

heat source for diffusion
diffusion occurs due to conc. gradient.

in particular chapter no. 5
(in particular direction)

Q. How does diffusion occur?
How does diffusion of atom in solids occur.

Step wise migration of atoms
from one lattice site to another
lattice site.

For diffusion atoms to occur it requires two conditions.

- (i) They must be an empty adjacent site
- (ii) The atom must have sufficient energy to break bonds with its neighbouring atoms and then cause lattice distortion in during its displacement.

Diffusion in solids \rightarrow Vacancy & interstitial diffusion.

Diffusion in liquids/gases \rightarrow Brownian motion.

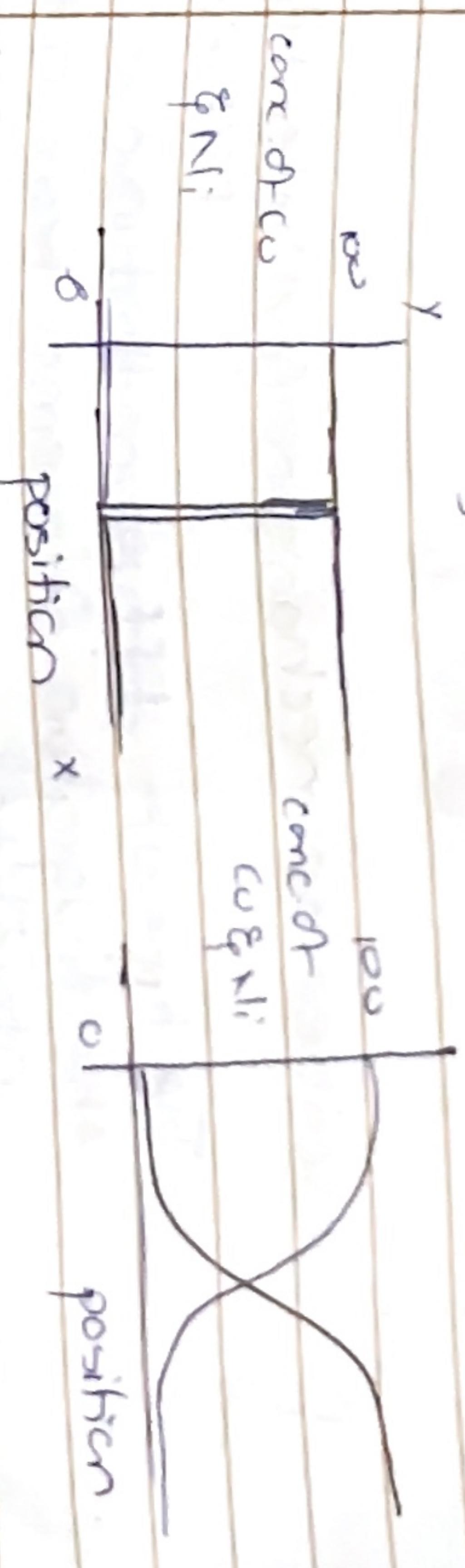
Q. self diffusion:-

Diffusion that occurs in the pure metals in which atoms of the same type are exchanging position is called as self diffusion.

Q. Impurity diffusion:-

Also known as the inter-diffusion that occurs due to exchange of positions between atoms of different materials.

\Rightarrow This indicates that one metal diffuses into another. E.g Cu - Ni



Q. Describe the mechanism of Diffusion by Vacancy

"It involves interchange of atoms from normal lattice position to an adjacent vacant lattice site"

- It depends upon the presence of vacant lattice sites in a structure.
- It can occur more at elevated temps because they create vacant lattice site.
- The motion of the diffusing atom & vacancy in this mechanism are opposite to one another

- Both interdiffusion & self diffusion can occur by this mechanism.

- Energy requirement for vacancy diffusion is illustrated as



- Q. Describe the mechanism for 'interstitial Diffusion'

The type of diffusion that involve the migration of atoms from one interstitial position to a neighbouring one which is empty.

- The mechanism is followed by interdiffusion of impurities such as H, C & O which have atoms small enough to fit in the interstitial positions.

- Q. Why is interstitial diffusion faster than vacancy diffusion?

In most metals the interstitial diffusion occurs more rapidly than vacancy diffusion because:

- i) The interstitial atoms are smaller and thus more mobile E.g. H, C, N, O etc.

- ii) The interstitial sites are usually more empty than vacancies.

