

Chapter 5: Diffusion

Diffusion: the movement of particles in a solid from an area of **high** concentration to an area of **low** concentration, resulting in the uniform distribution of the substance

Diffusion is process which is NOT due to the action of a **force**, but a result of the random movements of atoms (**statistical problem**)

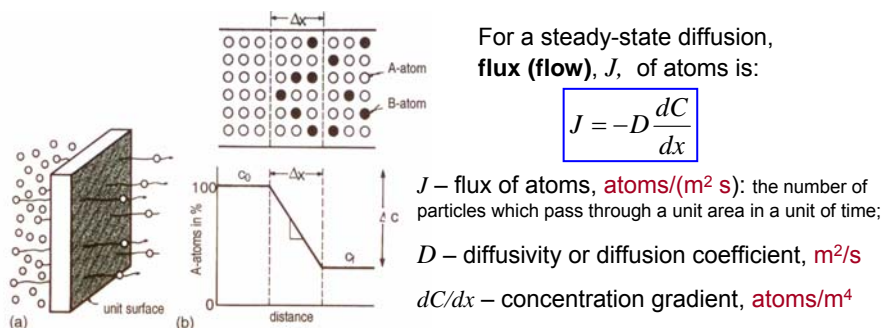
1. Diffusivity and 2 Fick's laws
2. Atomistic mechanisms of diffusion
3. Temperature dependence and Arrhenius plot
4. Industrial applications
 - carburized steel,
 - dopants in silicon

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5.1 Steady-State Diffusion

Consider diffusion of solute atoms (b) in solid state solution (AB) in direction x between two parallel atomic planes (separated by Δx)

- if there is **no changes with time** in C_B at these planes – such diffusion condition is called **steady-state diffusion**



Recall: Solvent – the majority atom type (or host atoms): **Solute** – the element with lower concentration

Substitutional – a solid solution in which the solute atoms are replaced by solute

Interstitial – solute atoms are located in gaps between host atoms

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Fick's first law of diffusion

$$J = -D \frac{dC}{dx}$$

For steady-state diffusion condition (**no change in the system with time**), the net flow of atoms is equal to the diffusivity D times the diffusion gradient dC/dx

$$J \left(\frac{\text{atoms}}{\text{m}^2 \text{s}} \right) = -D \left(\frac{\text{m}^2}{\text{s}} \right) \frac{dC}{dx} \left(\frac{\text{atoms}}{\text{m}^3} \times \frac{1}{\text{m}} \right)$$

'-' sign: flux direction is from the higher to the lower concentration; i.e. it is the opposite to the concentration gradient

Diffusivity D depends on:

1. Diffusion mechanism
2. Temperature of diffusion
3. Type of crystal structure (bcc > fcc)
4. Crystal imperfections
5. Concentration of diffusing species

Solute	Solvent (host structure)	Diffusivity (m ² /s)	
		500°C (930°F)	1000°C (1830°F)
1. Carbon	FCC iron	$(5 \times 10^{-15})^*$	3×10^{-11}
2. Carbon	BCC iron	10^{-12}	(2×10^{-9})
3. Iron	FCC iron	(2×10^{-23})	2×10^{-16}
4. Iron	BCC iron	10^{-20}	(3×10^{-14})
5. Nickel	FCC iron	10^{-23}	2×10^{-16}
6. Manganese	FCC iron	(3×10^{-24})	10^{-16}
7. Zinc	Copper	4×10^{-18}	5×10^{-13}
8. Copper	Aluminum	4×10^{-14}	10^{-10} M^2
9. Copper	Copper	10^{-18}	2×10^{-13}
10. Silver	Silver (crystal)	10^{-17}	10^{-12} M^2
11. Silver	Silver (grain boundary)	10^{-11}	
12. Carbon	HCP titanium	3×10^{-16}	(2×10^{-11})

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Non-Steady-State Diffusion

In practice the **concentration** of solute atoms at any point in the material changes **with time** – **non-steady-state diffusion**

For non-steady-state condition, diffusion coefficient, D - NOT dependent on time:

Second Fick's law of diffusion:
$$\frac{dC_x}{dt} = \frac{d}{dx} \left(D \frac{dC_x}{dx} \right)$$

If $D \neq D(x)$, in 1D case:

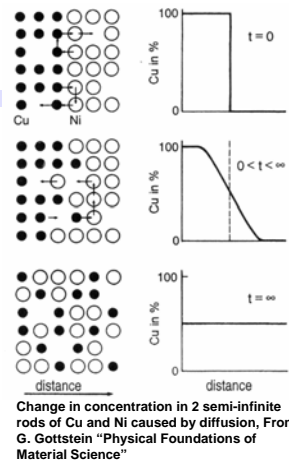
$$\frac{dC_x}{dt} = D \frac{\partial^2 C}{\partial x^2}$$

The rate of compositional change is equal to the diffusivity times the rate of the change of the concentration gradient

In 3D case:

$$\frac{dC_x}{dt} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)$$

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Non-Steady-State Diffusion (continued)

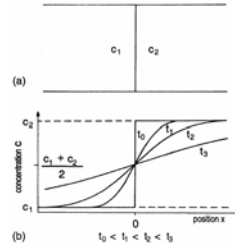
With specific initial or boundary conditions this partial differential equations can be solved to give the concentration as function of spatial position and time $c(x, y, z, t)$

Let us consider two rods with different concentrations c_1 and c_2 which are joined at $x=0$ and both are so long that mathematically they can be considered as infinitely long

The concentration profile at $t = 0$ is discontinuous at $x = 0$:

$x < 0, c = c_1; x > 0, c = c_2$

We can obtain solution of: $\frac{dC_x}{dt} = D \frac{\partial^2 C}{\partial x^2}$



$$c(x,t) - c_1 = \frac{c_2 - c_1}{\sqrt{\pi}} \int_{-\infty}^{\frac{x}{2\sqrt{Dt}}} e^{-\xi^2} d\xi = \frac{c_2 - c_1}{2} \left(1 + \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right)$$

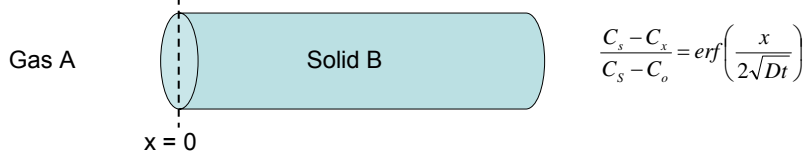
where $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\xi^2} d\xi$, is known as the error function

$$z = \frac{x}{2\sqrt{Dt}}$$

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Gas diffusion into a solid

Let us consider the case of a gas A diffusing into a solid B



C_s – surf. C of element in gas diffusing into the surface

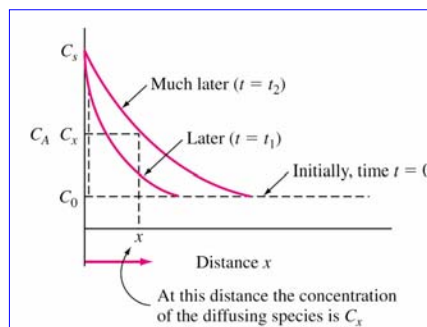
C_o – initial uniform concentration of element in solid

x – distance from surface

D – diffusivity of diffusing solute element

t – time

erf – mathematical function called **error function**

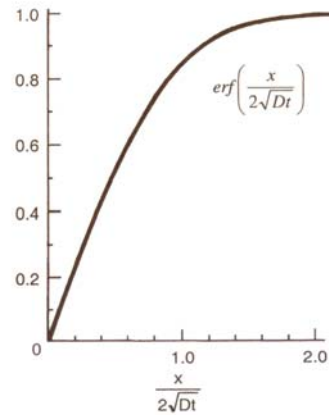


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Error function

Curve of the error function $erf(z)$ for

$$z = \frac{x}{2\sqrt{Dt}}$$



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

Q: Consider the gas carburizing of a gear of 1018 steel (C 0.18 wt %) at 927°C. Calculate the time necessary to increase the C content to 0.35 wt % at 0.40 mm below the surface of the gear. Assume the C content at the surface to be 1.15 wt % and that the nominal C content of the steel gear before carburizing is 0.18 wt %. D (C in γ iron) at 927°C = 1.28×10^{-11} m²/s

5.2 Atomistics of Solid State Diffusion

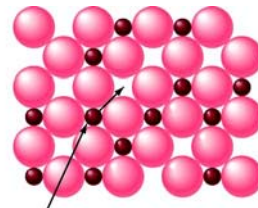
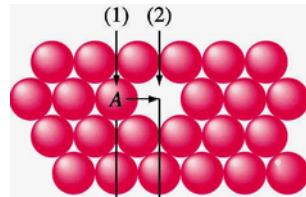
• Diffusion mechanisms:

1. **Vacancy** (substitutional) diffusion – migration of atom in a lattice assisted by the presence of vacancies

