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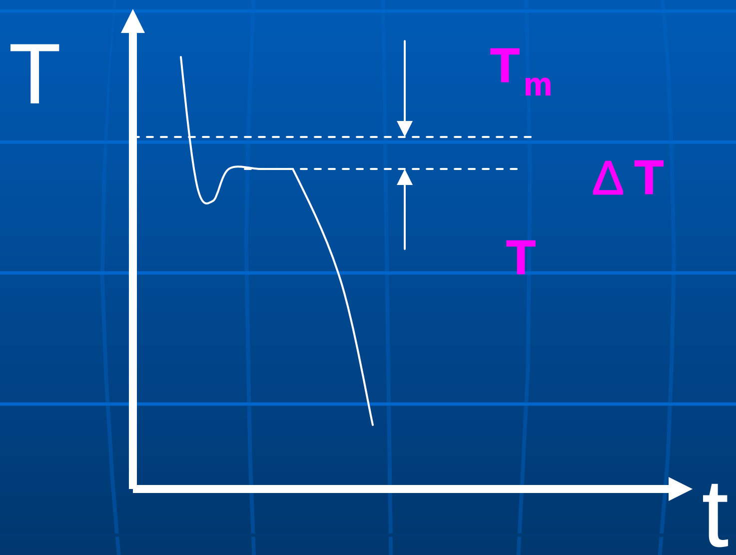


冷却过程中的结晶温度　T
平衡状态时的结晶温度　T_m

$\Delta T = T_m - T$

.

$$G_S - G_L = \Delta G < 0$$

S > 0 T

$$S_L > S_S$$

G = *H* - *TS* *G* *T*

$$dG \big/ dT = -S$$

G_L-T

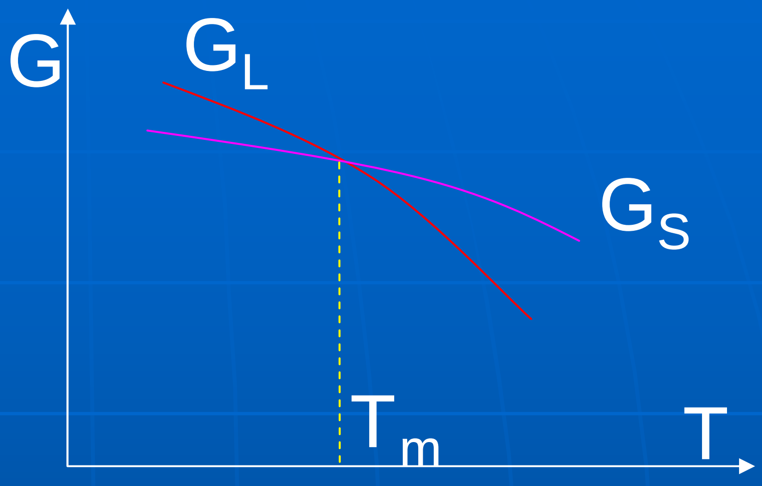
G_S-T

T_m

$G_L = G_S$

$G_S - G_L = \Delta G < 0$

$T < T_m$



(S) (L) $G = f(T)$

ΔG

$$\Delta G = G_S - G_L = (H_S - H_L) - T(S_S - S_L),$$

$$H_S - H_L = -L_m; S_S - S_L = -\Delta S_m = -L_m / T_m$$

$$\Delta G = -L_m \Delta T / T_m$$

1.

2.

3.

4.

5.

:

1.

(1).   :

， ΔG_V ，

σ ， ：

$$\Delta G = V \bullet \Delta G_V + A \bullet \sigma$$
$$= -\frac{4}{3}\pi r^3 \bullet \Delta G_V + 4\pi r^2 \bullet \sigma$$

： $\Delta G' = -4\pi r^2 \cdot \Delta G_v + 8\pi r \cdot \sigma = 0$

：

$$r = \frac{2\sigma}{\Delta G_V}$$

r_C

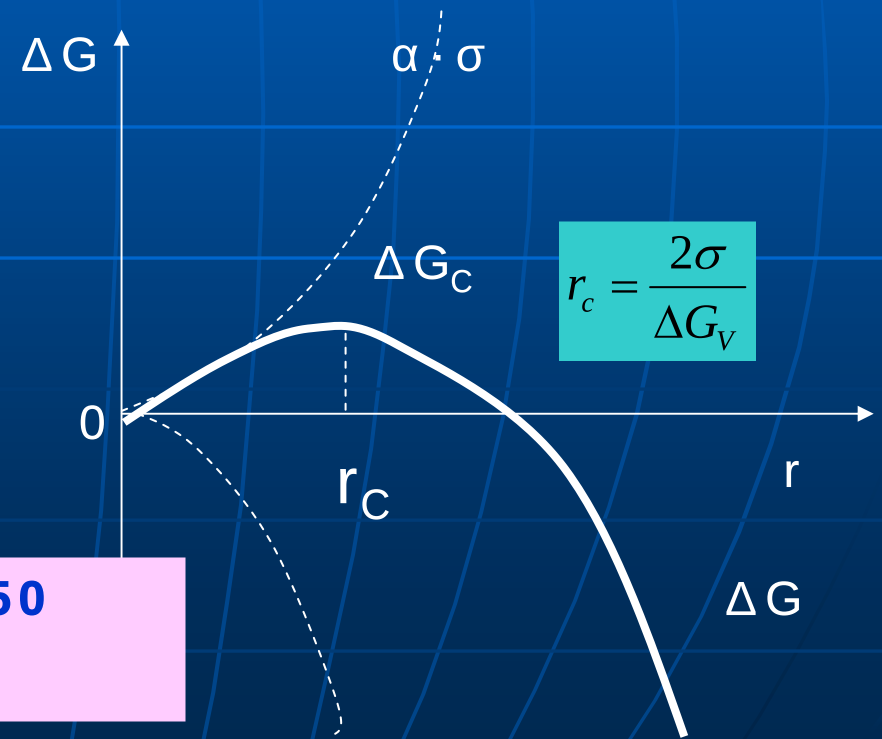
$$\Delta G_c = -\frac{4}{3}\pi \cdot r^3 \bullet \Delta G_V + 4\pi \cdot r^2 \bullet \sigma$$

$$= -\frac{4}{3}\pi \cdot \left(\frac{2\sigma}{\Delta G_V}\right)^3 \bullet \Delta G_V + 4\pi \cdot \left(\frac{2\sigma}{\Delta G_V}\right)^2 \bullet \sigma = \frac{16\pi \cdot \sigma^3}{3\Delta G_V{}^2}$$

$$= 4\pi \cdot r^2 \cdot \frac{\sigma}{3} = \frac{A \cdot \sigma}{3}$$

$\Delta G = \Delta H - T\Delta S$, $\Delta G = 0$, $\Delta S = \Delta H / T_0$,

$$\Delta G_V = \Delta H - \frac{T\Delta H}{T_0} = \frac{\Delta H}{T_0}(T_0 - T)$$



$$r_c = \frac{2\sigma}{\Delta G_V}$$

讨论:

1) $T=T_m$, 不成核;

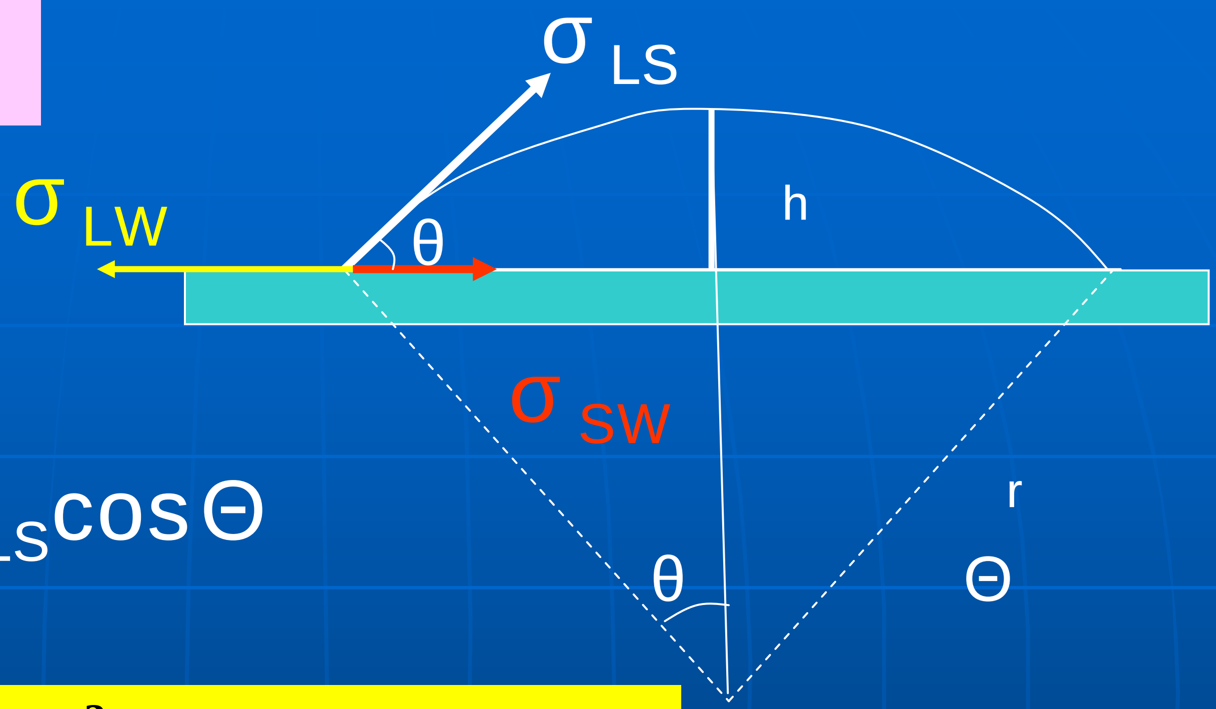
2) $\Delta T > 0$, 必要条件;

3) $r_n > r_C$, 核长大.