- iii) Smaller atoms (interstitial) therefore less energy required to break from neighbouring atoms!

- Q. Describe the mechanism of "substitutional diffusion"

"The type of diffusion in which the different atoms exchange position with vacancies".

- * substitutional / Host impurity generally does not follow this mechanism. Thus it applies to substitution of impurities with a structure. It depends upon:

- i) number of vacancies.

- ii) Activation energy to exchange.

Q.

How diffusion is important in processing?
Industrial applications of diffusion.

Case - Surface Hardening:-

The phenomena of diffusing carbon atoms into the host's iron atoms at the surface.

Advantages:-

(i) The phenomena makes the host material hard to deform, as C-atoms lock the planes from shearing.

(ii) The phenomena makes the material hard to crack, as C-atoms pull surface in compression.

Doping:-

Example:- doping phosphorus in silicon

for n-type semiconductors.

① deposit P rich layers on surface of silicon
② heat it and n-type semiconductor is made.

Q.

Diffusion flux:-

The diffusion can be quantified by the diffusion flux (J).
mass / moles of atoms 'M' diffusing through $\frac{1}{A}$ to a unit surface / cross-sectional area of a solid per unit time.

$$J = \frac{M}{At.} \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}} / \frac{\text{kg m}^2}{\text{s}}$$

Q.

