2018 Fall

Advanced Solidification

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4.5 Dendritic Growth

Contents for previous class

For aspects of dendritic growth

(a) Total amount of solid formed as a function of initial supercooling of the liquid

(b) Speed of growth as a function of the temperature of the liquid

(c) Direction of growth in relation to the structure of the growing crystal

(d) Spacing and relative lengths of the branches

(1) Total amount solidified. Assumption: liquid is cooled to a uniform temperature (below T_E), isolated so that no heat may enter or leave it. → "Total amount of Dendritic growth"

$$S = \frac{2C_L \Delta T}{2L - (C_L - C_S)\Delta T} \quad \Rightarrow \quad S \approx C\Delta T/L.$$

Others → "Filing in" stage

(much slower than the dendritic growth)

(2) Speed of growth

: depends on the shape and size of the tip and on its temperature

a) Steady state theory

Maximum value of v :

When $(T_E - T_i) = (T_i - T_A) \longrightarrow v = K(\Delta T)^2/4\rho\sigma T_E$ (here, $\Delta T = T_E - T_A$)

$$v \propto (\Delta T)^2$$

b) Non-steady state theory

Growth vs. branching of dendrite
: periodicity of process

→ overall control: by heat flow into a colder liquid ~ unchanged

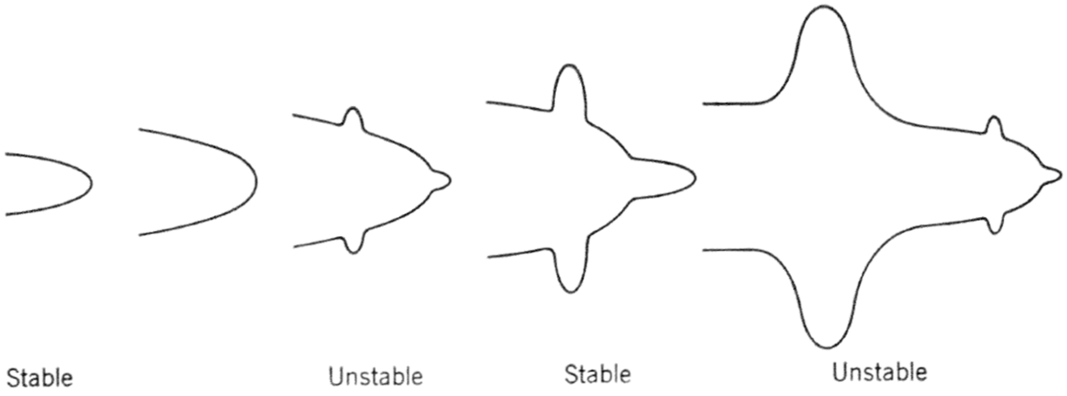


Fig. 4.14. Branching of dendrites.

* EXPERIMENTAL OBSERVATION OF RATE OF DENDRITIC GROWTH

(1) Growth in solid substrate at the same ΔT faster than free growth case

(2) lead dendrite with diffuse interface grew much faster than that with smooth interface

(3) R data: Scattering

∵ a) Dendrites, which were nucleated by local cooling of the melt, grew with random orientations

b) A member of a row < a spike isolated dendrite

Each dendrite of a 2D array will grow even more slowly as a result of their mutual interferernce by the overlapping of their thermal fields.

(4) $v \propto (\Delta T)^2$ **: a good linear relationship to ΔT~175° supercooling;beyond that point~fall into 2 classes**

(5) Although the departure of the tip temp. from equilibrium is small, this difference has an important influence on the tip radius and on the rate of growth.
(growth rate ∝ temp gradient & radius)

(C) Direction of dendrite growth

the arms of dendrites always grow in crystallographically determined directions, each of which is the axis of a pyramid whose sides are the most closely packed planes.

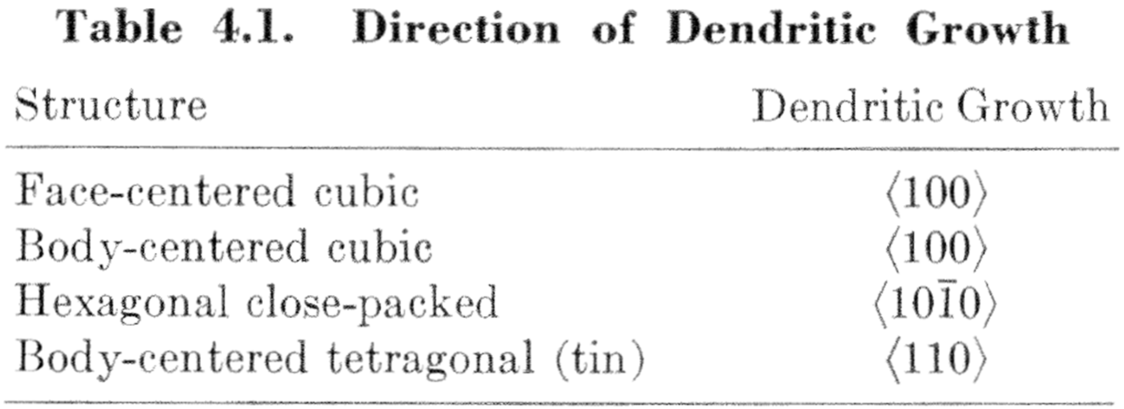


Table 4.1. Direction of Dendritic Growth

Structure	Dendritic Growth
Face-centered cubic	$\langle 100 \rangle$
Body-centered cubic	$\langle 100 \rangle$
Hexagonal close-packed	$\langle 10\bar{1}0 \rangle$
Body-centered tetragonal (tin)	$\langle 110 \rangle$

- According to these generalizations, the “dendrite arms” should always be orthogonal in the cubic and tetragonal and should form angles of 60° for the hexagonal close-packed metals.

