DIFFUSION IN SOLIDS

- FICK'S LAWS
- KIRKENDALL EFFECT
- ATOMIC MECHANISMS

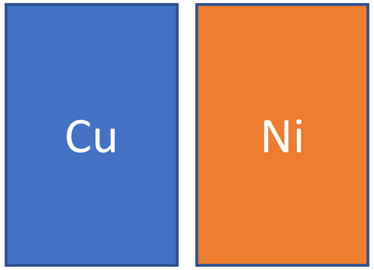
Diffusion in Solids
P.G. Shewmon
McGraw-Hill, New York (1963)

Diffusion

- Mechanism of material transport by atomic motion
- Driven by *thermal energy* and a *gradient*
- Thermal energy → thermal vibrations → Atomic jumps

Gradient
- Concentration / chemical potential
- Electric
- Magnetic
- Stress

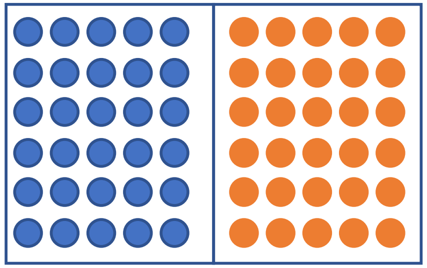
Time dependent mechanism



When I bring it together, do they start diffusing ?

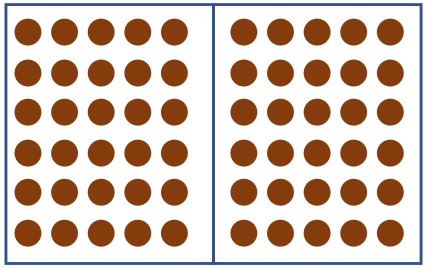
Ink in water diffuses immediately!

Initial



What happens to the concentration of each species ?

Final



❑ Flux (J) *(restricted definition)* → Flow / area / time [Atoms / m^2 / s]

Fick's I law

$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

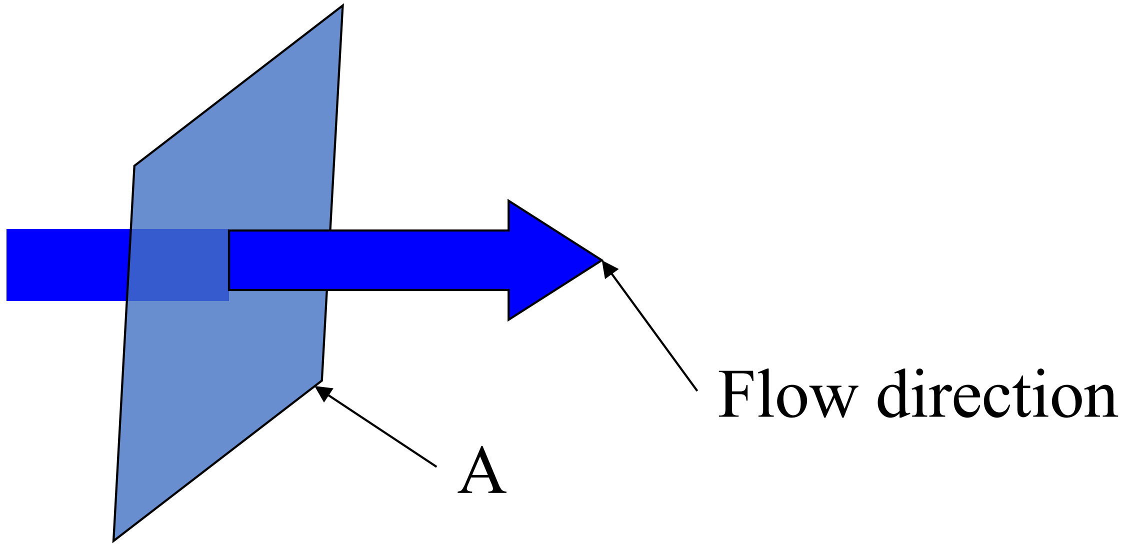
No. of atoms crossing area A per unit time

