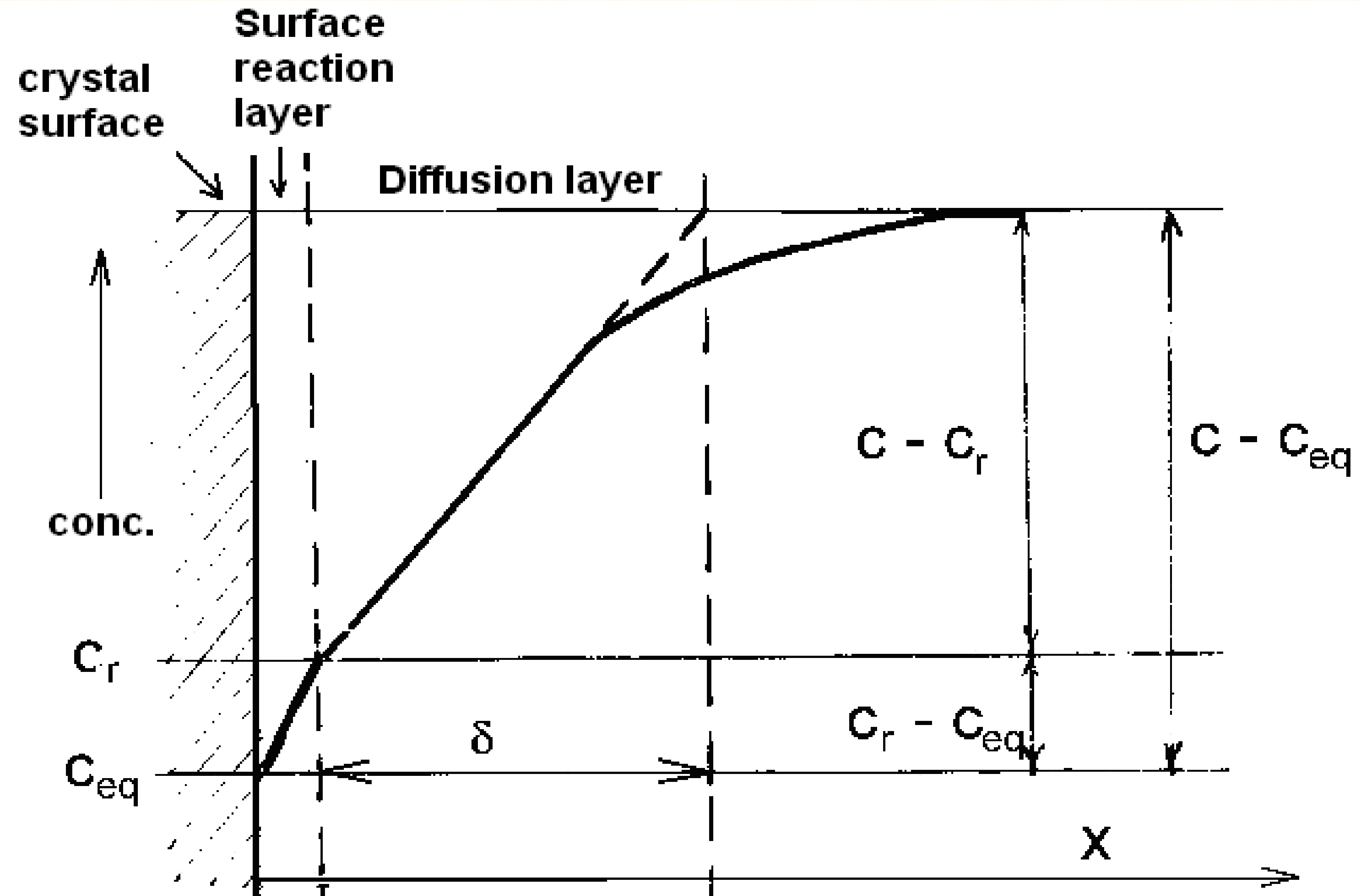
