Chapter 2.
Diffusion

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Contents

- Mathematics of diffusion
- Driving force of diffusion
- Atomistic of diffusion
  - ✓ Substitutional diffusion, Interstitial diffusion
  - ✓ Self diffusion, tracer diffusion, Vacancy diffusion
- Interdiffusion
- Fast diffusion path
- Moving boundary problem
- D = D(c)

Diffusion

❖ **Mechanism by which matter transported through matter**

– Rate of mass transport

$$\text{Flux } (J) = \frac{mass}{area \times time} \quad [\frac{Kg}{m^2 \cdot s}] = [\frac{g}{cm^2 \cdot s}]$$

Adoff Fick assumed that $J \propto$ conc. grad.

– Fick's First Law

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

Flux is opposite to conc. grad.

D : diffusion coefficient, diffusivity, related to atomic mobility

⇒ depends on microstructure of materials

Diffusion Coefficient (Diffusivity)

❖ Magnitude of D in various media

Gas : $D \approx 10^{-1}\ cm^2/s$

Liquid : $D \approx 10^{-4} \sim 10^{-5}\ cm^2/s$

Solid

Materials near melting temp. $D \approx 10^{-8}\ cm^2/s$

Elemental semiconductor (Si, Ge) $D \approx 10^{-12}\ cm^2/s$

Ceramic → trace of impurity change its value

ex) Age of universe ~ 10^{17} sec., diffusion distance = $\sqrt{Dt}$

Gas : $\sqrt{10^{16}} = 10^{8}\,cm = 1000\,km$

Liquid : $\sqrt{10^{12}} = 10^{6}\,cm = 10\,km$

Solid near T_m = 300*m*

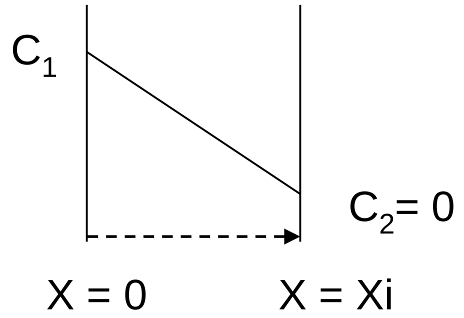
Fick's First Law

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

- Fick's First Law always applies.
  (except non-Fickian diffusion ex) Organic solvent in glassy polymer)

- When we are at steady state [$J \neq J(t)$], Fick's First Law tells whole story.

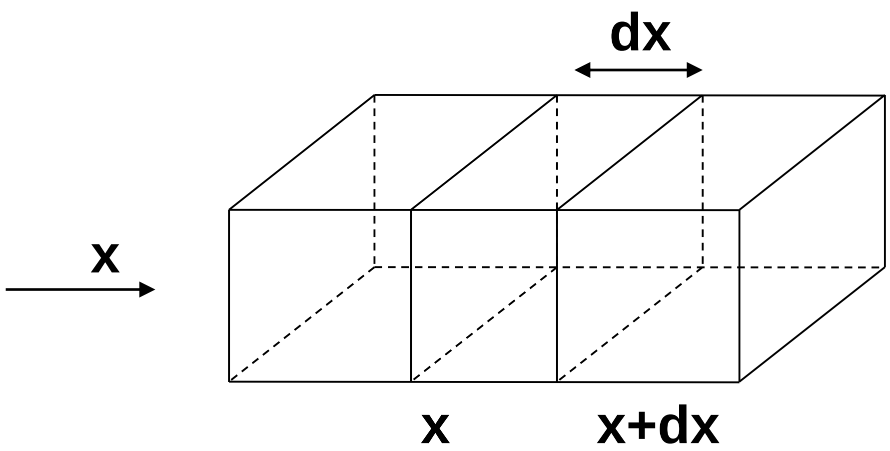
ex) diffusion through plate



$C(x) = ?$

Fick's Second Law

What happens during transient state? [$J = J(t)$]



❖ Mass balance on volume element:

