Universidad
Carlos III de Madrid
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MATERIALS SCIENCE AND ENGINEERING

TOPIC 2. STRUCTURE OF MATERIALS IV

Topic 2.4:

- **Mass transport: diffusion.**

DEFINITION OF DIFFUSION

Diffusion (transport phenomena): mechanisms by which material is transported through the material.

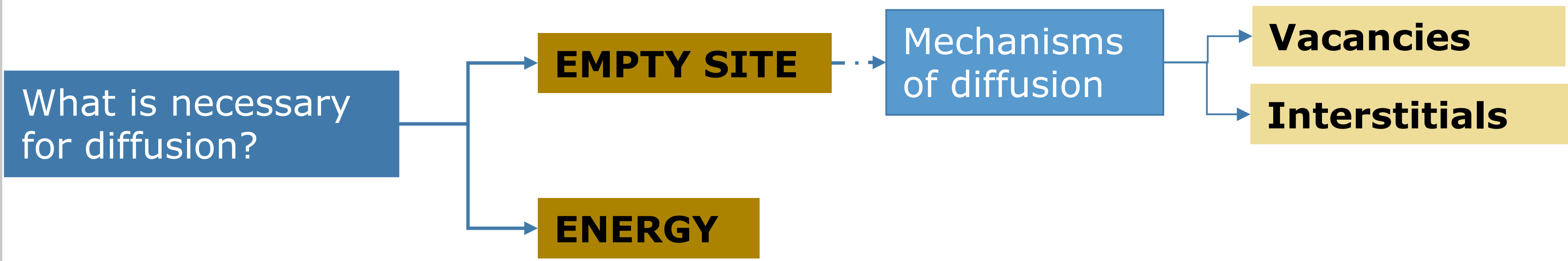
Diffusion in solids ⇒ movement of atoms within a solid ➔ The thermal vibrations in solids permit movement of some atoms ➔ Phenomena that need thermal activation

Diffusion: movement of atoms through the material.

STRUCTURE VS DIFFUSION

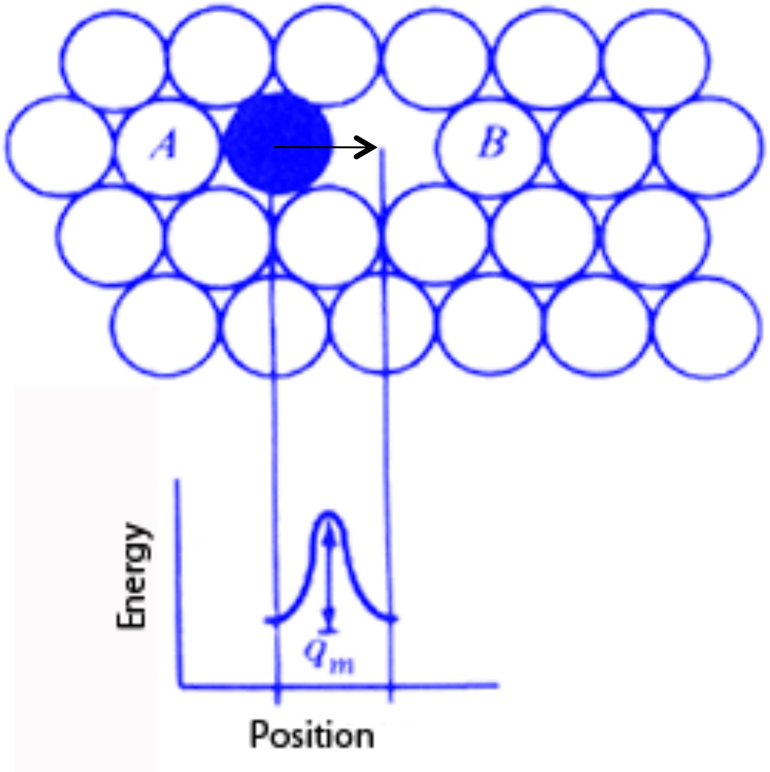
DIFFUSION is RAPID in...	DIFFUSION is SLOWER in...
Open crystalline structures	Compact crystalline structures
Materials with low T_m	Materials with high T_m
Increasing the T	Covalent materials
Small species	Large species