Ex.: self diffusion of Cu atoms in Cu crystal

2. **Interstitial** diffusion – movement of atoms from one interstitial site to another neighboring interstitial site without permanent displacement any of the atoms in the matrix crystal lattice

Ex.: C diffusion in BCC iron



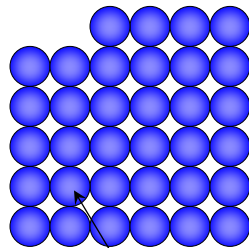
Interstitial atom
diffusing into
interstitial vacancy

Vacancies

The simplest point defect is the **vacancy (V)** – an atom site from which an atom is missing

Vacancies are always present; their number N_V depends on temperature (T)

$$N_V = N \times e^{-\frac{E_V}{kT}}$$



N_V - # of vacancies

N - number of lattice sites

E_V – energy required to form a vacancy

k – Boltzmann constant

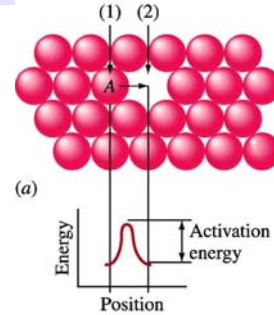
$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$; or $8.62 \times 10^{-5} \text{ eV K}^{-1}$

T – absolute temperature

Vacancy (Substitutional) Diffusion Mechanism

Substitutional (in homogeneous system - self-diffusion, in heterogeneous system – solid state solutions)

- Vacancies are always present at any T
- As T increases \Rightarrow # of vacancies increases \Rightarrow diffusion rate increases
- Move atom A (from (1) to (2)) = move vacancy from (2) to (1)..?



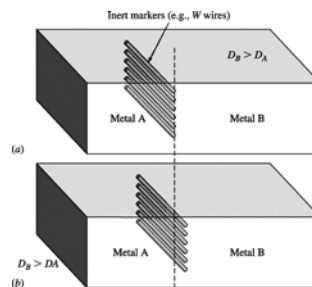
Metal	Melting point (°C)	Crystal structure	Temperature range studied (°C)	Activation energy	
				kJ/mol	kcal/mol
Zinc	419	HCP	240–418	91.6	21.9
Aluminum	660	FCC	400–610	165	39.5
Copper	1083	FCC	700–990	196	46.9
Nickel	1452	FCC	900–1200	293	70.1
α iron	1530	BCC	808–884	240	57.5
Molybdenum	2600	BCC	2155–2540	460	110

higher $T_{\text{melt}} \Rightarrow$ stronger bonding between atoms \Rightarrow high activation energy to move V

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Kirkendall effect

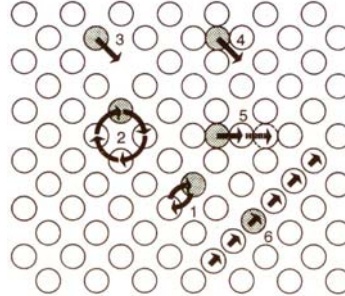
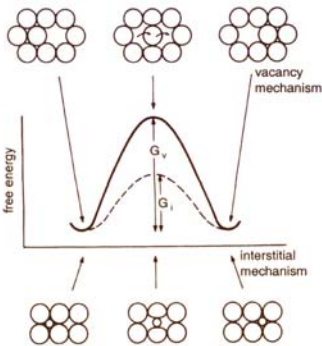
- Marker at the diffusion interface move slightly in the opposite direction to the most rapidly moving species \Rightarrow vacancies can move!



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Possible mechanisms of self-diffusion and their activation energy

1. Neighboring atoms exchange sites
2. Ring mechanism
3. Vacancy mechanism
4. Direct interstitial mechanism
5. Indirect interstitial mechanism



	Migration	Formation	Total
1	8 eV	-	8 eV
3	1 eV	1 eV	2 eV
4	0.6 eV	3.4 eV	4 eV
6	0.2 eV	3.4 eV	3.6 eV

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Anisotropy Effects

Table 5.2. Diffusion coefficient of various non-cubic metals parallel (\parallel) and perpendicular (\perp) to the basal plane.