(flux) × (area) = (rate of change of conc.) × (volume)

$$J \cdot A = V \frac{\partial C}{\partial t}$$

$$J_x A - J_{x+dx} A = \frac{\partial C}{\partial t} A dx \qquad (1)$$

Fick's Second Law (2)

Get J_{x+dx} by Tayler Series Expansion about J_x

$$J_{x+dx} = J_x + \frac{\partial J_x}{\partial x} dx + \frac{1}{2}\frac{\partial^2 J_x}{\partial x^2}(dx)^2 + \cdots \qquad \textbf{(2)}$$

From Eq. (1) and (2)

$$-\frac{\partial C}{\partial t} = \frac{\partial J_x}{\partial x} = \frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}\right) = -D\frac{\partial^2 C}{\partial x^2} - \underbrace{\frac{\partial C}{\partial x}\frac{\partial D}{\partial x}}_{=\left(\frac{\partial D}{\partial C}\right)\left(\frac{\partial C}{\partial x}\right)^2}$$

$$\therefore \quad \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \left(\frac{\partial D}{\partial C}\right)\left(\frac{\partial C}{\partial x}\right)^2$$

⇒ Fick's Second Law

When $D \neq D(c)$

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

2nd order linear partial diff. eq.

Unifying Power of Mathematics

- Kreyszig " Advanced Engineering Mathematics"
  Ch.11 " Partial Differential Equation"

Wave Eq. $$\frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2}$$ Ch 11-2

Heat Eq. $$\frac{\partial u}{\partial t} = c^2 \frac{\partial^2 u}{\partial x^2}$$ Ch 11-5

- 2 B.C. + 1 I.C. ⇒ solution *C(x,t)*
- linearity ⇒ solutions are additive.

- To solve
  - Separation of variables
  - Laplace Transformation
  - Fourier Transformation

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$ 3 차원

$$= D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right)$$ Cylindrical

$$= D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right)$$ Spherical.

Ref: Kreyszig Ch 11.6 이후 공부

J. Crank, "The Mathematics of Diffusion.",
Shewman, " Diffusion in Solids"

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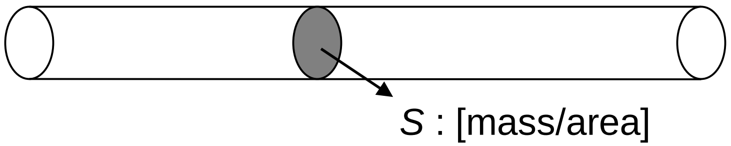
Solution of Diffusion Equation

Ref: Shewmon "Diffusion in Solids"

❖ **Case I) Thin Film Solution**

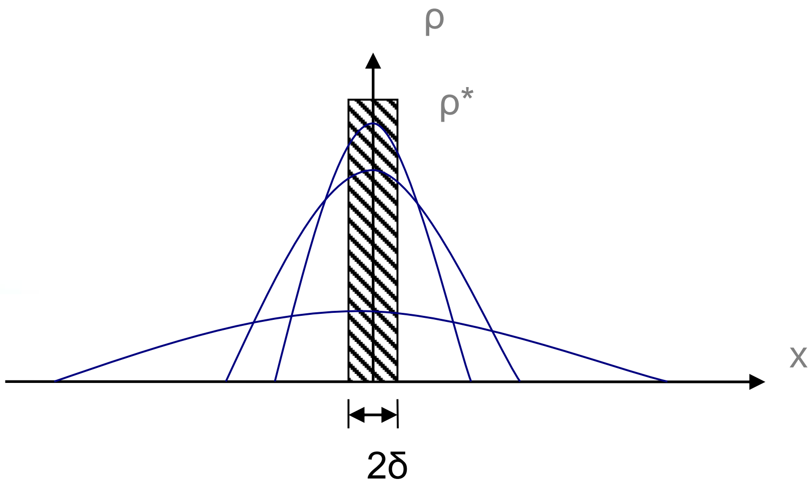
✓ Quantity of *S* of solute plated as a thin film on one end of a long rod of solute free material

✓ Similar solute free rod attached against solute.



ρ (x,t)?