Steady-state Diffusion:-
FICK'S FIRST LAW

Steady-state diffusion in a single (x) direction

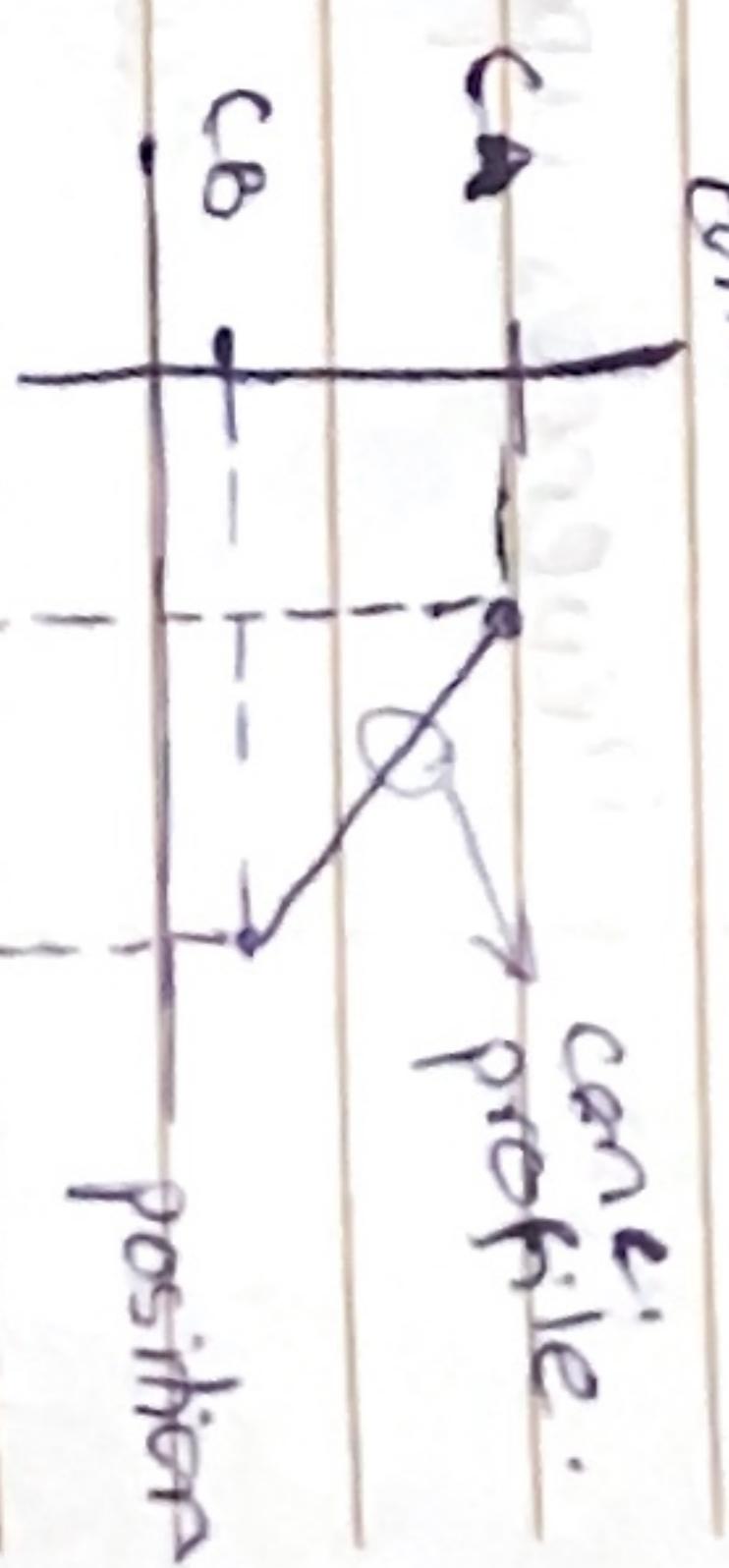
$$J = -D \left(\frac{dc}{dx} \right)$$

$\xrightarrow{\text{negative sign indicates const. of diffusion}}$ conc. gradient
 $\xrightarrow{\text{prop (diffusion coefficient). driving force.}}$ m^2/s .

gradient

conc.

$$\frac{dc}{dx} = \frac{c_A - c_B}{x_A - x_B}$$



$$\Delta C \Rightarrow \text{kg/m}^3.$$

Example 5.1 :-

$$T = 700^\circ\text{C}, \quad x_A = 5\text{mm}, \\ J = ? \quad x_B = 10\text{mm}.$$

$$C_A = 1.2 \text{ kg/m}^3, \quad D = 3 \times 10^{-11} \text{ m}^2/\text{s}, \\ C_B = 0.8 \text{ kg/m}^3.$$

(ii) It is independent of time but depends on temperature.
 (iii) It depends upon type of crystal imperfection.

→ Diffusion is faster along dislocation lines than through bulk crystal.

$$J = -D \frac{\Delta C}{\Delta x} \\ J = - (3 \times 10^{-11}) \times \frac{(1.2 - 0.8) \text{ kg/m}^3}{3 \times 10^{-4} \text{ m}^2/\text{s}} \\ J = - (5 \times 10^{-3} - 10 \times 10^{-3}) \text{ m}$$

$$J = \frac{\text{kg}}{\text{m}^2 \cdot \text{s}}.$$

(iv) Depends upon the type of crystal & host lattice.

Q. What does Fick's First law depends upon:

$$J = -D \frac{dc}{dx}.$$

→ interstitial diffusion is easier in BCC than FCC.

v) Depends upon the diffusion mechanism.