Metal	Structure	$D_{0\parallel}$	$D_{0\perp}$	Q_{\parallel}	Q_{\perp}	D_{\perp}/D_{\parallel} $T = 0.8T_m$
		$[cm^2/s]$	$[cm^2/s]$	$[kJ/mol]$	$[kJ/mol]$	
Be	hcp	0.52	0.68	157	171	0.31
Cd	hcp	0.18	0.12	82.0	78.1	1.8
α -Hf	hcp	0.28	0.86	349	370	0.87
Mg	hcp	1.5	1.0	136	135	0.78
Tl	hcp	0.4	0.4	95.5	95.8	0.92
Sb	rhomb	0.1	56	149	201	0.098
Sn	diamond	10.7	7.7	105	107	0.4
Zn	hcp	0.18	0.13	96.4	91.6	2.05

From G.Gottstein "Physical Foundations of Material Science"

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Carbon diffusion in Fe

Jump frequency Γ [s^{-1}] of an atom is given by:

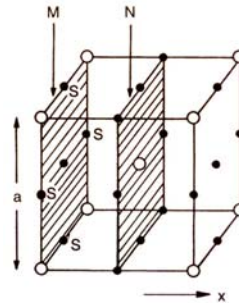
$$\Gamma = \nu \times e^{-\frac{G_m}{kT}}$$

Usually $\nu \cong 10^{13}$ [s^{-1}] vibrational frequency of the atom

There is a fundamental relationship between the jump frequency Γ and the diffusion coefficient D which is independent of mechanism and crystal structure:

$$D = \frac{\lambda^2}{6} \times \Gamma = \frac{\lambda^2}{6\tau}$$

λ – the jump distance of the diffusing atom
 $\tau = 1/\Gamma$ – the time interval between two jumps



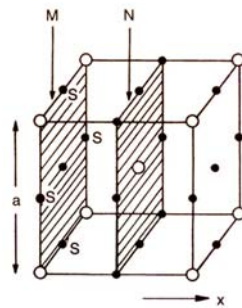
$$J = J_{MN} - J_{NM}$$

$$J = C_M^A \times \Gamma \times \frac{1}{4} \times \frac{2}{3} - C_N^A \times \Gamma \times \frac{1}{4} \times \frac{2}{3}$$

$$D = \frac{\Gamma a^2}{24}$$

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Carbon diffusion in Fe



Can be derived from an atomistic considerations of the diffusion processes

C atoms are located on the octahedral interstitial sites (black circles)

$$J = J_{MN} - J_{NM}$$

Only $\frac{1}{4}$ of possible jumps of C atoms lead to flux in $+x$

Only $\frac{2}{3}$ of all C atoms can jump in x direction

$$D = \frac{\lambda^2}{6} \times \Gamma = \frac{\lambda^2}{6\tau}$$

$$D = \frac{\Gamma a^2}{24}$$

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5.3 Effects of T on diffusion in solids

- Diffusion rate in a system will increase with temperature:

$$D = D_o \times e^{-\frac{E_A}{RT}}$$

D – diffusivity, m²/s

D_o . proportionality constant, m²/s, independent of T

E_A – activation energy for diffusing species, J/mol

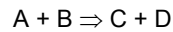
R – molar gas constant

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; or $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$

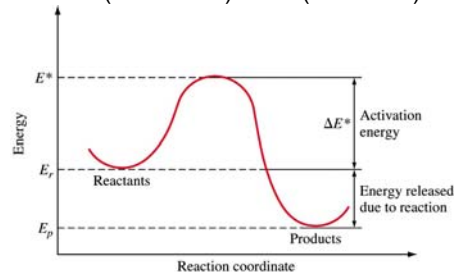
T – absolute temperature

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Activation energy



A (initial state) \Rightarrow A* (final state)



- only a fraction of the molecules or atoms in a system will have sufficient energy to reach E^*
- A thermally active process is one which requires a definite amount of thermal energy to overcome an *activation energy* barrier and enter the reactive state

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Boltzmann's equation

- On the basis of **statistical analysis**, Boltzmann's results showed that the probability of finding a molecule or atom at an energy level $E^* >$ the average energy E of all the molecules or atoms in a system at a particular temperature T , K, was:

$$\text{Probability} \propto e^{-\frac{E^* - E}{kT}}$$

where $k_B = 1.38 \times 10^{-23}$ J/(atom K) - Boltzmann's constant

- The fraction of atoms or molecules in a system having energies $> E^*$ at a given T (where E^* is much greater than the average energy of any atom or molecule):

$$\frac{n}{N_{total}} = C \times e^{-\frac{E^*}{kT}}$$

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Arrhenius Rate Equation

The rate of many chemical reaction as a function of temperature as follows:

$$\text{Rate of reaction} = C \times e^{-\frac{E_A}{RT}}$$

C – rate constant, independent of T

E_A – activation energy

R – molar gas constant

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; or $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$

