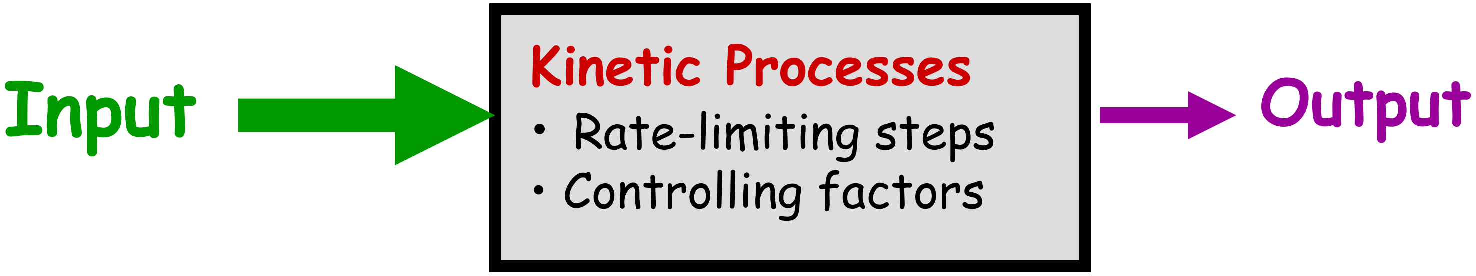
Thermodynamics vs. Kinetics

- Thermodynamics:
  - To study the direction of a reaction, or if a reaction can take place. ($\Delta G<0$)
  - To study the equilibrium states in which state variables of a system do not change with time.
- Kinetics:
  - To study the rates and paths of a reaction adopted by the systems approaching equilibrium.
  - To study the rate-limiting steps of a reaction
  - To study the controlling factors of the rate-limiting steps



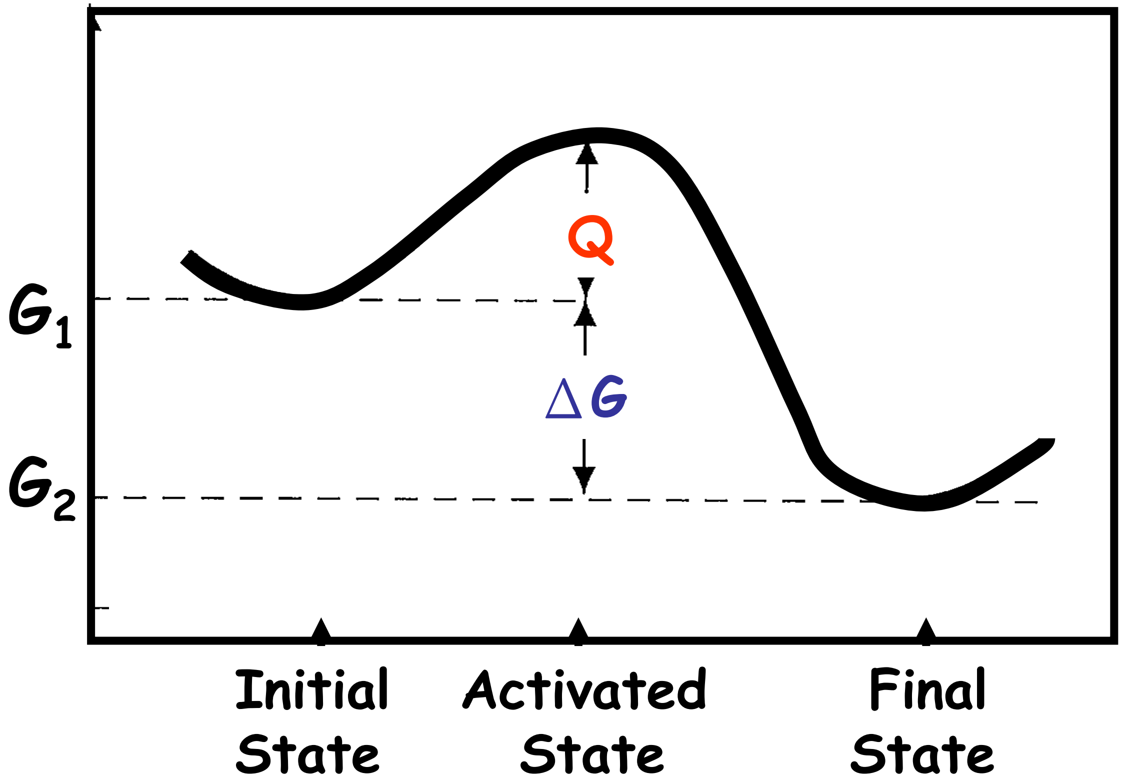
Input

Kinetic Processes

- Rate-limiting steps
- Controlling factors

Output

Thermodynamics vs. Kinetics



Reaction Rate α (Kinetic factor) x (Thermodynamic factor)

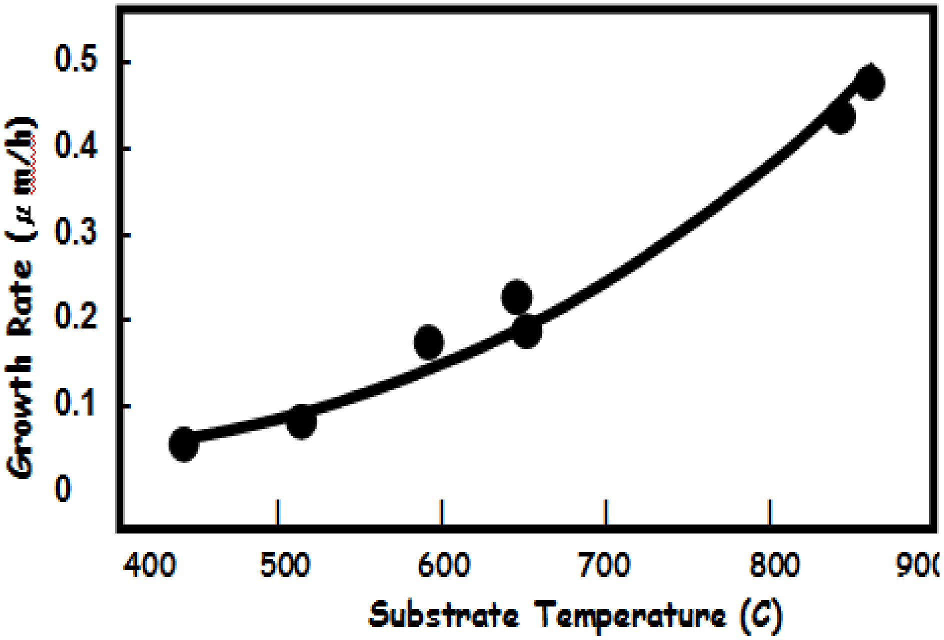
* Kinetic factor relates to Q (activation energy), while the thermodynamic factor relates to the driving force, $\Delta G = G_2 - G_1$.

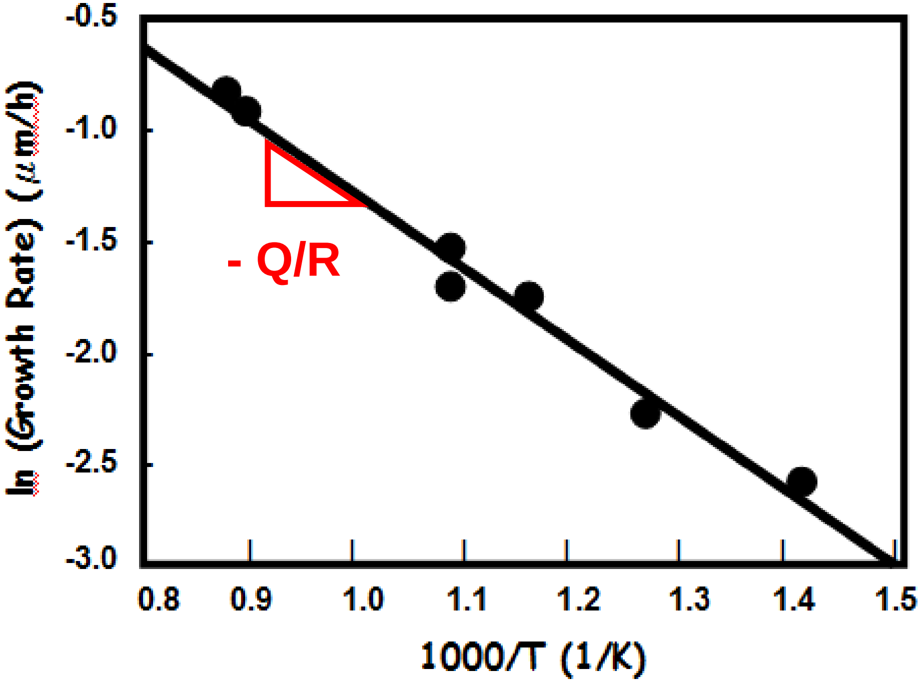
* The thermodynamic factor decides the direction of a reaction, while the kinetic factor, the rate of reaction.

Kinetic theory: The reaction rate is proportional to the probability to reach activated state that follows the Arrhenius rate equation, exp(-Q /RT).

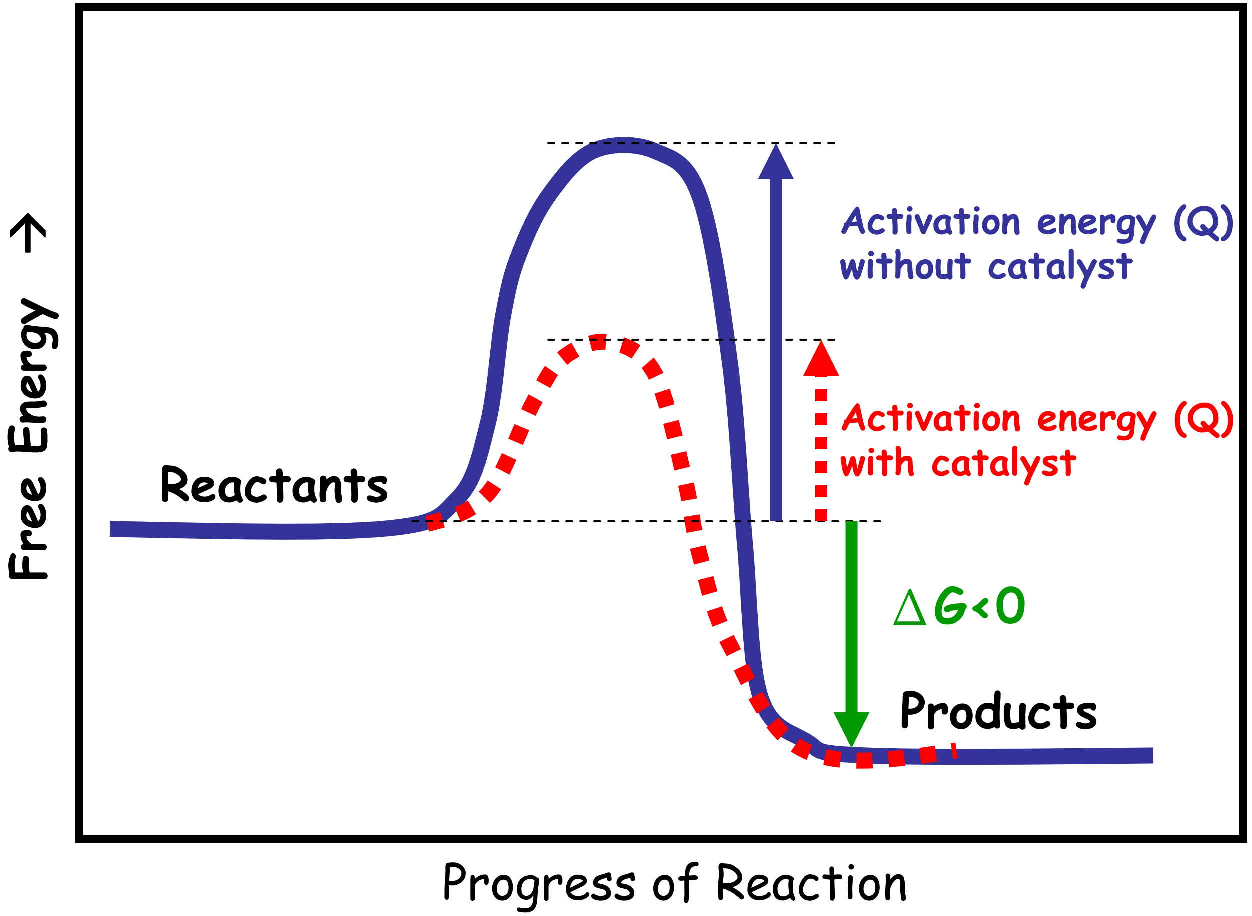
* The activation energy (Q) can be obtained from the slope of curve plotted as ln(reaction rate) vs. 1/T

Example: For diamond growth by CVD from reaction of methane and hydrogen





Kinetic factor increased by changing temperature or adding catalysts.



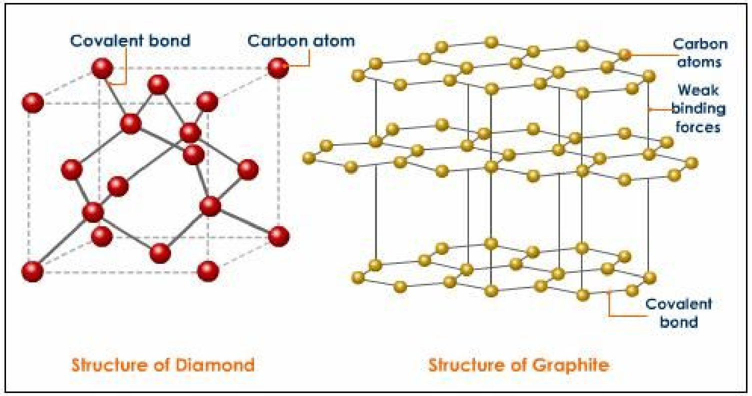
Examples: (1) $N_2 + 3H_2 = 2NH_3$ using iron as a catalyst

(2) $2CO + 2NO = 2CO_2 + N_2$ using Pt and Rh as catalysts for catalytic converters used in automobile

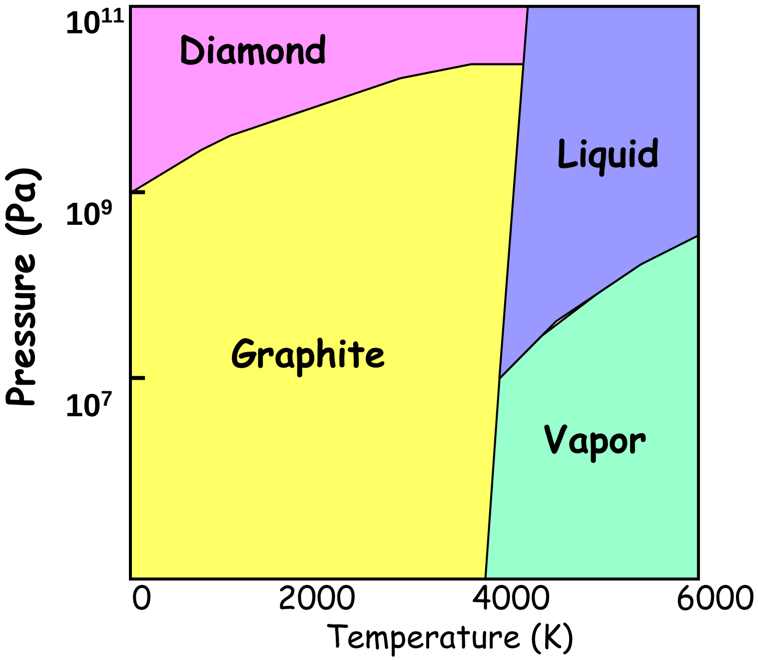
Examples: Thermodynamically favorable but kinetically unfavorable phase changes

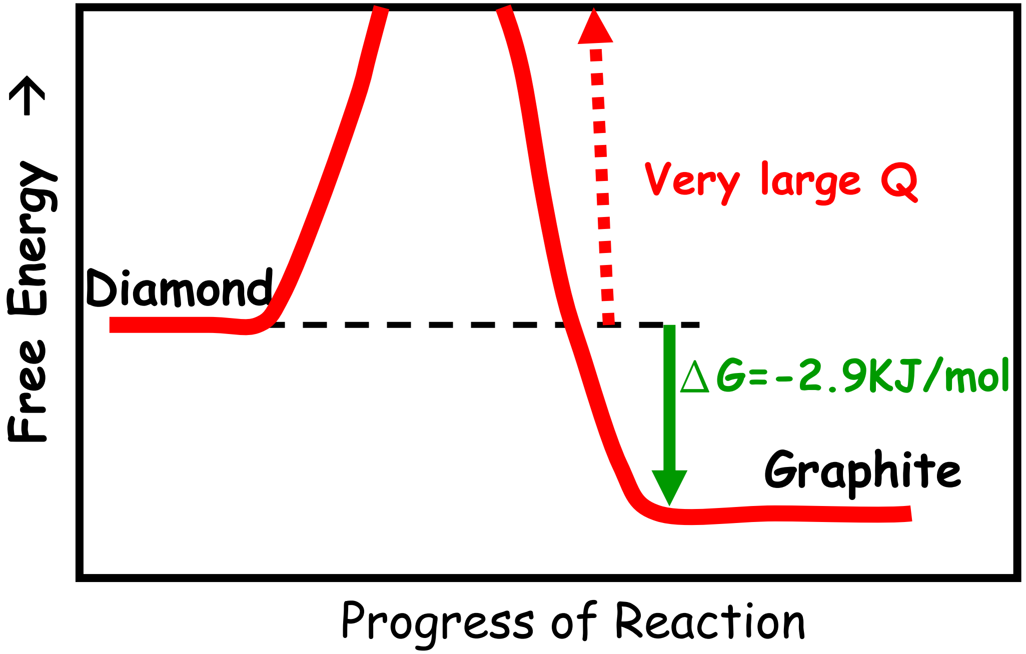
(1) Is a diamond forever?

