Diffusion and Phase Transformation

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- **Course Outline**
- **1. Diffusion**
  - **(a) Diffusion equation solutions – steady and transient states**
  - **(b) Diffusion with moving boundary**
  - **(c) Diffusion in heterogeneous systems – controlling kinetics**
  - **(d) Atomic theory of diffusion**
  - **(e) Diffusion in dilute and concentrated solutions**
- **2. Phase Transformation**
  - **(a) Nucleation - homogeneous and heterogeneous**
  - **(b) Growth with and without composition change**
  - **(c) Overall transformation kinetics**
  - **(d) Spinodal decomposition**
-
- **Textbooks and References**
- **1. P.G. Shewmon, Diffusion in Solids, 2nd ed., McGraw-Hill**
- 2. D.R. Poirier and G.H. Geiger, Transport Phenomena in Materials Processing, 2nd ed., TMS publication, 1994.
- 3. J. Crank, Mathematics of Diffusion, 2nd ed., Oxford University Press, 1975.
- 4. H.S. Carslaw and J.C. Jaeger, Conduction of Heat in Solids, 2nd, ed., Oxford University Press, 1959.
- 5. A.K. Jena and M.C. Chaturvedi, Phase Transformations in Materials, Prentice Hall, NJ, 1992.
- **6. D.A. Porter, K.E. Easterling and Y. Sherif, Phase Transformations in Metals and Alloys, 3rd ed., CRC**
- **Press, 2009.**
- 7. J.W. Christian, The Theory of Transformations in Metals and Alloys, Pergamon Press, 1975.
- 8 R. W. Balluffi, S. M. Allen and W. C. Carter, Kinetics of Materials, Wiley, 2005.

- **Grading**

Quizzes (2)	30%
Midterm test	25%
Final test	40%
Class attendance -random quizzes	5%

No aid sheet, No open book and No take home

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

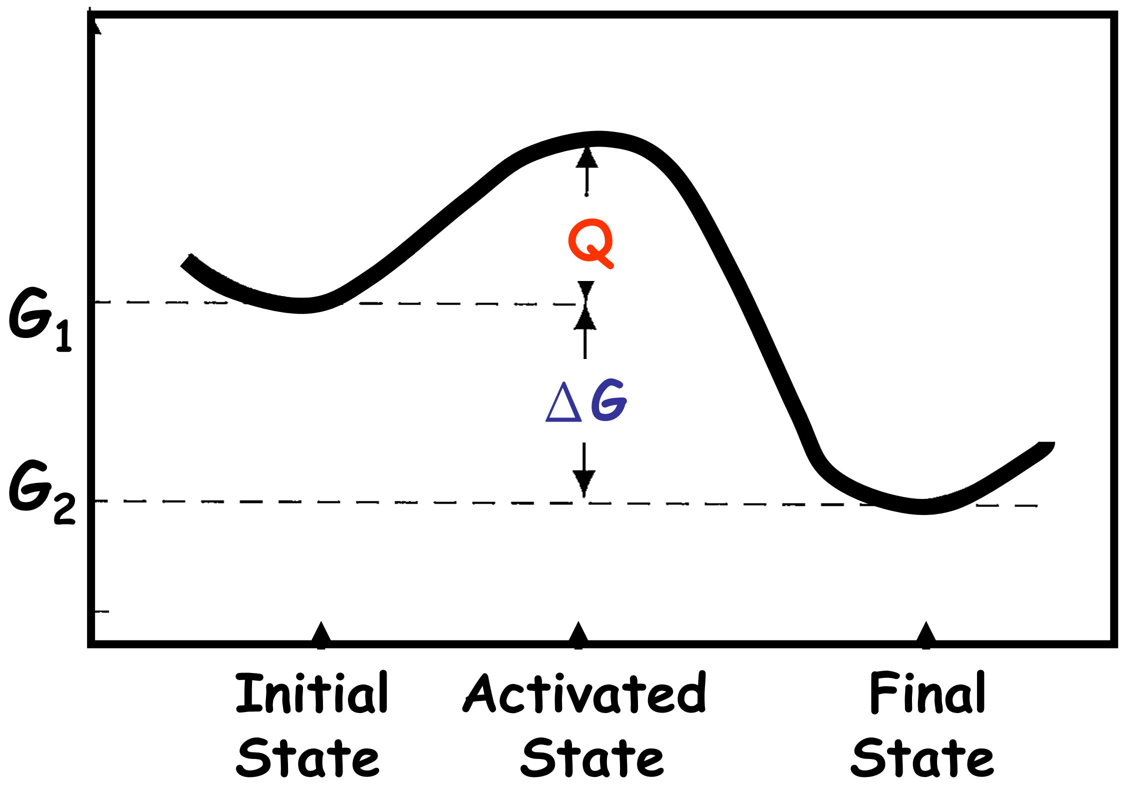
Input

Kinetic Processes

- Rate-limiting steps
- Controlling factors

Output

Thermodynamics vs. Kinetics



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

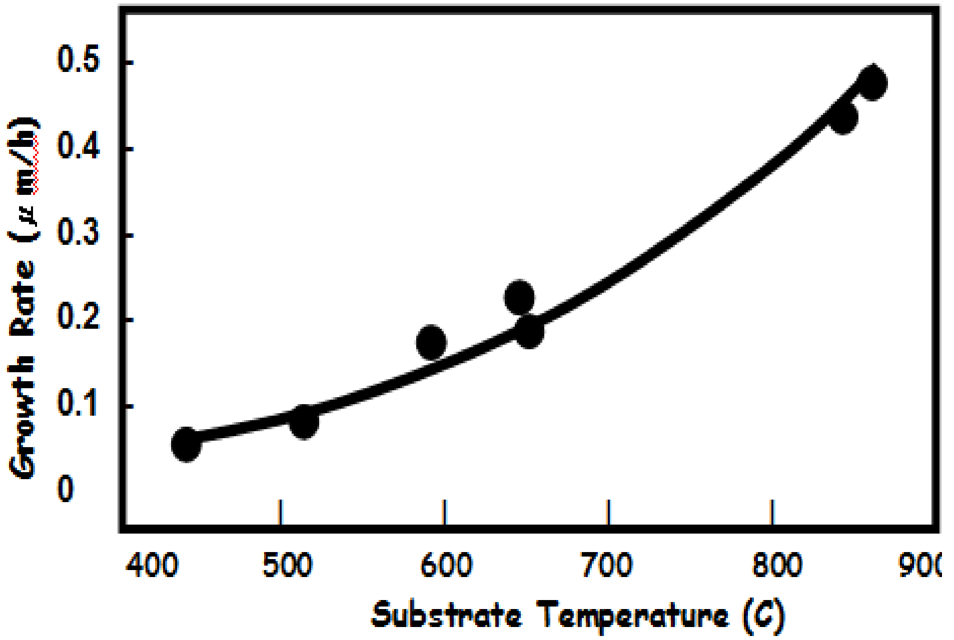
* Kinetic factor relates to Q (activation energy), while the thermodynamic factor relates to the driving force, $\Delta G=G_2-G_1$.

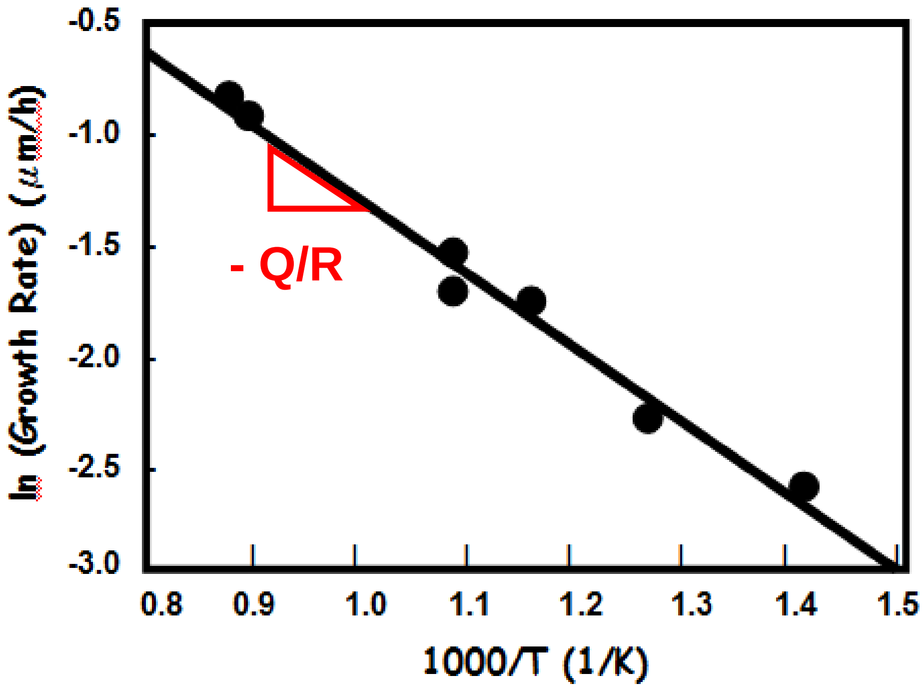
* The thermodynamic factor decides the direction of a reaction, while the kinetic factor, the rate of reaction.

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

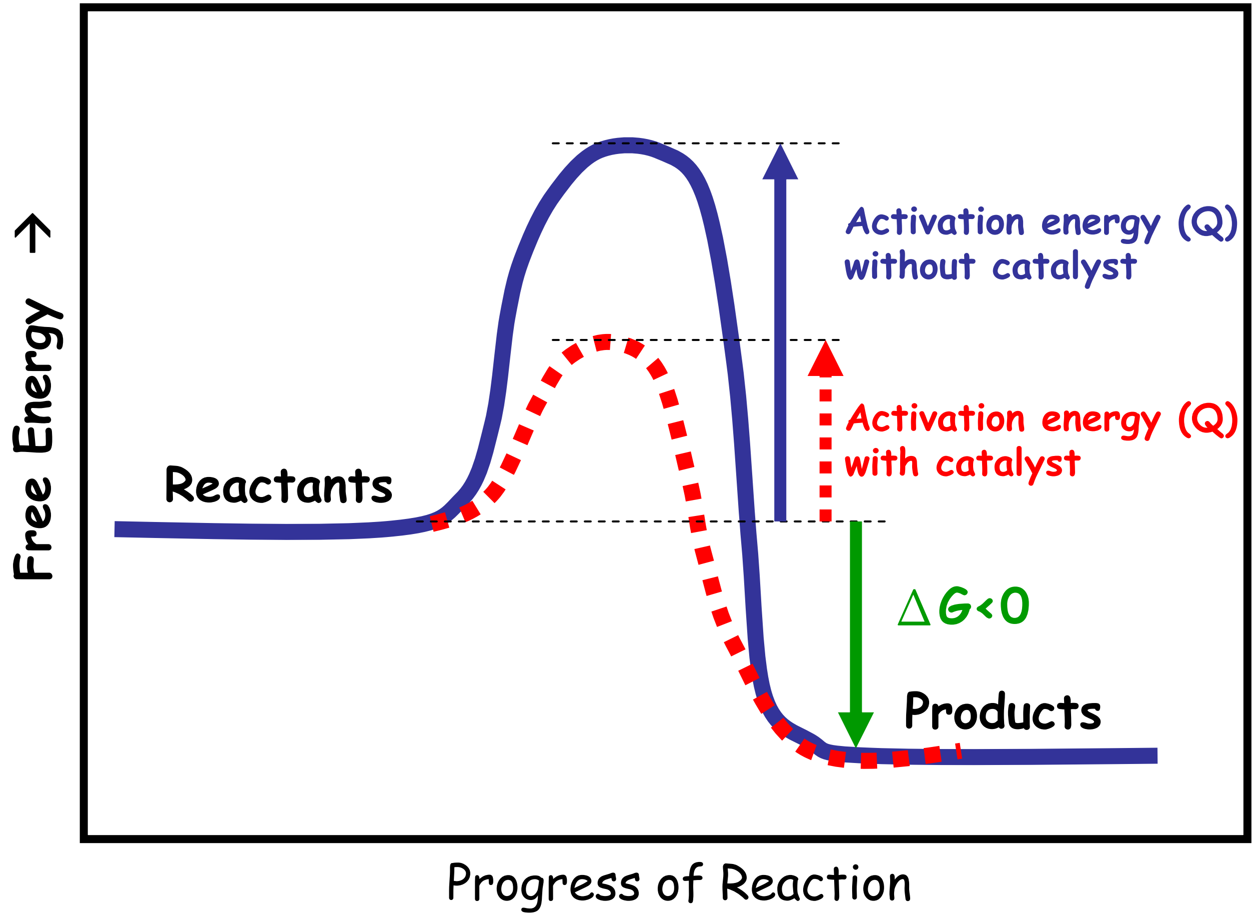
* The activation energy (**Q**) can be obtained from the slope of curve plotted as ln(reaction rate) vs. 1/T

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





Kinetic factor increased by changing temperature or adding catalysts.



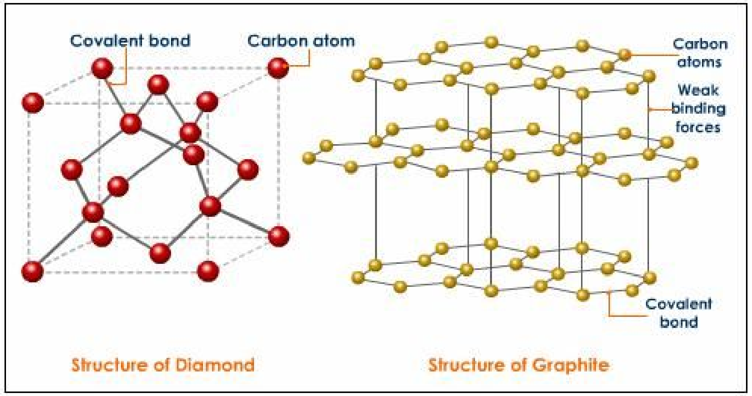
Examples: (1) $N_2 + 3H_2 = 2NH_3$ using iron as a catalyst

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

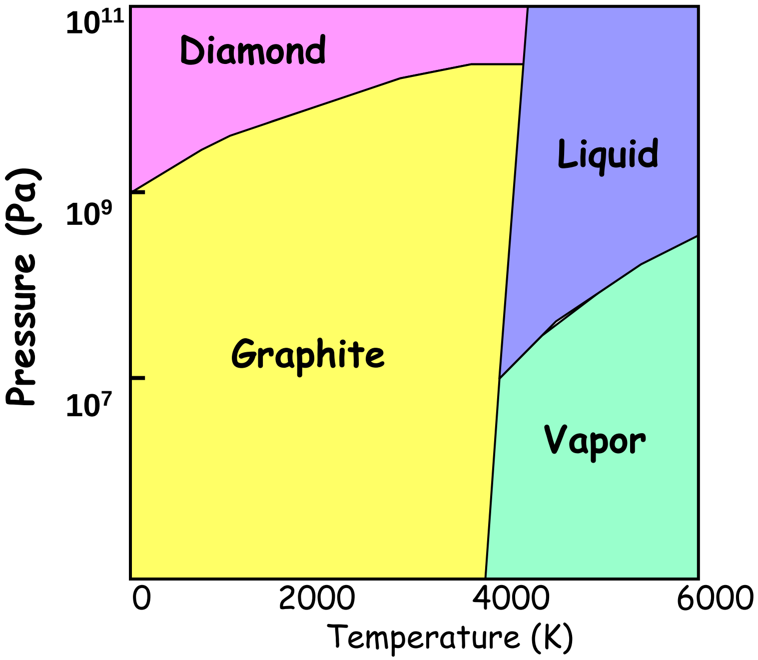
Examples: Thermodynamically favorable but kinetically unfavorable phase changes

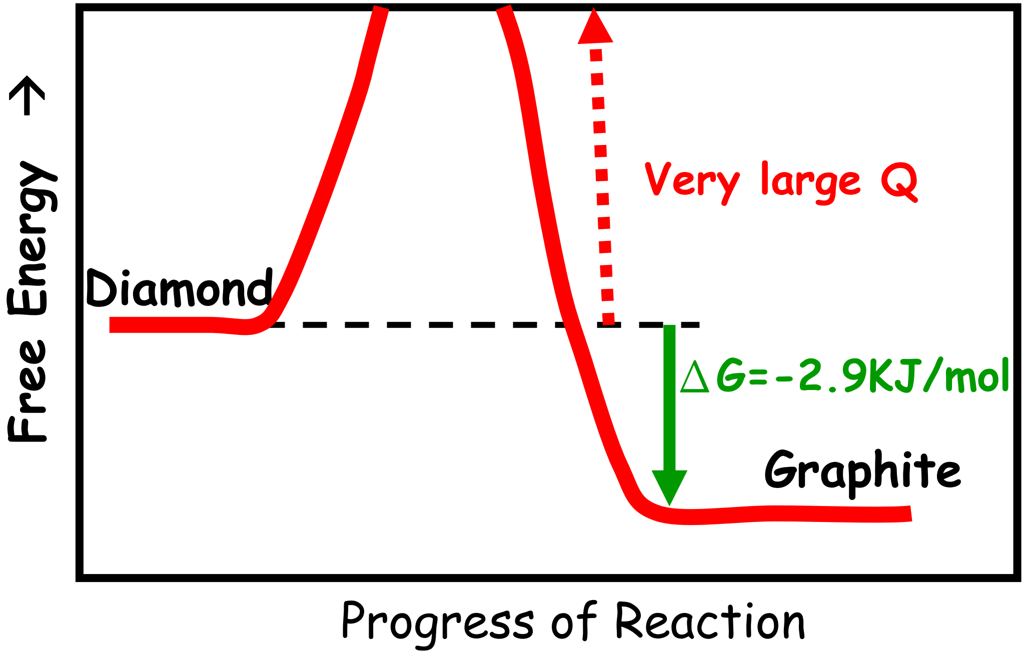
(1) Is a diamond forever?

Diamond

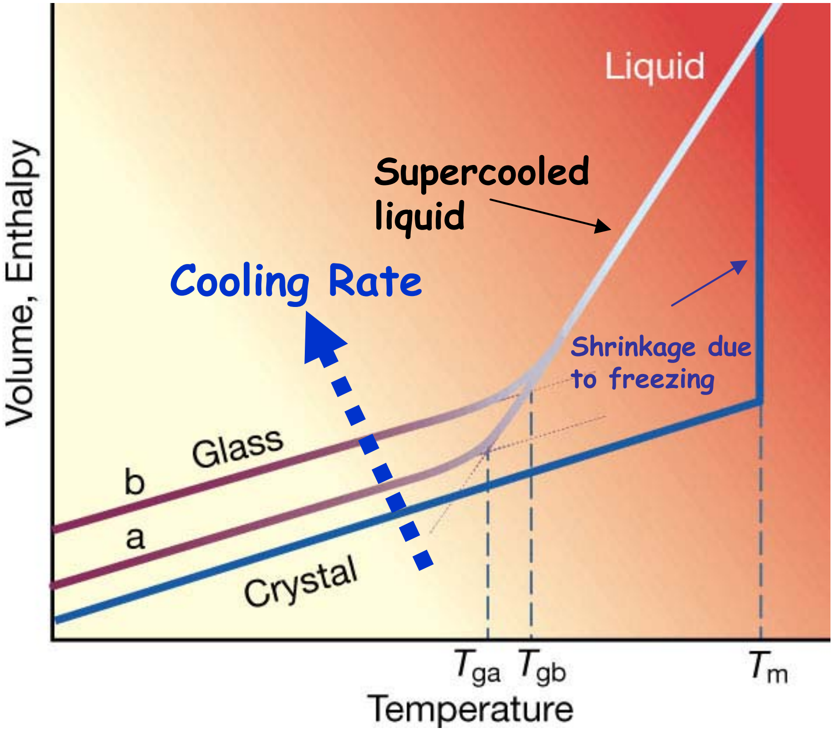


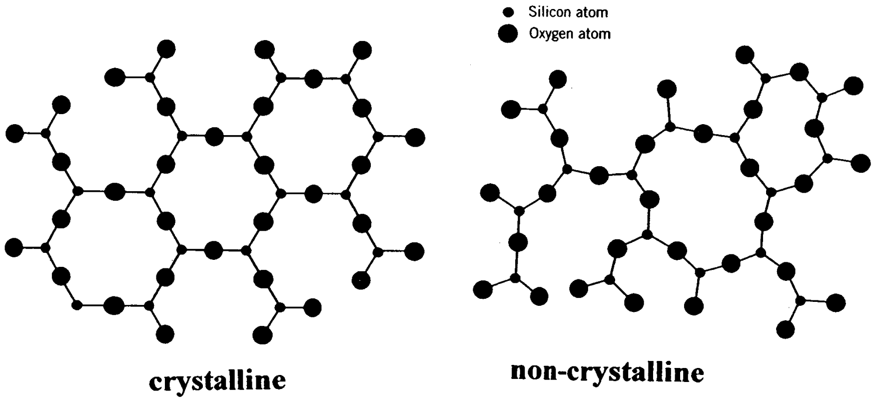
Graphite

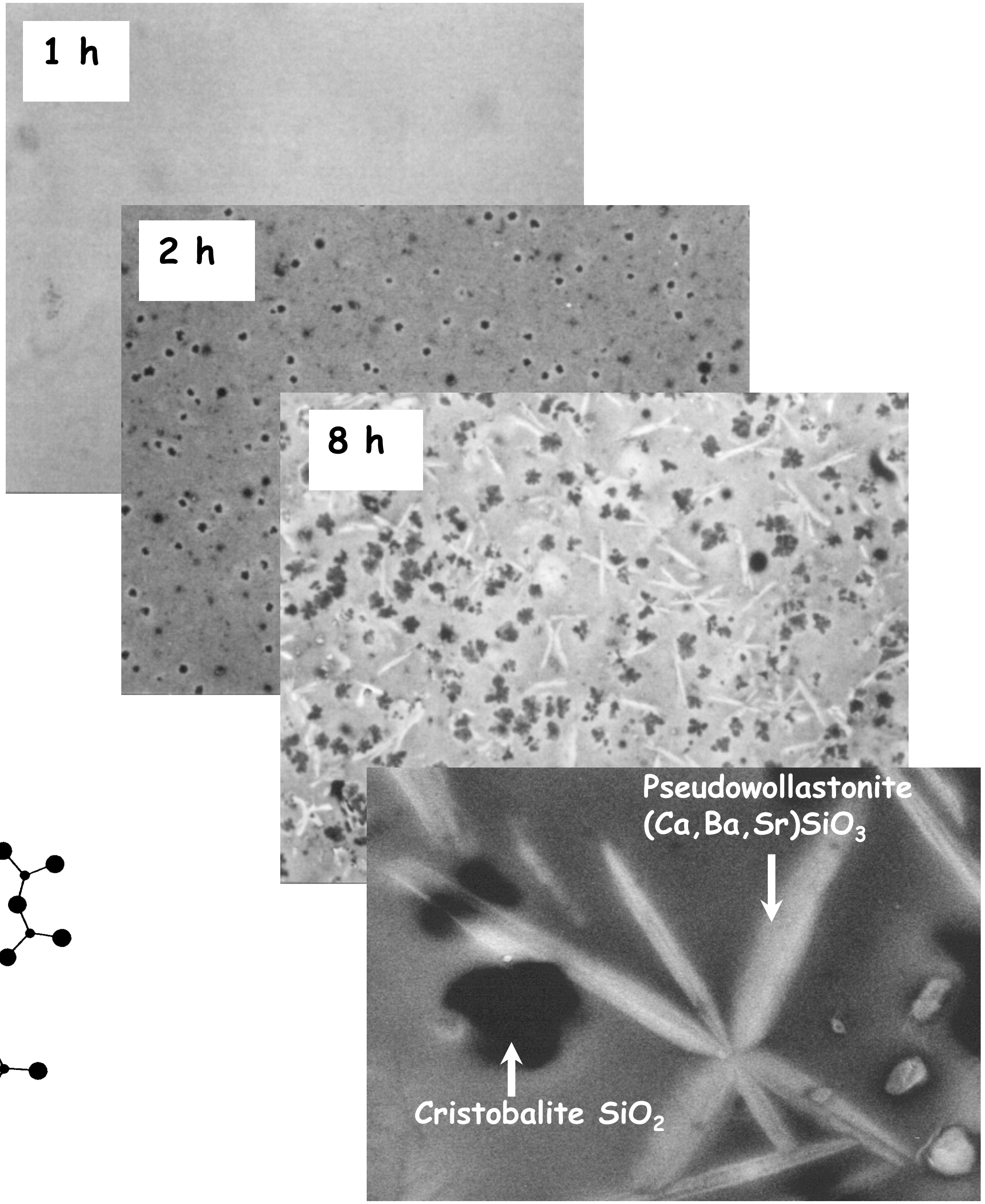




(2) Crystallization of glasses



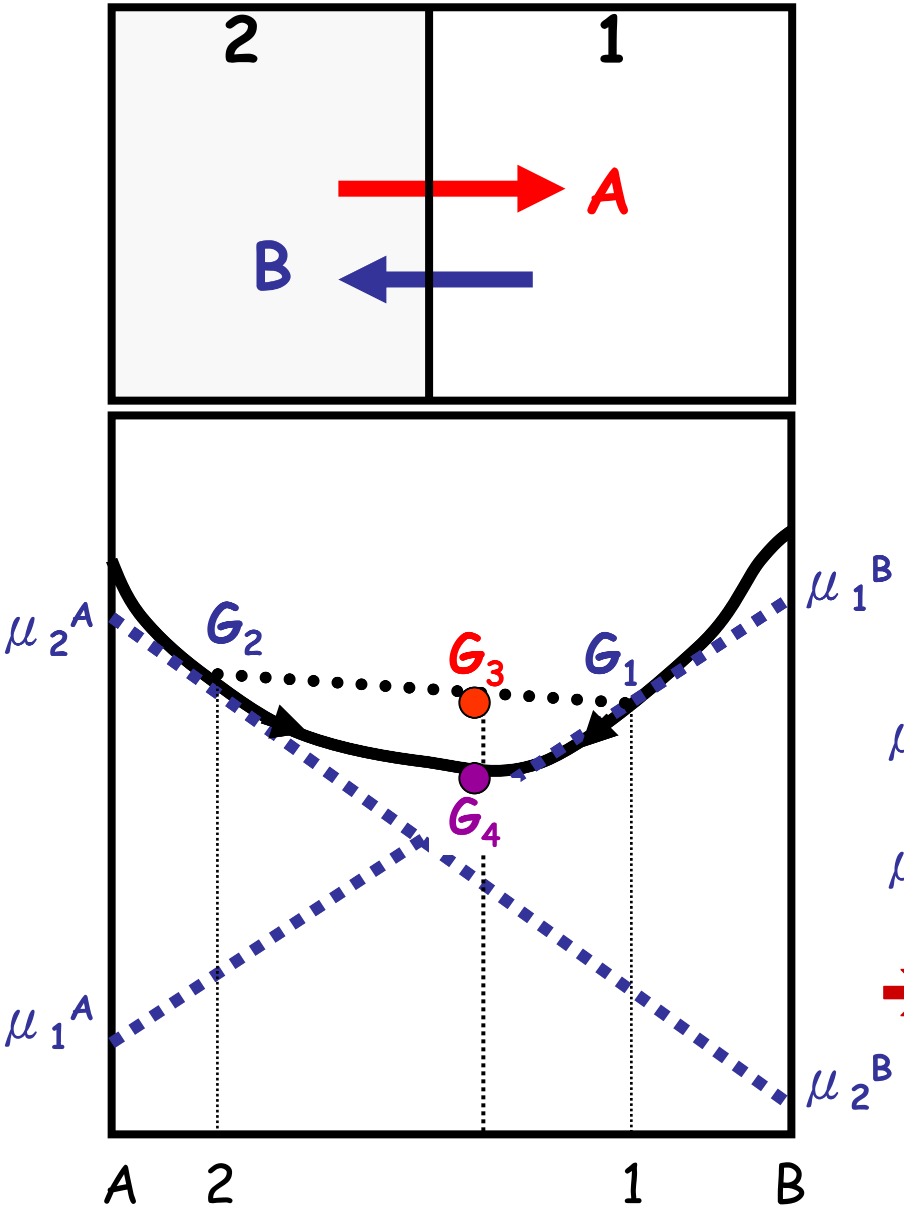




$CaO-SrO-BaO-B_2O_3-SiO_2$ glass-ceramics annealed at 875°C

Diffusion driven by decrease in chemical potential

* Down-hill diffusion



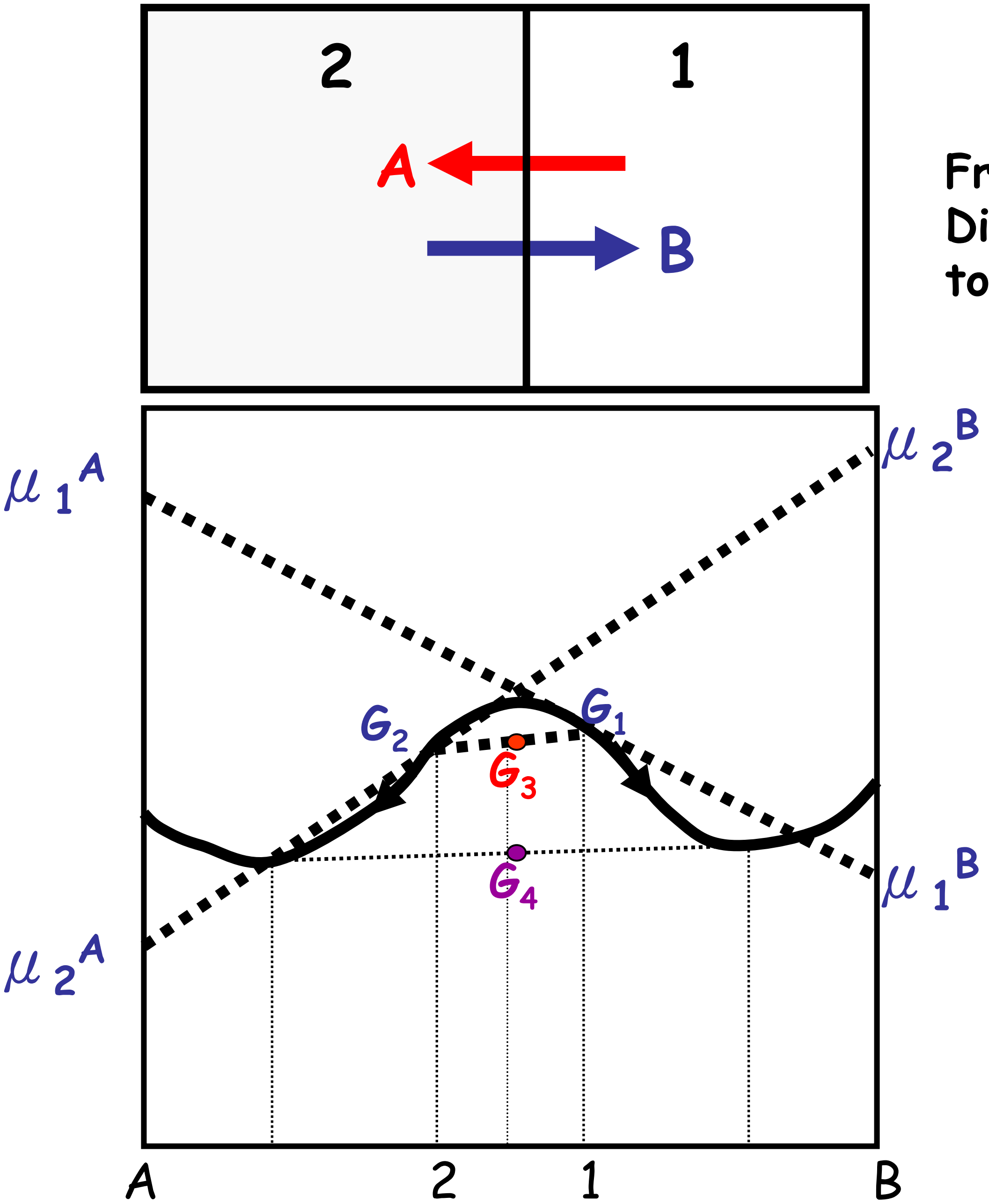
Free energy of diffusion couple = G_3
Diffusion taking place to homogenize
to obtain G_4

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

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

→Down-hill Diffusion

* Up-hill Diffusion



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 (2) to (1)**

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

→Up-hill Diffusion

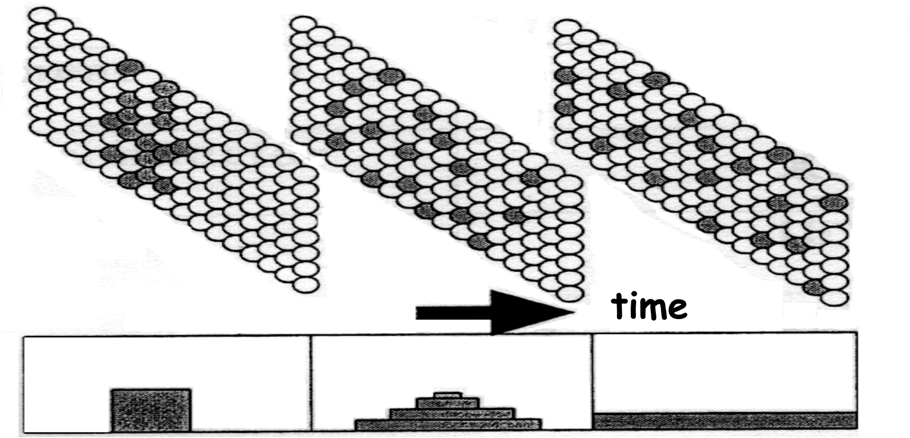
$$Driving \quad force \ \alpha \ \frac{\partial \mu}{\partial x} \ (not \frac{\partial C}{\partial x})$$

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

$B : Mobility, \quad F : Force$

Diffusion:

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



General scheme for transport phenomena

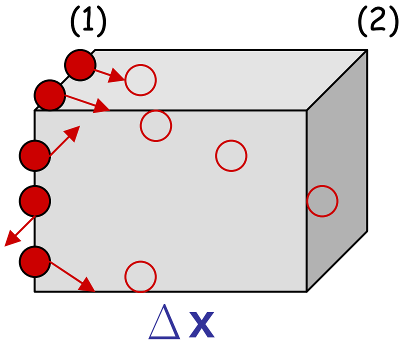
	Flux	α	Driving force	α	Gradient in potential
Matter	J	α	dC/dx	α	Concentration potential
Heat	q	α	dT/dx	α	Temperature potential
Electricity	I	α	dϕ/dx	α	Electrical potential

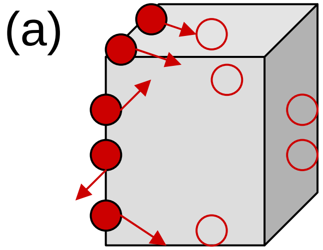
$J = -D\nabla C$ $(Fick's\ Law)$ D: diffusivity

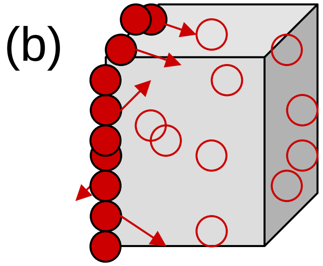
$q = -k\nabla T$ $(Fourier's\ Law)$ k: thermal conductivity

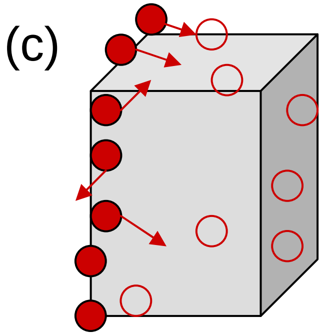
$I = -\sigma\nabla\phi$ $(Ohm's\ Law)$ σ: electrical conductivity

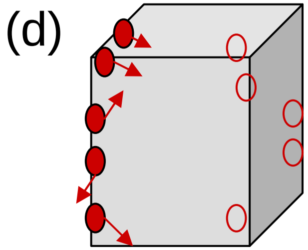
Fick's First Law











Rate of particles reaching surface (2):
number of particles/time =1

To increase the rate:

(a) Reducing thickness (∆x)
(b) Increasing number of particles (∆C)
(c) Increasing area (A)
(d) Reducing particle size (D)
(e) Increasing temperature (D) ($D=D_o\exp(-Q/RT)$)

$$\mathrm{v}\ (Rate) = \frac{\Delta n}{\Delta t} \ \alpha \ \frac{\Delta C}{\Delta x} \cdot A$$

$$\frac{\mathrm{v}}{A} = J\ (Flux) = \frac{\Delta n}{\Delta t \cdot A} \ \alpha \ \frac{\Delta C}{\Delta x}$$

$$= -D \frac{\partial C}{\partial x} \quad (\mathrm{D : Diffusivity})$$

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

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

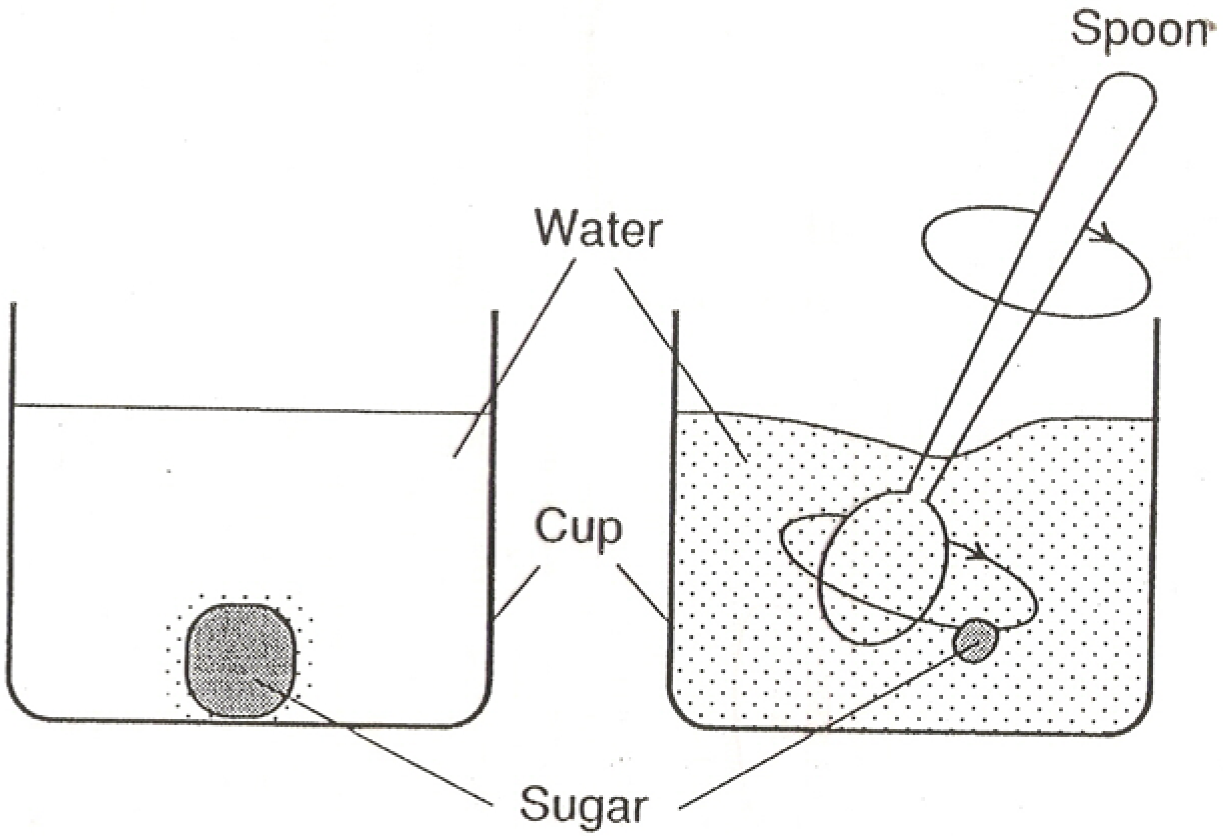
- **Flux (J)** : Mass/(area · time), e.g., g/(cm^2 · sec)
- **Minus (-):** Matter moves from high to low concentration.
- **Diffusivity (D):** Diffusivity related to atomic mobility and crystal structure, e.g., cm^2/sec (independent of concentration gradient)
- **Concentration gradient ($\frac{\partial C}{\partial x}$):** Gradient in "Mass Potential," e.g., g · cm^{-3}/cm

Magnitude of Diffusivity

Species	Diffusivity (cm^2/sec)
Solids (metals near M.P.)	10^{-8}
Elemental Semiconductors	10^{-12}
Liquids	10^{-4}-10^{-5}
Gases	10^{-1}

Note: Liquids and gases in liquids and gases generally dominated by convection flow, rather than diffusion.

Diffusion << Convection



Diffusion
(Slower)

Convection
(Faster)

Steady State:

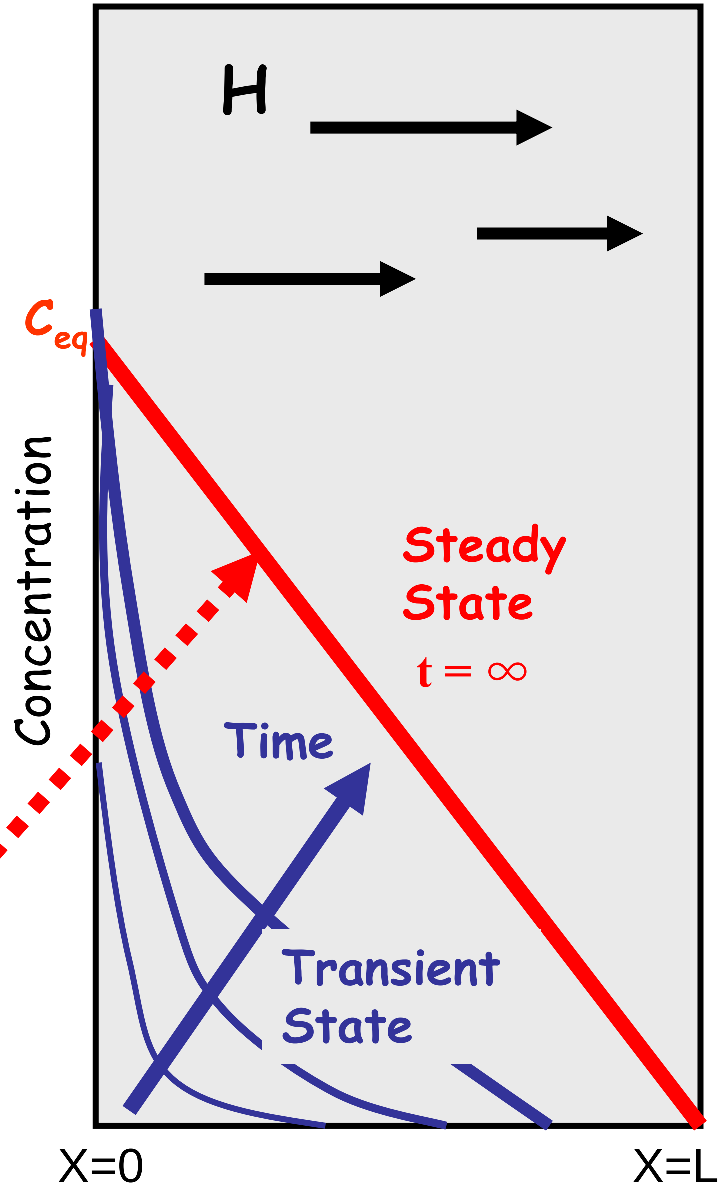
Concentration at a given point is invariant with time

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

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

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

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



Key: to describe C(x,t) quantitatively

Equilibrium State: No Flux

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

Steady State: Constant flux if the area is fixed.

