Diffusion

Preliminary concepts

A composition variable quantifies the amount of substance or material present in the system.

Examples:-

1) substitutional solid : Al - Li, Al - Cu

mole fraction $X_A = \frac{n_A}{n_A + n_B}$ n_A = No of A atoms

$X_B = \frac{n_B}{n_A + n_B}$ n_B = No of B atoms

$X_A + X_B = 1$

usually has a length scale in its definition eg: volume (V)

concentration

$$C_A = \frac{n_A}{V} = \frac{n_A / n_A + n_B}{V / n_A + n_B} = \frac{X_A}{V_m}$$

V_m → molar volume

$$C_B = \frac{n_B}{V} = \frac{X_B}{V_m}$$

2) Interstitial atoms : C in Fe → FeC_x

Li in CoO_2 → Li_xCoO_2 (cathode material)

H in Pd → storage

$X = \frac{n}{M}$ M = No of interstitial sites or No of unit cells

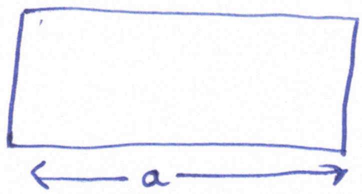
$C = \frac{n}{V}$

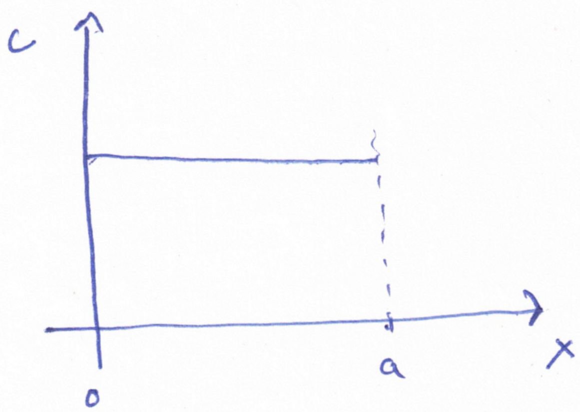
A single phase in equilibrium

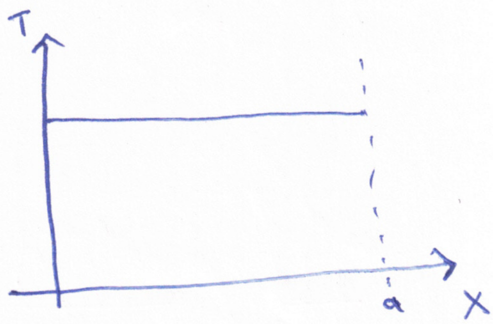
→ constant T and P, no ~~ex~~ inhomogeneous stresses