DIFFUSION MECHANISMS



DIFFUSION MECHANISMS

Self-diffusion: atoms exchanging positions are of the same type (pure metals)



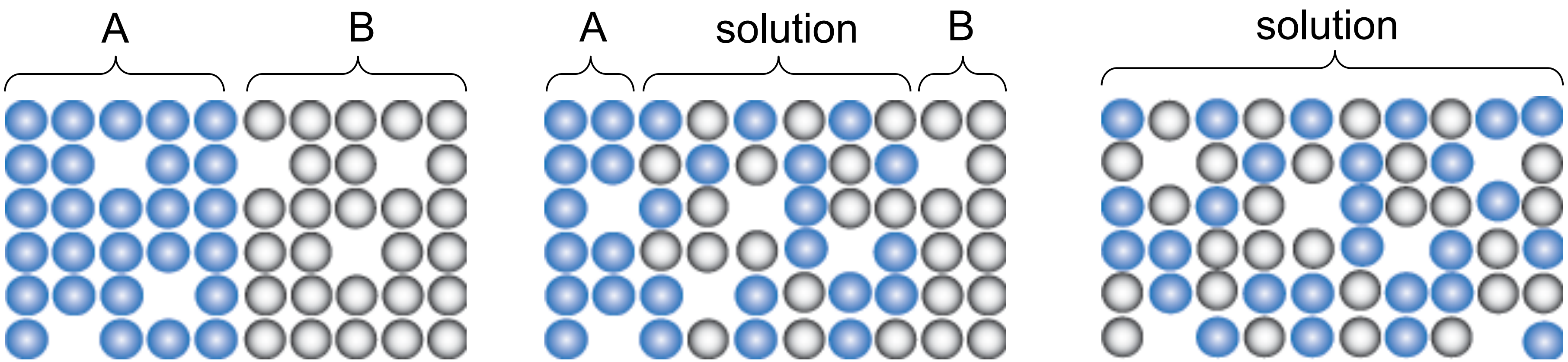
ɔtential Energy of atoms as a
ction of their position

VACANCY DIFFUSION

Atoms movement

1) $\uparrow E_{thermal}$ to overcome $E_{activation}$
2) Displacement of vacancies or defects. Vacancies are defects in equilibrium and are always present.

As $\uparrow T \Rightarrow \left\{ \begin{array}{l} \uparrow [\text{defects}] \\ \uparrow E_{thermal} <> E_{act} \end{array} \right\} \Rightarrow \uparrow$ diffusion



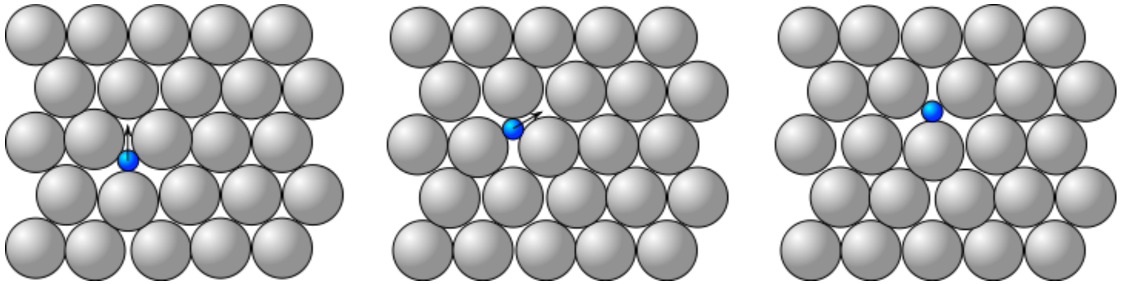
ACTIVATION ENERGY

- When $\uparrow T_{melting} \Rightarrow E_a \uparrow$
- Given that if $T_m \uparrow \Rightarrow E_{bond} \uparrow$