- The general explanation for the crystallographic features of dendritic growth must be related to anisotropy of the relationship between growth rate and kinetic driving force.→ Independence of growth direction and thermal conditions.

*** But, there is, so far, no way of measuring the anisotropy of growth rate.**

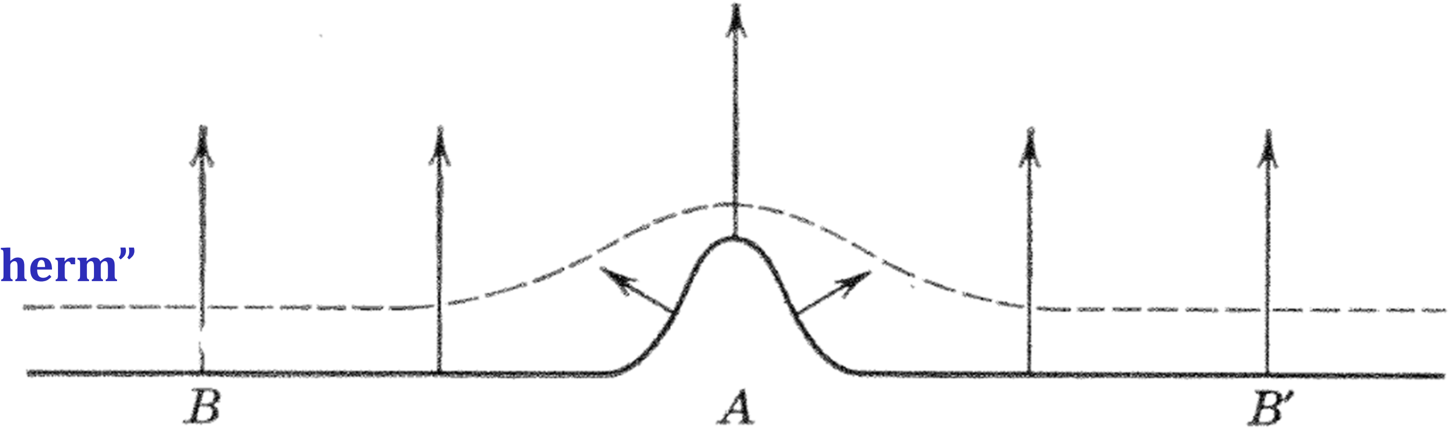
(d) Spacing and relative lengths of the branches

DIRECT OBSERVATION OF DENDRITE SHAPE

*** Spacing of dendrite arms**

Weinberg and Chalmer: ΔT ↑ → spacing of primary dendrite ↑

Increasing in spacing (qualitative explaination):
The region of the surface surrounding a developing instability have a smaller gradient of supercooling than regions that are undisturbed.



“ Isotherm”

Fig. 4.26. Temperature distribution near a dendrite branch.

ΔT ↑ → Production rate of liquid ↑ → AB distance ↑
(the gradient is insufficient to allow arms to develop).