$\Delta T \approx 0.2T_m$, 150~250

<20

(2).



$$\sigma_{LW} = \sigma_{SW} + \sigma_{LS} \cos \Theta$$

$$V_s = \frac{\pi r^3}{3}(2 - 3\cos\theta + \cos^3\theta)$$

$$A_{SL} = 2\pi rh = 2\pi r\left(r - r \bullet \cos\theta\right) = 2\pi \cdot r^2\left(1 - \cos\theta\right)$$

$$\alpha_{SW} = \pi r^2 \sin^2\theta = \pi r^2(1 - \cos^2\theta)$$

$\Delta G = V_S \cdot \Delta G_V + \alpha_{LS} \cdot \sigma_{LS} + \alpha_{SW} \cdot (\sigma_{SW} - \sigma_{LW})$

$$= \frac{\pi \cdot r^3}{3}(2 - 3\cos\vartheta + \cos^3) \cdot \Delta G_V$$

$$\Delta G = (-\frac{4}{3}\pi \cdot r^3 \cdot \Delta G_V + 4\pi \cdot r^2 \cdot \sigma) \cdot \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

$= \Delta G_C \cdot f$

$$f = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

,

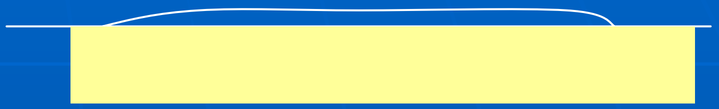
$$r_c^* = \frac{2\sigma_{SL}}{\Delta G_V}$$

$$\Delta G = \Delta G_C \cdot f$$

讨论

1. θ = 0, , ,

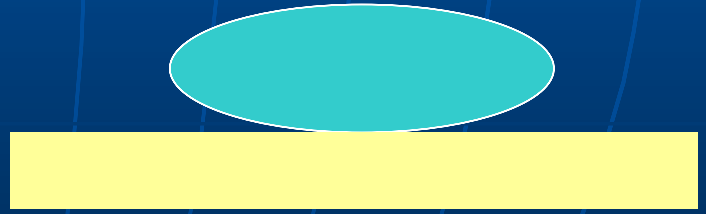
,



2. θ = 90°, $\Delta G = \Delta G/2$

$$f = \frac{(2+0)(1-0)^2}{4} = \frac{1}{2}$$

3. θ = π

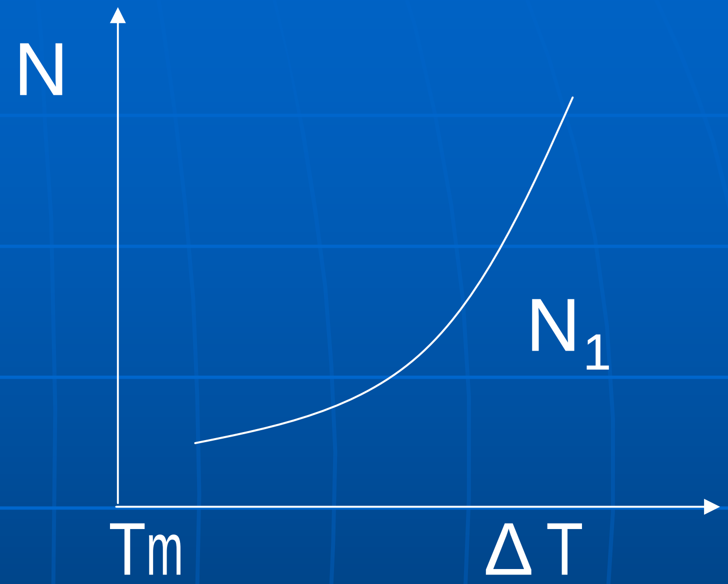


$$f = \frac{(2-1)(1+1)^2}{4} = 1$$

,

(3). *N*

/cm^3.sec



n rc ,

N , :

$$\frac{dn}{N} = -\frac{\Delta G}{k \cdot T},$$

$$\int_n^N \frac{dn}{n} = \ln\frac{n}{N} = -\frac{\Delta G}{kT}$$

ΔT

$$\frac{n}{N} = e^{-\frac{\Delta G}{kT}}$$

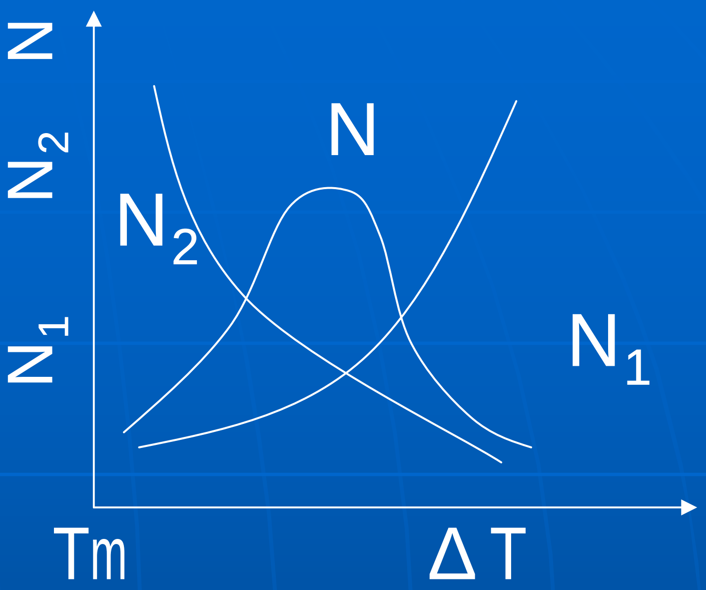
K

ΔT

α r_C ΔG_c

$$N_1 \propto \exp\left(-\Delta G_c/(kT)\right)$$

b



ΔT

$$N_2 \propto \exp\left(-Q/(kT)\right)$$

N:

$$N = N_1 \bullet N_2 = K\exp\left(-\Delta G_c/(kT)\right) \bullet \exp\left(-Q/(kT)\right)$$

2.

(1).

ΔG$_s$

x

$$\Delta G_s/(NkT_m) = ax(1-x) + x\ln x + (1-x)\ln(1-x)$$

K: T$_m$

α = ξ ΔS$_m$/R Jαckson , ΔS$_m$, R

ξ η

v(Z) ξ = η/v

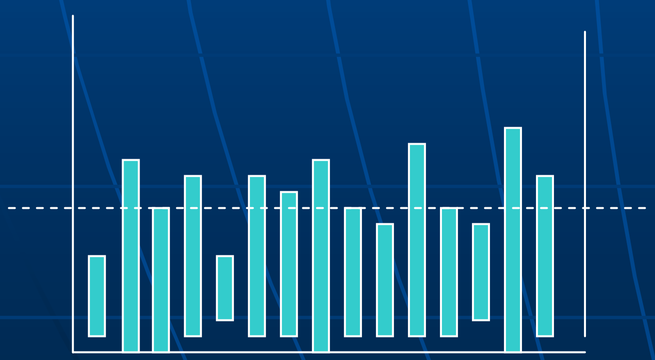
α

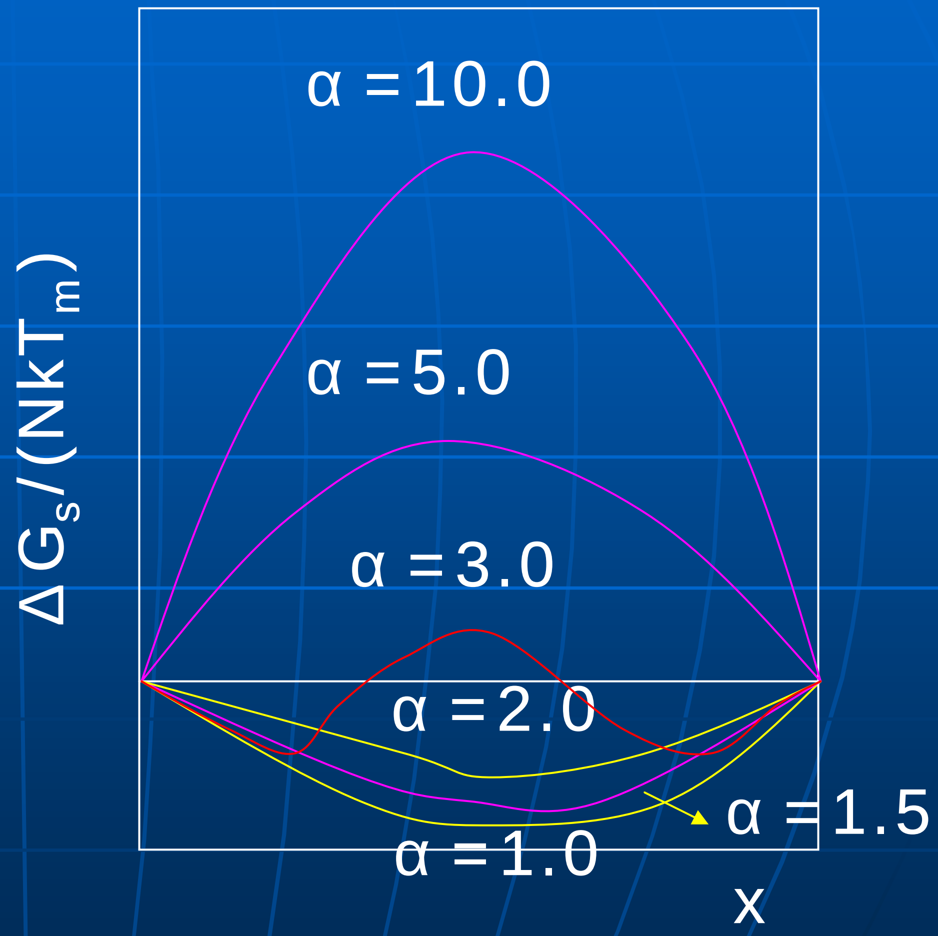
$(\Delta G_s/NkT_m)$ x 3

I.