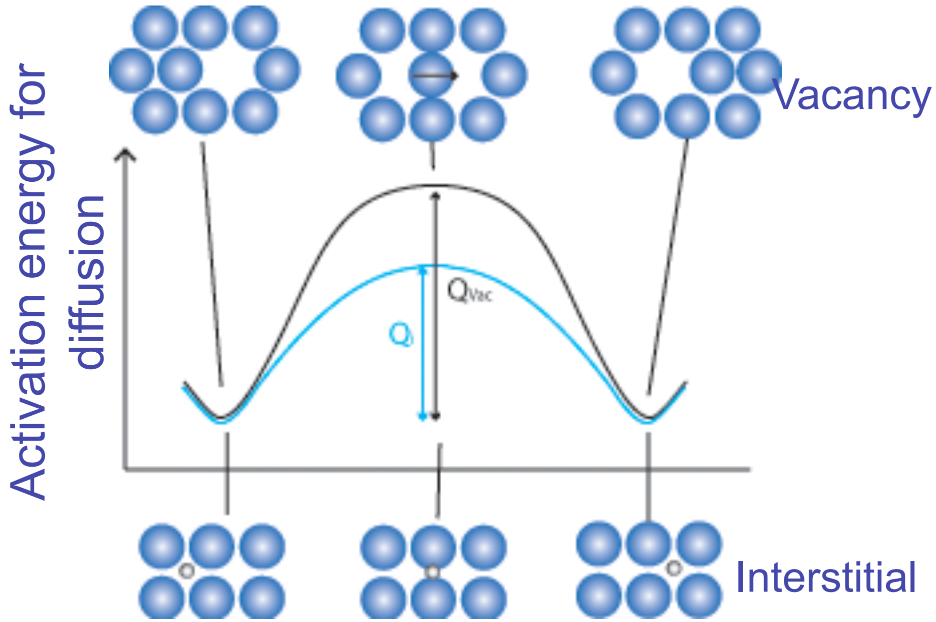
	Melting Temperature (°C)	Crystal structure	Activation energy (kJ/mol)
Zinc	419	HCP	91.6
Aluminium	660	FCC	165
Copper	1083	FCC	196
Nickel	1452	FCC	293
Molybdenum	2600	BCC	460

INTERSTITIAL DIFFUSION

Atoms in interstitial positions are displaced to other interstitial positions **without displacing** permanently any atoms of the matrix



The atoms that diffuse interstitially are small with respect to the matrix (i.e.: in metals: C, H, O, N)

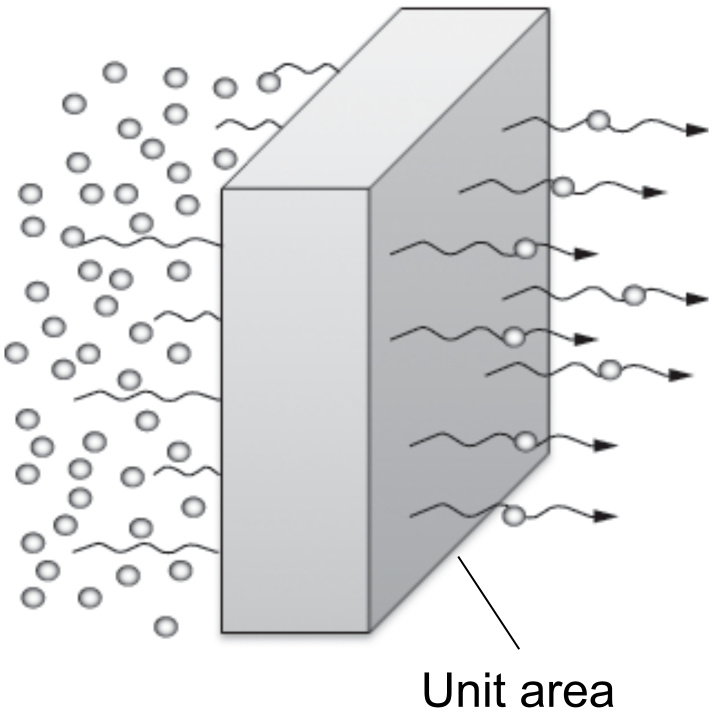


Interstitial diffusion :