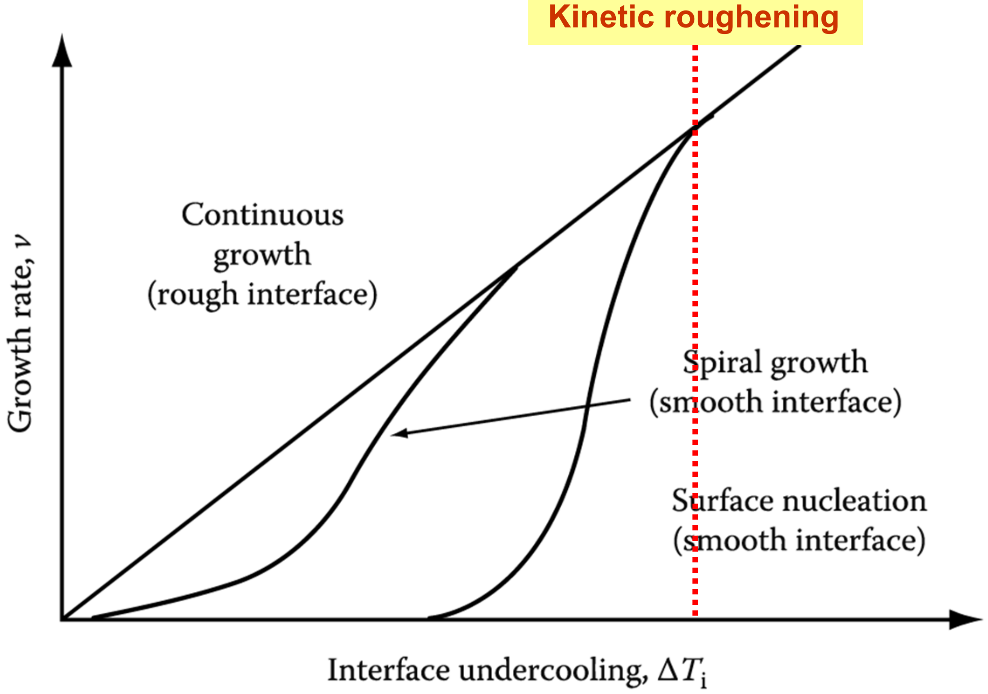
Solidification: Liquid → Solid

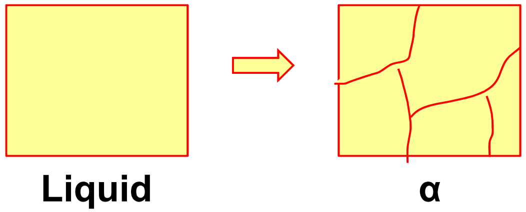
1) Pure Metals: Nucleation and Growth

a) homogeneous Nucleation or Heterogeneous Nucleation

- Undercooling ΔT
- Interfacial energy
  γ_{SL} / S(θ) wetting angle

b) Growth of solid





No compositional change during solidification

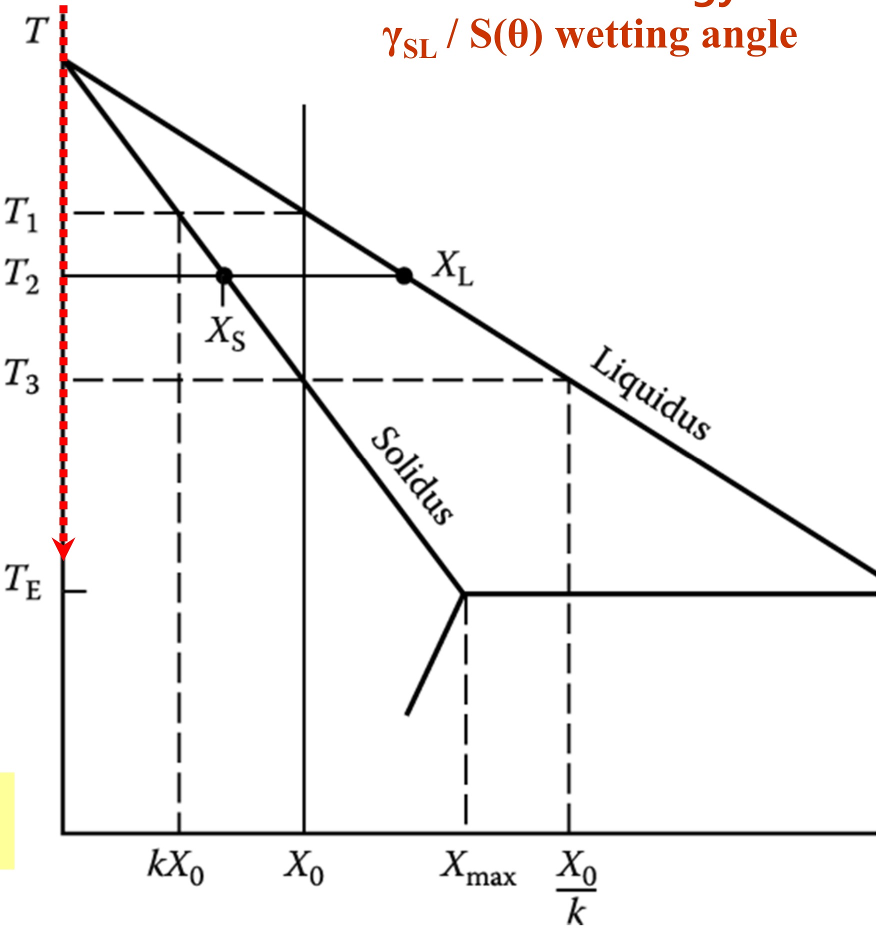


Fig. 4.19 A hypothetical phase diagram.

"Alloy solidification"

1. Solidification of single-phase alloys

- **Three limiting cases**

1) Equilibrium Solidification: perfect mixing in solid and liquid

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

3) No Diffusion in Solid, Perfect Mixing in Liquid

- Planar S/L interface → unidirectional solidification

- Superheated liquid

- Cellular and Dendritic Solidification

- Supercooled liquid

Chapter 5. Redistribution of solute during solidification

5.2 The Distribution Coefficient

Distribution coefficient or partition coefficient, ***k***

a) **Equilibrium distribution coefficient** $k_0 = C_S/C_L$ Characteristic of the system

- Not necessarily a constant for a given system
  (∵liquidus & solidus line may not be so related as to maintain a constant ratio)

- Independent of the speed of the motion of the interface

b) **Effective distribution coefficient** $k_E = C_S/C_0$ Depends of the conditions under which solidification takes place

C_S is formed at some instant by solidification of a liquid of **average concentration** C_0