α 2

: ,

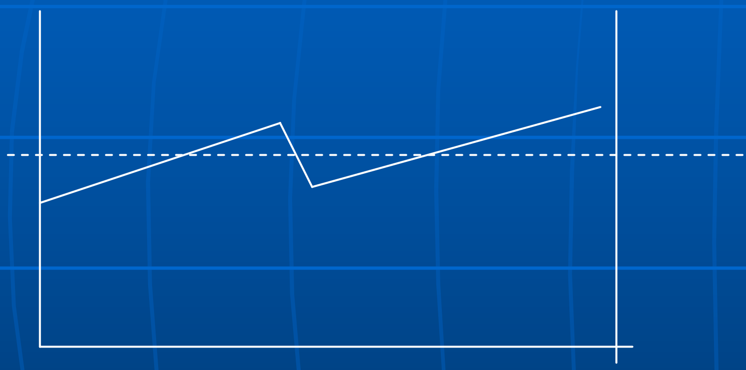


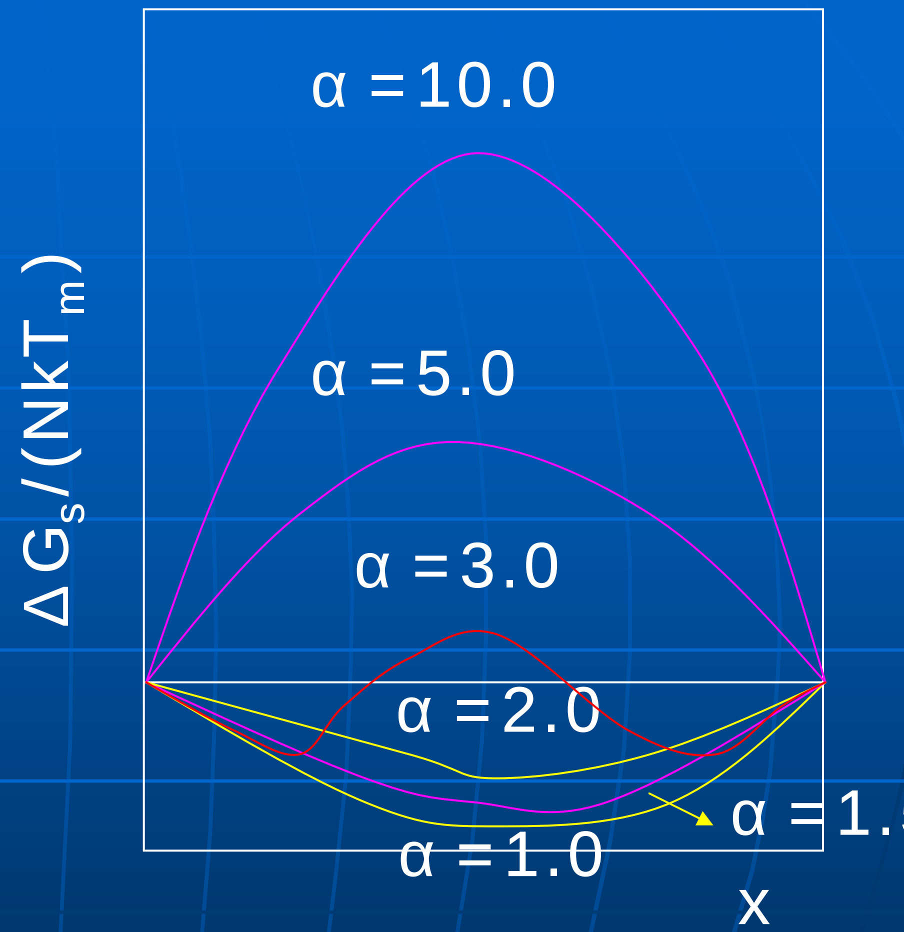


α x

II.X 0.5

$x \to 0$ $x \to 1$





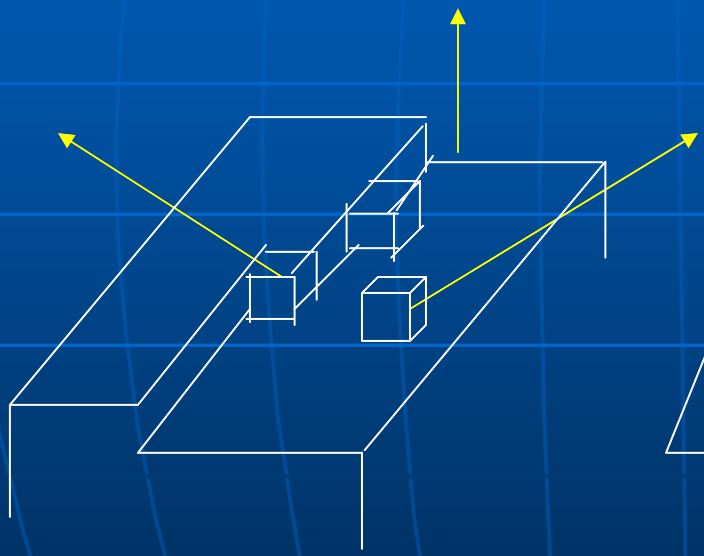
:

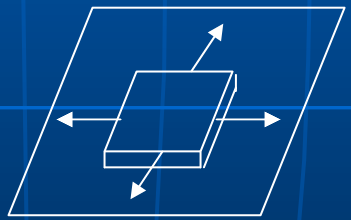
. Δ α

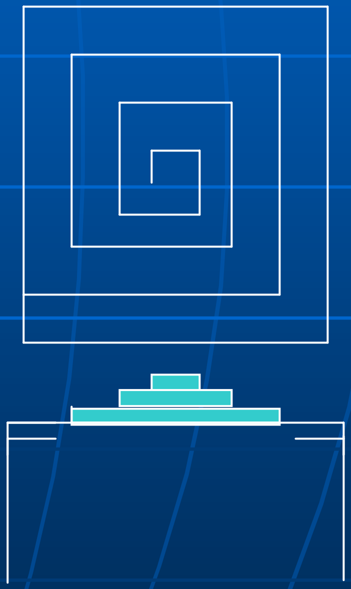
, Ge, Si

(2).

α. (   )







ΔT_k

R:

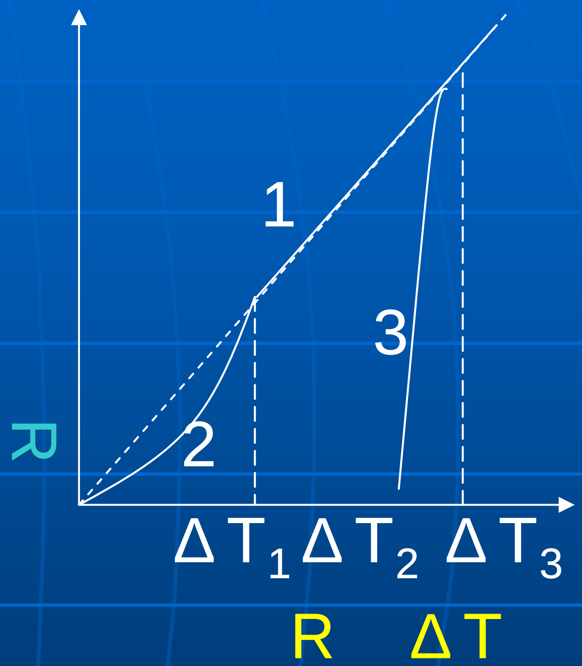
$$R = \mu_2 \exp\left[-b / \Delta T_k\right], \Delta T_k = 1 - 2^\circ C$$

:

$$R = \mu_3 \Delta T_k^2$$

μ_3

b. ( )



ΔT_k

$$R = \mu_1 \Delta T$$

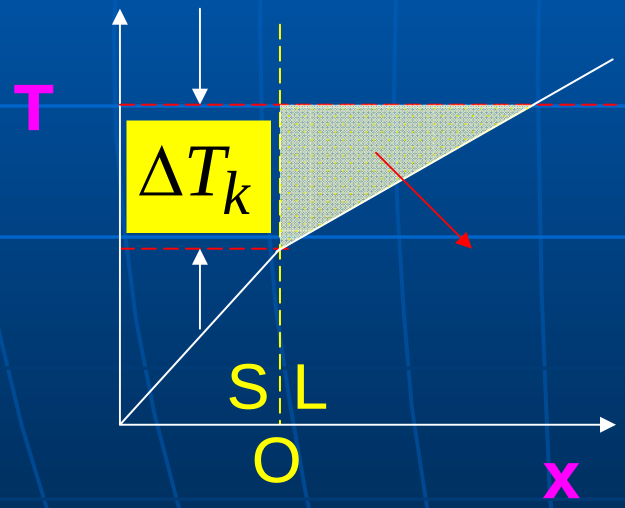
1-

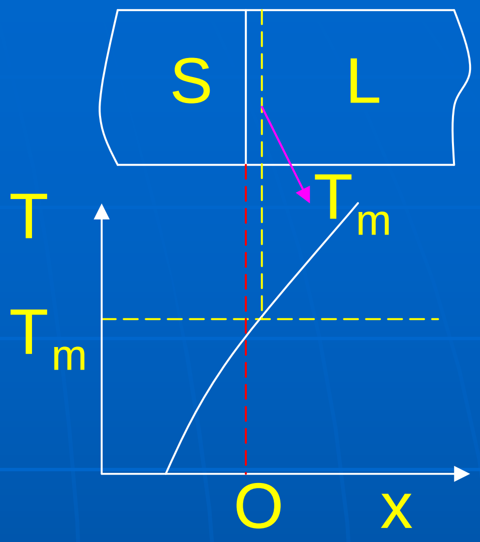
2-

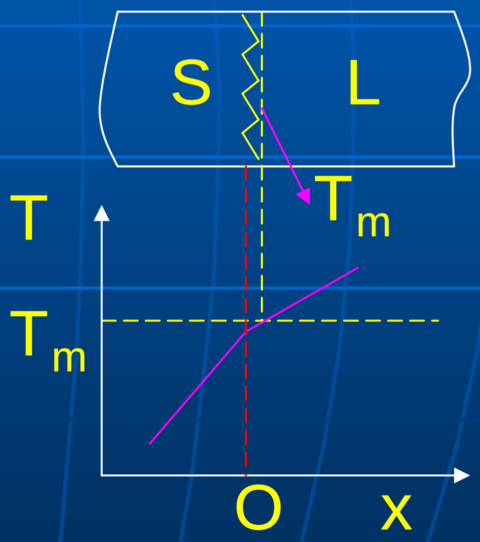
3-

(3).

α .