- Has E_a< Diffusion of Vacancies
- It is more rapid
- There are many more interstitial sites than vacancies

STEADY STATE DIFFUSION : Fick's 1st law

The rate at which the atoms diffuse in a material can be measured by a diffusion ***flux,* J** defined as the nº of atoms that passing through a plane of unit area per unit time



Flux density ⇒ Fick´s 1st Law

$$J = -D\frac{\delta C}{\delta x}$$

J=nº atoms (or mass) per unit surface and time along distance x (at/m^{2}s or kg/m^{2}s)

δC/δx= concentration gradient in x direction (at/m^3 or kg/m^3)

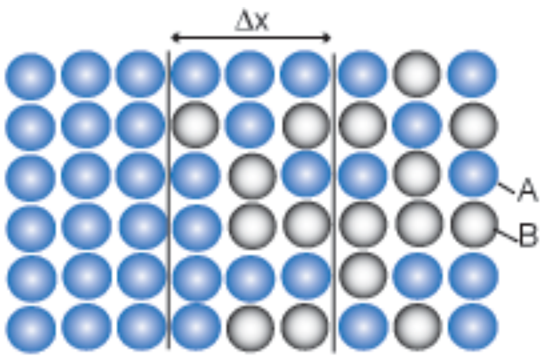
D= diffusivity or **diffusion coefficient** (m^2/s)

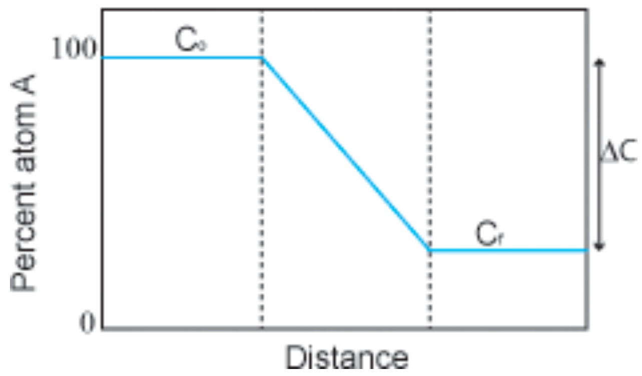
DRIVING FORCE = Composition gradient

STEADY STATE DIFFUSION : Fick's 1st law

Steady state conditions: The concentration of solute atoms at any point does not change with time.
The diffusion flux does not change with time

$$\frac{\partial J}{\partial t} = 0$$

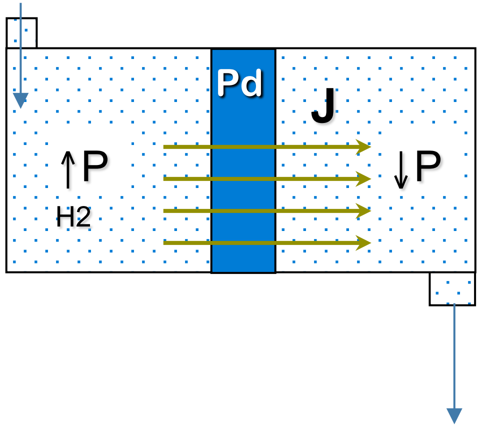


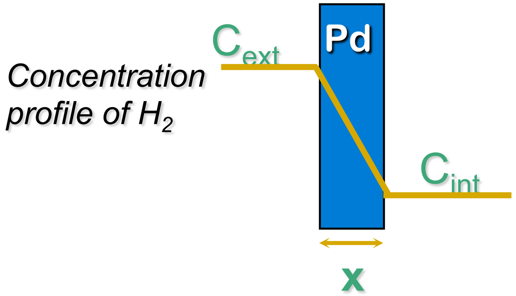


It is created putting in contact 2 materials with different composition. **J** at a T is constant only if the compositions are constant on each side ➔ if the composition gradient is constant