Diamond

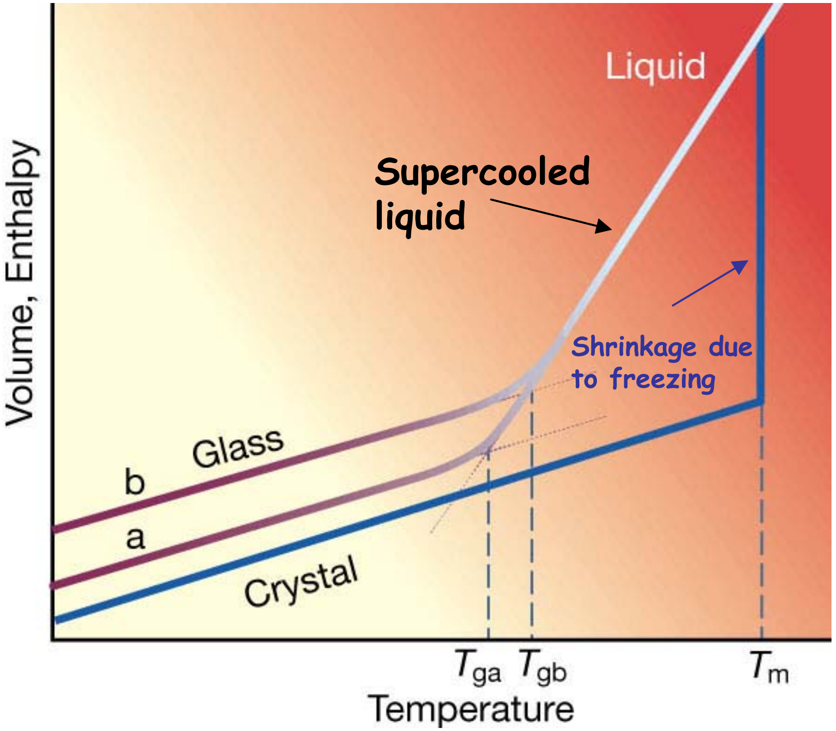


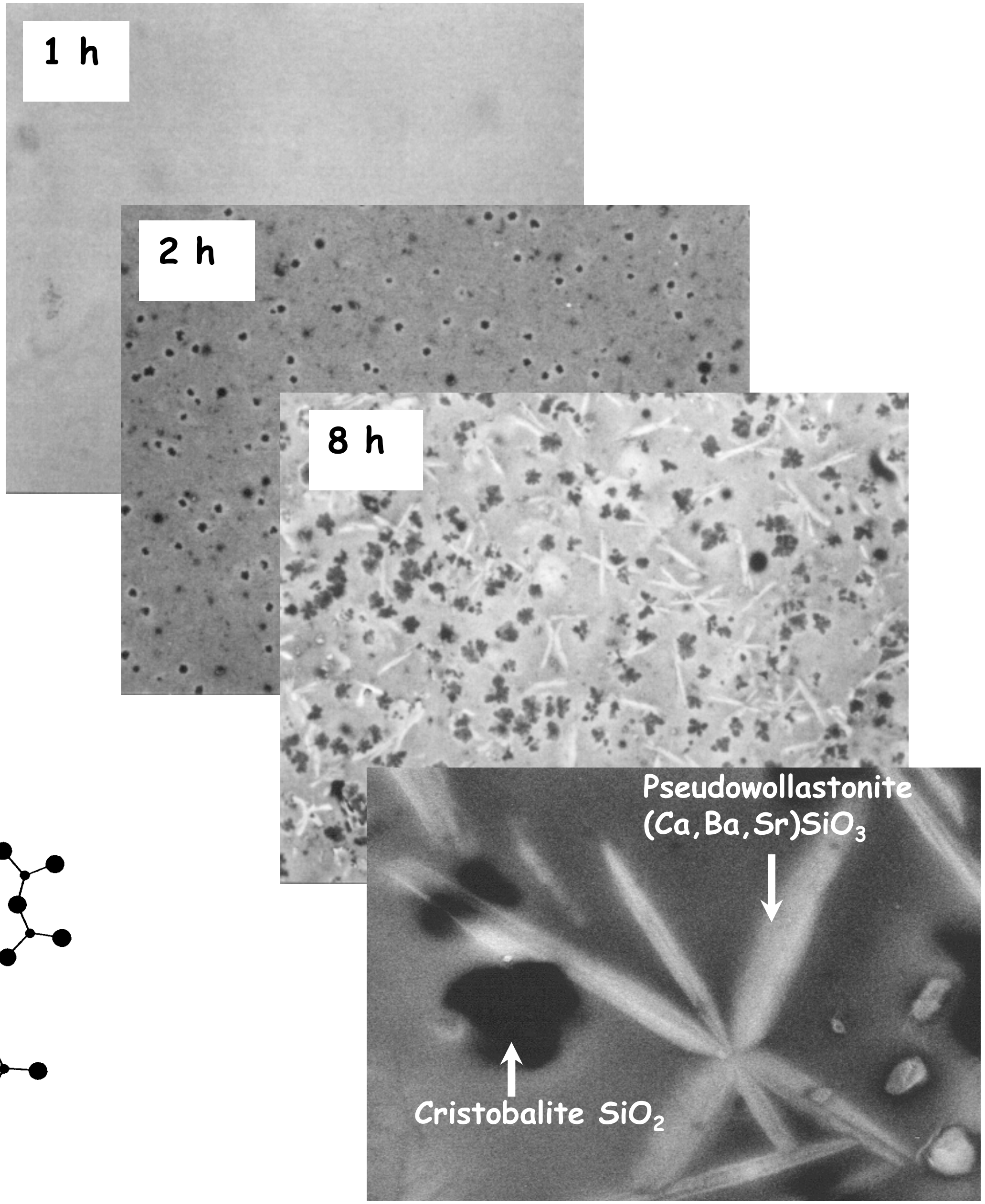
Graphite



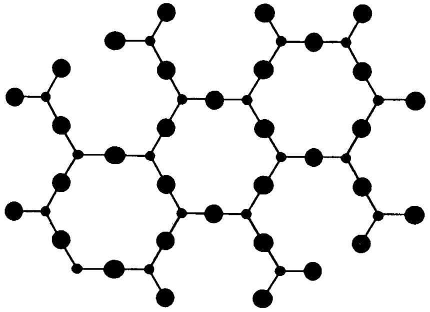


(2) Crystallization of glasses

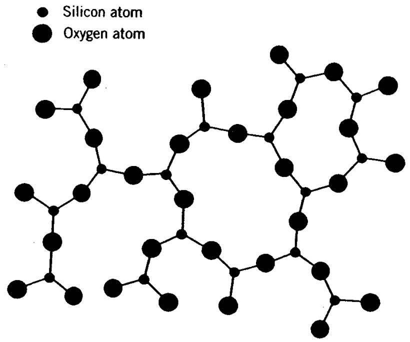




$CaO-SrO-BaO-B_2O_3-SiO_2$ glass-ceramics annealed at 875°C



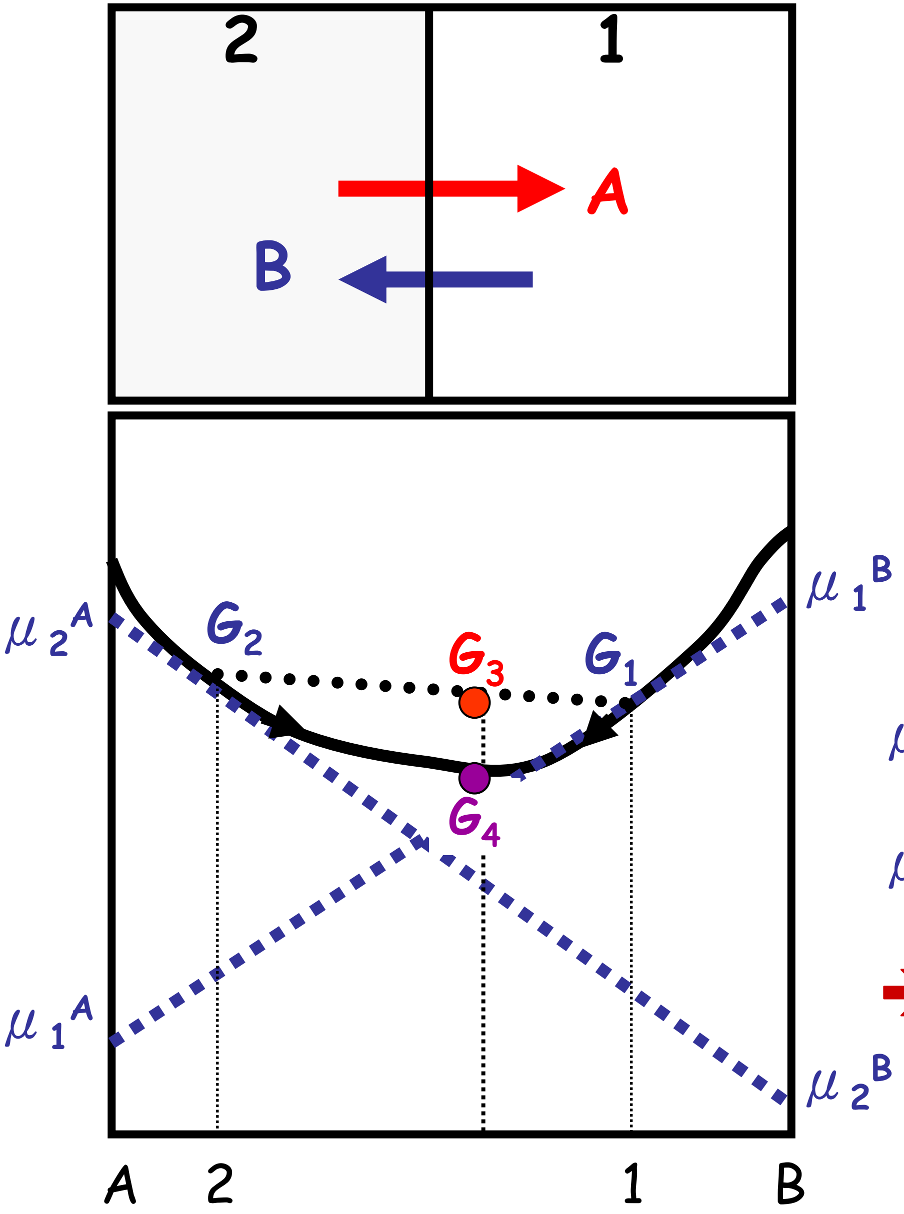
crystalline



non-crystalline

Diffusion driven by decrease in chemical potential

* Down-hill diffusion



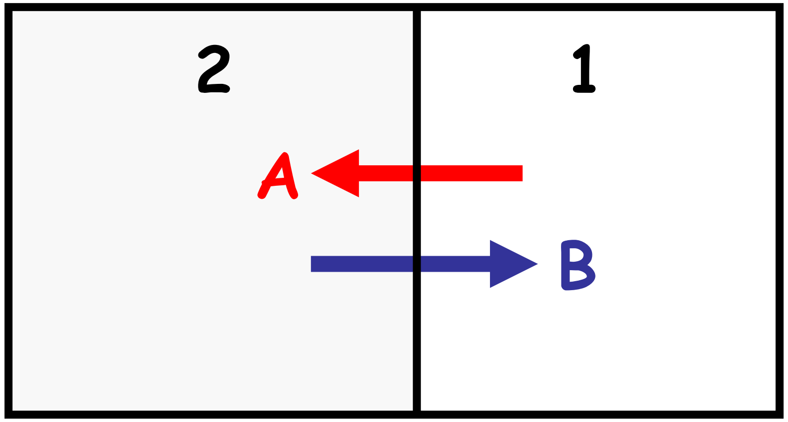
Free energy of diffusion couple = G_3
Diffusion taking place to homogenize to obtain G_4

$\mu_1^B > \mu_2^B$ →B diffusing from (1)→(2)

$\mu_2^A > \mu_1^A$ →A diffusing from (2)→(1)

→Down-hill Diffusion

* Up-hill Diffusion



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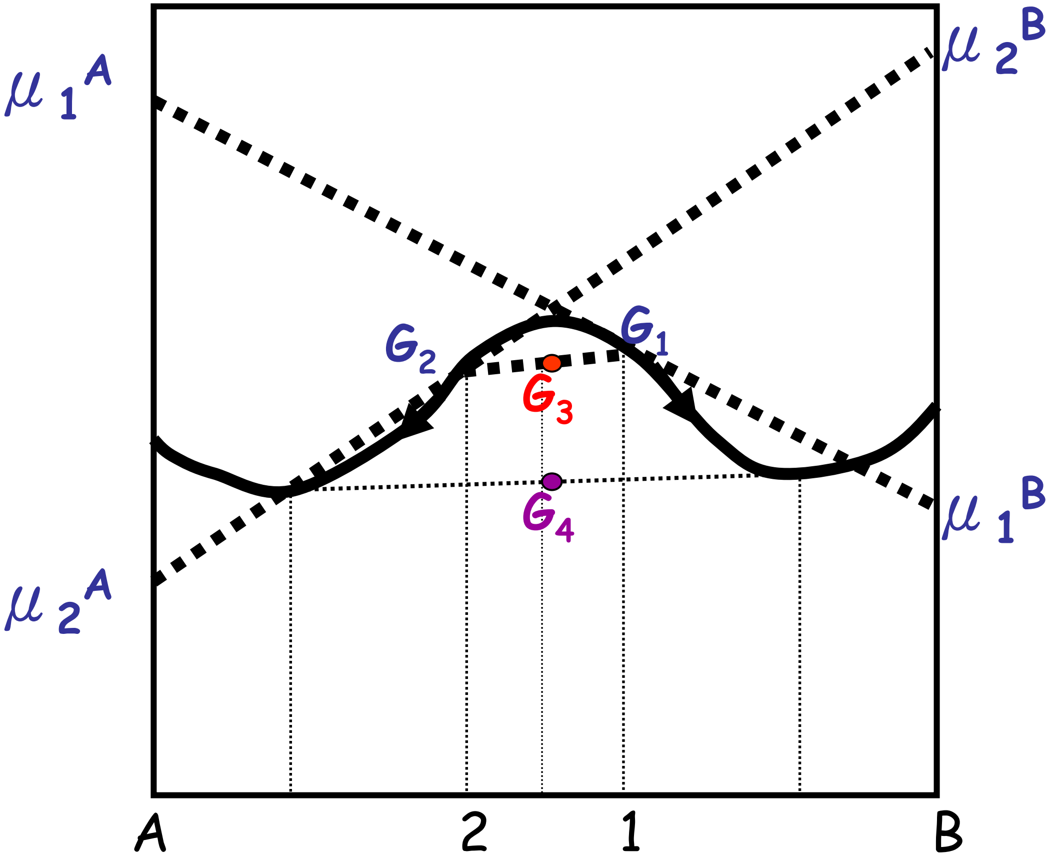


$\mu_1^B < \mu_2^B$ →B diffusing from (2) to (1)

$\mu_2^A < \mu_1^A$ →A diffusing from (1) to (2)

→Up-hill Diffusion

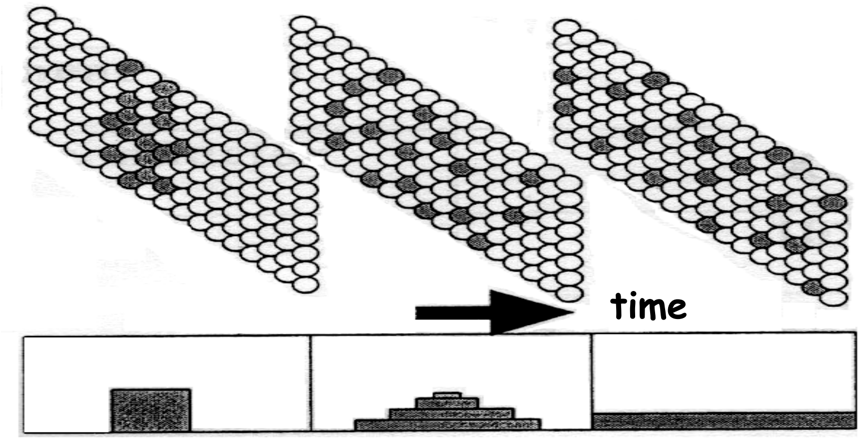
$$Driving \quad force \quad \alpha \quad \frac{\partial \mu}{\partial x} \quad (not \frac{\partial C}{\partial x})$$

$$J = Cv = C \cdot (B \cdot F) = C \cdot B(-\frac{\partial \mu}{\partial x})$$

$B : Mobility, \quad F : Force$

Diffusion:

Process by which matter is transported through matter as a result of molecular motions



General scheme for transport phenomena

	Flux	α	Driving force	α	Gradient in potential
Matter	J	α	dC/dx	α	Concentration potential
Heat	q	α	dT/dx	α	Temperature potential
Electricity	I	α	dϕ/dx	α	Electrical potential

$$J = -D\nabla C \quad (Fick's\ \ Law)$$

D: diffusivity

$$q = -k\nabla T \quad (Fourier's\ \ Law)$$

k: thermal conductivity

$$I = -\sigma\nabla\phi \quad (Ohm's\ \ Law)$$

σ: electrical conductivity

Fick's First Law:

Species migrates from a region of high concentration to a region of low concentration ; in general the rate of diffusion is proportional to the concentration gradient