Diffusion coefficient/ diffusivity

Cross-sectional area

Concentration gradient

Matter transport is down the concentration gradient



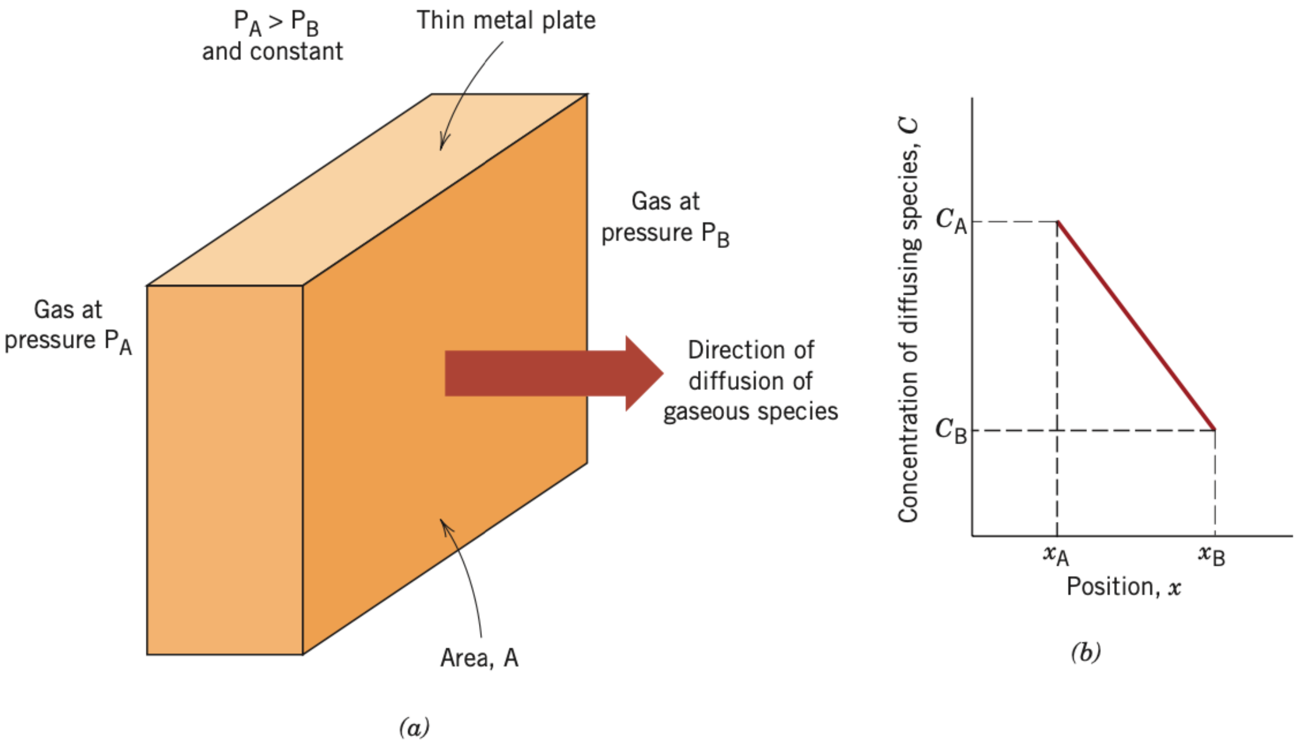
- As a first approximation assume D $\neq$ f(t)

Steady State Diffusion

Constant flux of the species

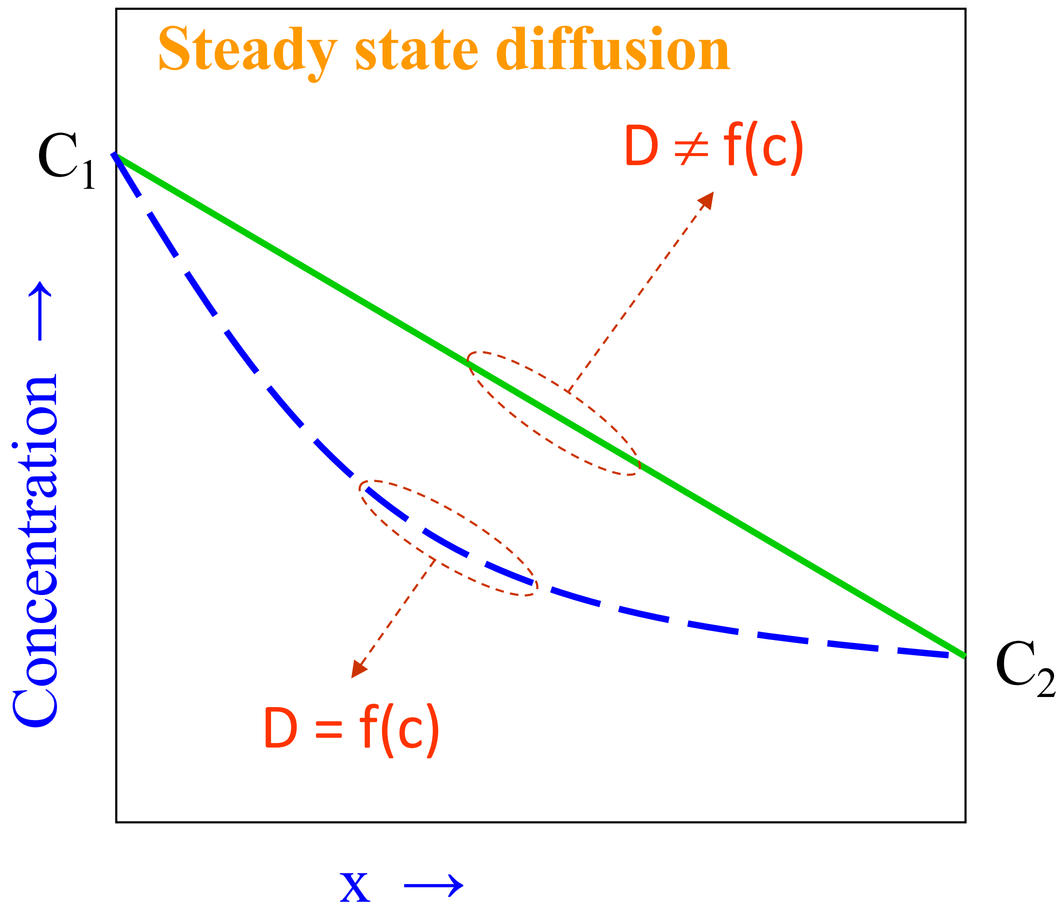
→ $J = \frac{dn}{dt}\frac{1}{A}$ is a constant!