STEADY STATE DIFFUSION : example

Example: Diffusion of inert gas through a layer of Pd. H_2 Purification





$$\frac{\Delta C}{\Delta x} = \frac{C_{ext} - C_{int}}{x_1 - x_2}$$

Determine the thickness of a plate of Pd with transversal area of $0.2 m^2$ so that it can purify $1.733 \cdot 10^{-3}$ kg/h of hydrogen, if the hydrogen concentration at the side of high pressure of the plate is 1.5 kg/m^3 and at the side of low pressure is 0.3 kg/m^3. The diffusion coefficient of hydrogen in Pd is $1 \cdot 10^{-8}$ m^2/s.

$$J = -D\frac{\Delta C}{\Delta x}$$

The total mass of purified hydrogen depends on the flow of atoms that have passed though the Pd plate surface:

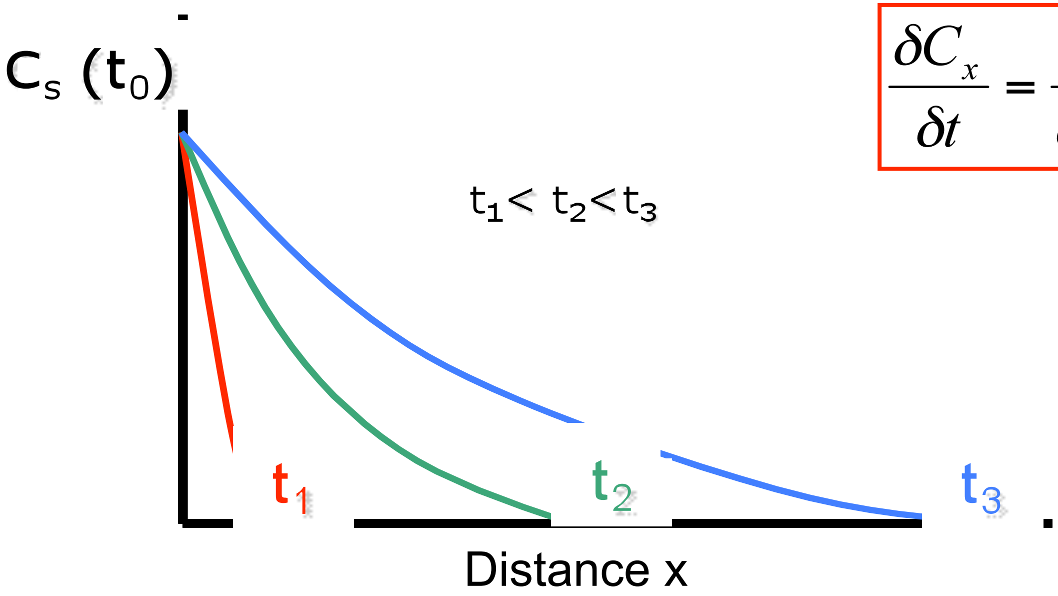
$$\text{flux} = \frac{\text{mass}}{\text{area} \cdot \text{time}} \Rightarrow J = \frac{1.73 \cdot 10^{-3}}{0.2} = 8.65 \cdot 10^{-3}\frac{kg}{m^2 h} = 2.4 \cdot 10^{-6}\frac{kg}{m^2 s}$$

$$J = -D\frac{\delta C}{\delta x} \approx -D \cdot \frac{(C_a - C_b)}{\Delta x} = 1.0 \cdot 10^{-8}\frac{(1.5 \cdot -0.3)}{\Delta x} = 2.4 \cdot 10^{-6} kg \cdot m^{-2} \cdot s^{-1} \Rightarrow \Delta x = 5mm$$

NON-STEADY STATE DIFFUSION : Fick's 2nd law

For the majority of materials ⇒ diffusion is ***non-steady state (transient)***: The concentration of solute atoms at any point of the material changes with time.

