \text{ is the pre-exponential factor}$$

## Why concentration of carbon in $\alpha$ -Fe with BCC structure is less than $\gamma$ -Fe with FCC structure?

- First let us consider FCC structure ( $\gamma$ -Fe)



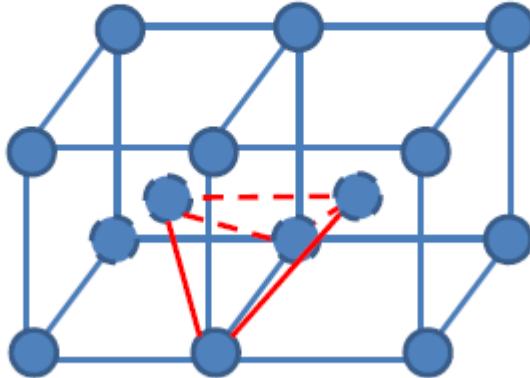
- Packing factor of FCC lattice 0.74
- This indicates the presence of voids. Let us discuss it more elaborately.
- In a FCC crystal there are mainly two types of voids:

Tetrahedral: coordination number (CN) is 4. That means the void is surrounded by 4 atoms.

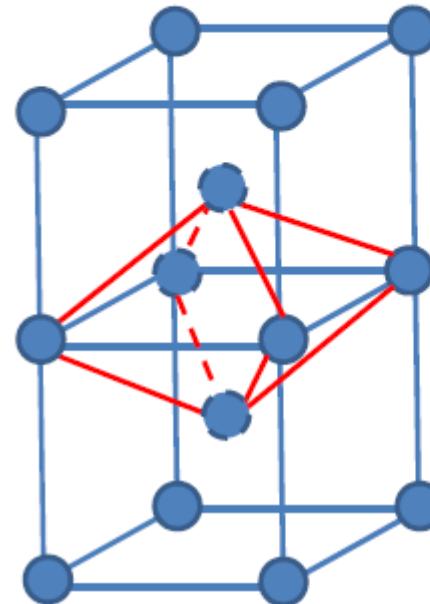
Octahedral: CN is 6. That means the void is surrounded by 6 atoms.

- There are 8 tetrahedral voids in a unit cell. That means 2 voids per atom.
- There are 4 octahedral voids in a unit cell. That means 1 void per atom.
- However, impurities prefer to occupy octahedral voids.
- Because the ratio of the radius of the tetrahedral void to atom is 0.225 and the same for the octahedral void is 0.414.
- The ratio of the radius of the carbon atom (size is 77 pm) to Fe (when it has FCC crystal) is 0.596.
- So when a carbon atom occupies any void, lattice will be distorted to increase the enthalpy.
- Distortion will be less if it occupies the octahedral voids.
- Although it increases the enthalpy, carbon atoms will be present up to a certain extent because of the gain in entropy, as explained previously, which decreases the free energy.

## Now let us consider the BCC unit cell ( $\alpha$ - Fe)



Tetrahedral void



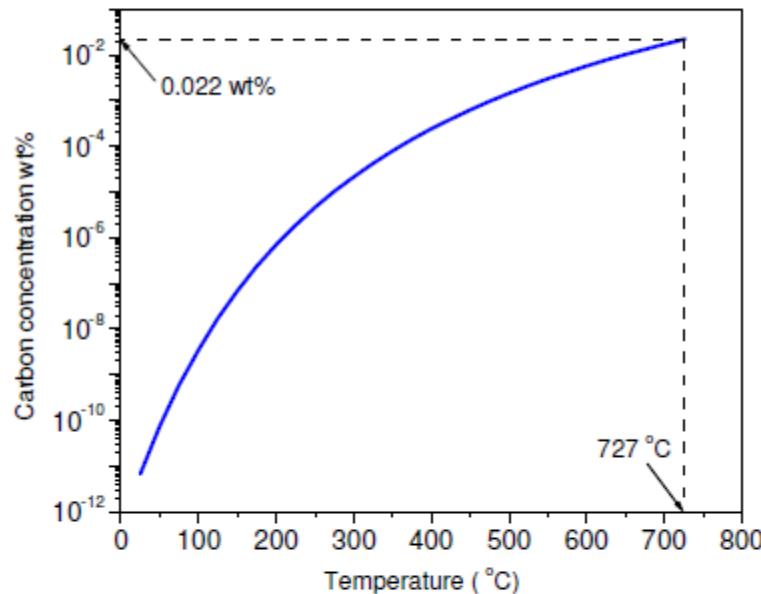
Octahedral void

- Packing factor of BCC lattice 0.68
- So total void in a BCC unit cell is higher than FCC cell.
- However, there are 12 (6 per atom) tetrahedral and 6 (3 per atom) octahedral voids present.
- This number is higher than the number of voids present in a FCC unit cell.