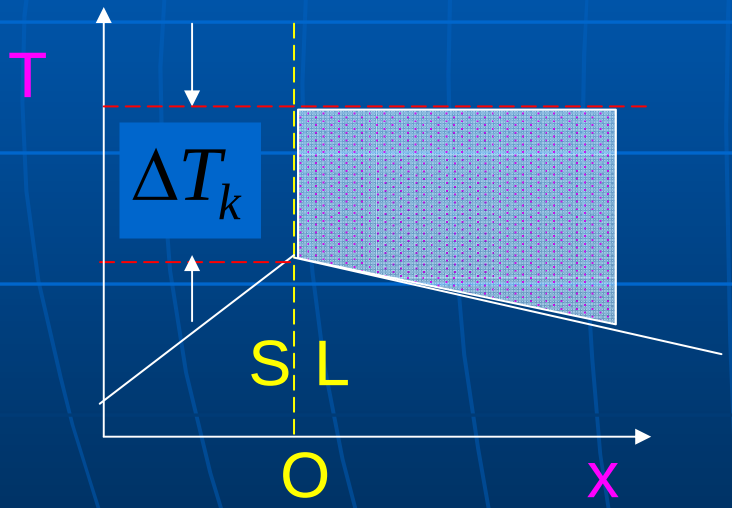
$$G_L = dT/dx > 0$$

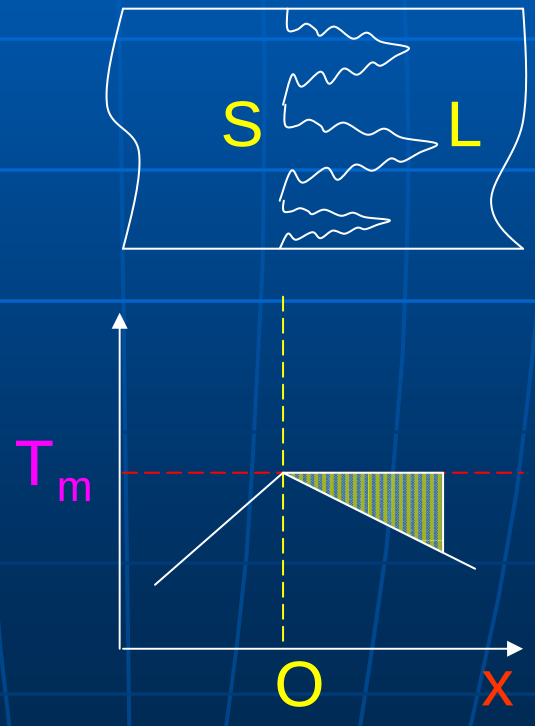
ΔT_k

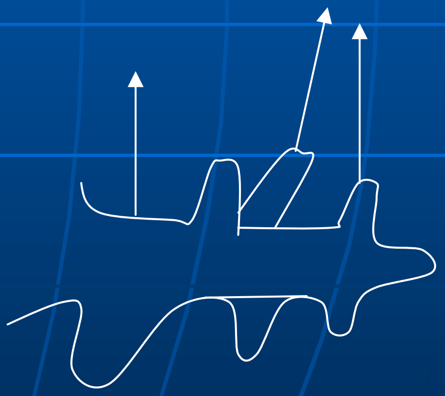
(x)

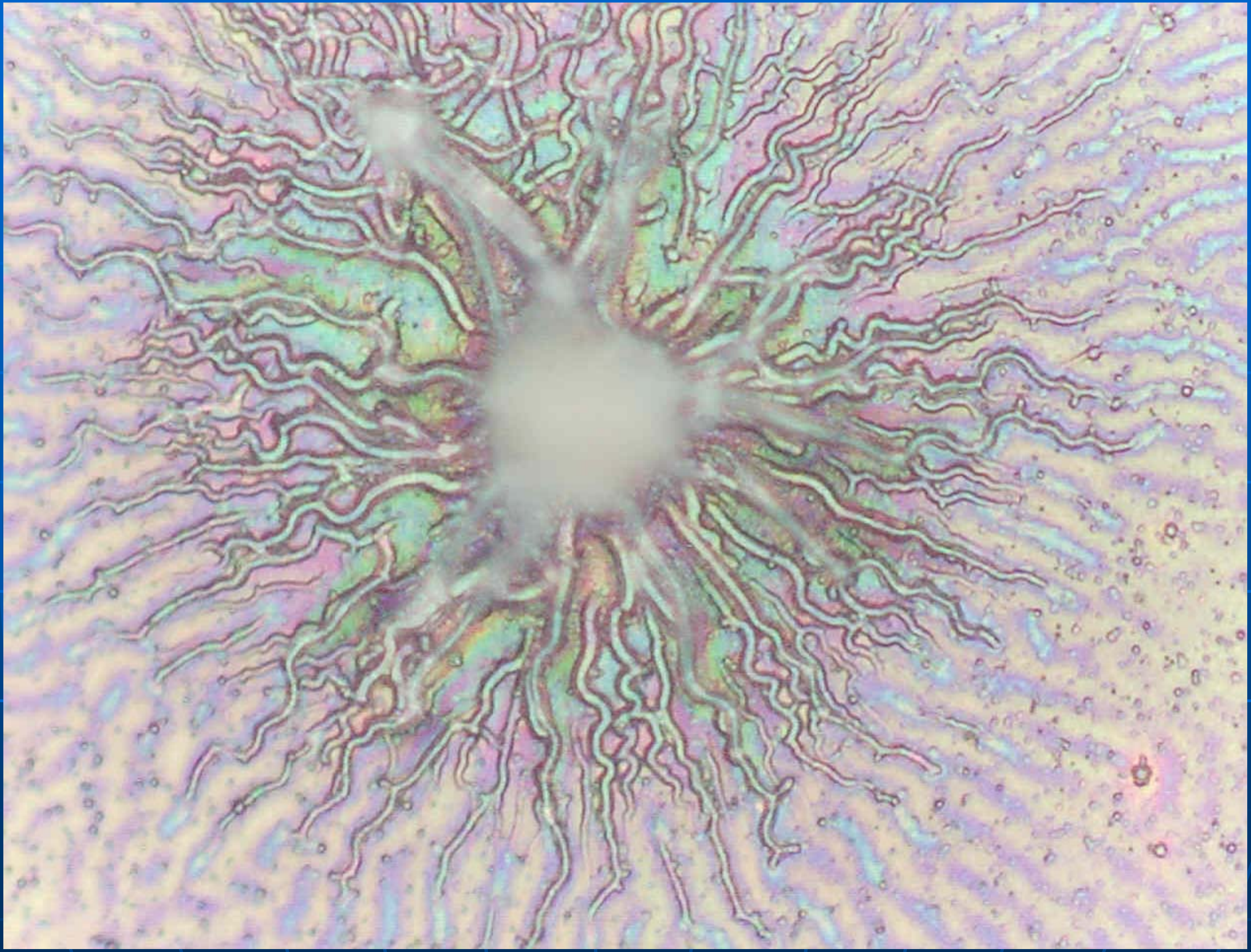
b.

