Date . .

Chap. 2. Diffusion.

In Chap. 1. → talked about the stability or equil^{m} arrangement of atoms in alloys.

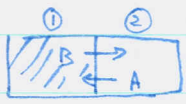
Phase transf → concerns about timing factor to reach the equil^{m}.

- Any rxns in alloys occur to accomplish intermediate or final equil^{m}.
- In the same context, diffusion occurs to reduce G of a sys.

* Two examples.

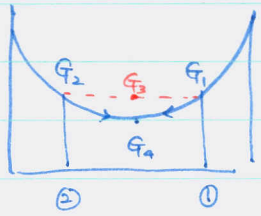
Figure 2.1.

case I B-rich



A-rich.

composition

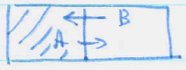


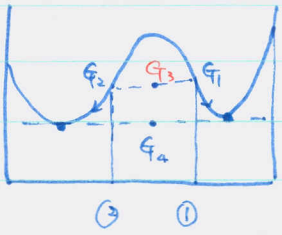
* general case

diffusion occurs to reduce and eliminate the conc. grad.

"down-hill diffusion"

case II





* Miscibility gap.

A. B. diffuse towards the regions of high conc.

"up-hill diffusion

both to reduce "G_{total}" !!

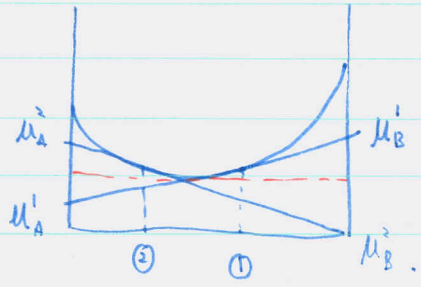
from where the chem. pot. of A. B is high

to where " is low.

$\mu_A^2 > \mu_B^2$

↓

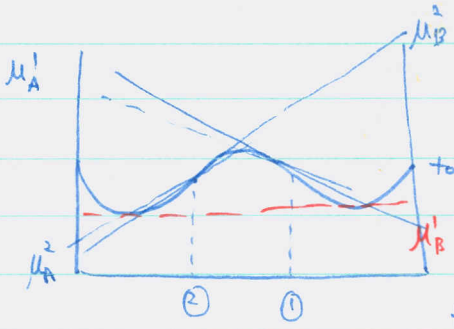
to reduce μ_A^2.



$\mu_B^1 > \mu_A^1$

↓

to reduce μ_B^1



$\mu_B^2 > \mu_A^2$

↓

to reduce

$\mu_A^1 > \mu_B^1$

↓

to reduce.

∴ better to express the driving force for diffusion in terms of a chem. pot. gradient.

Use this approach. → but case I is more common, easy to measure conc. grad. compared to μ.

∴ diffusion - related to conc. grad.

Date . .

2.1. Atomic Mechanisms of Diffusion.

Two common mechanisms.

- Substitutional atoms by a vacancy mech.
- interstitial atoms (small) by forcing their way bet'n the larger atoms.

Substitutional.

- oscillates w/ vibrational E. of $3kT$. $E \propto T.(K)$.
  assume freq. of the vib. is const. ∴ amplitude ↑ as T ↑ ∴ → E↑
- If an atom oscillates violently in the vicinity (on next to) of a vacancy, it can jump to the vac. site.
  ∴ Probability (to jump into a vac. site) ≅ P (to acquire suff. vib. E)

∴ migration rate → related to jump. freq. → conc. of vac. = f(T).

Interstitial

- when the size of a solute atom ≪ that of the solvent.
- fcc octahedral site - in the middle of the unit cell or mid way along the cubic edges.
  bcc. edge-centering or face-centering positions.
- conc. of interstitial atom is low ∴ occupies small fraction of available sites
  → ∴ each interstitial often surrounded by vac. → jump to overcome the strain energy barrier.

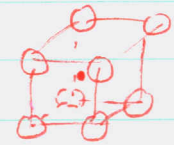
interstial-vac pairs = Frenkel defects

+ charge vac - - charge vac = Schottkey defect

Date . .

2.2. Interstitial Diffusion (1D).

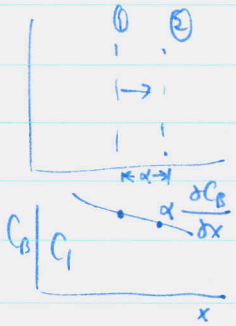
1. I.D. as a Random Jump Process.



how the I.D. diffusion is related to the Random Jump.