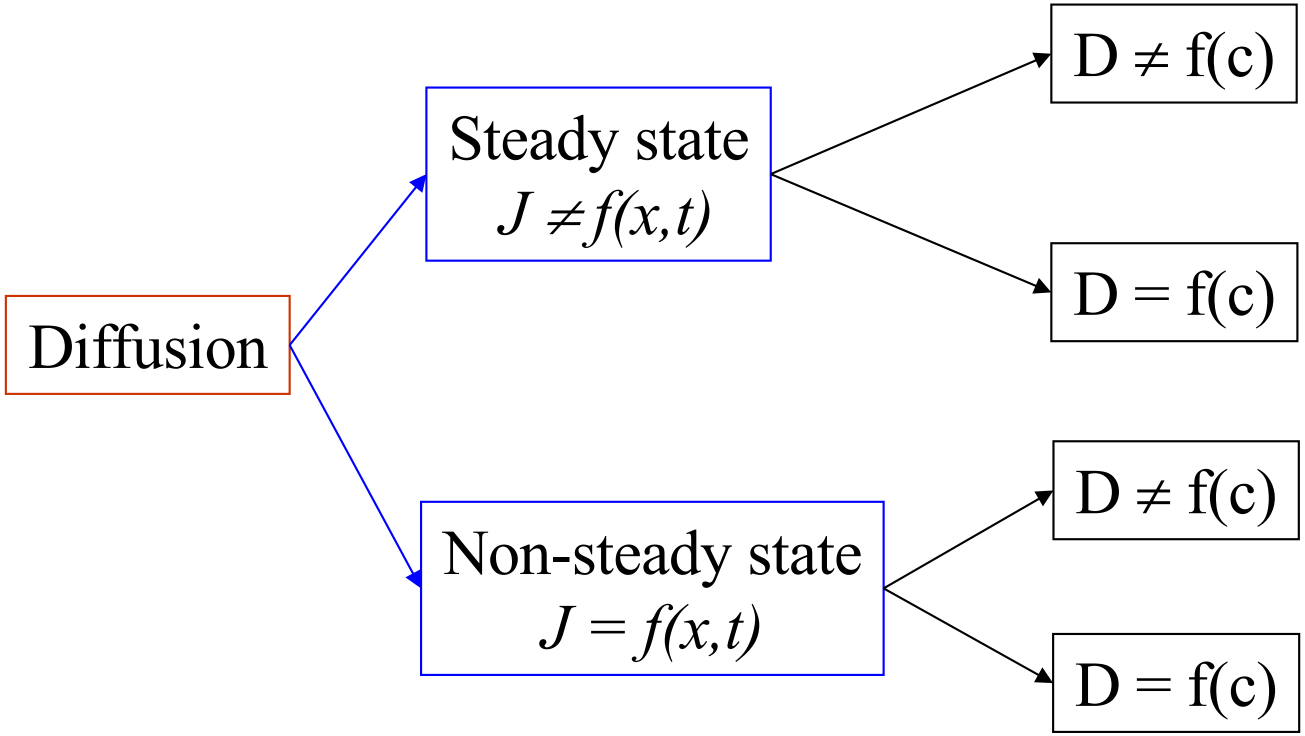
The solution to the Fick's 1st equation – linearly varying concentration



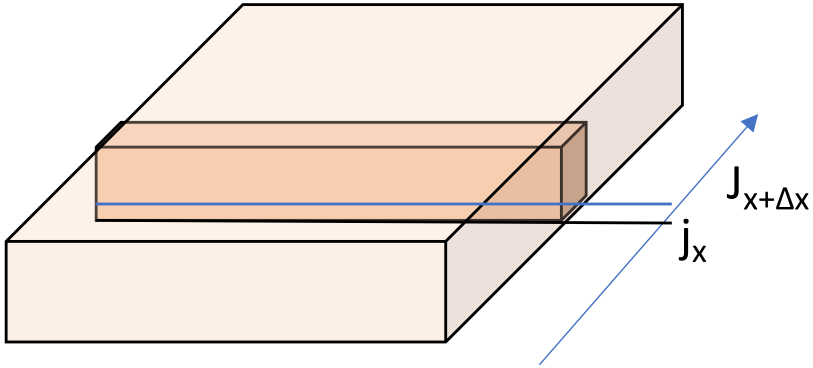
Steady State Diffusion

Solutions to the Fick when the diffusivity is a function of the concentration




Diffusion
Steady state
$J \neq f(x,t)$
Non-steady state
$J = f(x,t)$
D ≠ f(c)
D = f(c)
D ≠ f(c)
D = f(c)

Non-steady state



Flux is non-uniform!

If the current density at two points x and x+Δx are different,
That means, there is accumulation/depletion.

