$C_A)_{Gas} = 0.30276 \; C_A)_{liquid}$

$\downarrow$

$\underline{H}$.

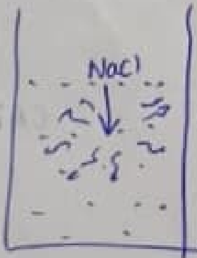
Crystallisation

convert liquid Solution to solid Crystals

Liquid Solution $\longrightarrow$ Solid Crystals

$\downarrow$

bring it to supersaturated state. Which is a meta stable state.

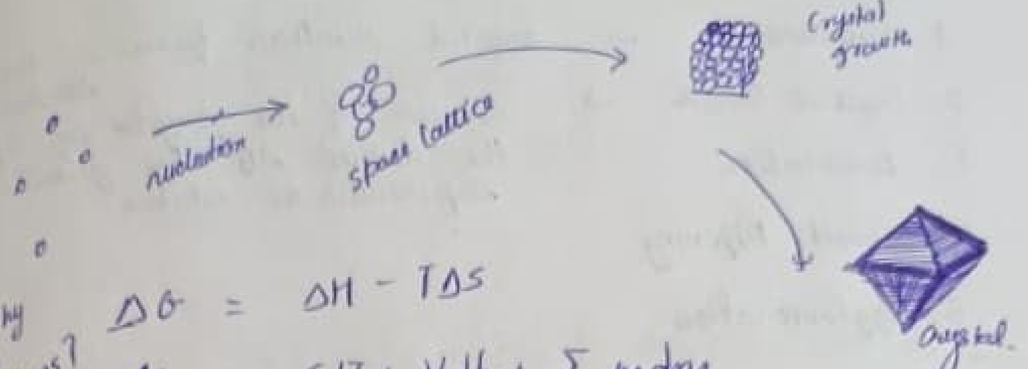


- dissolution until Saturation Condition
- at saturation condⁿ, Solute conc. is termed as Solubility.
- Solubility is a function of temp. Generally as Temp↑ Solubility↑

Difference b/w Precipitation & Crystallization

involves MT | does not Involve MT

Find Out
what is Melt Crystallization



why it happens?

$$\Delta G = \Delta H - T\Delta S$$

$$dG = -SdT + Vdp + \sum_A \mu_A dn_A$$

$$\mu_A = \frac{\partial G}{\partial n_A}, \quad n_A = \frac{\rho_i V}{M_A}$$

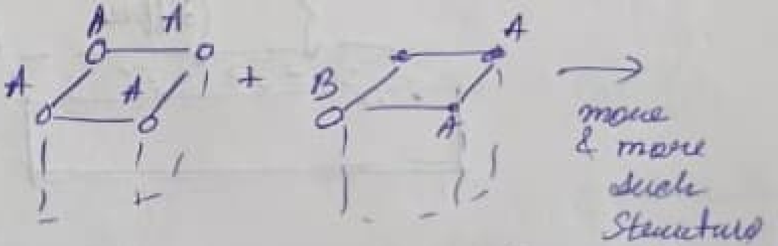
$$\mu_A = \frac{\partial G}{\partial \left(\frac{\rho_A V}{M_A}\right)}$$