Fig. 2.5. - equal prob. of the atom jumping to every one of the 6 adj. sites (parent atoms on a simple cubic lattice)

- if the plane (1) contains n_1 (β-atoms) $/m^2$.



(successful atom) jump rate [jump/sec]

(2.1) $\vec{J}_\beta = \frac{1}{6}\Gamma_\beta n_1$ (atoms $/m^2 \cdot$ sec). (1) → (2)

$\overleftarrow{J}_\beta = \frac{1}{6}\Gamma_\beta n_2$ (") (2) → (1)

(2.2) $\therefore \overset{(net)}{J_\beta} = \frac{1}{6}\Gamma_\beta (n_1 - n_2)$

when α = the separation dist. of planes (1) and (2).

$C_\beta(1) = n_1/\alpha \cdot 1$ (atoms/m^3), $C_\beta(2) = n_2/\alpha \cdot 1$ (atoms/m^3)

$\therefore n_1 - n_2 = \alpha (C_\beta^{(1)} - C_\beta^{(2)})$.

공간이동 방향이 conc. 낮은 곳으로

and Fig 2.5 → $C_\beta^{(1)} - C_\beta^{(2)} = -\alpha \cdot \frac{\partial C_\beta}{\partial x}$.

①/4?

(2.3) (net flow) $\therefore \boxed{J_\beta = -\left(\frac{1}{6}\Gamma_\beta \alpha^2\right)\frac{\partial C_\beta}{\partial x}}$ atoms $/m^2 \cdot$ sec.

(2.4) Fick's first law of Diffusion. $\boxed{= -D_\beta \frac{\partial C_\beta}{\partial x}}$ where $\frac{1}{6}\Gamma_\beta \alpha^2 = D_\beta$.

Intrinsic diffusivity or diff. coeff.

unit [atoms/m^2·s] = [m^2/sec][atoms/m^4]

(2.4) for I.D. based on a simple cubic lattice, $\Gamma_\beta \neq f$(conc.) good for random diff. in cubic.

In non-cubic $D_\beta = f$(direction-Xtallographic) hcp. monoclinic etc.

Date . .

- Still $D = f(\text{Comp.} = \text{conc.})$. in real alloys

  ex. γ-Fe 1000°C 2.5×10^{-11} m²/sec at 0.15 wt % C.

  7.7×10^{-11} m²/sec at 1.4 wt. % C.

  to release the strain E induced by C int.

  ex. γ-Fe 1000°C lattice para (= a) = 0.37 nm

  $\therefore \alpha = 0.37/\sqrt{2} = 0.26$ nm for Fe. $D_B = \frac{1}{6}\Gamma_B \alpha^2$

  using 2.5×10^{-11} m²/sec as D, $\therefore \Gamma_c = 2 \times 10^9$ jumps/sec.

  If the vib. freq. of C $\sim 10^{13}$, then $\frac{1}{10^4}$ success rate.

- random walk – the direction of each new jump – indep. of that of previous jump.

- Random walk in 3-D

  after n steps w/ jump dist. α 증명은 뒤!!

  avg. (jumps) displacement of an atom $= \alpha\sqrt{n}$ from its org. posit

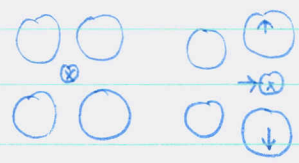
  ($\because n = \Gamma t$)

(2.5) $\therefore$ after a time t. $r = \alpha\sqrt{n} = \alpha\sqrt{\Gamma t}$ where $D = \frac{1}{6}\Gamma\alpha^2$

(2.6) $= 2.4\sqrt{Dt}$

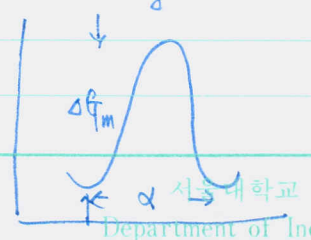
$\therefore r \propto \sqrt{Dt}$.

2. Effect of Temp – Thermal Activation.



- occasional violent oscillation of an int. atom – on some coincidence of the matrix & int. atom movement → results in an advance of an atom.

- factors controlling F, the effect of Temp.



ΔG_m = activation E.

Date . .