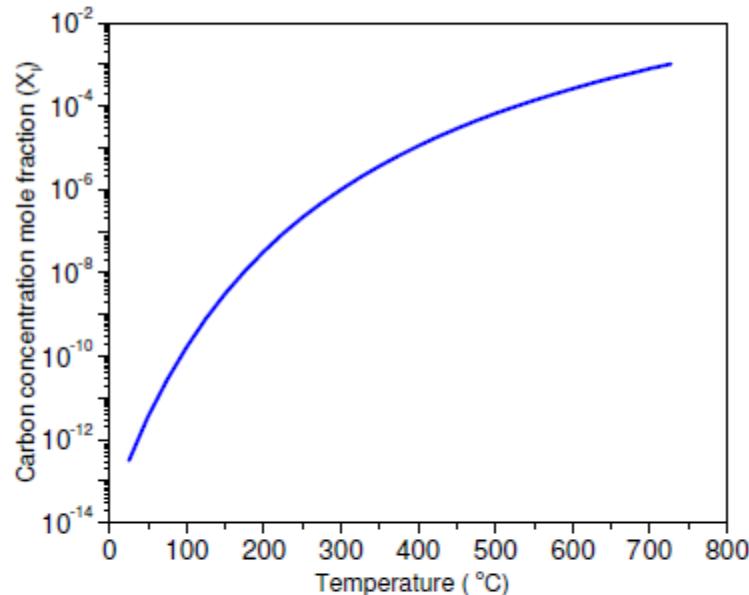
- Unlike voids in FCC lattice, in a BCC lattice the voids are distorted. That means if an atom sits in a void, it will not touch all the host atoms.
- The ratio of the radius of tetrahedral void to atom is 0.29 and the radius of octahedral void to atom is 0.155.
- The ratio of the radius of the C atom (size is 77 pm) to Fe (when it has BCC crystal) is 0.612.
- So it is expected that in a BCC unit cell, impurities should prefer tetrahedral voids.
- However, although the octahedral void size is small, planar radius which has 4 atoms on the same plane is 79.6 pm, which is larger than the C atom size. That means it needs to distort only other two atoms.
- On the other hand if C sits in the tetrahedral void it has to distort all four atoms.
- So in  $\alpha$  – Fe with BCC unit cell C occupies the octahedral voids

- Now the octahedral void size in  $\gamma$ -Fe (FCC) is higher than  $\alpha$ -Fe (BCC).
- So naturally the distortion in a BCC cell will be higher and the activation energy for impurities to occupy a void in a BCC cell also will be higher.
- This is the reason that we find much lower solubility limit of C in  $\alpha$ -Fe.
- Let us consider the C concentration in  $\alpha$ -Fe (BCC)

$$Wt\% = 240 \exp\left(-\frac{77300 \text{ J/mole}}{RT}\right)$$



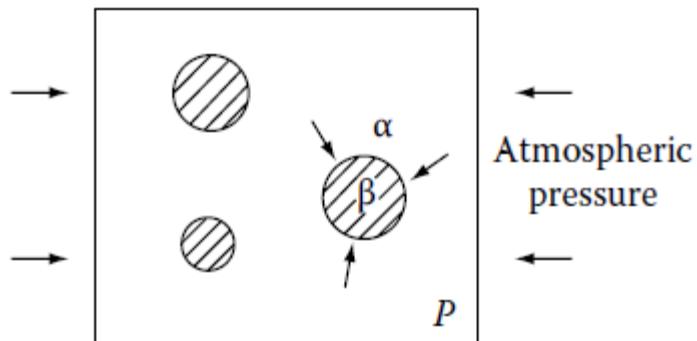
$$\text{In terms of mole fraction } X_I = 11.2 \exp\left(-\frac{77300 \text{ J/mole}}{RT}\right)$$



- At 727 °C, carbon concentration in  $\alpha$ -Fe is maximum (0.022 wt%), which is equivalent to mole fraction of  $\sim 10^{-3}$ . That means there is one C atom present in a cube of 10 atoms in each direction. That further means that only one carbon atom is present in 3000 octahedral voids

# The Influence of Interfaces on Equilibrium

Interphase interfaces are extremely important in early stages of phase transformation.