$$\frac{\Delta G}{\Delta\left(\frac{\rho_A V}{M_A}\right)} = \mu_A$$

as crystal grows $V\uparrow$

$\mu\downarrow$

Soln A + B



Primary Nucleation

(a) Homogeneous nucleation

↳ no influence from external forces / elements

(b) Heterogeneous nucleation

↳ external forces needed

Secondary Nucleation

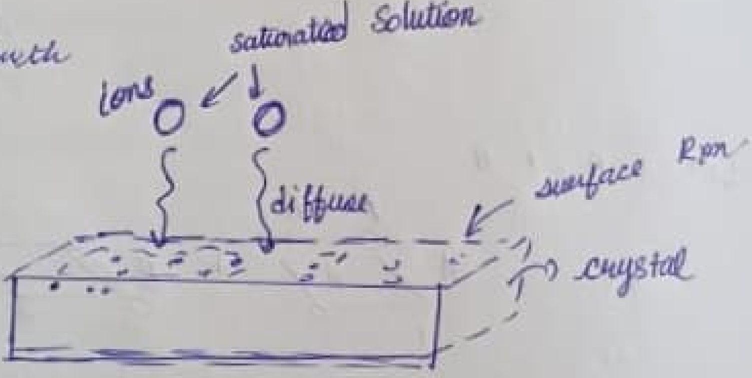
(a) Fluid Shear Nucleation

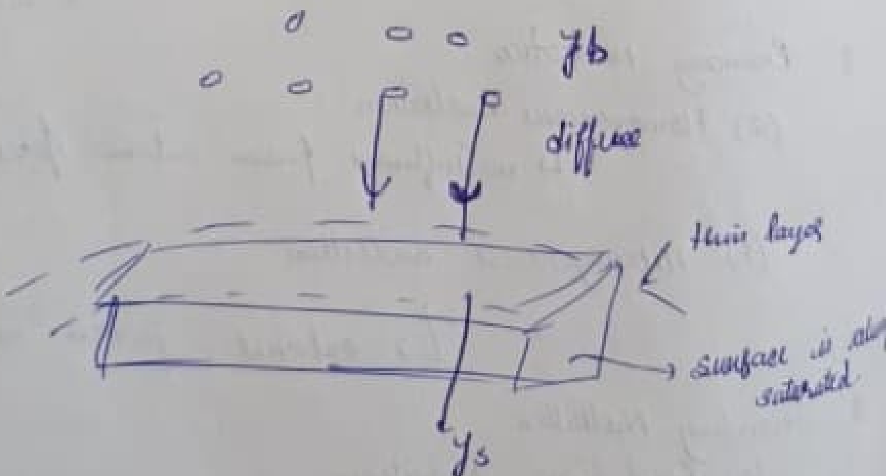
(b) Contact Nucleation

Steps of Crystallisation

1. Nucleation → crystal creation from a supe Solution
2. Crystal Growth → increase of the crystal size of the desired size by growth supersaturated solution
3. Dissolution
4. Ostwald Ripening
5. Agglomeration

Crystal Growth





Steady state

$$N_A = \frac{\dot{m}_p}{\text{Surface area}} \qquad (m_p = f(t))$$

$$N_A = k_y (y_b - y_i)$$

Sherwood correlation (flow over particle).

$$= k_s (y_i - y_s)$$

$$= K (y_b - y_s)$$

$$\boxed{\frac{1}{K} = \frac{1}{k_y} + \frac{1}{k_s}}$$

$$N_A = \frac{\dot{m}_p}{S_p} = K(\underbrace{y_b}_{\text{Super Saturated Sol}^n} - \underbrace{y_s}_{\text{Solubility}})$$

$$\dot{m}_p = \frac{dm_p}{dt}, \quad m_p = \rho_p \times V_p$$

$$V_p = \underline{a} \cdot L^3$$ ↳ assuming cube shape (mathematical technique)

$$\frac{S_p}{V_p} = \frac{6}{L} \qquad \frac{6aL^2}{aL^3}$$

$$S_p = \frac{6}{L} \cdot (aL^3) = 6aL^2.$$

$$\dot{m}_p = \frac{d}{dt}(\rho_p a L^3) = a\rho_p 3L^2 \frac{dL}{dt}.$$ → Growth rate