$$j_x - j_{x+\Delta x} = \frac{\partial c}{\partial t}\Delta x$$

Δx is the small segment thickness
C – species concentration m^{-3}

$$(j_{x+\Delta x} - j_x)/\Delta x = \frac{\partial j}{\partial x}$$

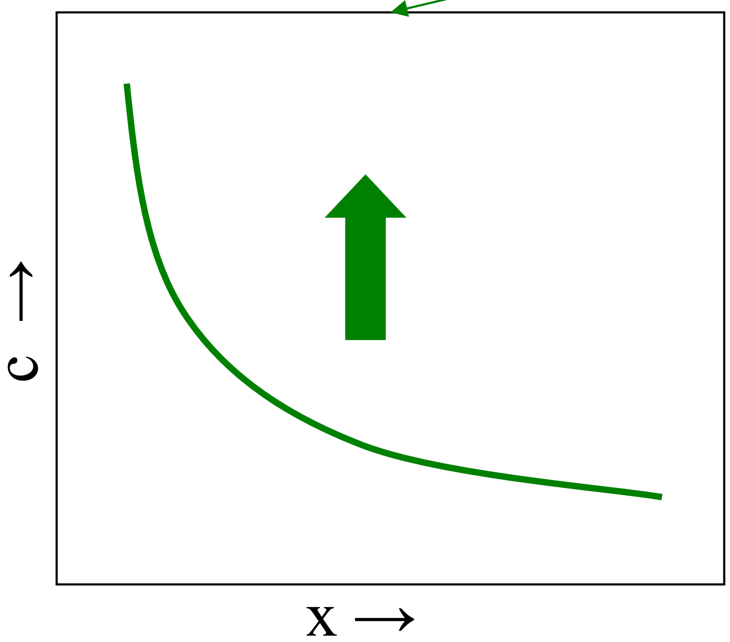
$$\frac{\partial c}{\partial t}\Delta x = -\frac{\partial j}{\partial x}\Delta x$$

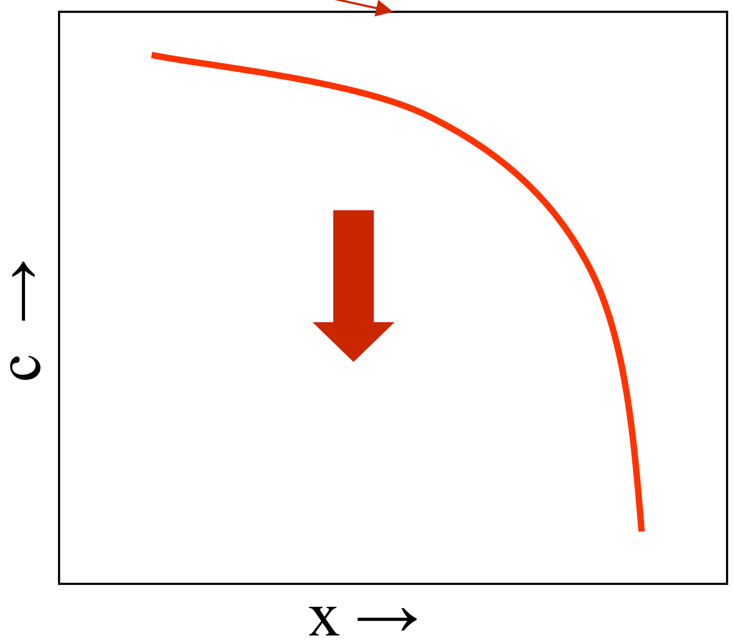
$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}\left[-\frac{D\partial c}{\partial x}\right]$$

This is also called as the continuity equation.

$$\left(\frac{\partial c}{\partial t}\right) \square D \frac{\partial^2 c}{\partial x^2}$$

RHS is the curvature of the c vs x curve





LHS is the change is concentration with time

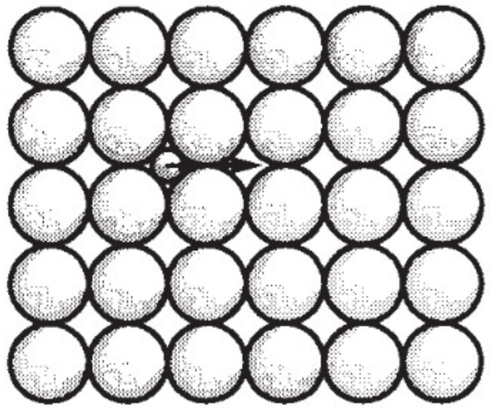
+ve curvature ⇒ c ↑ as t ↑

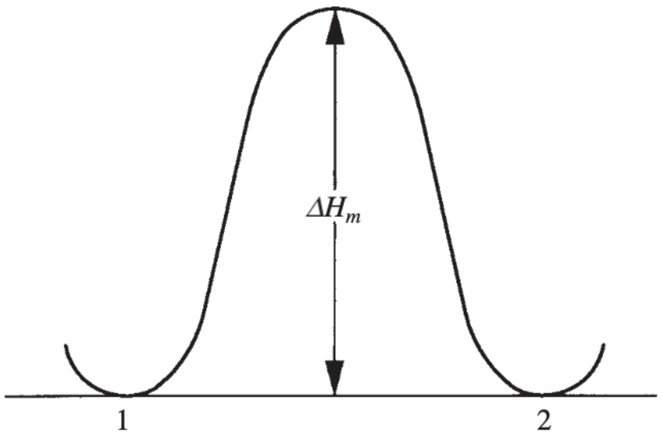
–ve curvature ⇒ c ↓ as t ↑

Diffusion mechanisms

Interstitial diffusion

The solute/diffusing atom is very small!