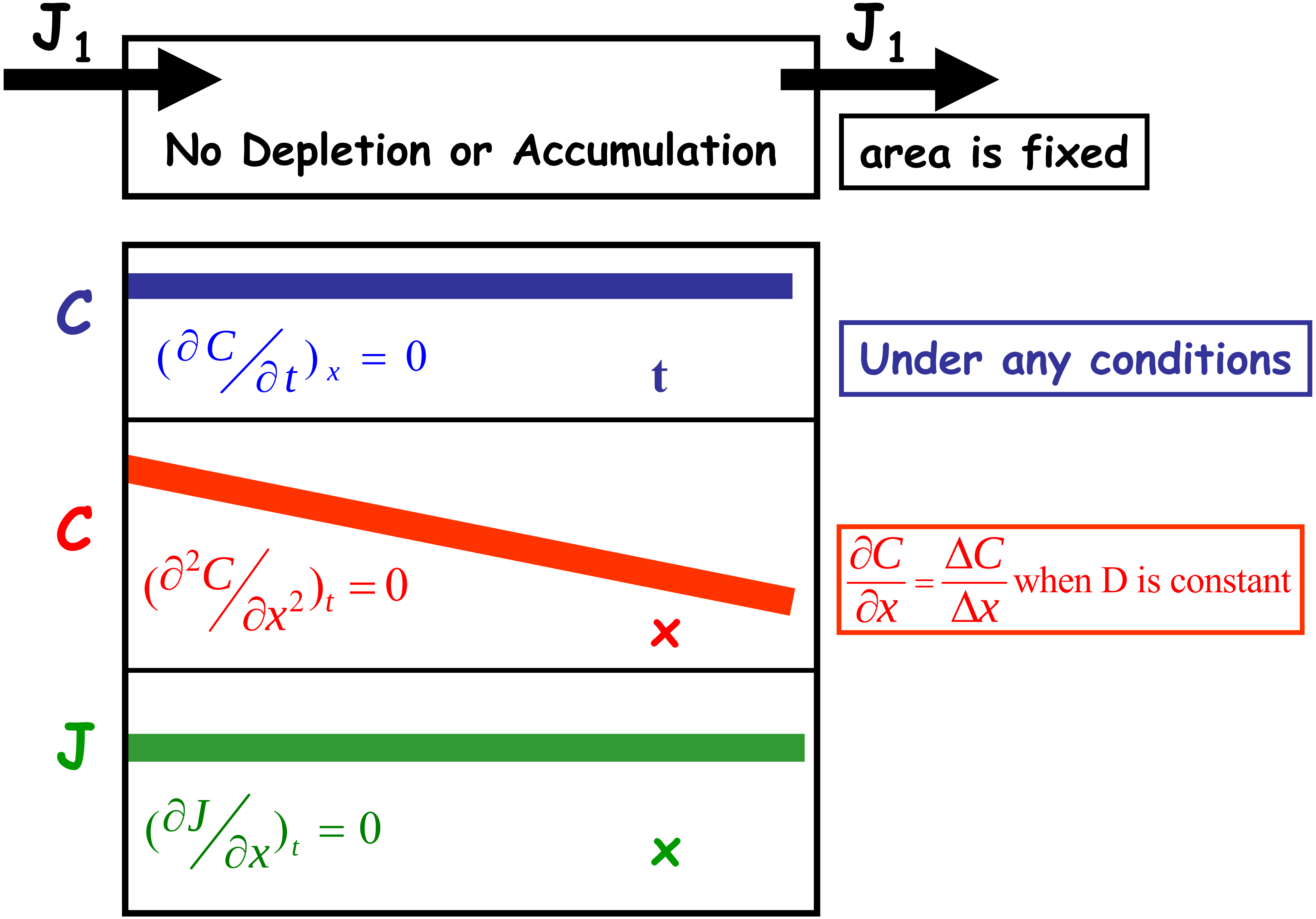
$$(\frac{\partial \mu}{\partial t})_x = 0 = (\frac{\partial C}{\partial t})_x$$

μ : Chemical Potential

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

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

Steady State:



J_1

J_1

No Depletion or Accumulation

area is fixed

C

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

Under any conditions

C

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

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

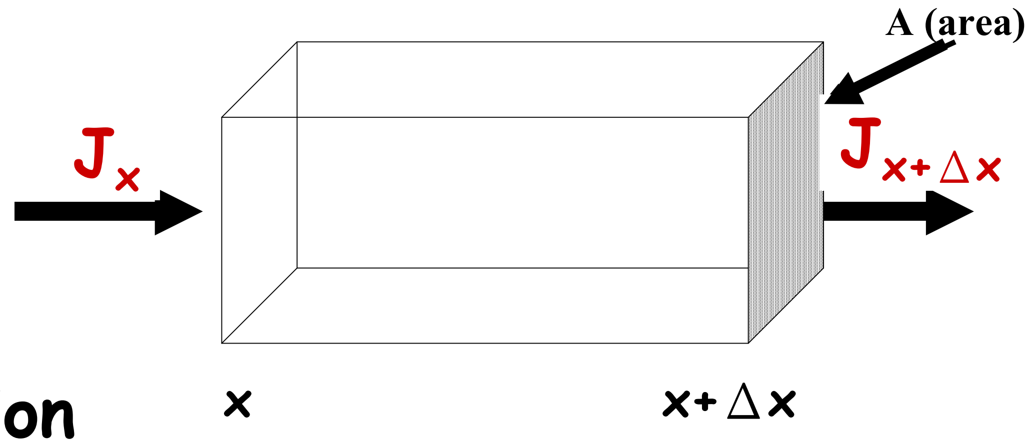
J

$(\partial J / \partial x)_t = 0$ ×

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

From Taylor Series

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

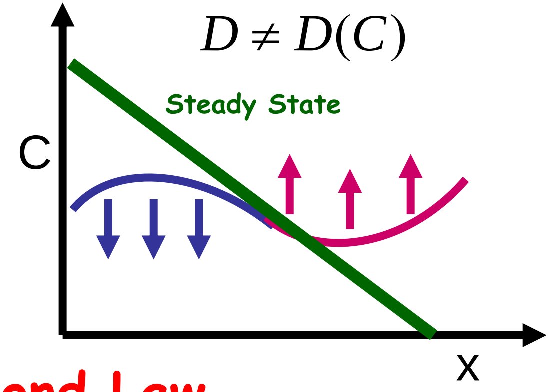
$$\boxed{\begin{aligned} J_x A - (J_x + \frac{\partial J}{\partial x} dx) A &= \frac{\partial C}{\partial t} A \cdot \Delta x \\ -\frac{\partial J}{\partial x} dx \cdot A &= \frac{\partial C}{\partial t} A \cdot \Delta x \end{aligned}}$$

Fick's Second Law (cont.)

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

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

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



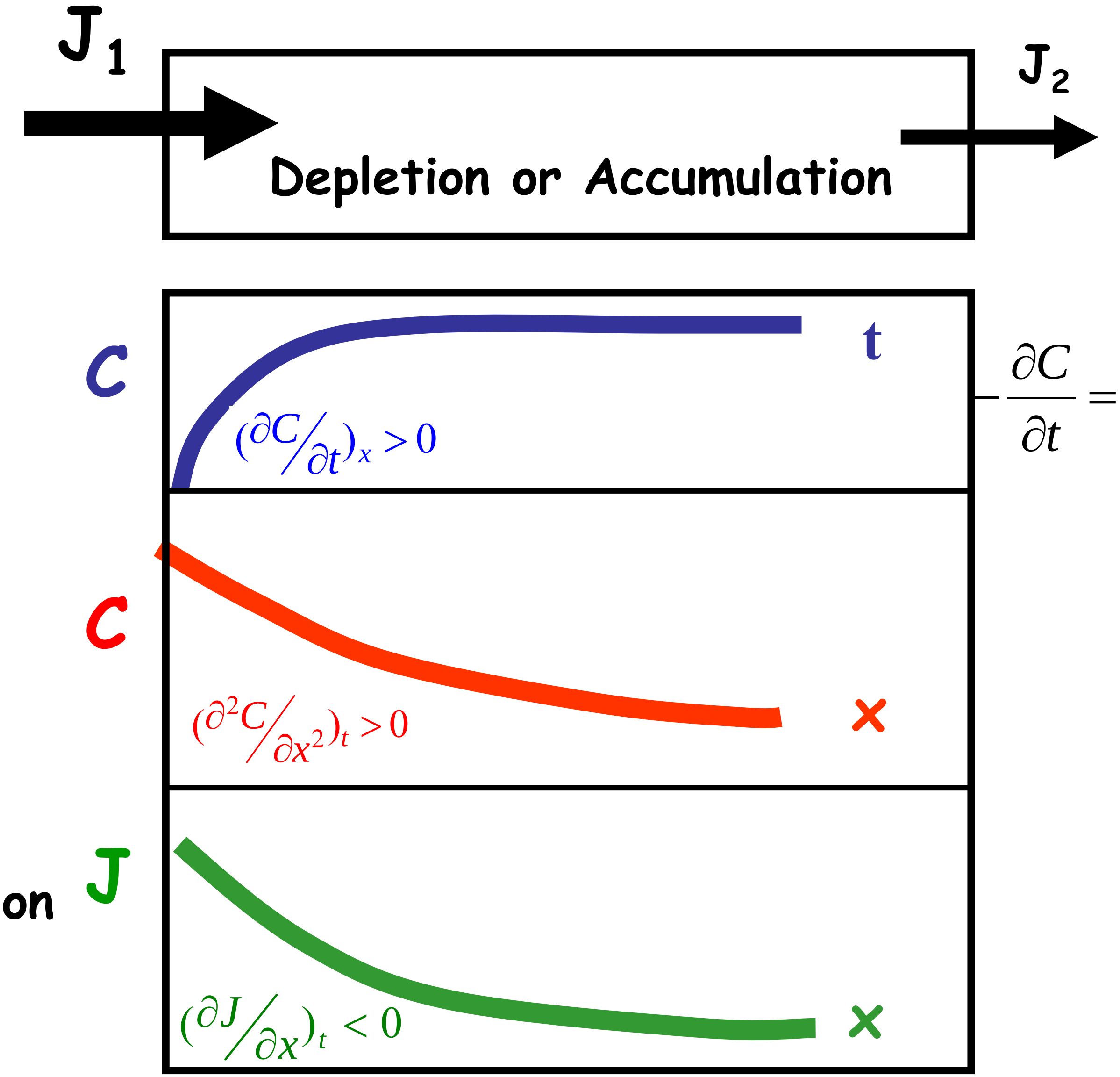
when $D \neq D(C) \rightarrow \frac{\partial D}{\partial C}=0$

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

Linear partial differential equation

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

Transient State:



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

If $J_2 < J_1$
→ Accumulation

Steady State

Cartesian coordinate in one dimension

$$\left(\frac{\partial C}{\partial t}\right)_x = D\frac{\partial^2 C}{\partial x^2} = 0$$

if C= f(r)

Cylindrical coordinate

$$\frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) = 0$$

Spherical coordinate

$$\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) = 0$$

(D is constant)

Application of Steady State

- Infinite cylinder
- Decarburization or Carburization in single-phase Fe-C alloy
- No phase transformation involved
- Steady state reached ($(\frac{\partial C}{\partial t})_x = 0$)
- Diffusion controlling process

  (Equilibrium concentrations reached on both sides)

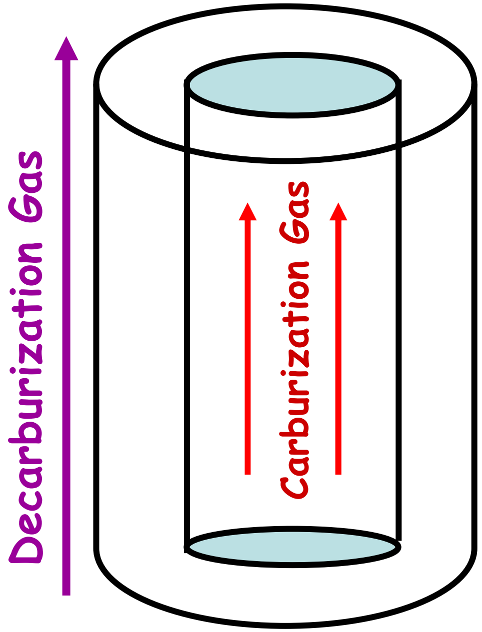
- To find D(C) in Fe-C alloy

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

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

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

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

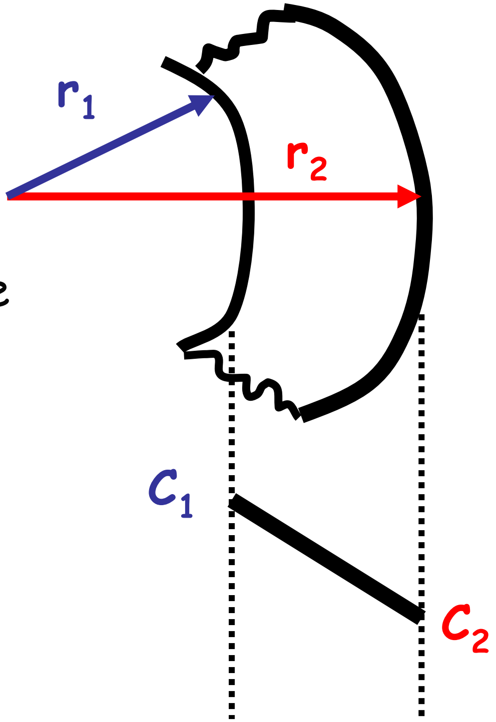


Infinite Cylinder (area is not fixed)

For steady radial diffusion through the wall of the hollow cylinder, the Laplace equation in cylindrical coordinate is

$$Steady \quad State: \left(\frac{\partial C}{\partial t}\right)_x = 0$$

$$Cylindrical \quad coordinate: \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial Z^2} = 0$$



If the concentration depends only on the radial coordinate

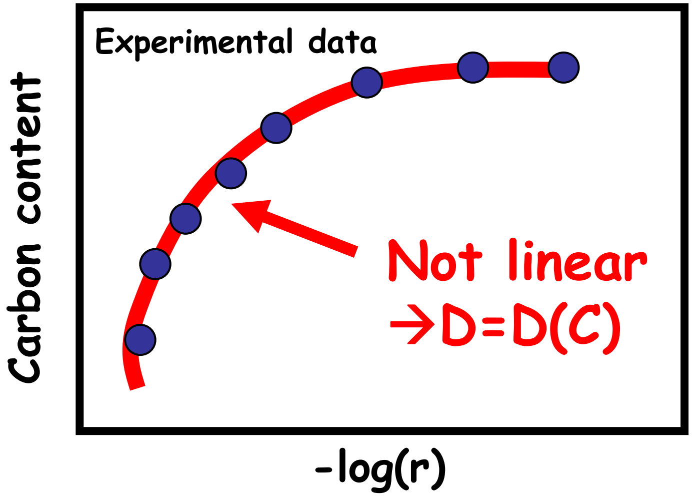
$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) = 0 \rightarrow \frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} = 0 \rightarrow C(r) = A + B\ln r$$

B.C.: $C(r_1, t) = C_1$, $C(r_2, t) = C_2$

$$\frac{C - C_2}{C_1 - C_2} = \frac{\ln\left(r / r_2\right)}{\ln\left(r_1 / r_2\right)}$$

A plot of C versus *ln*(r) should be a straight line if diffusion is the rate-controlling step and D is constant.

Diffusion of carbon in γ-Fe



The above analysis can not be applied

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

→The quantity of carbon passing through the tube per unit time (j) is constant and independent of r:

j (mass/time) = 2πrlJ$_r$ (Flow Rate)

Area: 2πrl is not constant
r: Radius
l: Length of cylinder
J_r: Local flux

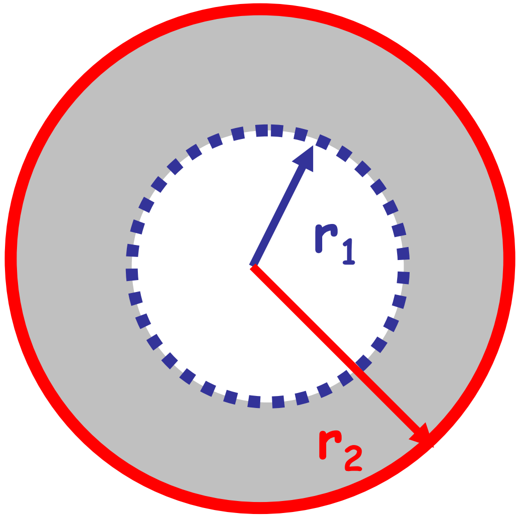
$$J_r=-D\frac{\partial C}{\partial r}$$

$$j=2\pi rl\left(-D\frac{\partial C}{\partial r}\right)\rightarrow\quad\frac{j}{2\pi lD}=-r\frac{\partial C}{\partial r}=-\frac{\partial C}{\partial \ln(r)}$$

Steady State (diffusion area is not fixed)

$$(\frac{\partial C}{\partial t})_x = D\frac{\partial^2 C}{\partial x^2} = 0$$

Cylinder



Diffusion area of 2πrl is not fixed

$$j_1 = \frac{\Delta m_1}{\Delta t} = j_2 = \frac{\Delta m_2}{\Delta t}$$

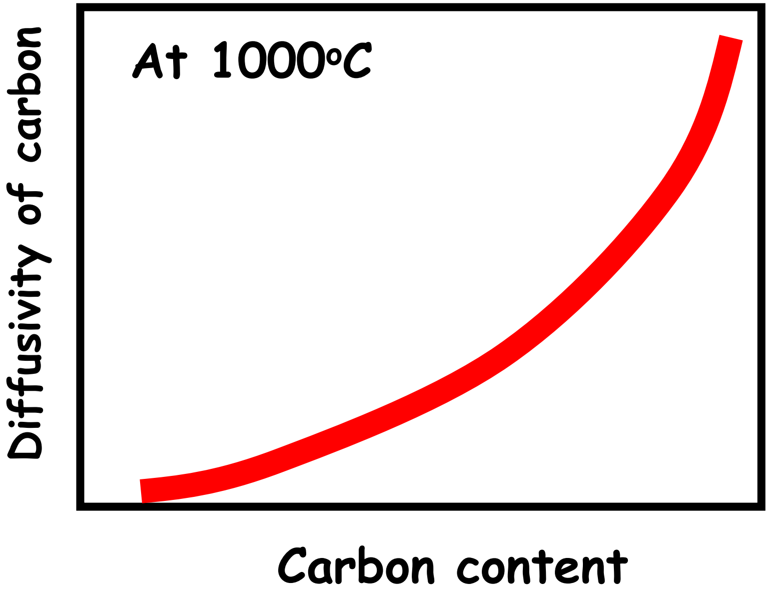
$$2\pi r_1 l J_{r1} = 2\pi r_2 l J_{r2}$$

$$r_1 J_{r1} = r_2 J_{r2}$$

$$r_1 < r_2 \Rightarrow J_{r1} > J_{r2}$$

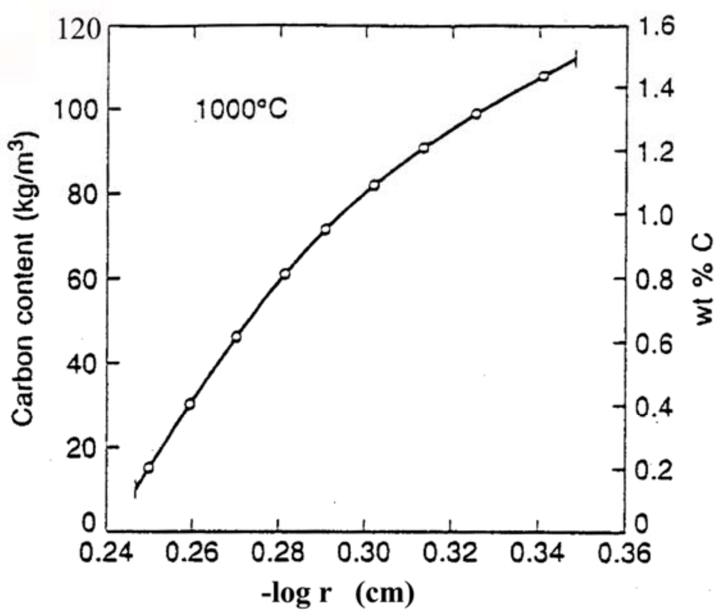
$$\frac{-j}{2\pi l D} = \frac{\partial C}{\partial \ln(r)}$$

For a given experiment, j can be determined by chemical analysis, and then we can determine D from the slope of the plot of C versus ln(r).



Concentration profile of carbon in the wall of a hollow steel cylinder under conditions of steady-state diffusion.

$$\frac{-j}{2\pi l D} = \frac{\partial C}{\partial \ln(r)}$$



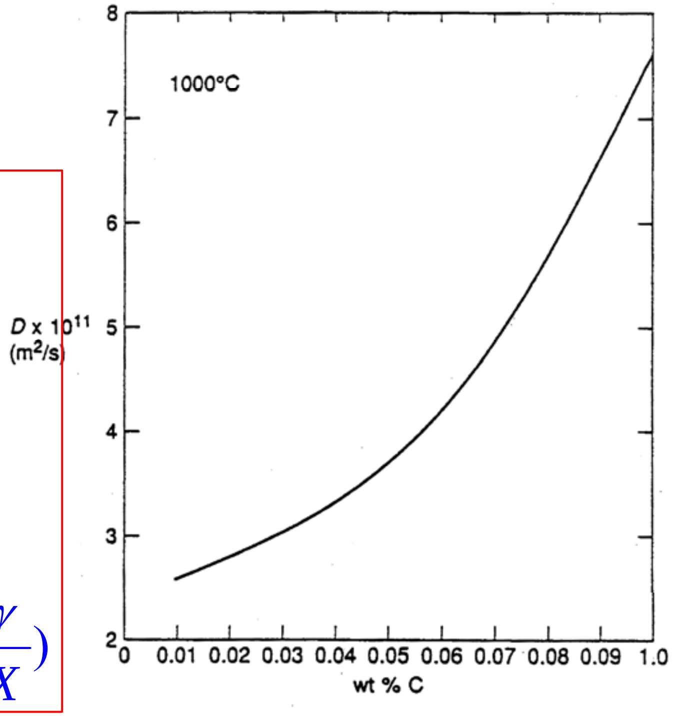
Diffusion coefficient of carbon in iron varying with its concentration at 1000℃

$$J = C\cdot \mathrm{v} = C\cdot(B\cdot F) = CB\left(-\frac{\partial\mu}{\partial x}\right)$$

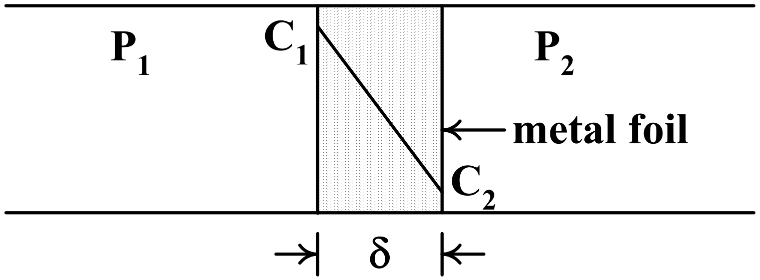
$$= -BRT\left(\frac{\partial \ln a}{\partial x}\right)C \equiv -D^{I}\frac{\partial C}{\partial x}$$

$$BRT\frac{\partial \ln a}{\partial x} = D^{I}\frac{\partial \ln C}{\partial x}$$

$$\therefore D^{I} = BRT\frac{\partial \ln a}{\partial \ln C} = BRT\frac{\partial \ln X\gamma}{\partial \ln X} = BRT\left(1+\frac{\partial \ln\gamma}{\partial \ln X}\right)$$



Steady State Diffusion (area is fixed)



$$\frac{1}{2}H_2 \Leftrightarrow [H]_{metal\ foil}$$

Sievert's law

$$k_{\text{equilibrium constant}} = \frac{[H]_{metal\ foil}}{\sqrt{P_{H_2}}}$$

- * Diffusion of hydrogen gas through the metal foil is the rate-limiting step.
- *Equilibrium concentrations (C_1 and C_2) on both sides, determined by the local partial pressures.
- *Steady State achieved.

$$C_1 = [H]_{metal-1} = k\sqrt{P_{H_2-1}}$$

$$C_2 = [H]_{metal-2} = k\sqrt{P_{H_2-2}}$$

P(H_2-1) and P(H_2-2) are partial pressures of hydrogen on sides 1 and 2, respectively

$$\frac{\partial C}{\partial x} = -\frac{C_1 - C_2}{\delta} = -\frac{k}{\delta}(\sqrt{P_{H_2-1}} - \sqrt{P_{H_2-2}})$$

$$J_x = -D\frac{\partial C}{\partial x} = +\frac{Dk}{\delta}(\sqrt{P_{H_2-1}} - \sqrt{P_{H_2-2}})$$

Consider an iron tank that contains H_2 gas at a pressure of P_o at a temperature of T_o. If the pressure outside the tank is zero, after what time the pressure in the tank has decreased to half of its original value?

Rate of loss of mass from tank ($\Delta m/\Delta t$)
= mass diffusion flux through walls (J_xA)

Assuming H_2 is an ideal gas

$$\frac{dm}{dt} = \frac{MV}{RT}\frac{dP}{dt}$$

(M: molecular weight of H_2 and
V: volume of tank)

(PV=nRT=(m/M)RT)

$$J_x = -\frac{Dk}{\delta}\sqrt{P}$$

$$J_x A = \frac{dm}{dt}$$

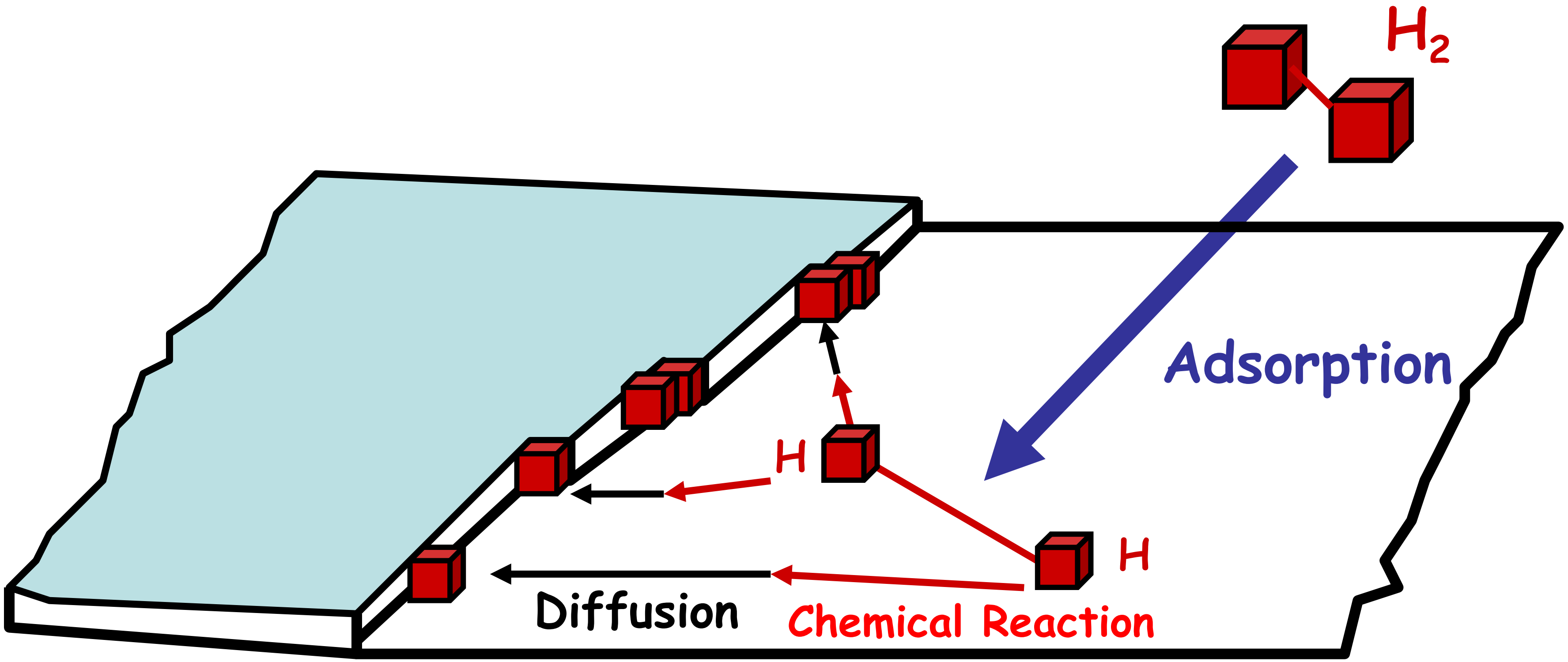
(A: Area of the tank)

$$\Longrightarrow \quad -\frac{DkA}{\delta}\sqrt{P} = \frac{MV}{RT}\frac{dP}{dt}$$

$$\int_{P_0}^{P}\frac{dP}{\sqrt{P}} = -\int_0^t \frac{DkART}{\delta MV}\,dt$$

(k :equilibrium constant)

H_2 Permeation through Metal Foil



$$J_{reaction} = kP^n$$

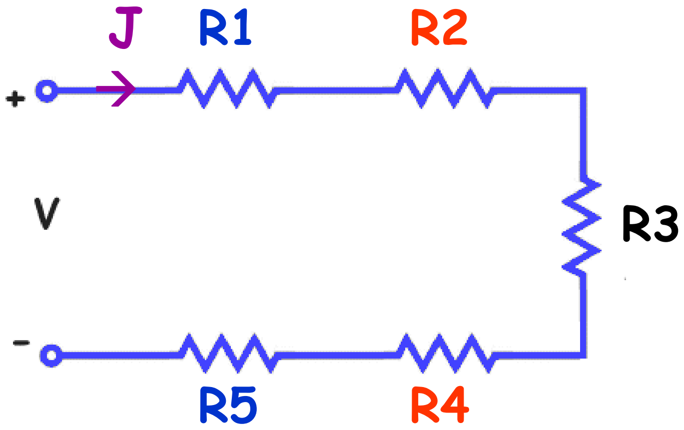
k: Reaction rate constant
P: Partial pressure of H_2

$$J_{adsorption} = \frac{\alpha P}{\sqrt{2\pi M k_B T}}$$

α : Sticking coefficient
M : Molecular weight

H_2 Permeation through Metal Foil

1. Adsorption
2. Chemical Reaction
3. Diffusion
4. Chemical Reaction
5. Desorption



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

$$J = -\frac{\partial C}{\partial x / D} \equiv I = \frac{V}{R}$$

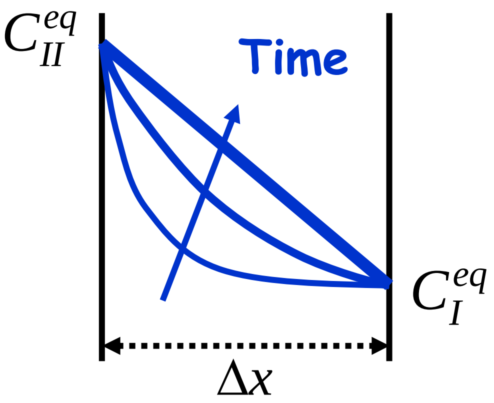
Process with steps in series the slowest one controls the whole reaction, and the rest reach their equilibrium states.

Steady State

(1) Diffusion controlling process

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

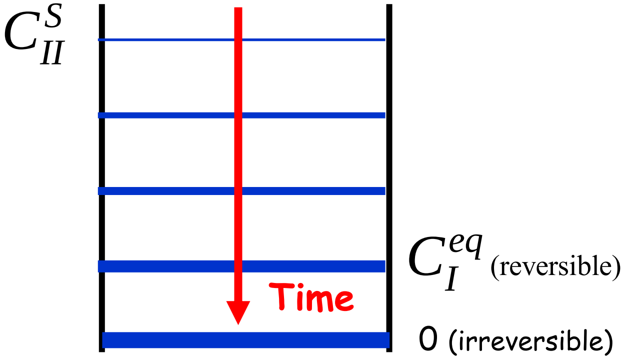
Since ΔC is fixed by chemical reactions (assuming constant D), J is inversely proportional to Δx.



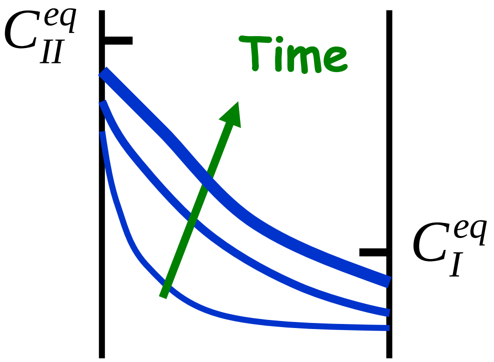
(2) Reaction controlling process

J is independent of Δx, and

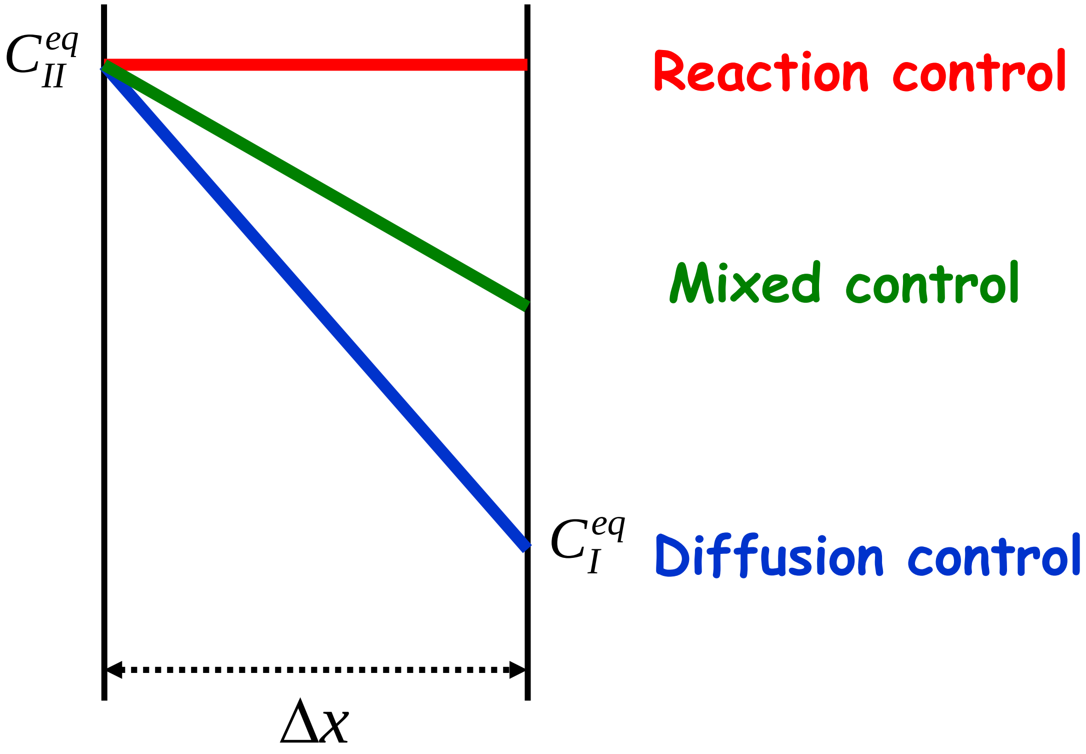
D is inaccessible.



(3) Mixed controlling process



(4) Extreme Cases



Steady State

J: constant (fixed A)

$$\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x} = -\frac{\partial}{\partial x}(-D\frac{\partial C}{\partial x}) = 0$$

D is not necessary to be constant.

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

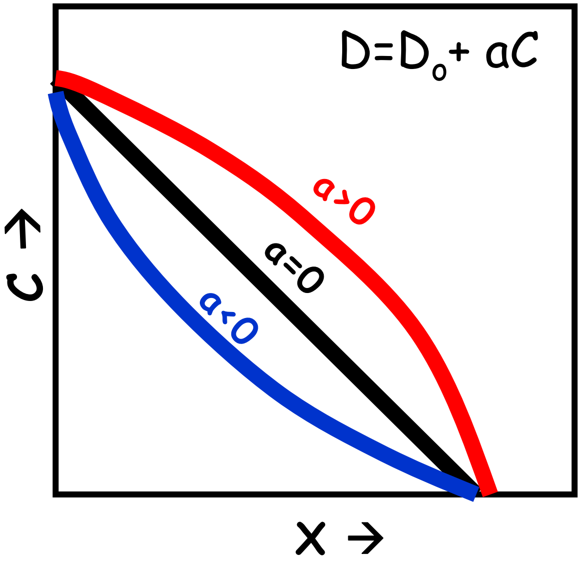
$$= D\frac{\partial^2 C}{\partial x^2} + (\frac{\partial C}{\partial x})^2 \frac{\partial D}{\partial C}$$

(a) steady state and D≠D(C)

$$\frac{\partial C}{\partial t} = 0 \Rightarrow D\frac{\partial^2 C}{\partial x^2} = 0 \Rightarrow \frac{\partial C}{\partial x} = \text{constant}$$

(b) steady state and D=D(C) $e.g., D > 0 \quad and \quad \frac{\partial D}{\partial C} = a$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + (\frac{\partial C}{\partial x})^2 a = 0$$



$$(1) a > 0 \quad D\frac{\partial^2 C}{\partial x^2} < 0 \rightarrow convex\ (\cap)$$

$$(2) a = 0 \quad D\frac{\partial^2 C}{\partial x^2} = 0 \rightarrow straight\quad line\ (\text{-})$$

$$(3) a < 0 \quad D\frac{\partial^2 C}{\partial x^2} > 0 \rightarrow concave\ (\cup)$$

(C) Steady State, D=D(x)

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

$$J\,dx = -D\,dC$$

$$if \quad D = ax$$

$$J\,dx = -ax\,dC$$

$$\frac{dx}{x} = -a\frac{dC}{J}$$

$$\ln x = -\frac{a}{J}C$$

$$\frac{\partial C}{\partial x} = -\frac{J}{a}\frac{1}{x}$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{J}{a}\frac{1}{x^2}$$

$$*a > 0 \quad D\frac{\partial^2 C}{\partial x^2} > 0$$

$$*a < 0 \quad D\frac{\partial^2 C}{\partial x^2} < 0$$

Steady state

J : constant

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

(1) D ≠ D(C)

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

I.C. C(0, 0) = C_0

C(x, 0) = C_i

B.C. C(0,t)=C_0

$$J\Delta x = -D\Delta C$$

$$J(0-x) = -D(C_0 - C_i)$$

$$C_i - C_o = -\frac{Jx}{D}$$

(2) D = D(C) = aC

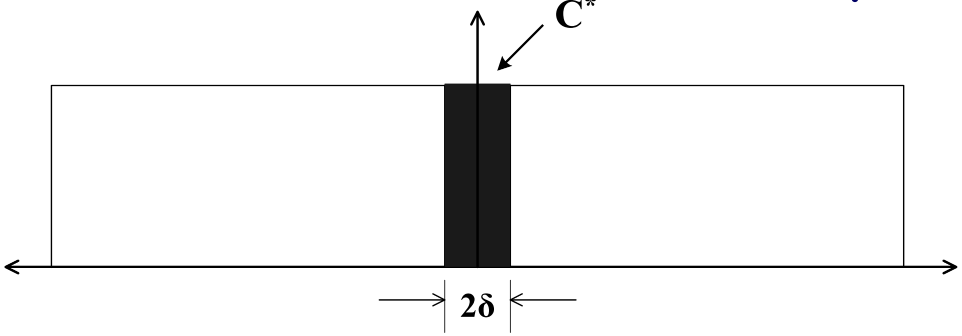
$$J = -aC\frac{\partial C}{\partial x}$$

$$\int_0^x \frac{J}{a}dx = \int_{C_o}^{C_i} -C\,dC \Longrightarrow \frac{Jx}{a} = -\frac{1}{2}(C_i^2 - C_0^2)$$

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 C(x,t).