⇒ means it has constant (or) uniform concentration and Temperature

e.g block of metal like ~~steel~~ pure iron



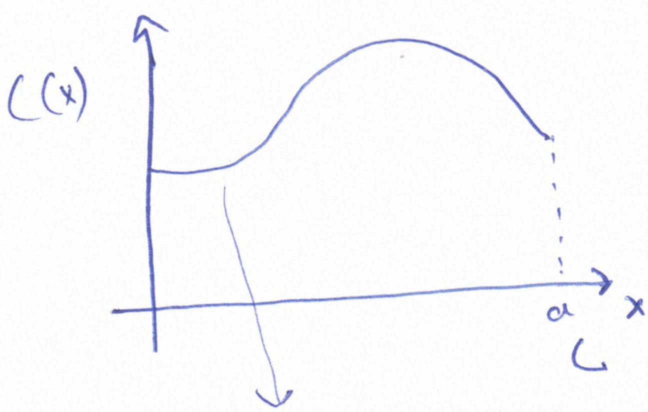


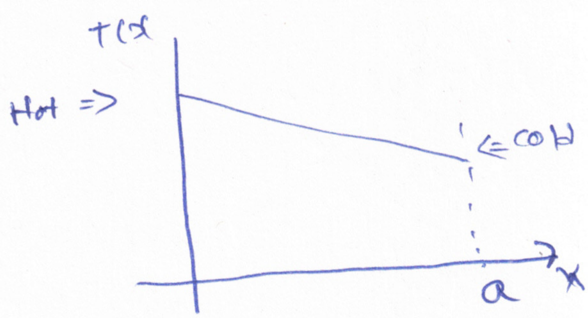


usually materials are out of equilibrium

⇓

non uniform concentration (or) temperature





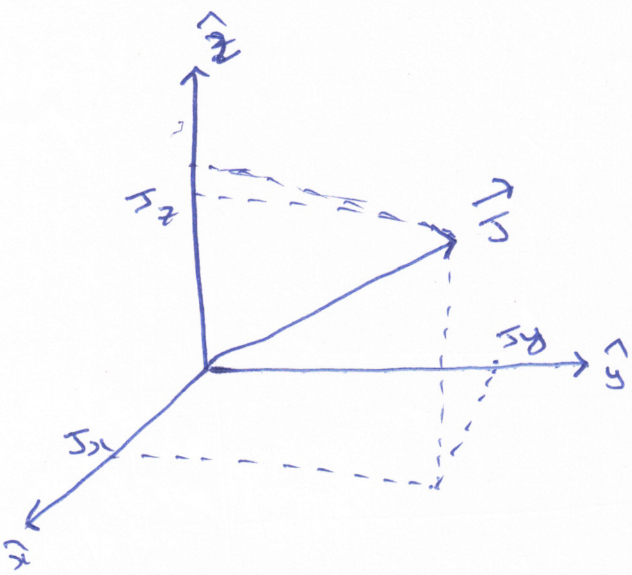
→ This creates a diffusion event moving the material towards equilibrium (uniform distribution

→ concentration variation creates diffusive "FLUX"

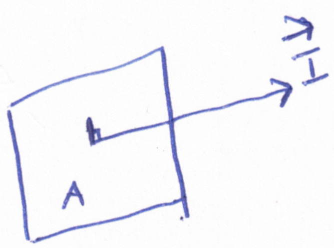
Flux : * a measure of flow per unit area
* usually denoted by $\vec{J}$ (a vector)
* Flux can be different in different directions

$$\vec{J} = (J_x, J_y, J_z)$$

$$\vec{J} = J_x \hat{x} + J_y \hat{y} + J_z \hat{z}$$



$\vec{J}$ is equal to the net number of atoms that cross a unit area per unit time



$\vec{I}$ = current of atoms passing area A $\perp^{er}$ the surface

$$\vec{J} = \frac{\vec{I}}{A}$$

units :

1) mole fraction : $x_A = \frac{n_A}{n_A + n_B}$ = unitless

2) concentration : $C_A = \frac{n_A}{V}$ = mole/m^3

3) flux : J_A = no of atoms crossing per area per time

$$= \frac{mole}{m^2 \cdot s} = \frac{mole}{cm^2 \cdot s}$$

common to use cm

Fick's First Law

- phenomenological observation
(or)
emphérical observation

→ It is a consititutive relation that links two physical quantities typically "cause" and "effect".

e.g Interstitial atoms (only one diffusing species)

$$\boxed{\vec{J} = -D\,\vec{\nabla} c}$$

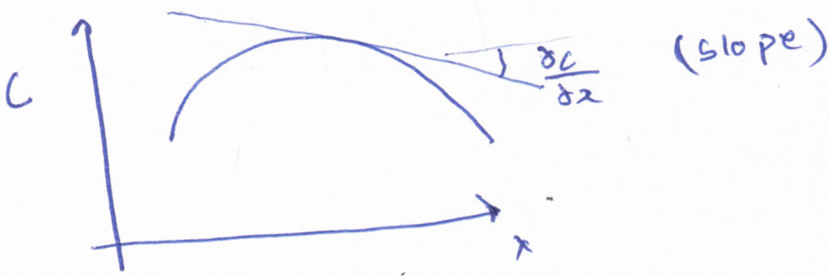
gradient operator

$$\vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

- this operation turns a scalar field into a vector

$$\vec{\nabla} c = \left(\frac{\partial c}{\partial x}, \frac{\partial c}{\partial y}, \frac{\partial c}{\partial z}\right)$$

in 1-dimension → $J = -D\,\dfrac{\partial c}{\partial x}$



D = diffusion coefficient
= Tells you how mobile the atoms are in the system

} depends on many factors such as T, crystal structure, atomic size etc

large D => mobile atoms
small D => slugsish atoms

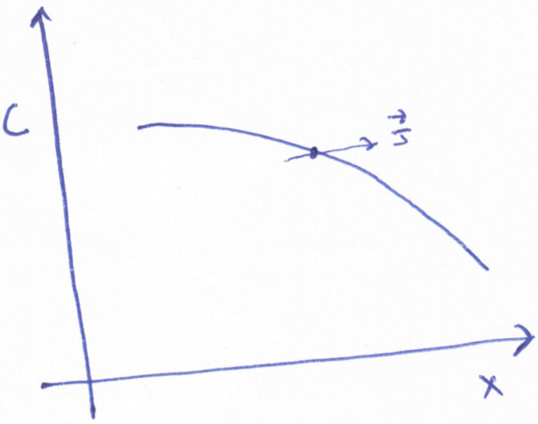
units of D :