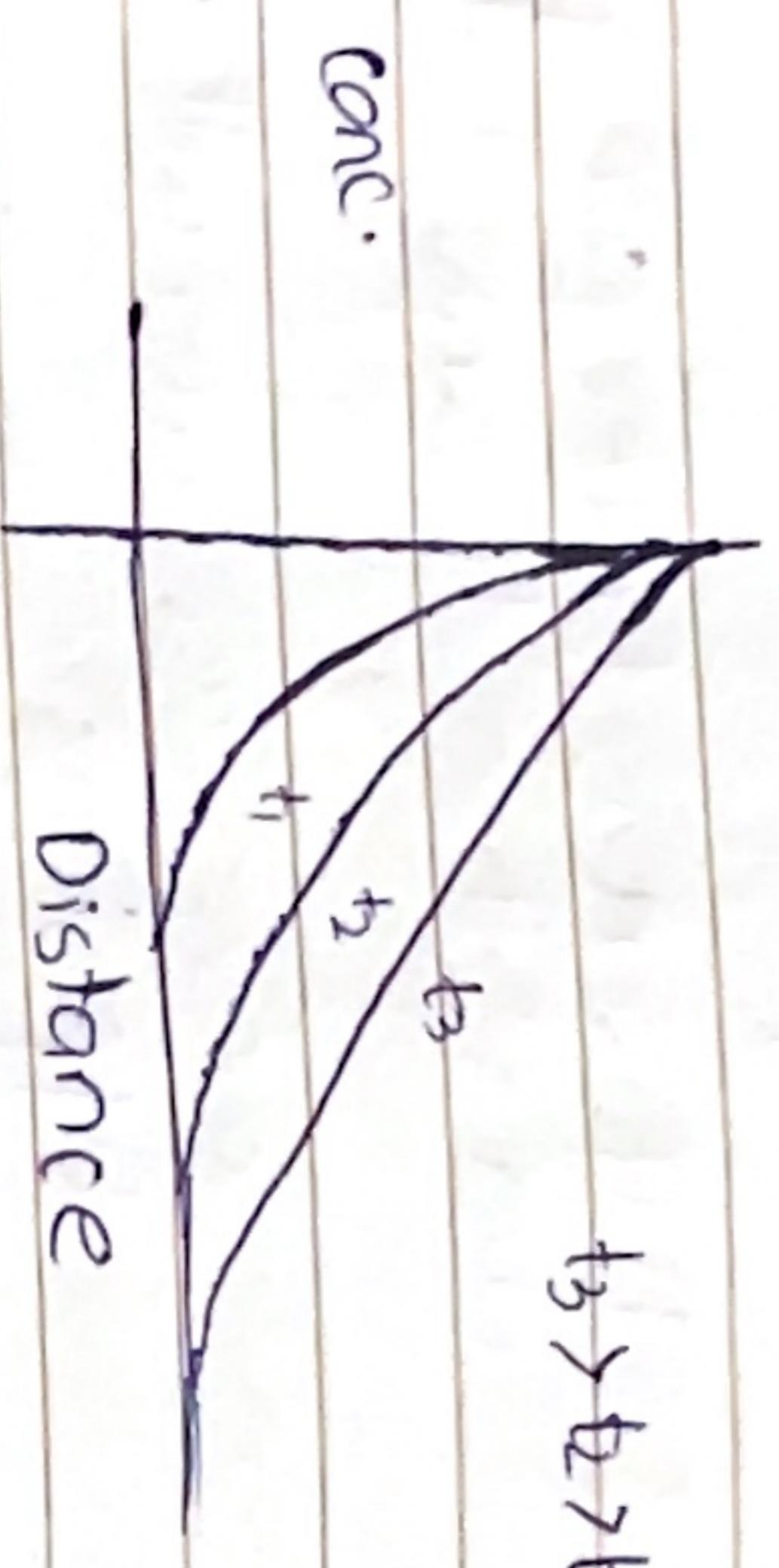
- substitutional
- interstitial.

$\frac{dy}{dx}$

FICK'S SECOND LAW

J (diffusion flux) and the conc. gradient at some particular point in a solid vary with time.

The phenomena is illustrated as with non-steady diffusion taken in various times



$$\bar{J} = \frac{m_x}{A \Delta t}$$

$$m_x = \bar{J}_x A \Delta t \quad \text{--- (1)}$$

Similarly mass leaving the volume at $\Delta x + x$ at time interval Δt .

$$m_{x+\Delta x} = \bar{J}_{x+\Delta x} A \Delta t \quad \text{--- (2)}$$

Now using equ (1) & (2)

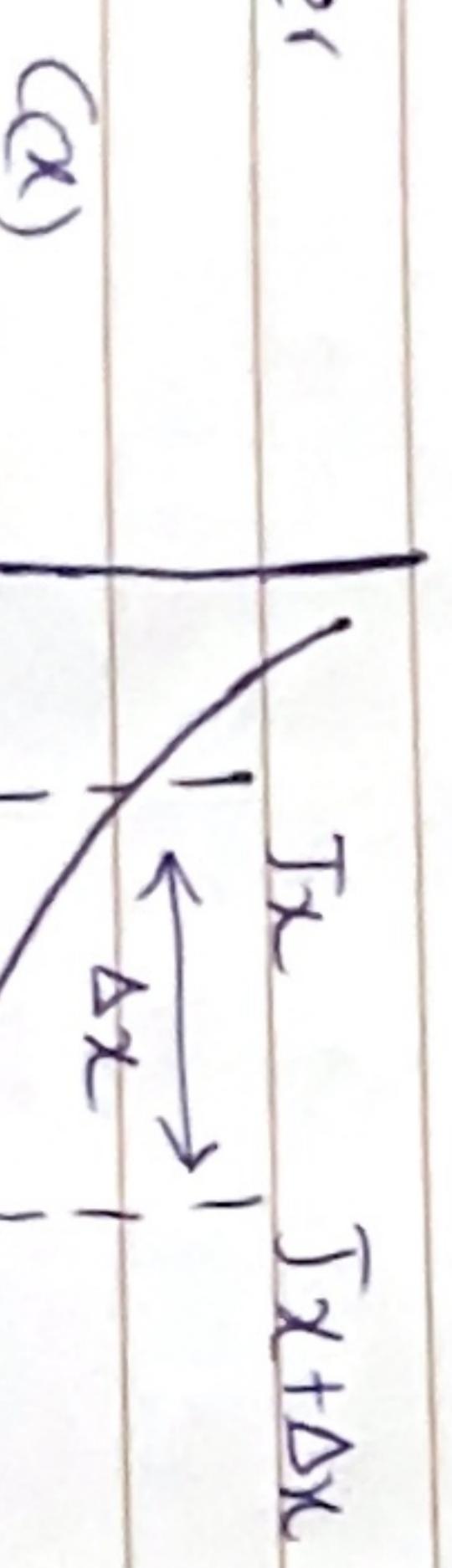
$$\frac{\delta c}{\delta t} \Rightarrow \frac{\Delta}{x} (D \frac{\delta^2 c}{\delta x^2})$$