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

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

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: $\sqrt{Dt} >> 2\delta$)

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

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

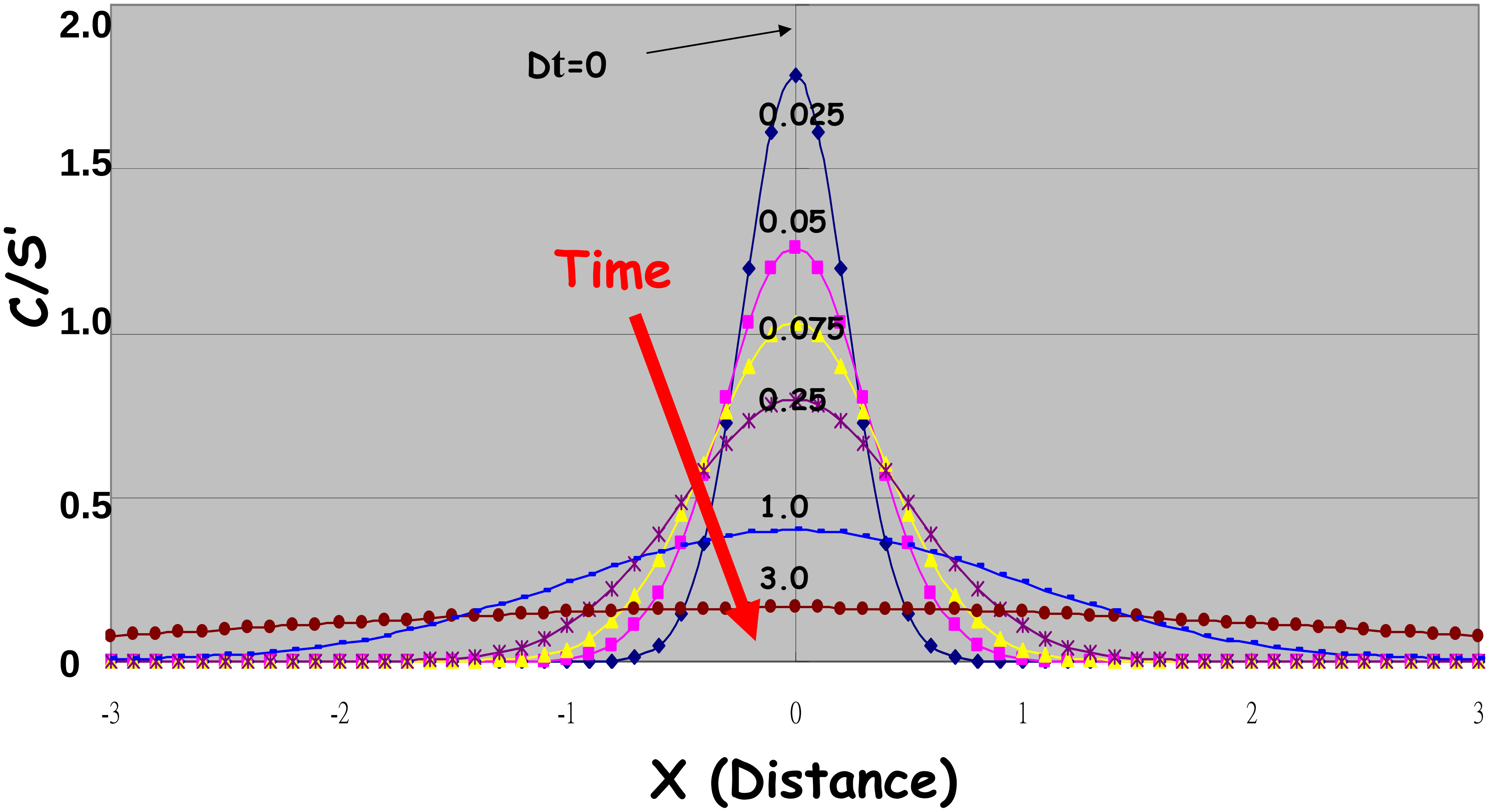
Taking the natural logarithm of both sides yields

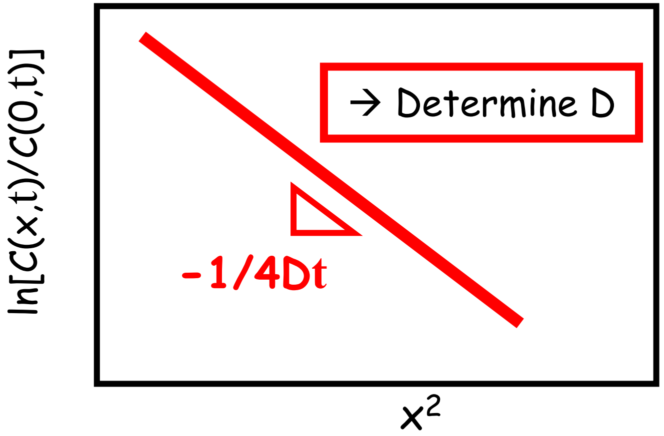
$$\ln(\frac{C(x,t)}{C(0,t)}) = -\frac{x^2}{4Dt}$$

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

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

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





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

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

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

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

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

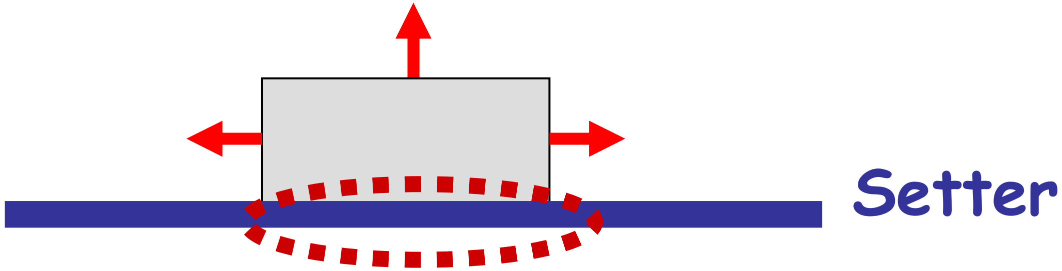
$$C(x,t)=\frac{S'}{2\sqrt{\pi Dt}}\exp(-1)=\frac{C(0,t)}{e} \leftarrow \text{this plane is determined.}$$

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

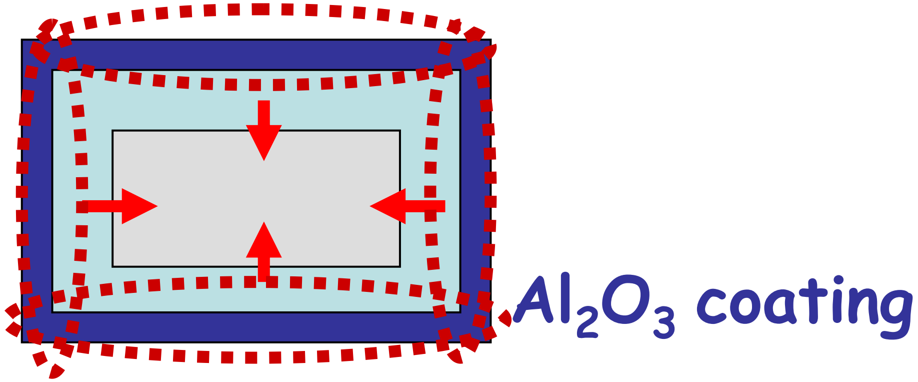
$$\frac{\partial C}{\partial x}\Big|_{x=0} = 0 \Rightarrow \text{Impermeable Boundary}$$

Examples:

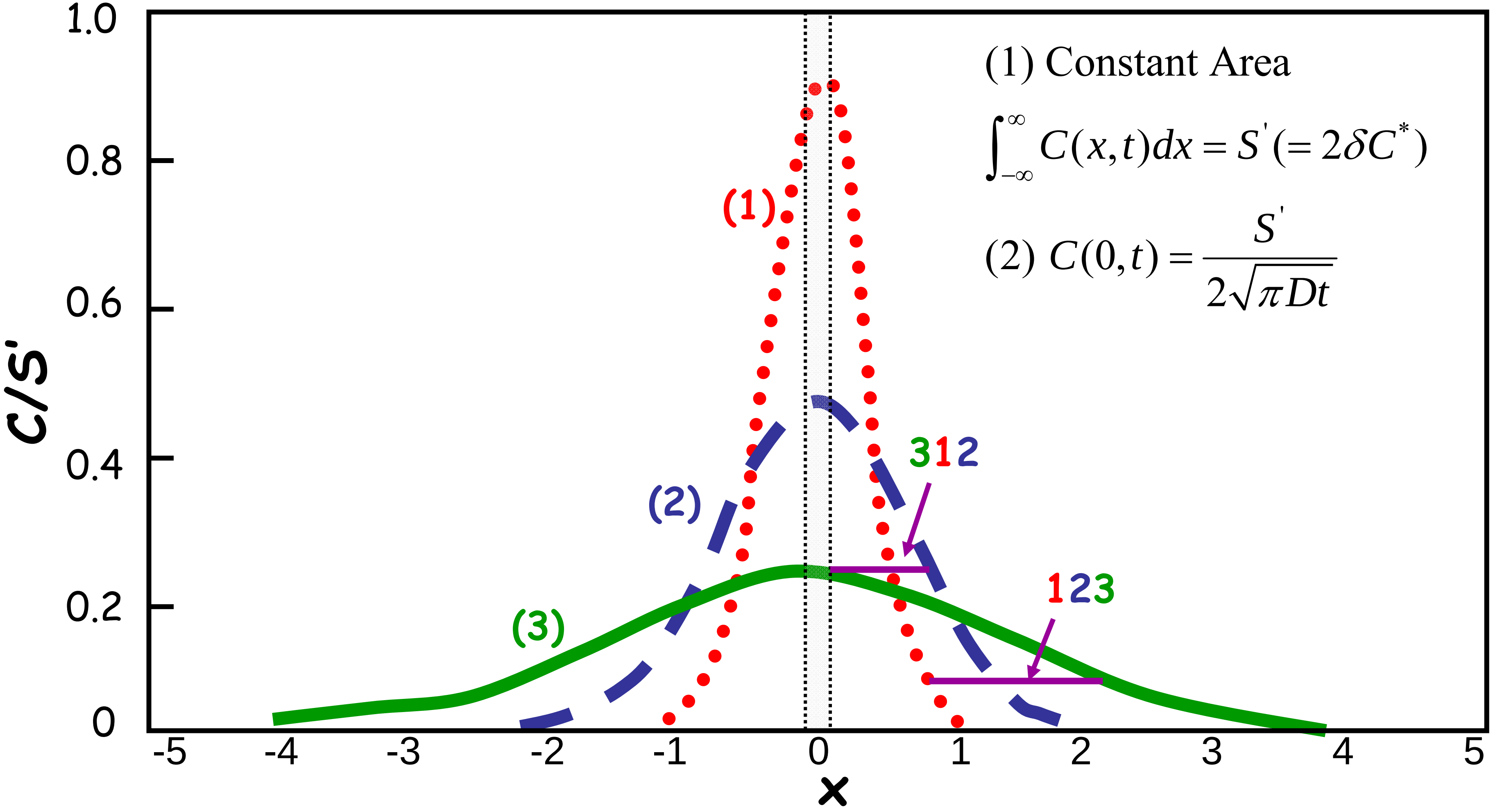
(1)



(2)



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



(1) Constant Area

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

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

Concentration-distance curves for an instantaneous plane source.

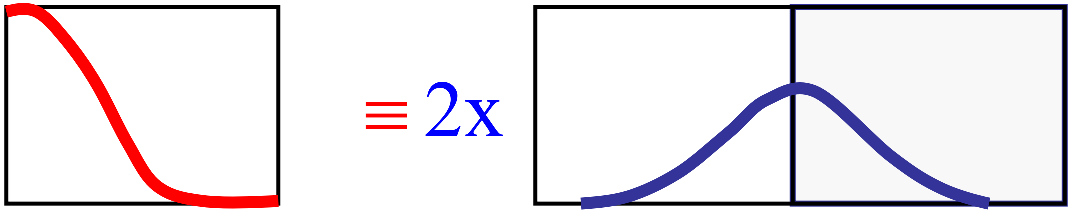
Thin Film Solution → Gaussian Concentration Distribution

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

$$\int_{-\infty}^{\infty}\exp(\frac{-x^2}{4Dt})dx=2\sqrt{\pi Dt}$$

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

(4) Reflection at a boundary (e.g. metal coated with oxides)



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

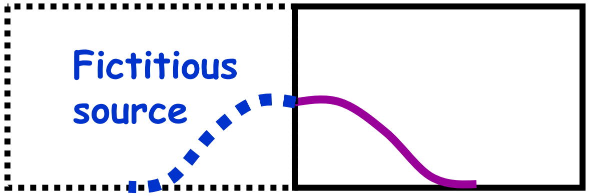
- * Reflection and superposition are mathematically sound
- * Linear sum of the two solutions is itself a solution

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

Superposition and Reflection

$$\frac{\partial C}{\partial x}\Big|_{x=0} = 0$$

$$\equiv$$



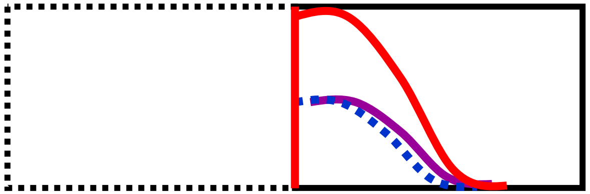
$$C(x,t) = \frac{S'}{2\sqrt{\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right) \quad x > 0$$

$$+$$

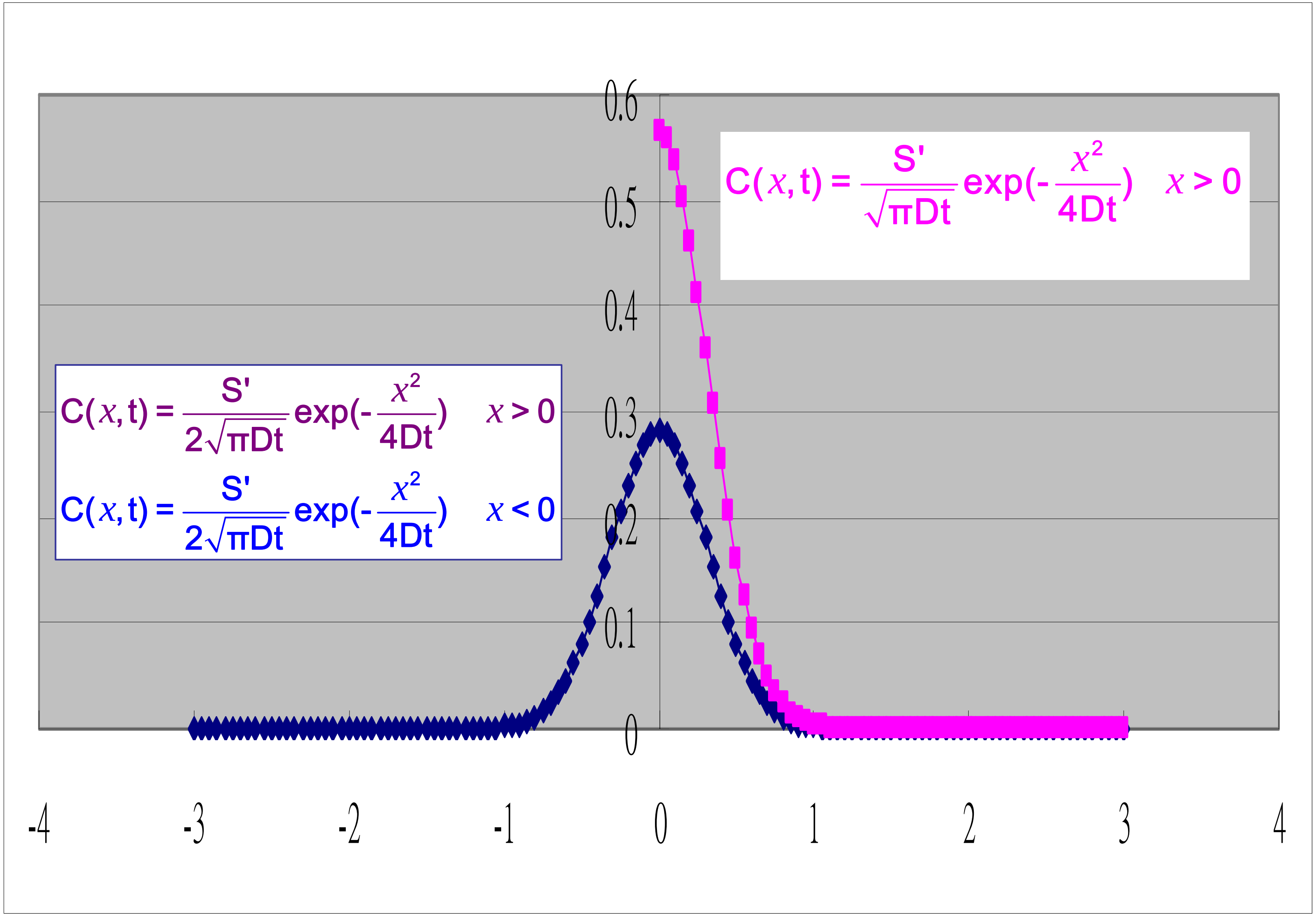
$$C(x,t) = \frac{S'}{2\sqrt{\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right) \quad x < 0$$

$$\equiv$$

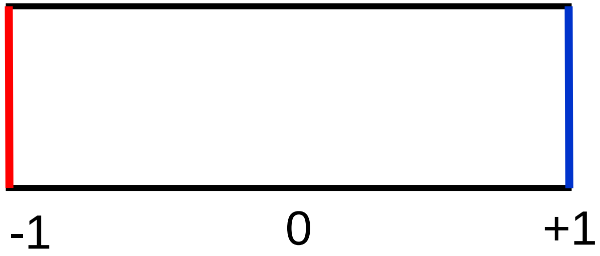
$$=$$



$$C(x,t) = \frac{S'}{\sqrt{\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right) \quad x > 0$$


$C(x,t) = \frac{S'}{\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt}) \quad x > 0$
$C(x,t) = \frac{S'}{2\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt}) \quad x > 0$
$C(x,t) = \frac{S'}{2\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt}) \quad x < 0$
0.6
0.5
0.4
0.3
0.2
0.1
0
-4
-3
-2
-1
0
1
2
3
4

Superposition and Reflection



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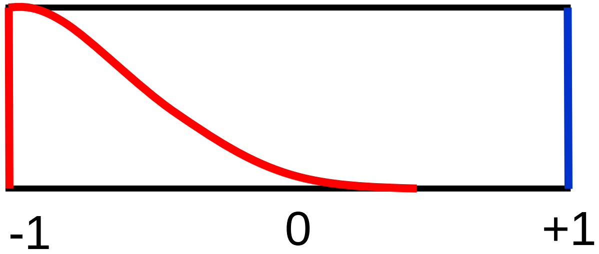
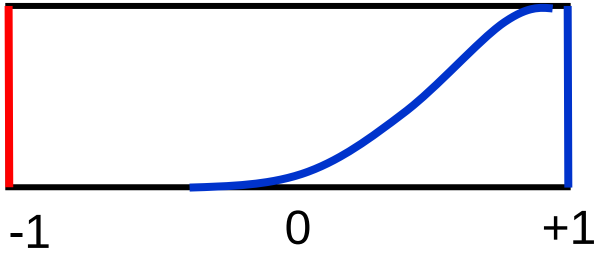


$$C(x,t) = \frac{S'}{\sqrt{\pi D t}} \exp\left(-\frac{(x+1)^2}{4Dt}\right)$$

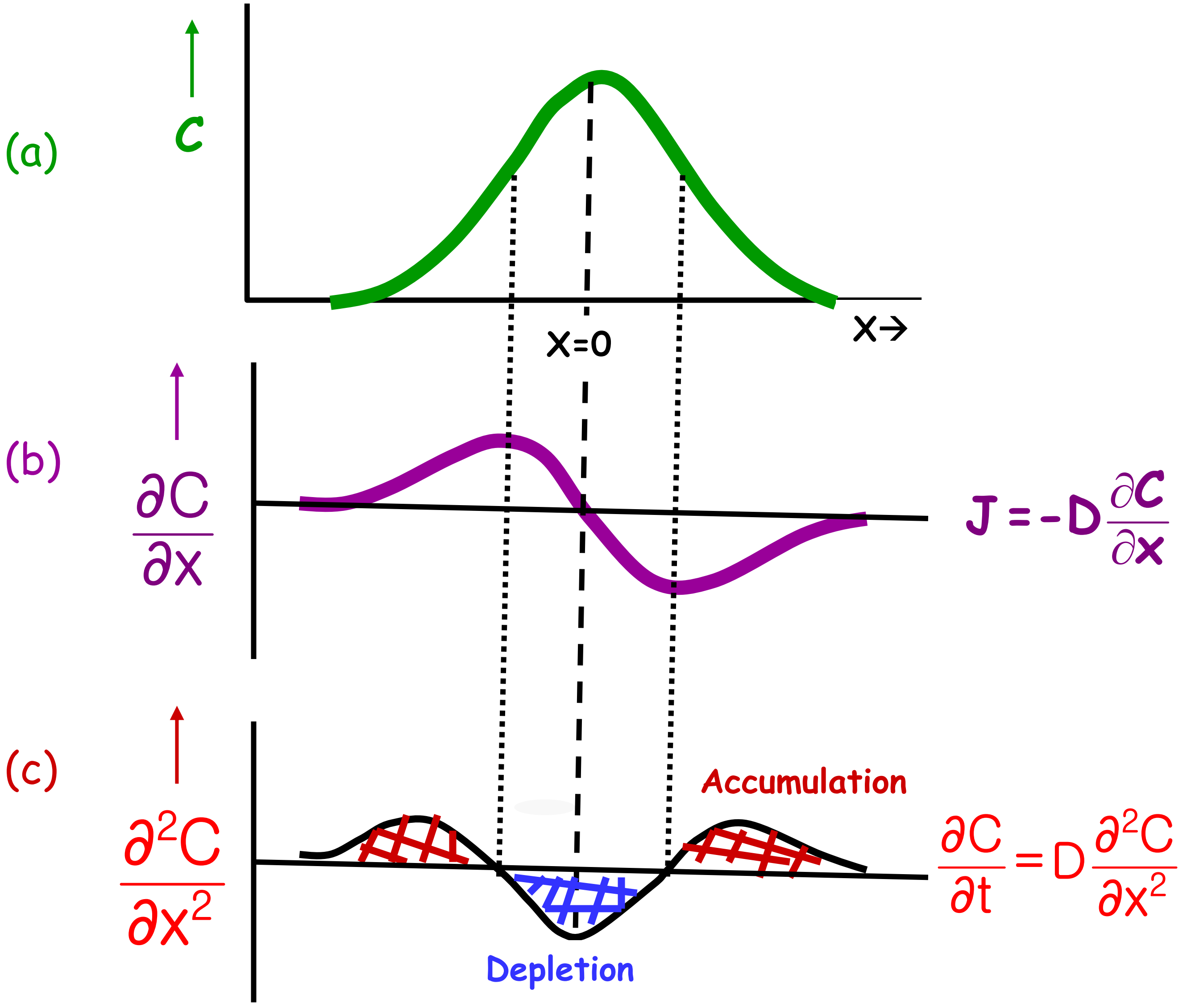
+



$$C(x,t) = \frac{S'}{\sqrt{\pi D t}} \exp\left(-\frac{(x-1)^2}{4Dt}\right)$$

$$C(x,t) = C(x,t) + C(x,t) = \frac{S'}{\sqrt{\pi D t}}\left[\exp\left(-\frac{(x+1)^2}{4Dt}\right) + \exp\left(-\frac{(x-1)^2}{4Dt}\right)\right]$$

Thin Film Solution

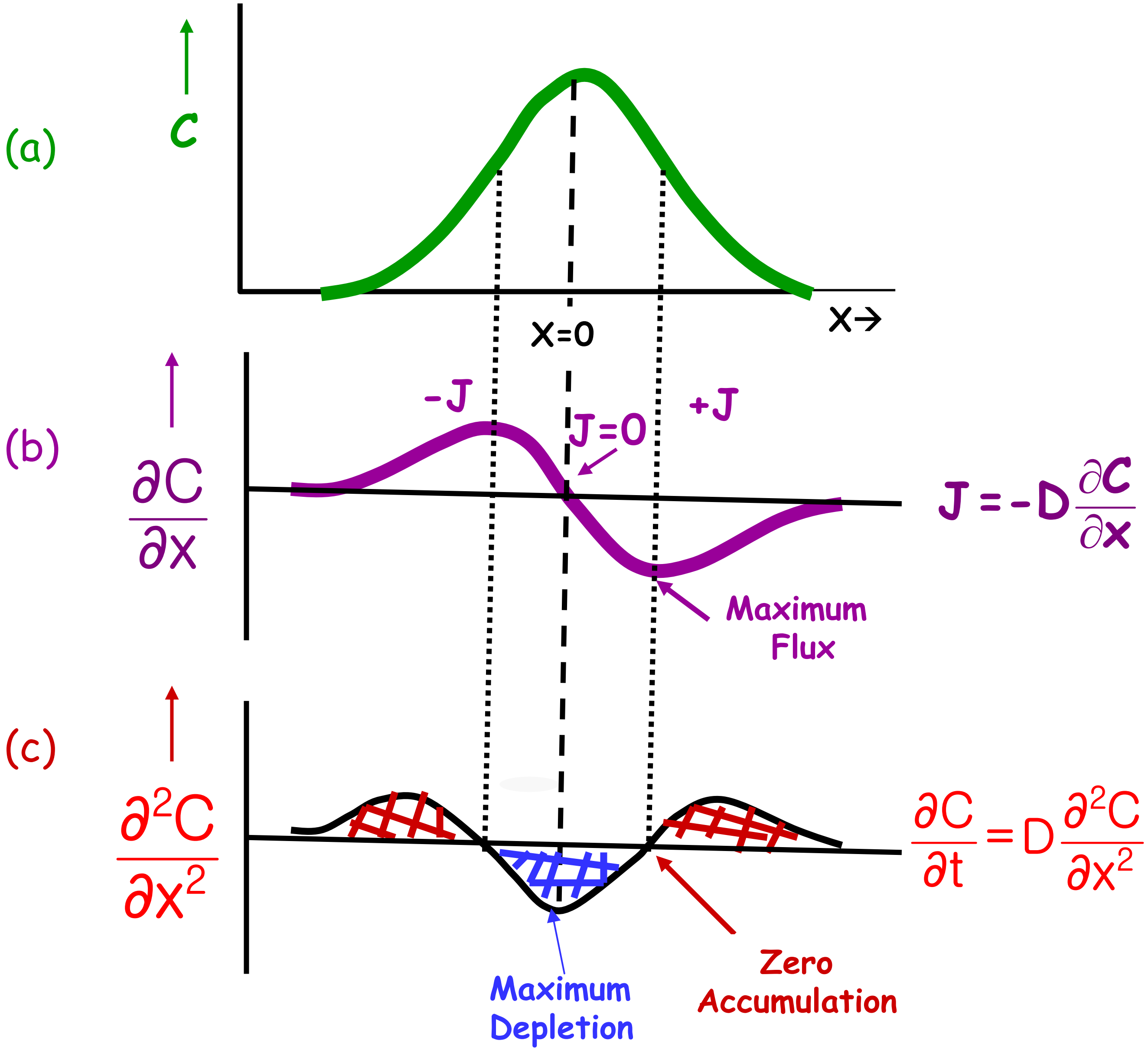


$$J = -D\frac{\partial C}{\partial x}$$

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

* Please derive (b) and (c)

Thin Film Solution



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

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

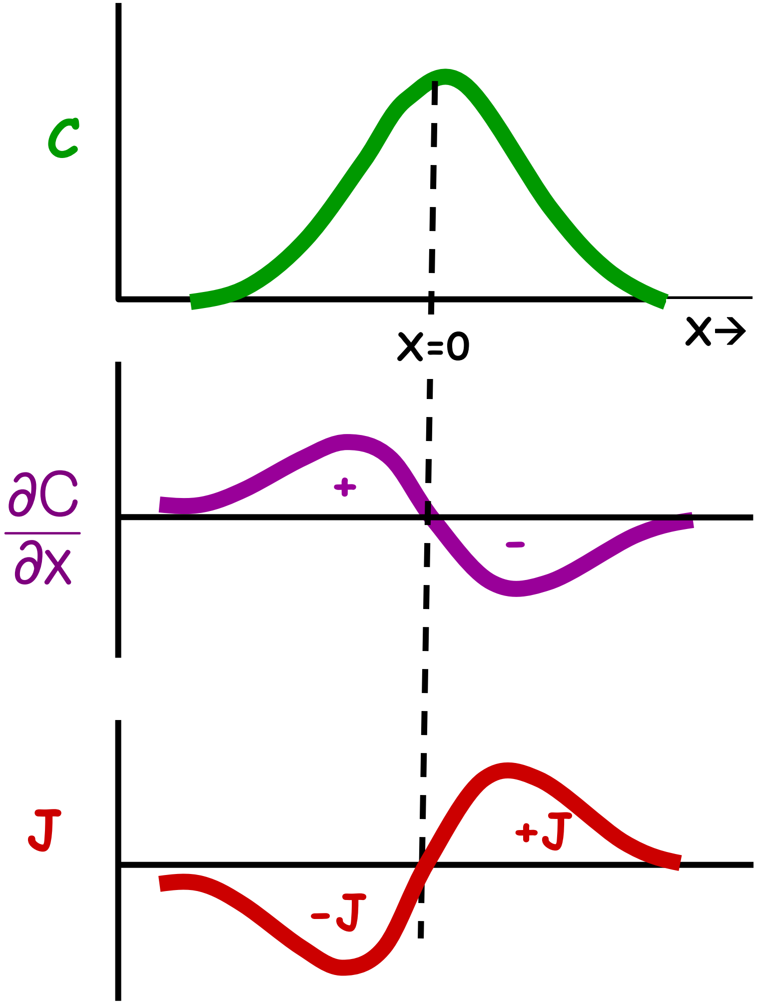
Thin Film Solution

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

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

$$x < 0 \qquad \frac{\partial C}{\partial x} > 0 \qquad J < 0$$

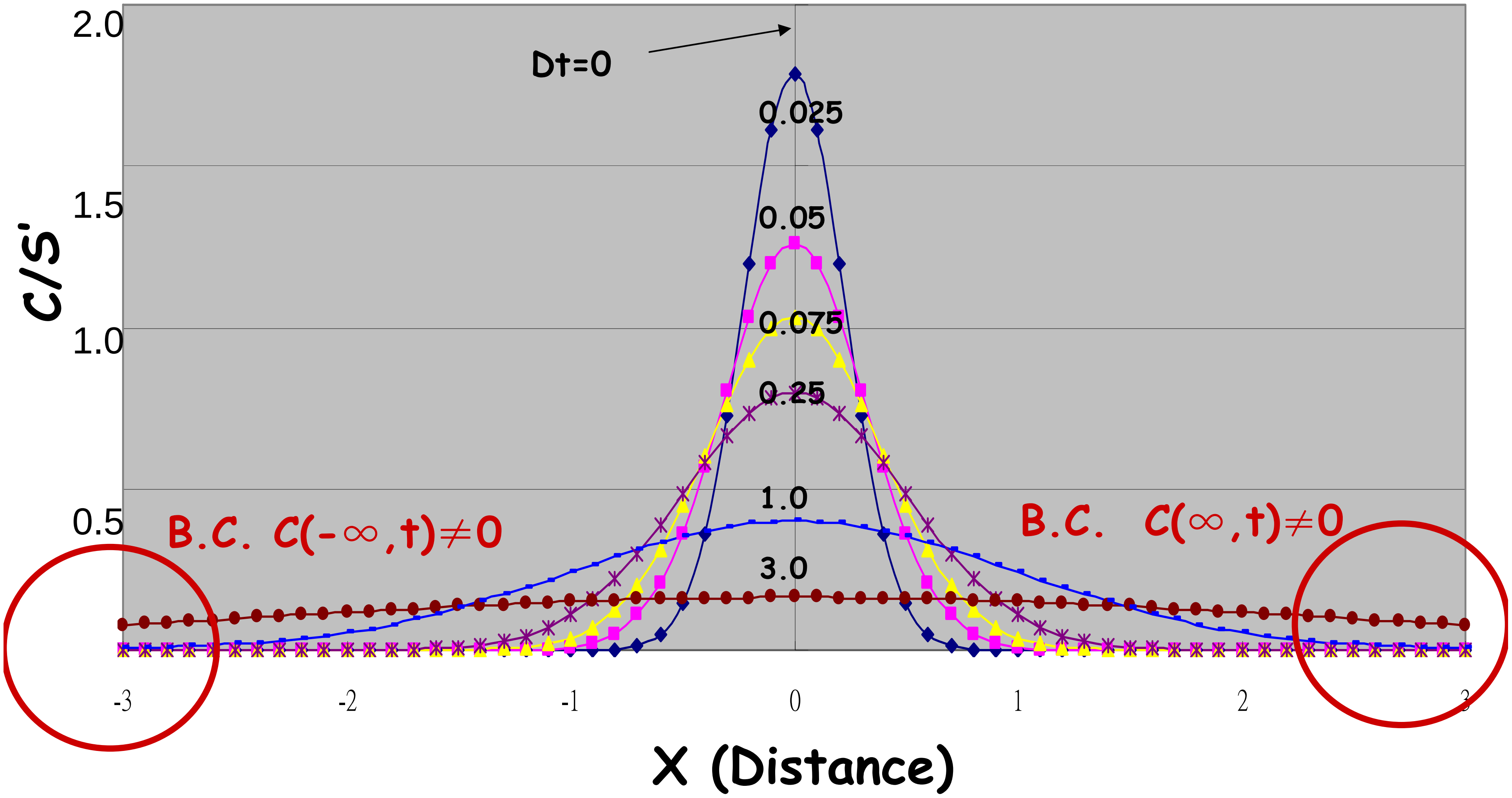
$$x > 0 \qquad \frac{\partial C}{\partial x} < 0 \qquad J > 0$$



Flux to the left is negative
Flux to the right is positive

Leak Test

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

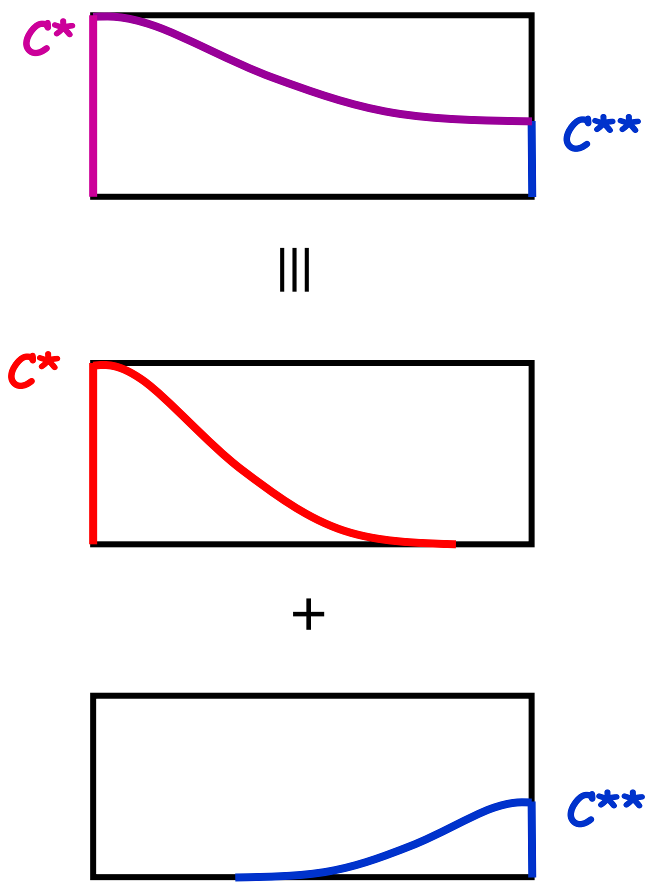


B.C. C(-∞,t)≠0

B.C. C(∞,t)≠0

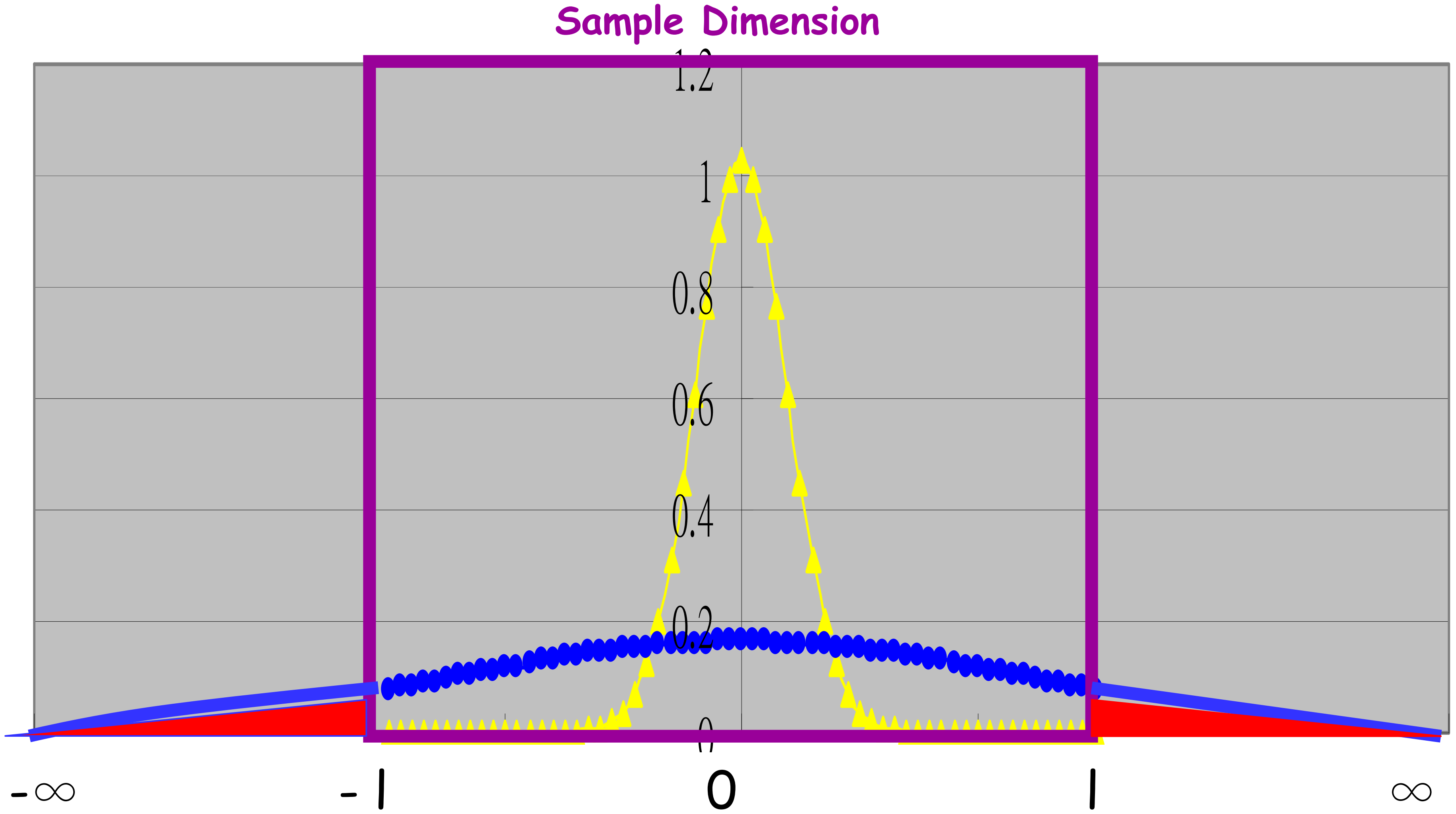
Leak Test

(Superposition and Reflection)



Concentration at a given point will be higher than that of "Infinite Case" because of reflection.

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.