Non stationary state ⇒ The substances come to an end through extinction



$$\frac{\delta C_x}{\delta t} = \frac{\delta}{\delta x}\left(D\frac{\delta C}{\delta x}\right)$$

Cx ≠ cnt.
D ≠ f(t)

The diffusion flux and concentration gradient at some particular point in the solid vary with time, resulting in net accumulation or depletion of diffusing species

NON-STEADY STATE DIFFUSION : Fick's 2nd law

HYPOTHESIS: if D ≠ f(C) i.e. diffusion coeff. is independent of composition (there is no interaction between diffusing atoms)

$$\frac{\delta C_x}{\delta t} = D\frac{\delta^2 C}{\delta x^2}$$

boundary conditions need to be defined according to experiment

Rate of composition change **=** DIFFUSIVITY **x** Rate of composition gradient change

For Boundary conditions:

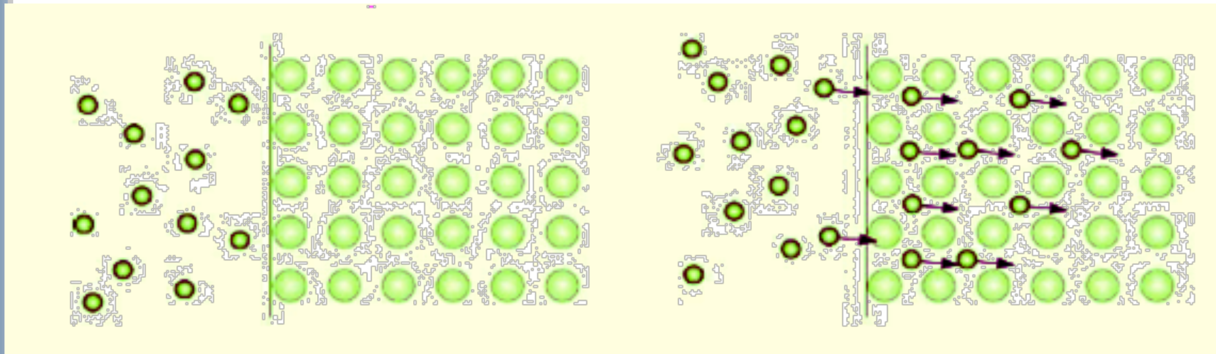
t=0, C=C_0 at 0 ≤x ≤∞.
t>0, → C=C_s at x=0 (surface concentration cnt.)
→ C=C_0 at x=∞

$$\frac{C_x - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

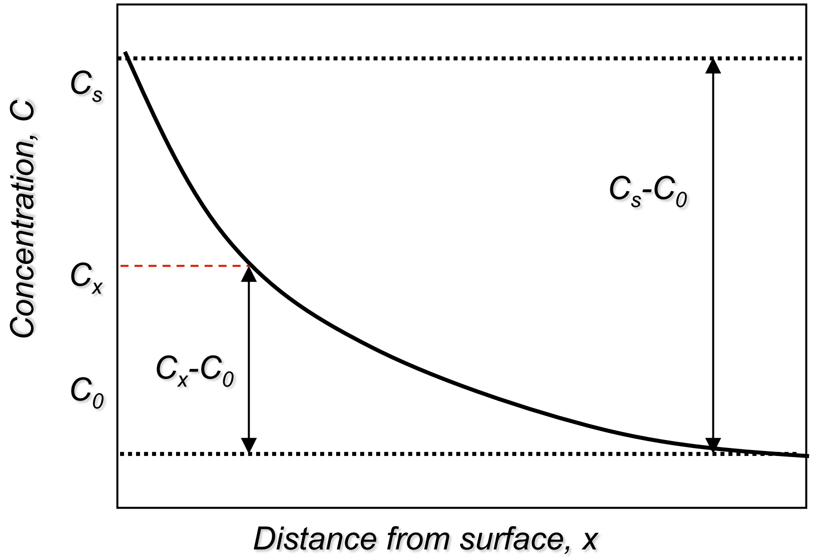
C_x = concentration at a distance x after time t
Erf = Gaussian error function