$$\left[\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2} \right]$$

$$\begin{aligned} \Delta m &= m_x - m_{x+\Delta x} \\ &= \bar{J}_x A \Delta t - \bar{J}_{x+\Delta x} A \Delta t. \end{aligned}$$

Derivation of Fick's 2nd law.

Consider



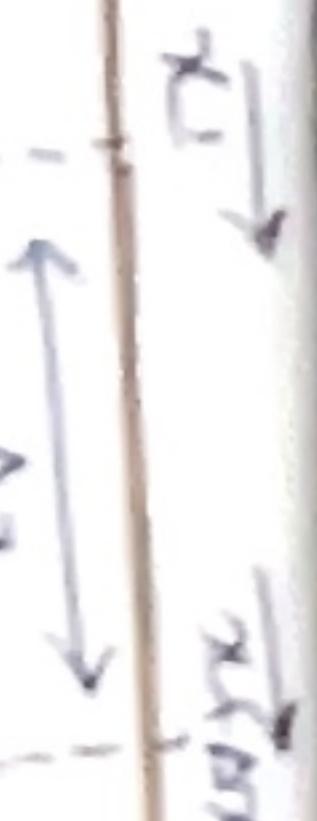
The change in conc. is

$$\Delta C = \frac{\Delta m}{\Delta V} \Rightarrow -\frac{\Delta J A \Delta t}{A \Delta x}$$

$$\text{Conc. } \frac{x_1}{x_1 + \Delta x} \text{ Galaxy}$$

$\frac{dy}{dx}$

Consider a body



$$\text{Volume} \Rightarrow A \Delta x$$

Now mass entering a volume ΔV in time interval Δt .

$$\bar{J} = \frac{m_x}{A \Delta t}$$

$$m_x = \bar{J}_x A \Delta t \quad \text{--- (1)}$$

Similarly mass leaving the volume at $\Delta x + x$ at time interval Δt .

$$m_{x+\Delta x} = \bar{J}_{x+\Delta x} A \Delta t \quad \text{--- (2)}$$

Now using equ (1) & (2)

$$\frac{\delta c}{\delta t} \Rightarrow \frac{\Delta}{x} (D \frac{\delta^2 c}{\delta x^2})$$

$$\left[\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2} \right]$$

$$\begin{aligned} \Delta m &= m_x - m_{x+\Delta x} \\ &= \bar{J}_x A \Delta t - \bar{J}_{x+\Delta x} A \Delta t. \end{aligned}$$

$$= (\bar{J}_x - \bar{J}_{x+\Delta x}) A \Delta t.$$

The change in conc. is

$$\Delta C = \frac{\Delta m}{\Delta V} \Rightarrow -\frac{\Delta J A \Delta t}{A \Delta x}$$

$$\Rightarrow -\frac{\Delta J A \Delta t}{A \Delta x} \text{ Galaxy}$$

$$\frac{\Delta C}{\Delta t} = - \frac{\Delta j}{\Delta x}$$

App limit on b.s

$$\text{limit } \frac{\Delta C}{\Delta t} = \lim_{\Delta x \rightarrow 0} - \frac{\Delta j}{\Delta x}$$

$$\frac{\partial C}{\partial t} = - \frac{\partial j}{\partial x}$$

by Fick First law

$$\bar{j} = - D \frac{\partial C}{\partial x}$$

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

Boundary Conditions.

initially:-

$$t=0 ; C=C_0 \text{ at } 0 \leq x \leq \infty$$

$$(i) \quad t>0 \quad C=\epsilon_x \text{ at } x=0.$$

$$(ii) \quad t>0 \quad C=C_\Theta \text{ at } x=\infty.$$

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$$

Solution of expression ①
is only possible when
physically meaningful
boundary conditions are specified.