Error Function

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

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

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

Complementary Error Function

$$1 - erf(z) = erfc(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty \exp(-u^2)du$$

$$\text{Small} \quad z \rightarrow erf(z) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n z^{2n+1}}{(2n+1)n!}$$

$$\text{Large} \quad z \quad (z \geq 3) \rightarrow erfc(z) = \frac{\exp(-z^2)}{\sqrt{\pi}} (\frac{1}{z} - \frac{1}{2z^3} + \ldots\ldots\ldots)$$

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

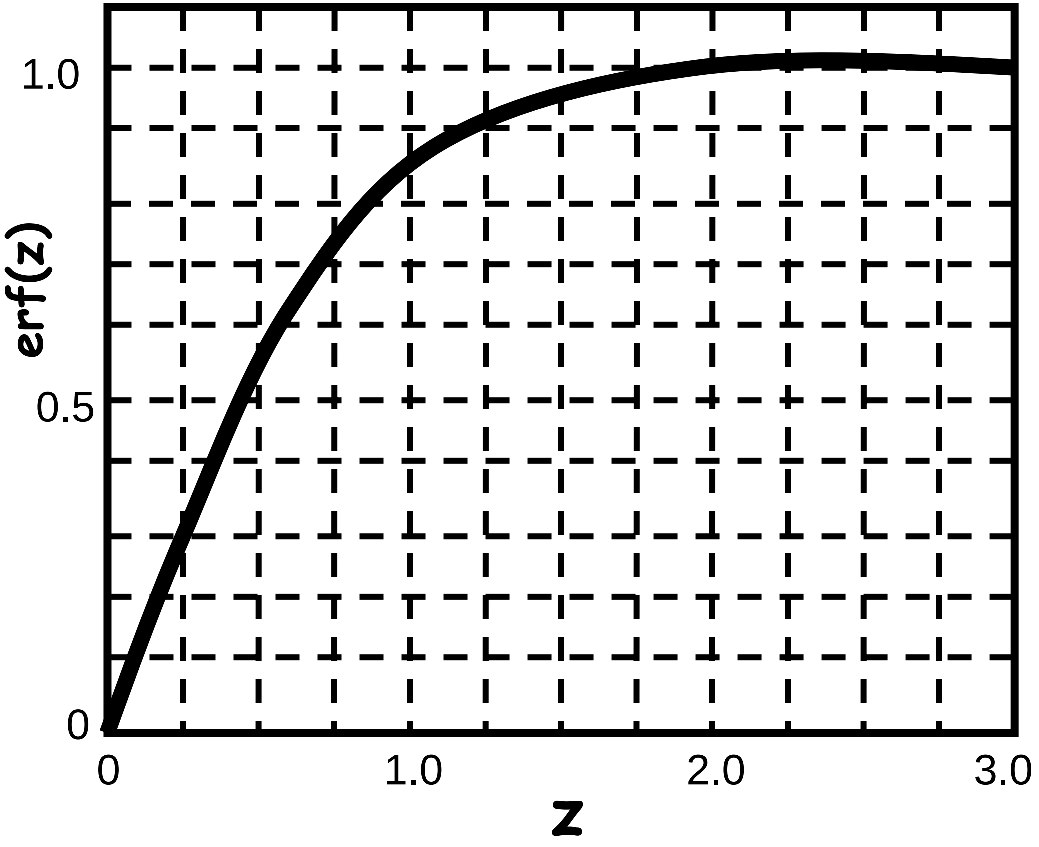
$$\frac{d^2(erf(z))}{dz^2} = -\frac{4z}{\sqrt{\pi}} \exp(-z^2)$$

Error Function

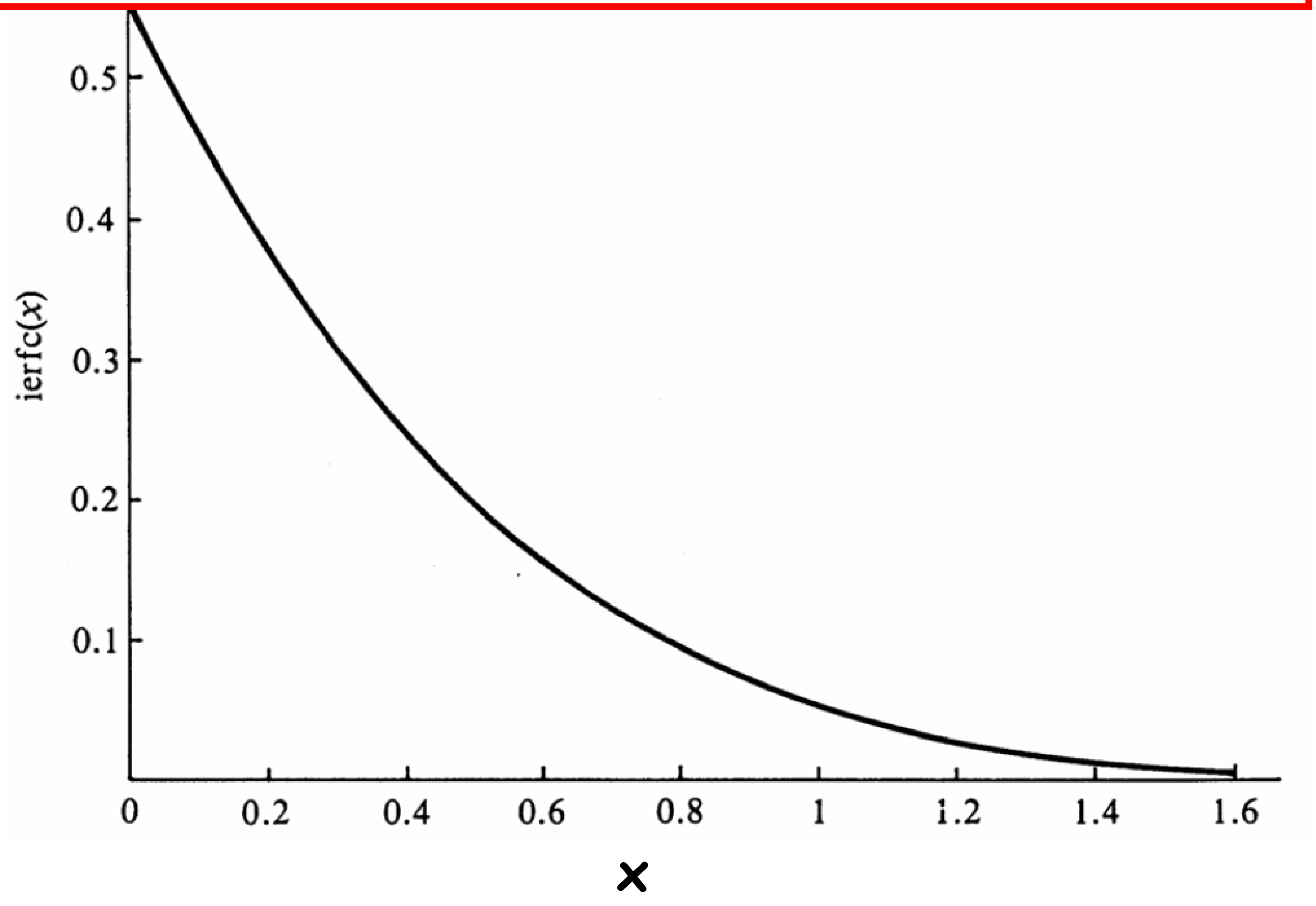
$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2) du$$

Table 1-1. The Error Function

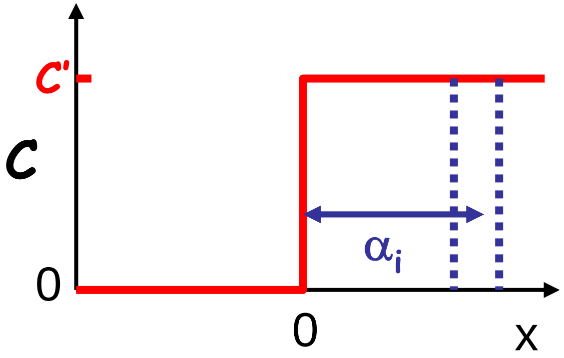
z	erf(z)	z	erf(z)
0	0	0.85	0.7707
0.025	0.0282	0.90	0.7969
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	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



$$ierfc(x) = \int_x^\infty erfc(u)du = \frac{1}{\sqrt{\pi}}\exp(-x^2) - x[1 - erf\,(x)]$$



Solution for a pair of Semi-infinite Solids



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

$$C(x,0)=C' \qquad x>0$$

$$B.C.\quad C(\infty,t)=C'$$

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

Superposition

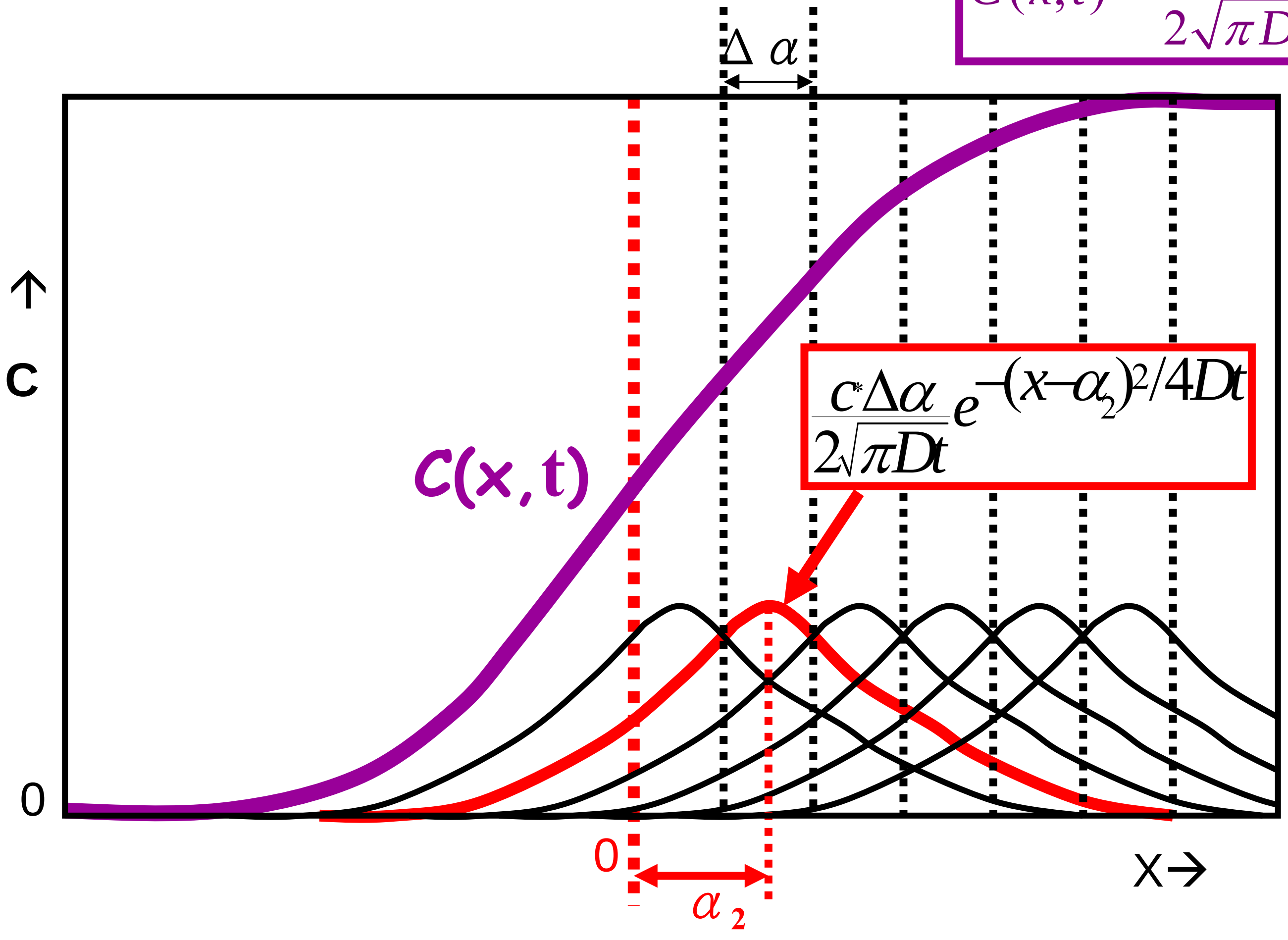
(1) No interaction from adjacent slabs

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

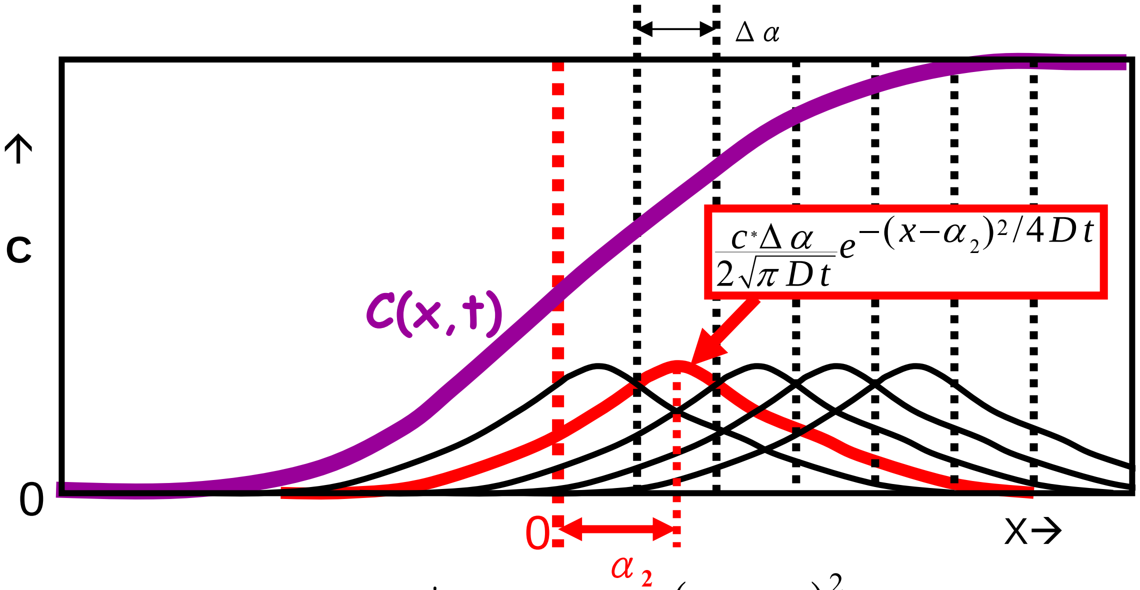
$$C(x,t) = \frac{C'}{2\sqrt{\pi Dt}} \sum_{i=1}^{n} \Delta\alpha \exp\left(-\frac{(x-\alpha_i)^2}{4Dt}\right)$$

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

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



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



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

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

Sum the solution of all thin slabs

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

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

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

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

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

By definition of error function

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

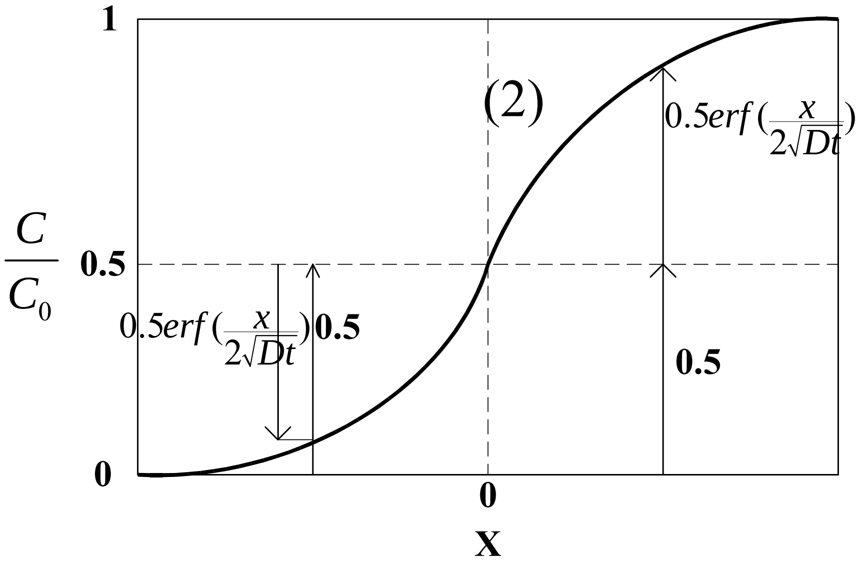
$$erf(\infty) = 1 \quad erf(0) = 0$$

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

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

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

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



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

(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.)

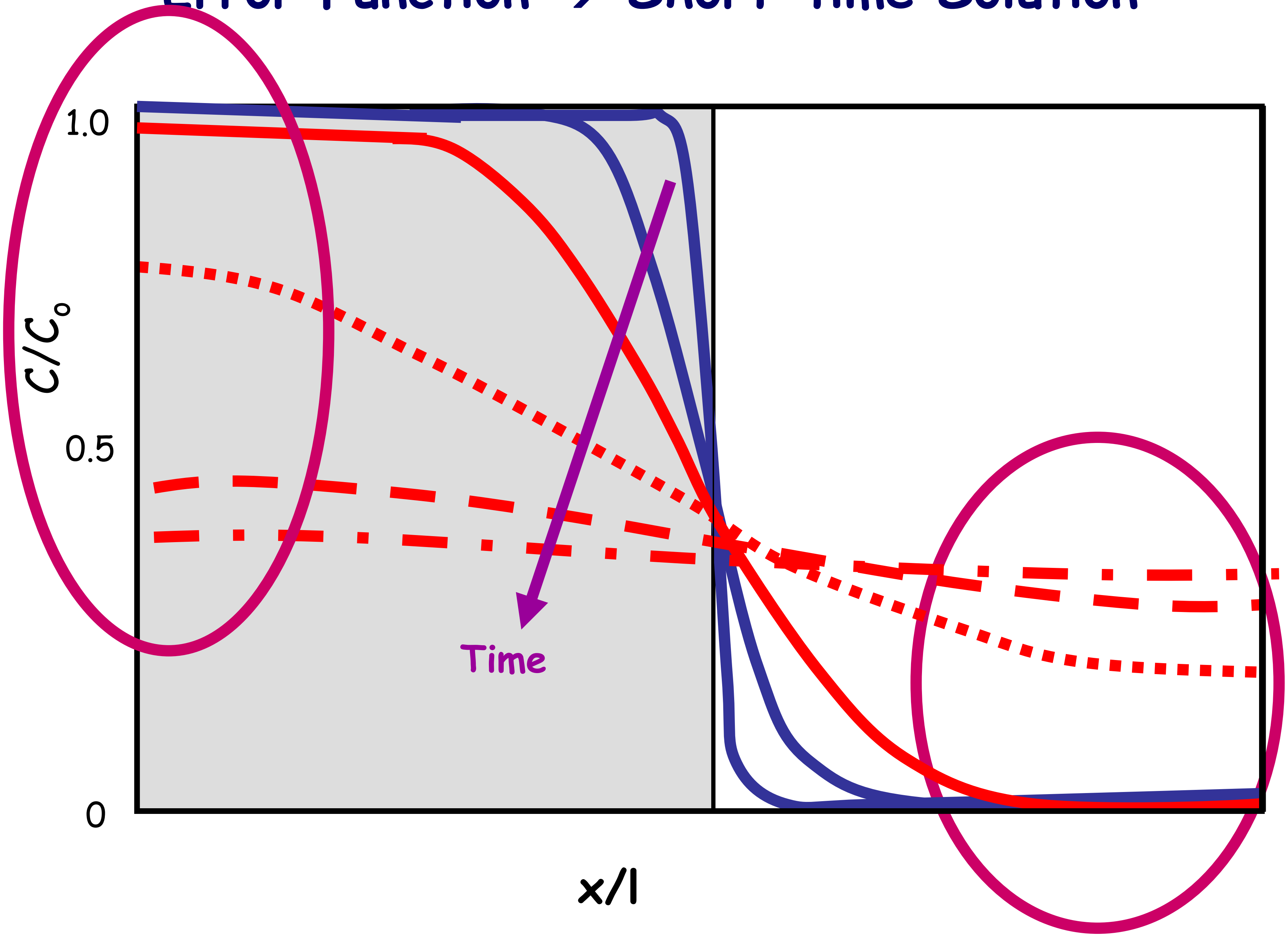
(4) $J_{x=0} = -D\frac{\partial C}{\partial x}|_{x=0} = -\frac{C_0}{2}\sqrt{\frac{D}{\pi t}}$ (-:to the left)

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

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

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.

Error Function → Short-time Solution

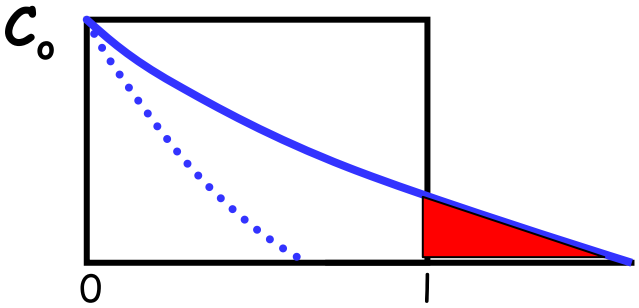


The above analyses are only good for an "**Infinite Slab**".
If it is not infinite, the diffusion will be reflected
back into the specimen when it reaches the end of the bar, and
concentration in that region will be higher than the above solution.

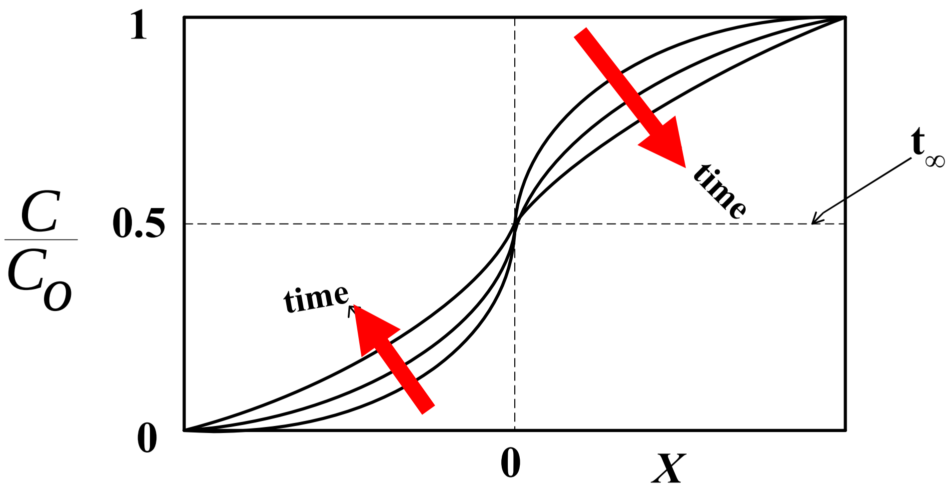
Q: How long is long enough to be considered infinite?

Leak Test

Arbitrarily taking 0.1% as a sufficiently insignificant concentration



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



Using B.C. to solve the problem

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

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

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

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

Examples

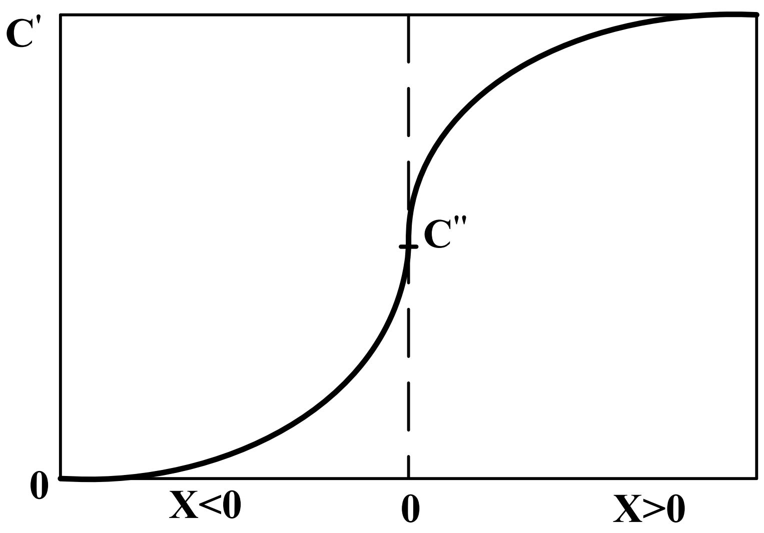
(1) if $C(0, t) = 0$ $\qquad C(x,t) = C' erf\left(\frac{x}{2\sqrt{Dt}}\right)$

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

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

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

(next page)



B.C.

$$C(0,t) = C''$$

$$C(\infty,t) = C'$$

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

$x < 0$

$$C(x,t) = A + Berf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C(0,t) = C'' = A$$

$$C(-\infty,t) = 0 \rightarrow A = B = C''$$

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

$x > 0$

$$C(0,t) = C'' = A$$

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

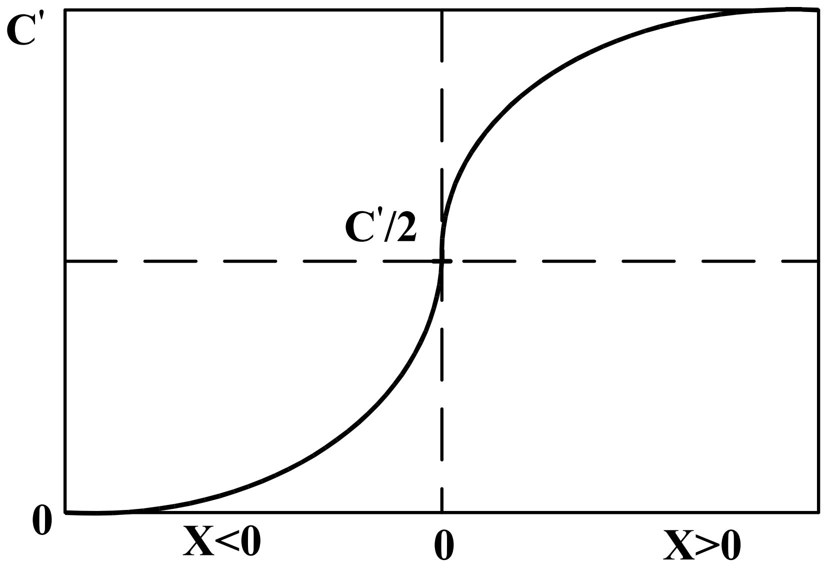
$$C(x,t) = C'' + (C' - C'')erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$if \quad C'' = \frac{C'}{2}$$

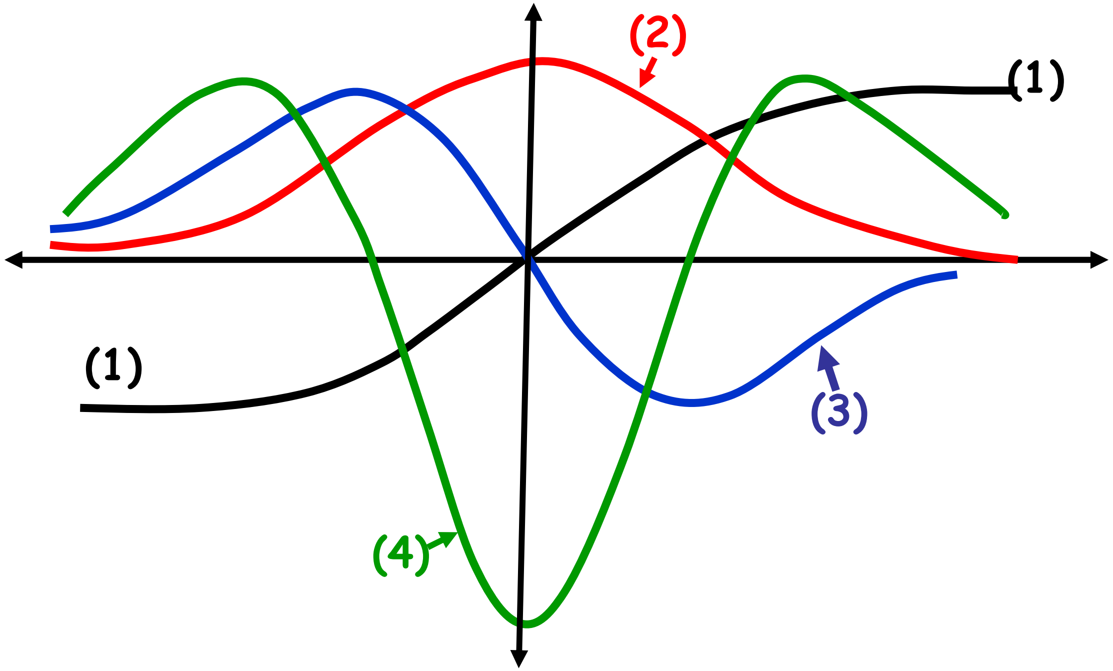
$$x < 0, \quad C(x,t) = \frac{C'}{2}(1 + erf(\frac{x}{2\sqrt{Dt}}))$$

$$x > 0, \quad C(x,t) = \frac{C'}{2} + (C' - \frac{C'}{2})erf(\frac{x}{2\sqrt{Dt}})$$

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



Error Function & its Derivatives



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

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

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

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

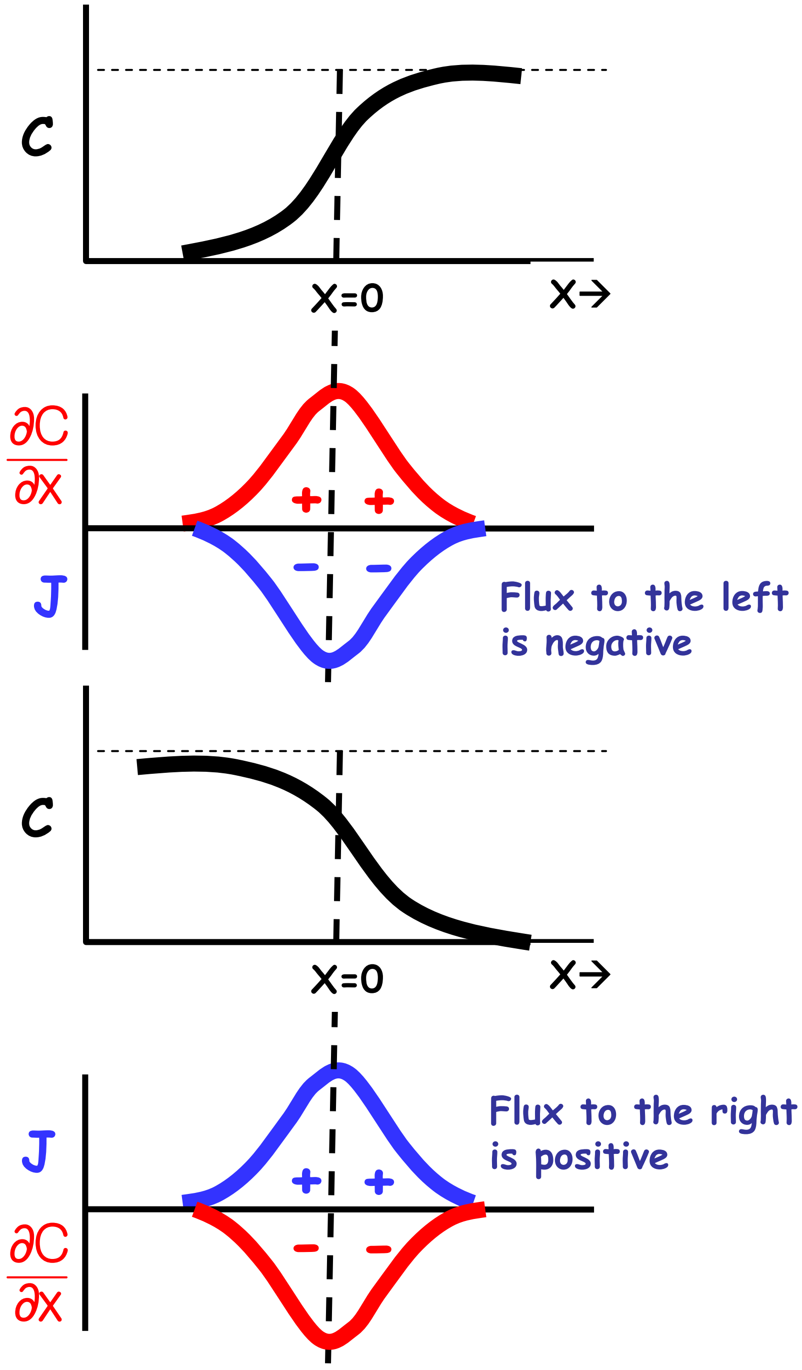
Note: (2) is the thin film solution

Semi-infinite Solution

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

$$\frac{\partial C}{\partial x} = \frac{B}{\sqrt{\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right)$$

$$B > 0 \qquad \frac{\partial C}{\partial x} > 0 \qquad J < 0$$

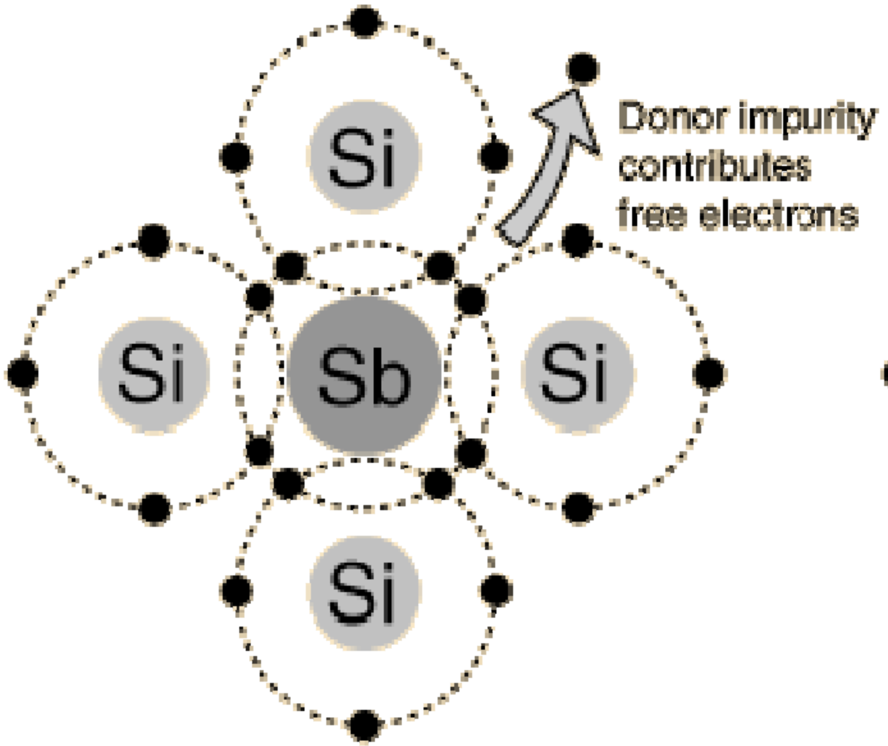


Flux to the left
is negative

Flux to the right
is positive

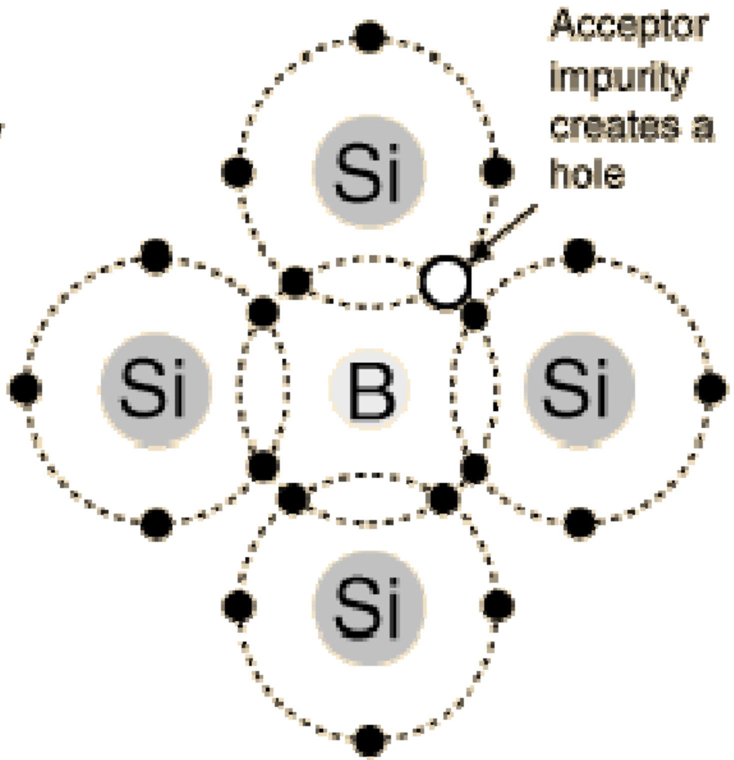
Doping of Semiconductors

n-type



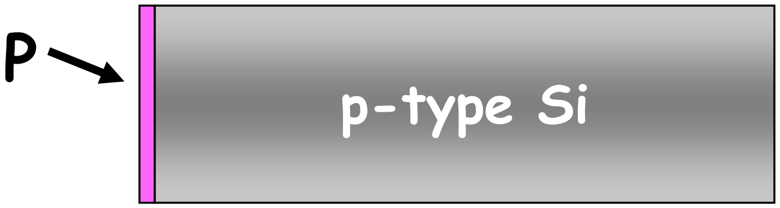
Donors: Sb, As, P

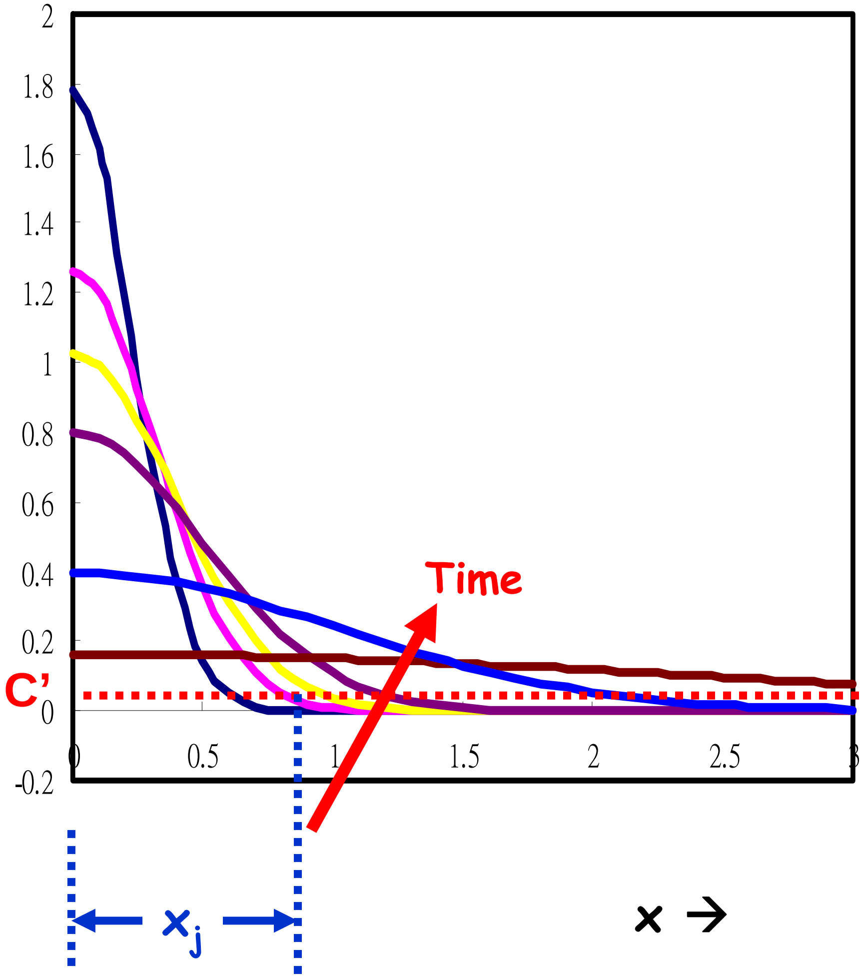
p-type



Acceptors: B, Al, Ga

Diffusion from a Limited Source (thin film)





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

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

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

:Gaussian function

Example: p-n junction

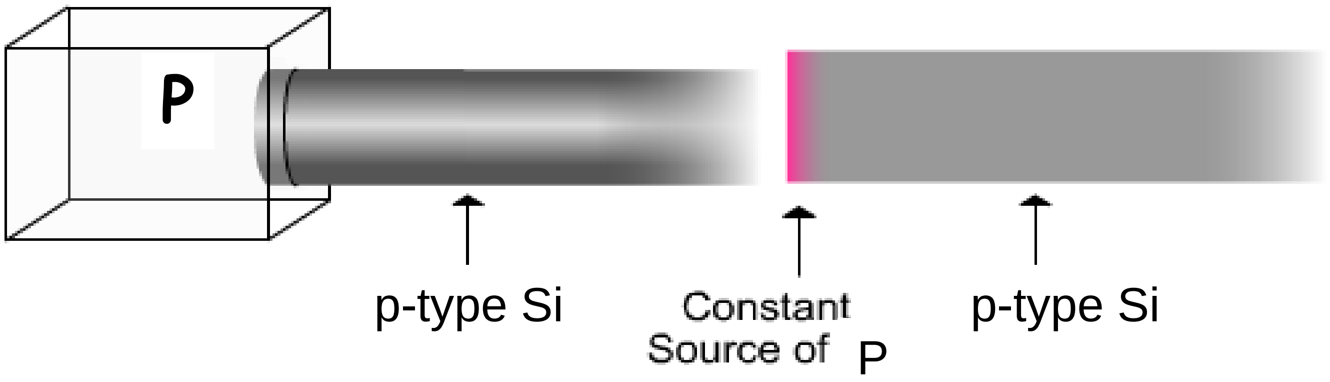
C'= Background Concentration

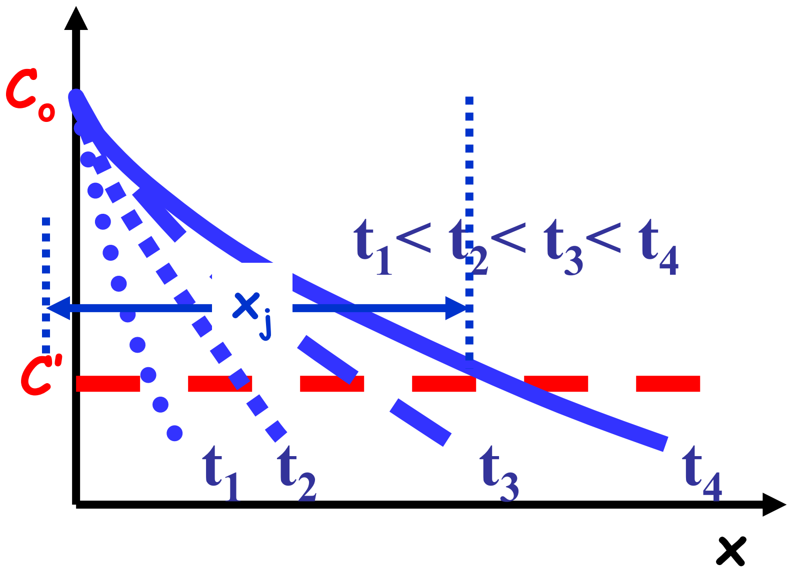
$$C > C' \quad (p \rightarrow n \;\; or \;\; n \rightarrow p)$$

$$C' = \frac{S_0}{\sqrt{\pi D t}} \exp\left(-\frac{{x_j}^2}{4Dt}\right)$$

x_j = junction distance

Diffusion from a Constant Source





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

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

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

: the amount of dopant entering the base

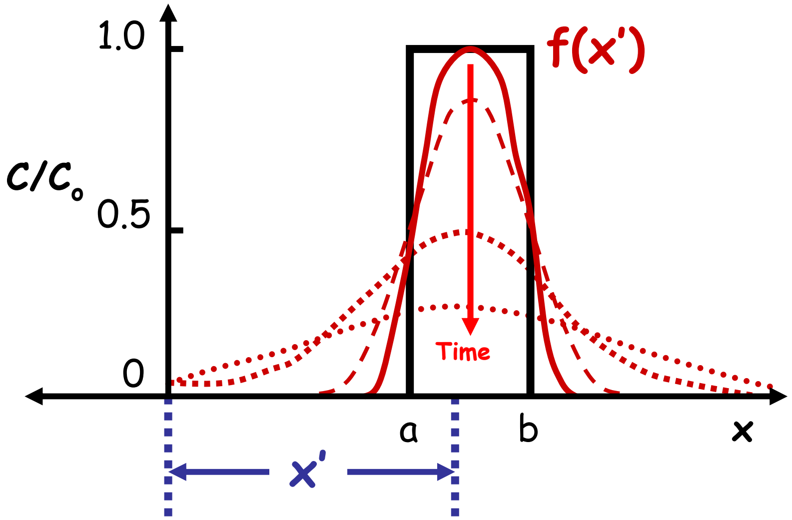
Example: p-n junction

C'= Background Concentration

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

$$C' = C_0 \, erfc(\frac{x_j}{2\sqrt{Dt}});$$ x_j : junction distance

Example



$$I.C.\quad C(x,0)=f(x')\quad a<x<b$$

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

$$C(x,t)=\lim_{\Delta x'\to 0}\sum_{n=1}^{\infty}\frac{f(x')\Delta x'}{2\sqrt{\pi Dt}}\exp\left(-\frac{(x-x')^2}{4Dt}\right)$$

$f(x')$: initial distribution of concentration

when $\Delta x' \to 0$

$$C(x,t)=\int_{-\infty}^{\infty}\frac{f(x')}{2\sqrt{\pi Dt}}\exp\left(-\frac{(x-x')^2}{4Dt}\right)dx'$$

$$=\left(\int_{-\infty}^{a}+\int_{a}^{b}+\int_{b}^{\infty}\right)\left(\frac{f(x')}{2\sqrt{\pi Dt}}\exp\left(-\frac{(x-x')^2}{4Dt}\right)\right)dx'$$

$$=\int_{a}^{b}\frac{f(x')}{2\sqrt{\pi Dt}}\exp\left(-\frac{(x-x')^2}{4Dt}\right)dx'$$

when $f(x')=C_i$

$$C(x,t)=\int_{a}^{b}\frac{C_i}{2\sqrt{\pi Dt}}\exp\left(-\frac{(x-x')^2}{4Dt}\right)dx'$$

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

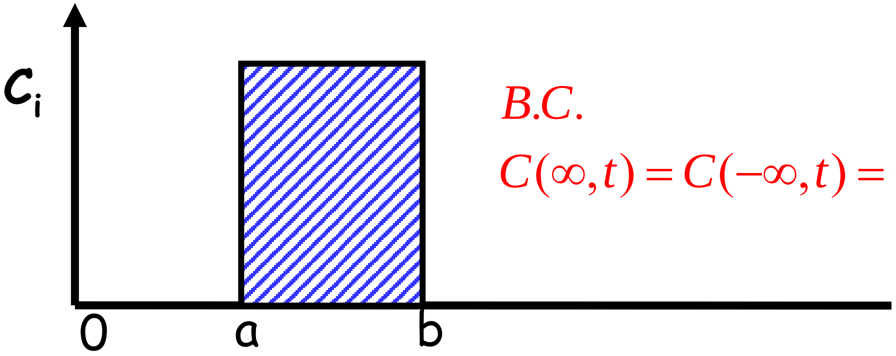
$$x^{'}=a \quad u=\frac{x-a}{2\sqrt{Dt}}, \quad x^{'}=b \quad u=\frac{x-b}{2\sqrt{Dt}}$$

$$C(x,t)=\int_{\frac{x-a}{2\sqrt{Dt}}}^{\frac{x-b}{2\sqrt{Dt}}}\frac{C_i}{2\sqrt{\pi Dt}}\exp(-u^2)(-2\sqrt{Dt})du$$

$$=-\frac{C_i}{\sqrt{\pi}}\int_{\frac{x-a}{2\sqrt{Dt}}}^{\frac{x-b}{2\sqrt{Dt}}}\exp(-u^2)du$$

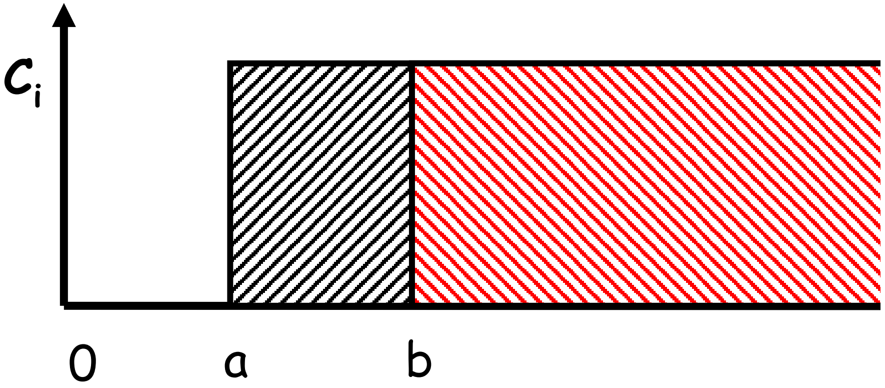
$$=-\frac{C_i}{\sqrt{\pi}}\frac{\sqrt{\pi}}{2}[erf(\frac{x-b}{2\sqrt{Dt}})-erf(\frac{x-a}{2\sqrt{Dt}})]$$

$$=\frac{C_i}{2}[erf(\frac{x-a}{2\sqrt{Dt}})-erf(\frac{x-b}{2\sqrt{Dt}})]$$



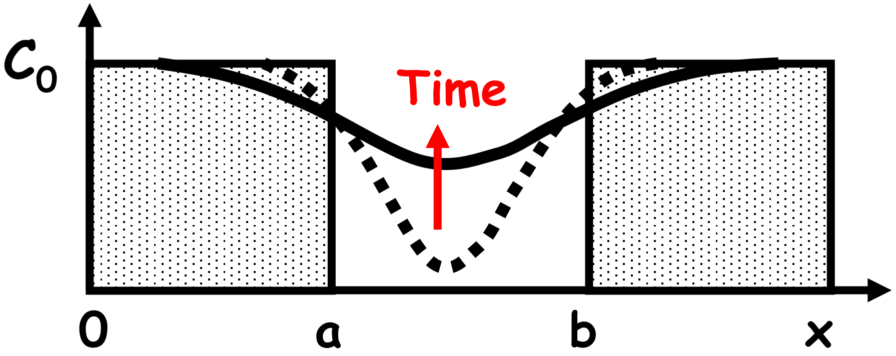
B.C.