$$\dot{m}_p = 3\rho_p a L^2 G.$$

[$N_A = \frac{\dot{m}_p}{S_p} = K(y_b - y_s)$

$N_A = \frac{3\rho_p a L^2 G}{6aL^2}$

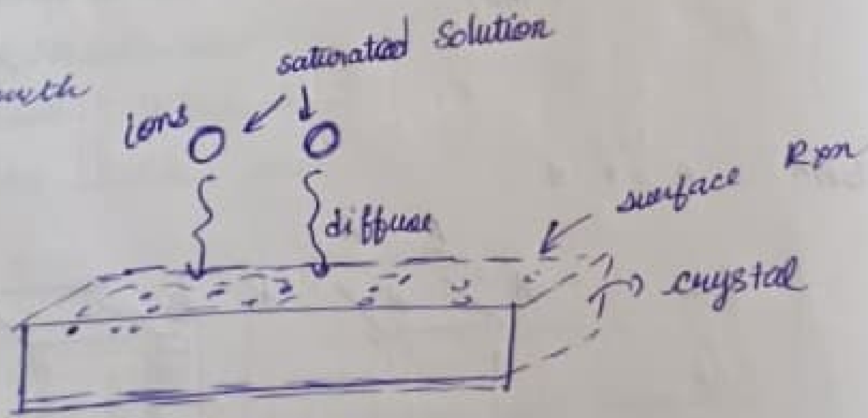
$N_A = \frac{\rho_p G}{2} = K(y_b - y_s)$]

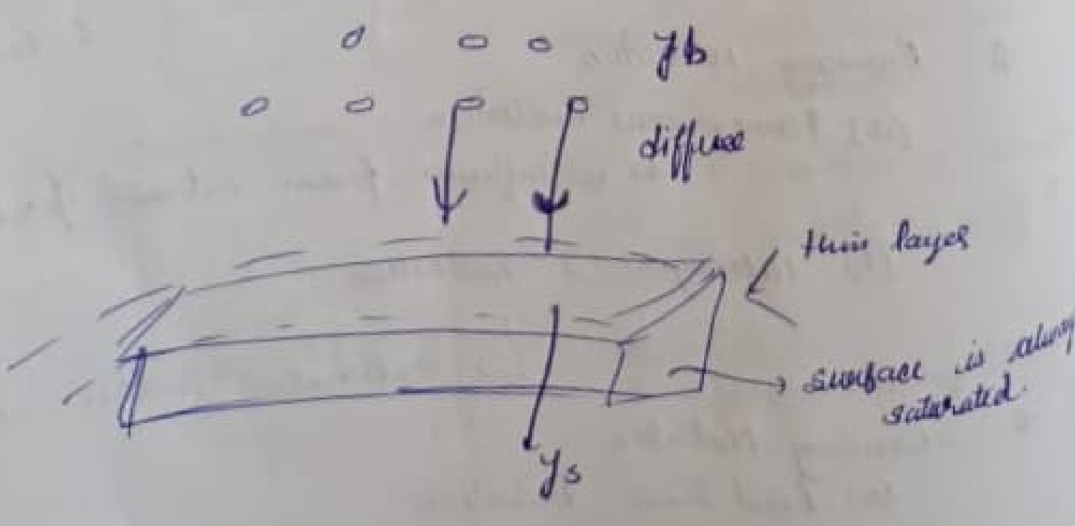
$$G = \frac{dL}{dt} = \frac{2K(y_b - y_s)}{\rho_p}.$$

Steps of Crystallisation

1. Nucleation → crystal creation from a supersat Solution
2. Crystal Growth → increase of the crystal size up to the desired size by growth from supersaturated solution
3. Dissolution
4. Ostwald Ripening
5. Agglomeration

Crystal Growth





Steady state

$$N_A = \frac{\dot{m}_p}{\text{Surface area}} \quad (m_p = f(t))$$

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$$= K (y_b - y_s)$$

$$\boxed{\frac{1}{K} = \frac{1}{k_y} + \frac{1}{k_s}}$$

$$N_A = \frac{\dot{m}_p}{S_p} = K (y_b - y_s)$$

y_b: Super Saturated Sol^n

y_s: Solubility

$$\dot{m}_p = \frac{dm_p}{dt}, \quad m_p = \rho_p \times V_p$$

$$V_p = a \cdot L^3$$

L, assuming cube shape. (mathematical technique)