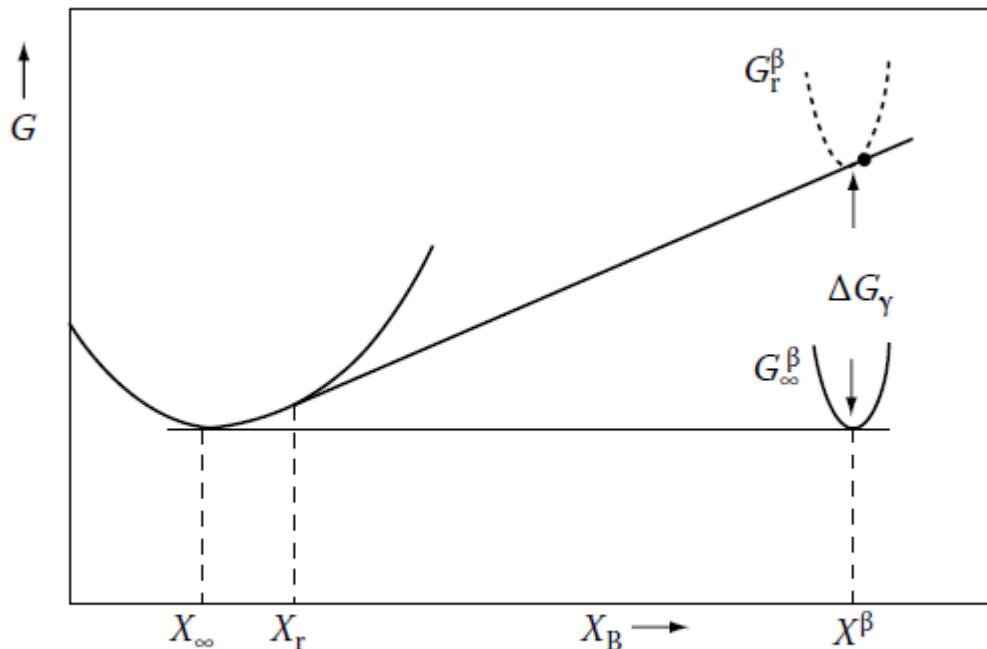
If  $\alpha$  phase acts 1 atm P,  $\beta$  phase is subjected to an extra  $\Delta P$  due to the curvature of  $\alpha/\beta$  interface.

If  $\gamma$  is the interfacial energy, and  $r$  is the spherical particle radius;

$$\Delta P = \frac{2\gamma}{r}$$

By definition, Gibbs Free Energy contains «PV» term and increase in P causes an increase in free energy G, by amount of  $\Delta G$ ;

$$\Delta G = \Delta P \cdot V \quad \text{which is actually} \quad \Delta G_\gamma = \frac{2\gamma V_m}{r} \quad ; V_m \text{ is molar volume of } \beta\text{-phase}$$

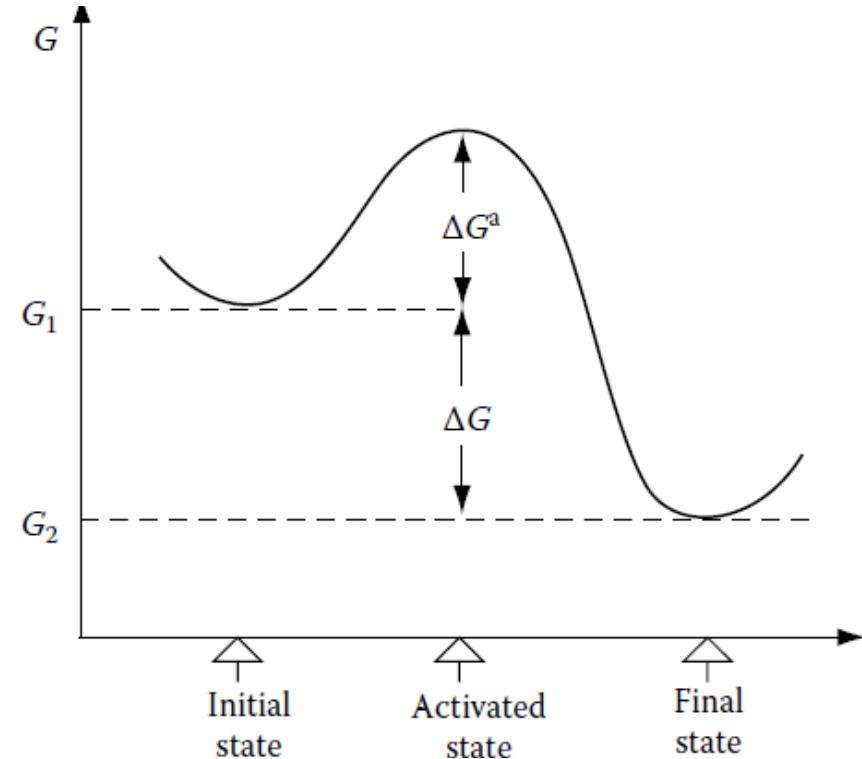


The effect of interfacial energy on the solubility of small particles.