NON-STEADY STATE DIFFUSION : Fick's 2nd law

Example: diffusion of a gas (with constant surface concentration) in the interior of a semi infinite solid (carbon diffusion in steel, saturation of a metal with atmospheric gases)



$$\frac{C_x - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$



z	erf (z)	z	erf (z)
0.00	0.0000	0.70	0.6778
0.01	0.0113	0.75	0.7112
0.02	0.0226	0.80	0.7421
0.03	0.0338	0.85	0.7707
0.04	0.0451	0.90	0.7969
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.00	0.8427
0.15	0.1680	1.10	0.8802
0.20	0.2227	1.20	0.9103
0.25	0.2763	1.30	0.9340
0.30	0.3286	1.40	0.9523
0.35	0.3794	1.50	0.9661
0.40	0.4284	1.60	0.9763
0.45	0.4755	1.70	0.9838
0.50	0.5205	1.80	0.9891
0.55	0.5633	1.90	0.9928
0.60	0.6039	2.00	0.9953
0.65	0.6420		

C_t may be determined at any time and position if the parameters C_o, C_s and D are known

DIFFUSIVITY

Solute	Solvent Structure solvent	Diffisivity at 500ºC m^2/s	Diffisivity at 1000ºC m^2/s
Carbon	Iron FCC	$5 \times 10^{-15*}$	3×10^{-11}
Carbon	Iron BCC	10^{-12}	$2 \times 10^{-9*}$
Iron	Iron FCC	$2 \times 10^{-23*}$	2×10^{-16}
Iron	Iron BCC	10^{-20}	$3 \times 10^{-14*}$
Nickel	Iron FCC	10^{-23}	$2 \times 10^{-16*}$
Manganese	Iron FCC	$3 \times 10^{-24*}$	10^{-16}
silver	Silver (crystal)	-	10^{-12}
silver	Silver (grain boudnary)	10^{-11}	-
Carbon	Titanium HCP	3×10^{-16}	$2 \times 10^{-11*}$
*metastable phases			

FACTORS THAT INFLUENCE DIFFUSIVITY

a) Diffusion mechanism: Atom size

C diffuses interstitially in Fe-γ

Fe diffuses by vacancy diffusion in Fe-γ

b) Type of crystalline structure of the matrix lattice (solvent)

$D_{(C\ in\ Fe\text{-}\gamma,\ FCC)} = 5.10^{-15}\ m^2/s < D_{(C\ in\ Fe\text{-}\alpha,\ BCC)} = 10^{-12}\ m^2/s$

packing factor (BCC) < packing factor (FCC)

$d_{interatomic}$ (BCC) > $d_{interatomic}$ (FCC)

c) Type of imperfections or defects in the crystal:

Open structures (more holes) $\Rightarrow \uparrow D$

$D_{surface} > D_{grain\ boundary} > D_{volume}$

FACTORS THAT INFLUENCE THE DIFFUSIVITY

d) Concentration of species that diffuse

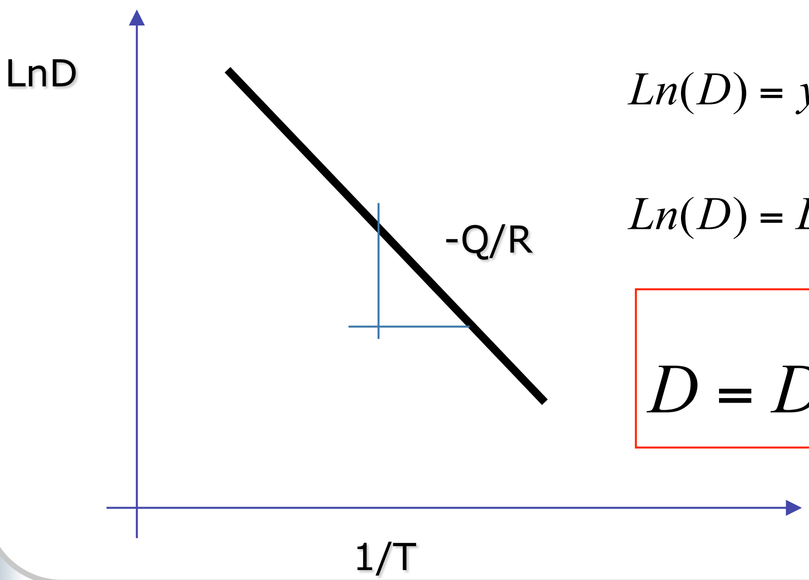
When we ↑ the concentration of solute atoms we modify D

e) Temperature

↑T ⇒ ↑D

Diffusion of atoms: when ↑ T , ↑ amplitude of vibration of atoms ⇒ greater probability of jump ⇒ D↑