- the fraction of atoms w/ ΔG = $\exp(-\Delta G/RT)$
  (or w/ ΔG more than avg. E)

- for the int. atoms υ freq. in x dir. successful atoms $= \upsilon \exp\left(-\frac{\Delta G_m}{RT}\right)$

성공적으로 next site으로 운동했것 (jump. freq)

- for an atom in 3-D w/ z sites to jump in.

(2.7) the jump freq. $\Gamma_B = z\upsilon \exp\left(-\frac{\Delta G_m}{RT}\right)$ migration

진동 freq.

where $\Delta G_m = \Delta H_m - T\Delta S_m$.

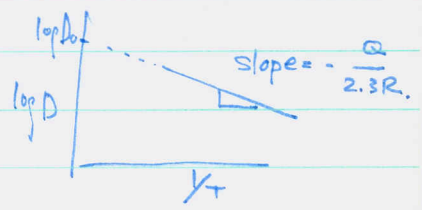
(2.8) $\therefore D_B = \left[\frac{1}{6}\alpha^2 z\upsilon \exp\frac{\Delta S_m}{R}\right] \exp\frac{-\Delta H_m}{RT}$

(2.9) $= D_{B0} \exp\left(\frac{-Q_{ID}}{RT}\right)$ where $\Delta H_m = Q_{ID}$.

$D_0 \neq f(T)$ D_{B0} agree w/ exp. measurements of diff. coeff. in subst and interstitial

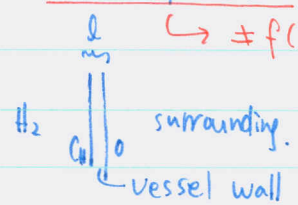
- Graphic representation.

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



3. Steady - State Diffusion.

↳ ≠ f(time)



$\frac{\partial C}{\partial x} = \frac{1 - C_H}{l}$

$D_H \neq f(\text{conc.})$

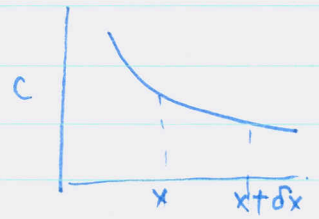
flux thru the wall

$\therefore J_H = \frac{D_H C_H}{l}$

S.S. is reached when the conc. everywhere reaches a const. value.

4. Nonsteady - State Diffusion

where the conc. changes w/ time and distance, 1st law won't work.

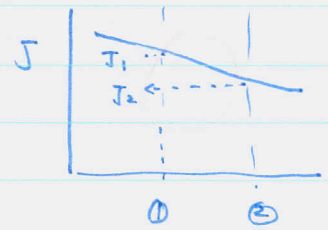


i) mass balance at ① ← (x와 x+δx 사이에 쌓이는 양 δC_B는 $J_1 - J_2$ 의 차이에 의한것)

in a small time δt

[atom/cm²·sec] $J_1 A \delta t$

at ② $J_2 A \delta t$. $J_1 > J_2$.



J changes w/ local D_B & $\frac{\partial C_B}{\partial x}$.

∴ the increase in conc. within the slice

$$\delta C_B = \frac{(J_1 - J_2) A \delta t}{A \delta x \ (= \text{vol.})} \quad (2.14)$$

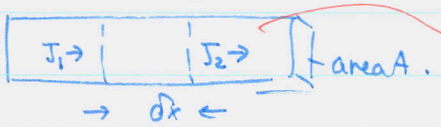


Fig. 2.8. 2nd law.

ii) → Another eq.

$$\Delta J = (J_2 - J_1) = \delta x \cdot \frac{\partial J}{\partial x}$$

$$J_2 = J_1 + \frac{\partial J}{\partial x} \delta x \quad (2.15)$$

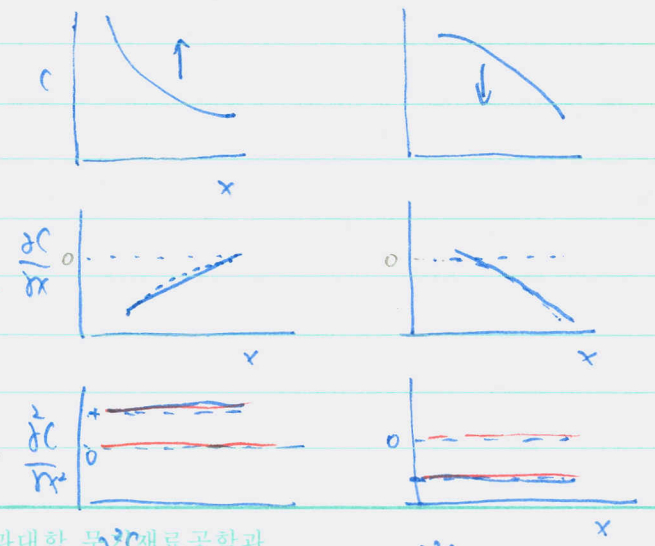
∴ iii) (2.14) → $J_2 = \cancel{J_1 + \frac{\delta C_B}{\delta t} \delta x} = J_1 - \frac{\partial C_B}{\partial t} \delta x$ as $\delta t \to 0$.