This free energy increase due to the interfacial energy is known as capillarity effect or **Gibbs-Thomson effect**

# The Kinetics of Phase Transformations

Thermodynamics can be used to calculate driving force for a transformation, but can't say how fast transformation will proceed. This is a subject of *Kinetics*.



If  $G_1$  and  $G_2$  are the free energies of the initial and final states, the driving force for the transformation will be  $\Delta G = G_2 - G_1$ . However, before the free energy of the atom can decrease from  $G_1$  to  $G_2$  the atom must pass through a so-called *transition* or *activated* state with a free energy  $\Delta G^a$  above  $G_1$ .

# The Kinetics of Phase Transformations

According to kinetic theory, the probability of an atom reaching the activated state is given by  $\exp(-\Delta G^a/kT)$  where  $k$  is Boltzmann's constant ( $R/N_a$ ) and  $\Delta G^a$  is known as the *activation free energy barrier*.

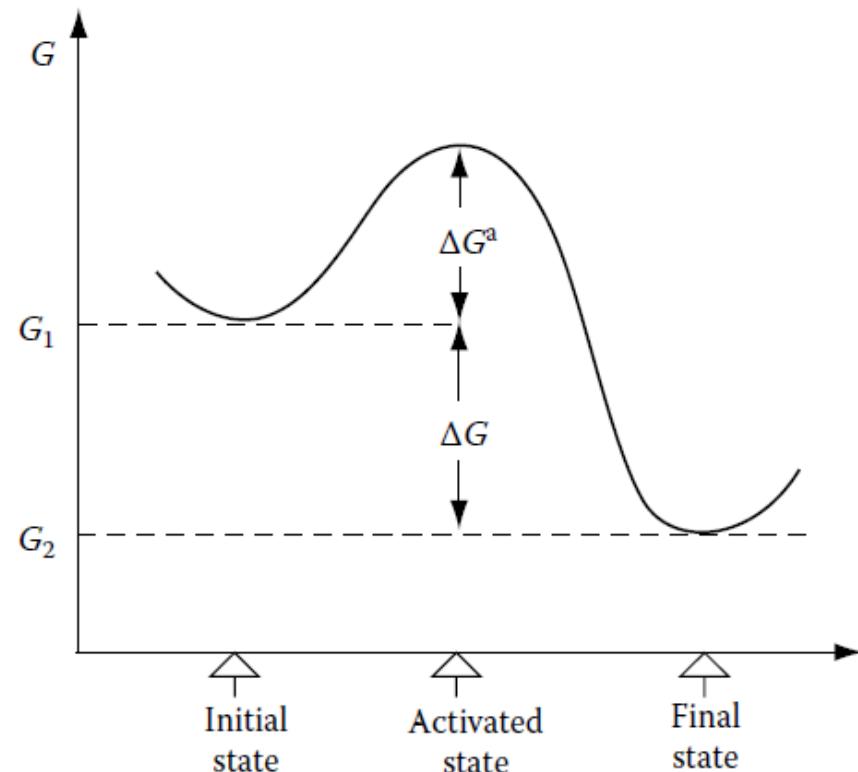
The rate at which a transformation occurs will depend on the frequency with which atoms reach activated state. Therefore we can write;

$$\text{rate} \propto \exp\left(-\frac{\Delta G^a}{kT}\right)$$

Putting  $\Delta G^a = \Delta H^a - T\Delta S^a$

$$\text{rate} \propto \exp\left(-\frac{\Delta H^a}{RT}\right)$$

**Arrhenius Rate Equation**



## DIFFUSION

Until now our concern was stable or equilibrium arrangements of atoms in an alloy. Phase transformation concerns those mechanisms by which a system attempts to reach this state and how long it takes.

One of the most fundamental processes that controls the rate at which many transformations occur is the diffusion of atoms.

What is the direction of diffusion? From high concentration to low concentration? Always? As can be seen in Fig. 2.1e and f the A and B atoms are diffusing from regions where the *chemical potential* is high to regions where it is low, i.e. *down* the chemical potential gradient in both cases.

In practice the first case is far more common than the second case, and it is usually assumed that diffusion occurs down concentration gradients. However, it can be seen that this is only true under special circumstances and for this reason it is better to express the driving force for diffusion in terms of a chemical potential gradient. Diffusion ceases when the chemical potentials of all atoms are everywhere the same and the system is in equilibrium.