One practically important solution is for a
semi-infinite solid in which the surface
conc. is held const. Frequently, the source
of the diffusing species is a gas phase...

(remaining theory from slides).

Initial conditions for ①.

(i) Before diffusion all the diffusion particles are arranged uniformly on the
surface with conc. C_0 .

(ii) the value of x is taken to be zero
and increases with distance in the solid.

(iii) The time is taken to be zero and increases
as the process begins.

Gaussian error function.

$$\frac{\partial^2 C}{\partial x^2} = \frac{C_0 - C_x}{D t}$$

$\frac{\partial C}{\partial x}$

Example 5.2 :-

$$T = 950^\circ C.$$

$$t = ?$$

$$C_0 = 0.25 \text{ wt}\%.$$

$$C_x = 0.8 \text{ wt}\%.$$

$$C_s = 1.20 \text{ wt}\%.$$

$$x = 0.50 \text{ mm} \\ = 0.5 \times 10^{-3} \text{ m} \quad \text{const carbon surface conc.}$$

$$D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}.$$

$$\frac{C_x - C_0}{C_s - C_0} \Rightarrow \frac{0.8 - 0.25}{1.20 - 0.25} \Rightarrow 1 - \text{erf} \left[\frac{5x \times 10^{-3}}{2\sqrt{1.6 \times 10^{-11} \times t}} \right]$$

Example 5.3 :-

$$D = 4.8 \times 10^{-14} \text{ m}^2/\text{s}$$

500°C

$$D = 5.15 \times 10^{-13} \text{ m}^2/\text{s}.$$

600°C

$$t_{500^\circ C} = ?$$

$$t_{600^\circ C} = 10 \text{ hr.}$$

$$\frac{x_{500}}{x_{600}} = \frac{x_{500}}{x_{600}}$$

$$\frac{D_{500}}{D_{600}} \frac{t_{500}}{t_{600}}$$

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794}$$

$$(2) \quad t_{500} = \frac{D_{600} t_{600}}{D_{500}} \Rightarrow \frac{(5.15 \times 10^{-13})(10 \text{ hr})}{4.8 \times 10^{-14}} \\ = 110.4 \text{ hours!}$$

$$z = 0.392$$

$$0.392 = 62.5 \text{ s}^{-1/2}$$

$$t = 25,400 \text{ s.}$$

$$t = 7.1 \text{ hrs.}$$

FACTORS AFFECTING DIFFUSION:-

(ii) Diffusing Species:-

The diffusing species and host material influences the diffusion coefficient D .

(iii) TEMP:-

Temp affects the diffusion coefficient.

$\uparrow D$ coefficient \propto Temp \uparrow

$$D = D_0 e^{-\frac{Q_d}{RT}}$$

\nwarrow

$D_0 = \text{pre-exponential}$
 temp (const) $D = \text{diffusion coefficient.}$

\rightarrow When Temp increases the vacancies increases.
 \rightarrow When temp increases the available energy to break bonds with T increases -