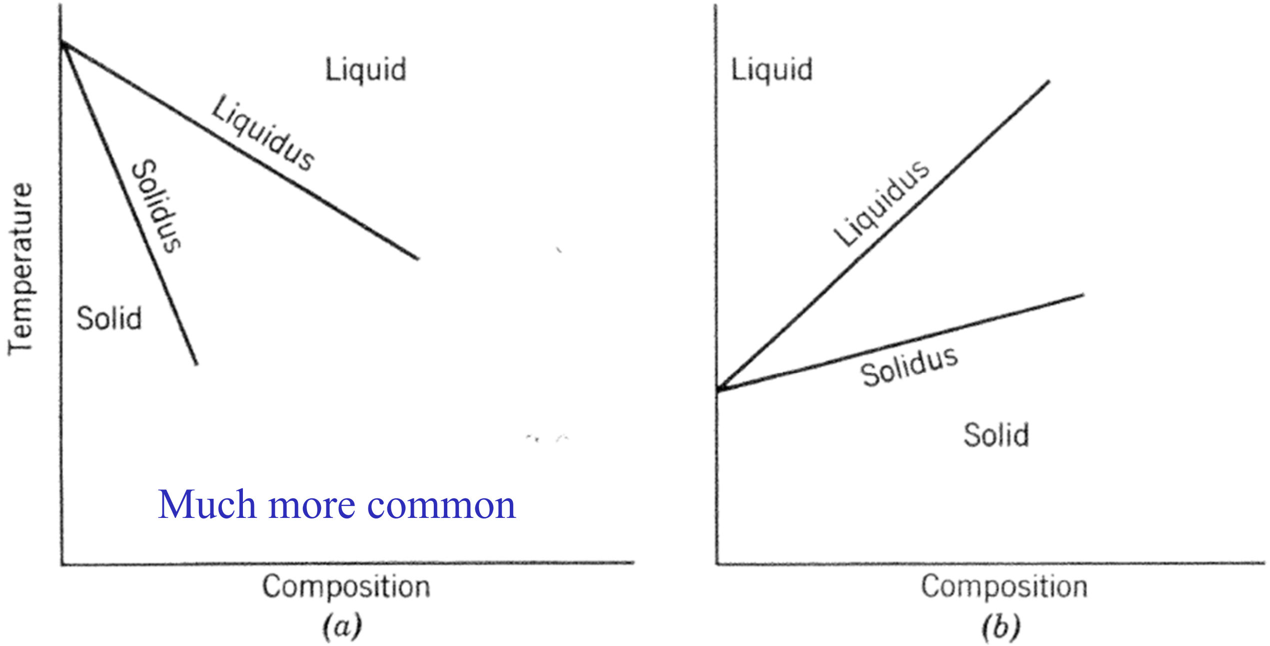


Fig. 5.1. Solidus-liquidus relationships for dilute binary alloys.

5.3 Rejection of solute

At solid-liquid interface

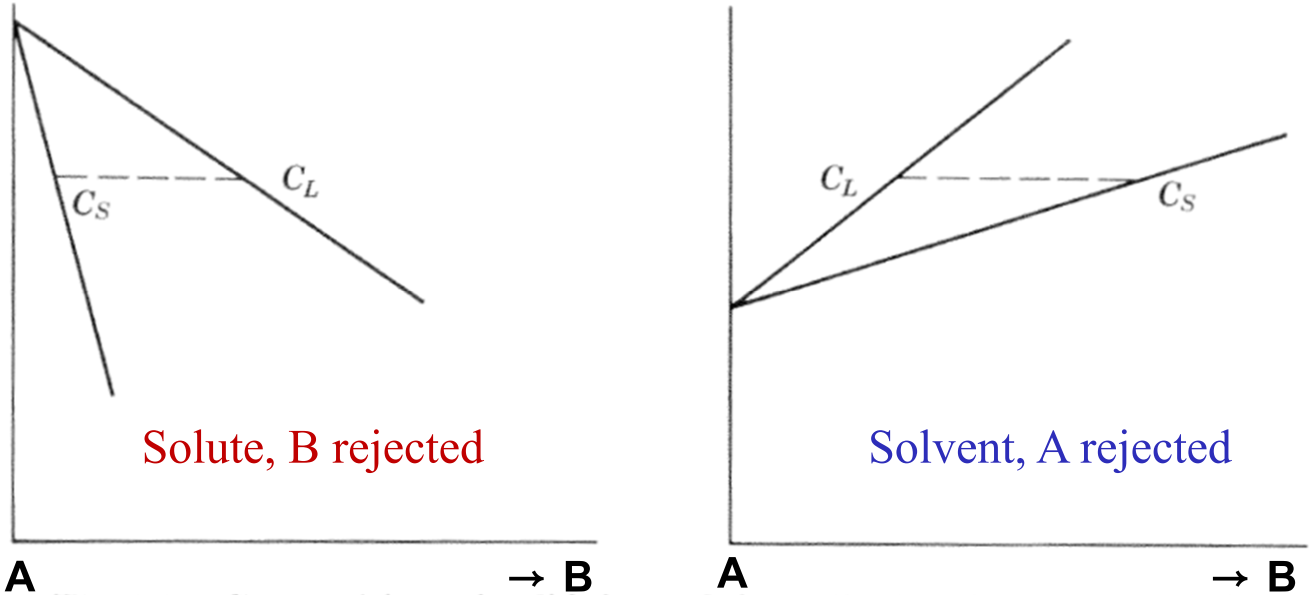


Fig. 5.3. Composition of solid formed from liquid of composition C_L.