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

- **Flux (J)** : **Mass/(area · time), e.g., g/(cm^2 · sec)**

- **Minus (-): Matter moves from high to low concentration.**

- **Diffusivity (D): Diffusivity related to atomic mobility and crystal structure, e.g., cm^2/sec (independent of concentration gradient)**

- **Concentration gradient ($\frac{\partial C}{\partial x}$): Gradient in "Mass Potential," e.g., g · cm^{-3}/cm**

Steady State:

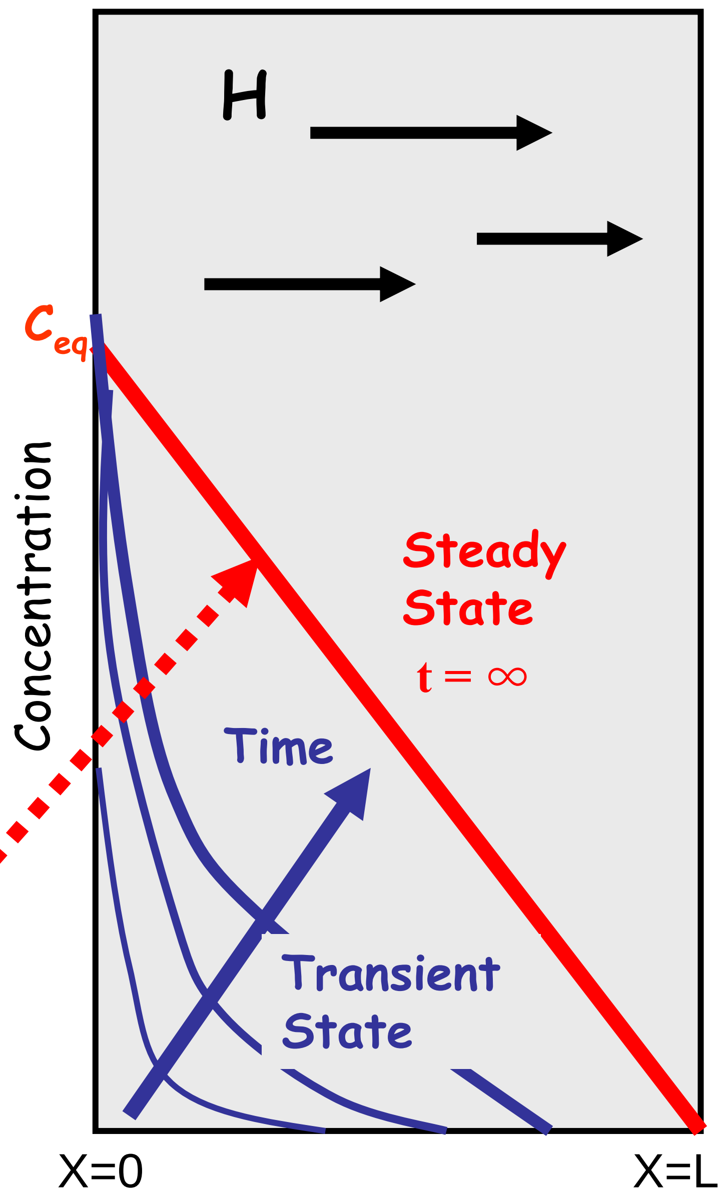
Concentration at a given point
is invariant with time

i.e., $C = C(x)$

$$\left(\frac{\partial C}{\partial t}\right)_x = 0$$

$J \neq J(x,t)$ when area is fixed

Steady State Solution: $C(x) = A + Bx = C_o - \frac{C_o}{L}x$



Key: to describe $C(x,t)$ quantitatively

Equilibrium State: No Flux

$$\left(\frac{\partial \mu}{\partial x}\right)_t = 0 = \left(\frac{\partial C}{\partial x}\right)_t$$

Steady State: Constant flux if the area is fixed.

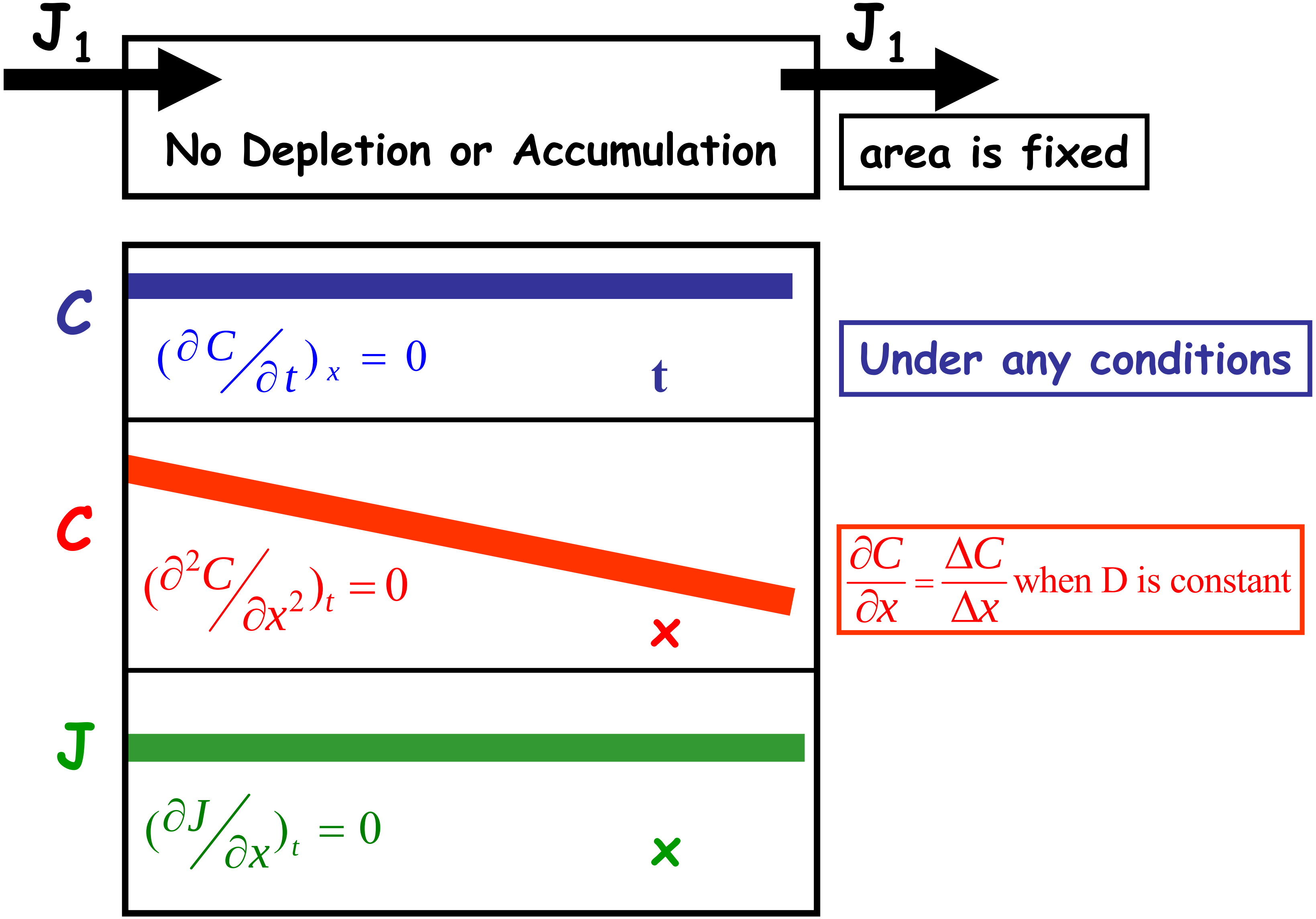
$$\left(\frac{\partial \mu}{\partial t}\right)_x = 0 = \left(\frac{\partial C}{\partial t}\right)_x$$

μ : **Chemical Potential**

$$\because \Delta\mu = \mathrm{RT}\ln(a) = \mathrm{RT}\ln(\gamma X)$$

$$\left(\frac{\partial \mu}{\partial x}\right)_t = \mathrm{RT}\left(\frac{\partial \ln(a)}{\partial x}\right)_t = \mathrm{RT}\left(\frac{\partial \ln(\gamma X)}{\partial x}\right)_t$$

Steady State:



No Depletion or Accumulation

area is fixed

$(\partial C/\partial t)_x = 0$ t

Under any conditions

$(\partial^2 C/\partial x^2)_t = 0$ ×

$\frac{\partial C}{\partial x} = \frac{\Delta C}{\Delta x}$ when D is constant

$(\partial J/\partial x)_t = 0$ ×

Fick's Second Law

Transient State: C=C(x,t), or J=J(x,t)

$(\frac{\partial C}{\partial t})_x \neq 0 \rightarrow$ accumulation or depletion of concentration exists

Mass Conservation

$$\frac{\partial m}{\partial t} = J_x A - J_{x+\Delta x} A = \frac{\partial C}{\partial t} A \cdot \Delta x$$ (A is fixed)

Flux · Area = Rate of change of concentration · volume

(g $\text{cm}^{-2}\text{sec}^{-1} \cdot \text{cm}^2$ = g $\text{cm}^{-3}\text{sec}^{-1} \cdot \text{cm}^3$)

From Taylor Series

$$\boxed{J_{x+\Delta x} = J_x + \frac{\partial J}{\partial x} dx} + \frac{\partial^2 J}{\partial x^2} \frac{dx^2}{2!} + \ldots\ldots\ldots$$

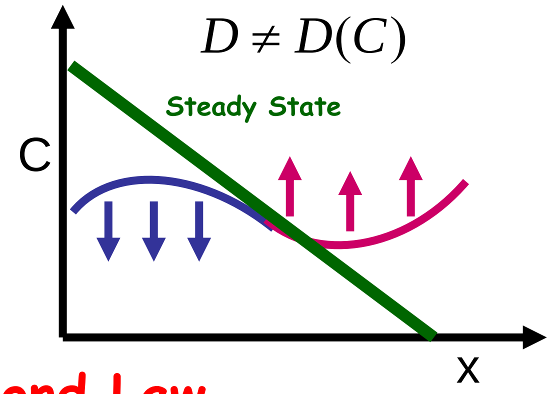
$$\boxed{\begin{aligned} & J_x A - (J_x + \frac{\partial J}{\partial x} dx) A = \frac{\partial C}{\partial t} A \cdot \Delta x \\ & -\frac{\partial J}{\partial x} dx \cdot A = \frac{\partial C}{\partial t} A \cdot \Delta x \end{aligned}}$$

Fick's Second Law (cont.)

$$-\frac{\partial C}{\partial t}=\frac{\partial J}{\partial x}=\frac{\partial}{\partial x}(-D\frac{\partial C}{\partial x})$$

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

$$=-D\frac{\partial^2 C}{\partial x^2}-\frac{\partial C}{\partial x}(\frac{\partial D}{\partial C}\frac{\partial C}{\partial x})$$



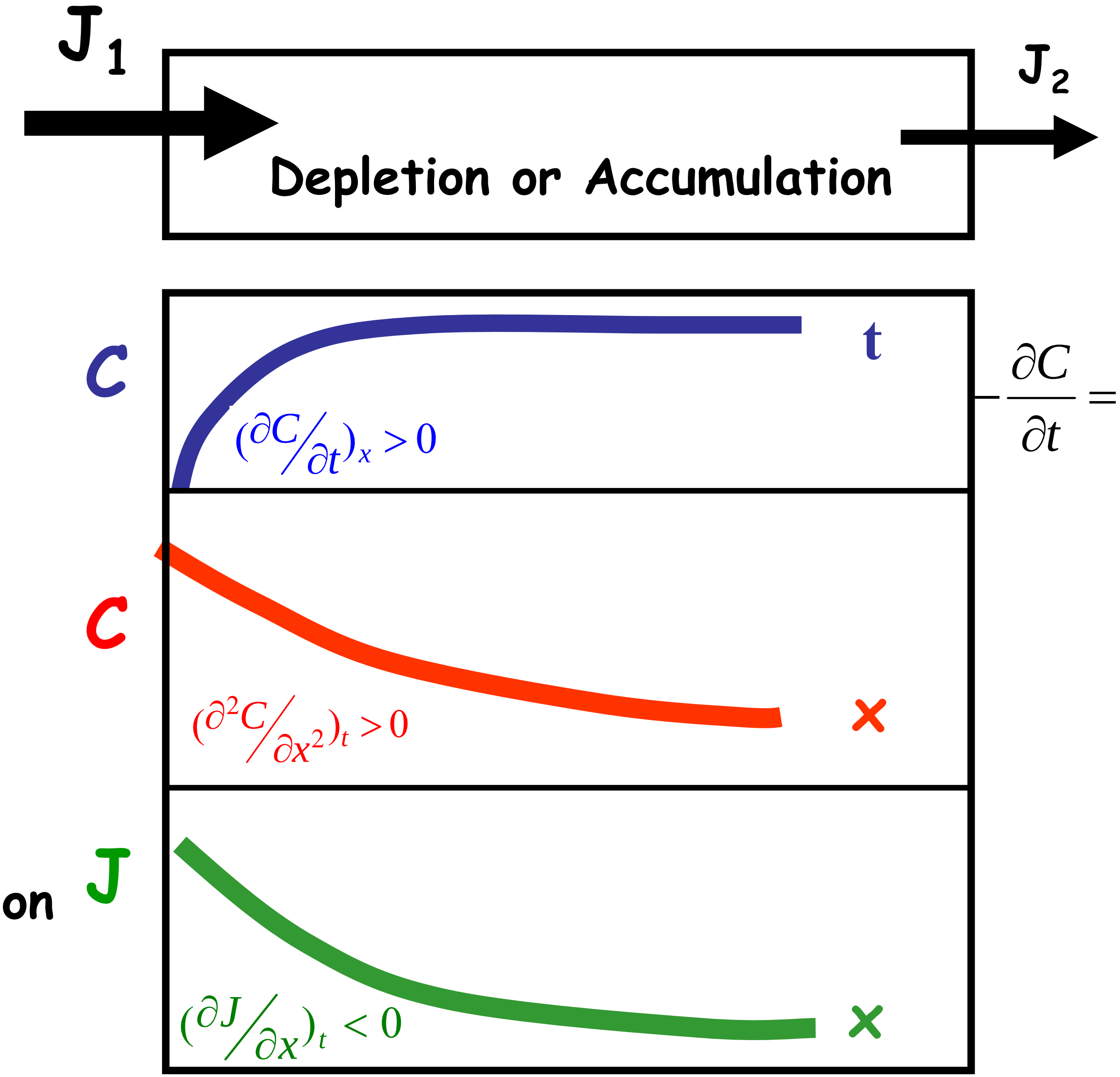
when $D\neq D(C)\rightarrow\frac{\partial D}{\partial C}=0$

$$\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}\rightarrow$$ **Fick's Second Law**

Linear partial differential equation

- **Solutions are additive**
- **Solutions require initial and boundary conditions**

Transient State:



J_1

J_2

Depletion or Accumulation

C $\quad$ t

$(\partial C/\partial t)_x > 0$

C

$(\partial^2 C/\partial x^2)_t > 0$

x

J

$(\partial J/\partial x)_t < 0$

x

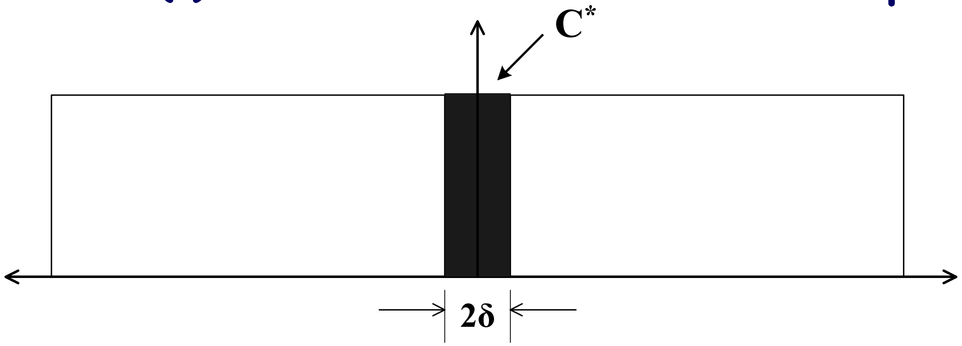
$$\frac{\partial C}{\partial t} = \frac{\partial J}{\partial x} = -D\frac{\partial^2 C}{\partial x^2}$$

If $J_2 < J_1$
→ Accumulation

Transient State --Thin-film solution (Infinite Sink)

A quantity of solute, S, is plated as a thin film on one end of a long rod of solute-free material, then a similar solute-free rod is welded to the plated end.

Annealed for time (t) → Determine concentration profile of the solute.