(2.16), (2.17) $$\therefore \frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x} = \frac{\partial}{\partial x}\left(D_B \frac{\partial C_B}{\partial x} \right)$$

Fick's 2nd Law.

if $D_B \neq f(\text{conc.})$

(2.18) $$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$



Ex. thin film or Homogenization model.

$\frac{\partial^2 C}{\partial x^2} > 0$ at all pts. all conc ↑ w/ t

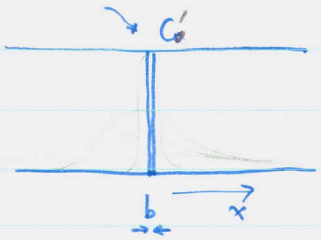
$\frac{\partial^2 C}{\partial x^2} < 0$ all conc ↓ w/ time.

Date

(Shewmon p15 -)

I. Diffusion in an infinite sys.

1. Thin film sol'n.



application of thin film → welded → diffuse for t.

A general sol'n for $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$ is $C(x,t) = \cancel{h(t)}\,A \cdot \exp\left(-\frac{x^2}{4Dt}\right)$

$$C(x,t) = \frac{bC_0'}{2\sqrt{\pi D t}} \exp\left[\frac{-x^2}{4Dt}\right] \quad \text{검명 뒤!} \quad (1.14)$$

where $\sqrt{Dt} > b$.

Is it correct sol'n? then show.

① satisfy $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$?

② " b.c. ?

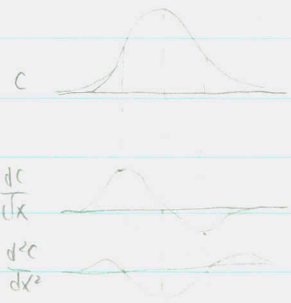
for $|x| > 0$ $C \to 0$ as $t \to \infty$

for $x = 0$ $C \to \infty$ as $t \to 0$.

③ yet the total quantity of solute $\int_{-\infty}^{\infty} C(x,t)\,dx = bC_0'$.

unit area (cm) solute/cm³

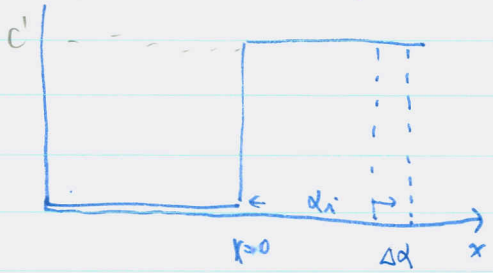
Charac. of this sol'n.



$x = \sqrt{4Dt}$ 이면 C decrease as $\frac{1}{\sqrt{t}}$ from eq (1.14)

$\exp\left(-\frac{x^2}{4Dt}\right)$ dist betn $x=0$, $\frac{C}{e}$ increases as $\sqrt{t}$.

3)' Sol'n for a pair of Semi-Infi Solids. pure A & B



$C = 0$ for $x < 0$ at $t = 0$

$C = C'$ for $x > 0$ at $t = 0$

Superposition of thinfilm sol'n. for many slices

$$C(x,t) \cong \frac{C'}{2\sqrt{\pi D t}} \sum_{1}^{n} \Delta\alpha_i \exp\left[\frac{-(x-\alpha_i)^2}{4Dt}\right]$$

C' [solute/cm³]
unit cross-section
∴ $C'\Delta\alpha_i$ = # of solute

(1) $$C(x,t) = \frac{C'}{2\sqrt{\pi D t}} \int_0^{\infty} \exp\left[\frac{-(x-\alpha)^2}{4Dt}\right] d\alpha, \quad \text{let } \frac{x-\alpha}{2\sqrt{Dt}} = u$$

(2) $$= \frac{C'}{\sqrt{\pi}} \int_{-\infty}^{x/2\sqrt{Dt}} \exp(-u^2)\,du.$$

Date . .