$$\ln D = \ln D_0 + \frac{-Q_d}{RT} \quad \textcircled{a}$$

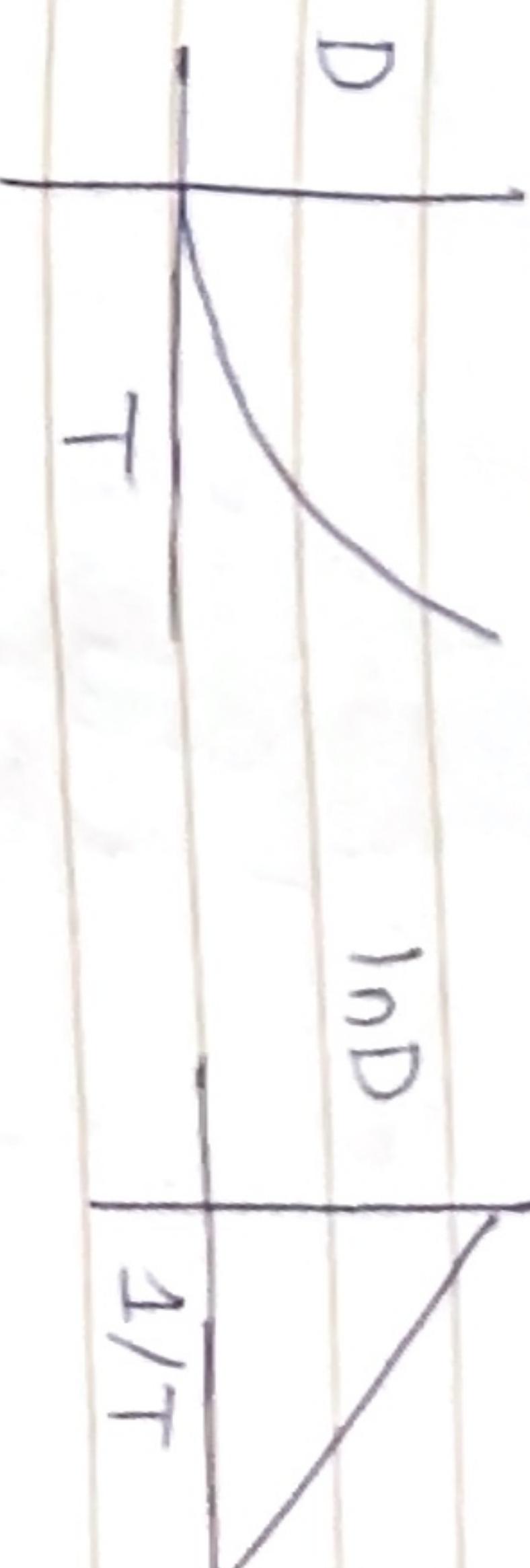
$$\ln D - \ln D_0 = -\frac{Q_d}{RT} \quad \textcircled{B}$$

$$\left[\begin{array}{l} T = \frac{Q}{R(\ln D_0 - \ln D)} \\ \quad \quad \quad \textcircled{2} \end{array} \right]$$

If from \textcircled{B}

$$\ln D_1 = \ln D_0 - \frac{Q_d}{RT_1}$$

$$\ln D_2 = \ln D_0 = \frac{Q_d}{RT_2}$$



$$\text{D.E.t.s} \\ C_x = 0.2 \text{ wt}\% \\ C_S = 1.00 \text{ wt}\%$$

$$C_x = 0.60 \text{ wt}\%.$$

$$\alpha = 0.75 \times 10^{-3} \text{ m.}$$

$$Dt = 6.24 \times 10^{-7} \text{ m}^2.$$

$$T_1 = 900^\circ\text{C}$$

$$T_2 = 1050^\circ\text{C}.$$

$$\frac{C_x - C_0}{C_S - C_0} = 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right).$$

$$D = D_0 e^{-\frac{Q_{\text{el}}}{RT}}$$

$$Dt = D_0 e^{-\frac{Q_{\text{el}}}{RT}}$$

C in γ -Fe means; 2.3×10^{-5}

$$\frac{0.6 - 0.2}{1 - 0.2} = 1 - \operatorname{erf} \left(\frac{0.75 \times 10^{-3}}{2\sqrt{Dt}} \right)$$

$$0.5 = \operatorname{erf} \left(\frac{0.75 \times 10^{-3}}{2\sqrt{Dt}} \right)$$

Using interpolation technique.

$$0.05 \quad 0.4755$$

$$0.5 \quad 0.5205$$

$$t = \frac{0.0271}{e^{(-\frac{17,810}{T})}}$$

$$900 - 1050^\circ\text{C}$$

$$\frac{z-0.45}{0.50-0.45} = \frac{0.5-0.4755}{0.5205-0.4755} \Rightarrow$$

$$- 900^\circ\text{C} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{use these values to get} \\ - 950^\circ\text{C} \\ - 1000^\circ\text{C} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{time but temp in Kelvin}$$

$$\operatorname{erf} \left(\frac{0.75 \times 10^{-3}}{2\sqrt{Dt}} \right) = 0.47.$$

Q. Define steady and non-steady state diffusion.

Steady state diffusion takes place at a constant rate that means once the process has started, the number of atoms/moles passing through an interface remains const. $\frac{dc}{dx} = \text{const}$.

Non-steady diffusion is a time dependant process in which the rate of diffusion is a function of time and varies with it.

$$\frac{dc}{dt} \neq \text{const.}$$