$$G_L = dT/dx < 0$$

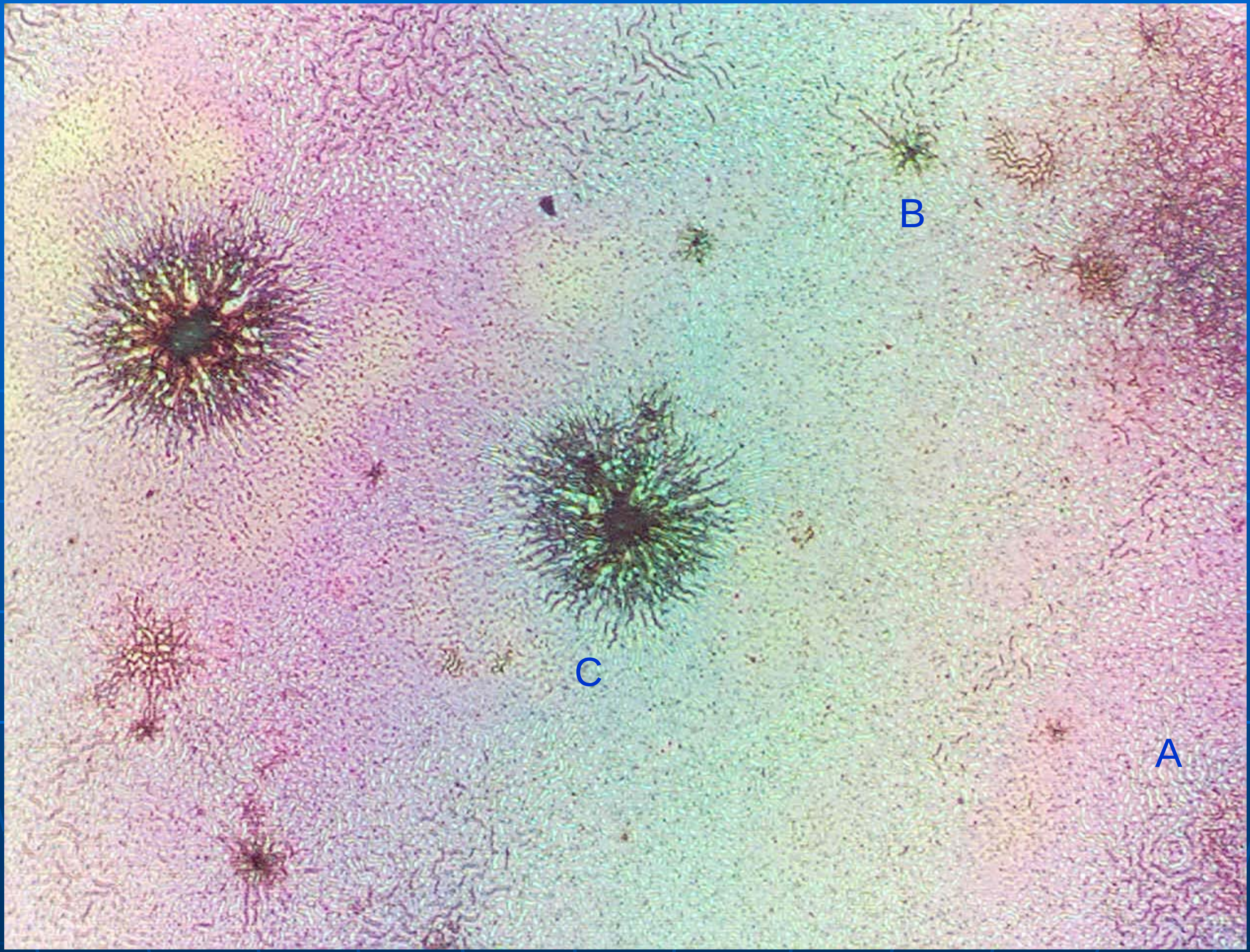








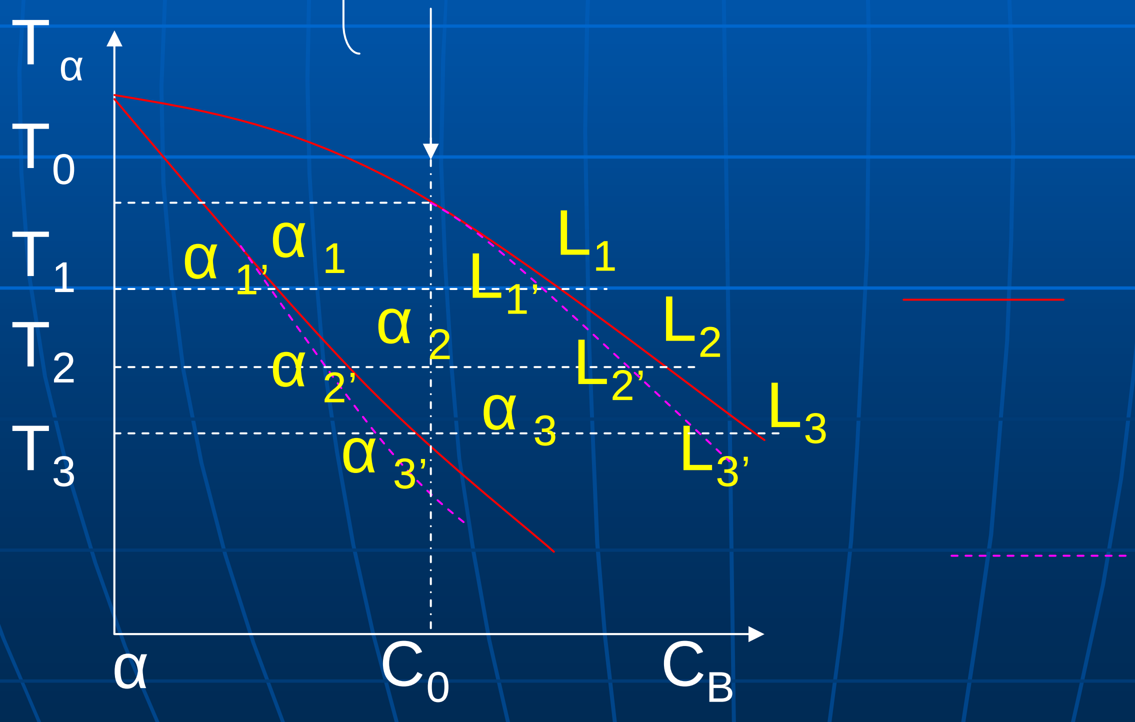
ZnO

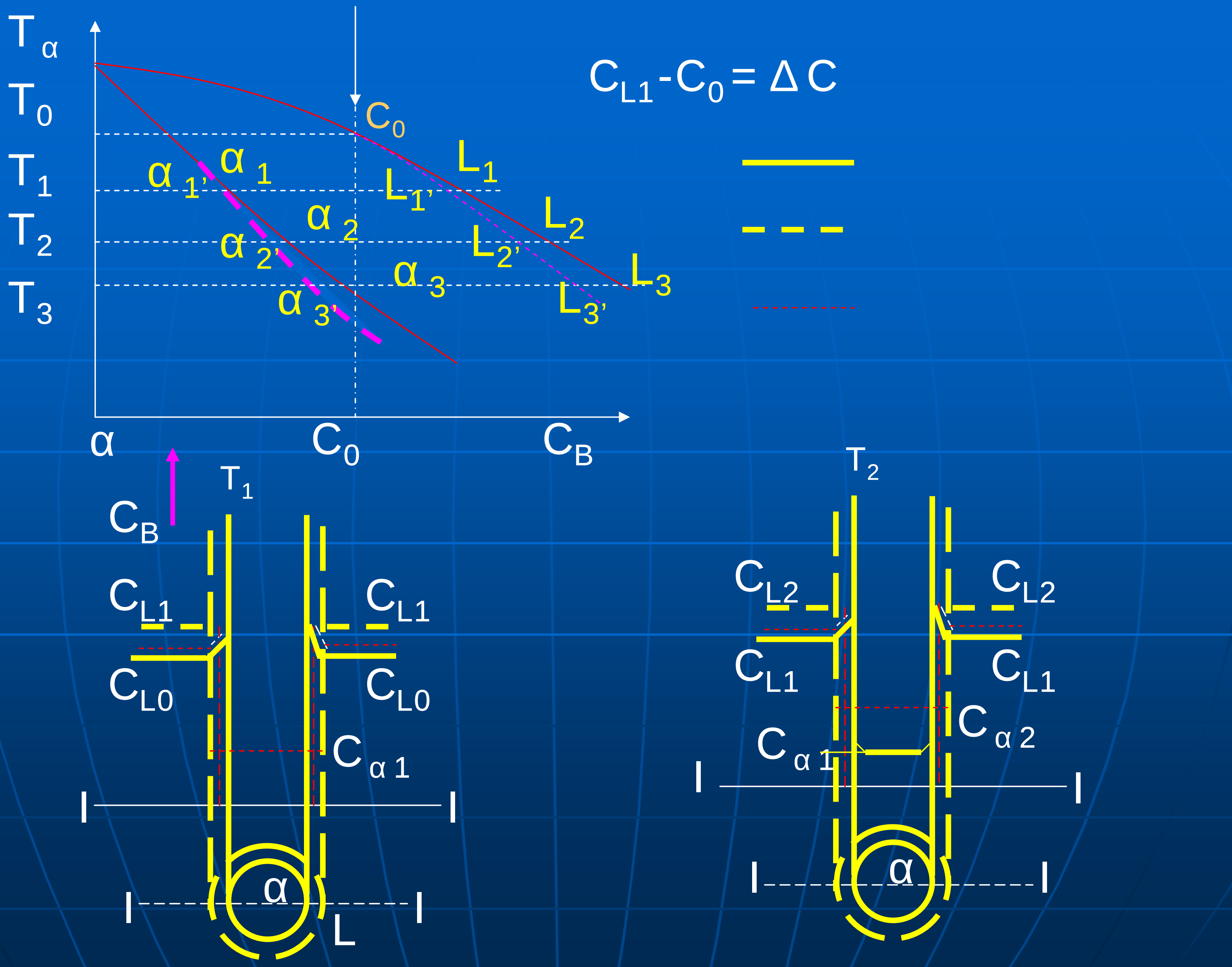


ZnO A B C

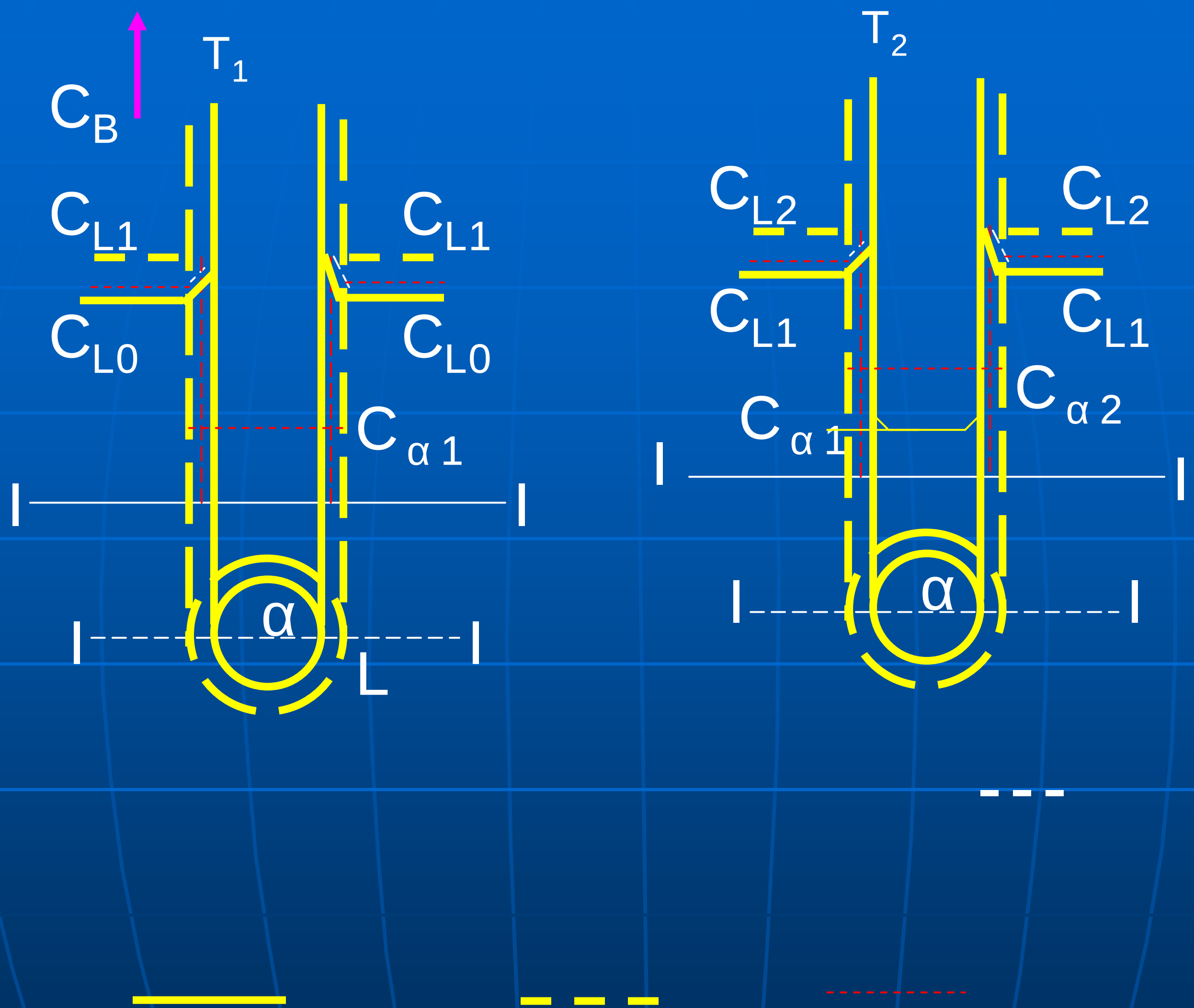
.