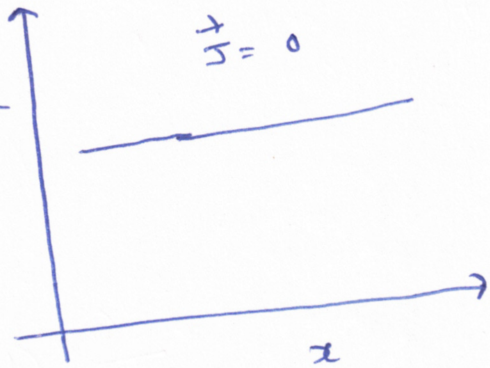
$$\frac{J}{\frac{\partial c}{\partial x}} = \frac{\frac{\text{mole}}{\text{cm}^2 \cdot \text{s}}}{\frac{\frac{\text{mole}}{\text{cm}^3}}{\text{cm}}} = \frac{\text{cm}^4}{\text{cm}^2 \cdot \text{s}} = \text{cm}^2/\text{s}$$

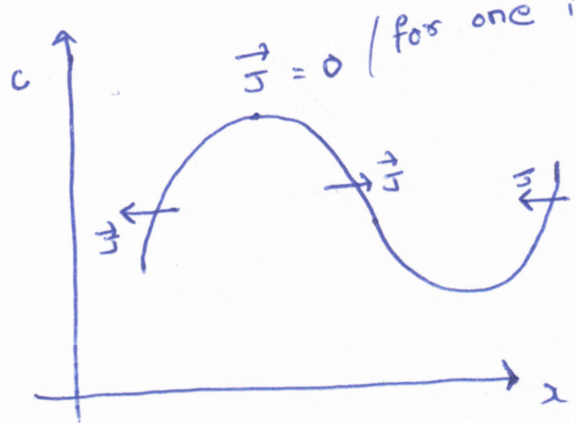
Imp → Fick's 1st law indicate that atoms diffuse down their concentration gradient

→ what is the direction of flux?

a)







(for one infinitesimal point)
↓
"c" is a continuum variable, so we can smooth it over

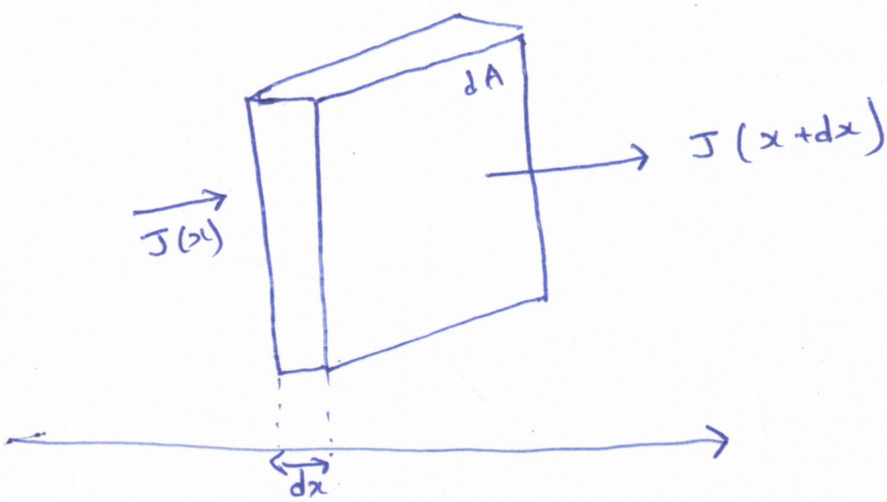
Ficks second Law: so far $\vec{J} = -D \vec{\nabla} c$

↳ brings time 't' into the picture

→ This is a conservation equation

→ atoms don't disapper → conserved

e.g: 1-dimension, flux J is in x- direction



volume, $V = dA \cdot dx$

→ No of particles in the volume, V $= C \cdot dA \cdot dx$

→ Rate of change of particles in V $= \frac{d}{dt}(c\, dA\, dx)$

why do the number of particles change?