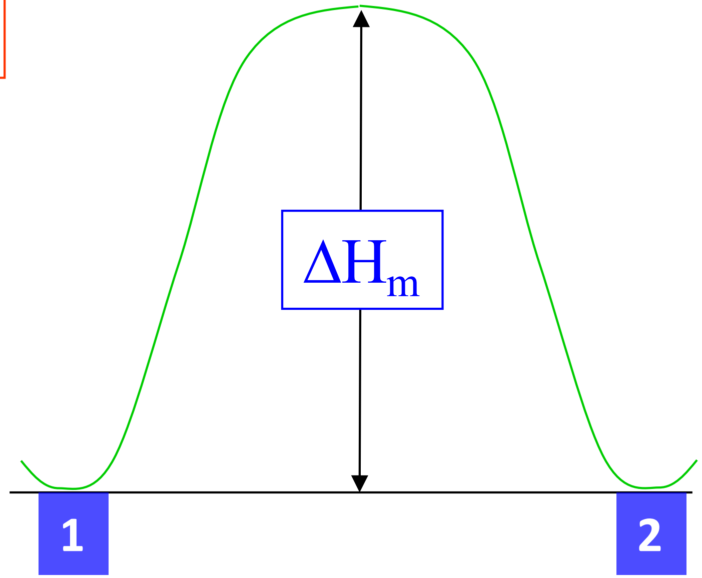


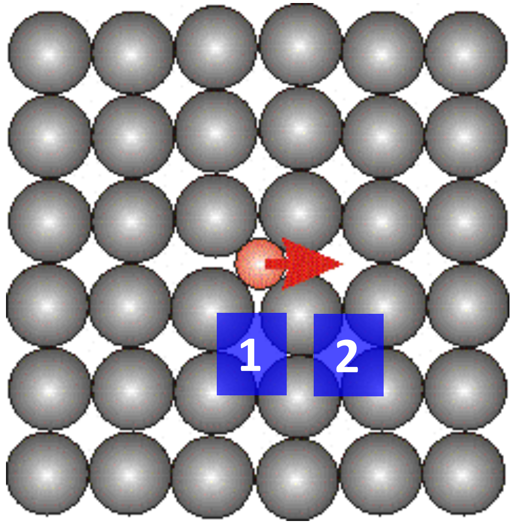


Momentary increase in the enthalpy is required for the interstitials to move from A -B

While A and B are both interstitial positions.

Interstitial Diffusion

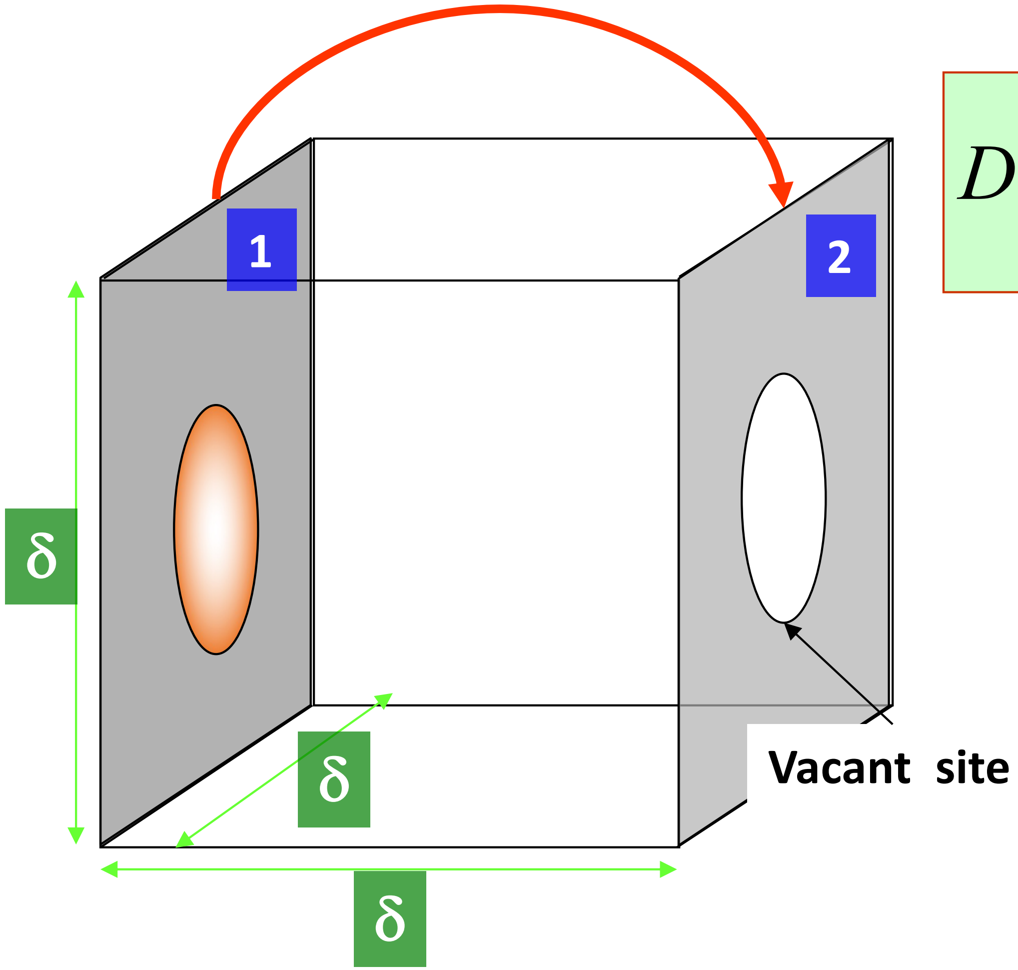




- At T > 0 K vibration of the atoms provides the energy to overcome the energy barrier ΔH_m (enthalpy of motion)
- $\nu \rightarrow$ frequency of vibrations, $\nu' \rightarrow$ number of successful jumps / time

$$\nu' \approx \nu \, e^{\left(-\frac{\Delta H_m}{kT}\right)}$$

- c = *atoms / volume*
- $c = 1 / \delta^3$
- *concentration gradient* $dc/dx = (-1 / \delta^3)/\delta = -1 / \delta^4$
- *Flux = No of atoms / area / time* $= \nu' / area = \nu' / \delta^2$



$$D \square \frac{J}{-(dc/dx)} \square \frac{\nu'}{\delta^2}\delta^4 \square \nu' \delta^2$$