* Both heat flow and solute diffusion are uniaxial
→ constant speed of interface

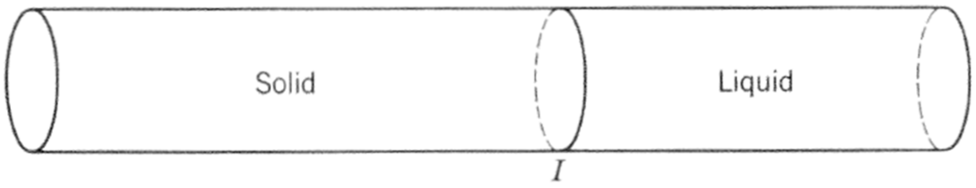


Fig. 5.4. Geometry of uniaxial solidification.

Assumption:

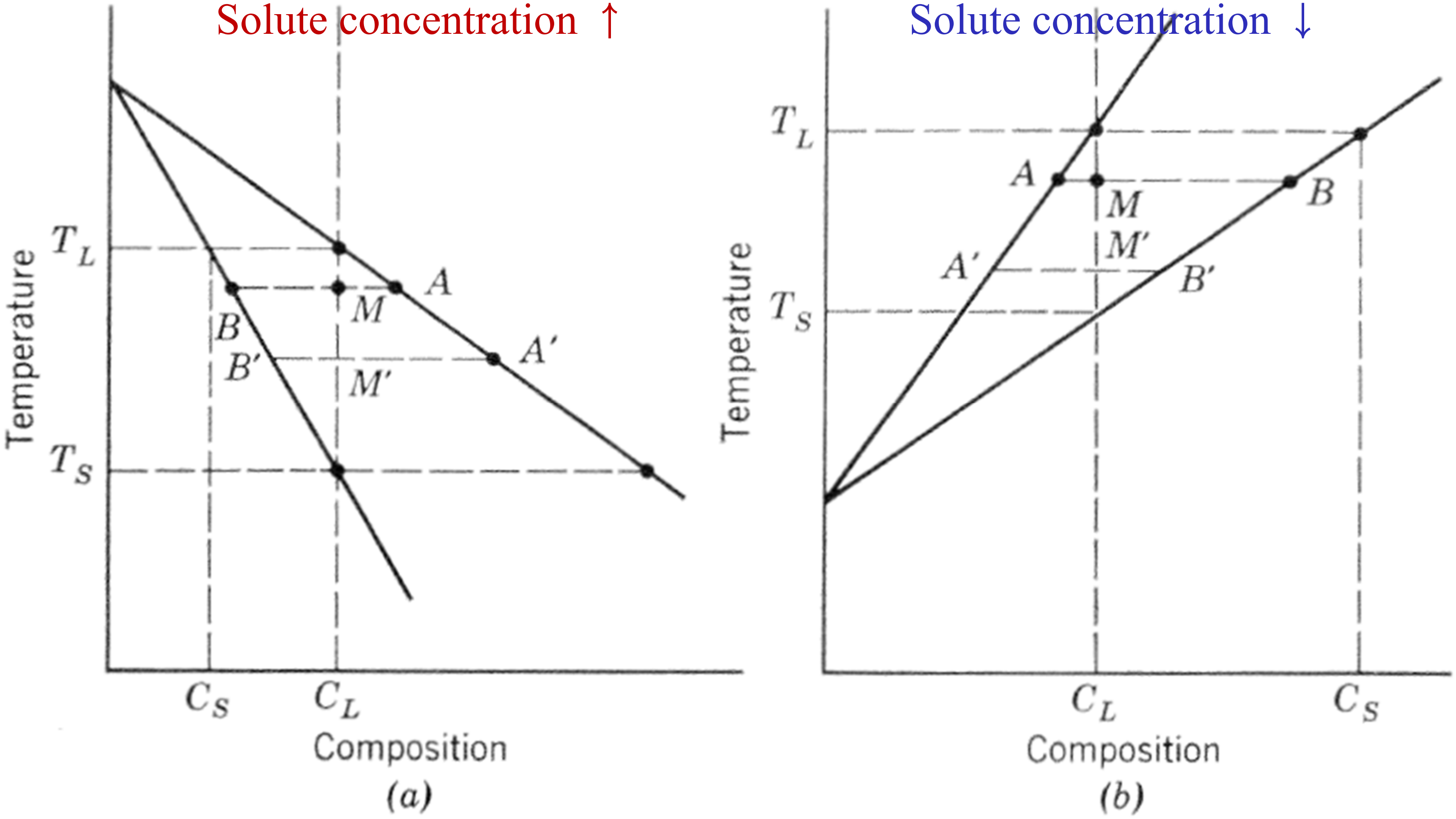
(a) all times completely mixed with the whole of remaining liquid.

(b) Transport is by diffusion only.