$$\frac{S_p}{V_p} = \frac{6}{L} \qquad \frac{6a L^2}{a L^3}$$

$$S_p = \frac{6}{L} (a L^3) = 6 a L^2$$

$$\dot{m}_p = \frac{d}{dt} (\rho_p a L^3) = a \rho_p 3L^2 \frac{dL}{dt}$$

$\frac{dL}{dt}$ → Growth rate

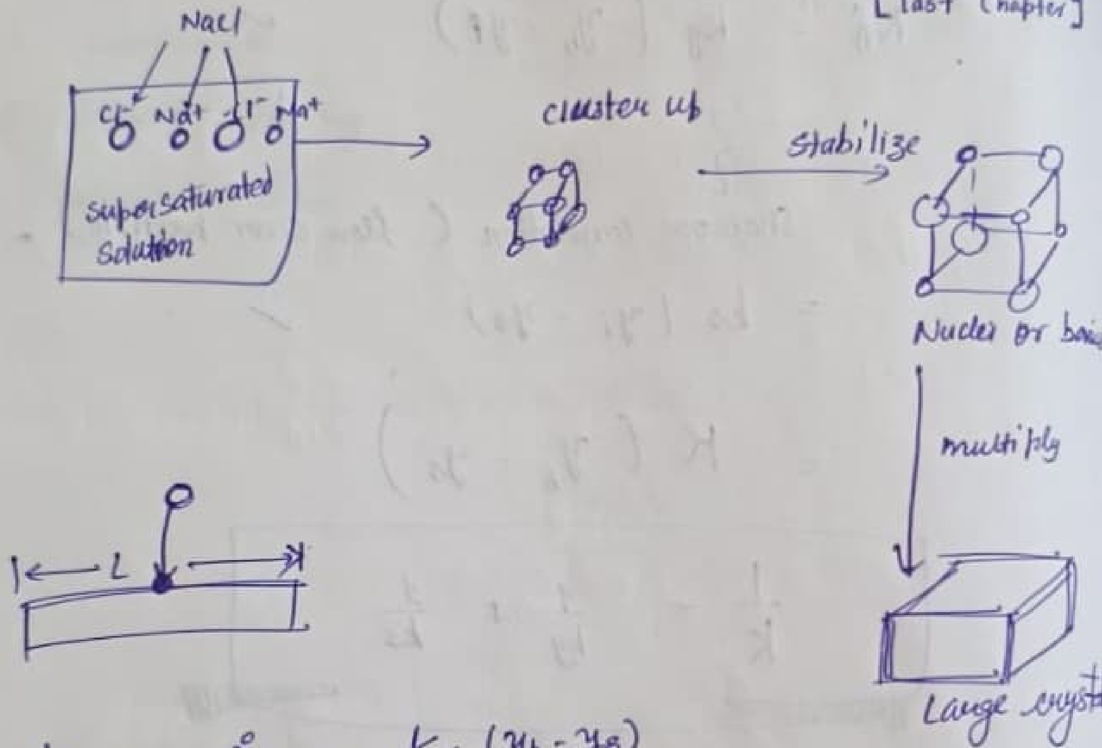
$$\dot{m}_p = 3 \rho_p a L^2 G$$

$$\left[\begin{array}{l} N_A = \frac{\dot{m}_p}{S_p} = K (y_b - y_s) \\ N_A = \frac{3 \rho_p a L^2 G}{6 a L^2} \\ N_A = \frac{\rho_p G}{2} = K (y_b - y_s) \end{array} \right]$$

$$G = \frac{dL}{dt} = \frac{2K (y_b - y_s)}{\rho_p}$$

Crystallisation Part

↳ From McCabe Smith
(Theory and Problems)
[last Chapter]

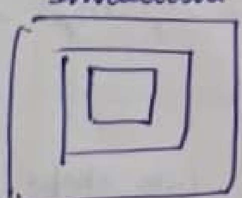


$$N_A = \frac{\dot{m}_p}{S_p} = K_y (y_b - y_s)$$

$$G = \frac{dL}{dt} = \frac{2K}{\rho_p} (y_b - y_s)$$

(growth rate)