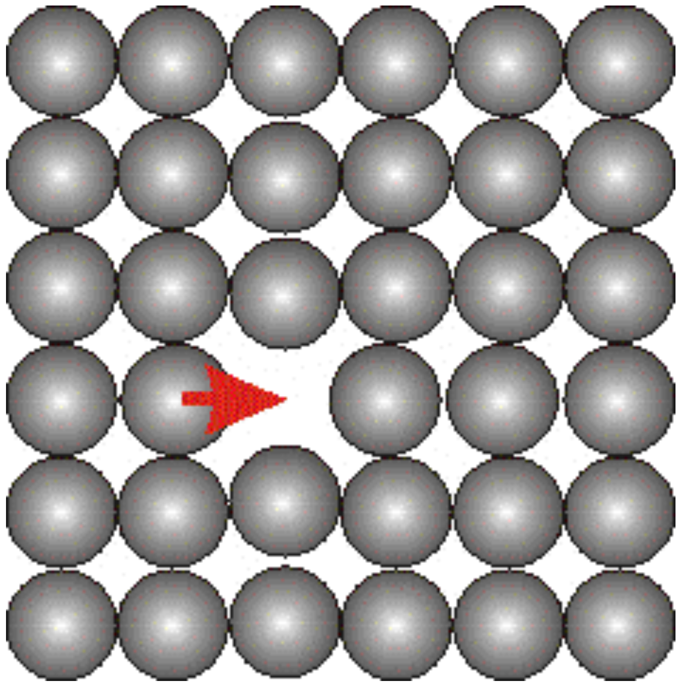
$$D \square \nu \, \delta^2 \, e^{\left(\frac{-\Delta H_m}{kT}\right)}$$

On comparison with

$$D \square D_0 \, e^{\left(-\frac{Q}{kT}\right)}$$

$$D_0 \square \nu \, \delta^2$$

2. Vacancy Mechanism



Substitutional Diffusion

- *Probability for a jump* α *(probability that the site is vacant) . (probability that the atom has sufficient energy)*
- $\Delta H_m \rightarrow$ *enthalpy of motion of atom*
- $\nu' \rightarrow$ *frequency of successful jumps*

$$\nu' \square \nu\, e^{\left(\frac{-\Delta H_f}{kT}\right)} e^{\left(\frac{-\Delta H_m}{kT}\right)} \longrightarrow \nu' \square \nu\, e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$$

As derived for interstitial diffusion $\longrightarrow$

$$D \square \frac{J}{-(dc/dx)} \square \frac{\nu'}{\delta^2}\delta^4 \square \nu'\delta^2$$

$$D \square \nu\, \delta^2\, e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$$

Temperature dependence of diffusivity

$$D \square D_0 \, e^{\left(-\frac{Q}{kT}\right)}$$

Arrhenius type

For interstitial

$$D \square \nu \, \delta^2 \, e^{\left(\frac{-\Delta H_m}{kT}\right)}$$

For substitutional

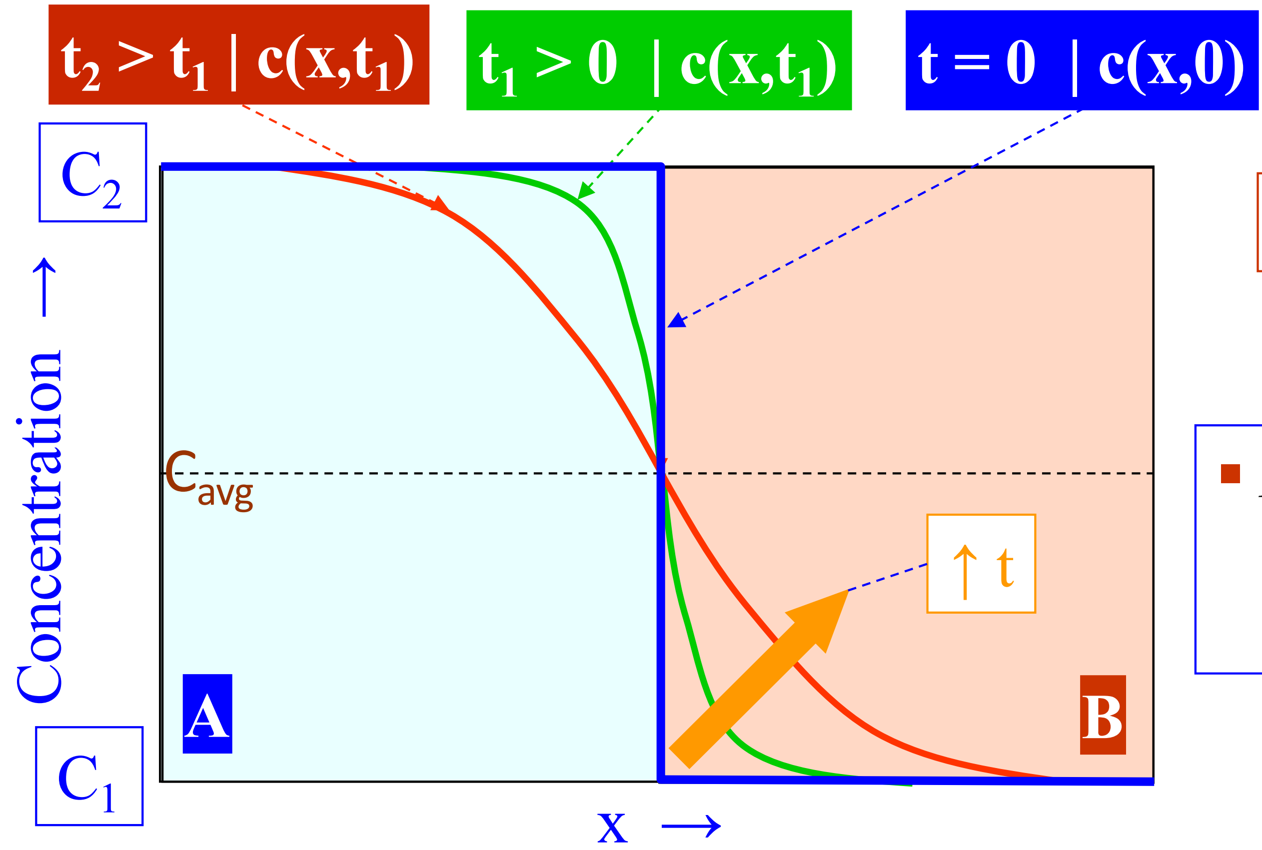
$$D \square \nu \, \delta^2 \, e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$$