* The incoming flux is different from outgoing flux

1) No of particles flowing in at x per time
$= dA \cdot J(x)$

2) No of particles flowing out at $x+dx$ per time
$= dA \cdot J(x+dx)$

taylor expansion

$= dA \cdot \left[J(x) + \frac{\partial J}{\partial x} dx + O(dx)^2 \right.$

3) Net no of particles flowing through the volume, V $= dA \left(J(x) - \left[J(x) + \frac{dJ}{dx} dx \right] \right. = \cancel{dA} = dA \cdot \frac{dJ}{dx}$

Both should be equal

$$\frac{\partial\left(c\, \partial A\, \partial x\right)}{\partial t} = -\partial A\, \frac{\partial J}{\partial x}\, dx$$

$$\Rightarrow \boxed{\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}}$$

generalized to 3-D

$$\Rightarrow \boxed{\frac{\partial c}{\partial t} = -\vec{\nabla}\cdot\vec{J}}$$

$\vec{\nabla}\cdot\vec{J}$ = divergence of J

$$= \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}$$

Summary of Fick's 2 laws

1st law

$$\vec{J} = -D\vec{\nabla}c$$

→ constitutive equation
→ D is a materials constant
→ empherical equation

2nd law

$$\frac{\partial c}{\partial t} = -\vec{\nabla}\cdot\vec{J}$$

→ conservation equation
→ valid if particles are not created or destroyed

Does 2nd law valid if we consider vacancies as species? what are sinks or sources of vacancies? Ans :- defects such as dislocation, GB's

$$\frac{\partial c}{\partial t} = \dot{n} - \vec{\nabla}\cdot\vec{J}$$

$\dot{n}$ = Source or sink term taking care of rate of creation or destruction of particles

→ Let's combine the two laws

$$\frac{\partial c}{\partial t} = \vec{\nabla}\left(D\,\vec{\nabla} c\right)$$

if D is constant

$$\boxed{\frac{\partial c}{\partial t} = D\,\nabla^2 c}$$

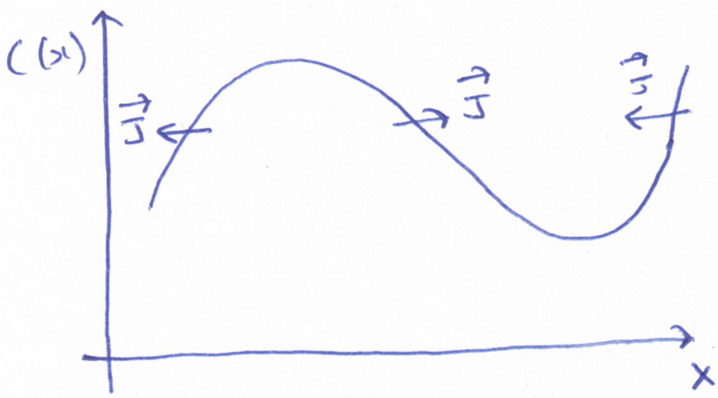
∇^2 = laplacian operator

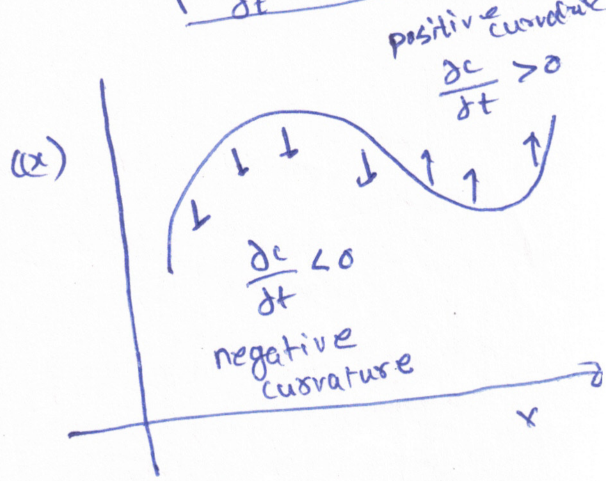
$$\nabla^2 c = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}$$

$$\boxed{\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}}$$

→ physical interpretation

$$J = -D\,\frac{\partial c}{\partial x}$$





ew comments on Diffusivity:

It connects two vectors, $\vec{J}$ and $\vec{\nabla} c$ ⇒ Hence its a 2nd order tensor