Invariant Crystal



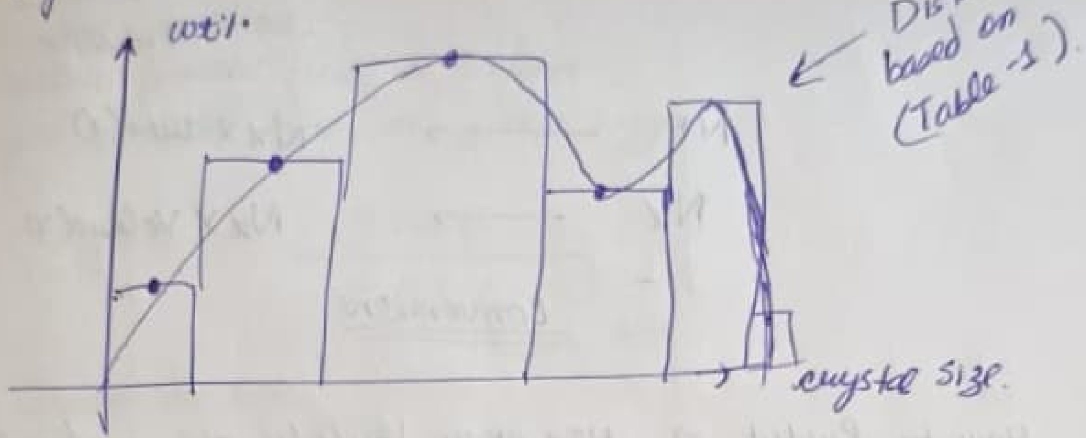
uniform growth.

$$\frac{dL}{dt} = \text{constant} = G$$

⇒ crystallisation
↓
crystals
↓
size is not same.

Crystals of Varying Size will be formed

Crystal Size Distribution (SD)

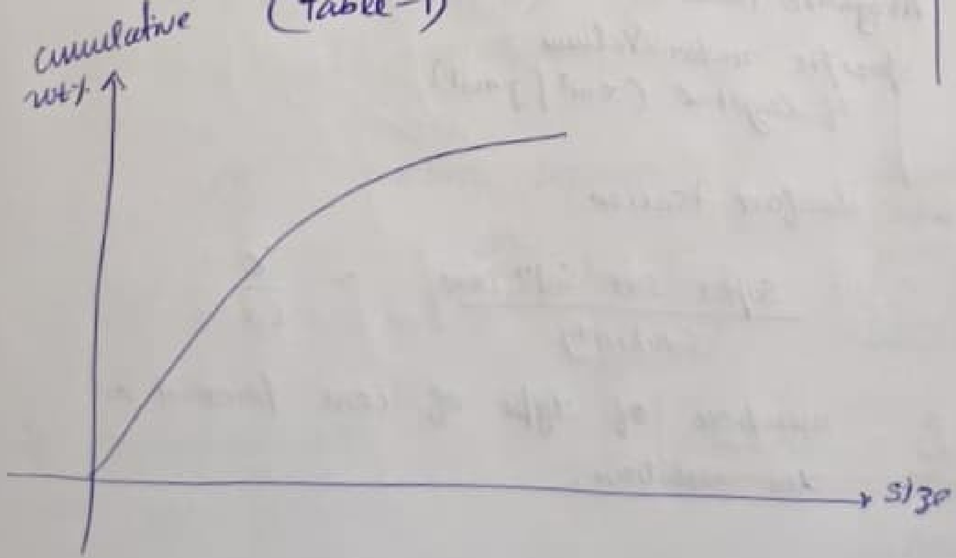


Size	wt %
1 μm	10%
2 μm	20%
3 μm	40%
10 μm	30%

(Table-1)

$\Rightarrow$ Cumulative wt %.