$$D_0 \square \nu \, \delta^2$$

$$Q = \begin{matrix} \Delta H_m \; for \; interstitial \\ \Delta H_m + \Delta H_f \; for \; substitutional \end{matrix}$$

Examples of diffusion:

1. Diffusion couple



Flux → $f(x)|_t$, $f(t)|_x$ ⇒ Non-steady state

- *If* $D = f(c)$
  $\Rightarrow c(+x,t) \neq c(-x,t)$
  i.e. asymmetry about y-axis

- $C(+x, 0) = C_1$
- $C(-x, 0) = C_2$

$$\left(\frac{\partial c}{\partial t}\right) = D\,\frac{\partial^2 c}{\partial x^2} \quad \rightarrow \quad c(x,t) = A - B\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Solution to 2º de with 2 constants
determined from Boundary Conditions and Initial Condition

- $Erf\,(\infty) = 1$
- $Erf\,(-\infty) = -1$
- $Erf\,(0) = 0$
- $Erf\,(-x) = -Erf\,(x)$

$$Erf\,(\gamma) = \frac{2}{\sqrt{\pi}}\int_0^{\gamma} \exp(-u^2)\,du$$

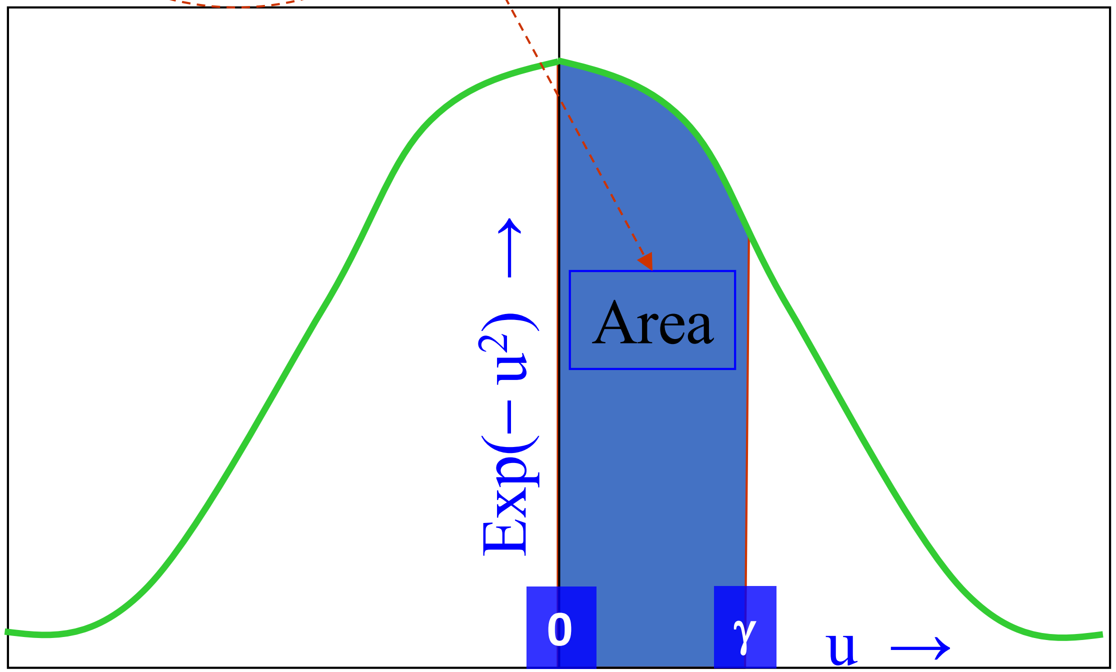


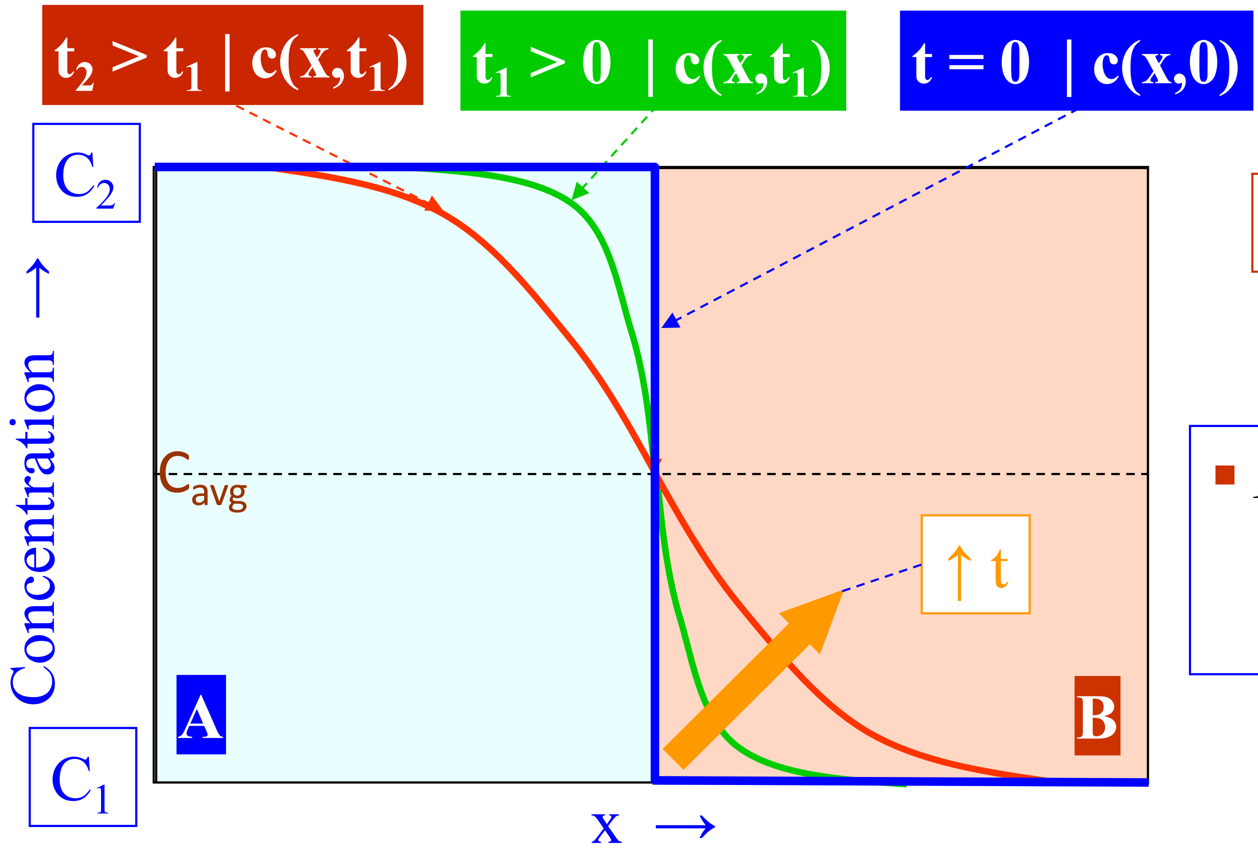
TABLE 8.1

The Error Function

z	erf (z)	z	erf (z)