(c) Motion of solute, by diffusion, in the solid

1) Equilibrium maintained at all times: perfect mixing in solid and liquid

When solidification start → liquidus temp ↓

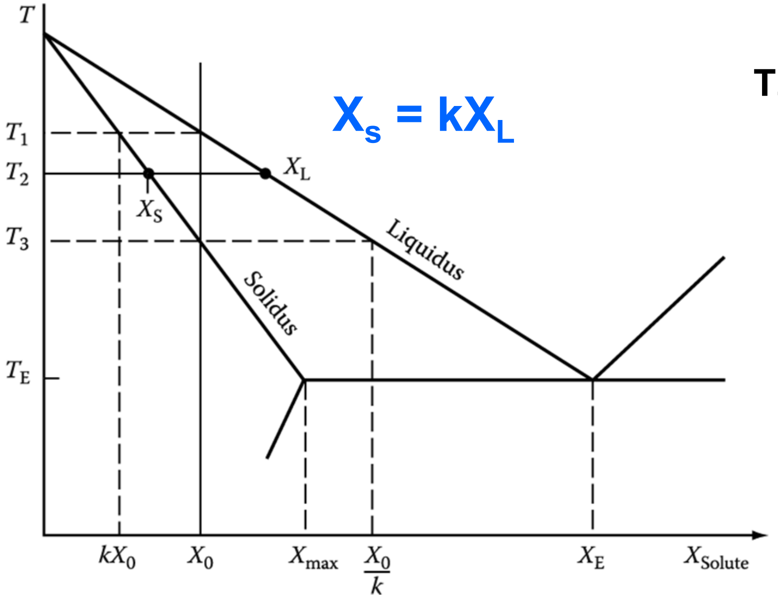

Solute concentration ↑

Solute concentration ↓

a) Total amount of solvent and solute remain unchanged.

b) The relative amount of solid and liquid are always given by the ratio AM/BM.

1) Equilibrium Solidification : perfect mixing in solid and liquid



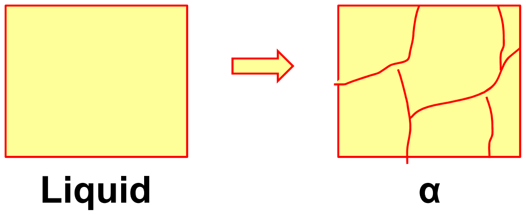
$X_s = kX_L$

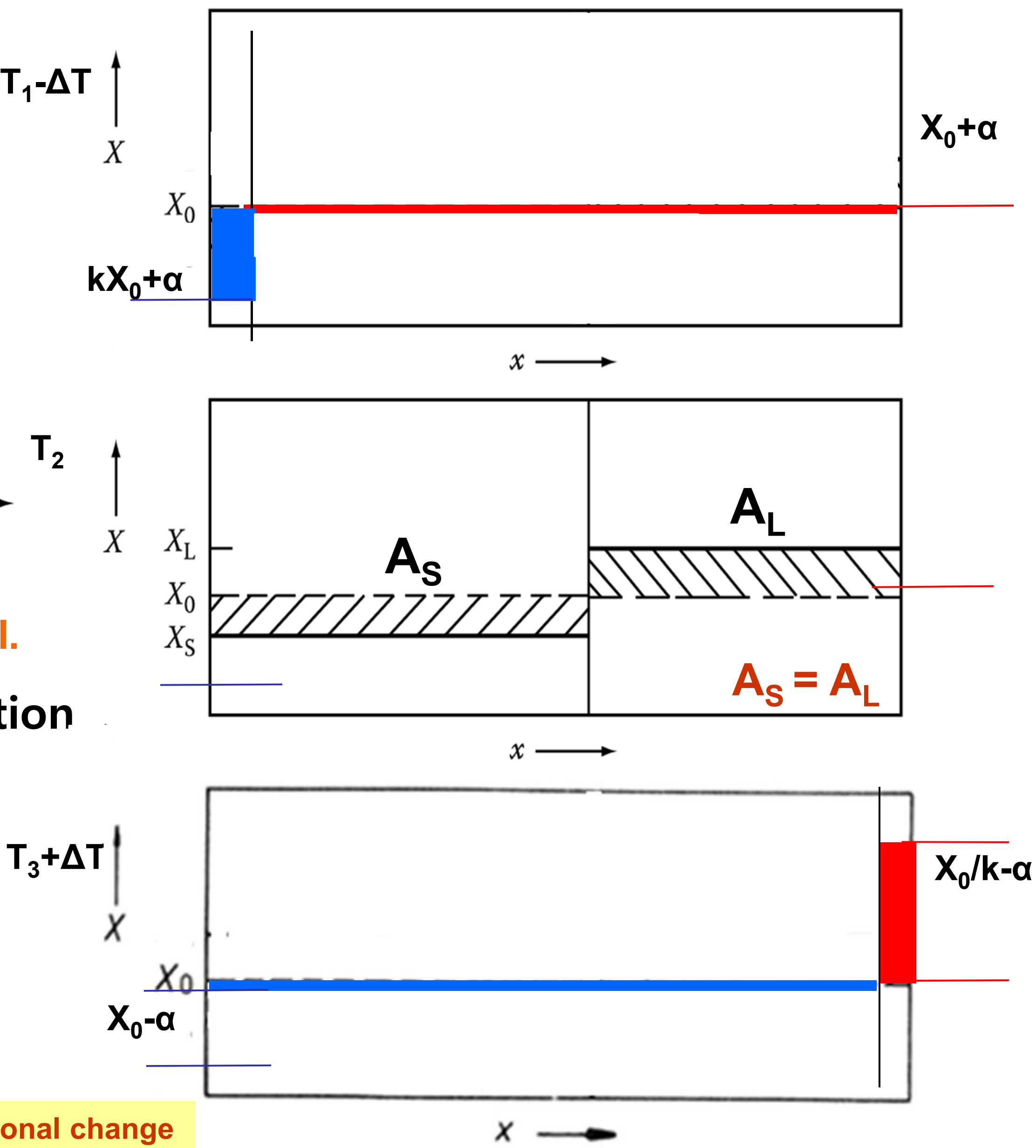
Conservation of solute requires the two shaded areas to be equal.