Size	wt %
1 μm	10%
2 μm	30%
3 μm	70%
4 μm	100%



Number of x size particle to mass

$N_x \longrightarrow \dfrac{N_x \times V_x \times \rho_x}{m_{total, x}}$

$N_x \longrightarrow N_x \times area(x)$

$N_x \longrightarrow N_x \times Volume(x)$

conversions

How to Predict ⇒ How many particles of a particular size.

Secondary

Primary Nucleation

↳ Homogeneous

↓

no. of nucleus / volume time

Nucleation rate

↓

$\dot{B}_0 = a \exp\left(- \dfrac{16 \pi \sigma^3 V_m^3 N_A}{3 \nu^2 (RT)^2 (\ln \alpha)^2} \right)$

(for Homogen)

(2)

N_A = Avogadro Number

V_m - specific molar Volume of crystal ($cm^3/g\,mol$)

σ = Surface tension

α = $\dfrac{\text{Super sat Sol}^n \text{ conc}}{\text{Solubility}} = \dfrac{C}{C_s}$

ν = number of type of ions present in the solution.

Kelvin Equation

Solubility = f (size)

at the same conditions,
smaller particles tend to dissolve,
larger particles tend to grow bigger.

$$\ln \alpha = \frac{4 V_m \sigma}{\nu R T L}$$

L → size

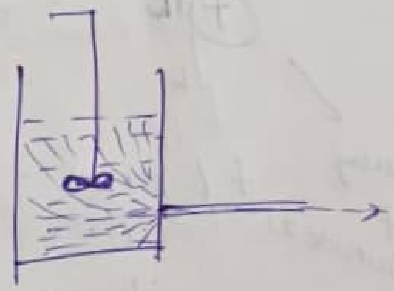
(*) Smaller the size,
higher the solubility

(*) for a given saturation level, estimation of the predominant size (L) can be obtained.

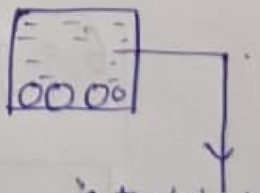
CSTR

$$\frac{\text{mixed suspension}}{\text{mixed product Removal}}$$

[MSMPR crystallizer]



(*) mother liquour or magma → Initially Supersaturated

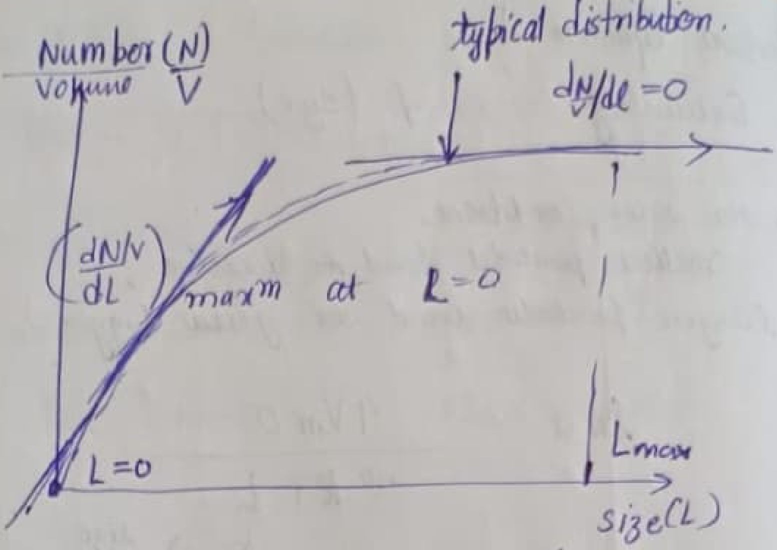


Saturated solⁿ or

If crystals are not in equillibrium with magma, then it is a supersaturated solution

Assumptions of MSMPR
* crystals are in equillibrium with magma
* magma is Saturated Solution
* McCabe ΔL Law ⇒ G is constant (Growth rate...)