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

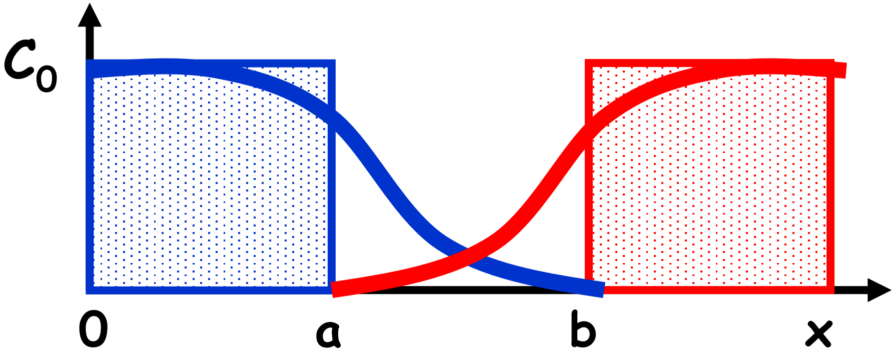


$$\frac{C_i}{2} erf\left(\frac{x-a}{2\sqrt{Dt}}\right) - \frac{C_i}{2} erf\left(\frac{x-b}{2\sqrt{Dt}}\right)$$

$$= \frac{C_i}{2}\left[erf\left(\frac{x-a}{2\sqrt{Dt}}\right) - erf\left(\frac{x-b}{2\sqrt{Dt}}\right)\right]$$



$$\equiv$$



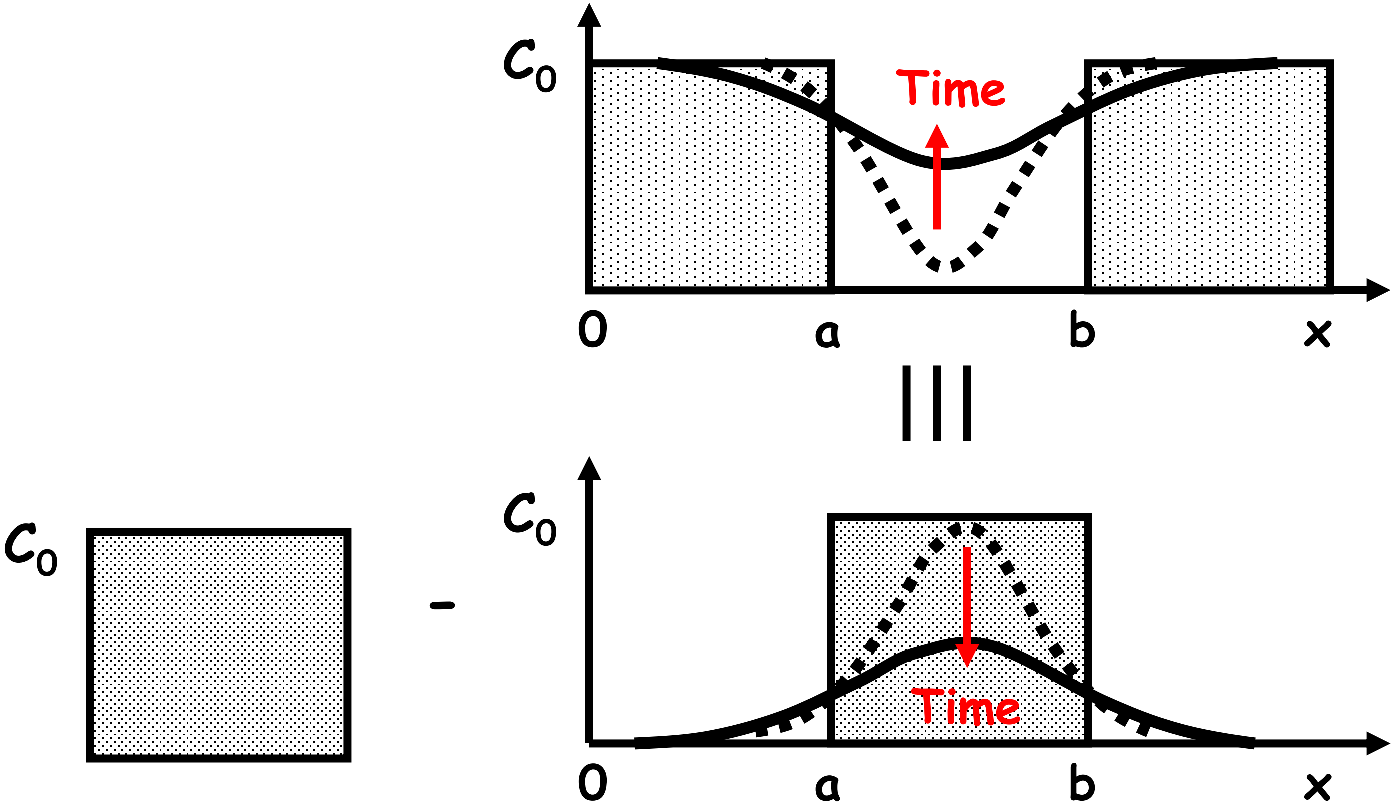
$$C(x,t)=\frac{C_o}{2}[1+erf(\frac{x-b}{2\sqrt{Dt}})]$$

+

$$C(x,t)=\frac{C_o}{2}[1-erf(\frac{x-a}{2\sqrt{Dt}})]$$

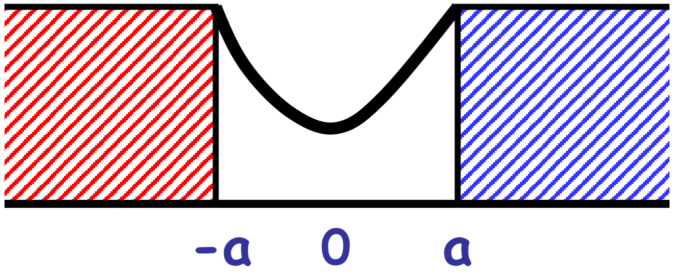
$$=$$

$$C(x,t)=C_o-\frac{C_o}{2}[erf(\frac{x-a}{2\sqrt{Dt}})-erf(\frac{x-b}{2\sqrt{Dt}})]$$



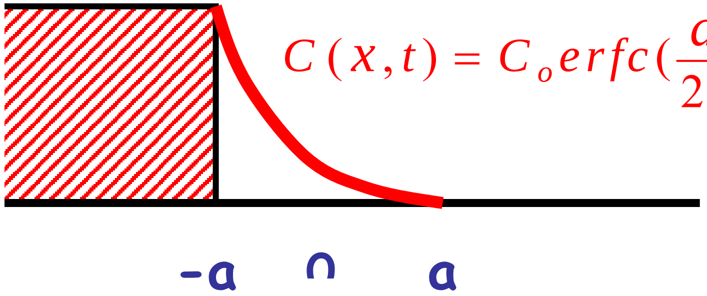
$$C(x,t) = C_o - \frac{C_o}{2}\left[erf\left(\frac{x-a}{2\sqrt{Dt}}\right) - erf\left(\frac{x-b}{2\sqrt{Dt}}\right)\right]$$

B.C. $C(-a,t)=C(a,t)=C_o$



|||

(a)

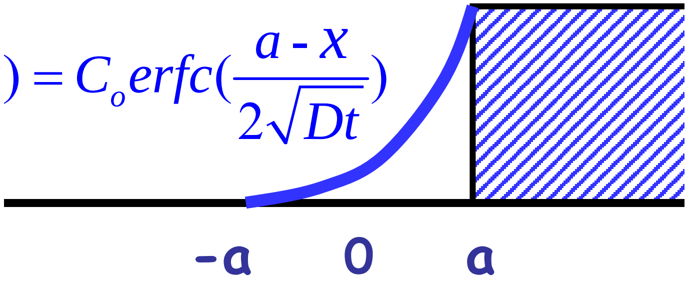


$$C(x,t) = C_o erfc(\frac{a+x}{2\sqrt{Dt}})$$

+

(b)

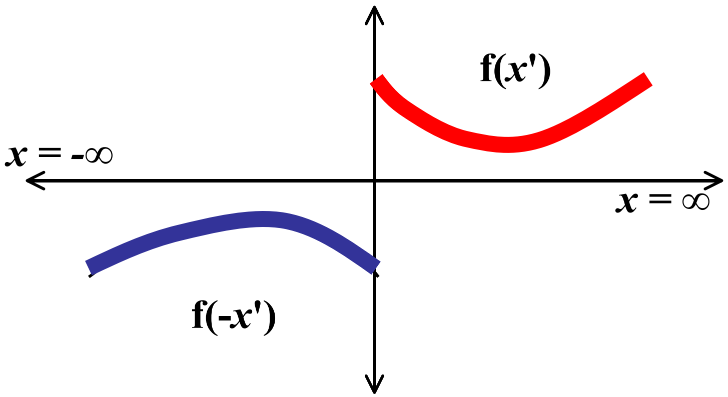
$$C(x,t) = C_o erfc(\frac{a-x}{2\sqrt{Dt}})$$



$$(a)+(b) = C(x,t) = C_o[erfc(\frac{a-x}{2\sqrt{Dt}}) + erfc(\frac{a+x}{2\sqrt{Dt}})]$$

Semi-infinite

(1)



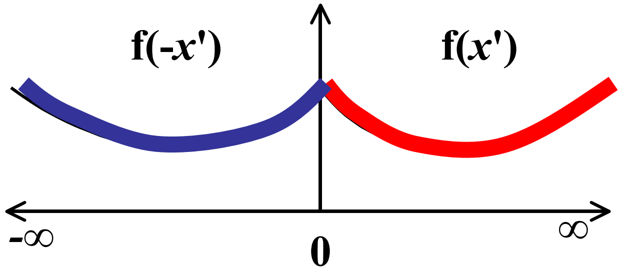
$$C(x,0) = f(x')$$

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

$$f(-x') = -f(x') \leftarrow odd\ \ function$$

$$C(x,t) = \int_{-\infty}^{0} \frac{f(-x')}{2\sqrt{\pi Dt}} \exp(-\frac{(x-x')^2}{4Dt})dx' + \int_{0}^{\infty} \frac{f(x')}{2\sqrt{\pi Dt}} \exp(-\frac{(x-x')^2}{4Dt})dx'$$

(2)

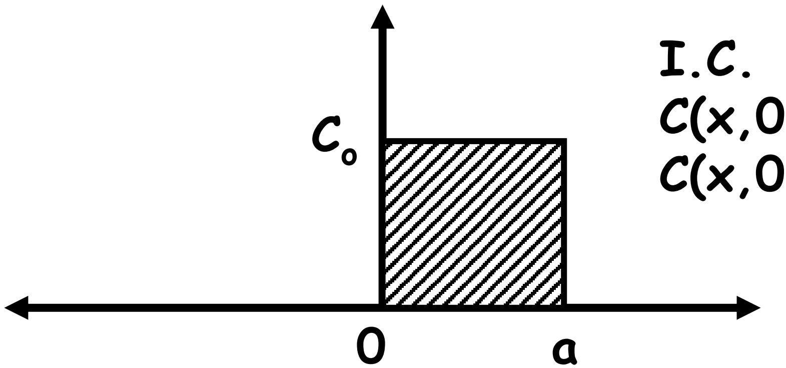


$$C(x,0) = f(x')$$

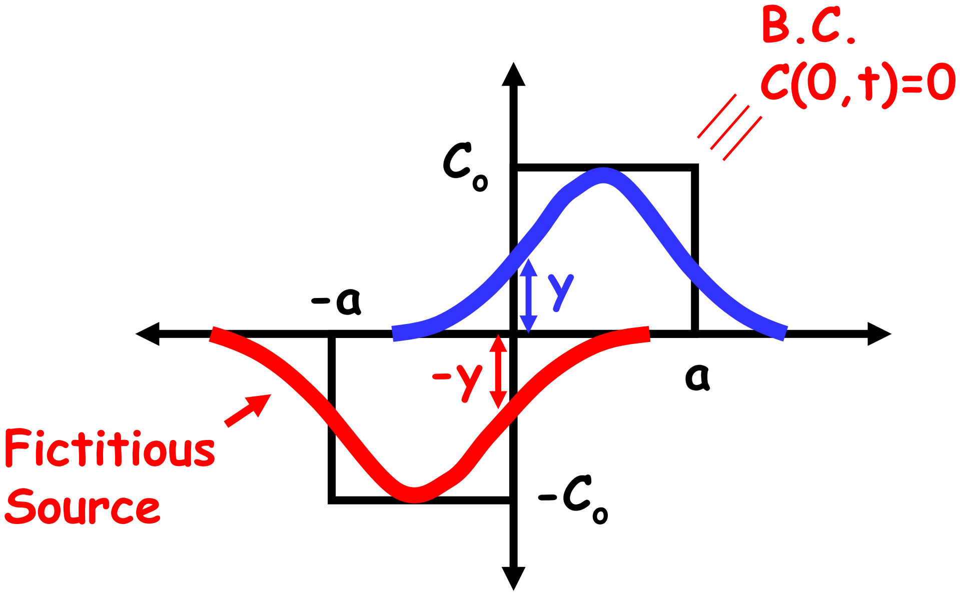
$$\frac{\partial C}{\partial x}(0,t) = 0$$

$$f(x') = f(-x') \leftarrow even\ \ function$$

$$C(x,t) = \int_{-\infty}^{0} \frac{f(-x')}{2\sqrt{\pi Dt}} \exp(-\frac{(x-x')^2}{4Dt})dx' + \int_{0}^{\infty} \frac{f(x')}{2\sqrt{\pi Dt}} \exp(-\frac{(x-x')^2}{4Dt})dx'$$



I.C.
$C(x,0)=C_o \quad 0 \le x \le a$
$C(x,0)=0 \quad x>a,\ x<0$



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

Fictitious Source

Equivalent I.C.

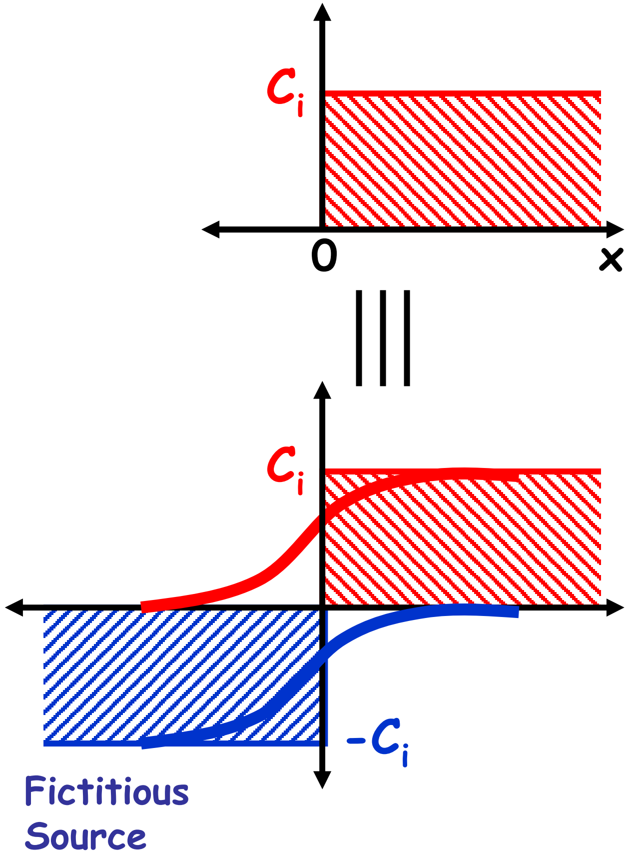
$C(x,0)=C_o \ 0 \le x \le a$
$C(x,0)=-C_o \ -a \le x \le 0$
$C(x,0)=0, x>a,\ x<-a$

$$C(x,t)=\frac{C_o}{2}[erf(\frac{x}{2\sqrt{Dt}})-erf(\frac{x-a}{2\sqrt{Dt}})]$$

$$+(-\frac{C_o}{2})[erf(\frac{-x}{2\sqrt{Dt}})-erf(\frac{-x-a}{2\sqrt{Dt}})]$$

$$=\frac{C_o}{2}[2erf(\frac{x}{2\sqrt{Dt}})-erf(\frac{x-a}{2\sqrt{Dt}})-erf(\frac{x+a}{2\sqrt{Dt}})]$$

Example



$I.C.$

$$C(x,0) = C_i \quad x > 0$$

$$C(x,0) = 0 \quad x < 0$$

$B.C.$

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

$$C(\infty,t) = C_i$$

$Equivalent \quad I.C.$

$$C(x,0) = C_i \quad x > 0$$

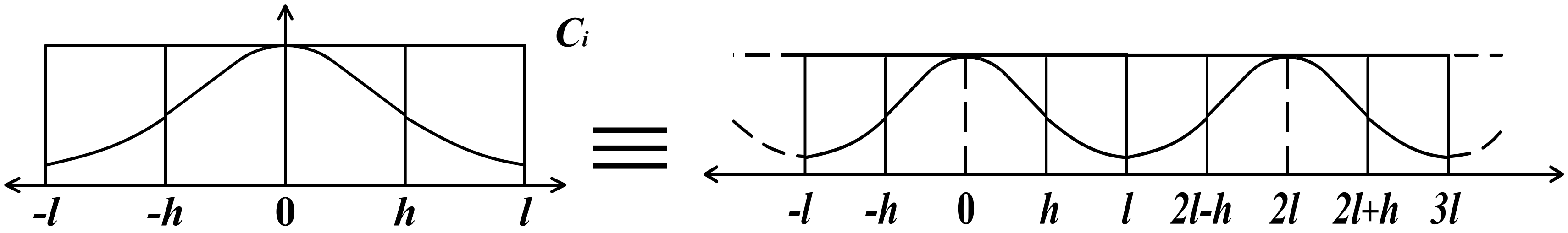
$$C(x,0) = -C_i \quad x < 0$$

$$C(x,t) = \int_{-\infty}^{0} \frac{f(x')}{2\sqrt{\pi D t}} \exp\left(-\frac{(x-x')^2}{4Dt}\right) dx' + \int_{0}^{\infty} \frac{f(x')}{2\sqrt{\pi D t}} \exp\left(-\frac{(x-x')^2}{4Dt}\right) dx'$$

$$f(x') = C_i, \quad x' > 0; \quad f(x') = -C_i \quad x' < 0$$

$$C(x,t) = C_i \, erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (x \geq 0)$$

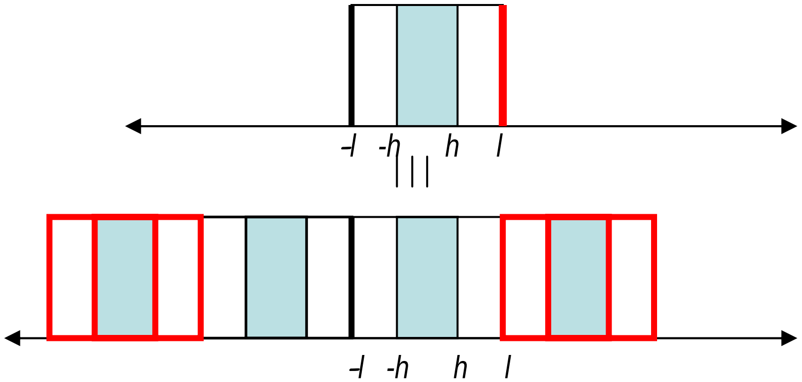
Example



I.C.

$$C(x,0)=C_i \quad -h \le x \le h$$

$$C(x,0)=0 \quad x<-h, x>h$$



B.C.

$$\frac{\partial C(x,t)}{\partial x}=0 \quad x=l, x=-l$$

Equivalent I.C.

$$C(x,0)=C_i \quad 2nl-h\le x\le 2nl+h\,, -\infty<n<\infty$$

$$C(x,t)=\int_{-\infty}^{\infty}\frac{f(x')}{2\sqrt{\pi Dt}}\exp(-\frac{(x-x')^2}{4Dt})dx'$$

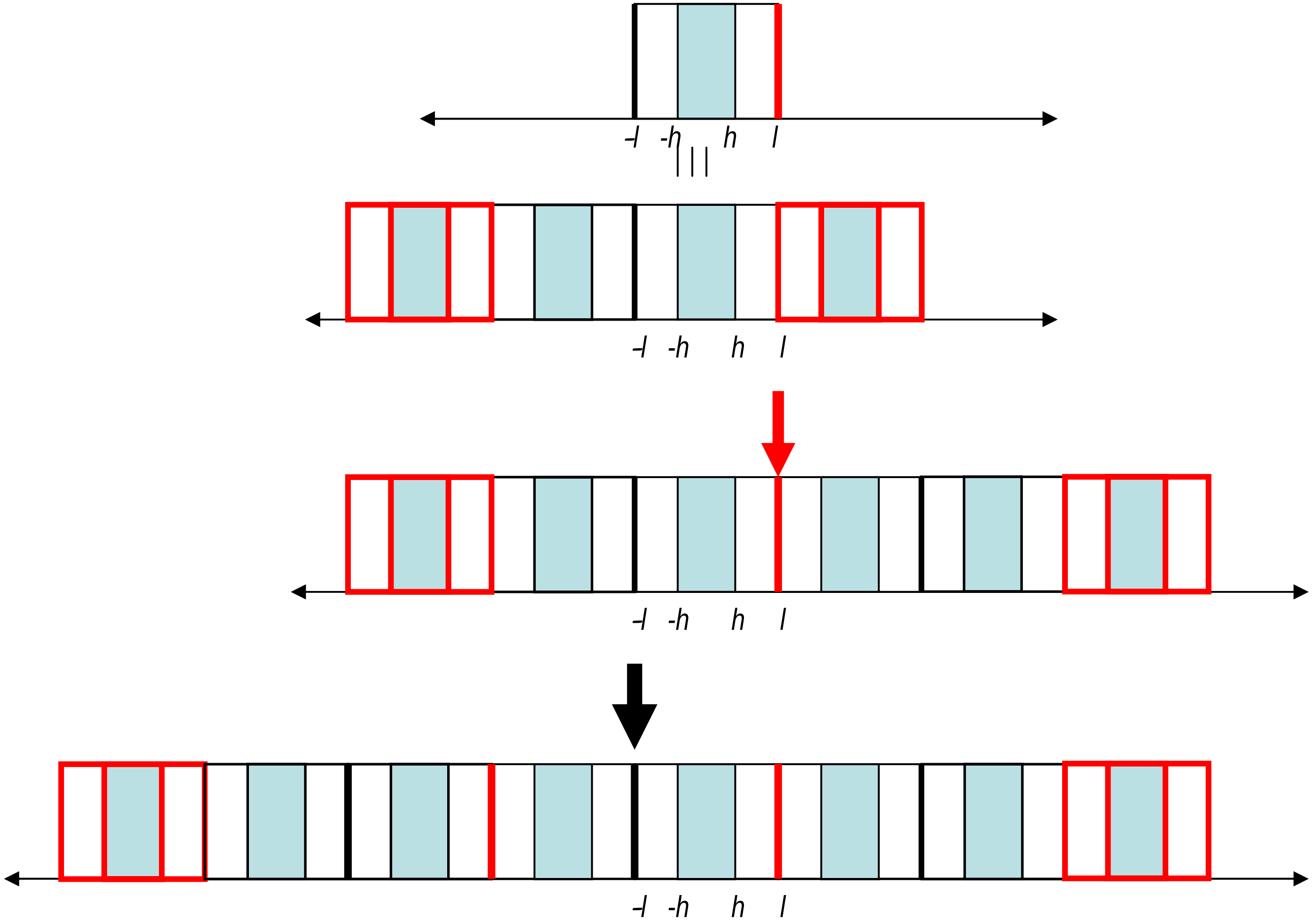
$$=\int_{2nl-h}^{2nl+h}\frac{C_i}{2\sqrt{\pi Dt}}\exp(-\frac{(x-x')^2}{4Dt})dx'$$

$$=\frac{C_i}{2}\sum_{-\infty}^{\infty}[erf(\frac{x-(2nl-h)}{2\sqrt{Dt}})-erf(\frac{x-(2nl+h)}{2\sqrt{Dt}})]$$

Example

B.C.

$$\frac{\partial C(x,t)}{\partial x} = 0 \quad x = l, x = -l$$



Equivalent I.C.

$$C(x,0) = C_i \quad 2nl - h \le x \le 2nl + h, -\infty < n < \infty$$

Example

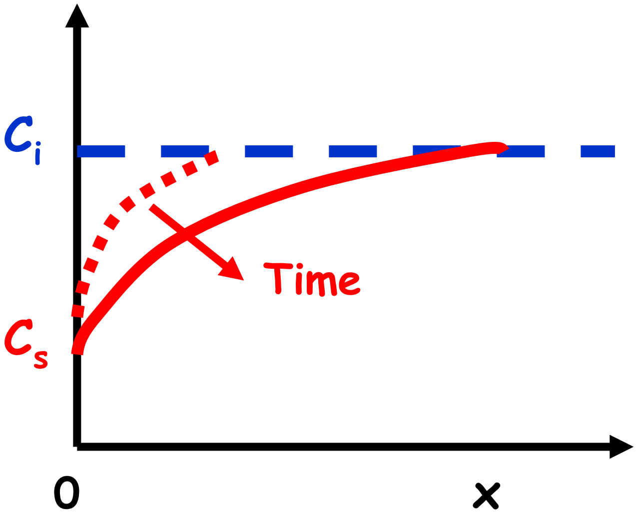
$$C(x,0) = C_i$$

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

$$Define \quad \theta = C - C_s$$

$$\theta(x,0) = C_i - C_s = \theta_i$$

$$\theta(0,t) = 0$$



$$\theta(x,t) = \theta_i erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C - C_s = (C_i - C_s) erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

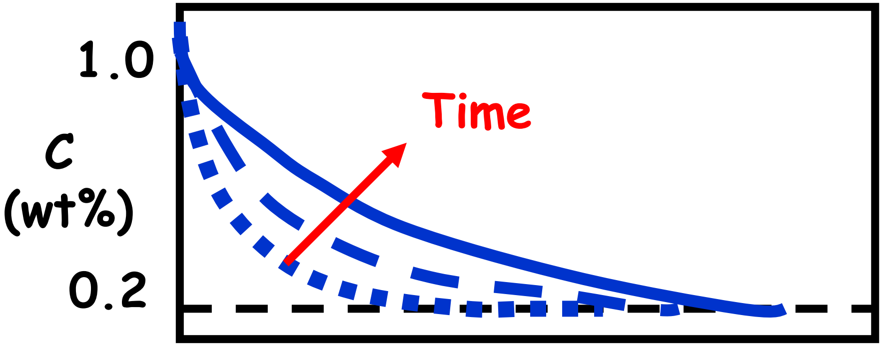
$$\frac{C - C_s}{C_i - C_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Example: Carburization

A piece of AISI 1020 steel is heated to 1255K and subjected to a carburizing atmosphere such that

$$2CO \Leftrightarrow CO_2 + C_{(s)} \qquad (1)$$

is in equilibrium with 1 wt%C in solution at the surface



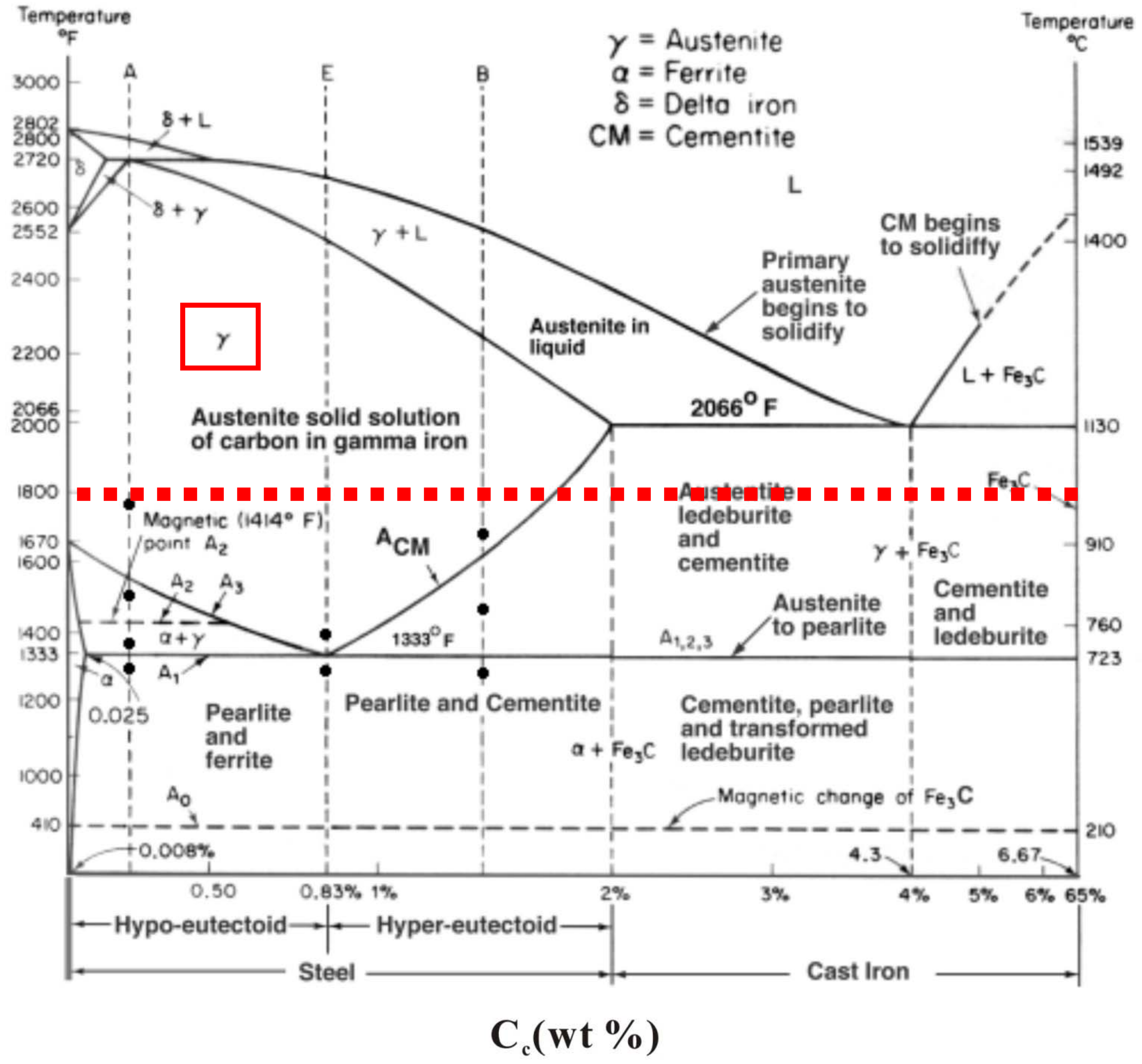
C_s is fixed by eq. (1) =1 wt%C
C_2=0.2 wt%C

$$D_c = 2x10^{-7}\,cm^2 s^{-1} \quad at \quad 1255K$$

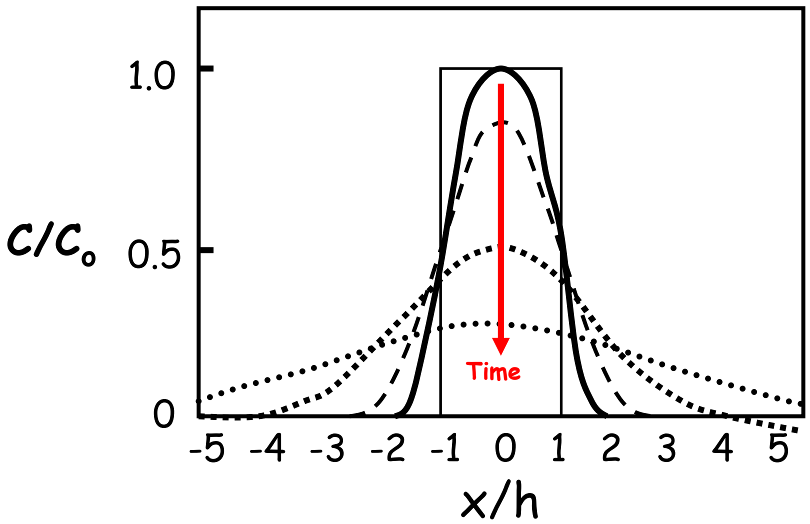
$$\boxed{\frac{C - C_s}{C_2 - C_s} = erfc\left(\frac{x}{2\sqrt{Dt}}\right)}$$

When t = 3600 s
C=0.35 wt%C at x = $5x10^{-2}$ cm

Fe-C Phase Diagram



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

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

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

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

$$\mathrm{X}(x)T'(t) = DT\mathrm{X}''$$

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

$$\frac{\mathrm{X}\dfrac{dT}{dt}}{\mathrm{X}T} = \frac{DT\mathrm{X}''}{\mathrm{X}T}$$

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

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

$\dfrac{\mathrm{X}''}{\mathrm{X}}$: 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

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

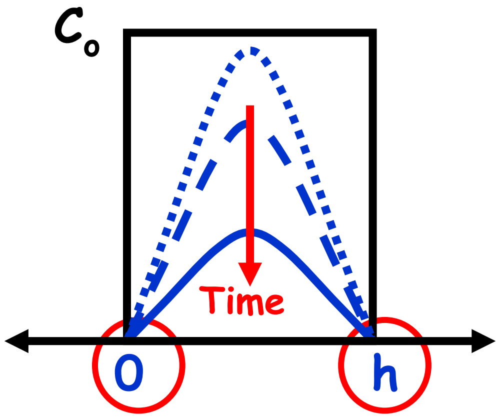
$$=T_0\exp(-\lambda^2Dt)(A'\sin\lambda x+B'\cos\lambda x)$$

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

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

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

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.

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

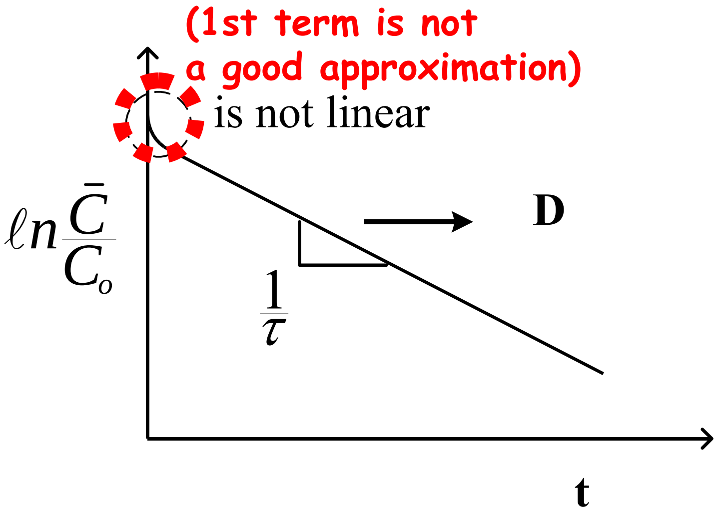
$$= \frac{8C_0}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^2}\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

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

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

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

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



(1st term is not a good approximation)

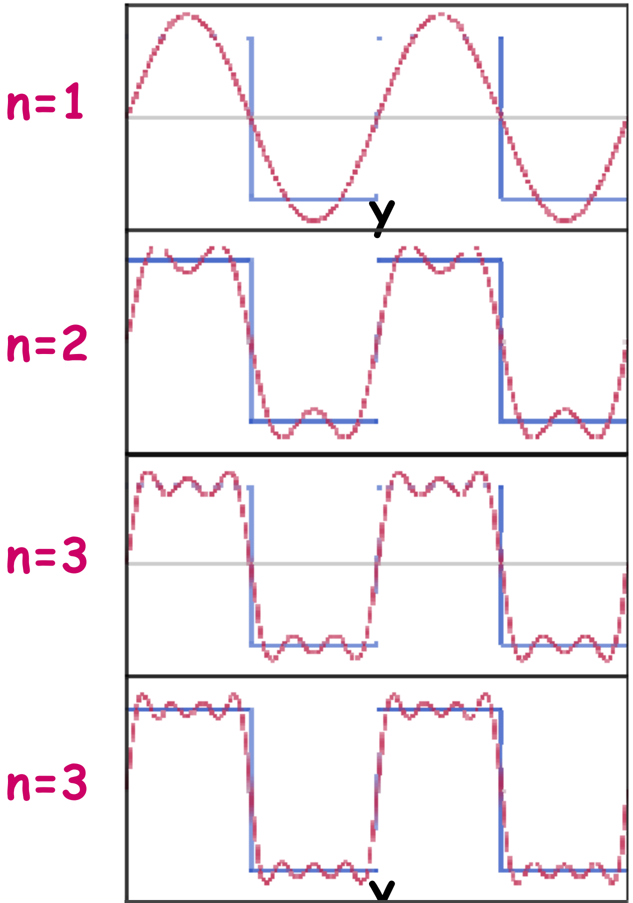
is not linear

Fourier Series

Example: **Initial concentration is a sum of sine series**

$$C_o = \sum_{n=1}^{\infty} A_n \sin(\lambda_n x)$$

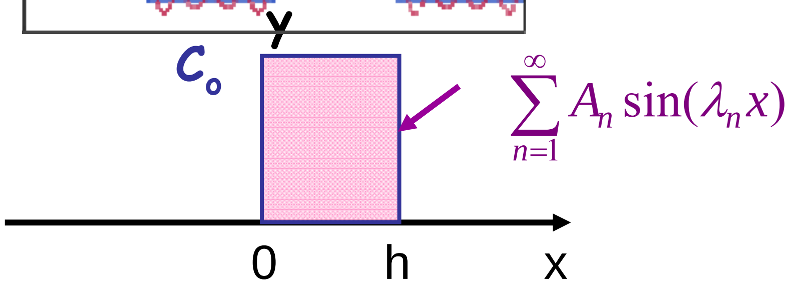
$$= \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi}{h} x\right)$$



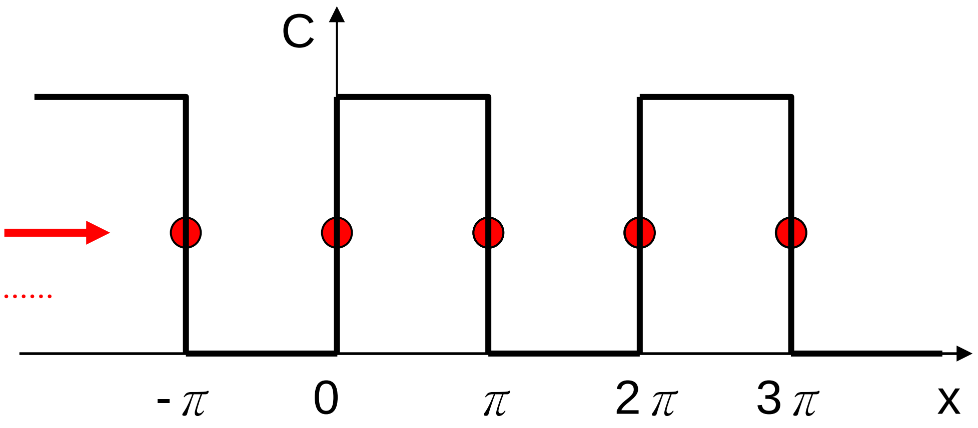
$$Y = \frac{\pi x}{h}$$

$$Y = \pi$$

$$\text{when} \quad x = h$$



Fourier Series



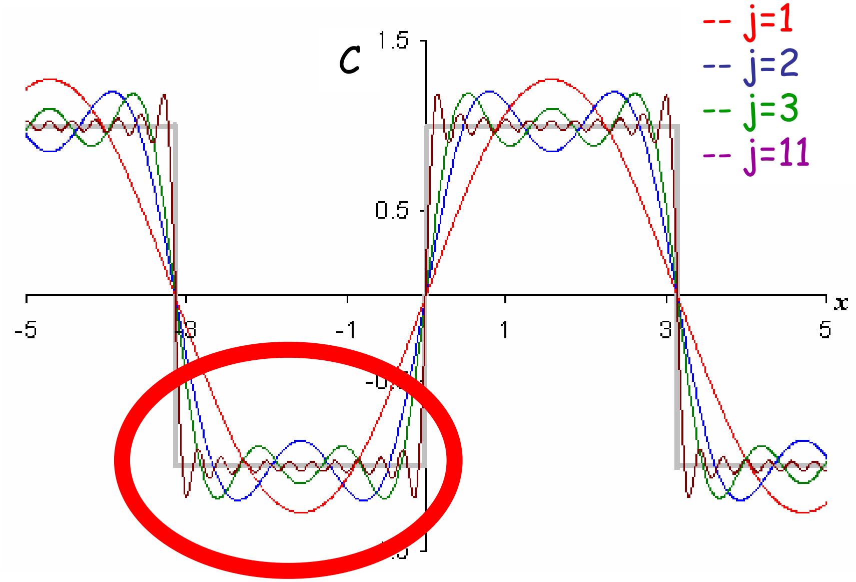
B.C.
$C(x,t) = 2$
$x = 0,\ \pm\pi,\ \pm 2\pi........$

$$C(x,0) = 2 + \frac{8}{\pi}\sum_{0}^{\infty}\frac{\sin(2j+1)x}{2j+1}$$

$$C_o(x,0) = 2, \quad C_1(x,0) = 2 + \frac{8}{\pi}\sin(x)$$

$$C_2(x,0) = 2 + \frac{8}{\pi}\sin(x) + \frac{8}{3\pi}\sin(3x)$$

$$C_{19}(x,0) = 2 + \frac{8}{\pi}\sin(x) + \frac{8}{3\pi}\sin(3x) + ...+ \frac{8}{39\pi}\sin(39x)$$