(1.18) $$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2)\,du.$$

$$\mathrm{erf}(\infty) = 1 \quad \& \quad \mathrm{erf}(-z) = -\mathrm{erf}(z).$$

$\mathrm{erf}(-z) = -\mathrm{erf}(z)$, $\mathrm{erf}(\frac{1}{2}) = \frac{1}{2}$

(1.19) $$\therefore C(x,t) = \frac{C'}{2}\left[1 + \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

$$1 - \mathrm{erf}(-\infty) + \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C'}{2}\left[\frac{2}{\sqrt{\pi}}\int_{-\infty}^{0} + \int_0^{\frac{x}{2\sqrt{Dt}}}\right]$$

$$\frac{x-\alpha}{2\sqrt{Dt}} = u$$

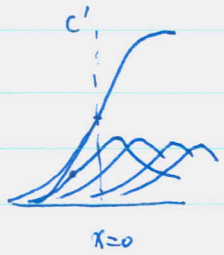
$$\frac{-d\alpha}{2\sqrt{Dt}} = du.$$

$$\therefore (1) = \frac{C'}{2\sqrt{\pi Dt}} \int_{\frac{x}{2\sqrt{Dt}}}^{-\infty} (-2\sqrt{Dt}) \exp(\,)$$

$$= \frac{C'}{\sqrt{\pi}} \int_{-\infty}^{\,''} \exp(-u^2)\,du$$

2) Decarburization.

i) From (1.19) $x=0$ $C = \frac{C'}{2}$ = const regardless of any t



then (1.19) is the sol'n for a homo alloy of solute C' held in an atmosphere which reduces the <u>surface conc. to $\frac{C'}{2}$</u> and keeps it there for all $t>0$.

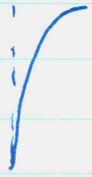
B.C. $C = \frac{C'}{2}$ for $x=0$ at $t>0$.
$C = C'$ for $x>0$ at $t=0$.

$$\frac{C'}{2} = \overset{\frac{C'}{2}}{A} + \overset{0}{B}\,\mathrm{erf}\,z$$

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

$$C' = \frac{C'}{2} + \frac{C'}{2}\,\mathrm{erf}(\infty)$$

ii) If the surface conc. is held at $c=0$ for all $t>0$.



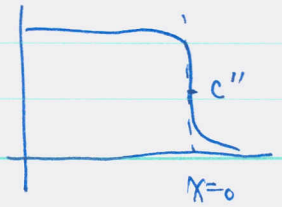
B.C $C = 0$ for $x=0$ at $t>0$
$C = C'$ for $x>0$ at $t=0$

$$0 = \overset{0}{A} + B\,\mathrm{erf}(0)$$
$$C' = A + B\,\mathrm{erf}(\infty)$$
$$\therefore B = C'$$

sol'n $$C(x,t) = C'\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\therefore C = C'\,\mathrm{erf}(z)$$

iii) If the surface conc. of an initially solute-free specimen is maintained at C'' for all $t>0$.



then (1.19) holds $x<0$, since $\mathrm{erf}(-z) = -\mathrm{erf}(z)$

$$C(x,t) = C''\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

B.C $C = C''$ for $x=0$ $t>0$
$C = 0$ for $x<0$ $t=0$.

$$C'' = A + B\,\mathrm{erf}(0) \quad ; C''$$
$$0 = A + B\,\mathrm{erf}(\infty)$$

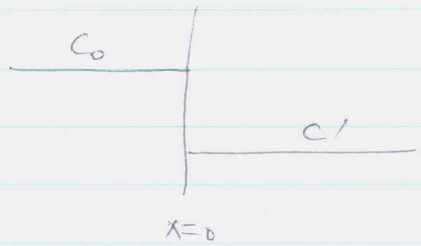
Date . .

IV 4) For a given boundary condition.