Assuming **$D \neq D(x)$ (Constant diffusivity)**

Fick's 2nd Law: $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

I.C. $C(x,0) = 0 \qquad |x| > \delta$

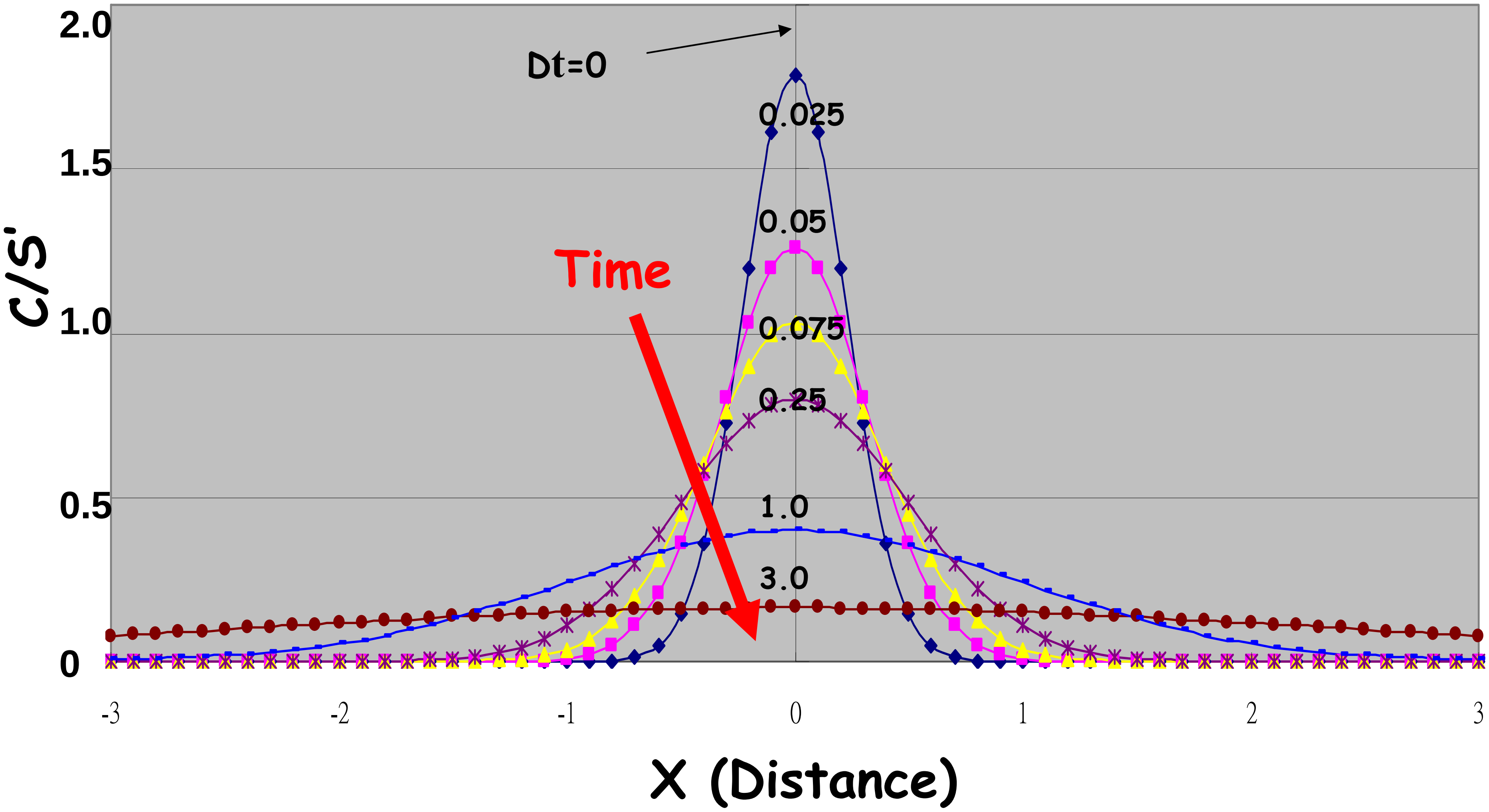
$C(x,0) = C^* \qquad |x| \leq \delta$

B.C. $C(\infty, t) = 0$

$C(-\infty, t) = 0$

Transient State --Thin-film solution (Infinite Sink)

$$C(x,t) = \frac{S'}{2\sqrt{\pi D t}} \exp(-\frac{x^2}{4Dt})$$



Conservation of mass

$$\int_{-\infty}^{\infty} C(x,t)dx = S^{'}(= 2\delta C^{*})$$

S'= g/cm^2 (Surface Concentration)
C*= g/cm^3

$$General \quad Solution: \ C(x,t) = \frac{A}{\sqrt{t}}\exp(-\frac{x^2}{4Dt})$$ (A: constant)

$$Particular \quad Solution: \ C(x,t) = \frac{S^{'}}{2\sqrt{\pi Dt}}\exp(-\frac{x^2}{4Dt})$$ (Note: $\sqrt{Dt} >> 2\delta$)

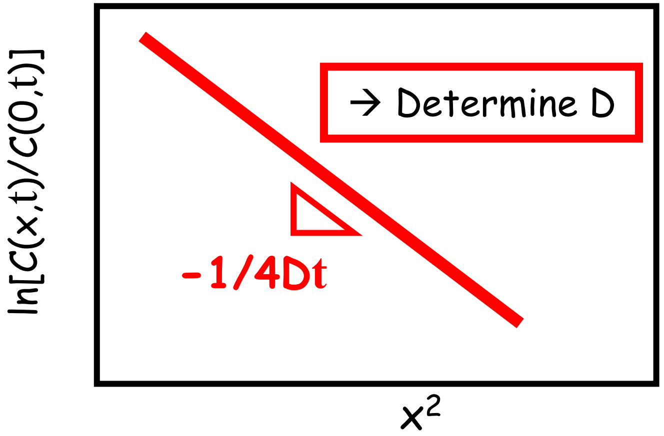
$$\because \quad C(0,t) = \frac{S^{'}}{2\sqrt{\pi Dt}}$$

$$C(x,t) = C(0,t)\exp(-\frac{x^2}{4Dt})$$

Taking the natural logarithm of both sides yields

$$\ln(\frac{C(x,t)}{C(0,t)}) = -\frac{x^2}{4Dt}$$

Thus a graph of $\ln(C(x,t)/C(0,t))$ against x^2 should yield a straight line with a slope of $-1/4Dt$.



$if \quad \ln(\frac{C(x,t)}{C(0,t)})\ vs.\ x^2$ is not a linear relation, D is a function of concentration. If it is linear, D is independent of concentration.

$$C(x,t) = \frac{S'}{2\sqrt{\pi D t}} \exp(-\frac{x^2}{4Dt})$$

$$(1) \frac{\partial C}{\partial x}|_{x=0} = 0 \Rightarrow \text{Impermeable} \quad \text{Boundary}$$

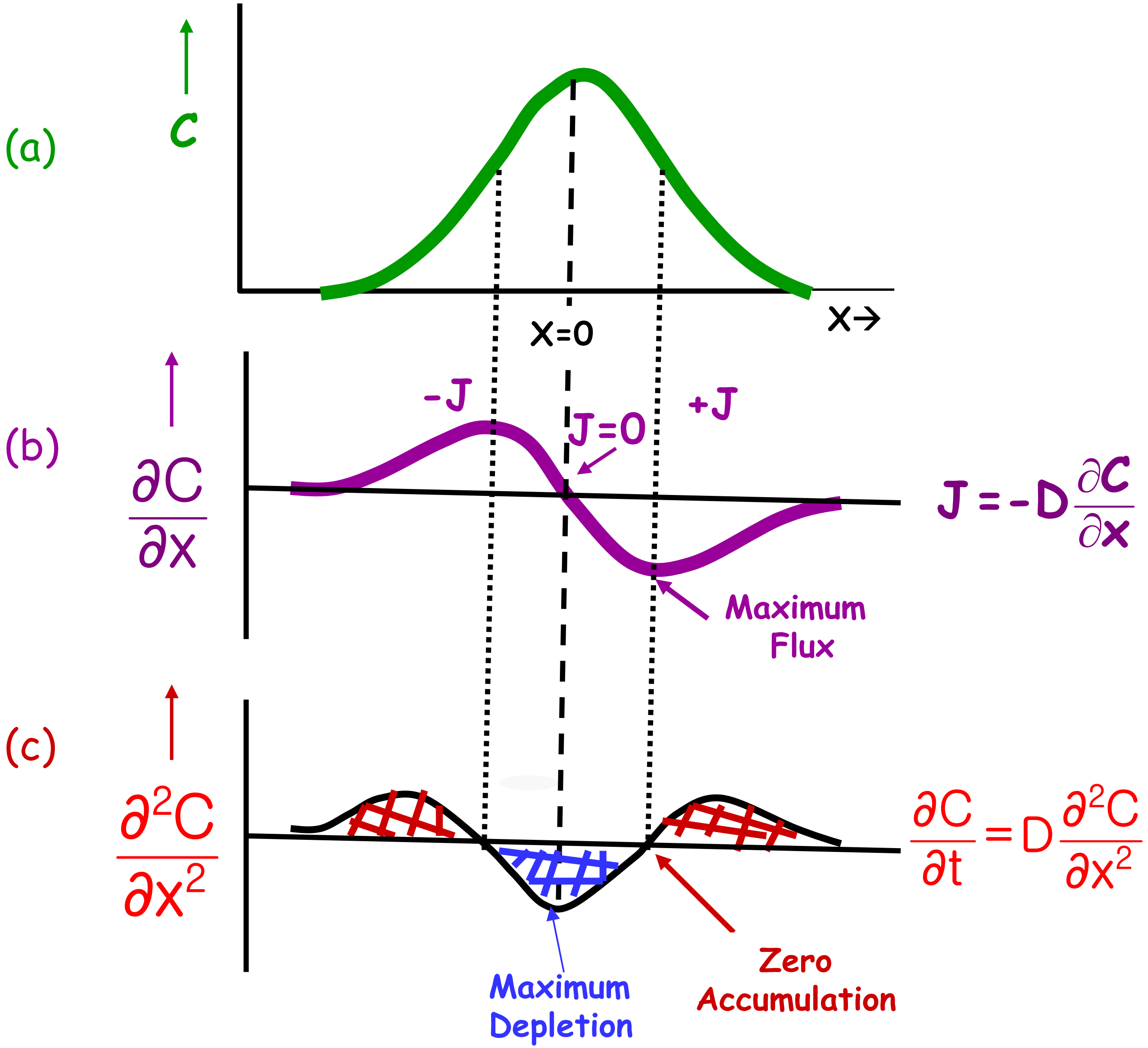
$$(2) C(0,t) = \frac{S'}{2\sqrt{\pi D t}} \Rightarrow C(0,t) \quad \alpha \quad \frac{1}{\sqrt{t}}$$

$$(3) when \quad \frac{x^2}{4Dt} = 1 \rightarrow x = 2\sqrt{Dt}$$

$$C(x,t) = \frac{S'}{2\sqrt{\pi D t}} \exp(-1) = \frac{C(0,t)}{e} \leftarrow \text{this} \quad \text{plane} \quad \text{is} \quad \text{determined.}$$

$$x \quad \alpha \quad \sqrt{t} \leftarrow this \quad plane\ (x = 2\sqrt{Dt}) \quad moves \quad away \quad from \quad x = 0.$$

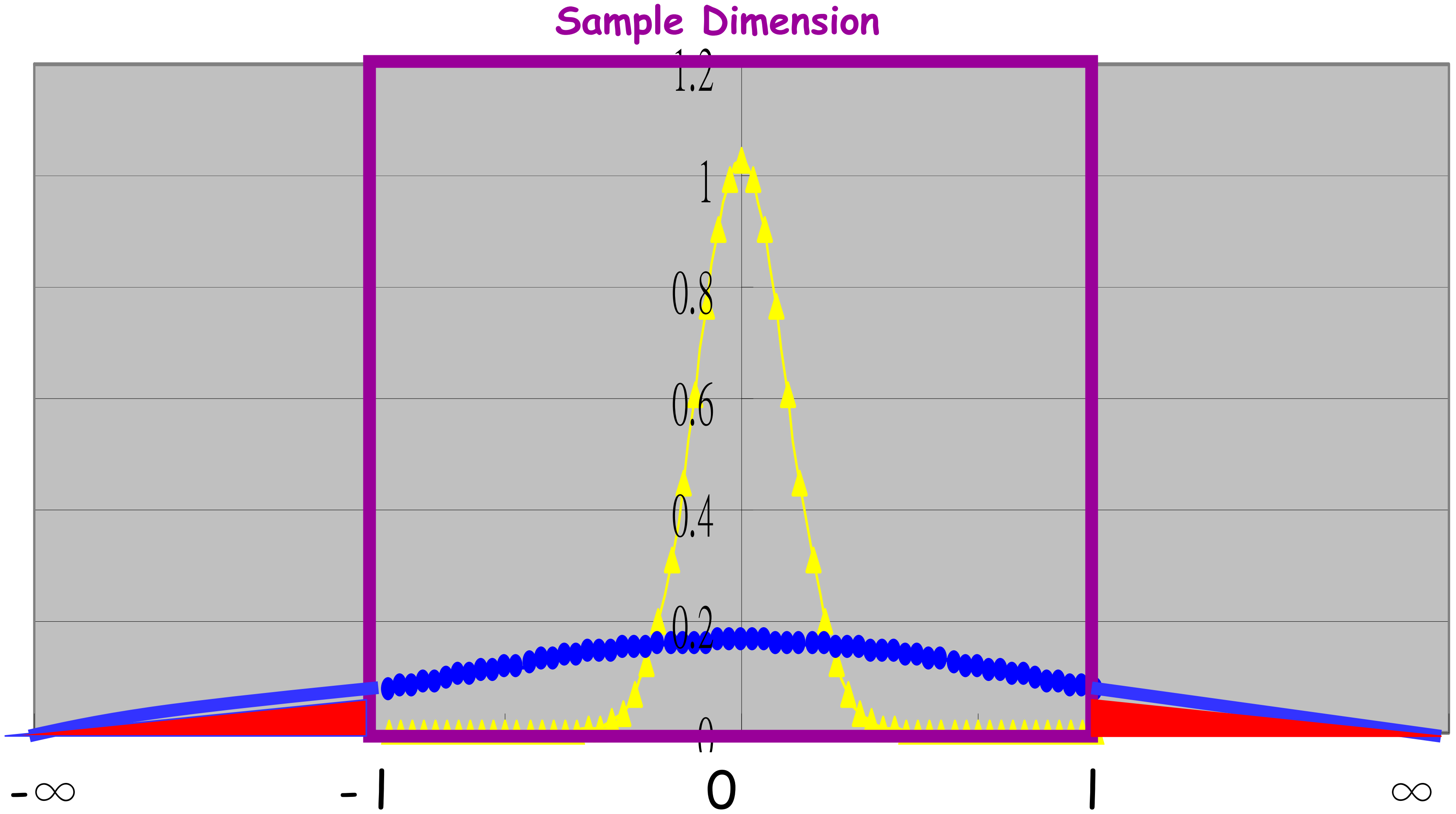
Thin Film Solution



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

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

Leak Test



The above analyses are only good for a thin film in the middle of an "**Infinite Bar**". If it is not infinite, the diffusion will be reflected back into the specimen when it reaches the end of the bar, and concentration in that region will be higher than the above solution.

Q: How long is long enough to be considered infinite?

Leak Test

Arbitrarily taking 0.1% as a sufficiently insignificant concentration

$$0.1\% = \frac{\int_l^\infty C(x,t)dx}{\int_0^\infty C(x,t)dx} = \frac{\int_l^\infty \frac{S'}{2\sqrt{\pi Dt}}\exp(-\frac{x^2}{4Dt})dx}{\int_0^\infty \frac{S'}{2\sqrt{\pi Dt}}\exp(-\frac{x^2}{4Dt})dx} = 10^{-3}$$

$$Let \quad u = \frac{x}{2\sqrt{Dt}}, \quad du = \frac{dx}{2\sqrt{Dt}}$$

$$x = \infty \quad u = \infty$$

$$x = l \quad u = \frac{l}{2\sqrt{Dt}}$$

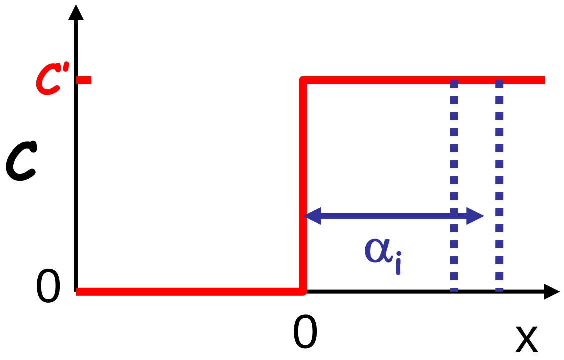
$$10^{-3} = \frac{\frac{S'}{\sqrt{\pi}}\int_{\frac{l}{2\sqrt{Dt}}}^{\infty} \exp(-u^2)du}{\frac{S'}{\sqrt{\pi}}\int_{0}^{\infty} \exp(-u^2)du}$$

$$= \frac{erfc(\frac{l}{2\sqrt{Dt}})}{1} = 1 - erf(\frac{l}{2\sqrt{Dt}})$$

$\therefore l = 4.6\sqrt{Dt}$ **(Check the Table of Error Function)**

$l \geq 4.6\sqrt{Dt}$ **The bar is considered to be long enough to use a thin-film solution with 99.9% accuracy.**

Solution for a pair of Semi-infinite Solids



$$
\begin{aligned}
I.C.\quad & C(x,0)=0 && x<0 \\
& C(x,0)=C' && x>0 \\
B.C.\quad & C(\infty,t)=C' \\
& C(-\infty,t)=0
\end{aligned}
$$