(*) Every crystal has same life time (residence time) in the crystalliser ... uniform



Number distribution can also be converted as Population Density Function

$$f = \frac{d(N/V)}{dL}$$

$$\int_{L}^{L+\Delta L} f \, dL = \int_{0}^{N/V} d\left(\frac{N}{V}\right)$$

why f outside??

$$f(L+\Delta L - L) = \frac{N}{V}$$

[for L to L + ΔL, Δf is very less, f ≈ constant]

$$f = \frac{N}{V\Delta L} \Rightarrow N = f V \Delta L$$

How may particles in the range L to L+ΔL

$$G = \frac{dL}{dt} = \text{constant} = \frac{L}{t_m}$$ → age of crystal

$$\boxed{L = G t_m}$$

$\therefore f \cdot \Delta L = \frac{\text{no. of Crystals}}{\text{volume}}$

$\therefore -\underbrace{\Delta f \cdot \Delta L}_{\text{no. of crystals taken out}}$ in time Δt

∵ uniform Distribution of crystals in the tank, Hence,

$\boxed{\text{number Ratio} = \text{Volume Ratio}}$

$$-\frac{\Delta f \; \Delta L}{f \; \Delta L} = \frac{\text{Volume of Product taken out in } \Delta t \text{ time}}{\text{Volume of soln in Crystallizer}}$$

Steady State Assumed.

Product flow rate $(m^3/sec) = Q$.

$$-\frac{\Delta f}{f} = \frac{Q \, \Delta t}{V_C}$$

$$-\frac{\Delta f}{\Delta t} = \frac{f Q}{V_C}.$$

$$\lim_{t \to 0} \left(-\frac{\Delta f}{\Delta t} \right) = \frac{f Q}{V_C}.$$

$$-\frac{df}{dt} = f \frac{Q}{V_C}$$

$$-\frac{df}{dL} \frac{dL}{dt} = \frac{f Q}{V_C} \qquad \left[\frac{dL}{dt} = G \right]$$

$$-\frac{df}{dL} \cdot G = \frac{Q f}{V_C}$$

$\frac{\text{Vol}}{\text{Vol/time}}$ $\quad \frac{V_C}{Q} = \tau =$ Residence time

$$-\frac{df}{dL} = \frac{f}{G\tau}$$

$$\star \boxed{-\frac{df}{f} = \frac{dL}{G\tau}} \Rightarrow \int_{f_0}^{f} \frac{df}{f} = \int_0^L -\frac{dL}{G\tau}$$

$$\ln f = -\frac{L}{G\tau}$$

$$f = f_0 e^{-L/G\tau}$$

Q $-\ln\left(\frac{f}{f^0}\right) = \frac{L}{GT}$

$$f = f_0 e^{-\frac{L}{GT}}$$

$\downarrow$ to predict crystals of a particular size.

mean size = Σ(size x fraction).

$f \longrightarrow$ gives no. of particles in size Range L to $L+\Delta L$

Cumulative Number fraction :- $\dfrac{\text{no. of particles from 0 to } L}{\text{Total no. of particles}}$

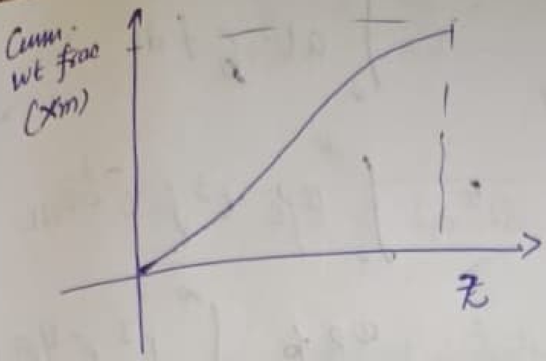
Cumulative Number fraction $= \dfrac{1}{\int_0^\infty f\,dL} \cdot \int_0^L f\,dL$