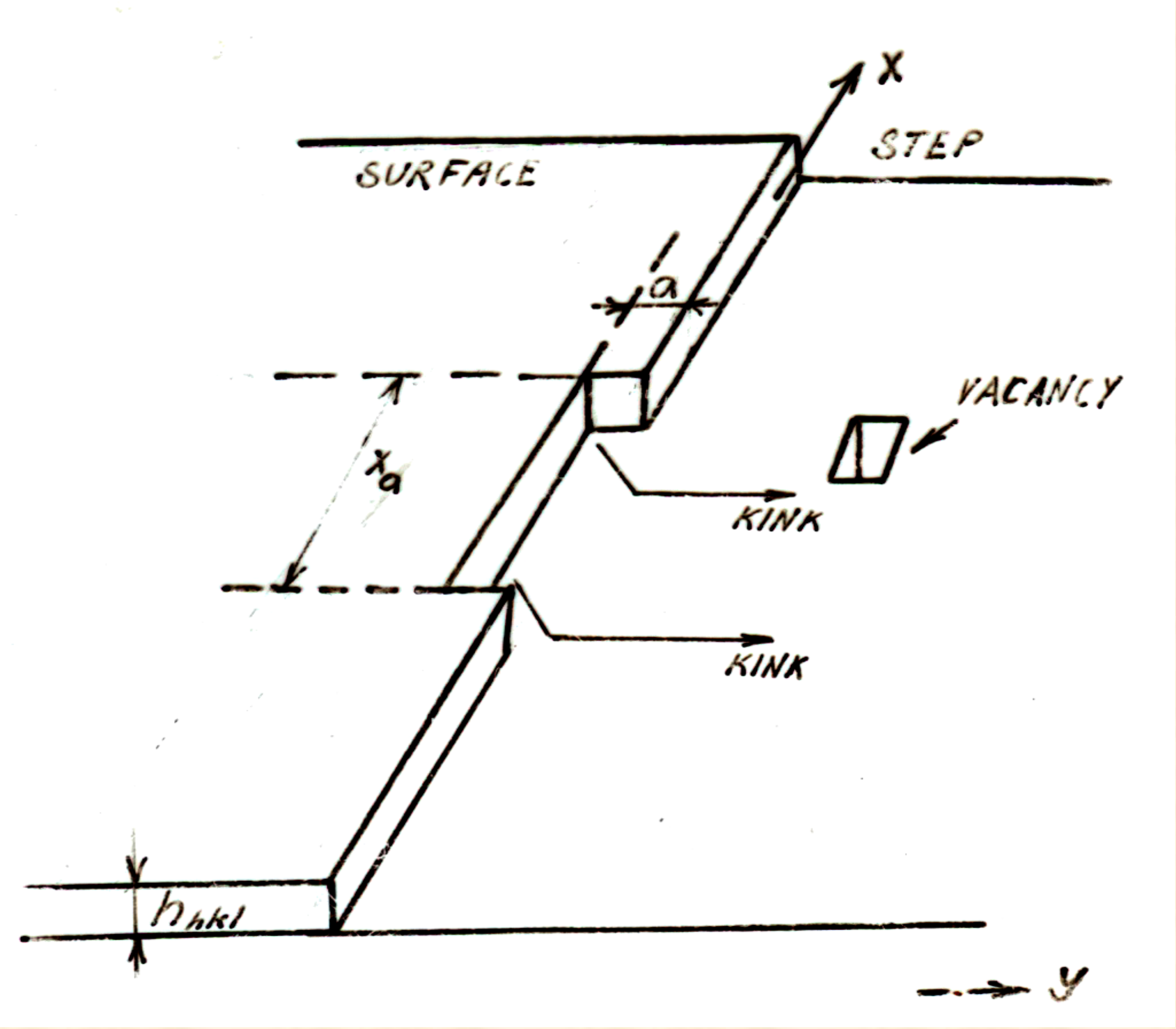
Diffusion model of crystal growth