$C = C_0$ for $x > 0$ at $t = 0$

$C = C'$ for $x < 0$ at $t = 0$

then the solution $C(x,t) - C_0 = \frac{C' - C_0}{2}\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$.



$$C(x,t) = \frac{C' - C_0}{2} + C_0 - \frac{C' - C^0}{2}\,\mathrm{erf}(\quad)$$

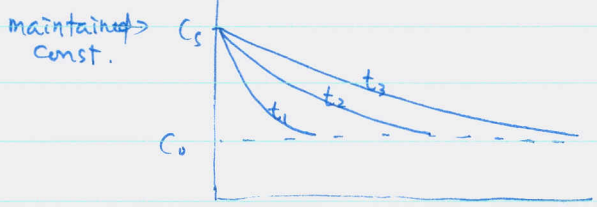
$$= \frac{C' + C_0}{2} - \frac{C' - C^0}{2}\,\mathrm{erf}(\quad)$$

Date . .

The Carburization of Steel.

1) carburization for a harder, wear-resistant surface using CH_4 or CO/CO_2. for γ-Fe.

- equil^{m} bet'n a gas mixture and surface C conc.



Analytical expression using Fick's 2nd law.

w/ B.C $C_B = C_s$ at $x=0$

$C_B = C_0$ at $x=\infty$.

↳ the original conc.

assuming $D \neq f(\text{conc.})$ and infinitely long bar.

(2.23) $$\boxed{C = C_s - (C_s - C_0)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$ where $\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z \exp(-y^2)\,dy$

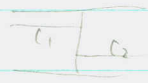
when $\mathrm{erf}(\frac{1}{2}) \cong \frac{1}{2}$ i.e. $x = \sqrt{Dt_1}$ $C = \frac{1}{2}(C_s + C_0)$

(2.24) i.e. $C = \frac{1}{2}(C_s + C_0)$ where $\frac{x}{2\sqrt{Dt}} \cong \frac{1}{2}$ → $x \simeq \sqrt{Dt}$

2) Decarburization.

(2.25) $$\boxed{C = C_0\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$ why? see back

3) two semi-infinite specimens.



if $C_1 = 0$, $C = \frac{C_2}{2}[1 + \mathrm{erf}(z)]$

$$\boxed{C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$ why? see back

~~Various Cases~~ (Shewmon P.7-19) 이 iv) of 5-2

~~A. Thin-film Sol'n.~~

Date . .

II. Diffusion in Finite System – Complete Homogenization.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$ separation of variables $C(x,t) = X(x)\,T(t)$

substitute this into → Fick's 2nd law. $X\frac{dT}{dt} = DT\frac{d^2X}{dx^2}$

rearrange $\frac{1}{DT}\frac{dT}{dt} = \frac{1}{X}\frac{d^2X}{dx^2} = -\lambda^2$ to be equal

↓ time fn only ↓ fn of dist. only

T, X function의 미분이 같을 수 있는 방법은 그 값이 상수 일 때이며 $+\lambda^2$ 인 경우임

i) then $\frac{1}{T}\frac{dT}{dt} = -\lambda^2 D$ $\therefore T = T_0 \exp(-\lambda^2 Dt)$ $T \to 0$ as $t \to \infty$

ii) similarly $\frac{d^2X}{dx^2} + \lambda^2 X = 0.$ sol'n $X(x) = A'\sin\lambda x + B'\cos\lambda x$

$\therefore$ sol'n $C(x,t) = (A\sin\lambda x + B\cos\lambda x)\exp(-\lambda^2 Dt)$

(1-27) $\therefore$ a peni'l sol. $C(x,t) = A_0 + \sum(A_n \sin\lambda_n x + B_n\cos\lambda_n x)\exp(-\lambda_n^2 Dt)$

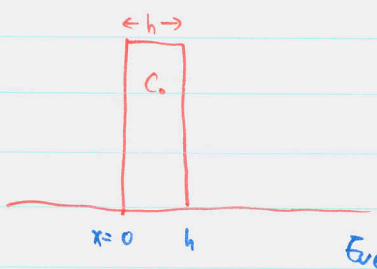
$\bar{c}$ 

$x=0,\ t=0$ $C_0 = \bar{C}$ $\therefore A_0 = \bar{C}$ $B_n = 0$

$x = l, 2l$ $C = \bar{C}$ $\lambda_n = \frac{\pi}{l_n}$ = periodicity

$\therefore C(x,t) = \bar{C} + \sum A_n \sin\left(\frac{\pi}{l_n}\right)x \exp\left\{-\left(\frac{\pi}{l_n}\right)^2 Dt\right\}$

Diffusion out of a slab



B.C. $C = C_0$ for $0 < x < h$ at $t = 0$

$C = 0$ for $x = h$, $x = 0$ at $t > 0$

Eventually the conc. in the slab → 0 $\therefore A_0 = 0$ 이다 (1.27)

Since $C = 0$ at $t > 0$, $x = 0$. $B_n \Rightarrow 0$

$C = 0$ $x = h$ $\sin\lambda_n h = 0$ $\therefore \lambda_n h = n\pi$

$\therefore \lambda_n = \frac{n\pi}{h}$ n any + integer.