Example:

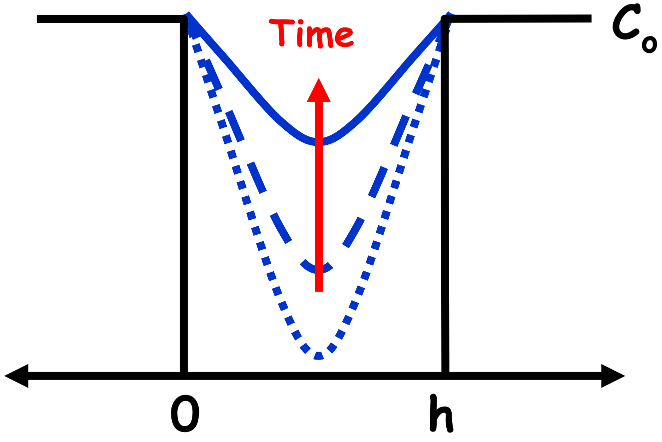
$I.C.$

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

$$C(x,0)=C_0 \ x<0, x>h$$

$B.C.$

$$C(x,t)=C_0 \quad x=0,h$$

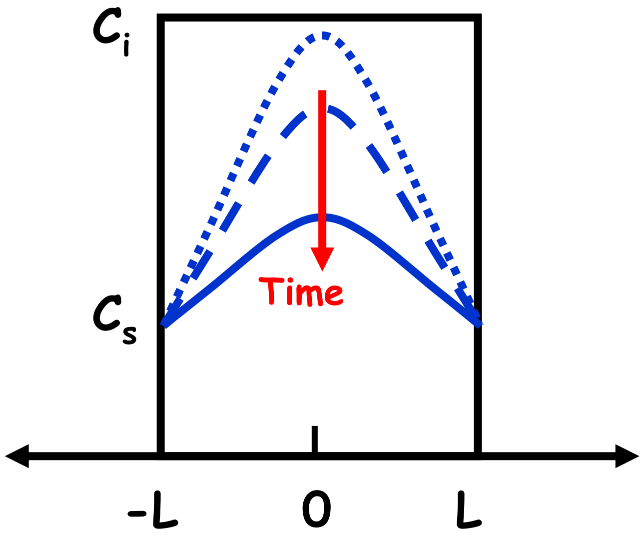


$$C=C_0-\frac{4C_0}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\sin(\frac{(2j+1)\pi x}{h})\exp(-(\frac{(2j+1)\pi}{h})^2 Dt)$$

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

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

Example:



I.C.

$$C(x,0) = C_i \quad -L < x < L$$

$$C(x,0) = 0 \quad x < -L, x > L$$

B.C.

$$\frac{\partial C}{\partial x}(0,t) = 0$$

$$C(\pm L,t) = C_s$$

$$\frac{C - C_s}{C_i - C_s} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\cos\left(\frac{(2n+1)\pi}{2}\frac{x}{L}\right)\exp\left(-\frac{(2n+1)^2\pi^2}{4}\frac{Dt}{L^2}\right)$$

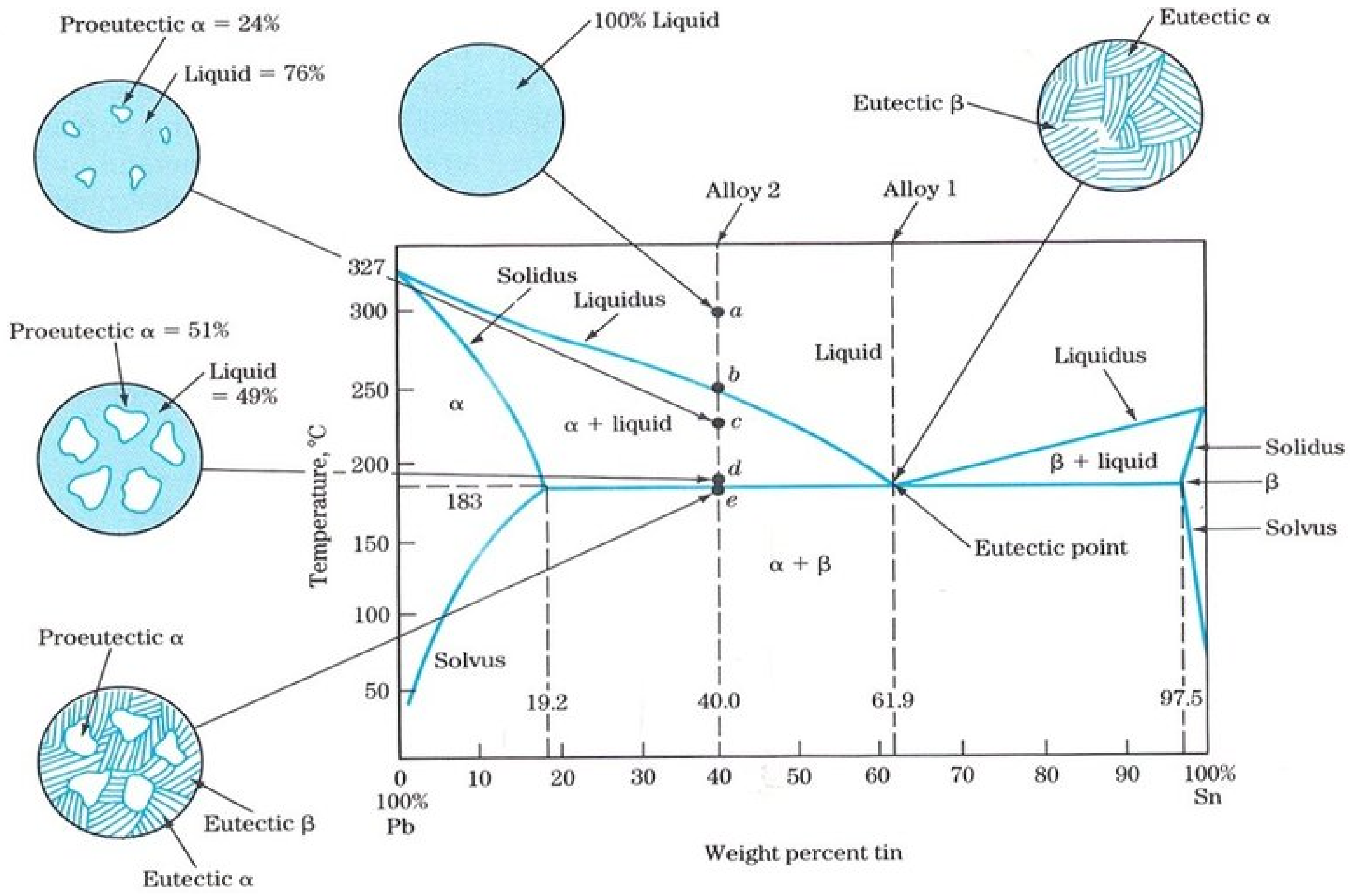
$$\overline{C} = \frac{1}{L}\int_0^L C(x,t)dx$$

$$\frac{\overline{C} - C_s}{C_i - C_s} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2\pi^2}{4}\frac{Dt}{L^2}\right]$$

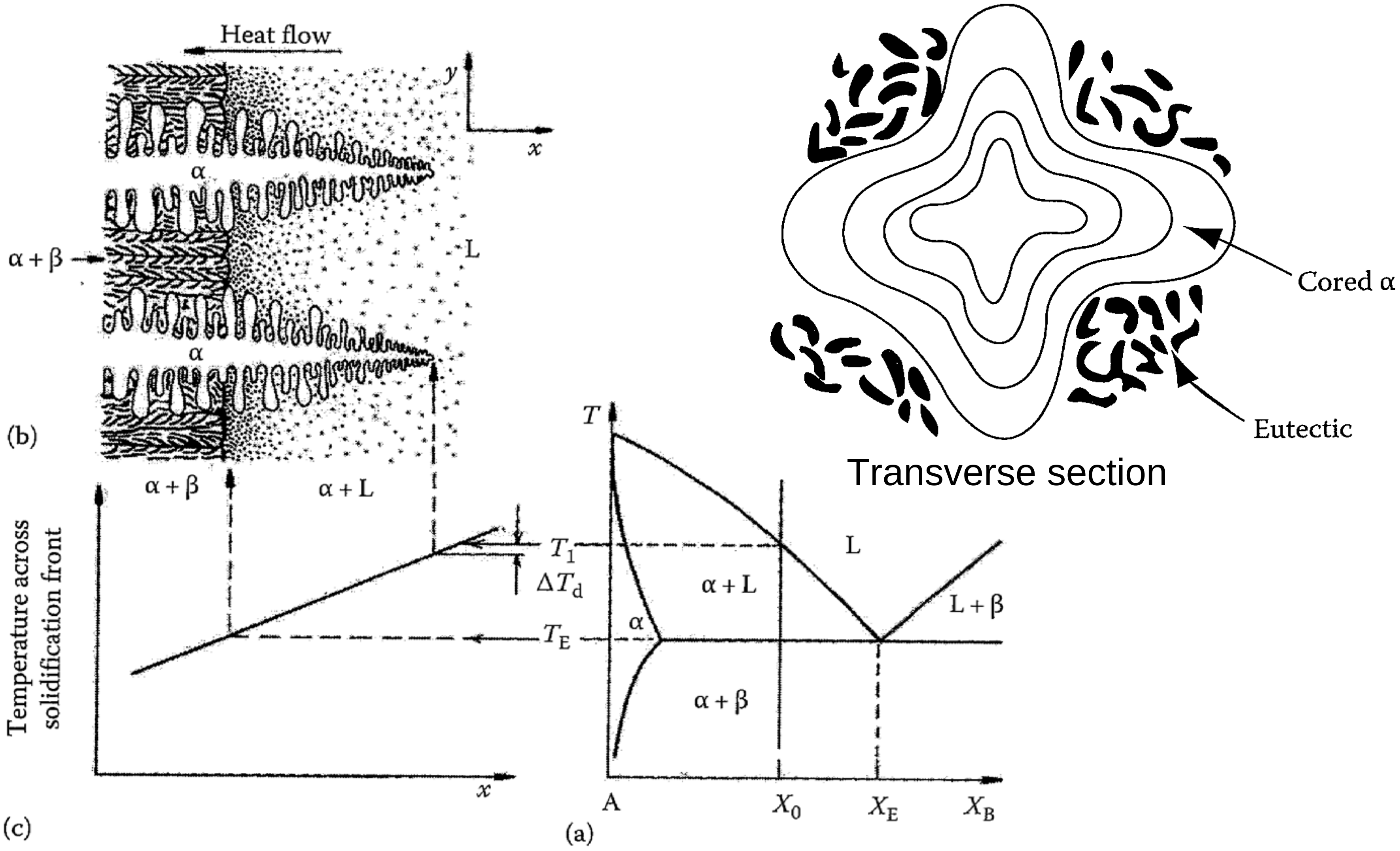
$$\approx \frac{8}{\pi^2}\exp\left(-\frac{t}{\tau}\right) \quad \text{(only the first term is taken)}$$

$$\text{where} \quad \tau = \frac{4L^2}{\pi^2 D}$$

Phase Transformation in Pb-Sn Alloy System



Solidification of an off-eutectic Alloy -- Coring

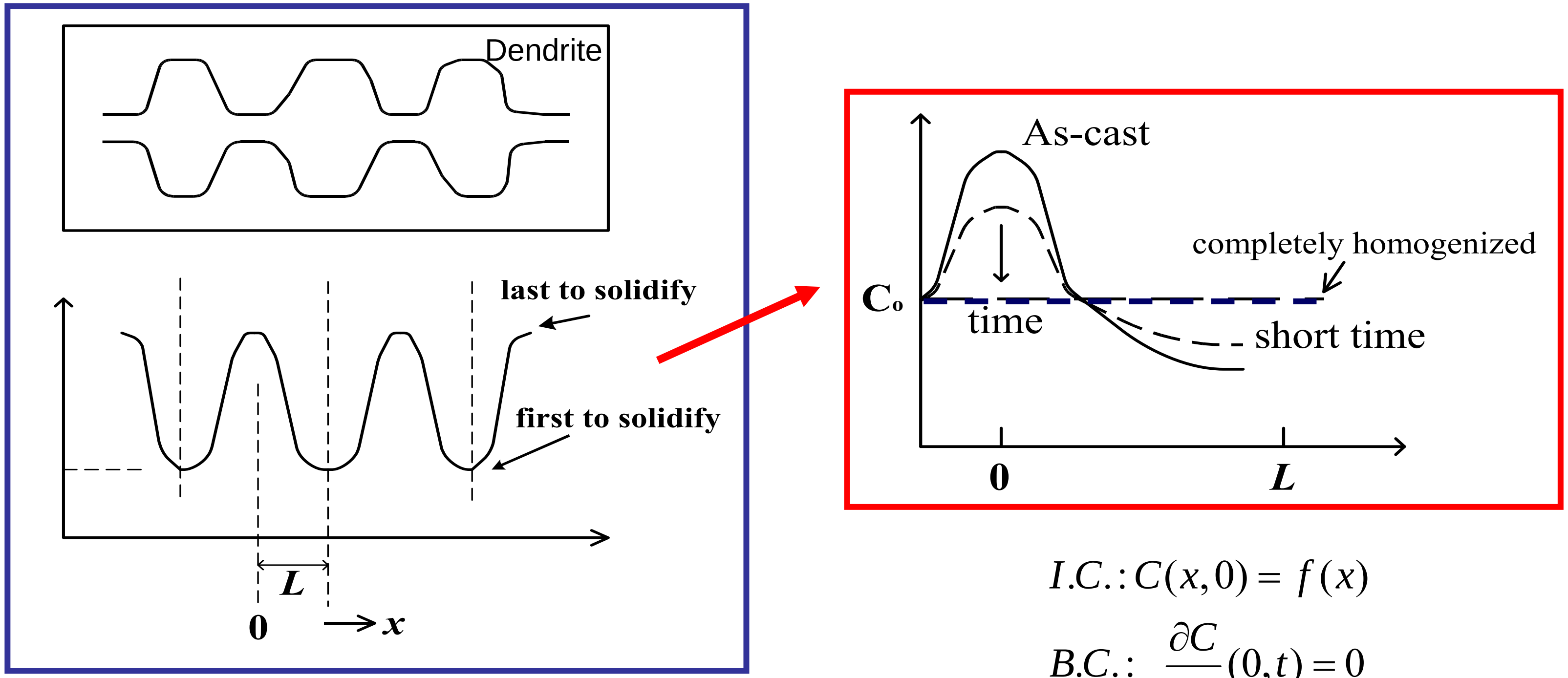


Transverse section

FIGURE 4.37
Solidification of an off-eutectic alloy in a temperature gradient. (a) Alloy composition in relation to the phase diagram. (b) Schematic solidification front. (c) Temperature variation across solidification front (isotherms normal to *x*).

Example : **Homogenization of Alloys**

Coring: Diffusion of most alloying element in the solid state is too slow to maintain a solid if uniform concentration is in equilibrium with the liquid during solidification.



$$I.C.: C(x,0) = f(x)$$

$$B.C.: \quad \frac{\partial C}{\partial x}(0,t) = 0$$

$$\frac{\partial C}{\partial x}(L,t) = 0$$

$$C(x,t) = C_0 + \sum A_n \cos\frac{n\pi x}{L}\exp(-n^2\pi^2\frac{Dt}{L^2})$$

$$A_n = \frac{2}{L}\int_0^L f(x)\cos\frac{n\pi x}{L}dx$$

(Ref: Crank's Book p.63)

Table 13.2 The relative change in average composition for the basic shapes

Diffusion in a slab of semithickness, L

I.C.: $C(x,0) = C_i,$

B.C.: $C(L,t) = C_s,$

$$\frac{\partial C}{\partial x}(0,t) = 0.$$

Solution:

$$\frac{\bar{C} - C_s}{C_i - C_s} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2}{4}\,\frac{Dt}{L^2}\right]. \tag{13.43}$$

Diffusion in solid circular cylinder of radius, R

I.C.: $C(r,0) = C_i,$

B.C.: $C(R,t) = C_s,$

$$\frac{\partial C}{\partial r}(0,t) = 0.$$

Solution:

$$\frac{\bar{C} - C_s}{C_i - C_s} = \sum_{n=1}^{\infty}\frac{4}{\xi_n^2}\exp\left[\frac{-\xi_n^2 Dt}{R^2}\right], \tag{13.45}$$

where $\xi_n = 2.405, 5.520, 8.654, 11.792, 14.931$, when $n = 1, 2, 3, 4, 5$, etc.[*]

Diffusion in spheres of radius, R

The same set of initial and boundary conditions as for the cylinder above:

$$\frac{\bar{C} - C_s}{C_i - C_s} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left[\frac{-n^2\pi^2 Dt}{R^2}\right]. \tag{13.46}$$

---

[*] ξ_n are roots of the equation $J_0(x) = 0$, where $J_0(x)$ is the Bessel function of zero order.

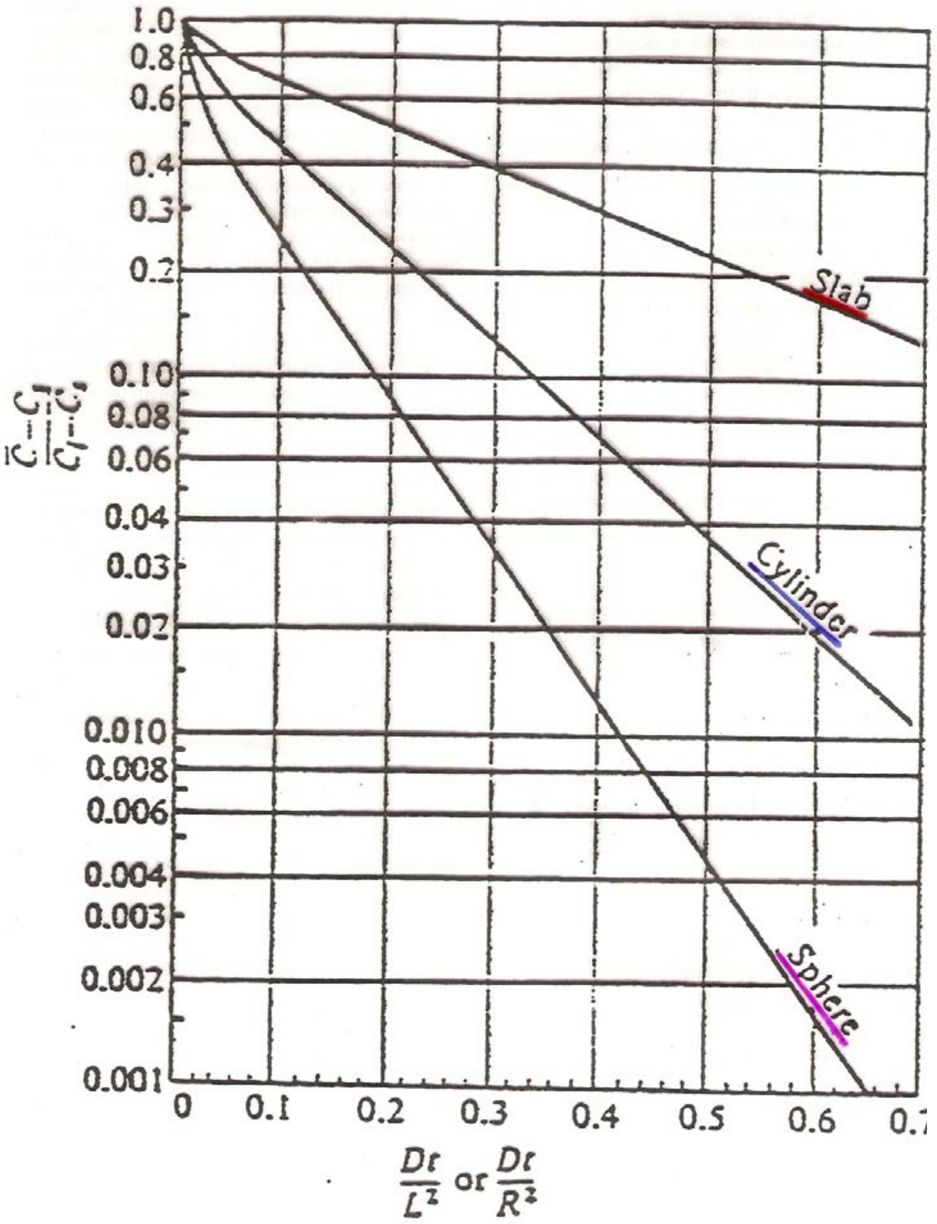
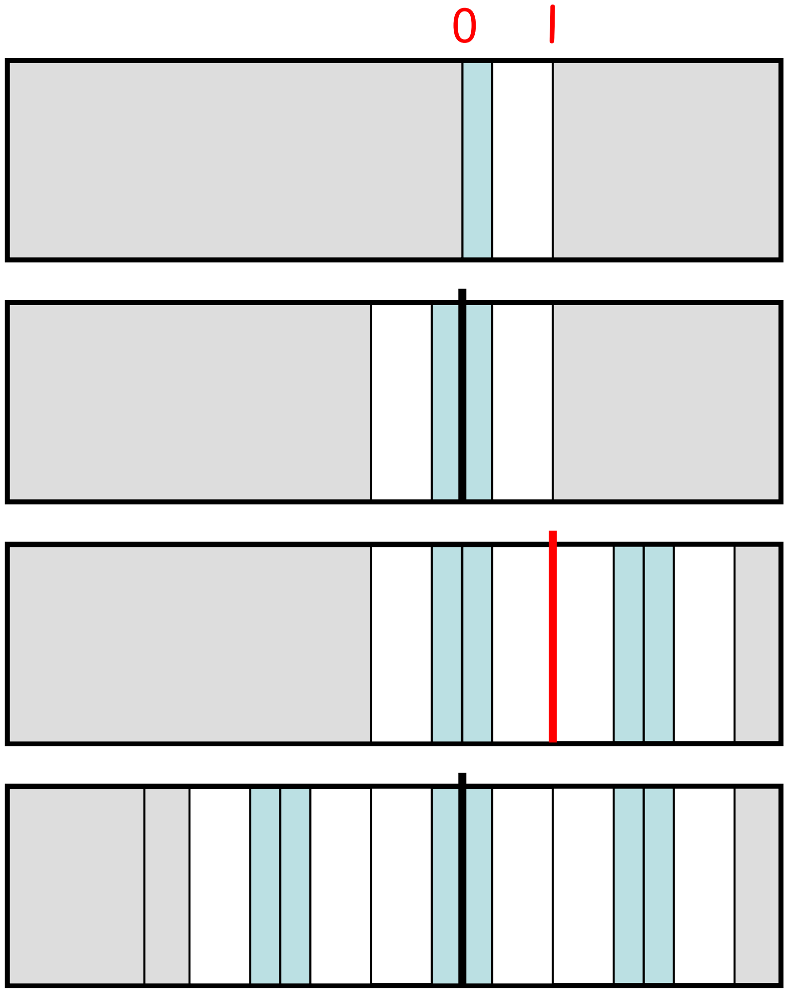


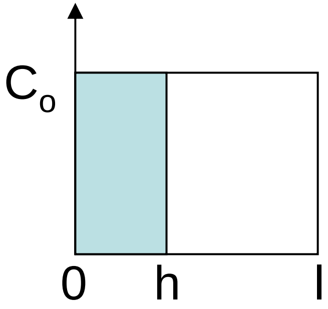
Fig. 13.6 The relative change in average composition for the
shapes. R = radius, and L = semithickness.

Numerical Approximations
Error Function Series

$$\frac{\partial C}{\partial x} = 0 \; at \; x = 0 \; and \; x = l.$$



Sequence of mirror reflection to provide no-flow boundary conditions



I.C.

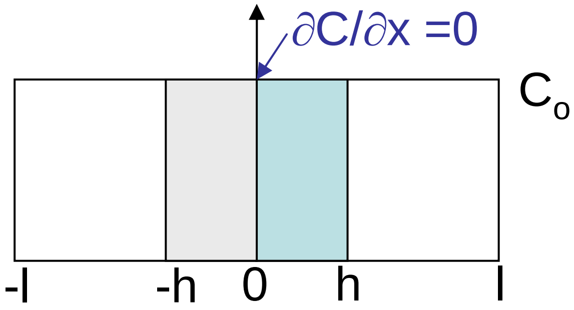
$$C(x,0)=C_o \qquad 0\le x\le h$$

$$C(x,0)=0 \qquad h<x<l$$

B.C.

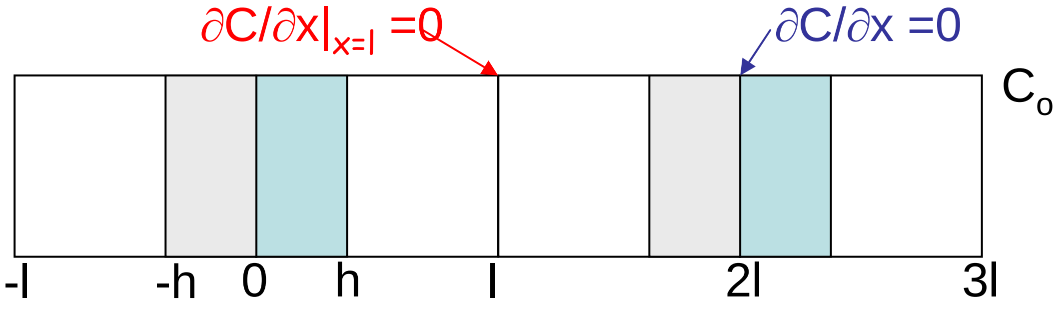
$$\frac{\partial C}{\partial x}=0 \qquad x=0,\ x=l$$

$\downarrow$ $\because \partial C/\partial x|_{x=0}=0$



$$C(x,t)=\int_{-h}^{h}\frac{C_o}{2\sqrt{\pi Dt}}\exp(-\frac{(x-x')^2}{4Dt})dx'$$

$\downarrow$ $\because \partial C/\partial x|_{x=l}=0$



$$C(x,t)=\int_{-h}^{h}\frac{C_o}{2\sqrt{\pi Dt}}\exp(-\frac{(x-x')^2}{4Dt})dx'+\int_{2l-h}^{2l+h}\frac{C_o}{2\sqrt{\pi Dt}}\exp(-\frac{(x-x')^2}{4Dt})dx'$$

$$\frac{\partial C}{\partial x}\Big|_{x=0} = 0, \qquad \frac{\partial C}{\partial x}\Big|_{x=l} = 0 \ldots\ldots\ldots$$

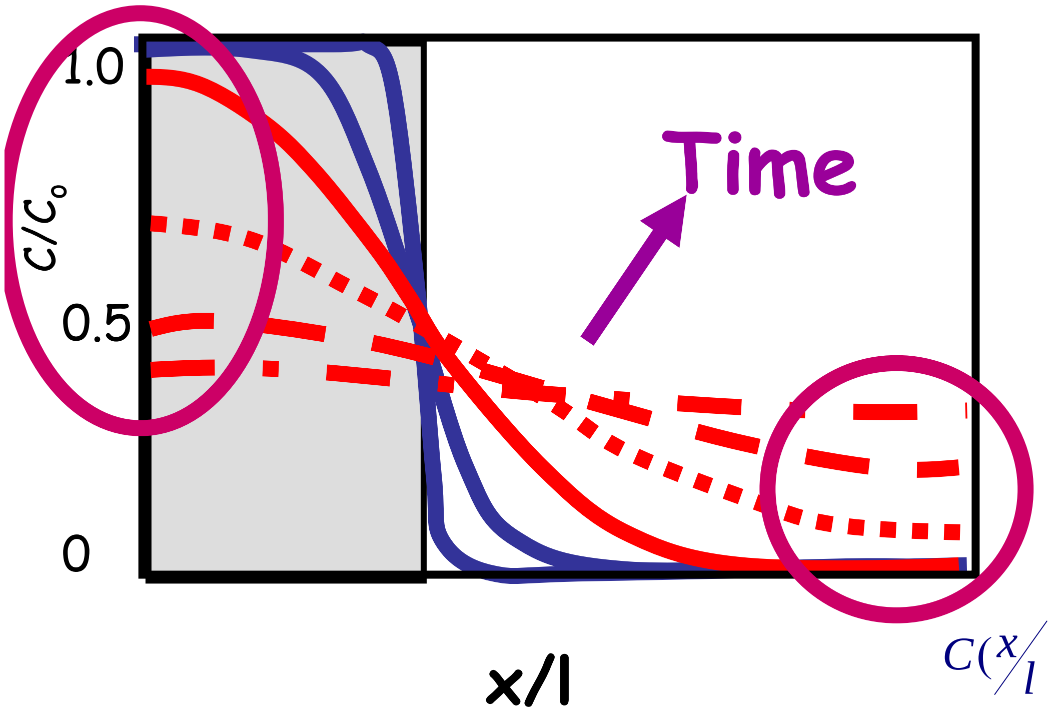
$$C(x,t) = \sum_{0}^{\pm\infty} \int_{2nl-h}^{2nl+h} \frac{C_o}{2\sqrt{\pi D t}} \exp\left(-\frac{(x-x')^2}{4Dt}\right) dx'$$

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

$$C(x,t) = \frac{C_o}{2}\left(\sum_{0}^{\pm\infty}\left[erf\left(\frac{x-2nl+h}{2\sqrt{Dt}}\right) - erf\left(\frac{x-2nl-h}{2\sqrt{Dt}}\right)\right]\right)$$

$$0 \le x \le l$$

Error Function (3 terms)

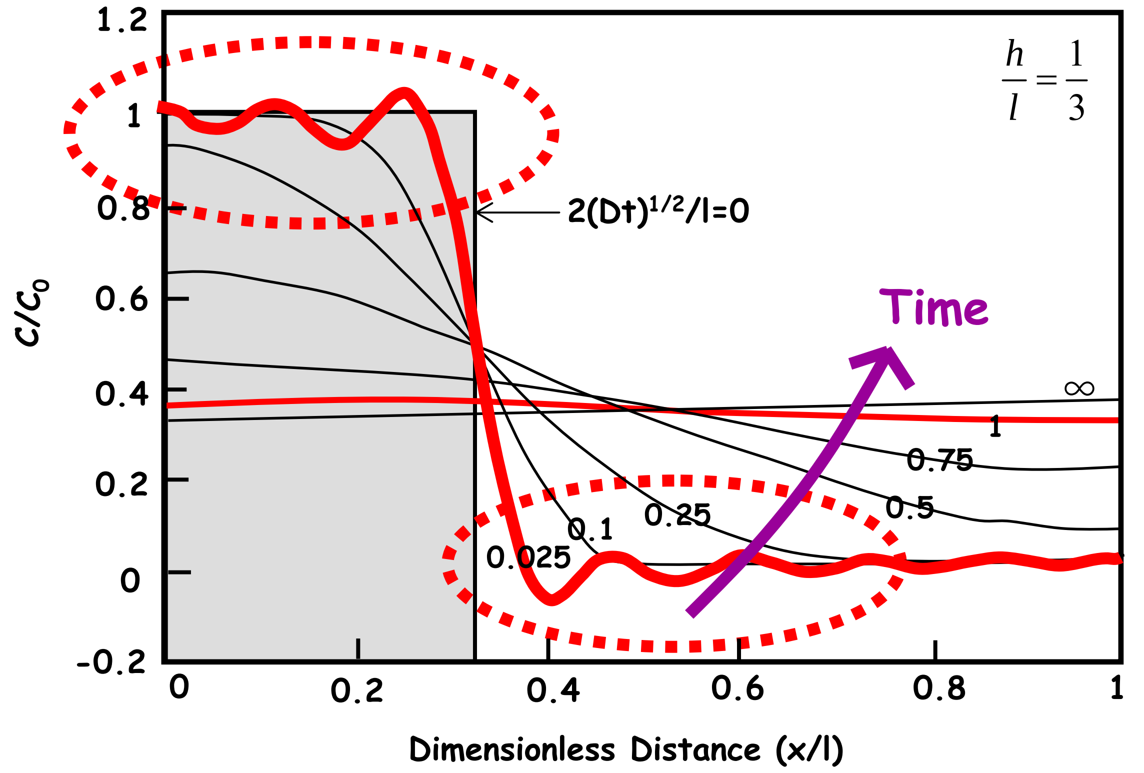


$$\frac{h}{l} = \frac{1}{3}$$

$$\frac{C(x/l, t; \frac{1}{3})}{C_0} \approx \frac{1}{2}\left\{\begin{array}{l} [erf(\frac{\frac{x}{l}+\frac{1}{3}}{\frac{2\sqrt{Dt}}{l}}) - erf(\frac{\frac{x}{l}-\frac{1}{3}}{\frac{2\sqrt{Dt}}{l}})] \\ +[erf(\frac{\frac{x}{l}+2+\frac{1}{3}}{\frac{2\sqrt{Dt}}{l}}) - erf(\frac{\frac{x}{l}+2-\frac{1}{3}}{\frac{2\sqrt{Dt}}{l}})] \\ +[erf(\frac{\frac{x}{l}-2+\frac{1}{3}}{\frac{2\sqrt{Dt}}{l}}) - erf(\frac{\frac{x}{l}-2-\frac{1}{3}}{\frac{2\sqrt{Dt}}{l}})] \end{array}\right\}$$

Note: When $2\sqrt{Dt}/l$ increases, more error function terms would be needed because error functions spread indefinitely and therefore do not provide support of the no-flow boundary conditions.

Fourier Series (15 terms)

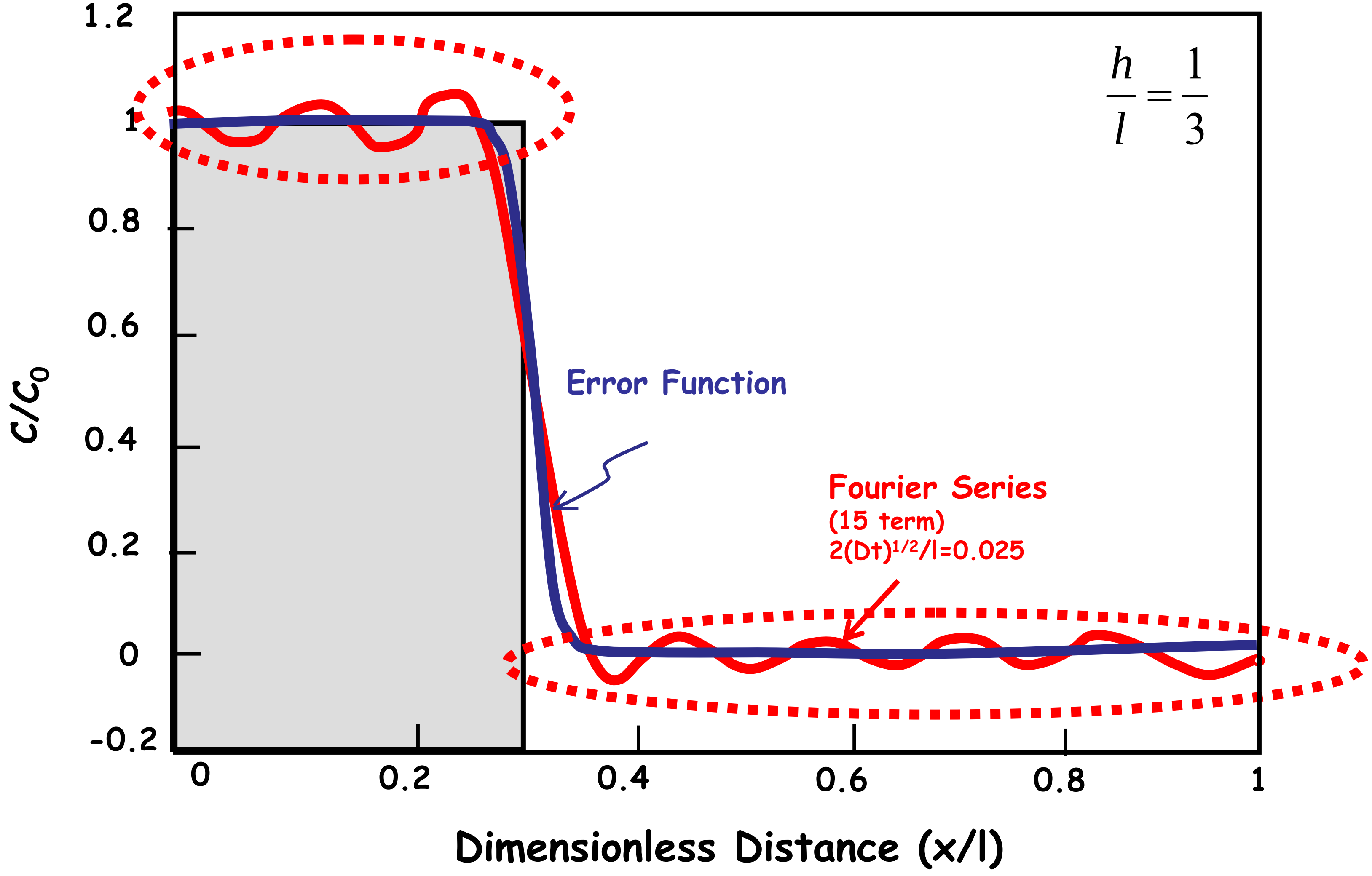


$$\frac{C(x,t)}{C_0}=\frac{1}{3}+\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin(\frac{n\pi}{3})\cos(\frac{n\pi x}{l})\exp[-(\frac{n\pi}{2})^2(\frac{2\sqrt{Dt}}{l})^2]$$

Note: At short times (small $2\sqrt{Dt}/l$), more Fourier terms would be needed to eliminate spurious ripples and negative concentrations in the solution.

Short Time Solution

$$\frac{2\sqrt{Dt}}{l} = 0.025$$



Method of Laplace Transform

Laplace transform to the diffusion equation is to remove the time variable leaving an ordinary differential equation, the solution of which yields the transform of the concentration as a function of the space variables (x,y,z). (Solve p.d.e. by making it an o.d.e.)

Definition

$$F(p) = \int_0^\infty e^{-pt} f(t)dt$$

F(p) is called the Laplace transform of the original function f(t), and denoted by L(f(t))

$$L(f) = F(p) = \int_0^\infty e^{-pt} f(t)dt$$

This operation is called Laplace Transform.

$$f(t) = L^{-1}(F)$$

is called inverse transform or inverse of F(p)

$f(t)$	$L(f)$	$f(t)$	$L(f)$
1	$1/p$	e^{at}	$\dfrac{1}{p-a}$
t	$1/p^2$	$\cos(wt)$	$\dfrac{p}{p^2+w^2}$
t^2	$2!/p^3$	$\sin(wt)$	$\dfrac{w}{p^2+w^2}$
t^n	$n!/p^{n+1}$	$\cosh(at)$	$\dfrac{p}{p^2-a^2}$
		$\sinh(at)$	$\dfrac{a}{p^2-a^2}$

$$L(f') = pL(f) - f(0)$$

$$L(f'') = p^2 L(f) - pf(0) - f'(0)$$

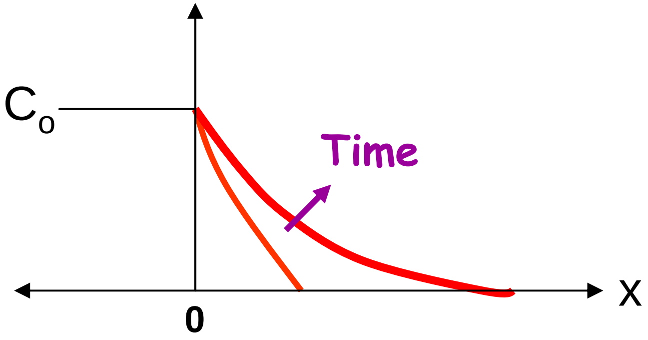
Example: Semi-infinite System

I.C.

$$C(x,0) = 0 \qquad x > 0$$

B.C.