concentration driving force for a two-step process

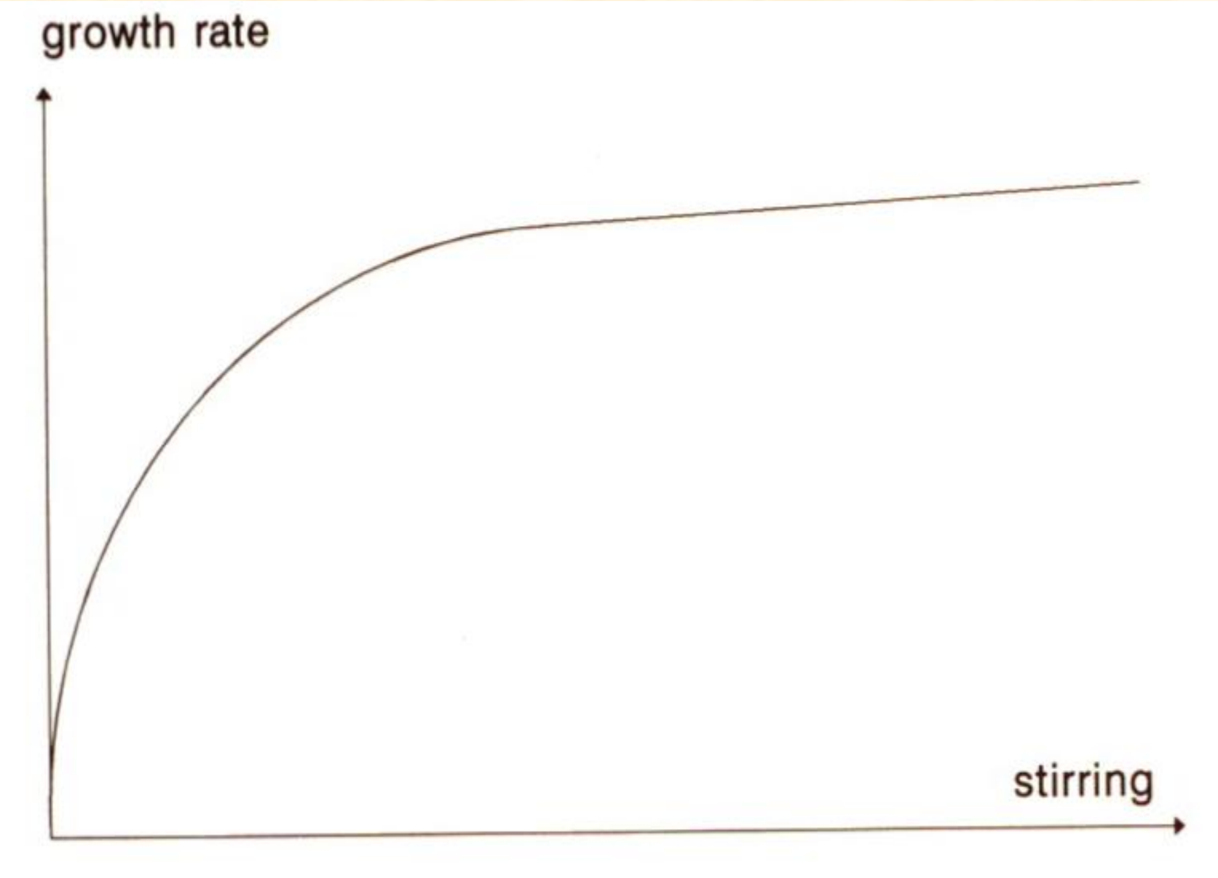


Incorporation of particles into the crystal lattice **(surface reaction)**



Intensification of the crystallization process by mixing …. When it is expedient ?

Limit of stirring



Crystallization - Examples

$$W = \frac{1}{K} = \frac{1}{k_d} + \frac{1}{k_r} = W_d + W_r$$

Resistance of Crystalization process

$$W_r = \frac{1}{k_r}$$

Resistance of Surface reaction

Resistance of Diffusion process

$$W_d = \frac{1}{k_d} = \frac{\partial}{D}$$

Example - control process

$D = 1{,}7.10^{-10} m^2/s$

$\partial = 43.10^{-6} m$

$k_R = 67{,}8.10^{-6} m/s$

??? k_d , W_d , W_r , W

if W = 100 % , that W_d = ? % , W_r = ? %

Crystallization - Examples

Example 1: Crystallisation rate

In the crystallization of technical sugar solutions, which are in accordance with the diffusion theory of crystal growth, the following quantities were found:

- Diffusion coefficient $D = 1{,}7 \cdot 10^{-10}\ m^2/s$
- Diffusion layer thickness $\delta = 43 \cdot 10^{-6}\ m$
- Rate constant of the surface reaction $k_r = 68 \cdot 10^{-6}\ m/s$

Calculate the **rate constant of the diffusion** $\mathbf{k_D}$ and the total crystallisation constant **K**. Decide **which of the processes is the control** and what is the **relative proportion** of diffusion on the total resistance W. Resistance is defined as the reciprocal value of the velocity constant.

Rate constant and resitance calculation

The rate constant of diffusion:

$$\mathbf{k_D = D\ /\ \delta} = 1{,}7.10^{-10}\ m^2/s\ /\ 43.10^{-6}\ m = \mathbf{3{,}95\ .\ 10^{-6}\ m/s}$$

The rate constant of the surface reaction **$k_r >> k_D$** ,
from which it follows that the crystallization process
is controlled by diffusion !