1. ----





$C_{L1} - C_0 = \Delta C$
Tα
T0
T1
T2
T3
C0
L1
L1'
L2
L2'
L3
L3'
α 1'
α 1
α 2
α 2'
α 3
α 3'
α
C0
CB
T1
CB
CL1
CL0
CL1
CL0
Cα 1
α
L
T2
CL2
CL1
CL2
CL1
Cα 2
Cα 1
α



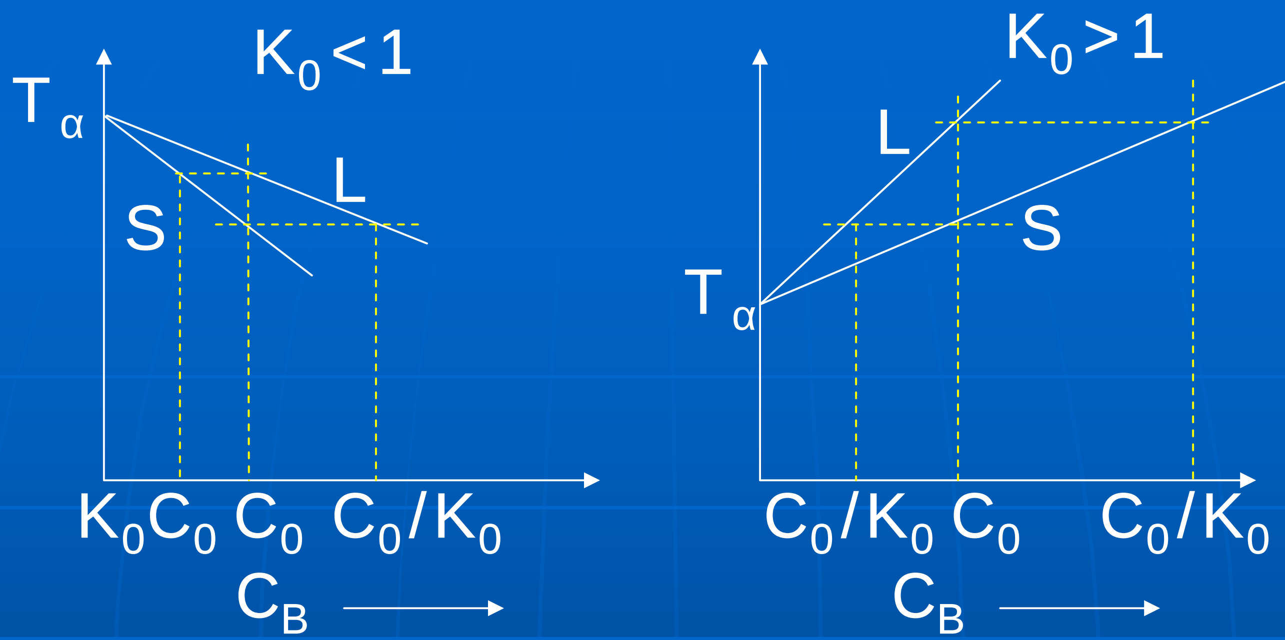
C_B
T_1
C_{L1}
C_{L1}
C_{L0}
C_{L0}
$C_{\alpha 1}$
I
I
α
I
I
L
T_2
C_{L2}
C_{L2}
C_{L1}
C_{L1}
$C_{\alpha 2}$
$C_{\alpha 1}$
I
I
α
I
I

α **A**

2.

.

1.



K_0

(1). K_0 $K_0=C_S/C_L$

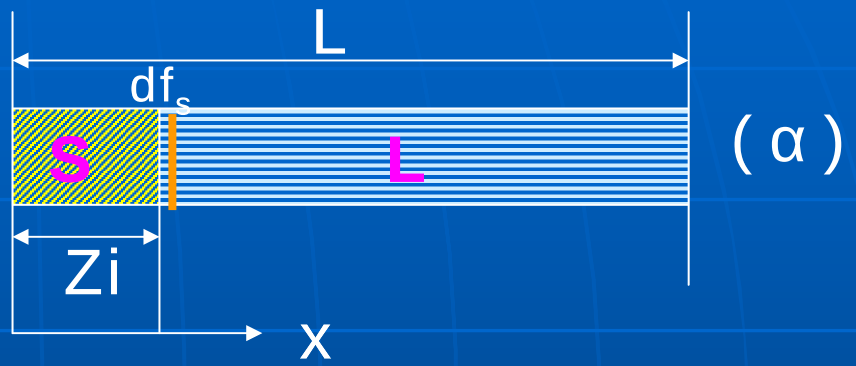
(2).

$C_S=K_0C_L$

(3).

2. 液相内溶质可充分均匀混合

$f_S = Z_i / L$



$$(C_L - C_S) df_s = (1 - f_s - df_s) dC_L$$

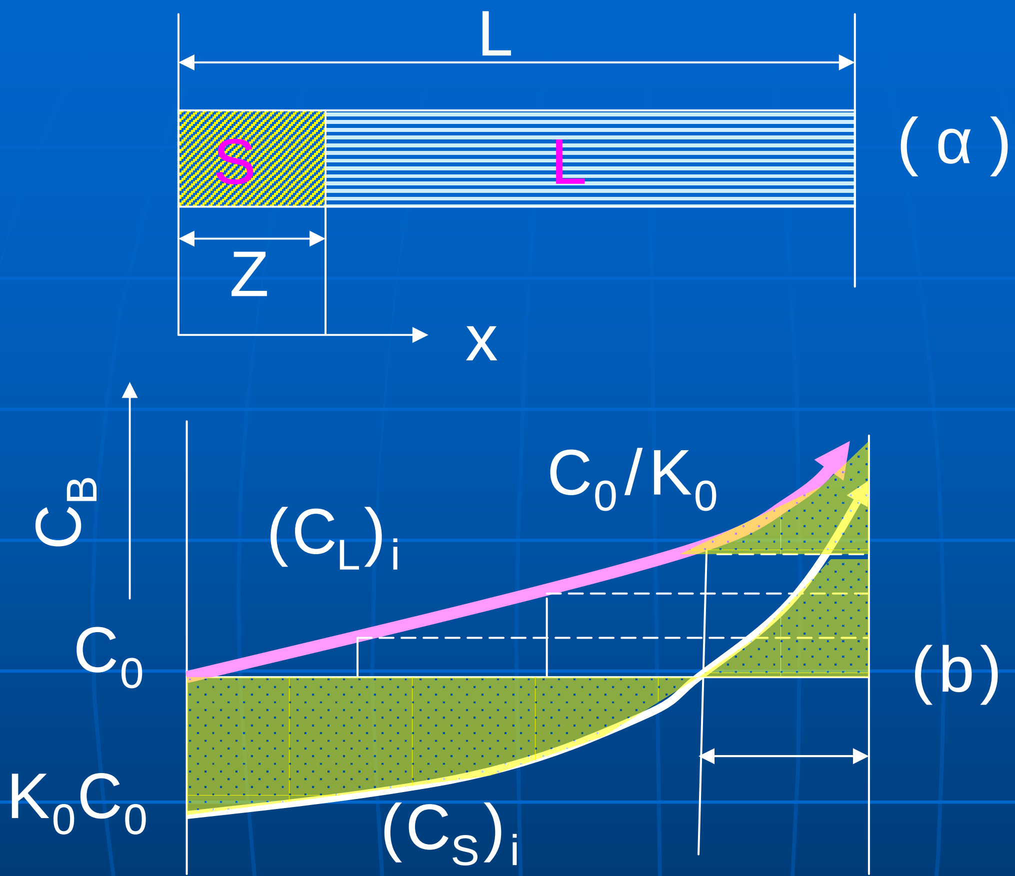
$(C_L - K_0 C_L) df_s = (1 - f_s) df_s - df_s dc_L$,

$dC_L / C_L = (1 - k_0) df_s / (1 - f_s)$, $\ln C_L = (k_0 - 1)\ln(1 - f_s) + \ln C$