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



(Note: diffusion in a semi-infinite medium, x>0 when the boundary is kept at a fixed concentration. e.g. doping problem)

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

multiplying both sides by e^{-pt} and integrating with respect to time from 0 to ∞, one obtains

$$\int_0^\infty e^{-pt}\frac{\partial^2 C}{\partial x^2}dt - \frac{1}{D}\int_0^\infty e^{-pt}\frac{\partial C}{\partial t}dt = 0$$

Assuming the orders of differentiation and integration can be interchanged

$$\int_0^\infty e^{-pt}\frac{\partial^2 C}{\partial x^2}dt = \frac{\partial^2}{\partial x^2}\int_0^\infty Ce^{-pt}dt = \frac{\partial^2 \overline{C}}{\partial x^2}$$

$$Note: \quad \overline{C} = L(C) = F(p) = \int_0^\infty C(x,t)e^{-pt}dt$$

$$\int_0^\infty e^{-pt}\frac{\partial C}{\partial t}dt = pL(C) - \underset{\text{I.C.}}{C(0)} = p\overline{C} - 0$$

Note: $L(f') = pL(f) - f(0)$

$$\frac{\partial^2 \overline{C}}{\partial x^2} - \frac{p}{D}\overline{C} = 0$$

$$\overline{C} = A_1 e^{-\sqrt{p/D}\cdot x} + A_2 e^{\sqrt{p/D}\cdot x}$$

B.C.: $C(0,t) = C_0 \qquad L(C_0) = \dfrac{C_0}{p} = \overline{C}$

$$C(\infty,t) = 0 \rightarrow A_2 = 0$$

$$\overline{C} = A_1 e^{-\sqrt{p/D}\,0} = \frac{C_0}{p} \rightarrow A_1 = \frac{C_0}{p}$$

$$\overline{C} = \frac{C_0}{p} e^{-\sqrt{p/D}\cdot x}$$

From Table $L^{-1}(\overline{C}) = C$

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

Example

$$I.C.$$

$$C(x,0)=0 \qquad -l<x<l$$

$$B.C.$$

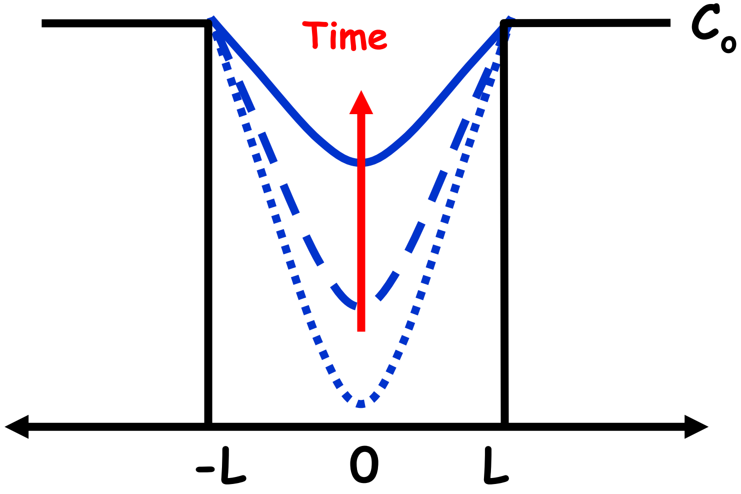
$$C(x,t)=C_0 \qquad x=l, x=-l$$

$$\frac{\partial C(0,t)}{\partial x}=0$$

$$\frac{\partial^2 \overline{C}}{\partial x^2}-\frac{p}{D}\overline{C}=0 \qquad 0<x<l$$

$$\frac{\partial \overline{C}}{\partial x}=0 \qquad \text{at } x=0$$

$$\overline{C}=\frac{C_0}{p} \qquad \text{at } x=l,\ x=-l$$



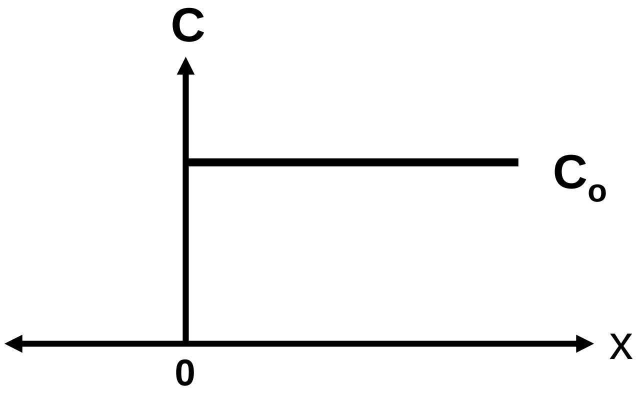
$$\overline{C}=\frac{C_0\cosh(\sqrt{p/D}\cdot x)}{p\cosh(\sqrt{p/D}\cdot l)}$$

$$\text{Note: } \cosh(x)=\frac{e^{x}+e^{-x}}{2}$$

Note: please check Crank's Book pages 22-24 to have the solution

$$C=C_0-\frac{4C_0}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\exp\left(-\frac{(2n+1)^2\pi^2}{4}\frac{Dt}{l^2}\right)\cos\left(\frac{(2n+1)\pi}{2}\frac{x}{l}\right)$$

Example: Constant Flux at the surface



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

$$B.C.:\ C(\infty,t)=C_0$$

$$J(0,t)=A=-D\,{}^{\partial C(0,t)}\!/_{\partial x}$$

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

$$\frac{\partial^2\overline{C}}{\partial x^2}-\frac{p}{D}\overline{C}=-\frac{C_0}{D}$$

$$\overline{C}=k_1e^{\sqrt{\frac{p}{D}}x}+k_2e^{-\sqrt{\frac{p}{D}}x}+k_3$$

$$\because C(\infty,t)=C_0\rightarrow k_1=0$$

$$\overline{C}(x,p)=k_2e^{-\sqrt{\frac{p}{D}}x}+k_3$$

$$L(-D\frac{\partial C(0,t)}{\partial x})=-D\frac{\partial\overline{C}(0,p)}{\partial x}=L(A)=\frac{A}{p}$$

$$\frac{\partial\overline{C}(0,p)}{\partial x}=-\frac{A}{Dp}$$

$$\frac{\partial\overline{C}(x,p)}{\partial x}=-\sqrt{\frac{p}{D}}k_2e^{-\sqrt{\frac{p}{D}}x}$$

$$\frac{\partial\overline{C}(0,p)}{\partial x}=-\sqrt{\frac{p}{D}}k_2=-\frac{A}{Dp}$$

$$k_2 = \frac{A}{D^{1/2} p^{3/2}}$$

To get k_3, go back to partial differential equations

$$\frac{\partial^2 \overline{C}(x,p)}{\partial x^2} - \frac{p}{D}\overline{C}(x,p) = -\frac{C_0}{D}$$

$$\because \; \overline{C}(x,p) = k_2 e^{-\sqrt{\frac{p}{D}}x} + k_3$$

$$\frac{p}{D}k_2 e^{-\sqrt{\frac{p}{D}}x} - \frac{p}{D}[k_2 e^{-\sqrt{\frac{p}{D}}x} + k_3] = -\frac{C_0}{D}$$

$$-\frac{p}{D}k_3 = -\frac{C_0}{D} \Rightarrow k_3 = \frac{C_0}{p}$$

$$\overline{C}(x,p) = \frac{A}{D^{1/2} p^{3/2}} e^{-\sqrt{\frac{p}{D}}x} + \frac{C_0}{p} \qquad (*)$$

$$q = \sqrt{p/D} \qquad \text{(Ref:Crank Book No.9)}$$

$$L^{-1}\left(\frac{e^{-qx}}{pq}\right) = 2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} e^{-\frac{x^2}{4Dt}} - x\,erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{e^{-qx}}{pq} = \frac{D^{1/2} e^{-\sqrt{\frac{p}{D}}x}}{p^{\frac{3}{2}}}$$

multiplied by $\frac{A}{D}$

$$L^{-1}[eq.(*)] = \frac{A}{D} L^{-1}(\text{Crank No.9}) + L^{-1}\left(\frac{C_o}{p}\right)$$

$$C(x,t)=\frac{A}{D}\left\{2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}e^{-\frac{x^2}{4Dt}}-x\,erfc\left(\frac{x}{2\sqrt{Dt}}\right)\right\}+C_0$$

Check $\quad C(x,0)=C_0$

$$-D\frac{\partial C(0,t)}{\partial x}=A$$

$$\frac{\partial C(x,t)}{\partial x}=\frac{A}{D}\left\{2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}e^{-\frac{x^2}{4Dt}}\left(-\frac{2x}{4Dt}\right)-erfc\left(\frac{x}{2\sqrt{Dt}}\right)-x\frac{\partial}{\partial x}\left(erfc\left(\frac{x}{2\sqrt{Dt}}\right)\right)\right\}$$

$$\frac{\partial C(0,t)}{\partial x}=-\frac{A}{D}\Rightarrow A=-D\frac{\partial C(0,t)}{\partial x}$$

$$C(0,t)=\frac{2A}{D}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}+C_0$$

Solutions for Variable D

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

$\frac{\partial D}{\partial x}$ 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

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

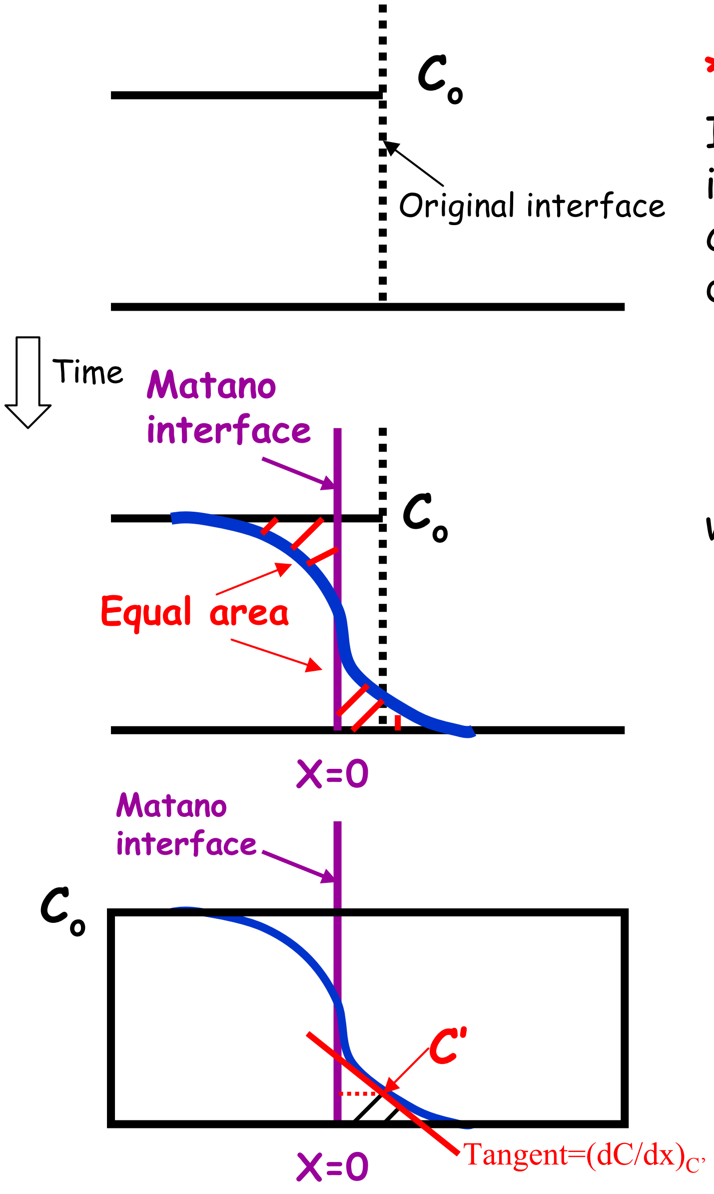
$$= \frac{1}{t}\frac{\partial}{\partial \eta}(D\frac{\partial C}{\partial \eta})$$

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

Example: Infinite System

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

$C(x,0)=0 \quad x>0 \rightarrow \eta = \infty$



*** 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

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

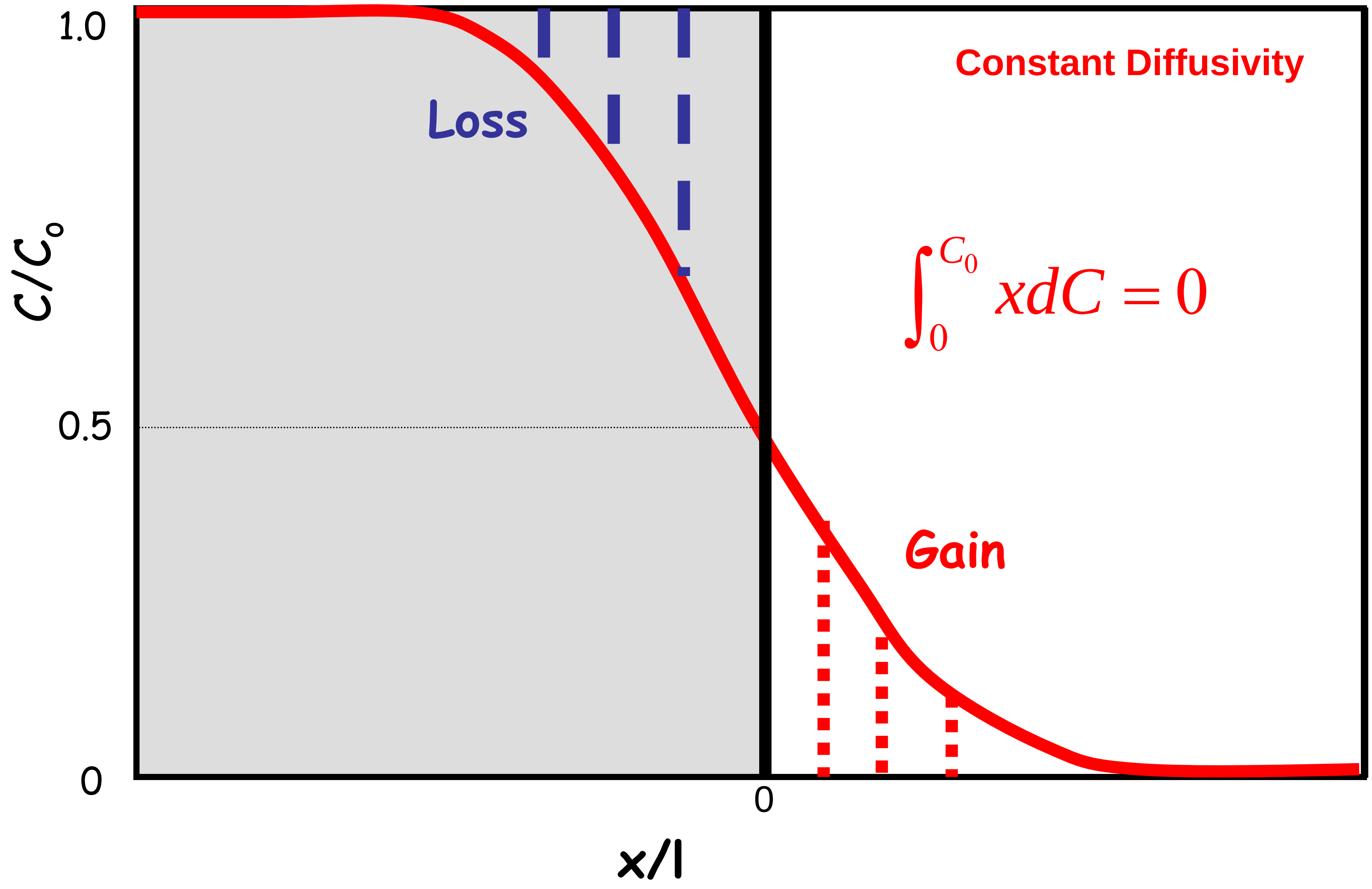
which expresses the equality of the two shaded areas.

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

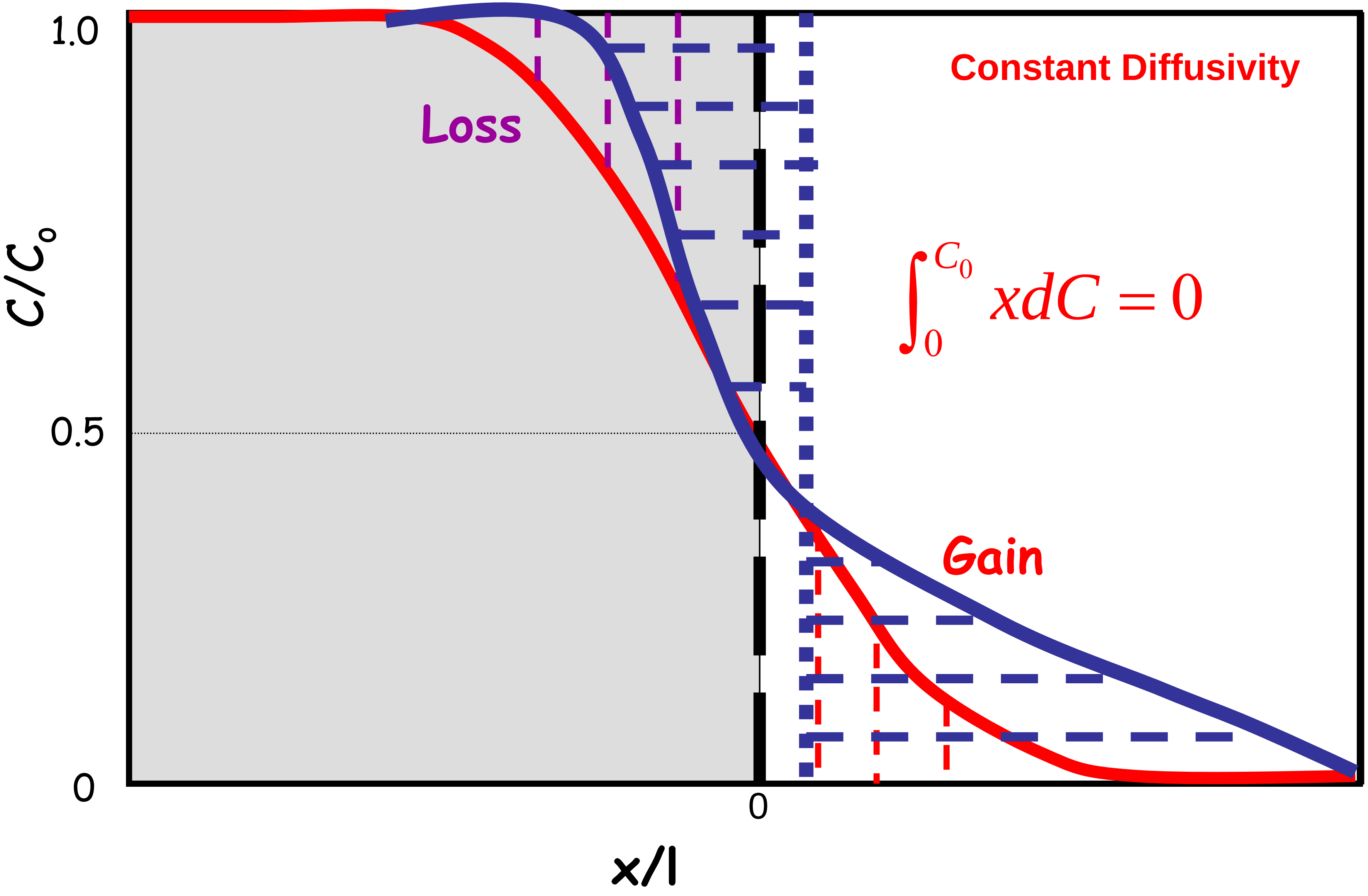
$$-\frac{1}{2}\int_0^{C'} \frac{x}{\sqrt{t}}\,dC = D\frac{\partial C}{\partial \eta}\Big|_0^{C'} = D\frac{dC}{d(\frac{x}{\sqrt{t}})}\Big|_0^{C'} = D\sqrt{t}\,\frac{dC}{dx}\Big|_0^{C'}$$

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

Error-Function Solution



Error-Function Solution

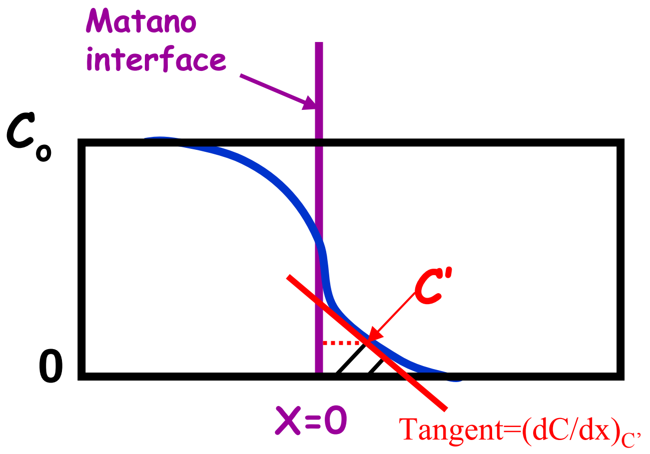


$$\int_{0}^{C_0} x\,dC = 0$$

D increases with decreasing concentration

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

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

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

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

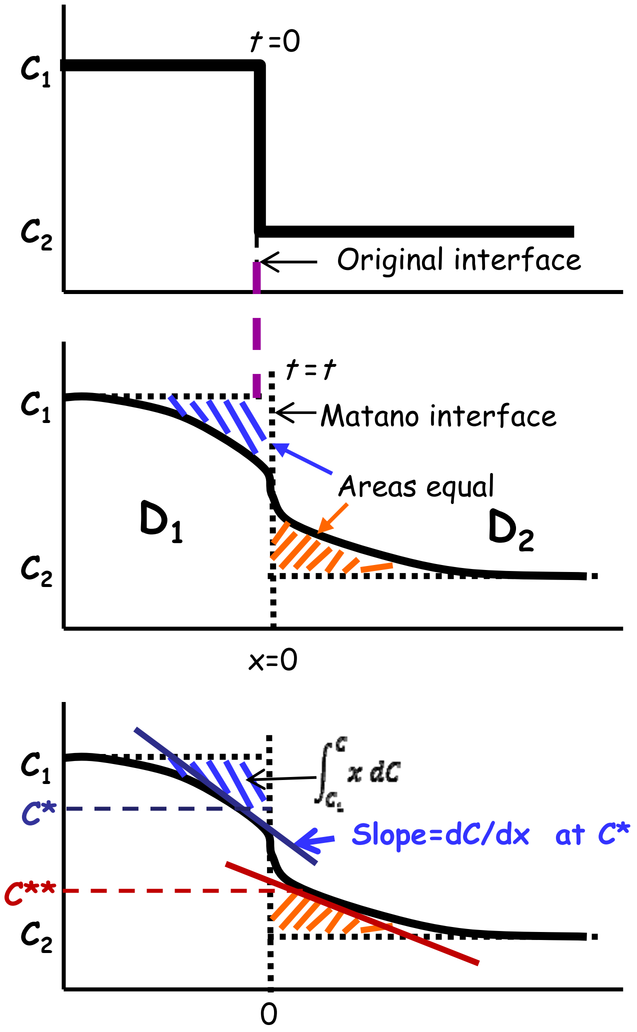
which is an additional boundary condition and determines the location of Matano interface.

x=0 plane (Matano interface) determined by

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

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

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

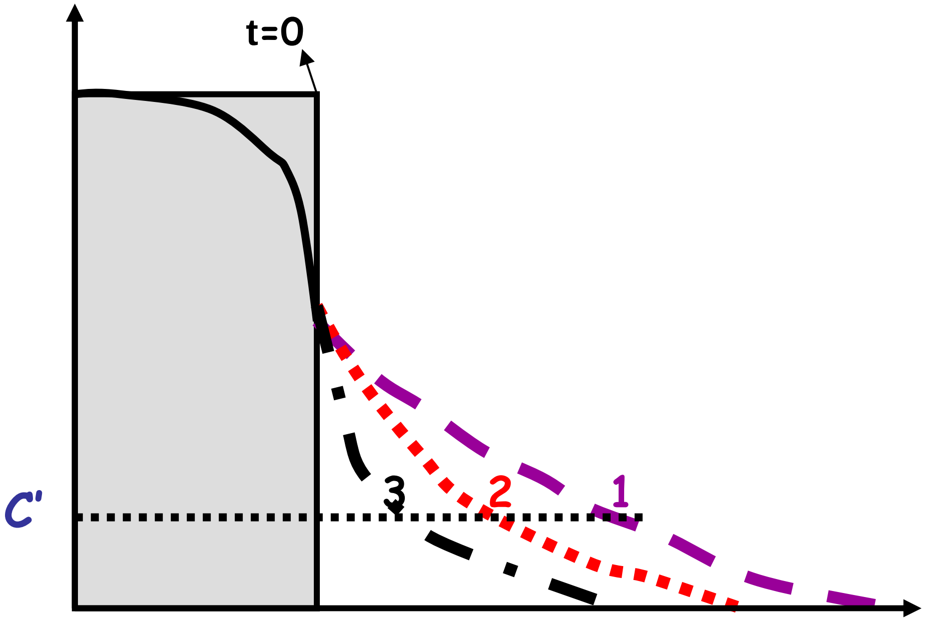


$$D(C') = \frac{-1}{2t}\left(\frac{dx}{dC}\right)_{C'} \int_0^{C'} x\,dC$$

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

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

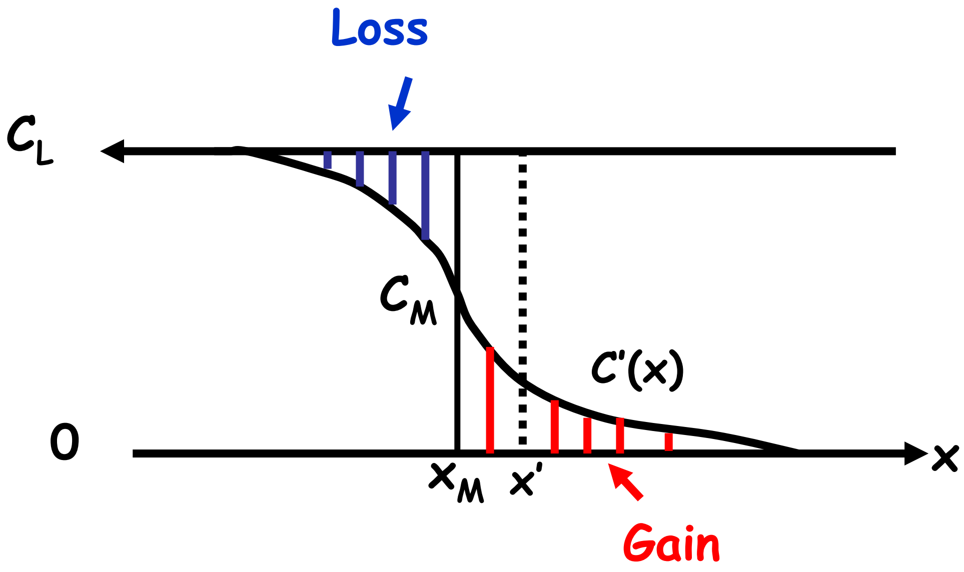
$$\text{Area}: \int_{C_1}^{C^*} x\,dC = \int_{C^{**}}^{C_2} x\,dC$$



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

$$D^1(C') > D^2(C') > D^3(C')$$

Matano Interface



x': Original interface
x_M: Matano interface

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

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

$$\int_{-\infty}^{x_M} [C_L - C(x)]dx = \int_{x_M}^{\infty} [C(x) - 0]dx$$

Integrated by parts $(\int udv = uv - \int vdu)$

$$[C_L - C(x)]\cdot x \,\Big|_{-\infty}^{x_M} - \int_{C_M}^{C_L} xdC$$

$$= [C(x) - 0]\cdot x \,\Big|_{x_M}^{\infty} - \int_{C_M}^{0} xdC$$

$$B.C.:\ C(-\infty, t) = C_L ; C(\infty, t) = 0$$

$$(C_L - C_M)x_M - \int_{C_M}^{C_L} xdC + (C_M - 0)x_M$$

$$+\int_{C_M}^{0} xdC = 0$$

$$(C_L - 0)x_M - \int_{C_M}^{C_L} xdC + \int_{C_M}^{0} xdC = 0$$

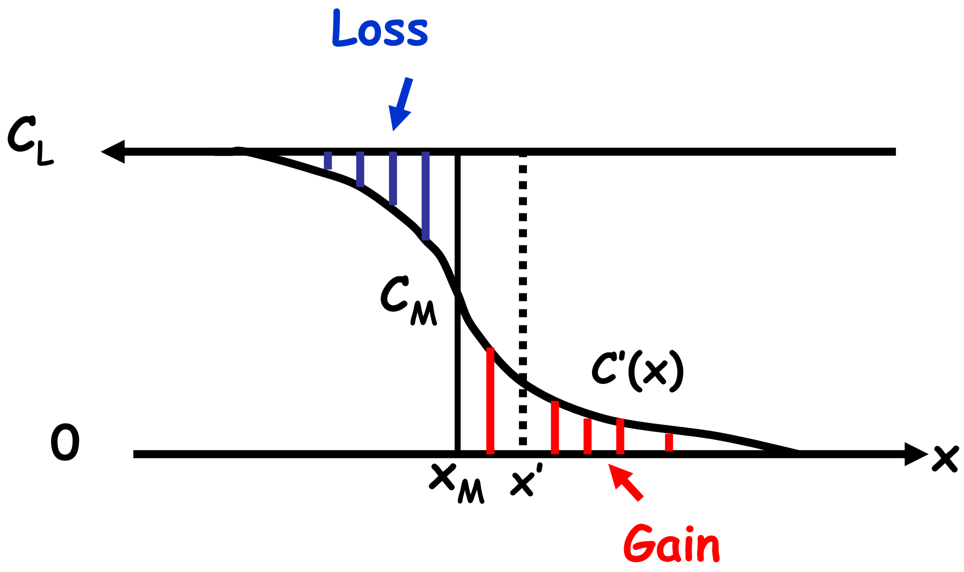
$$(C_L - 0)x_M - \left(\int_{C_M}^{C_L} xdC + \int_{0}^{C_M} xdC\right) = 0$$

If the coordinate of the Matano interface, x_M, is selected as the origin of the x-axis, i.e., $x_M=0$, then

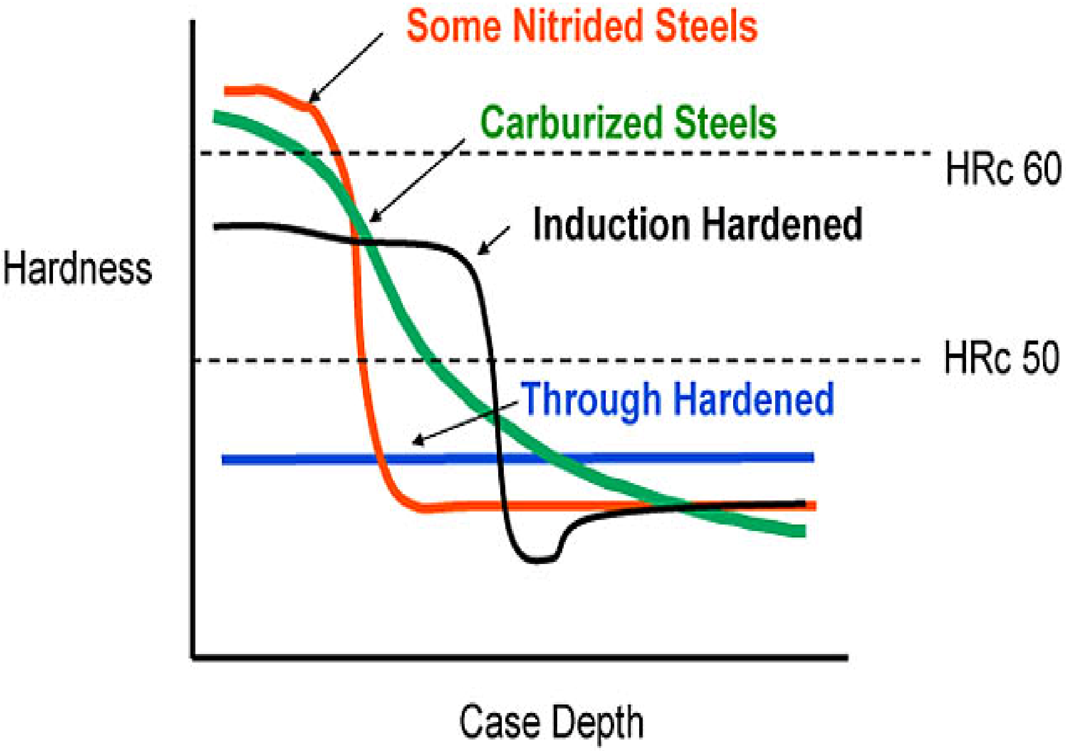
$$\int_0^{C_M} x\,dC + \int_{C_M}^{C_L} x\,dC = 0$$

$$\int_0^{C_L} x\,dC = \int_0^{C_L} \eta\,dC = 0$$

Although the location of $x_M=0$ is not known a priori, it may be found from concentration-distance data by balancing the area denoted Loss against the area of Gain.



Hardening of Steels

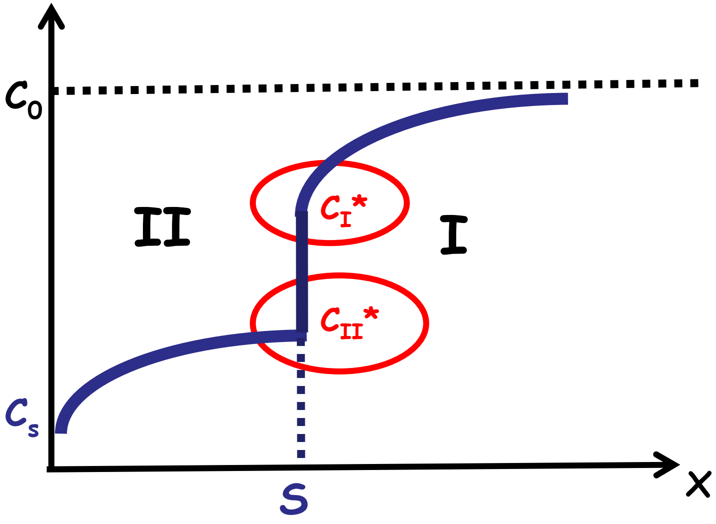


THROUGH HARDENING In order to harden steel, the iron mix must contain a certain amount of carbon. Carbon dissolves in molten iron. In through hardening steel, there is a high level of carbon added to the iron mix. When the component is heat treated, it becomes hard all the way through from the surface to the core, hence the term “through hardened”. Through-hardened steel components are relatively brittle and can fracture under impact or shock load.

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

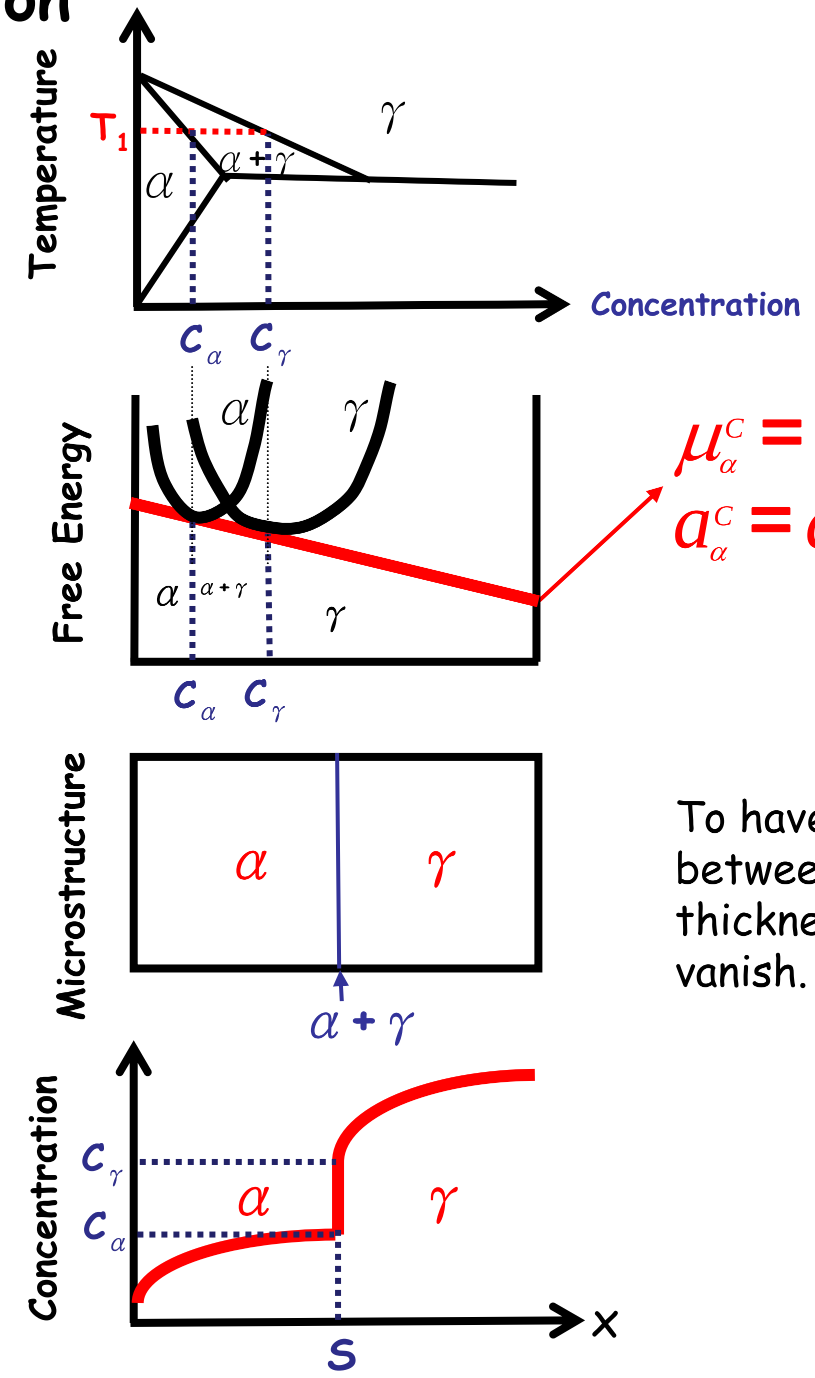
$C_I^* = kC_{II}^*$

k : partition ratio between phases

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

Kinetic Issue $dS/dt = ?$

Decarburization

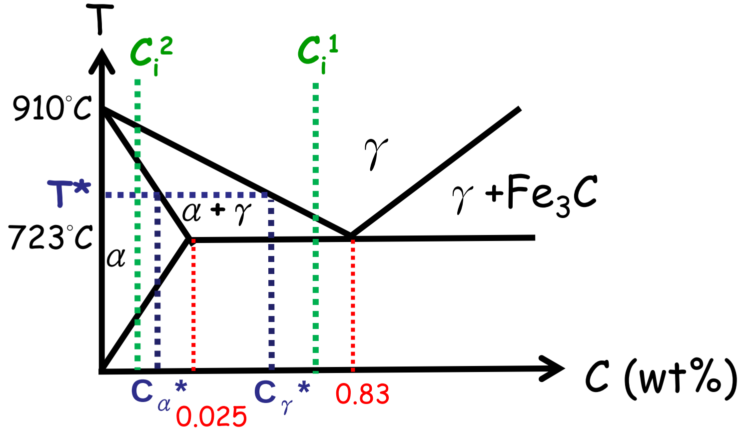


$$\mu_\alpha^C = \mu_\gamma^C \text{ or}$$

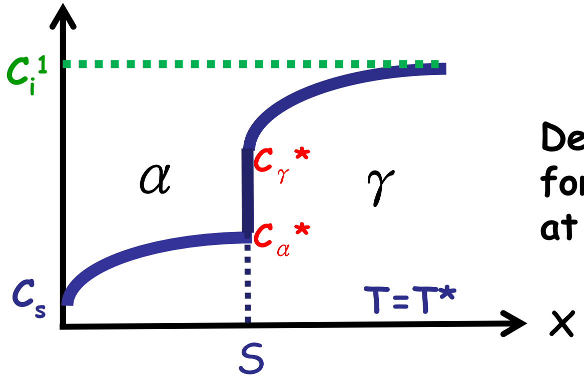
$$a_\alpha^C = a_\gamma^C$$

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

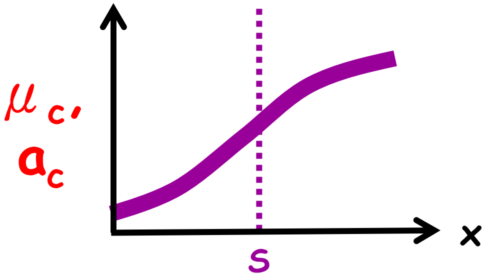
Carburization: α-Fe → γ-Fe
Decarburization: γ-Fe → α-Fe



Decarburization



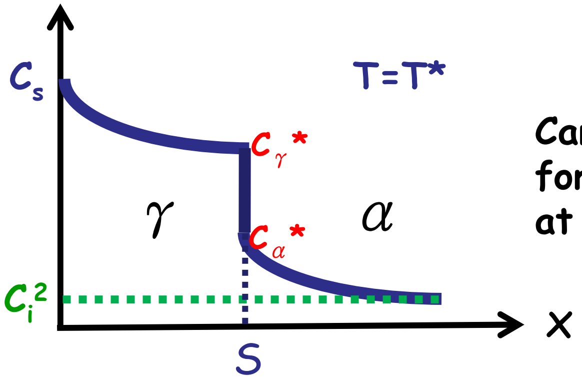
Decarburization forming α phase at the interface