Superposition

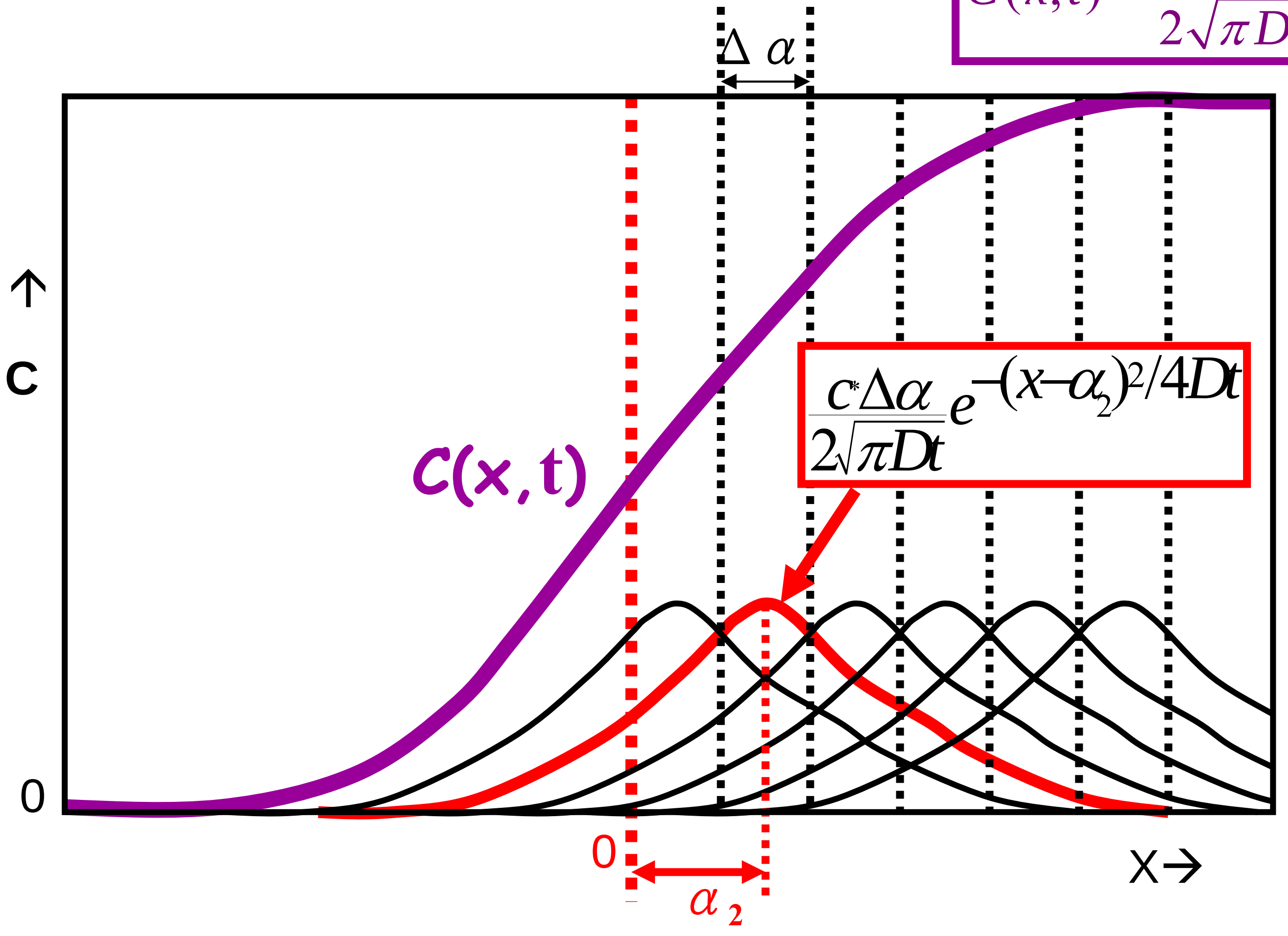
(1) No interaction from adjacent slabs

(2) Superposition of the distributions from the individual slabs since the diffusion equation is linear and additive.

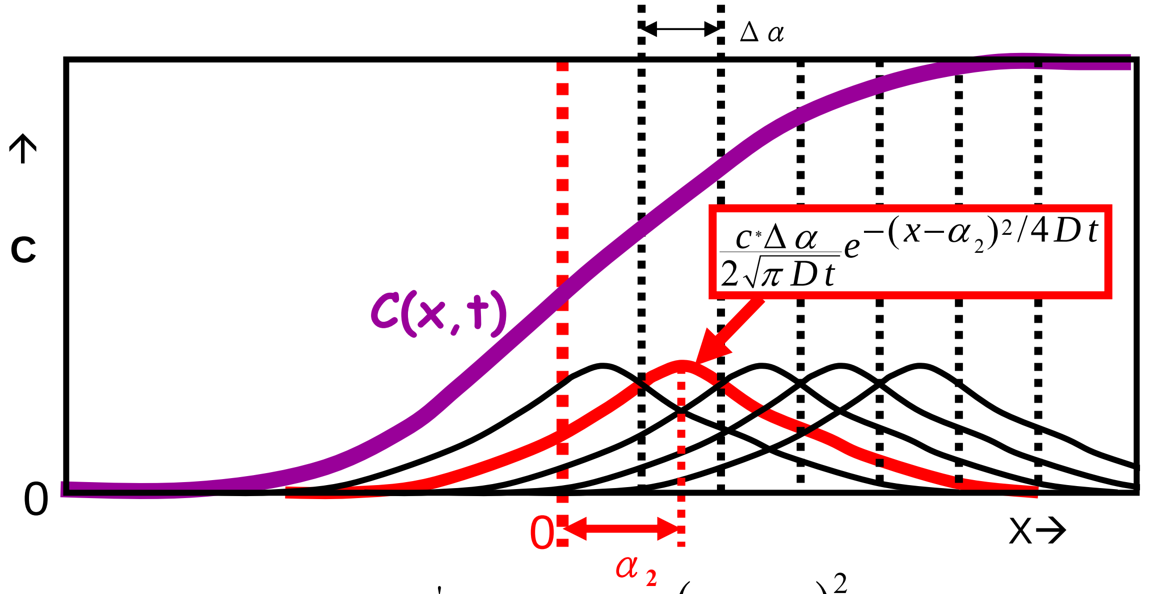
$$C(x,t) = \frac{C'}{2\sqrt{\pi D t}} \sum_{i=1}^{n} \Delta\alpha \exp(-\frac{(x-\alpha_i)^2}{4Dt})$$

$$\Delta\alpha \to 0 \quad n \to \infty$$

$$C(x,t) = \frac{C'}{2\sqrt{\pi D t}} \int_0^{\infty} \exp(-\frac{(x-\alpha_i)^2}{4Dt}) d\alpha$$



$$\frac{c^*\Delta\alpha}{2\sqrt{\pi Dt}} e^{-(x-\alpha_2)^2/4Dt}$$



$$C_i(x,t) = \frac{C'\Delta\alpha}{2\sqrt{\pi Dt}}\exp(-\frac{(x-\alpha_i)^2}{4Dt})$$

$$Note:\ S = C'\Delta\alpha$$

Sum the solution of all thin slabs

$$C(x,t) = \frac{C'}{2\sqrt{\pi Dt}}\sum_{i=1}^{n}\Delta\alpha\exp(-\frac{(x-\alpha_i)^2}{4Dt})$$

$$\Delta\alpha \to 0 \quad n \to \infty$$

$$C(x,t) = \frac{C'}{2\sqrt{\pi Dt}}\int_0^{\infty}\exp(-\frac{(x-\alpha_i)^2}{4Dt})d\alpha$$

Substituting $u = \frac{x-\alpha}{2\sqrt{Dt}}, \quad d\alpha = -2\sqrt{Dt}\,du$

$$\alpha = 0 \rightarrow u = \frac{x}{2\sqrt{Dt}}$$

$$\alpha = \infty \rightarrow u = -\infty$$

$$C(x,t) = -\frac{C^{'}}{\sqrt{\pi}}\int_{\frac{x}{2\sqrt{Dt}}}^{-\infty} \exp(-u^2)du$$

reverse limits of integration and split integral

$$C(x,t) = \left(\int_{-\infty}^{0} + \int_{0}^{\frac{x}{2\sqrt{Dt}}}\right)\frac{C^{'}}{\sqrt{\pi}}\exp(-u^2)du$$

By definition of error function

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

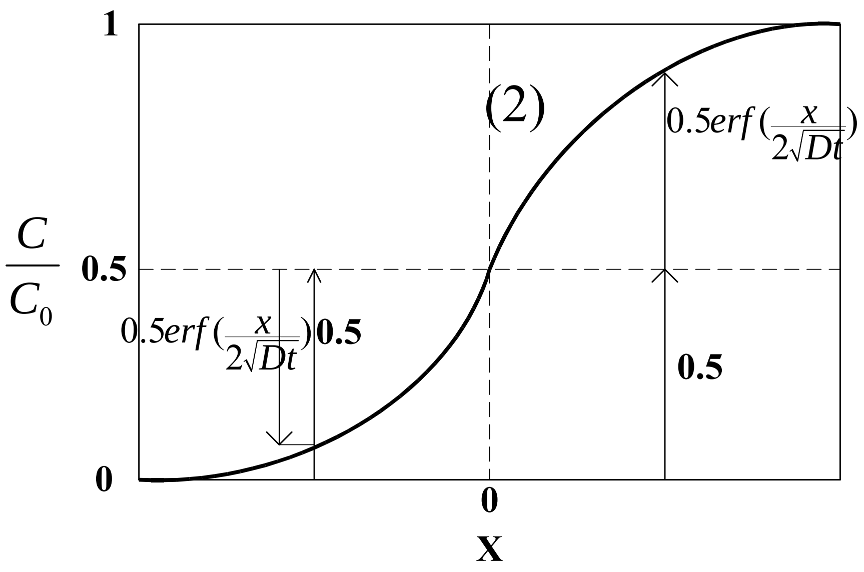
$$erf(\infty) = 1 \quad erf(0) = 0$$

$$erf(-z) = -erf(z)$$

$$C(x,t) = \frac{C^{'}}{\sqrt{\pi}}\left[\int_{-\infty}^{0}\exp(-u^2)du + \int_0^{\frac{x}{2\sqrt{Dt}}}\exp(-u^2)du\right]$$

$$= \frac{C^{'}}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{2} + \frac{\sqrt{\pi}}{2}erf\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

$$= \frac{C^{'}}{2}\left[1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$



Note:
If the concentration is fixed (C=C*), the term of $x/2\sqrt{Dt}$ is then also fixed. This means that the penetration distance is a function of the square root of the diffusion time. For example, if a diffusion penetration of 0.1mm develops in one hour, it will take 4 hours to develop a penetration of 0.2 mm.

$$\frac{C}{C_0}=\frac{1}{2}[1+erf(\frac{x}{2\sqrt{Dt}})]$$

(1) $x>0 \quad \frac{C}{C_0}=0.5+\frac{1}{2}erf(\frac{x}{2\sqrt{Dt}})$

$x<0 \quad \frac{C}{C_0}=0.5-\frac{1}{2}erf(\frac{|x|}{2\sqrt{Dt}})$

(2) $\frac{x}{2\sqrt{Dt}}=1\rightarrow\frac{C}{C_0}=0.921$

which varies with time as $x=2\sqrt{Dt}$

(all compositions except $C/C_o=0.5$).

(3) $x=0\rightarrow\frac{C}{C_0}=\frac{1}{2}$ (implicit B.C.)

(4) $J_{x=0}=-D\frac{\partial C}{\partial x}|_{x=0}=-\frac{C_0}{2}\sqrt{\frac{D}{\pi t}}$ (-:to the left)

(5) Total mass crosses the plane at $x=0$

$$\frac{M}{A}=\int_0^t Jdt=-C_0\sqrt{\frac{Dt}{\pi}} \qquad \text{(A:area)}$$

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If it is not infinite, the diffusion will be reflected
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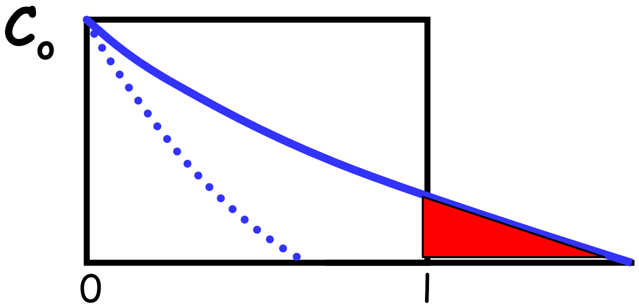
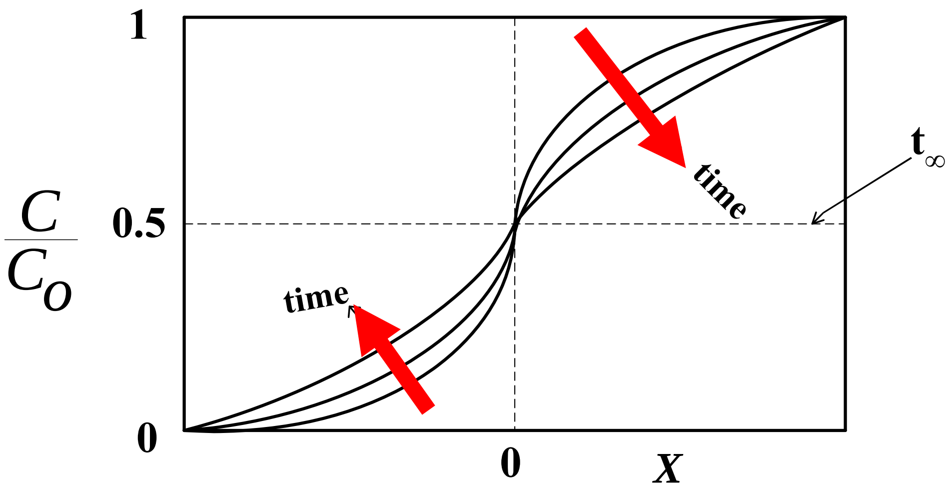
Arbitrarily taking 0.1% as a sufficiently insignificant concentration



$$0.1\% = \frac{\int_l^\infty C(x,t)dx}{\int_0^\infty C(x,t)dx} = \frac{\int_l^\infty \frac{1}{2} C_0[1 - erf(\frac{x}{2\sqrt{Dt}})]dx}{\int_0^\infty \frac{1}{2} C_0[1 - erf(\frac{x}{2\sqrt{Dt}})]dx} = 10^{-3}$$



Using B.C. to solve the problem

$$C(x,t) = A + B\cdot erf(\frac{x}{2\sqrt{Dt}})$$

$$C(\infty,t) = C' = A + B$$

$$C(-\infty,t) = 0 = A - B \quad \Rightarrow A = B = \frac{C'}{2}$$

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

Examples

(1) if $C(0, t) = 0$ $\quad C(x,t) = C' erf(\frac{x}{2\sqrt{Dt}})$

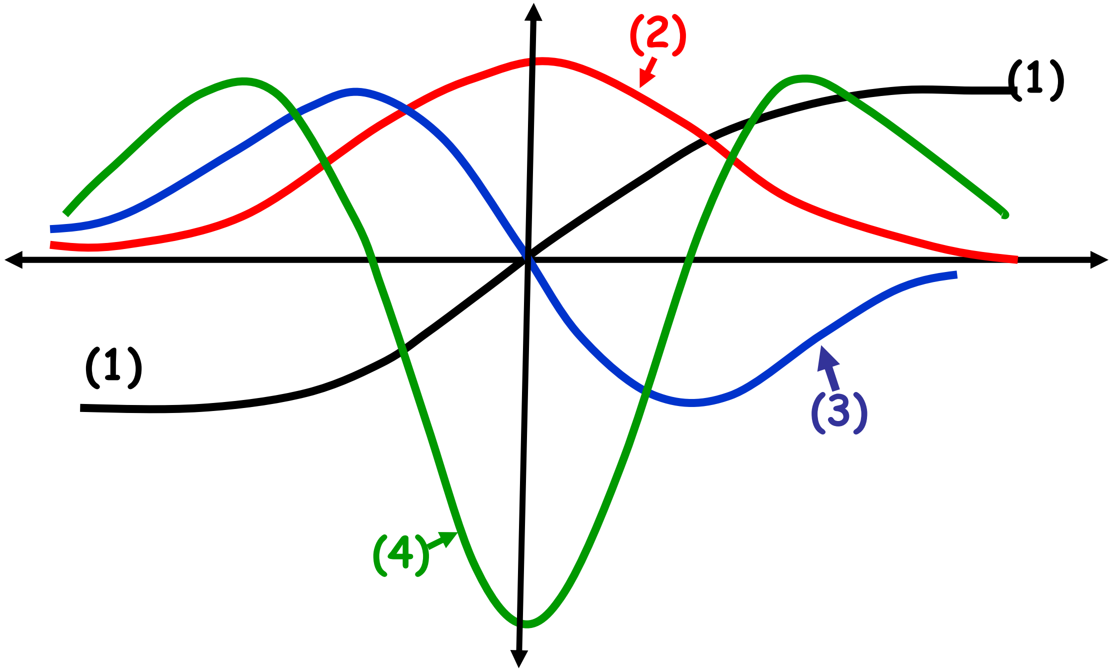
(2) if $C(0, t) = C'' = A$, $C(\infty, t) = C'$

$$C(x,t) = C''[1 + erf(\frac{x}{2\sqrt{Dt}})], \quad x < 0$$

$$\frac{C - C''}{C' - C''} = erf(\frac{x}{2\sqrt{Dt}}), \quad x > 0$$

(next page)