* Equilibrium solute concentration

$kX_0 \leq X_s \leq X_0$

$X_0 \leq X_L \leq X_0/k < X_E$





Compositional change during solidification

1) Equilibrium Solidification : perfect mixing in solid and liquid

a) Solid is at all times in equilibrium with the liquid →
"diffusion in Solid ~ fast enough" → no concentration gradient

* The assumption demands that

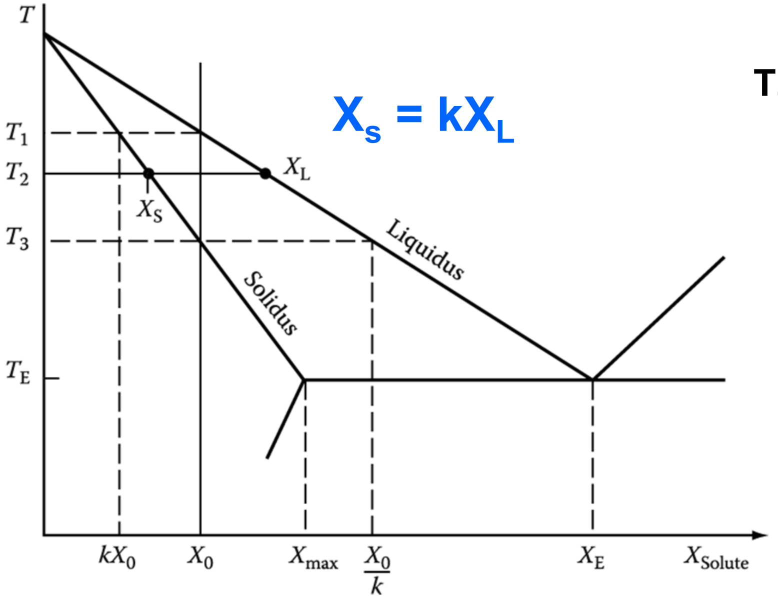
① the rate of advance of the interface is slow compared with the diffusion rate of the relevant solute in the solid

② diffusion distance (total distance through which the interface moves) is small.
(for example, geological process, the time scale is extremely long by human or industrial standards)

b) Among metallurgical processes, the largest effect of diffusion during solidification is probably to be found in the case of carbon and nitrogen in steel, since these interstitial solutes have very much higher diffusion coefficients than substitutional solutes.

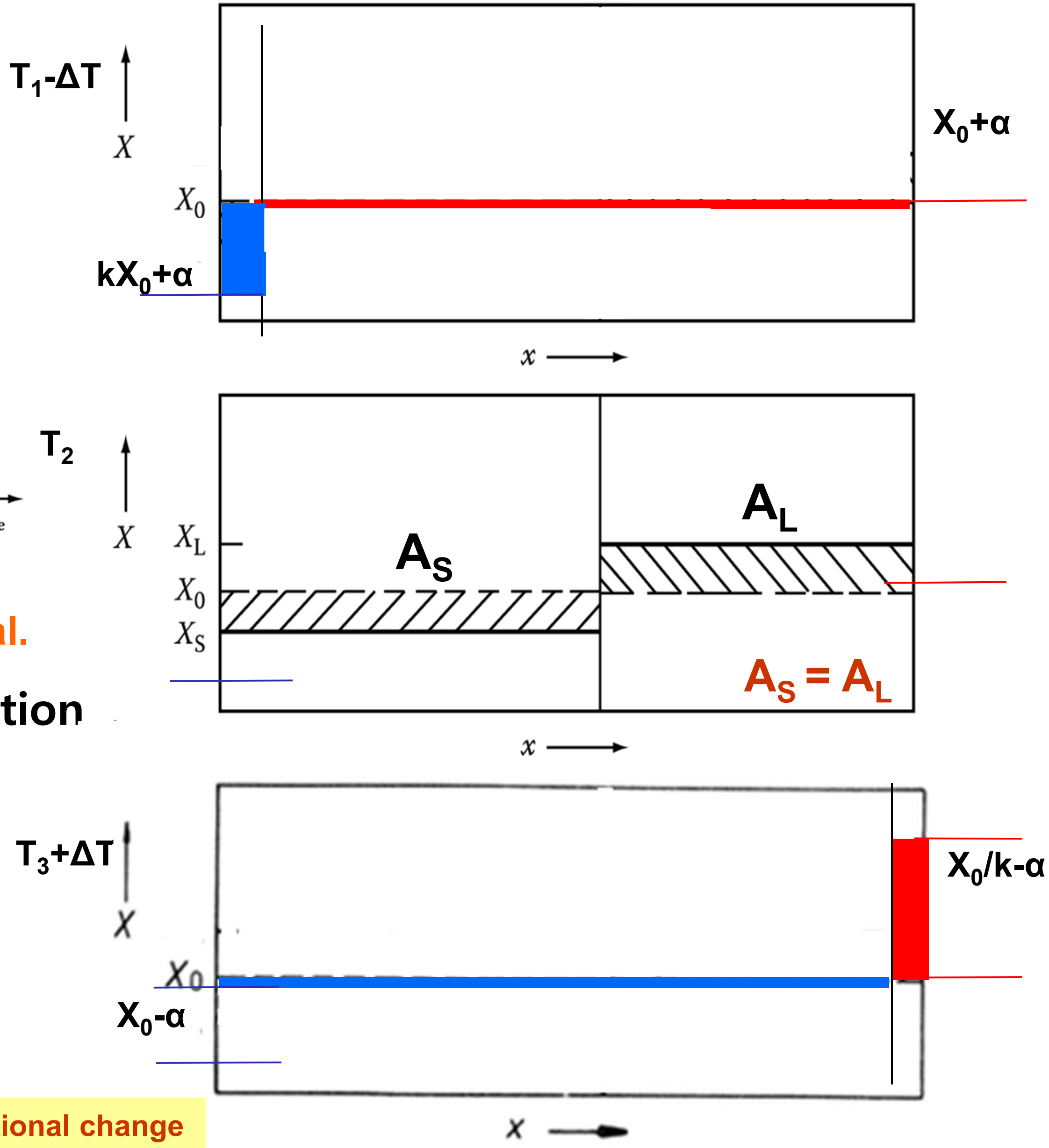
c) It should also be remembered that a significant amount of diffusion can also take place after solidification while the material is cooling down. → page 178