T – absolute temperature

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Typical Arrhenius Plot

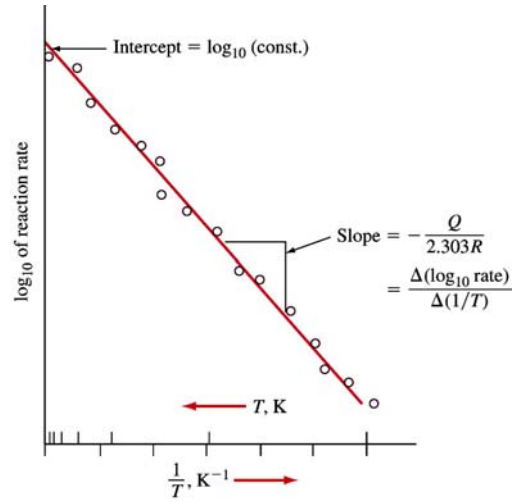
If we rewrite in natural log plot:

$$\ln \text{rate} = \ln C - \frac{E_A}{RT}$$

$$\left. \begin{array}{l} \ln \text{rate} = a \\ \ln C = b \\ x = \frac{1}{T} \end{array} \right\} y = b + m \times x$$

or in logarithmic log plot:

$$\log_{10} \text{rate} = \log_{10} C - \frac{E_A}{2.303RT}$$



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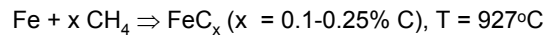
Q.: The diffusivity of Ag atoms in solid silver metal is $1.0 \times 10^{-17} \text{ m}^2/\text{s}$ at 500°C and $7.0 \times 10^{-13} \text{ m}^2/\text{s}$ at 1000°C . Calculate the activation energy (J/mole) for the diffusion of Ag in Ag in the T range 500 to 1000°C .

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5.4 Industrial applications

Steel Hardening by Gas Carburizing

In the gas carburizing process for steel parts, the parts are placed in a furnace in contact with a gas rich in CO-CH₄ mixture at ~927°C.

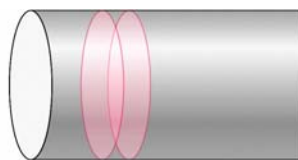


- The C from the gas diffuses into the surface of the steel part and increases the C content of the outer surface region of the part.
- The higher C concentration at the surface makes the steel harder in this region
- A steel part can thus be produced with a hard outer layer and a tough low C steel inner core (important, for example, for many types of gears)

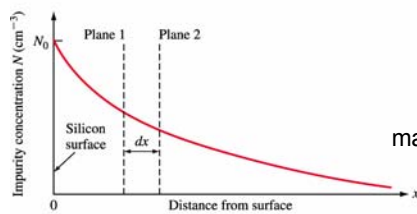
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Dopants activation

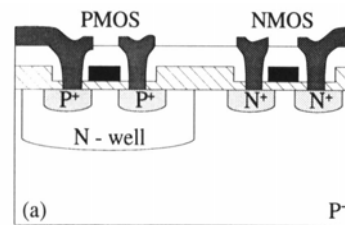
Dopants can be incorporated into Si wafer to change their electrical conducting characteristics



(a)

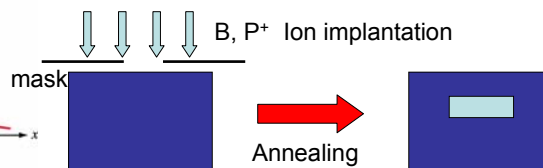


(b)



(a)

Si - bulk



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Q: If boron, B, is diffused into a thick slice of Si with no previous B in it at a temperature of 1100°C for 5 h, what is the depth below the surface at which the concentration is 10^{17} atoms/cm³ if the surface concentration is 10^{18} atoms/cm³? $D = 4 \times 10^{-13}$ cm²/s for B diffusing in Si at 1100°C.

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Summary

- **Diffusion:** the movement of particles in a solid from an area of **high** concentration to an area of **low** concentration, resulting in the uniform distribution of the substance

- **Fick's first diffusion law:** for steady-state diffusion condition (no change in the system with time), the net flow of atoms is equal to the diffusivity D times the diffusion gradient dC/dx

$$J = -D \frac{dC}{dx}$$

- **Fick's second diffusion law:** The rate of compositional change is equal to the diffusivity times the rate of the change of the concentration gradient

$$\frac{dC_x}{dt} = D \frac{\partial^2 C}{\partial x^2}$$

- **Diffusion rate** in a system will increase with **temperature:**

$$D = D_o \times e^{-\frac{E_A}{RT}}$$

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