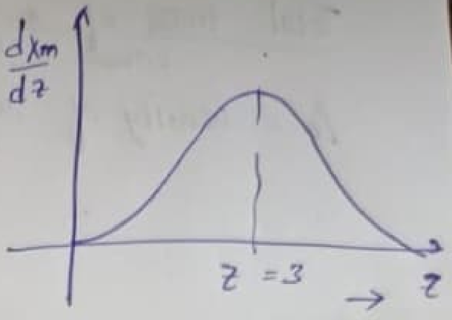
Cumulative Area fraction $= \dfrac{\int_0^L L^2 f\,dL}{\int_0^\infty L^2 f\,dL}$

Cum Vol. frac / wt frac $= \dfrac{\int_0^L L^3 f\,dL}{\int_0^\infty L^3 f\,dL}$.

wt fraction = volume fraction $= \dfrac{\int_0^L L^3 f^0 e^{-\frac{L}{G\tau}} dL}{\int_0^\infty L^3 f^0 e^{-\frac{L}{G\tau}} dt}$

Cum. wt frac $= 1 - \left(1 + z + \frac{z^2}{2} + \frac{z^3}{6}, \ldots\right)e^{-z}$





People found that at $z = 3 = \frac{L_{\text{predominant}}}{G\tau}$ the major population is found.

$\uparrow f_o \quad \uparrow G$

$$\lim_{L \to 0} \frac{d(N/V)}{dt} = \left(\lim_{L \to 0} \frac{d(N/V)}{dL} \right) \frac{dL}{dt}$$

$\Rightarrow \frac{\text{no. of nuclei}}{\text{Volume} \times \text{time}} = B_o$

$$\boxed{B_o = f_o \cdot G}$$

$\downarrow$

nucleation rate.

$$\frac{\text{Total no. of crystals}}{\text{volume}} \left(\frac{N_c}{V} \right) = \int_0^\infty f \cdot dL$$

$$= \int_0^\infty f_o e^{-z} dL$$

$z = \frac{L}{G\tau}$

$$= \int_0^\infty f_o G\tau \, e^{-z} d\left(\frac{L}{G\tau}\right)$$

$$= f_o G\tau \underbrace{\int_0^\infty e^{-z} dz}_{1}$$

$\Rightarrow$

$$\frac{\text{Total no. of crystals}}{\text{volume}} = f_o G\tau$$

$$= \boxed{\frac{N_c}{V} = B_o \tau}$$

Total $\frac{\text{mass of crystals}}{\text{volume}} = \int_0^\infty a L^3 \rho_c f \, dL$

ρ_c = Density of crystal

$$= \int_0^\infty a \rho_c L^3 f_0 e^{-\frac{L}{G\tau}} dL$$

$$= a \rho_c f_0 \int_0^\infty L^3 e^{-L/G\tau} dL$$

$$= 6 a \rho_c f_0 (G\tau)^4$$

$$\frac{\frac{n_c}{V}}{\frac{w_c}{V}} = \frac{f_0 G \tau}{6 a \rho_c f^0 (G\tau)^4}$$

$\frac{\text{number}}{\text{mass}}$ -- $\frac{n_c}{w_c} = \frac{1}{6 a \rho_c (G\tau)^3}$

$$L_{pr} = 3 G\tau \Rightarrow \boxed{\frac{L_{pr}}{3} = G\tau}$$

$$\frac{n_c}{W_c} = \frac{9}{2 a \rho_c (L_{pr}^3)}.$$

\# assume MSMPR

$\Rightarrow$ no. of nuclei formed = no of crystals formed.

$\Rightarrow$ $\frac{\text{no. of nuclei formed}}{\text{volume} \times \text{time}} = \frac{\text{no. of crystals formed}}{\text{volume} \times \text{time}}$

crystals production rate = c (wt/time)

$$B^0 = \frac{c \times \frac{n_c}{W_c}}{V_c} \quad \left(\frac{\text{number}}{\text{mass}}\right)$$

$$B^0 = \frac{c}{V_C} \times \frac{n_C}{W_C}$$

$$B^0 = \frac{q_C}{2a \rho_C L_{pr}^3 V_C}$$

Read Yourself → types of Industrial Crystallizers. (short Qns on them will come in Exam)