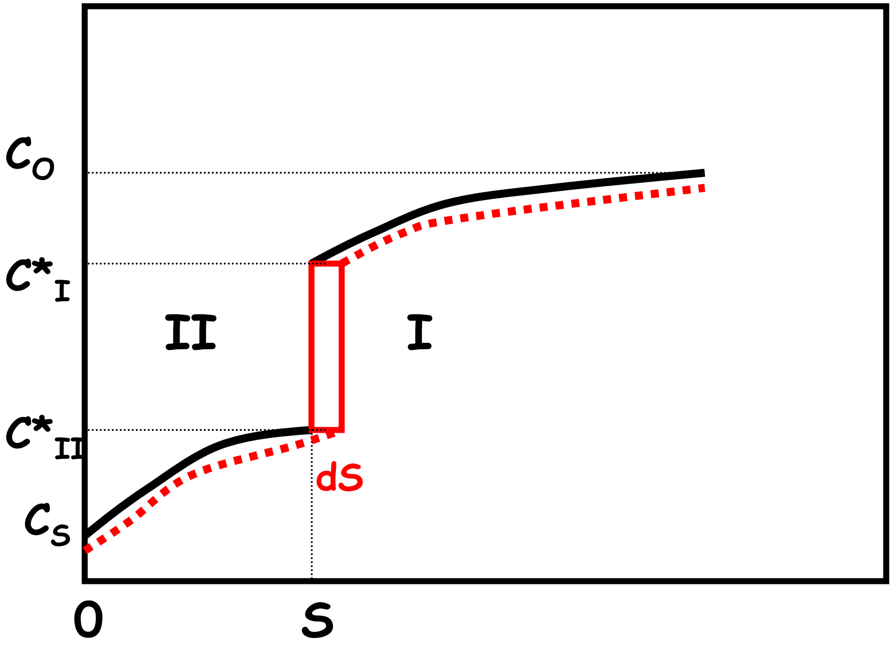
$\mu_\alpha^C = \mu_\gamma^C$ at x=S

where α and γ coexist

Carburization



Carburization forming γ phase at the interface



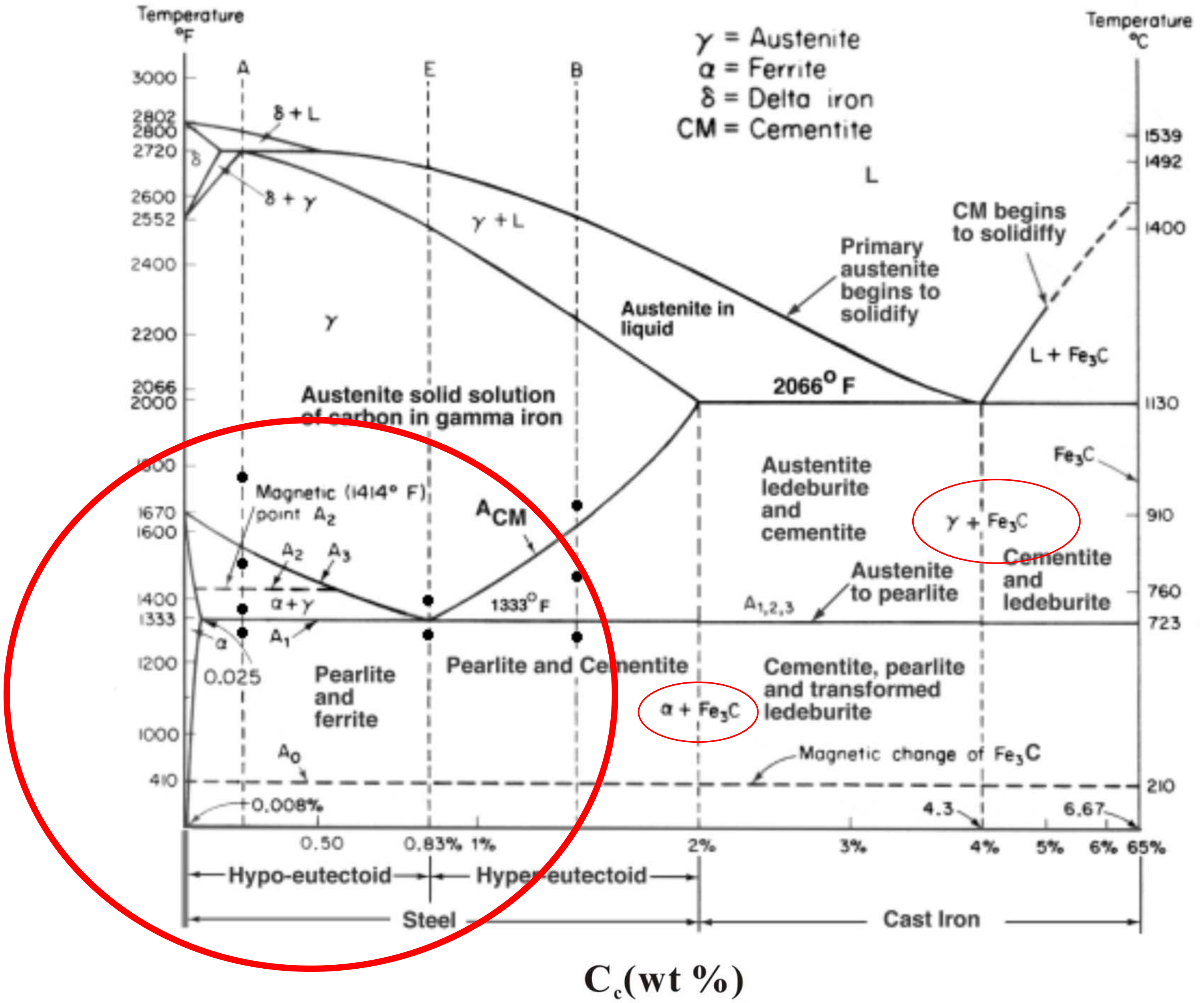
Mass Conservation

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

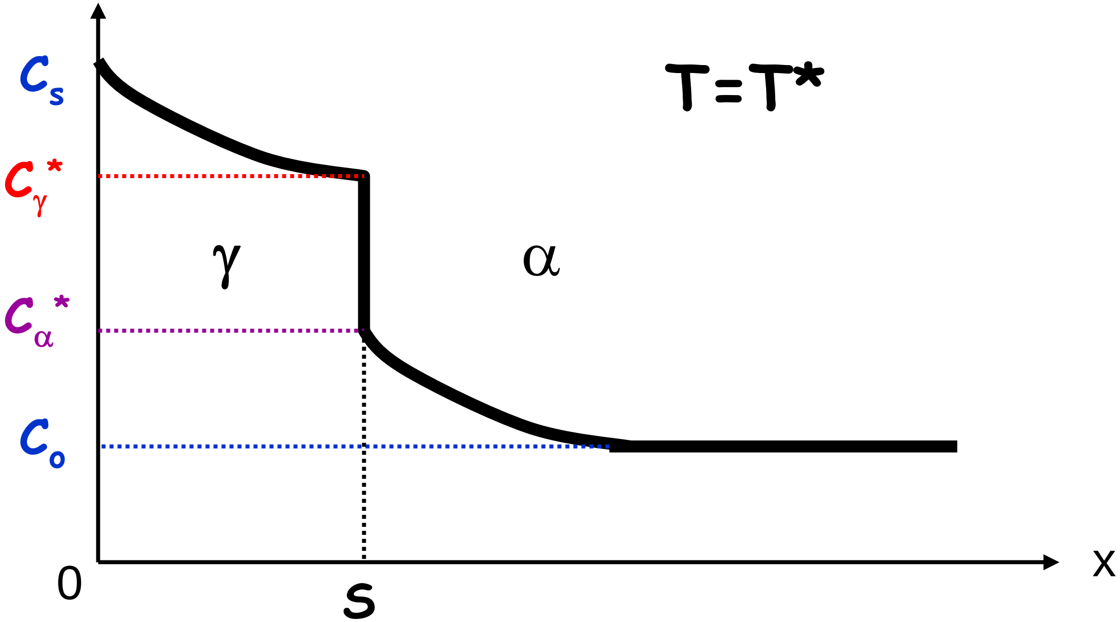
$$J_{II} - J_I = -D_{II}\left(\frac{\partial C_{II}}{\partial x}\right)_{x=S} - \left(-D_I \frac{\partial C_I}{\partial x}\right)_{x=S}$$

A: area for diffusion: constant

Fe-C Phase Diagram



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

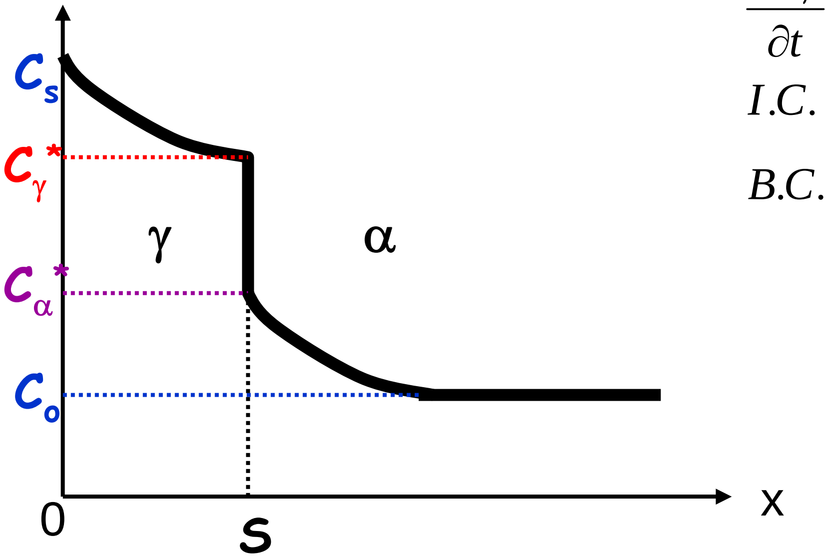
* $$D_C \neq D(C) \quad D_\alpha^C \neq D_\gamma^C$$

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

Fick's 2nd law

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

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



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

$B.C.:$ *in* α *phase*

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

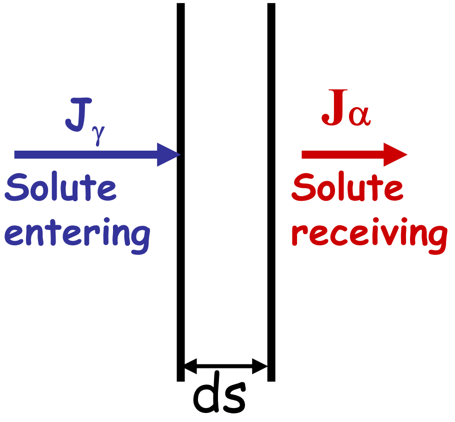
$$C = C_0 \quad at\ x = \infty$$

in γ *phase*

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

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

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

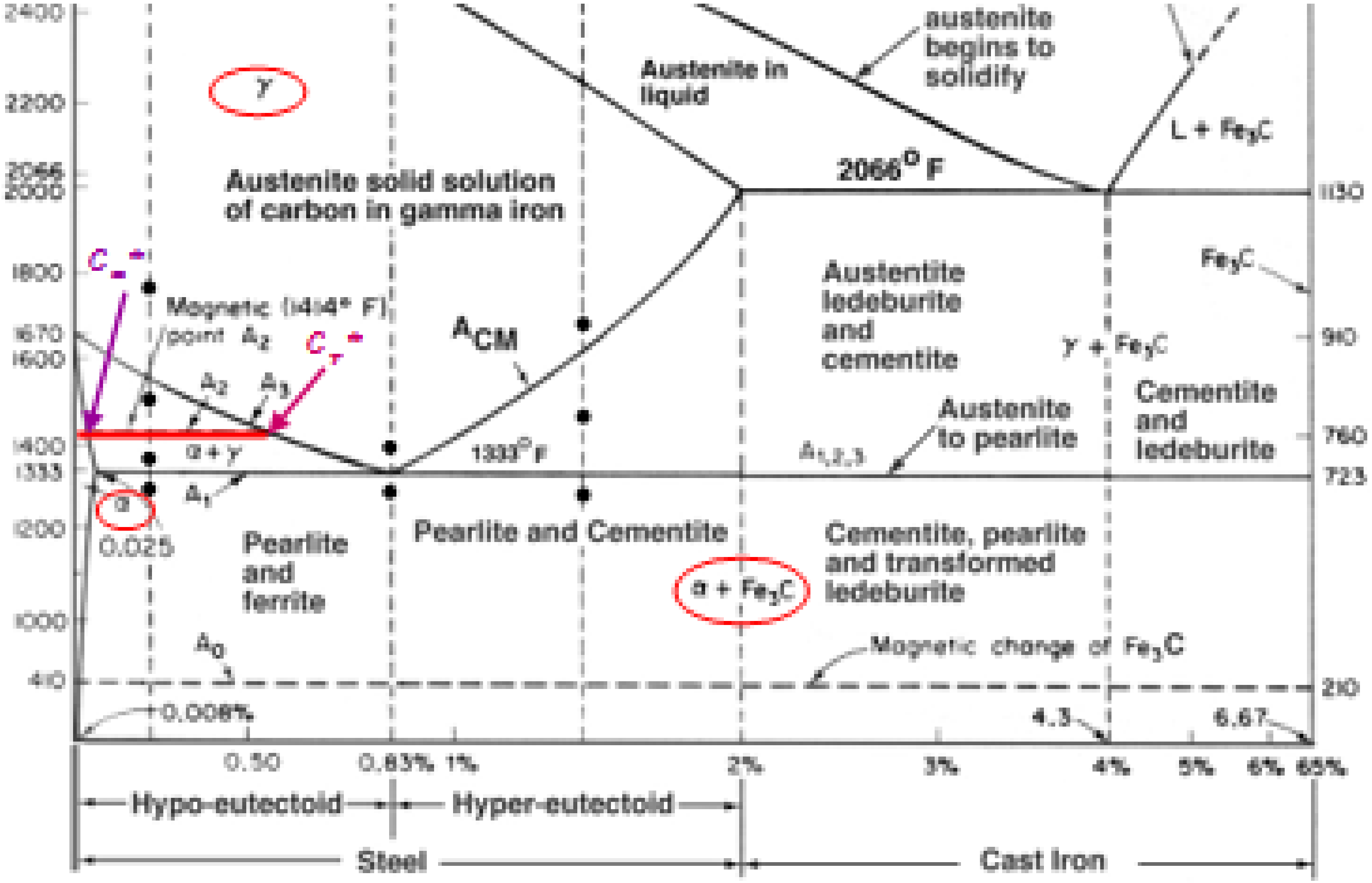


At $x = S$

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

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

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


2400
2200
2066
2000
1800
1670
1600
1400
1333
1200
1000
410
γ
Austenite solid solution of carbon in gamma iron
Austenite in liquid
austenite begins to solidify
L + Fe$_3$C
2066° F
1130
C_α*
Magnetic (1414° F) point A$_2$
C_γ*
A$_{CM}$
Fe$_3$C
910
A$_2$
A$_3$
α + γ
1333° F
Austentite ledeburite and cementite
γ + Fe$_3$C
Cementite and ledeburite
Austenite to pearlite
A$_{1,2,3}$
760
723
A$_1$
α
0.025
Pearlite and ferrite
Pearlite and Cementite
α + Fe$_3$C
Cementite, pearlite and transformed ledeburite
A$_0$
Magnetic change of Fe$_3$C
210
0.008%
4.3
6.67
0.50
0.83%
1%
2%
3%
4%
5%
6%
6.5%
Hypo-eutectoid
Hyper-eutectoid
Steel
Cast Iron

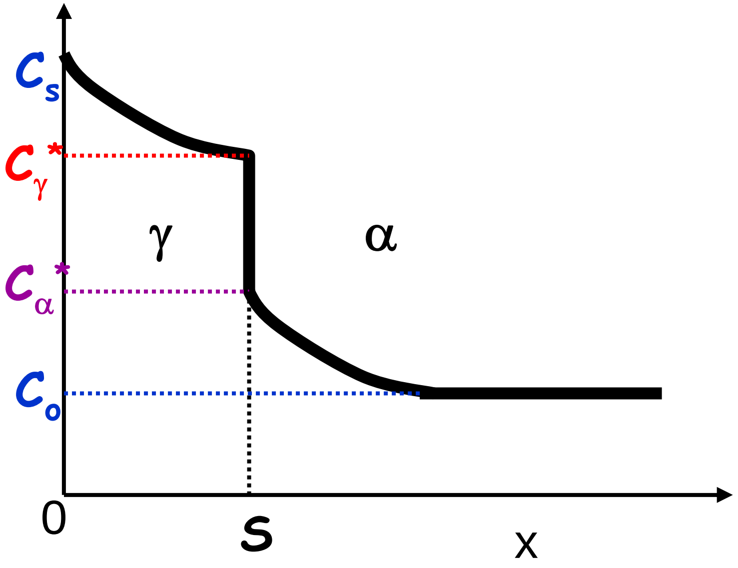
C_c(wt %)

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 ($\because$ diffusion controlling process)

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

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

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

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

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

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

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

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

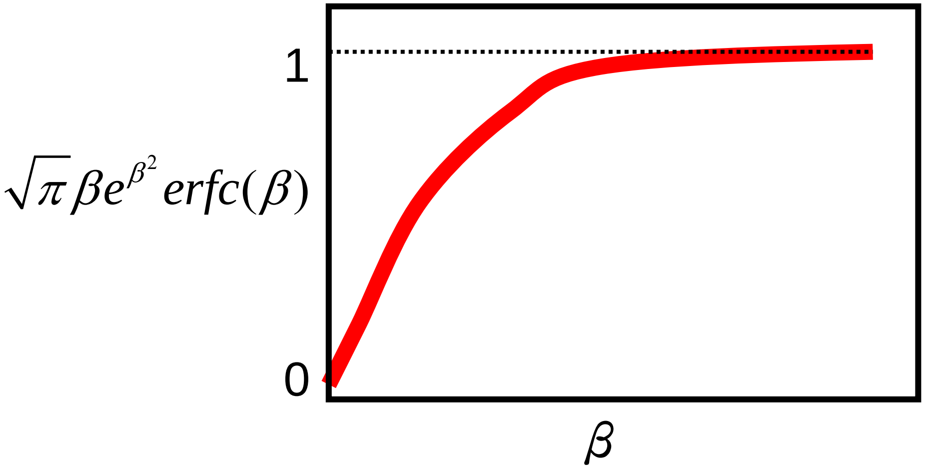
$$\left.\begin{array}{l} C_s + B' erf(\beta) = C_\gamma^* \\ C_0 + B erfc(\beta\phi^{1/2}) = C_\alpha^* \end{array}\right\}$$

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

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

$\rightarrow$ solve β by trial and error

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



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)

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

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

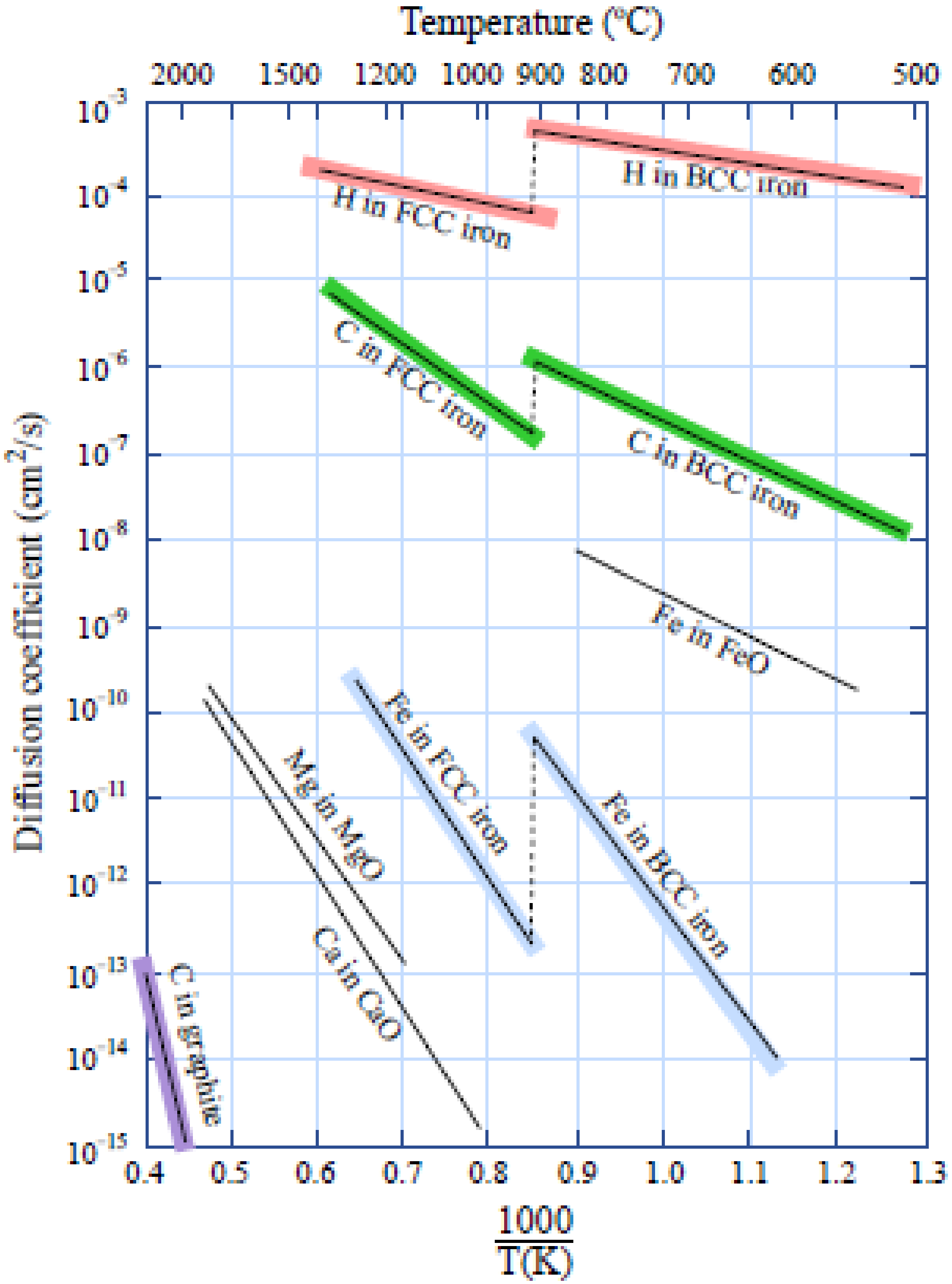
$$(C_\alpha^* - C_\gamma^*) = \frac{C_s - C_\alpha^*}{\sqrt{\pi}\,\beta e^{\beta^2}\,erf(\beta)} - \frac{C_\gamma^* - C_0}{\sqrt{\pi}\,\beta\phi^{1/2} e^{\beta^2\phi} erfc(\beta\phi^{1/2})}$$

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

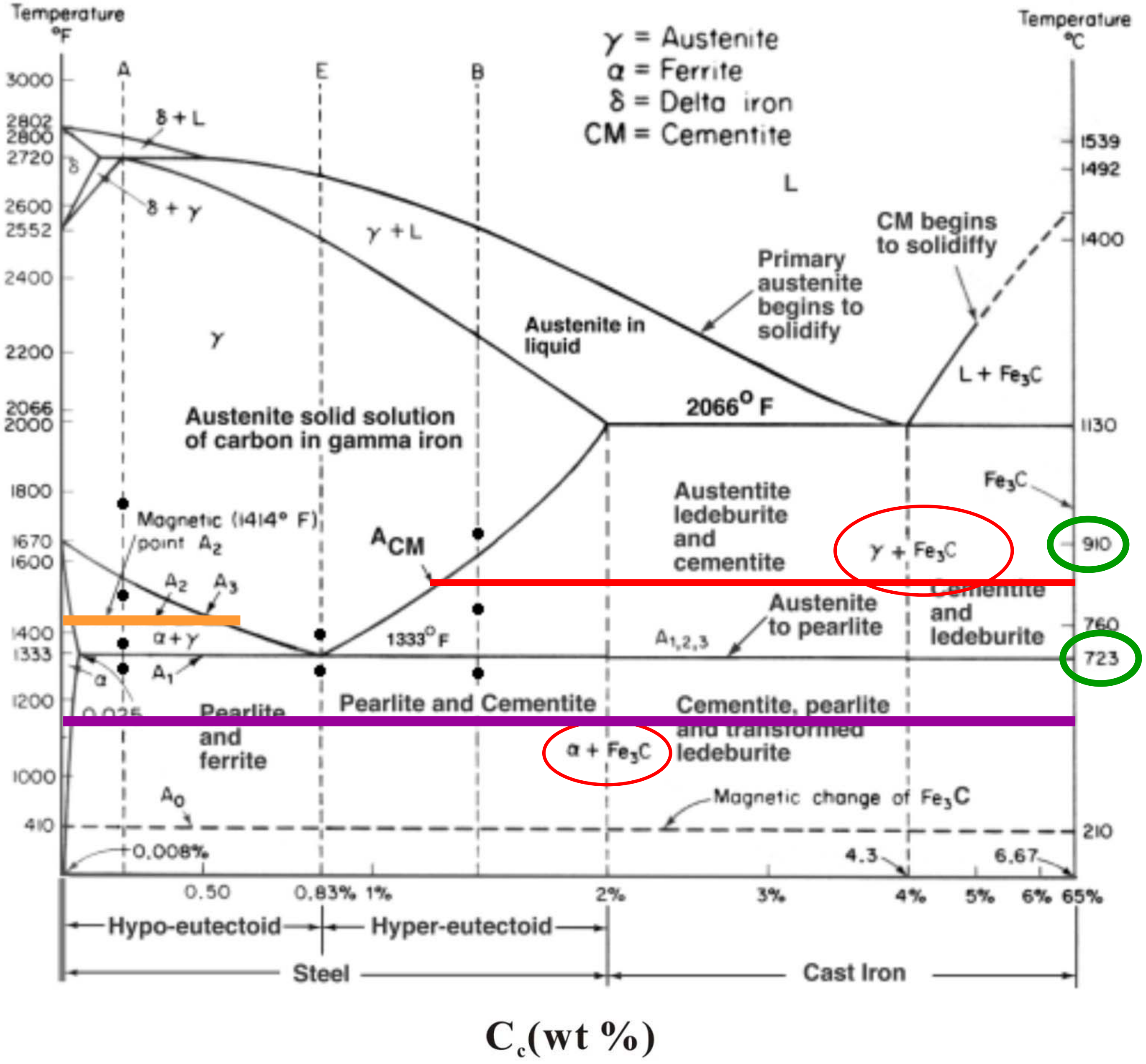
$$0.22 = \frac{0.01}{f(\beta)} - \frac{(0.24 - 0.4)}{f(\beta\phi^{1/2})}$$

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

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

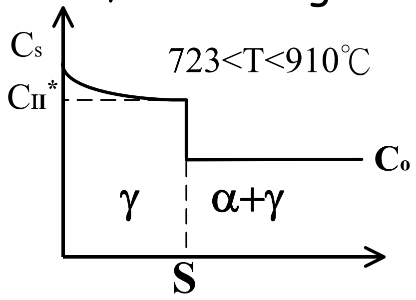

Temperature (°C)
2000
1500
1200
1000
900
800
700
600
500
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
Diffusion coefficient (cm^2/s)
H in BCC iron
H in FCC iron
C in FCC iron
C in BCC iron
Fe in FeO
Mg in MgO
Fe in FCC iron
Fe in BCC iron
Ca in CaO
C in graphite
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
$\frac{1000}{T(K)}$

Fe-C Phase Diagram

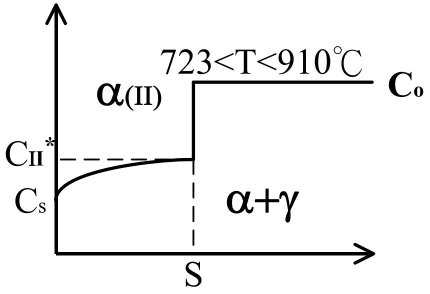


Formation of a single-phase layer from an initial two-phase mixture

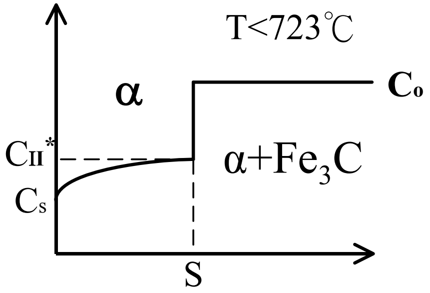
In the two-phase region, the average composition, C_o, is assumed to be uniform, which requires, in effect, that the grain size is small and that second-phase dispersion is uniform.



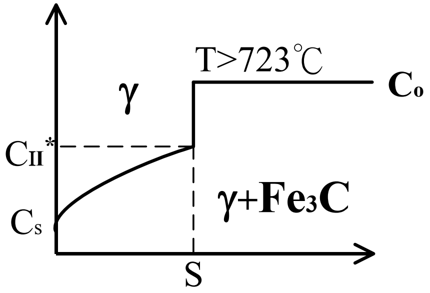
Carburization



De-carburization



De-carburization



De-carburization

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

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

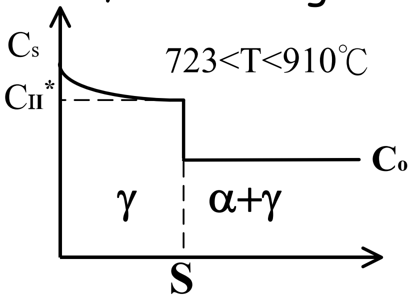
$$C_s-C_{II}^*=B_2 erf(\beta)$$

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

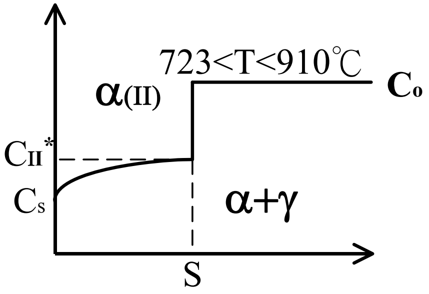
eliminate $B_2 \Rightarrow \frac{1}{\sqrt{\pi}}\left(\frac{C_s-C_{II}^*}{C_{II}^*-C_0}\right)=\beta\exp(\beta^2)erf(\beta)$

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

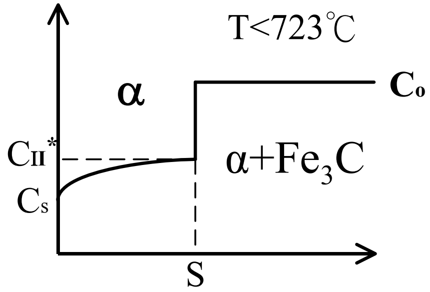
In the two-phase region, the average composition, C_o, is assumed to be uniform, which requires, in effect, that the grain size is small and that second-phase dispersion is uniform.



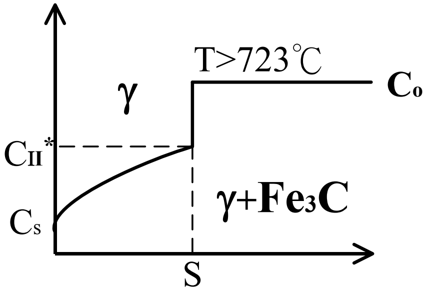
Carburization



De-carburization



De-carburization



De-carburization

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

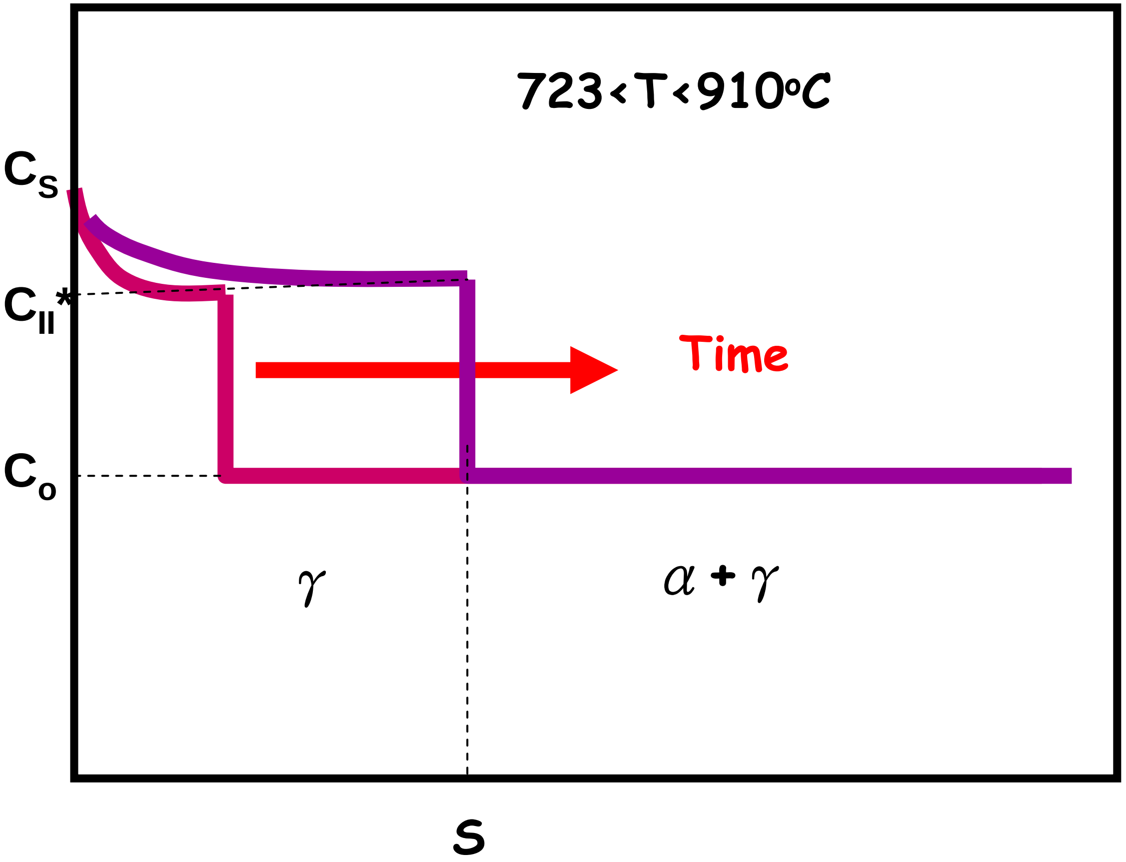
$$-D_{II}\left(\frac{\partial C_{II}}{\partial x}\right)_{x=s} = (C_{II}^{*} - C_0)\frac{dS}{dt}$$

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

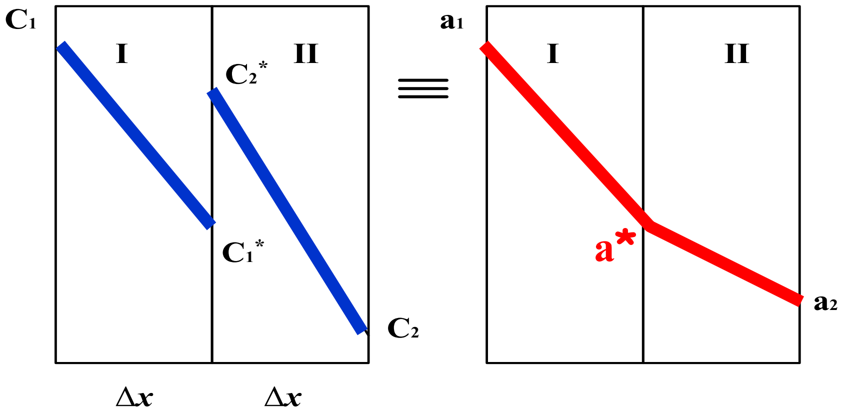
$$C_{II}^{*} - C_0 = \frac{B_2 \exp(-\beta^2)}{\sqrt{\pi}\beta}$$

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

Carburization Process



Steady state without Interfacial resistance (immobile boundary)



Concentration profile **Chem. activity profile**

$$J_1 = D_1 \frac{C_1 - C_1^*}{\Delta x}$$

$$J_2 = D_2 \frac{C_2^* - C_2}{\Delta x}$$

$a^* = k_2 C_2^*$

$a^* = k_1 C_1^*$

$C_1^* = k C_2^*$

$k_2 = k_1 k$

k_1 and k_2 are activity coefficient

k is a partition coefficient

Steady State → $J_1 = J_2$

No interfacial resistance → $\dfrac{C_1^*}{C_2^*} = k\ (const)$

$$C_1^* = C_2^* \cdot k = k\left(\frac{D_1 C_1 + D_2 C_2}{D_2 + k D_1}\right)$$

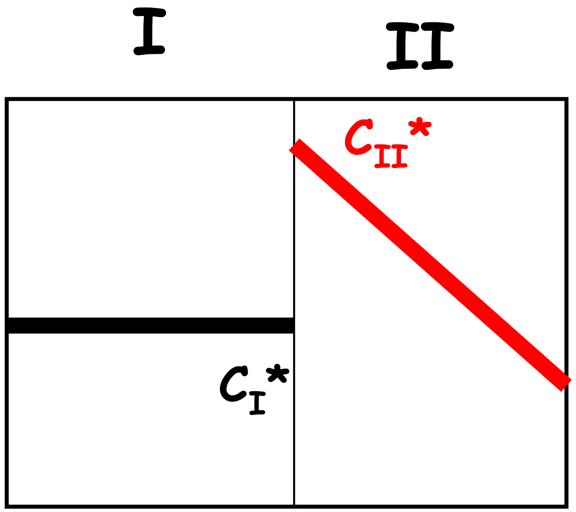
Note:

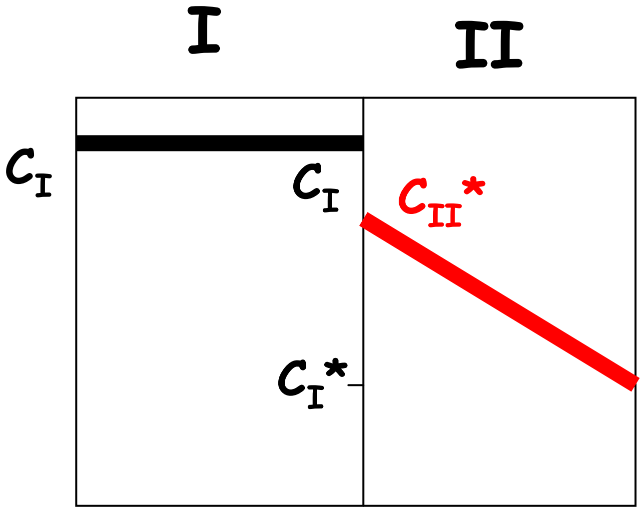
$D_1 >> D_2 \rightarrow C_1^* = C_1$

$D_1 << D_2 \rightarrow C_2^* = C_2$

$D_I >> D_{II}$

Diffusion Control in Phase II

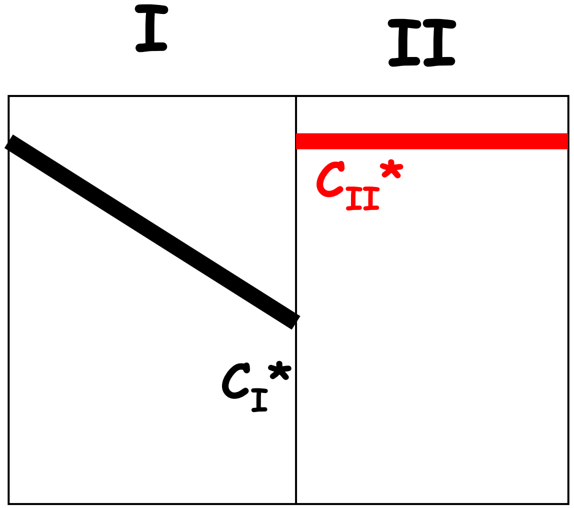


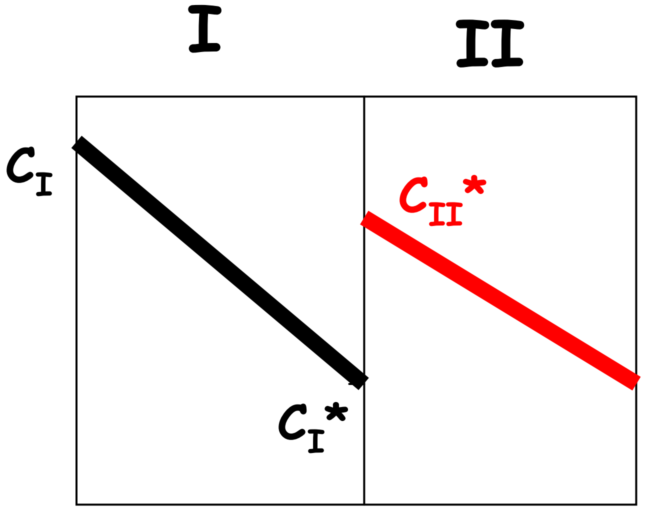


Reaction @ interface of Phase I & diffusion control in Phase II

$D_I << D_{II}$

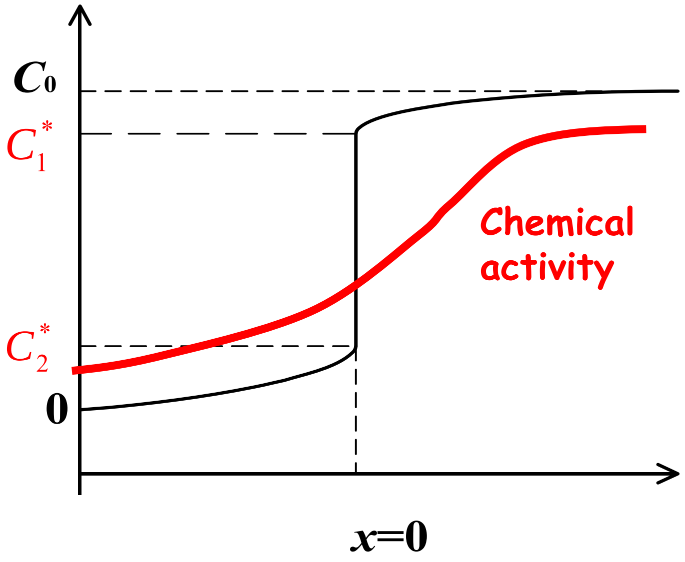
Diffusion Control in Phase I





Mixed diffusion control

Infinite composite system without Interfacial Resistance



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

$$C(x,0) = 0 \quad x < 0$$

$$B.C.: C(0,t) = C_1^* \quad x = 0^+$$

$$C(0,t) = C_2^* \quad x = 0^-$$

No accumulation at the interface

$$\frac{C_2^*}{C_1^*} = k \quad at\ x = 0$$

$$D_1 \frac{\partial C_1}{\partial x_1} = D_2 \frac{\partial C_2}{\partial x_2} \quad at\ x = 0$$

(immobile boundary)

$$C_1 = A_1 + B_1 erf\left(\frac{x}{2\sqrt{D_1 t}}\right) \quad x > 0$$

$$C_2 = A_2 + B_2 erf\left(\frac{x}{2\sqrt{D_2 t}}\right) \quad x < 0$$

$$C_1 = \frac{C_0}{1 + k\left(\frac{D_2}{D_1}\right)^{1/2}} \left\{1 + k\left(\frac{D_2}{D_1}\right)^{1/2} erf\left(\frac{x}{2\sqrt{D_1 t}}\right)\right\}$$

$$C_2 = \frac{kC_0}{1 + k\left(\frac{D_2}{D_1}\right)^{1/2}} erfc\left(\frac{|x|}{2\sqrt{D_2 t}}\right)$$

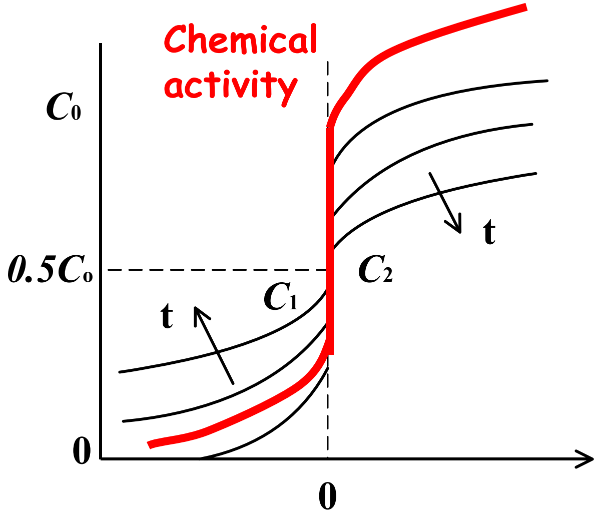
$$C_1^*(0,t) = \frac{C_0}{1 + k\left(\frac{D_2}{D_1}\right)^{1/2}}$$

$$C_2^*(0,t) = \frac{kC_0}{1 + k\left(\frac{D_2}{D_1}\right)^{1/2}}$$

(both of them are fixed)

($k=1$, $D_2/D_1=1$ → $C_1^*=C_2^*=C_o/2$)

Composite system with Interfacial Resistance (immobile boundary)



Contact Resistance at x=0

$$D_1\frac{\partial C_1}{\partial x}=h(C_1-C_2)\quad x=0$$

$$D_1\frac{\partial C_1}{\partial x}=D_2\frac{\partial C_2}{\partial x}=h(C_1-C_2)$$

The concentrations on either side of the interface are no longer constant, but each approaches the equilibrium value of $1/2C_0$ relatively slowly. (if $D_1=D_2$)

$$C_1=\frac{C_0}{1+(\frac{D_2}{D_1})^{1/2}}\{1+(\frac{D_2}{D_1})^{1/2}\{erf(\frac{x}{2\sqrt{D_1t}})+\exp(h_1x+h_1^2D_1t)\cdot erfc[\frac{x}{2\sqrt{D_1t}}+h_1\sqrt{D_1t}]\}\}$$

$$C_2=\frac{C_0}{1+(\frac{D_2}{D_1})^{1/2}}\{erfc(\frac{|x|}{2\sqrt{D_2t}})-\exp(h_2x+h_2^2D_2t)\cdot erfc(\frac{|x|}{2\sqrt{D_2t}}+h_2\sqrt{D_2t})\}$$

$$h_1=\frac{h}{D_1}\{1+(\frac{D_1}{D_2})^{1/2}\}$$

$$h_2=\frac{h}{D_2}\{1+(\frac{D_2}{D_1})^{1/2}\}$$

h: Chemical reaction rate constant at interface

(if $D_2=D_1$, $C_1(0,\infty)=C_2(0,\infty)=C_o/2$)