$f_s = 0$ $C_L = C_0$, C C_0

$$C_L = C_0 (1 - fs)^{(K_0 - 1)} = C_0 f_L^{(K_0 - 1)}$$

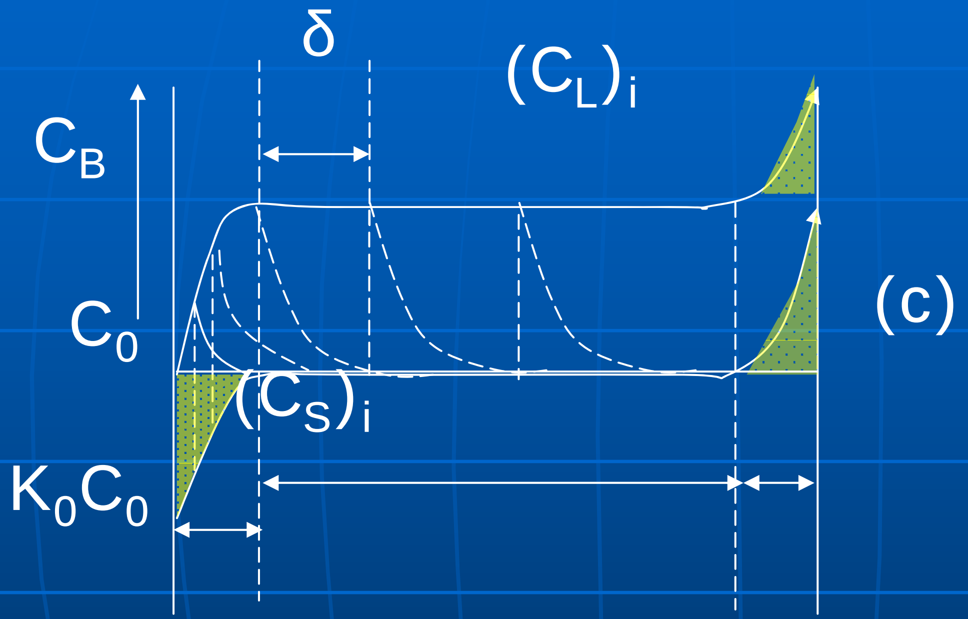
$$C_S = K_0 C_0 (1 - fs)^{(K_0 - 1)}$$

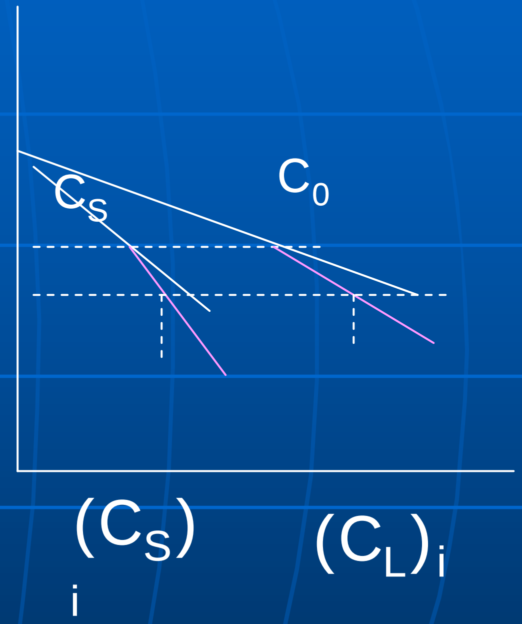


$$C_L = C_0(1 - fs)^{(K_0 - 1)} = C_0 f_L^{(K_0 - 1)}$$

$$C_S = K_0 C_0 (1 - fs)^{(K_0 - 1)}$$

3. 液相内溶质仅靠扩散混合





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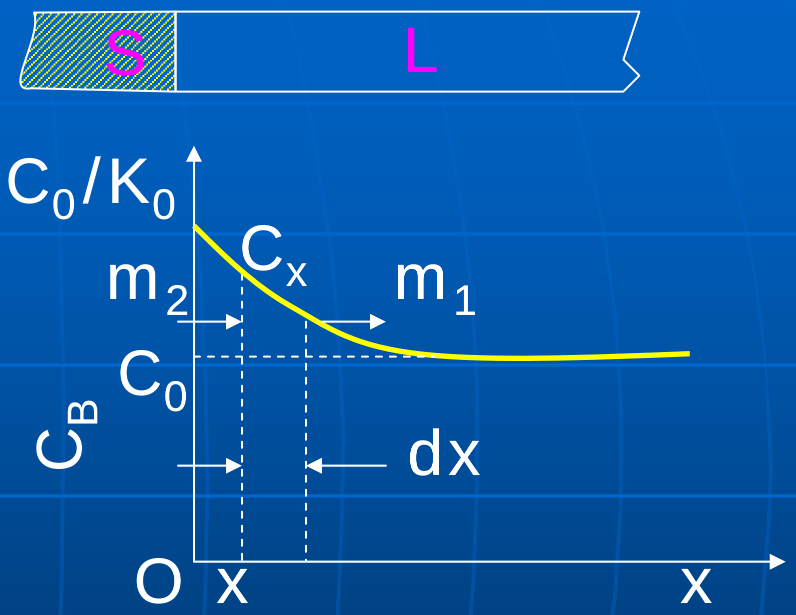


S
L
C0/K0
Cx
m2
m1
C0
CB
dx
O
x
x

(δ max)

(1). $$\frac{dm_1}{dx} = -D\frac{d^2C_x}{dx^2}$$

(2). $$R \cdot \frac{\partial C_L}{\partial x}$$

$$\frac{d^2C_x}{dx^2} = -DR \cdot \frac{\partial C_L}{\partial x}$$

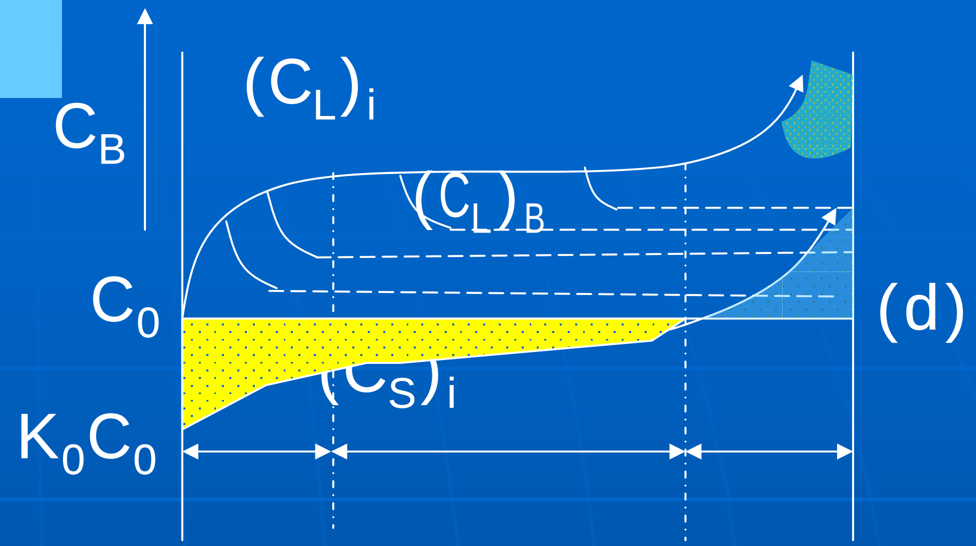
$$C_x = Be^{-\frac{Rx}{D}} + A$$

$X=0$ $C_L=C_0/K_0=A+B$. $B=C_L-A$

$x \to \infty$, $C_L=C_0$, $B=C_0/K_0-C_0$

$$C_x = C_0\left[1+\frac{1-K_0}{K_0}\exp\left(-\frac{Rx}{D}\right)\right]$$

4. 液相内溶质部分混合



(δ_{max})

(1).

$$dm_1 / dx = -Dd^2C_x / dx^2$$

(2).

$$C_x = C_0\left[1 + \frac{1-K_0}{K_0}\exp\left(-\frac{Rx}{D}\right)\right]$$

$(C_L)_i$ $(C_L)_B$ $(C_L)_i/(C_L)_B$

$$K_e = K_0 K_1 = \left[(C_S)_i/(C_L)i\right] \bullet \left[(C_L)_i/(C_L)_B\right] = (C_S)_i/(C_L)_B$$

K_0

$$K_e = K_0 / \left[K_0 + (1 - K_0)e^{-R\delta/D}\right]$$

$$(C_L)_B = C_0(1 - Z/L)^{K_e - 1} = C_0(1 - fs)^{K_e - 1}$$

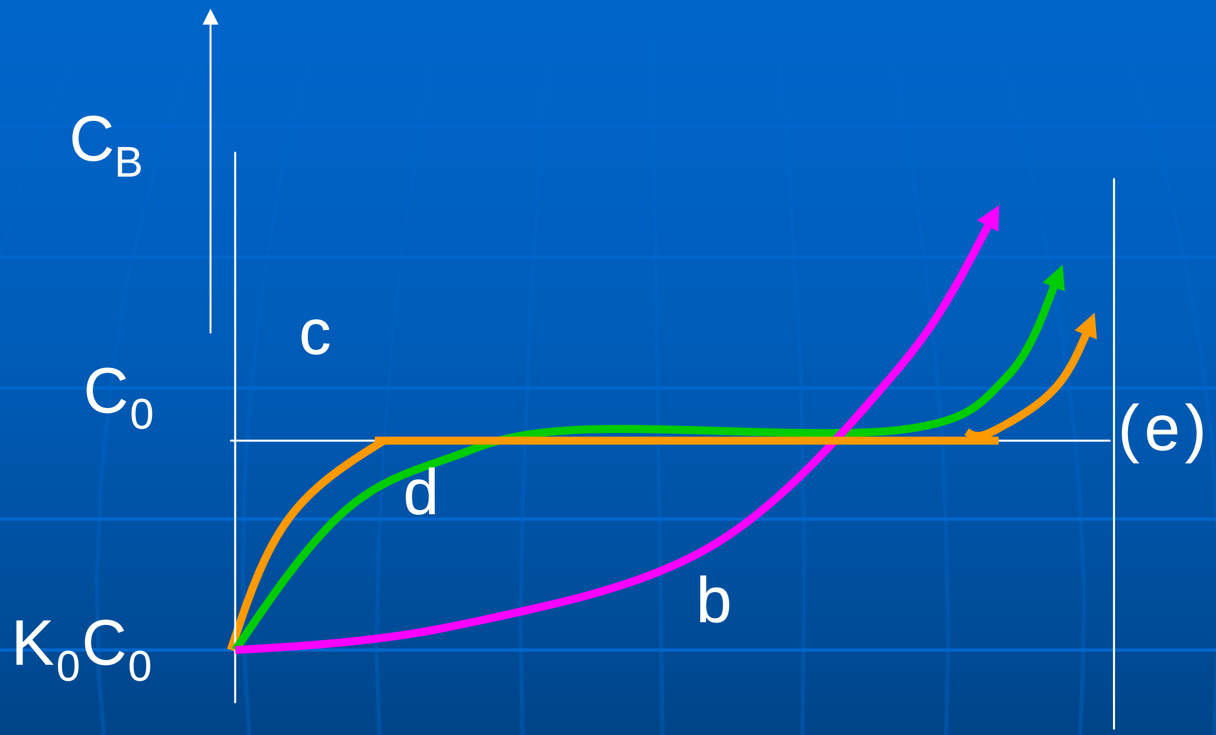
$$C_S = K_e C_0(1 - Z/L)^{K_e - 1} = K_e C_0(1 - fs)^{K_e - 1}$$

(1). R $\delta \to 0$ $K_e = K_0$

(2). R $\delta = \delta_{max}$ $K_e = 1$

(3). $K_0 < K_e < 1$

K_0 K_e



C_B
c
C_0
(e)
d
b
K_0C_0

.