(1.28) $\therefore C_0 = \sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{h}$

Date . .

multiple both sides w/ $\sin\left(\frac{p\pi x}{h}\right)$ & integrate x over the range $0<x<h$.

$$\int_0^h C_0 \sin\left(\frac{xp\pi}{h}\right) dx = \sum A_n \int_0^h \sin(xp\pi/h)\sin(xn\pi/h)\,dx.$$

orthogonal fn.

$$= -C_0\frac{h}{p\pi}\cos\left(\frac{xp\pi}{h}\right)\Big]_0^h$$

$$= -C_0\frac{h}{p\pi}\left[\cos(p\pi) - \cos 0\right]$$

① if $p = 2, 4 \ldots = 0$

$p = 1, 3 \ldots = \frac{2hC_0}{p\pi}$

$\int_0^\infty$ " $= 0$ unless $p = n$.

$= \frac{h}{2}$. if $p = n$.

$$\therefore A_n = \frac{2}{h}\int_0^h C_0 \sin(nx\pi/h)\,dx. = 0 \text{ for all even values of } n$$

$$= \left(\frac{2}{h}\right)\left(-\frac{hC_0}{n\pi}\right)\left[\cos(n\pi) - \cos 0\right] = \frac{4C_0}{n\pi} \text{ for all odd } \text{"}.$$

(1.30) $$\therefore A_n = A_j = \frac{4C_0}{(2j+1)\pi} \quad j = 0, 1, 2.$$

odd

The sol'n $$C(x,t) = \frac{4C_0}{\pi}\sum_0^\infty \frac{1}{(2j+1)}\sin\frac{(2j+1)\pi x}{h}\exp\left(-\left[\frac{(2j+1)\pi}{h}\right]^2 Dt\right)$$

in a short time, only few terms useful $\because \exp(-t)$

→ applies to the decarburization of a thin sheet of steel.

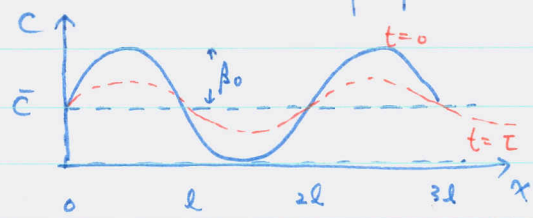
Your inquiries have separated you from your God

Date

5. Solutions to the Diff. Eq. (w/ Practical Examples)

Homogenization

ex. elimination of segregation in castings.



$0 < x < l$ negative C_B decrease

$l < x < 2l$ positive curvature

C_B increase

wave length

(2.19) $C = \bar{C} + \beta_0 \sin \frac{\pi}{l} x$ at $t = 0$.

mean comp — the amplitude of the initial conc.

Assume $D_B \neq f(\text{conc})$.

(2.20) at t, $C(t) = \bar{C} + \beta_0 \sin \frac{\pi x}{l} \exp\left(-\frac{t}{\tau}\right)$

(2.21) where τ (= relaxation time) $= \frac{l^2}{\pi^2 D_B}$ ⇐ find out where it's from!! see back!

at $x = \frac{l}{2}$, at time t the amplitude of the conc. profile

(2.22) $\beta = \beta_0 \exp\left(-\frac{t}{\tau}\right)$ → exponentially decrease.

at $t \to \infty$ $\beta \to 0$ $C \to \bar{C}$

- the speed to reach $\bar{C}$ is determined by τ

at $t = \tau$ $\beta = \beta_0/e = \beta_0/2.72$ 30% 까지 내려갔다

↳ $t = 0$

at $t = 2\tau$ $\beta = \beta_0/e^2 \cong \beta_0/10$ 10% "

from (2.21) the rate of homo'n ↑ rapidly as l ↓ (wavelength of fluctuation)

→ In practice, the conc. profile will not be sinusoidal but considered as a sum of infinite series of sine waves. → short wavelength (small influence) decay soon.

τ of long wavelength (dominant) determine homo process