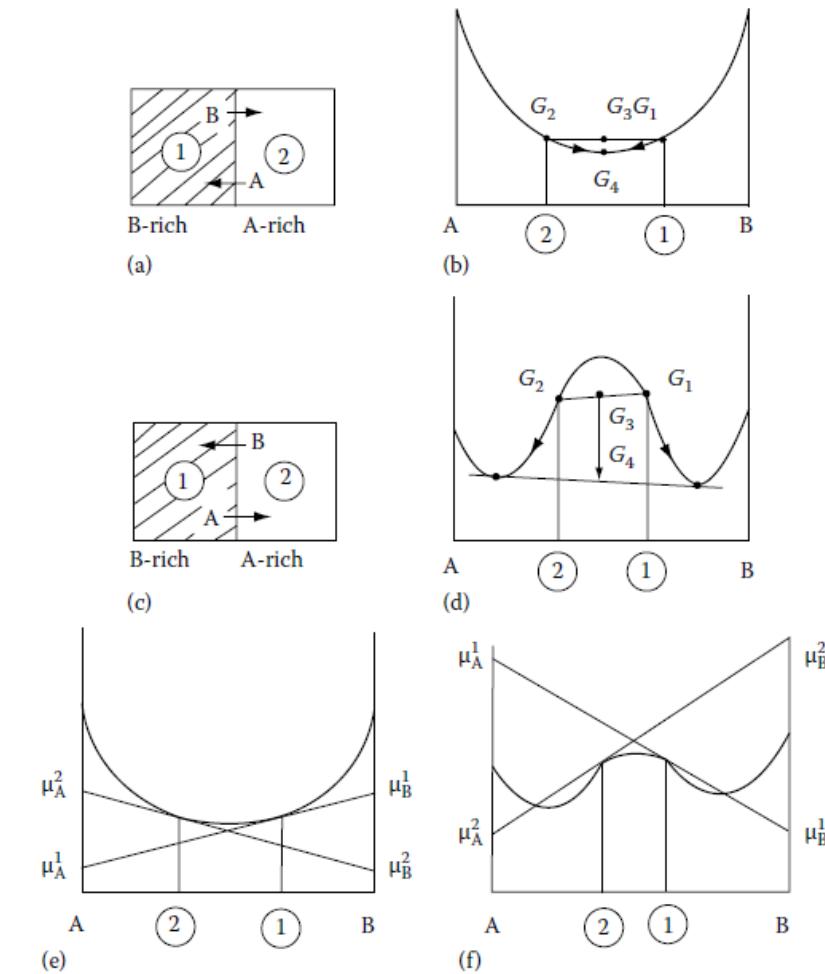


FIGURE 2.1

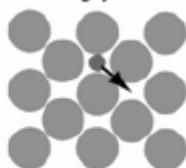
Free energy and chemical potential changes during diffusion, (a) and (b) 'down-hill' diffusion, (c) and (d) 'up-hill' diffusion, (e)  $\mu_A^2 > \mu_A^1$  therefore A atoms move from (2) to (1),  $\mu_B^2 > \mu_B^1$  therefore B atoms move from (1) to (2). (f)  $\mu_A^1 > \mu_A^2$  therefore A atoms move from (1) to (2),  $\mu_B^2 > \mu_B^1$  therefore B atoms move from (2) to (1).

## Atomic mechanism of diffusion

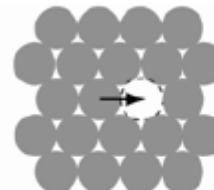
- Till now, we discussed the diffusion process without going to the atomic level.
- By measuring concentration profile, one can measure the diffusion coefficients.
- However, to get further insights on the diffusion process, we need to understand the atomic mechanism.
- It is almost impossible to track the jump of any particular atom.
- However, based on the experimental results, we can use logical arguments to explain the process in the atomic level.
- The aim of this topic is to explain the possible mechanisms without going to extreme complications.

Mainly there can be two types of diffusion:

Interstitial diffusion



Substitutional diffusion



- Solvent atoms
- Interstitial atoms
- Vacancy

- As we have seen before that all elements will have some impurities.
- C, O, H etc. are present in most of the metals in interstitial voids.
- Diffusion occurs by interstitial diffusion mechanism.
- Similarly vacancies are also always present.
- So substitutional diffusion is possible because of presence of vacancies.

Let us first consider random jump of atoms that is diffusion without the presence of any driving force.