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$



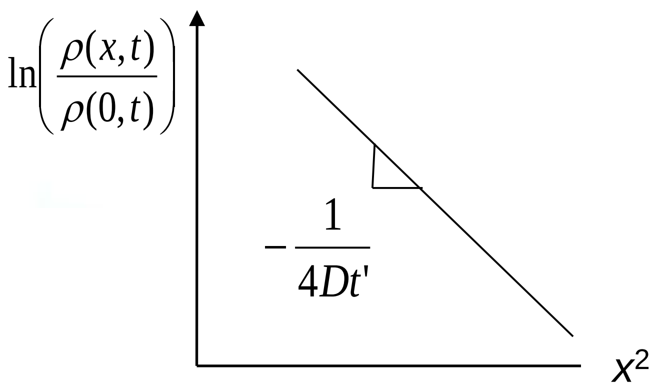
I.C. $\rho(x,0) = \rho^* \quad |x| < \delta$; $\quad 0 \quad$ otherwise

B.C. $\rho(\infty,t) = 0$; $\quad \rho(-\infty,t) = 0$

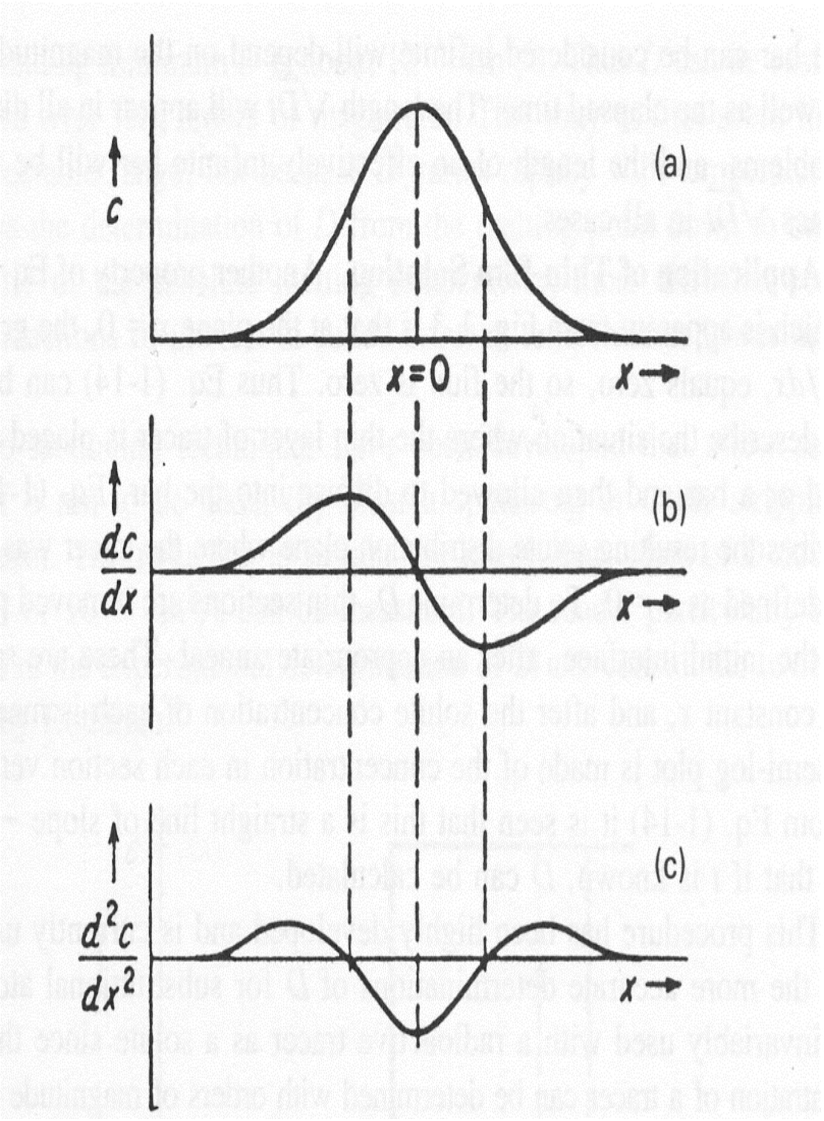
- Conservation of mass $\int_{-\infty}^{\infty} \rho dx = S$
- General Solution $\rho(x,t) = \frac{A}{\sqrt{t}} \exp(-\frac{x^2}{4Dt})$
- Particular Solution $\rho(x,t) = \frac{S}{\sqrt{4\pi Dt}} \exp(-\frac{x^2}{4Dt})$