0.000	0.0000	0.85	0.7707
0.025	0.0282	0.90	0.7970
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3268	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

Applications based on Fick's II law → *Determination of Diffusivity*

A & B welded together and heated to high temperature (kept constant → T_0)



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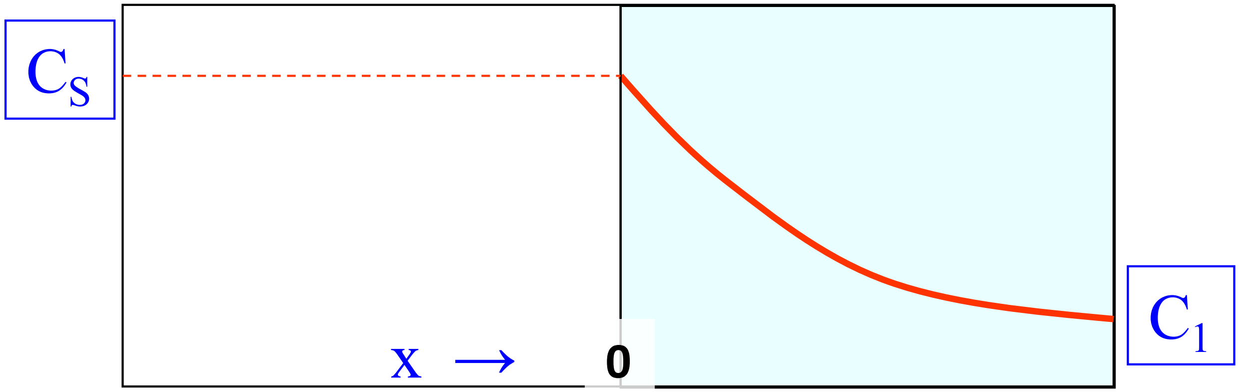
- $C(+x, 0) = C_1$
- $C(-x, 0) = C_2$

→

- $A = (C_1 + C_2)/2$
- $B = (C_2 - C_1)/2$

Applications based on Fick's II law → *Carburization of steel*

- Surface is often the most important part of the component, which is prone to degradation
- Surface hardenting of steel components like gears is done by carburizing or nitriding
- Pack carburizing → solid carbon powder used as C source
- Gas carburizing → Methane gas $CH_4\ (g) \rightarrow 2H_2\ (g) + C$ (diffuses into steel)



- $C(+x, 0) = C_1$
- $C(0, t) = C_S$

→

- $A = C_S$
- $B = C_S - C_1$