Error Function & its Derivatives



(1) $\mathrm{erf}(x)$

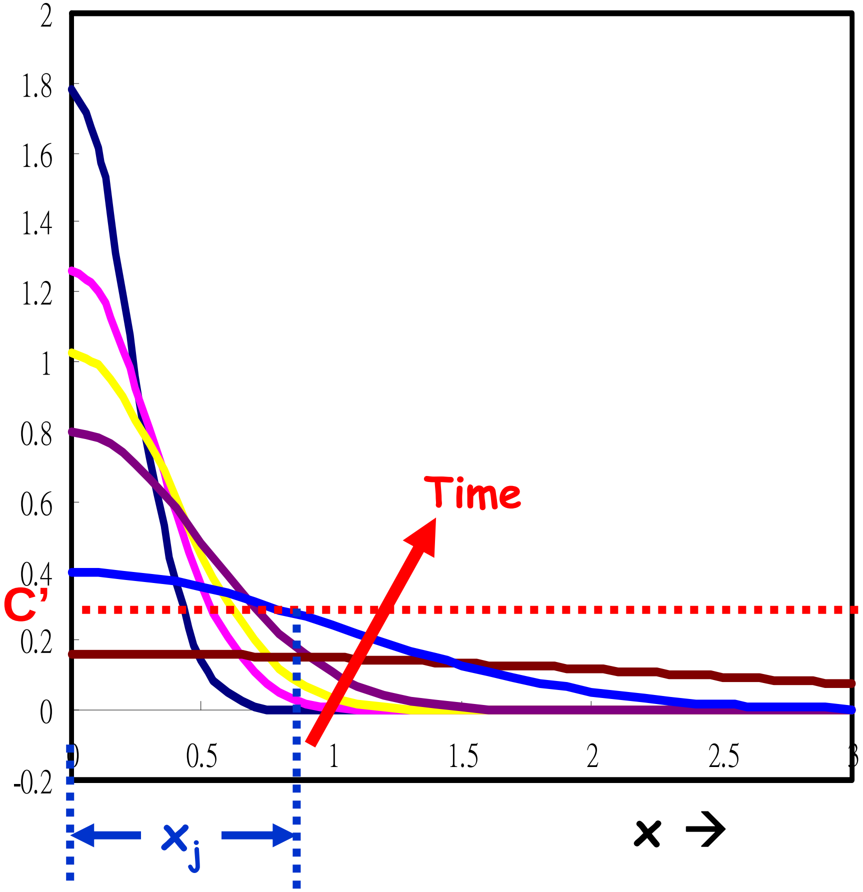
(2) $\dfrac{d(\mathrm{erf}(x))}{dx} \equiv$ (-)Flux

(3) $\dfrac{d^2(\mathrm{erf}(x))}{dx^2} \equiv$ *Accumulation*

(4) $\dfrac{d^3(\mathrm{erf}(x))}{dx^3}$

Note: (2) is the thin film solution

Diffusion from a Limited Source (thin film)



$$C(0,t) \neq \text{constant}$$

$$\int_0^\infty C(x,t)dx = S_0 \rightarrow \text{constant}$$

$$C(x,t) = \frac{S_0}{\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt})$$

:Gaussian function

Example: p-n junction

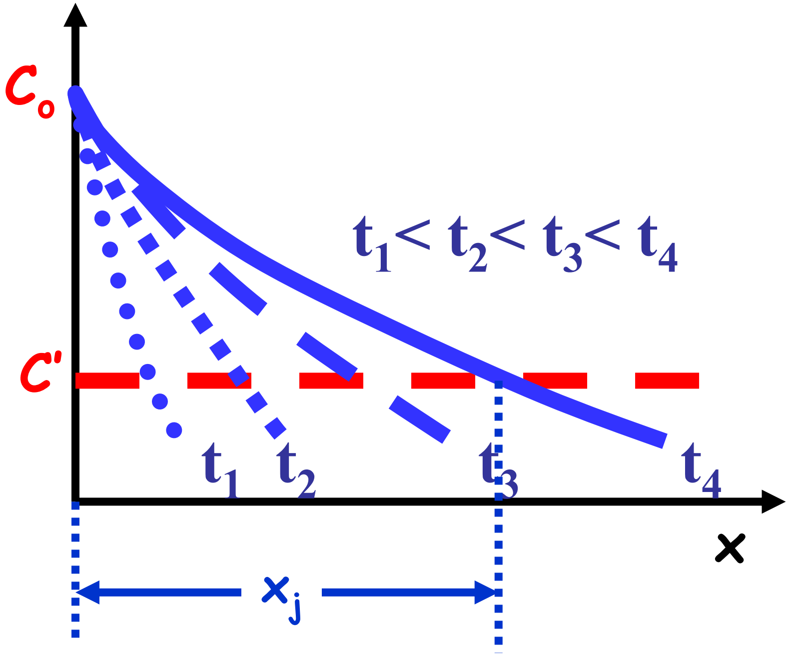
C'= Background Concentration

$$C > C' \quad (p \rightarrow n \;\; or \;\; n \rightarrow p)$$

$$C' = \frac{S_0}{\sqrt{\pi Dt}} \exp(-\frac{x_j^{\,2}}{4Dt})$$

$$x_j = \text{junction distance}$$

Diffusion from a Constant Source



$$C(0,t) = C_0$$

$$C(x,t) = C_0 erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$M = A \cdot \int_0^{\infty} C(x,t)dx = 2AC_0\sqrt{\frac{Dt}{\pi}}$$

: the amount of dopant entering the base

Example: p-n junction

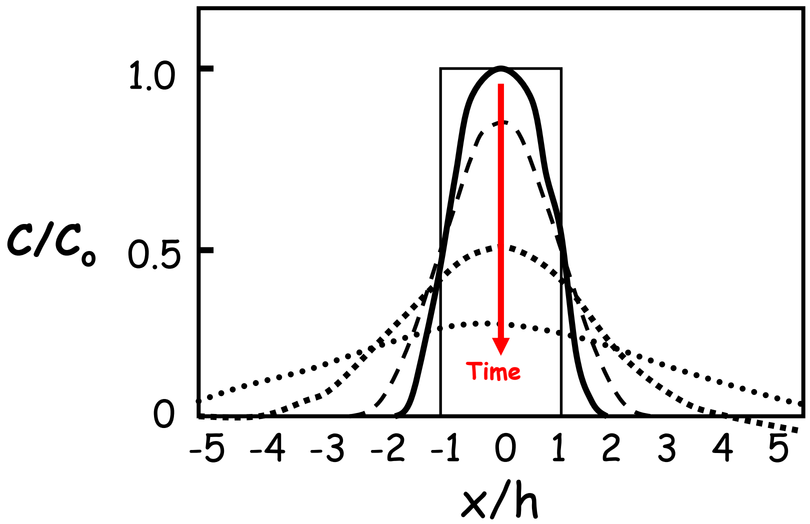
C′= Background Concentration

$$C > C' \quad (p \rightarrow n \;\; or \; n \rightarrow p)$$

$$C' = C_0\, erfc\left(\frac{x_j}{2\sqrt{Dt}}\right)$$

x_j : junction distance

Separation of Variables



- ✧Series Solutions
- ✧Small system + long time
- ✧**Real solution to all systems without assumptions of "Infinite System"**

Assuming the solution can be represented by

$$C(x,t) = X(x)T(t)$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad \text{assuming} \quad D \neq D(C)$$

$$X\frac{dT}{dt} = DT\frac{\partial^2 X}{\partial x^2}$$

$$X(x)T'(t) = DTX''$$

Divide both sides by $C(x,t)$

$$\frac{X\frac{dT}{dt}}{XT} = \frac{DTX''}{XT}$$

$$\frac{T'}{DT} = \frac{X''}{X}$$

$\frac{T'}{DT}$: function only of time

$\frac{X''}{X}$: function only of distance

Since they vary independently, both sides must be equal to a constant, designated as **$-\lambda^2$** where λ is a real number

$$\frac{1}{T}\frac{dT}{dt} = -\lambda^2 D$$

$$T = T_0 \exp(-\lambda^2 Dt)$$

where T_0 is a constant, **$-\lambda^2$ is chosen because one deals with the system in which any inhomogeneities disappear as time passes**, i.e., T approaches zero as time increases.

The equation in x is

$$\frac{d^2\mathrm{X}}{dx} + \lambda^2\mathrm{X} = 0$$

the solution to this equation is of the form

$$\mathrm{X}(x) = A^{'}\sin(\lambda x) + B'\cos(\lambda x)$$

where A′ and B′ are functions of λ

$$C(x,t) = \mathrm{X}(x)T(t)$$

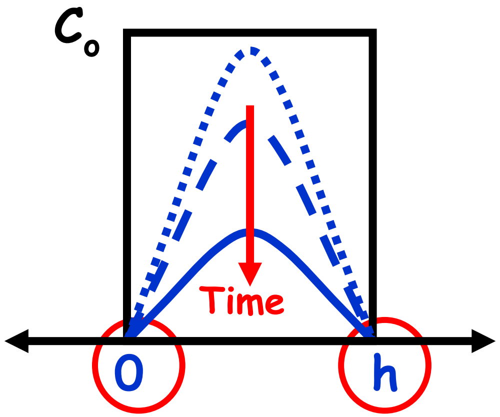
$$= T_0 \exp(-\lambda^2 Dt)(A^{'}\sin\lambda x + B'\cos\lambda x)$$

$$= (A\sin\lambda x + B\cos\lambda x)\exp(-\lambda^2 Dt)$$

But if this solution holds for any real value of λ, then a sum of solutions with different values of λ is also a solution. Thus in its most general form the product solution will be infinite series of the form

$$C(x,t) = \sum_{n=1}^{\infty}[(A_n \sin\lambda_n x + B_n \cos\lambda_n x)\exp(-\lambda_n{}^2 Dt)]$$

Example :"Diffusion out of a Slab"



$$I.C.\quad C(x,0)=C_o \quad 0<x<h$$

$$B.C.\quad C(x,\ t)=0 \quad x=0 \text{ and } x=h$$

$$\because C(0,t)=0 \Rightarrow B_n=0 \qquad C(x,t)=\sum_{n=1}^{\infty}[(A_n\sin\lambda_n x+B_n\cos\lambda_n x)\exp(-\lambda_n{}^2 Dt)]$$

$$C(h,t)=0 \Rightarrow \text{the argument of } \sin\lambda_n x \text{ is equal to zero}$$

$$\Rightarrow \lambda_n = {}^{n\pi}\!/_{h} \text{ where } n \text{ is a positive integer}$$

$$\therefore C(x,t)=\sum_{n=1}^{\infty}(A_n\sin\lambda_n x)(\exp(-\lambda_n{}^2 Dt))$$

$$C_0=C(x,0)=\sum_{n=1}^{\infty}A_n\sin\lambda_n x \quad (0<x<h)$$

$$=\sum_{n=1}^{\infty}A_n\sin(\frac{n\pi}{h}x)\rightarrow A_n=?$$

Multiplying both sides by $\sin({}^{p\pi x}\!/_{h})$ and integrate x over the range of $0\le x\le h$ to determine A_n

$$\int_0^h C_0\sin(\frac{p\pi x}{h})dx=\sum_{n=1}^{\infty}A_n\int_0^h\sin(\frac{n\pi x}{h})\sin(\frac{p\pi x}{h})dx$$

$$n\neq p\rightarrow\sum_{n=1}^{\infty}A_n\int_0^h\sin(\frac{n\pi x}{h})\sin(\frac{p\pi x}{h})dx=0$$

$$n=p\rightarrow\sum_{n=1}^{\infty}A_n\int_0^h\sin(\frac{n\pi x}{h})\sin(\frac{p\pi x}{h})dx=\frac{h}{2}A_n$$

$$A_n = \frac{2}{h}\int_0^h C_0 \sin(\frac{n\pi x}{h})dx = \frac{2C_0}{h}(-\frac{h}{n\pi})\cos(\frac{n\pi x}{h})\Big|_0^h = \frac{2C_0}{n\pi}\cos(\frac{n\pi x}{h})\Big|_h^0$$

$$= \frac{2C_0}{n\pi}[\cos(\frac{n\pi 0}{h}) - \cos(\frac{n\pi h}{h})] = \frac{2C_0}{n\pi}[1-\cos(n\pi)]$$

$$n : even \rightarrow A_n = 0$$

$$n : odd = 2j+1 \rightarrow A_n = \frac{4C_0}{n\pi} = \frac{4C_0}{(2j+1)\pi} \quad j = 0,1,2......$$

The solution is $C(x,t) = \frac{4C_0}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\sin(\frac{(2j+1)\pi x}{h})\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$

Note: Each successive term is smaller than the preceding one, and the percentage decreases between terms and increases exponentially with time. Thus after a short time has elapsed, the infinite series can be satisfactorily represented by only a few terms. To determine the error, we compare the ratio of the maximum values of the first and second terms (R)

$$R = 3\exp(\frac{8\pi^2 Dt}{h^2})$$

$$R = 100 \quad when \quad h = 4.75\sqrt{Dt}$$

$$t \geq \frac{h^2}{(4.75)^2 D}$$

The error in using the first term to represent C(x,t) is less than 1% at all points.

Degassing of Metals

It is difficult to measure the concentration of gas at various depths, and what is experimentally determined is the quantity of gas which has been given off or the quantity remaining in the metal. Therefore, the average concentration ($\bar{C}$) is used.

$$\bar{C} = \frac{1}{h}\int_0^h C(x,t)dx$$

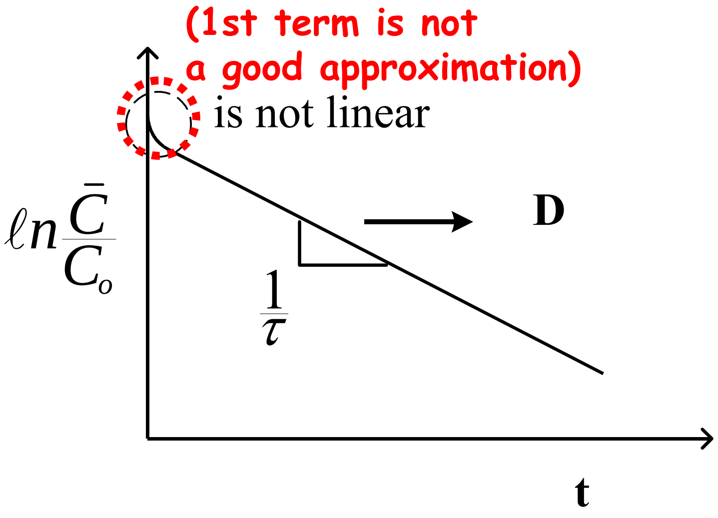
$$= \frac{8C_0}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^2}\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

When $\bar{C}(t) \le 0.8C_0$ the first term is a good approximation to the solution or when t is sufficiently large

$$\frac{\bar{C}}{C_0} = \frac{8}{\pi^2}\exp(-\frac{t}{\tau})$$

$$\tau = \frac{h^2}{\pi^2 D} \text{ : relaxation time}$$

$$\Rightarrow \text{Large } \tau \rightarrow \text{slow process}$$



Solutions for Variable D

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

$\frac{\partial D}{\partial x}$ makes this equation inhomogeneous, especially when D=D(C) or D(T) or D(t) or D(x).
The key in solving the above p.d.e. is to simplify the equation with x and t to x or t function.

Boltzman-Matano Analysis (D=D(C))

$$\eta = \frac{x}{\sqrt{t}}$$

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \eta}\frac{\partial \eta}{\partial t} = -\frac{1}{2}\frac{x}{t^{3/2}}\frac{\partial C}{\partial \eta}$$

and

$$\frac{\partial C}{\partial x} = \frac{\partial C}{\partial \eta}\frac{\partial \eta}{\partial x} = \frac{1}{\sqrt{t}}\frac{\partial C}{\partial \eta}$$

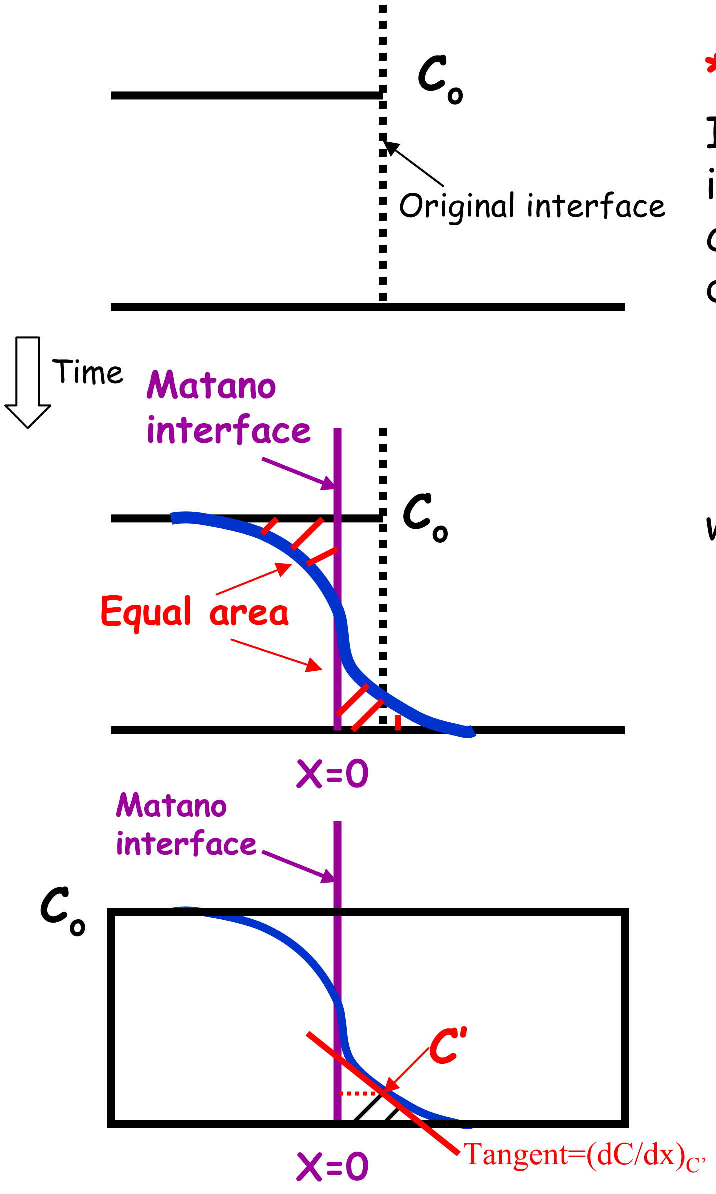
Therefore

$$-\frac{1}{2}\frac{x}{t^{3/2}}\frac{\partial C}{\partial \eta} = \frac{\partial}{\partial x}\left(\frac{D}{\sqrt{t}}\frac{\partial C}{\partial \eta}\right)$$

$$= \frac{1}{t}\frac{\partial}{\partial \eta}\left(D\frac{\partial C}{\partial \eta}\right)$$

$$-\frac{\eta}{2}\frac{\partial C}{\partial \eta} = \frac{\partial}{\partial \eta}\left(D\frac{\partial C}{\partial \eta}\right)$$

Example: Infinite System



I.C. $C(x,0)=C_o$ x<0→ $\eta = -\infty$
$C(x,0)=0$ x>0→ $\eta = \infty$

*** x=0 is not determined yet**

If $D \neq D(C)$, $C=C_o/2$ which determines x=0 for an infinite system. However, if $D=D(C)$ the above condition is no longer valid, the x=0 must be determined by

$$\int_0^{C_0} x\,dC = 0$$

which expresses the equality of the two shaded areas.