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = -\underbrace{\begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}}_{\text{tensor}} \begin{pmatrix} \frac{\partial c}{\partial x} \\ \frac{\partial x}{\partial y} \\ \frac{\partial c}{\partial z} \end{pmatrix}$$

for isotropic materials, cubic symmetry

$$D_{xx} = D_{yy} = D_{zz} = D, \quad \underset{i \neq j}{D_{ij}} = 0$$

→ If diffusivity changes with concentration $D(c)$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D(c) \nabla c \right]$$

in 1-D

$$\Rightarrow \quad \frac{\partial c}{\partial t} = D(c) \frac{\partial^2 c}{\partial x^2} + \frac{dD(c)}{dc} \left(\frac{\partial c}{\partial x} \right)^2$$

→ If diffusivity function of time, $D(t)$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D(t) \nabla c \right] = D(t) \nabla^2 c$$

we can do change of variabe

$$\tau_D = \int_0^t D(t')\, dt'$$

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \tau_D} \frac{\partial \tau_D}{\partial t} = \left(\frac{\partial c}{\partial \tau_D} \right) D(t)$$

$$\Rightarrow \quad \boxed{\frac{\partial c}{\partial \tau_D} = \nabla^2 c}$$

→ similar to master eqn

→ some times replace D.t with $\int_0^t D\, dt$ in the solution

→ If diffusivity is fn of direction

$$J_i = - \sum_i D_{ij} \frac{\partial c}{\partial x_j}$$

$$\frac{\partial c}{\partial t} = \hat{D}_{11} \frac{\partial^2 c}{\partial \hat{x}_1^2} + \hat{D}_{22} \frac{\partial^2 c}{\partial \hat{x}_2^2} + \hat{D}_{33} \frac{\partial^2 c}{\partial \hat{x}_3^2}$$

$$\hat{D} = \begin{bmatrix} \hat{D}_{11} & & 0 \\ & \hat{D}_{22} & \\ 0 & & \hat{D}_{33} \end{bmatrix}$$ eigen values

$[\hat{x}_1, \hat{x}_2, \hat{x}_3]$ eigen vectors

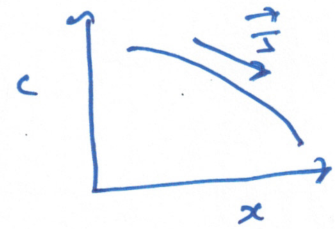
Finite difference method :-

→ This is a way to solve diffential equations

→ Let's take an example of diffusion

Ficks' First law : $\vec{J} = -D \frac{\partial c}{\partial x}$

$\downarrow$ Flux



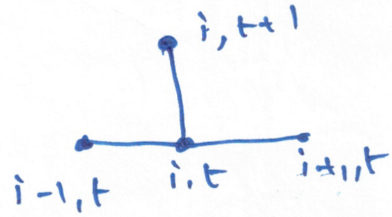
Fick's second law : $\frac{\partial c}{\partial t} = \frac{-\partial J}{\partial x}$

$\Rightarrow$ Diffusion eq :→ $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x} \right)$

for constant D

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

→ Foroward diffencing (explicit)



$$\frac{\partial c}{\partial t} = \frac{c_i^{t+1} - c_i^t}{\Delta t}$$

$$\frac{\partial^2 c}{\partial x^2} = D\left(\frac{c_{i+1}^t - 2c_i^t + c_{i-1}^t}{\Delta x^2} \right)$$

$$\Rightarrow c_i^{t+1} = c_i^t + \underbrace{\frac{D \Delta t}{\Delta x^2}}_{\alpha \le \frac{1}{2}} \left(\frac{c_{i+1}^t - 2c_i^t + c_{i-1}^t}{\Delta x^2} \right)$$

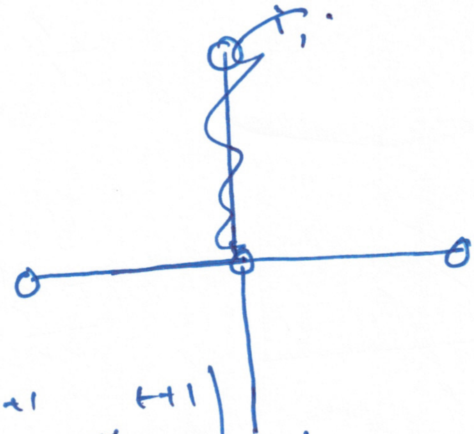
$$\Rightarrow \quad c_i^{t+1} = c_i^{t}(1-2\alpha) + \alpha\left(c\phi_{i+1}^{t} + c\phi_{i-1}^{t}\right)$$

$$\alpha \le 1/2$$

→ ~~Go ta eq~~

→ Backword differencing

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



$$\Rightarrow \quad \frac{\partial c}{\partial t} = \frac{c_i^{t+1} - c_i^{t}}{\Delta t}$$