D = f (T) Experimentally we find there is an Arrhenius type dependence :



$$Ln(D) = y_0 - \frac{Q}{R \cdot T}$$

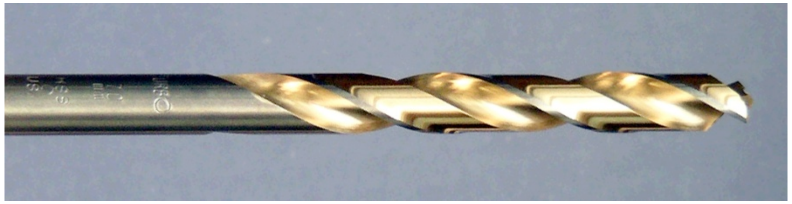
$$Ln(D) = Ln(D_0) - \frac{E_D}{R \cdot T}$$

$$D = D_0 e^{-\frac{E_D}{RT}}$$

D = diffusivity (m^2/s)
D_o = proportional coeff. (frequency factor)
E_D = activation energy necessary to produce the diffusive movement of 1 mol of atoms
R = gas constant
T = Temperature (K)

INDUSTRIAL APPLICATIONS EXAMPLES

- Cementation of gears $CH_4 – H_2$
- Fabrication of integrated circuits with Si wafers : diffusion of impurities.
- Si powder nitriding : Si_3N_4
- Diffusion soldering
- Sintering



Titanium nitride coated drill ; http://commons.wikimedia.org/wiki/File:Titanium_nitride_coating_90.jpg

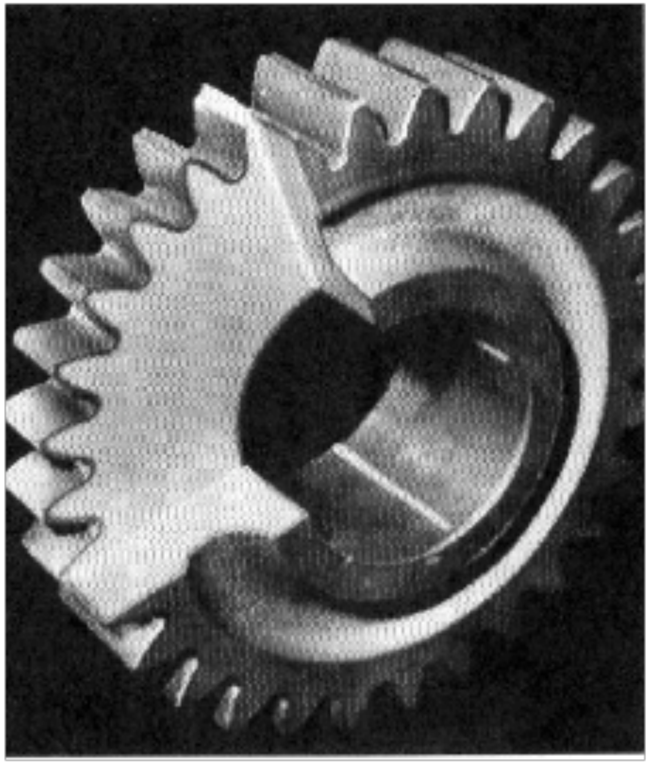
Aluminium Titanium Nitride coated Endmill recoated tools
http://commons.wikimedia.org/wiki/File:AlTiNCoatedEndmill_NanoShieldPVD_Thailand.JPG

CASE HARDENING - CEMENTATION

Case Hardening - Cementation (Interstitial diffusion) Diffusion of C atoms in the surface of a steel component .

The C atoms "block" the movement of dislocations, deform the lattice, make more difficult plastic deformation ➔ **Hardening**

The excess of C in the surface leaves a state of residual stresses in **compression**



William D. Callister, Jr. , Materials Science and Engineering : An Introduction, John Wiley & Sons, Inc.