- Atoms vibrate with Debye frequency at their positions with an average energy of  $3kT$ .
- Because of violent oscillation, sometimes it can acquire enough energy to cross the activation barrier to jump to another position.
- In this context atoms can be considered as restless, aimless, brainless matter, which tries to jump even without any gain or purpose.
- In the case of interstitial diffusion, if the concentration of atoms is very less, atom can jump randomly to any other position, since as discussed before that most of the interstitial voids will be vacant.
- For example, as shown before, at maximum composition of C in  $\alpha$ -Fe, only one octahedral void is occupied out of 3000 voids.
- In substitutional diffusion, however, the diffusion process is rather complicated since one particular atom can exchange position on the condition that vacancy is available next to it.
- We have shown before that, on average, near the melting point, only one vacancy is available out of 1000 atoms. So in general substitutional diffusion rate is much lower compared to the rate of interstitial diffusion.
- We shall discuss these two atomic mechanisms of diffusion one by one.

## Interstitial Diffusion

Although random atomic jump model usually doesn't fit in real alloys, experiments show that Fick's 1<sup>st</sup> law is still applicable (only if the diffusion coefficient  $D$  is made to vary with composition).

For ex; Diffusion coeff. of Carbon in FCC-Fe at 1000°C is  $2.5 \times 10^{-11} \text{ m}^2/\text{s}$  at 0.15 wt% C; but it is  $7.7 \times 10^{-11} \text{ m}^2/\text{s}$  in solutions containing 1.4 wt% C.

The reason for the increase of  $D_C^S$  with concentration is C atoms result in strain of Fe-lattice and making diffusion easier as the amount of strain increases.

## Diffusion Distance

For a random walk in 3D, after  $n$  steps of length  $\Delta x$  the 'average' atom will be displaced by a net distance  $\Delta x \sqrt{n}$  from its original position. (root mean square displacement after  $n$  steps)

Therefore after a time  $t$ , the average atom displaced a radial distance  $r$ , where

$$r = \Delta x \sqrt{(t/\tau)}$$

$$\text{by substituting } D = \frac{1}{6} \tau \Delta x^2 \Rightarrow r = 2.4 \sqrt{Dt}$$

$\sqrt{Dt}$  distance is very important in diffusion problems.

ex. lattice parameter of  $\gamma$ -Fe is 0.32 m  $\rightarrow$  jump distance

$$\text{is } \frac{a\sqrt{2}}{2} = 0.26 \text{ m. } D_c^{\gamma} \text{ at } 1000^\circ\text{C} = 2.5 \times 10^{-9} \text{ m}^2/\text{s}$$

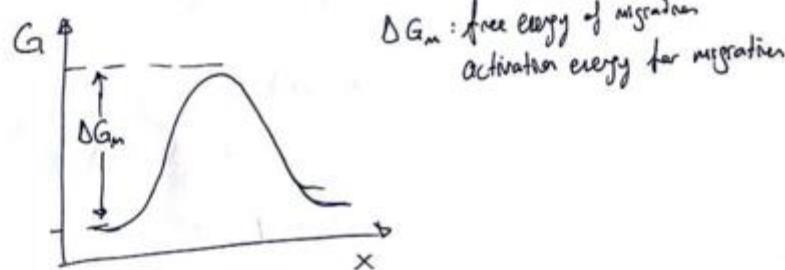
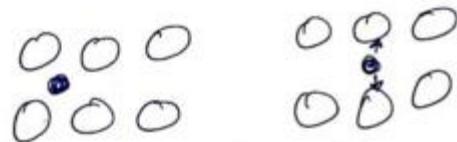
$$D = \frac{1}{6} \Gamma \Delta x^2 \Rightarrow \Gamma = 2 \times 10^9 \text{ jumps/s}$$

Typical vibrational freq. of atoms are in the range of  $10^{12}$  -  $10^{14}$

Let's take  $10^{13}$  for Carbon  $\Rightarrow$  1 attempt  $\approx 10^4$  results  
in a jump atom side to another

in 1 second, carbon diffuses in  $\gamma$ -Fe with a total movement  
of 0.5 meters, but only a net displacement of  $\approx 10 \mu\text{m}$ !

Effect of Temperature - Thermal Activation



In any system in thermal eq<sup>n</sup> the atoms are constantly colliding each other and changing their vibrational energy. On average, the fraction of atoms with an energy of  $\Delta G$  is given by  $\exp(-\Delta G/RT)$ .