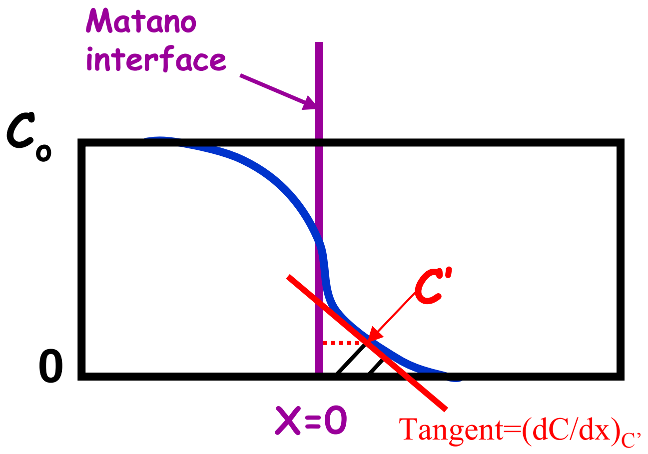
$$-\int_0^{C'} \frac{\eta}{2}\,dC = \int_0^{C'} d\left(D\frac{\partial C}{\partial \eta}\right)$$

$$-\frac{1}{2}\int_0^{C'} \frac{x}{\sqrt{t}}\,dC = D\frac{\partial C}{\partial \eta}\Big|_0^{C'} = D\frac{dC}{d\left(\frac{x}{\sqrt{t}}\right)}\Big|_0^{C'} = D\sqrt{t}\,\frac{dC}{dx}\Big|_0^{C'}$$

$$-\frac{1}{2}\int_0^{C'} x\,dC = Dt\frac{dC}{dx}\Big|_0^{C'}$$

For an infinite system

$$\frac{dC}{dx}=0 \quad when \quad C=0 \quad or \quad C=C_o \qquad \therefore \frac{dC}{dx}\Big|_0^{C_0}=0$$



Therefore

$$-\frac{1}{2}\int_0^{C_0} xdC = Dt\frac{dC}{dx}\Big|_0^{C_0}$$

$$\because \frac{dC}{dx}\Big|_0^{C_0}=0$$

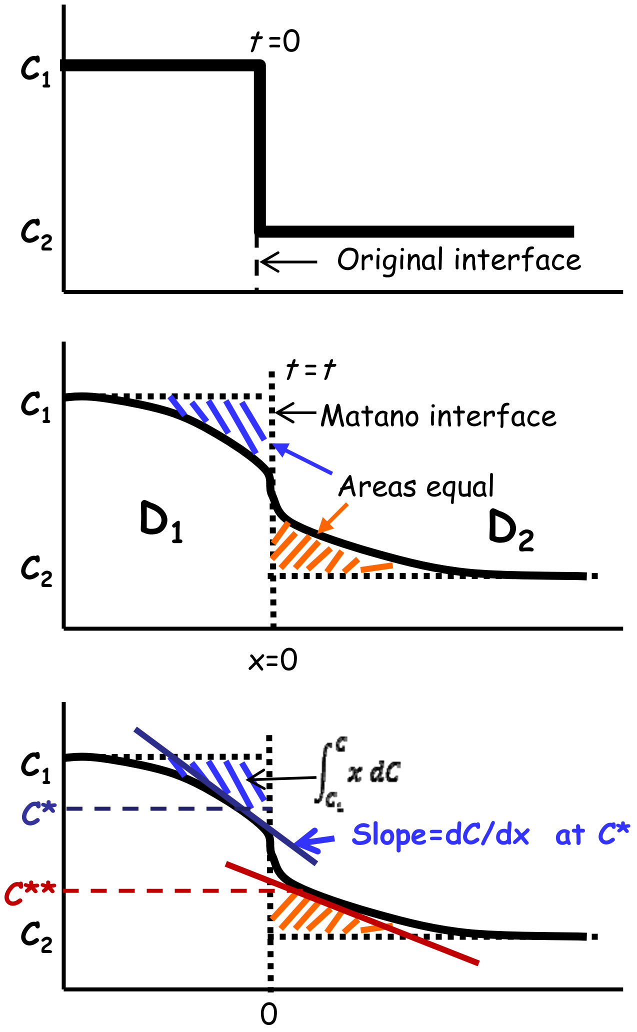
$$\therefore \int_0^{C_0} xdC = 0$$

which is an additional boundary condition and determines the location of Matano interface.

x=0 plane (Matano interface) determined by

$$\int_0^{C_0} xdC = 0$$

$$D(C')=\frac{-1}{2t}\left(\frac{dx}{dC}\right)_{C'}\int_0^{C'} xdC$$



$$D(C') = \frac{-1}{2t}\left(\frac{dx}{dC}\right)_{C'} \int_0^{C'} x\,dC$$

$$Slope: \frac{\partial C}{\partial x}\Big|_{C^*} > \frac{\partial C}{\partial x}\Big|_{C^{**}}$$

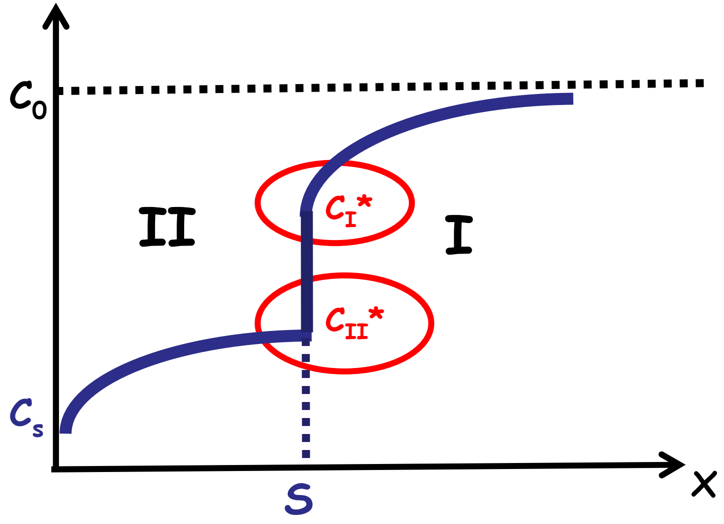
$$Diffusivity: D_{C^*} < D_{C^{**}}$$

$$Area: \int_{C_1}^{C^*} x\,dC = \int_{C^{**}}^{C_2} x\,dC$$

The Moving Boundary Problem

*Diffusion controlling process along with reaction at phase boundary

General Aspects



* C_I^* and C_{II}^*: equilibrium concentrations in phases I and II.

* $x > S$ $\quad \dfrac{\partial C_I}{\partial t} = D_I \dfrac{\partial^2 C_I}{\partial x^2}$

$x < S$ $\quad \dfrac{\partial C_{II}}{\partial t} = D_{II} \dfrac{\partial^2 C_{II}}{\partial x^2}$

* Diffusion controlling process

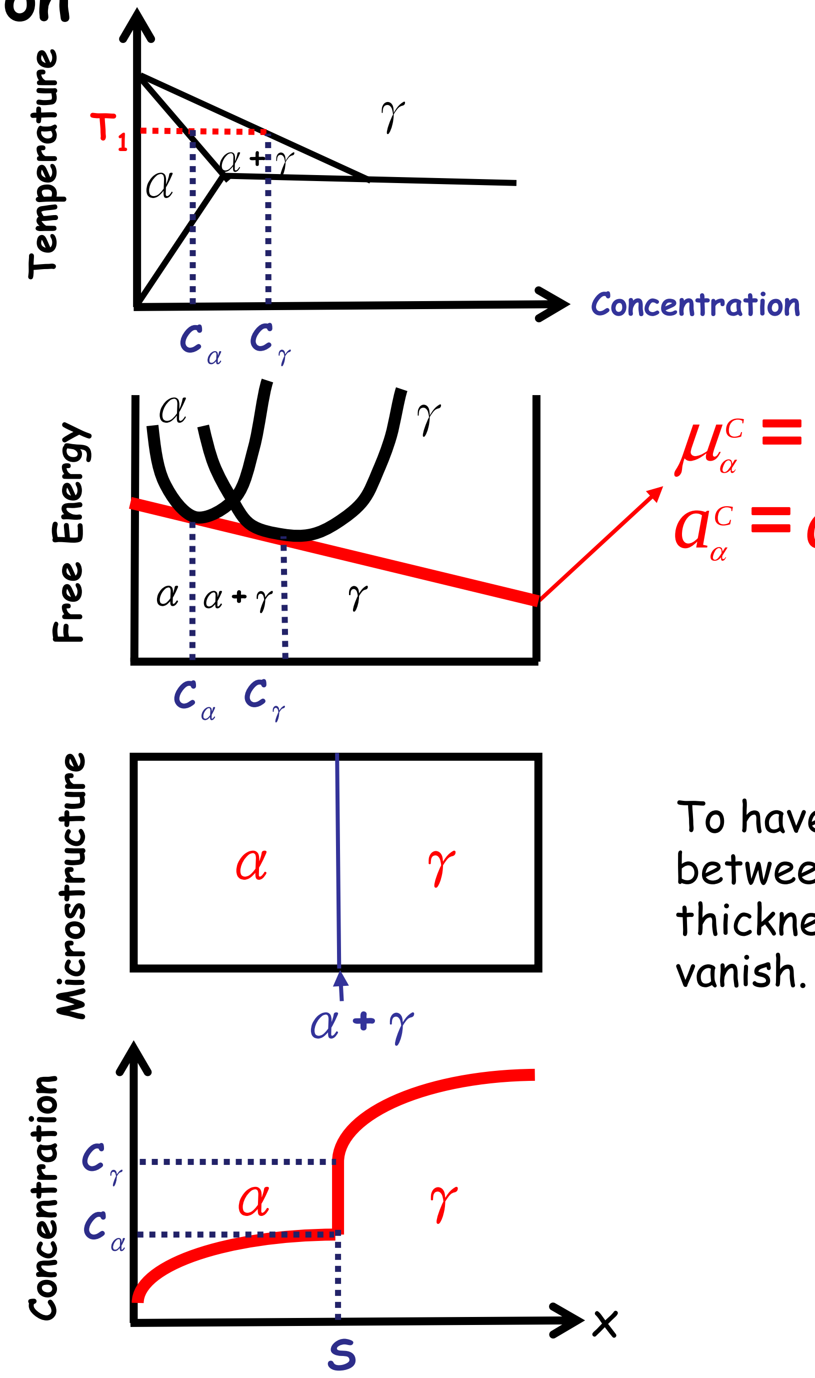
$C_I^* = kC_{II}^*$

k : partition ratio between phases

$$* \; D_I\left(\frac{\partial C_I}{\partial x}\right)_{x=S} - D_{II}\left(\frac{\partial C_{II}}{\partial x}\right)_{x=S} = (C_{II}^* - C_I^*)\frac{dS}{dt}$$

Kinetic Issue $dS/dt = ?$

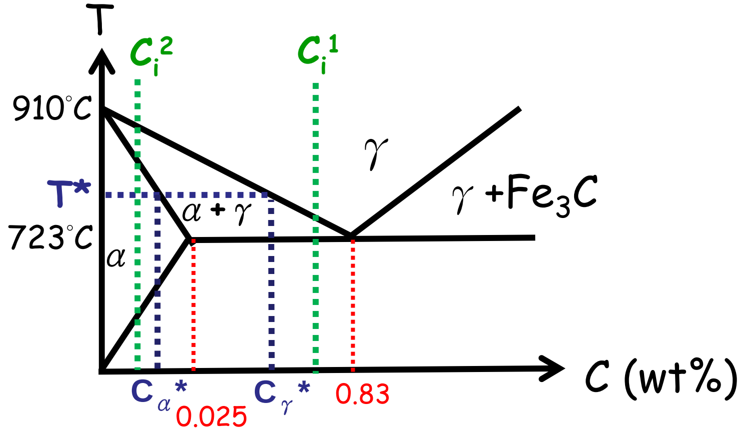
Decarburization



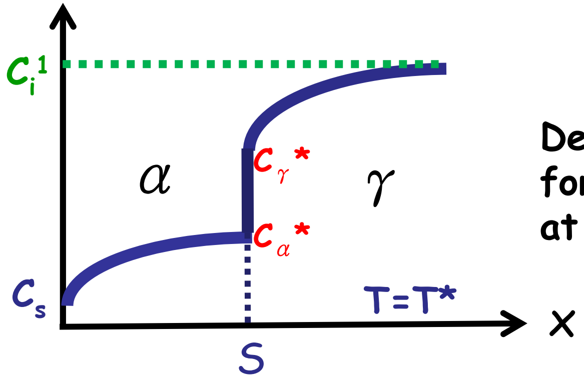
$$\mu_\alpha^C = \mu_\gamma^C \text{ or}$$
$$a_\alpha^C = a_\gamma^C$$

To have net diffusion flux between α and γ, the thickness of α + γ has to vanish.

Carburization: α-Fe → γ-Fe
Decarburization: γ-Fe → α-Fe

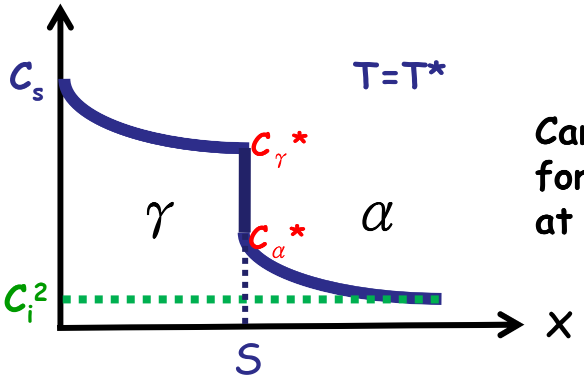


Decarburization

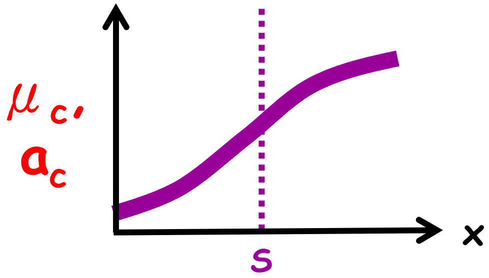


Decarburization forming α phase at the interface

Carburization

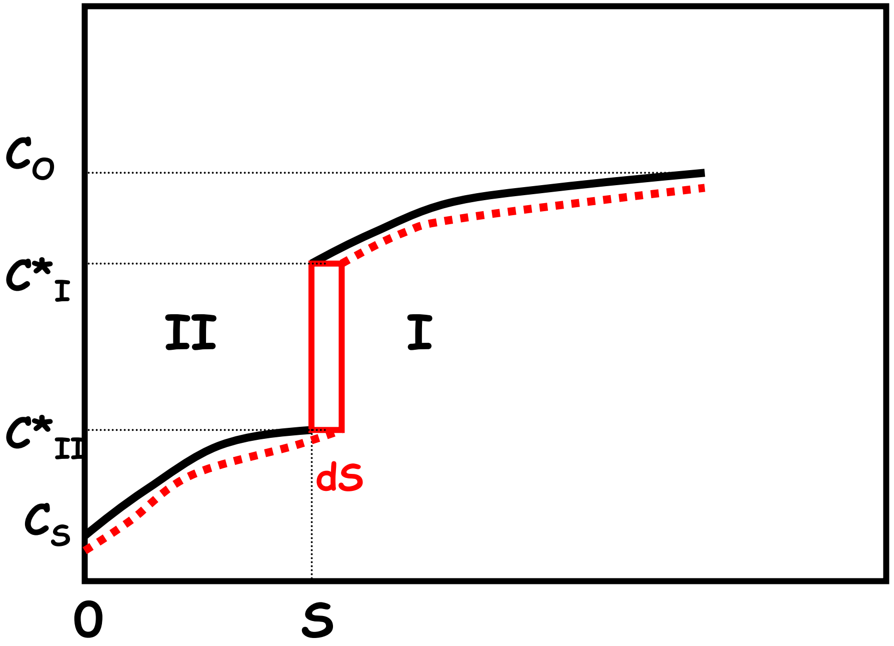


Carburization forming γ phase at the interface



$\mu_\alpha^C = \mu_\gamma^C$ at x=S

where α and γ coexist



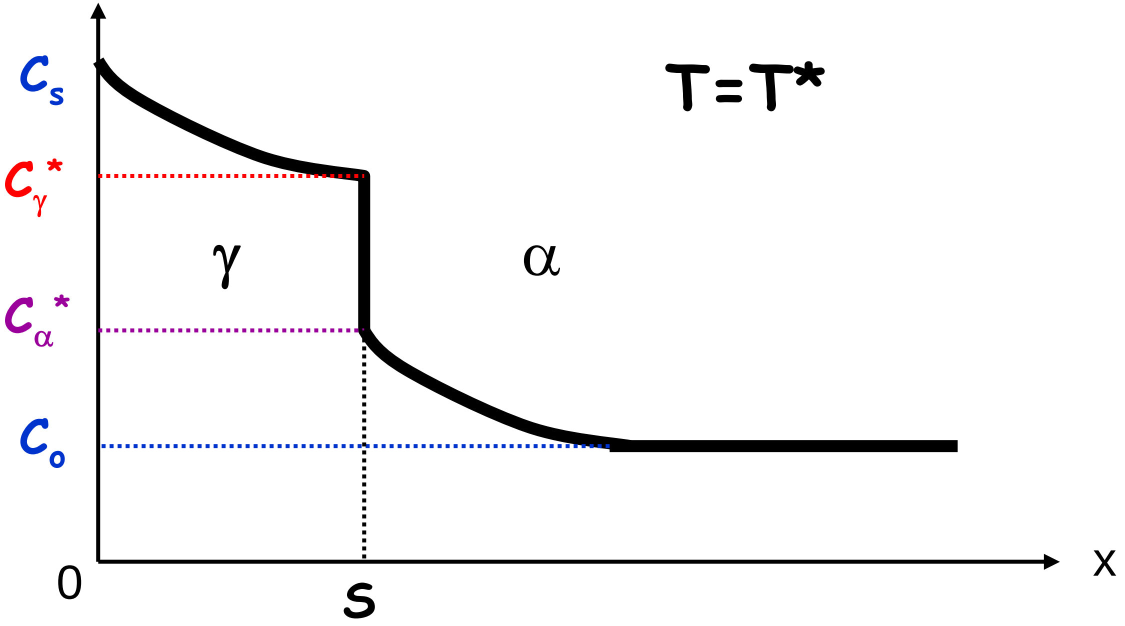
Mass Conservation

$$(J_{II} - J_I)A \cdot dt = (C^*_{II} - C^*_I)A \cdot dS$$

$$J_{II} - J_I = -D_{II}\left(\frac{\partial C_{II}}{\partial x}\right)_{x=S} - \left(-D_I \frac{\partial C_I}{\partial x}\right)_{x=S}$$