$$\rho(0,t) = \frac{S}{\sqrt{4\pi Dt}} \qquad \rho(0,t) \text{ drops off as } \frac{1}{\sqrt{t}}$$

- **in general** $\rho(x,t) = \rho(0,t) \exp(-\frac{x^2}{4Dt})$



Can measure D by this equation because it only needs the ratio of the concentration.


(a)
c
x=0
x
(b)
dc/dx
x
(c)
d²c/dx²
x

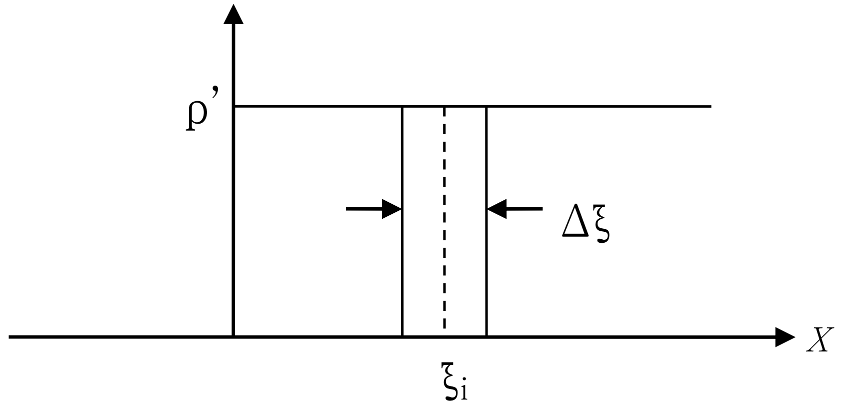
ex)  $0 < x < L$

S (mass/area)

$$\rho(x,t) = \frac{2S}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \qquad 0 < x < L$$

Solution of Diffusion Equation

❖ Case II) Pair of Semi-Infinite Solids



I.C. $\begin{cases} \rho(x,0) = 0 & x < 0 \\ \rho(x,o) = \rho' & x > 0 \end{cases}$

B.C. $\begin{cases} \rho(\infty,t) = \rho' \\ \rho(-\infty,t) = 0 \end{cases}$

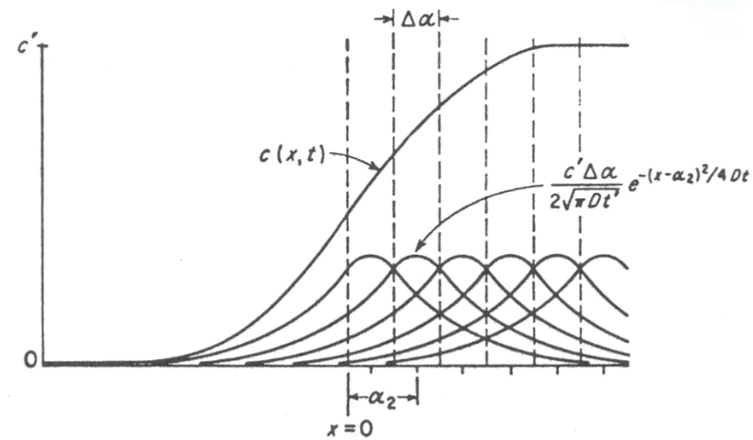
Sol) Thin film solution from slice at position x = ξ_i

$$\rho_i(x,t) = \frac{S}{\sqrt{4\pi Dt}} \exp\left(-\frac{(x-\xi\ )^2}{4Dt}\right) \qquad S = \rho'\Delta\xi$$

$$\rho(x,t) = \frac{\rho'}{\sqrt{4\pi Dt}} \sum_{i=1}^{n} \Delta\xi \exp\left(-\frac{(x-\xi_i)^2}{4Dt}\right)$$

in the limit as $\Delta\xi \rightarrow 0$ $n \rightarrow \infty$

$$\rho(x,t) = \frac{\rho'}{\sqrt{4\pi Dt}} \int_0^{\infty} \exp\left(-\frac{(x-\xi_i)^2}{4Dt}\right) d\xi$$