If the interstitial atom is vibrating with a mean freq.  $\nu$  in the  $x$  direction, it makes  $\nu$  attempts that are successful is given by  $\exp(\Delta G_m/RT)$ . If 2 sites are available to jump, jump freq. is given by;

$$\Gamma = 2\nu \exp\left(\frac{-\Delta G_m}{RT}\right)$$

$$\Delta G_m = \Delta H_m - T \Delta S_m ; \text{ combine with } D = \frac{1}{6} \Gamma \Delta x^2$$

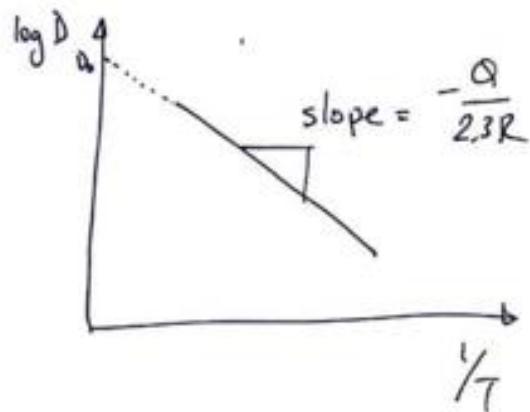
$$\Rightarrow D = \left[ \frac{1}{6} \Delta x^2 2\nu \exp \frac{\Delta S_m}{R} \right] \exp \frac{-\Delta H_m}{RT}$$

This can be simplified to an Arrhenius-type eq<sup>n</sup>.

$$D = D_0 \exp \frac{-Q_{ID}}{RT} \quad Q_{ID} = \text{activation energy for interstitial diffusion.}$$

$$\left[ D_0 = \frac{1}{6} \Delta x^2 2\nu \exp \frac{\Delta S_m}{R} \right] \quad Q_{ID} = \Delta H_m$$

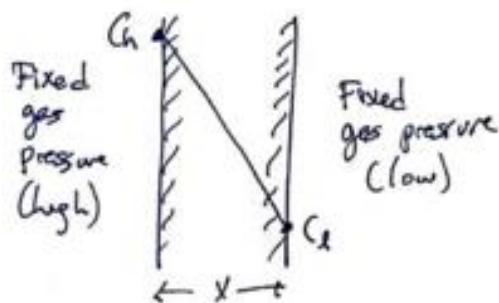
$$\log D = \log D_0 - \frac{Q}{2.3R} \left( \frac{1}{T} \right)$$



The slope of  $\log D$  vs  $1/T$  graph gives the activation energy for diffusion!

### Steady-State Diffusion

In steady state diffusion, concentration doesn't change with time



$$\frac{\partial C}{\partial x} = \frac{\Delta C}{\Delta x} = \frac{C_h - C_l}{0 - x} = -\frac{C_h - C_l}{x}$$

$$\text{Flux, } J = D \frac{C_h - C_l}{x}$$

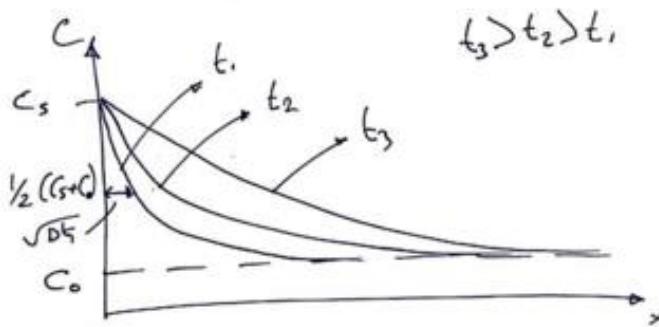
### Nonsteady-State Diffusion

In most practical situations, steady-state conditions are not established, which means concentration varies with distance and time.  
 → Fick's first law is invalid.

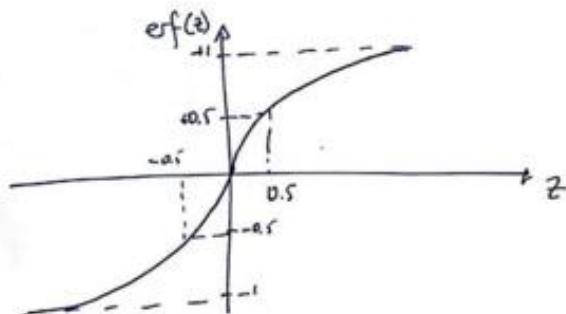
## Carburization of Steel

The aim is to increase carbon concentration in the surface of steel to achieve a harder wear-resistant surface. This is usually done by holding the steel in a gas mixture containing  $\text{CH}_4$  and/or  $\text{CO}$  at a  $T$  where it is austenite.

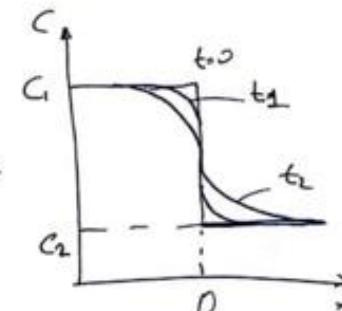
The concentration profile after different times is like;



$$C = C_s - (C_s - C_0) \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$



more accurate values are tabulated.



$t_2 > t_1 > 0$   
Conc. profiles when 2 bars of different comp. are annealed after welding.