But
$$\left.\frac{\partial^2 c}{\partial x^2}\right|_{t+1} = D\left(\frac{\phi_{i+1}^{t+1} - 2\phi_i^{t+1} + \phi_{i-1}^{t+1}}{\Delta x^2}\right)_{i,j}$$

$$\Rightarrow \quad -\alpha\, c_{i-1}^{t+1} + (1+2\alpha)\, c_i^{t+1} - \alpha\, c_{i+1}^{t+1} = c_i^{t}$$

→ always stable.

<u>Boundary conditions</u>:-

1) Dirchlet BC :- concentration is given

$c(x=0) = 0$

$c(x=1) = 7$

2) Newman BC :- Flux is given

$\cancel{\frac{dc}{dx}}\; J(x=0) = 2$

$\Rightarrow -D\left.\frac{\partial c}{\partial x}\right|_{x=0} = 2$

3) Mixed BC :-

Explicit Method: when D depends on x (I-D)

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

new term

does not depend on 't'

$$\Rightarrow \frac{C_i^{t+1} - C_i^t}{\Delta t} = \frac{\left(C_{i+1}^t - C_i^t\right)}{\Delta x}\frac{\left(D_{i+1} - D_i\right)}{\Delta x} + \frac{D_i}{\Delta x^2}\left(C_{i+1}^t - 2C_i^t + C_{i-1}^t\right)$$

$$\Rightarrow C_i^{t+1} = C_i^t + \frac{\Delta t}{\Delta x^2}\left[\left(C_{i+1}^t - C_i^t\right)\left(D_{i+1} - D_i\right) + D_i\left(C_{i+1}^t - 2C_i^t + C_{i-1}^t\right)\right]$$

β

$$\Rightarrow C_i^{t+1} = C_i^t + \beta\left[C_{i+1}^t D_{i+1} - \cancel{C_{i+1}^t D_i} - C_i^t D_{i+1} + \cancel{C_i^t D_i} + C_{i-1}^t D_i \cancel{C_{i+1}^t} - \cancel{2} D_i C_i^t + D_i C_{i-1}^t\right]$$

$$\Rightarrow \boxed{C_i^{t+1} = C_i^t\left(1 - \beta\left(D_{i+1} + D_i\right)\right) + C_{i+1}^t\left(\beta D_{i+1}\right) + C_{i-1}^t\left(\beta D_i\right)}$$

Implict Method: when D depends on x (1-D)

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

no "t" in D

$$\Rightarrow \frac{C_i^{t+1} - C_i^{t}}{\Delta t} = \frac{C_{i+1}^{t+1} - C_i^{t+1}}{\Delta x}\;\frac{D_{i+1}^{\cancel{t+1}} - D_i^{\cancel{t+1}}}{\Delta x} + D_i\left(\frac{C_{i+1}^{t+1} + C_{i-1}^{t+1} - 2C_i^{t+1}}{\Delta x^2}\right)$$

$$\Rightarrow C_i^{t+1} = C_i^{t} + \overbrace{\frac{\Delta t}{\Delta x^2}}^{\beta}\left(\left(C_{i+1}^{t+1} - C_i^{t+1}\right)\left(D_{i+1}^{\cancel{t+1}} - D_i^{\cancel{t+1}}\right)\right) + \beta D_i\left(C_{i+1}^{t+1} + C_{i-1}^{t+1} - 2C_i^{t+1}\right)$$

$$\Rightarrow C_i^{t+1} = C_i^{t} + \beta\Big[D_{i+1}^{\cancel{t+1}} C_{i+1}^{t+1} - \cancel{D_i^{\cancel{t+1}} C_{i+1}^{t+1}} - D_{i+1} C_i^{t+ \ldots} + \cancel{D_i C_i^{t+1}} + \cancel{D_i C_{i+1}^{t+1}} + D_i C_{i-1}^{t+1} - \cancel{2}D_i C^{t \ldots}$$

$$\Rightarrow \boxed{-\beta D_{i+1} C_{i+1}^{t+1} + \left(1+\beta\, D_{i+1} + D_i\right) C_i^{t+1} - \beta D_i C_{i-1}^{t+1} = C_i^{t}}$$