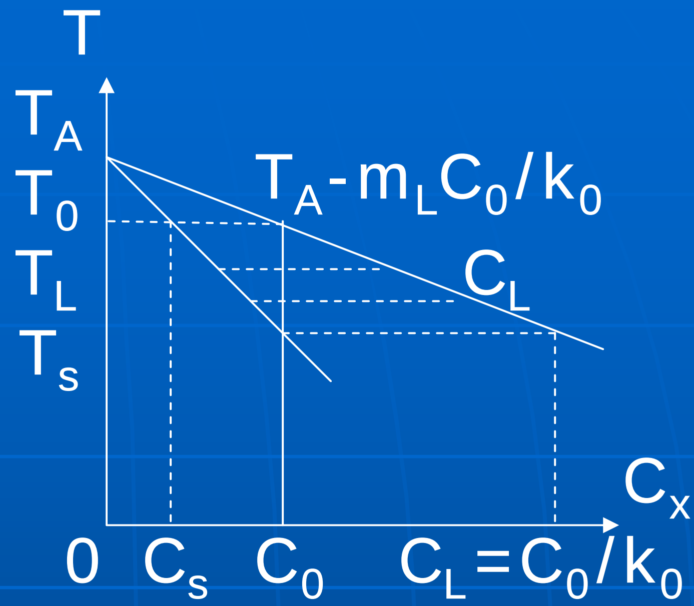
1.

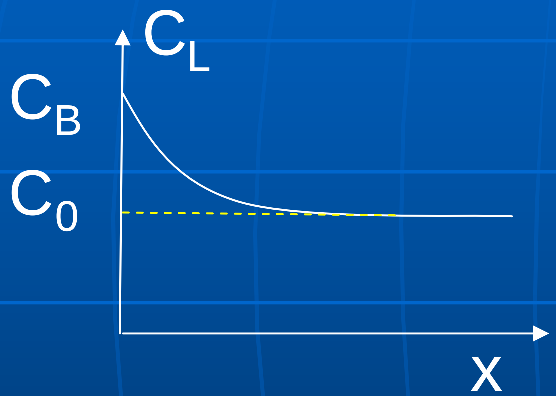
T m

2.

$$T_L = T_A - m_L C_L, m_L \qquad x = 0$$

$$C_L = C_0\left(1 + \frac{1-k_0}{k_0} e^{-Rx/D}\right), C_L = C_0\left(\frac{k_0 + 1 - k_0}{k_0}\right) = \frac{C_0}{k_0}$$



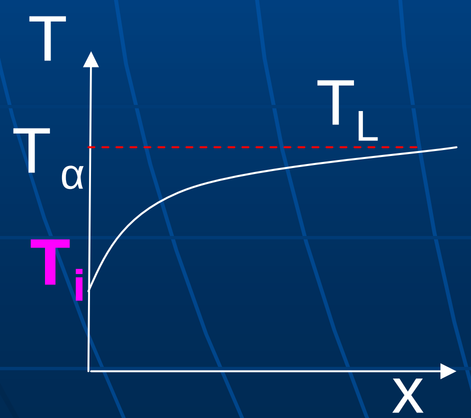


$$T_L = T_A - m_L C_0\left(1 + \frac{1-k_0}{k_0} e^{-Rx/D}\right) \qquad \mathbf{1}$$

$x = 0$,

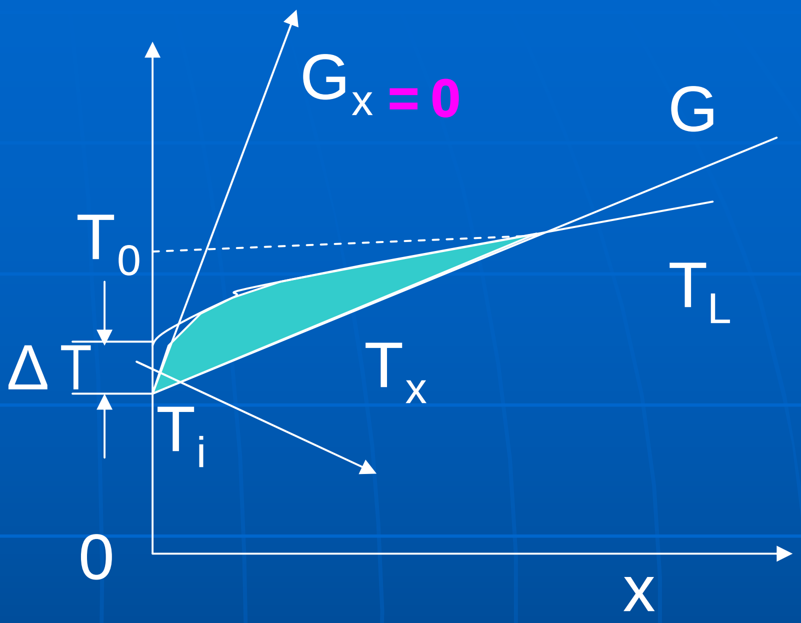
$$T_i = T_A - m_L C_0\left(1 + \frac{1-k_0}{k_0}\right)$$

$$= T_A - m_L C_0 \frac{k_0 + 1 - k_0}{k_0} = T_A - m_L \frac{C_0}{k_0}$$



G

$$T_x = T_i + Gx = T_A - m_L \frac{C_0}{k_0} + Gx$$



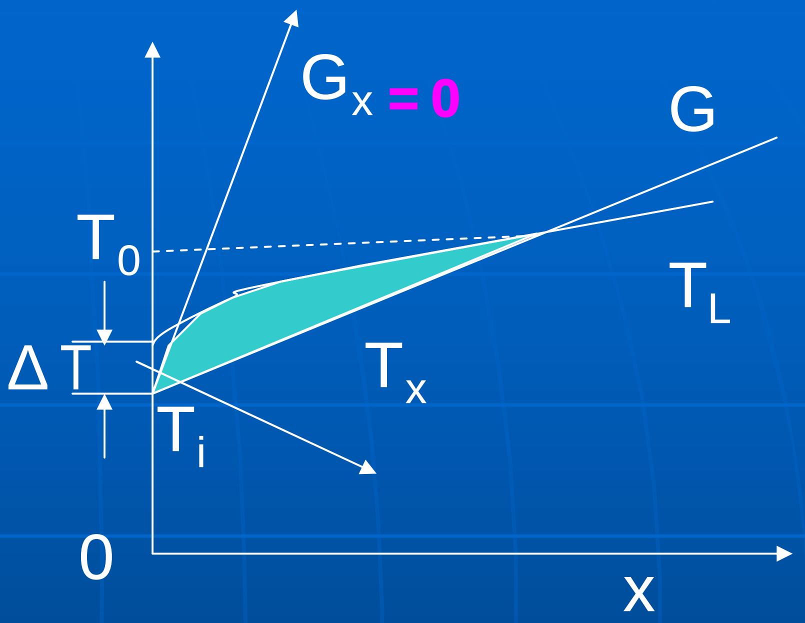
(1) T_L

$$\frac{dT_L}{dx} = -\frac{m_L C_0 (1-k_0)}{k_0} \bullet \left(-\frac{R}{D}\right) \bullet e^{-Rx/D},$$

$$x = 0 \qquad \left.\frac{dT_L}{dx}\right|_{x=0} = \frac{m_L C_0}{D} \bullet \frac{1-k_0}{k_0} R$$

曲线T_L斜率大于G，
则出现组分过冷，即

$$\frac{m_L C_0}{D} \cdot \frac{1-K_0}{K_0} \ge \frac{G}{R}$$



ΔT

D:

K_0

C_0:

m_L:

G:

R

G ↑

R ↓

T_L G

$$\frac{m_L C_0}{D}\frac{1-k_0}{k_0} \geq G/R$$

$\left\{ \begin{array}{l} G \uparrow \\ R \downarrow \end{array} \right.$

$\left\{ \begin{array}{l} G \\ R \end{array} \right.$

$\left\{ \begin{array}{l} D \\ K_0 \end{array} \right.$

C_0

m_L

.

1.

(1).

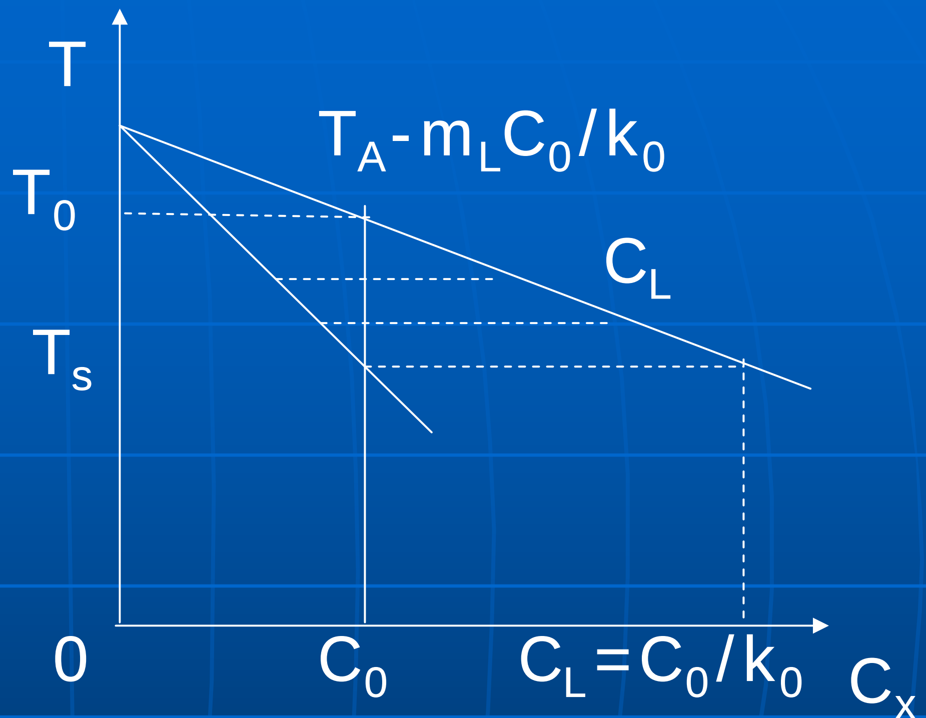
(2).

$$G/R \geq m_L C_0 (1-k_0) / D k_0$$

2.

(1). (   )

$$\frac{m_L C_0}{D}\frac{1-k_0}{k_0} \geq G/R$$



$$m_L = \frac{T_0 - T_S}{C_L - C_0} = \frac{T_0 - T_S}{C_0(\frac{1}{k_0} - 1)} = \frac{\Delta T_C}{C_0 \frac{1-k_0}{k_0}}$$

$$G/R \geq \frac{\Delta T_{C_0}}{D}$$

(2).