Note that; since  $\text{erf}(0.5) \approx 0.5$  the depth at which

the carbon concentration is midway between  $C_s$  and  $C_0$

is given by  $\frac{x}{2\sqrt{Dt}} \approx 0.5 \Rightarrow x \approx \sqrt{Dt}$

Therefore the thickness of carburized layer is  $\sqrt{Dt}$ .

(to obtain a twofold increase in penetration requires 4-fold time)

Carbon diffusn in  $\gamma$ -Fe at 1000°C,  $D = 4 \times 10^{-11} \text{ m}^2/\text{s}$ , which means

that a carburized layer 0.2 mm thick requires

$$\text{a time; } \frac{(0.2 \times 10^{-3} \text{ m})^2}{4 \times 10^{-11} \text{ m}^2/\text{s}} = 1000 \text{ s (17 mins)}$$

During decarburization of steel, surface concentration is reduced to a very low value ( $C_s \rightarrow 0$ )

$$\Rightarrow C = C_0 \text{ erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

Another situation; 2 semi-infinite specimens of different compositions  $C_1$  and  $C_2$  are joined together and annealed.

The relevant solution is;

$$C = \left( \frac{C_1 + C_2}{2} \right) - \left( \frac{C_1 - C_2}{2} \right) \text{ erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

z	erf(z)	z	erf(z)	z	erf(z)
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

## Substitutional Diffusion

In dilute interstitial alloys diffusion is simple because the diffusing atoms are always surrounded by 'vacant' sites to which they can jump.

In substitutional diffusion, an atom can jump only if there is a vacant site around (see fig.)



The simplest case for substitutional diffusion

i) self-diffusion.

## Self-Diffusion

The rate of self-diffusion can be measured experimentally by introducing a few radioactive A atoms ( $A^*$ ) into pure A and measuring the rate of penetration at various temperatures.

Since  $A^*$  and A are chemically identical, their jump frequencies will be almost same.  $\Rightarrow D_{A^*} = D_A = \frac{1}{6} \Delta x^2 \Gamma$

This equation was derived by assuming that each atomic jump is unrelated to the previous jump.

This was good approx. for interstitial diffusion, but not for self-diffusion.

$$\Rightarrow D_A^* = f D_A = f \frac{\Delta x^2}{6} ; \quad f: \text{correlation factor}$$

however, this effect is small and  $f$  is close to unity.

The probability of an adjacent site is vacant is given by  $z X_v$ ;  $z$  is the number of nearest neighbours and  $X_v$  is the probability that any one site is vacant; which is just the mole fraction of vacancies in the metal.

Combining the thermal energy of migration and vacant site probability;  $\Gamma = \nu z X_v \exp \frac{-\Delta G_m}{RT}$

( $\nu$  is temp-independent vibration frequency of atoms)

If vacancies are in thermodynamic equl<sup>M</sup>;  $X_v = X_v^e$

$$X_v^e = \exp \frac{-\Delta G_v}{RT} \Rightarrow D_A = \frac{1}{6} \Delta x^2 z \nu \exp \frac{-(\Delta G_m + \Delta G_v)}{RT}$$

$$D_A = \frac{1}{6} \Delta x^2 z \nu \exp \frac{\Delta S_m + \Delta S_v}{R} \exp \left( -\frac{\Delta H_m + \Delta H_v}{RT} \right)$$

For most metals  $v \approx 10^{13}$

In FCC metals  $z=12$  and  $\Delta x = \frac{a\sqrt{2}}{z}$

$$\Rightarrow D_A = D_0 \exp \frac{-Q_{SD}}{RT} \sim \text{activation energy for self-diffusion}$$

$$D_0 = \frac{1}{6} \Delta x^2 z v \exp \frac{\Delta S_m + \Delta S_v}{R} \quad \text{and} \quad Q_{SD} = \Delta H_m + \Delta H_v$$

Consider the effect of  $T$  on self-diffusion in Cu.

At 800°C the data give  $D_{Cu} = 5 \times 10^{-9} \text{ mm}^2/\text{s}$ .

The jump distance  $\Delta x$  in Cu = 0.25 nm

and from  $D = \frac{1}{6} \Delta x^2 \Gamma \Rightarrow \Gamma = 5 \times 10^5 \text{ jumps/s}$

After an hour at this  $T$ ,  $\sqrt{Dt} \approx 4 \mu\text{m}$ .

Extrapolating the data to 20°C  $\rightarrow D_{Cu} = 1 \times 10^{-34} \text{ mm}^2/\text{s}$

$\Gamma_{Cu} \approx 1 \times 10^{-20} \text{ jumps/s}$   $\rightarrow$  each atom would make one jump every  $10^{12}$  years!