변수변환

$$\begin{cases} \eta = \dfrac{x-\xi}{2\sqrt{Dt}} \\ d\xi = -2\sqrt{Dt}\, d\eta \end{cases}$$

$\xi = 0 \rightarrow \eta = \dfrac{x}{2\sqrt{Dt}}$

$\xi = \infty \rightarrow \eta = -\infty$

$$\rho(x,t) = -\frac{\rho'}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^{-\infty} \exp(-\eta^2) d\eta$$

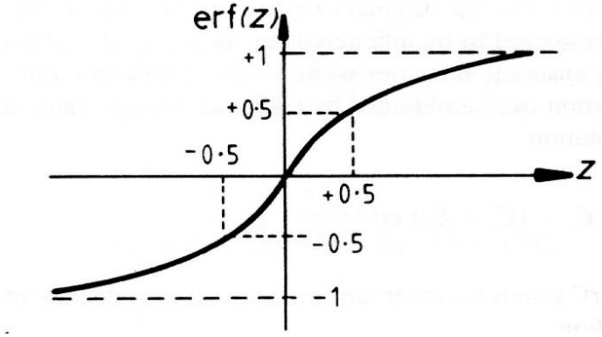
$$\left(\because \int e^{-z^2} dz \rightarrow erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2) d\eta \right)$$

$$= \frac{\rho'}{\sqrt{\pi}} \int_{-\infty}^{0} \exp(-\eta^2) d\eta + \frac{\rho'}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} \exp(-\eta^2) d\eta$$

일반적인 경우의 해 :

$$\rho(x,t) = A + B\, erf \frac{x}{2\sqrt{Dt}} = A' + B'\, erfc \frac{x}{2\sqrt{Dt}}$$

Error Function (erf)



$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2) d\eta$$

- erf (0) = 0, erf (∞) = 1
- erf (-z) = - erf (z) (odd function)
- erfc (z) = 1- erf (z) erfc (0) = 1 , erfc (∞) = 0

Power series expansion of error function

for small z, $$erf(z) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n z^{2n+1}}{(2n+1)^{n!}}$$

erf (z) ≈ z until ~ 0.6

Error Function Table

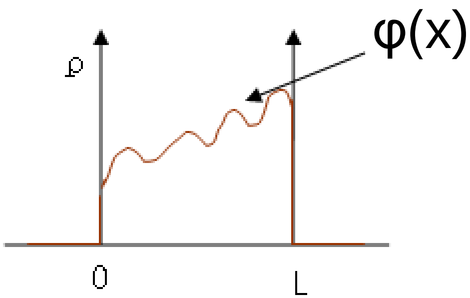
Table 1-1. The Error Function

z	erf(z)	z	erf(z)
0	0	0.85	0.7707
0.025	0.0282	0.90	0.7969
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	0.3286	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

Case III) General case

Can solve by Separation of variables,
Fourier Transformation,
Laplace transformation

공학수학 Ch 11-5



I.C. $\rho(x,0) = \varphi(x)$
Otherwise $\rho(x,0)=0$

Separation of Variables: $\rho(x,t) = X(x)T(t)$

$$\frac{\dot{T}}{DT} = \frac{X''}{X} = const.$$

Sol: $$\rho(x,t) = \sum_{n=1}^{\infty} B'_n \exp\left(-\frac{n^2\pi Dt}{L^2}\right)\sin\frac{n\pi x}{L}$$

Where $$B'_n = \frac{2}{L}\int_0^L \phi(s)\sin\frac{n\pi s}{L}ds$$