Rate constant and resitance calculation

The crystallization constant is defined as :

$$1/K = 1/k_r + 1/k_D$$

Resistance : $$W = W_r + W_D$$

Rate constant and resitance calculation

The crystallization constant is defined as :

$$1/K = 1/k_r + 1/k_D$$

Resistance : $W = W_r + W_D$

After fitting into the equation, we get :

$1/K = 3{,}74 \cdot 10^{-6}$ m/s

and **total resistance :** $W = 2{,}68 \cdot 10^{5}$ s/m

Rate constant and resitance calculation

Total resistance : $\mathbf{W = 2{,}68 \cdot 10^5}$ **s/m**

Resistance $\mathbf{W_r}$ = reciprocal value $\mathbf{1/k_r}$

$$\mathbf{W_r = 0{,}15 \cdot 10^5 \text{ s/m}}$$

Diffusion resistance $\mathbf{W_D}$ = reciprocal $\mathbf{1/k_D}$

$$\mathbf{W_D = 2{,}53 \cdot 10^5 \text{ s/m}}$$

The diffusion resistance $\mathbf{W_D}$ is **94%** of the total resistance **W**, which confirms that **the control is diffusion !!!**

Rate constant and resitance calculation (sum)

The rate constant of diffusion:

$\mathbf{k_D = D / \delta} = 1{,}7.10^{-10}\ m^2/s\ /\ 43.10^{-6}\ m = \mathbf{3{,}95\ .\ 10^{-6}\ m/s}$

The rate constant of the surface reaction $\mathbf{k_r >> k_D}$, from which it follows that the crystallization process **is controlled by diffusion** !

The crystallization constant is defined as : $\mathbf{1/K = 1/k_r + 1/k_D}$

After fitting into the equation, we get : $\mathbf{1/K = 3{,}74\ .\ 10^{-6}\ m/s}$

and **total resistance :** $\mathbf{W = 2{,}68\ .\ 10^5\ s/m}$

Reciprocal value $\mathbf{1/k_r}$ is : $\mathbf{W_r = 0{,}15\ .\ 10^5\ s/m}$

and reciprocal $\mathbf{1/k_D}$ is : $\mathbf{W_D = 2{,}53\ .\ 10^5\ s/m}$

The diffusion resistance $\mathbf{W_D}$ is **94%** of the total resistance **W**, which confirms that **the control is diffusion**..

Example 2 : Crystals calculation

Calculate the amount of crystals to achieve the desired target product size

What amount of crystals is required to initiate the crystallisation batch process if the following requirements for the slurry produced are given:

- the final weight of 40 t

- the final crystal content of 55% in suspension

- the average final crystal size of 1.4 mm.

Calculate the amount of crystals to achieve the desired target product size

The following were used to initiate (= inoculation):

a) Suspensions of microcrystals, so-called "slurries" with a particle size of 17 um (slurries containing 50% of crystals). It is believed that 25% of added crystals are dissolved in the industrial crystallizer.

b) Crystals with a mean size of 0.1 mm.

c) Suspension containing 40% crystals with a mean crystal size of 0.25 mm

Calculate the amount of crystals to achieve the desired target product size

Calculation:

For the calculation, we use the **volume factor $k_v = 0.75$,** where after the density $\rho = 1.59$ g / cm^3 has been applied to the shape defining factor,

$$\mathbf{V = k_v . L^3}$$

we get the relationship between the **mass m** (mg) and the **size** of the crystals

$$\mathbf{m = \mathit{k_v} . \rho . \mathit{L}^3 = 1{,}19 . \mathit{L}^3}$$

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Mass of the average crystal in the resulting product:

m_1 **(mg) = ???**

Number of crystals in the product:

N = ???

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Mass of the average crystal in the resulting product:

$$m_1 = 1{,}19 \cdot 1{,}43 = 3{,}27 \text{ mg}$$

Number of crystals in the product:

$$N = 40.10^9 \cdot\ 0{,}55 / 3{,}27 = 6{,}73.10^9$$

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Ad a) **Mass of 1 microcrystal:**

$m_1 = 1{,}19 \,.\, 0{,}0173 = 5{,}85 \,.\, 10^{-6}$ mg

Mass of the slurry:

$m_{sl} = 6{,}73.10^{9} \,.\, 5{,}85.10^{-6} \,.\, 100 / 50 \,.\, 1{,}25 = 98 \,.\, 10^{3}$ mg = 98 g

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Ad b) **Mass of 1 crystal of 0,1 mm**

$m_1 = 1{,}19 \,.\, 0{,}1^3 = 1{,}19 \,.\, 10^{-3}$ mg

Mass of crystals:

$m_k = 6{,}73.10^9 \,.\, 1{,}19.10^{-3} = 8\,{,}01.10^6$ mg $= 8{,}\,01$ kg

Calculate the amount of crystals to achieve the desired target product size

Calculation:

Ad c) **Mass of 1 crystal (L = 0,25 mm)**

$m_1 = 1{,}19 \,.\, 0{,}253 = 0{,}0186 \text{ mg}$

Suspension Weight

$m_s = 6{,}73.10^9 \,.\, 0{,}0186 \,.\, 100/40 = 0{,}313.10^9 \text{ mg} = 313 \text{ kg}$

END