A: area for diffusion: constant

Carburization



$$\frac{dS}{dt} = ?$$

known parameters:

C_γ^*, C_α^*, C_S, C_o, D_γ^C and D_α^C

Example: Carburization

*Chemical activity of carbon at surface can be set up by

$$2CO \underset{}{\overset{k}{\rightleftarrows}} C + CO_2$$

$$a_c = \frac{k[CO]^2}{[CO_2]}; \quad or$$

$$CH_4 \underset{}{\overset{k}{\rightleftarrows}} 2H_2 + C$$

$$a_c = \frac{k[CH_4]}{P_{H_2}^{\ 2}}$$

*Rate of advance of boundary controlled by diffusion of carbon in Fe. Therefore

$$x = S \qquad C_\gamma^* = kC_\alpha^*$$

$$(if \quad C_\gamma^* = C_\alpha^* \quad at \quad x = S \Rightarrow reaction \quad controlling \quad process)$$

* $C = C_\gamma^* \ at \ x = S^-$

$C = C_\alpha^* \ at \ x = S^+$

* Semi-infinite solid

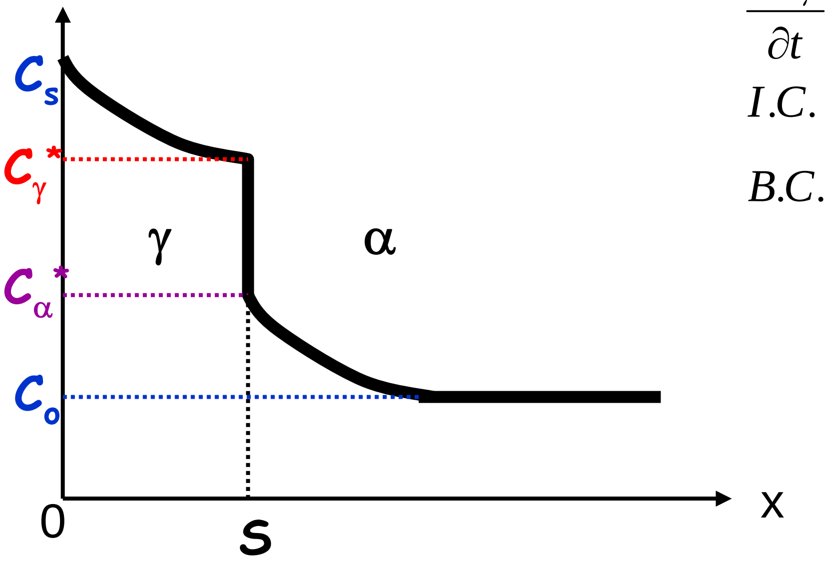
* $D_C \neq D(C) \quad D_\alpha^C \neq D_\gamma^C$

* $\Delta V_{\alpha \to \gamma} = 0$ mass flux requiring no density correction

Fick's 2nd law

$$\frac{\partial C_\alpha}{\partial t} = D^C_\alpha \frac{\partial^2 C_\alpha}{\partial x^2} \quad x > S$$

$$\frac{\partial C_\gamma}{\partial t} = D^C_\gamma \frac{\partial^2 C_\gamma}{\partial x^2} \quad 0 < x < S$$



$$I.C.: \quad C(x,0) = C_0$$

$B.C.:$ *in* α *phase*

$$C = C_\alpha^* \quad at \ x = S^+$$

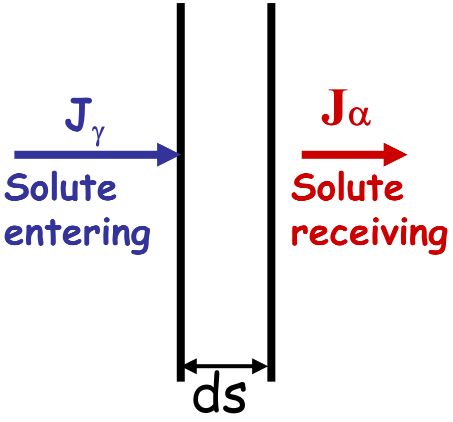
$$C = C_0 \quad at \ x = \infty$$

in γ *phase*

$$C = C_\gamma^* \quad at \ x = S^-$$

$$C = C_s \quad at \ x = 0$$

$$C(s,t) = C_\gamma^* = kC_\alpha^* \quad (k: Partition \quad Ratio)$$



At $x = S$

$$(J_\gamma - J_\alpha)dt = (C_\gamma^* - C_\alpha^*)dS$$

$$-D^C_\gamma \left(\frac{\partial C_\gamma}{\partial x}\right)_{x=s} + D^C_\alpha \left(\frac{\partial C_\alpha}{\partial x}\right)_{x=s} = (C_\gamma^* - C_\alpha^*)\frac{dS}{dt}$$

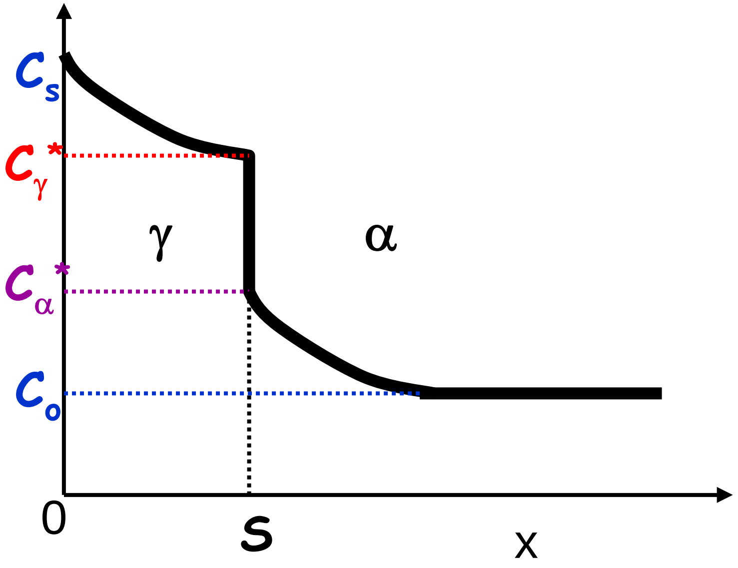
$$Note: (J_\gamma - J_\alpha)dt \cdot A = (C_\gamma^* - C_\alpha^*)dS \cdot A$$

In α phase

$$C_\alpha = A + B \cdot erfc\left(\frac{x}{2\sqrt{D_\alpha^C t}}\right), \quad x = \infty \rightarrow C_\alpha = C_0 = A$$

In γ phase

$$C_\gamma = A' + B' \cdot erf\left(\frac{x}{2\sqrt{D_\gamma^C t}}\right), \quad x = S \rightarrow C_\gamma = C_\gamma^*; \quad x = 0 \rightarrow C = C_s = A'$$



$$C_\alpha(x,t) = C_0 + B \cdot erfc\left(\frac{x}{2\sqrt{D_\alpha^C t}}\right)$$

$$C_\gamma(x,t) = C_s + B' \cdot erf\left(\frac{x}{2\sqrt{D_\gamma^C t}}\right)$$

At boundary $x = S \rightarrow C_\gamma = C_\gamma^*$

$$C_\gamma^* = C_s + B' \cdot erf\left(\frac{S}{2\sqrt{D_\gamma^C t}}\right)$$

C_γ^* and C_S are constants $\quad$ ($\because$ diffusion controlling process)

therefore $\dfrac{S}{2\sqrt{D_\gamma^C t}}$ is a constant too $\rightarrow \dfrac{S}{2\sqrt{D_\gamma^C t}} = \beta$ (constant)

$S = 2\beta\sqrt{D_\gamma^C t}$ where β is a constant

$$C_\gamma(S,t) = C_\gamma^* = C_s + B' erf\left(\frac{S}{2\sqrt{D_\gamma^C t}}\right) = C_s + B' erf(\beta)$$

Similarly

$$C_\alpha(S,t) = C_\alpha^* = C_0 + B\cdot erfc(\frac{S}{2\sqrt{D_\alpha^C t}}) = C_0 + B\cdot erfc(\frac{2\beta\sqrt{D_\gamma^C t}}{2\sqrt{D_\alpha^C t}})$$

Replace $\phi = \frac{D_\gamma^C}{D_\alpha^C}$

$$C_\alpha(S,t) = C_0 + B\cdot erfc(\beta\phi^{1/2}) = C_\alpha^*$$

$$-D_\gamma^C(\frac{\partial C_\gamma}{\partial x})_{x=s} = \frac{-D_\gamma^C B'}{2\sqrt{D_\gamma^C t}}\frac{2}{\sqrt{\pi}}\exp(-\frac{x^2}{4D_\gamma^C t})|_{x=s} \quad (1)$$

$$D_\alpha^C(\frac{\partial C_\alpha}{\partial x})_{x=s} = \frac{-D_\alpha^C B}{2\sqrt{D_\alpha^C t}}\frac{2}{\sqrt{\pi}}\exp(-\frac{x^2}{4D_\alpha^C t})|_{x=s} \quad (2)$$

$$Eq.(1)+(2) = (C_\gamma^* - C_\alpha^*)(\frac{\partial S}{\partial t})$$

$$S = 2\beta\sqrt{D_\gamma^C t}$$

$$\therefore \frac{dS}{dt} = \beta\sqrt{\frac{D_\gamma^C}{t}}$$ (Note: it is not a constant)

$$C_\gamma^* - C_\alpha^* = \frac{-B' e^{-\beta^2}}{\sqrt{\pi}\beta} - \frac{Be^{-\beta^2\phi}}{\sqrt{\pi}\beta\sqrt{\phi}}$$

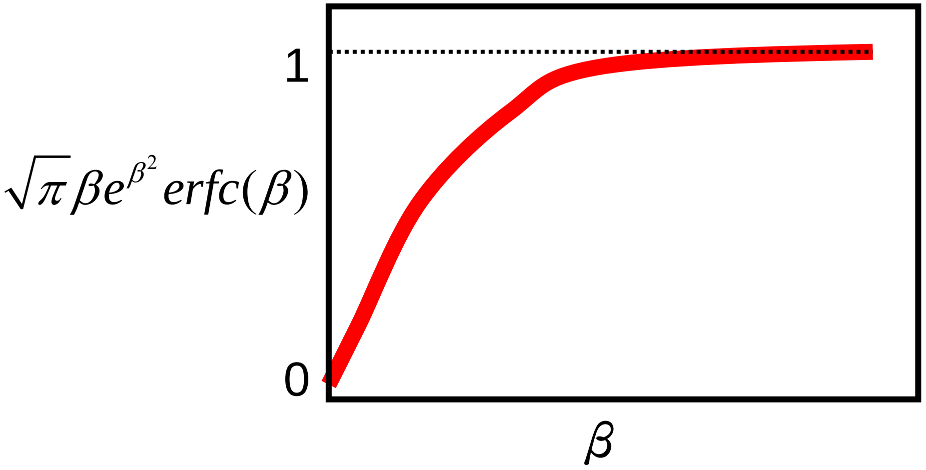
$$\left.\begin{aligned} &C_s + B'erf(\beta) = C_\gamma^* \\ &C_0 + Berfc(\beta\phi^{1/2}) = C_\alpha^* \end{aligned}\right\}$$

Use them to estimate B' and B, and then to solve β

$$C_\gamma^* - C_\alpha^* = \frac{C_s - C_\gamma^*}{\sqrt{\pi}\beta e^{\beta^2} erf(\beta)} - \frac{C_\alpha^* - C_0}{\sqrt{\pi}\beta\phi^{1/2} e^{\beta^2\phi} erfc(\beta\phi^{1/2})}$$

→ solve β by trial and error

→ then we get $S = 2\beta\sqrt{D_\gamma^C t}$ and $\frac{dS}{dt} = \beta\sqrt{\frac{D_\gamma^C}{t}}$



Note: the only unknown parameter in the above equation is β

$(C_\gamma^*, C_\alpha^*, C_s, C_0, D_\gamma^C$ and D_α^C are known parameters$)$

Example: **Decarburization**

0.4% Carbon Alloy Steel

T=800°C

C_s=0.01% (equilibrium by CO and CO_2)

t = 30 min → $S_{\alpha\text{-}Fe}$?

Answer: C_o=0.4%, C_s=0.01%

C_γ*=0.24%, C_α*=0.02% (Obtained from Fe-C Phase Diagram)

$$D_\alpha^C = 3\text{x}10^{-8};\quad D_\gamma^C = 2\text{x}10^{-6}\quad \text{cm}^2/\text{sec}$$

$$\phi = \frac{D_\gamma^C}{D_\alpha^C} = 66.6$$

$$(C_\alpha^* - C_\gamma^*) = \frac{C_s - C_\alpha^*}{\sqrt{\pi}\,\beta e^{\beta^2}\,erf\,(\beta)} - \frac{C_\gamma^* - C_0}{\sqrt{\pi}\,\beta\phi^{1/2} e^{\beta^2\phi}\,erfc(\beta\phi^{1/2})}$$

$$(0.02 - 0.24) = \frac{(0.01 - 0.02)}{f\,(\beta)} - \frac{(0.24 - 0.4)}{f\,(\beta\phi^{1/2})}$$

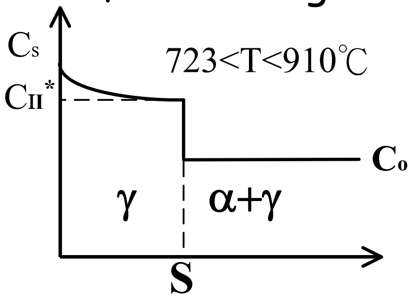
$$0.22 = \frac{0.01}{f\,(\beta)} - \frac{(0.24 - 0.4)}{f\,(\beta\phi^{1/2})}$$

$$by\quad trial\quad and\quad error \Rightarrow \beta = 0.144\quad (see\quad Figure)$$

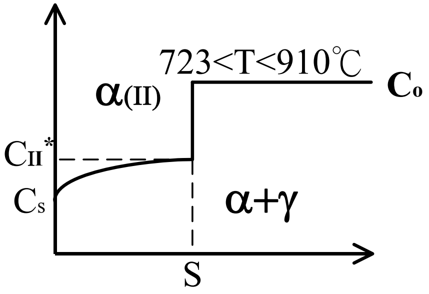
$$S = 2\beta\sqrt{D_\gamma^C t} = 0.0173\quad cm$$

Formation of a single-phase layer from an initial two-phase mixture

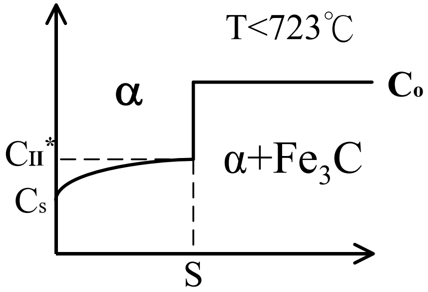
In the two-phase region, the average composition, C_0, is assumed to be uniform, which requires, in effect, that the grain size is small and that second-phase dispersion is uniform.



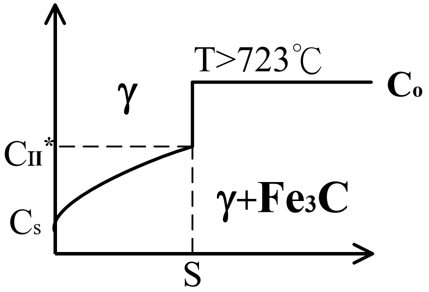
Carburization



De-carburization



De-carburization



De-carburization

$$C_{II}(S,t) = C_{II}^*$$

$$-D_{II}\left(\frac{\partial C_{II}}{\partial x}\right)_{x=s} = (C_{II}^* - C_0)\frac{dS}{dt}$$

$$C_s - C_{II}^* = B_2 erf(\beta)$$

$$C_{II}^* - C_0 = \frac{B_2 \exp(-\beta^2)}{\sqrt{\pi}\beta}$$

$$\text{eliminate} \quad B_2 \Rightarrow \frac{1}{\sqrt{\pi}}\left(\frac{C_s - C_{II}^*}{C_{II}^* - C_0}\right) = \beta \exp(\beta^2) erf(\beta)$$