1) Equilibrium Solidification : perfect mixing in solid and liquid



$X_s = kX_L$

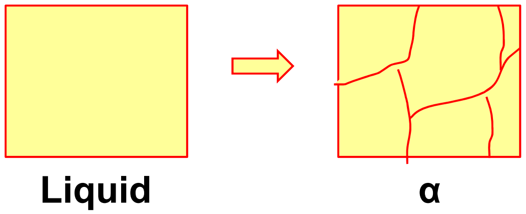
Conservation of solute requires the two shaded areas to be equal.



* **Equilibrium solute concentration**

$kX_0 \le X_s \le X_0$

$X_0 \le X_L \le X_0/k < X_E$



Compositional change during solidification

2) Mixing in the liquid by diffusion only: No diffusion in the solid

* 1) Equilibrium Solidification : Opposite extreme of perfect mixing in solid and liquid (solute or solvent) does not move→no mixing in either the solid or the liquid → L→S without composition change:"diffusionless solidification" of this kind may take place locally when the liquid is sufficiently supercooled. = "polymorphic transformation"

* For example, **$D_S << D_L$**

(**D_S ignored, D_L~normally**_all diffusion in the liquid is to the interface)

In the case of Equilibrium solidification

V (speed of advance of interface)= very slow ↔

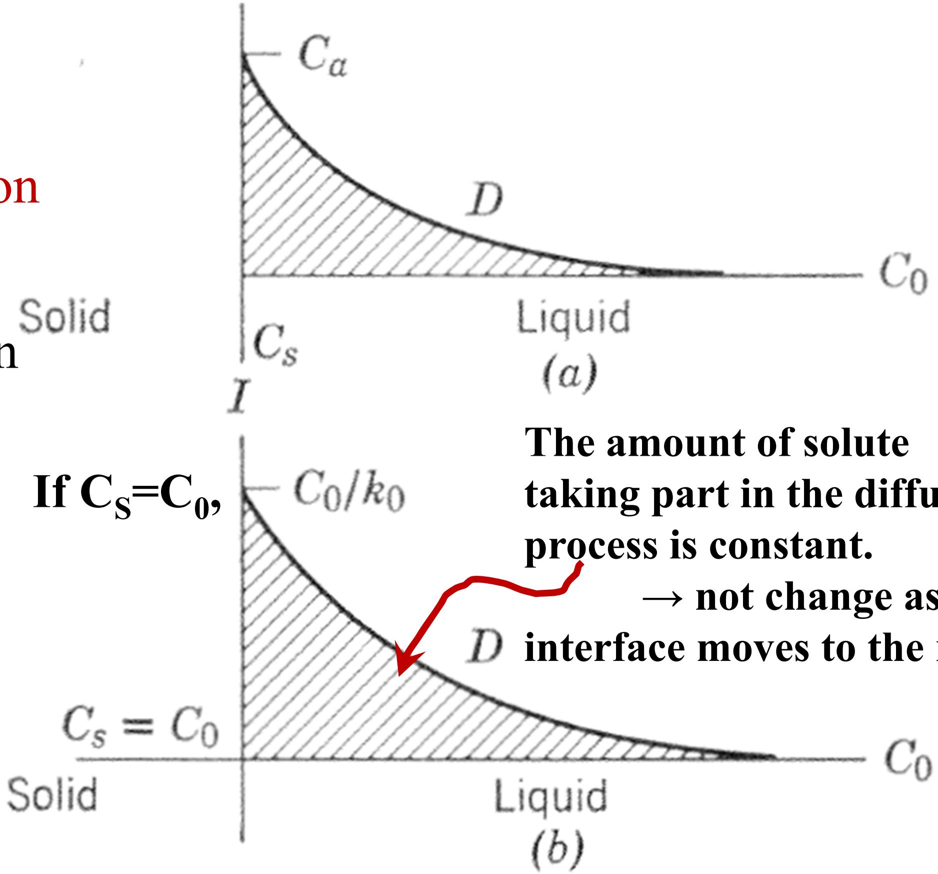
but in this case **$V_{interface}$ = *R* cm/sec**

$C_S/C_a = k_0$

C_0_initial composition of liquid

$k_E = C_S/C_0$

Here, C_a=solute concentration in the liquid at the interface



If C_S=C_0,

The amount of solute taking part in the diffusion process is constant.

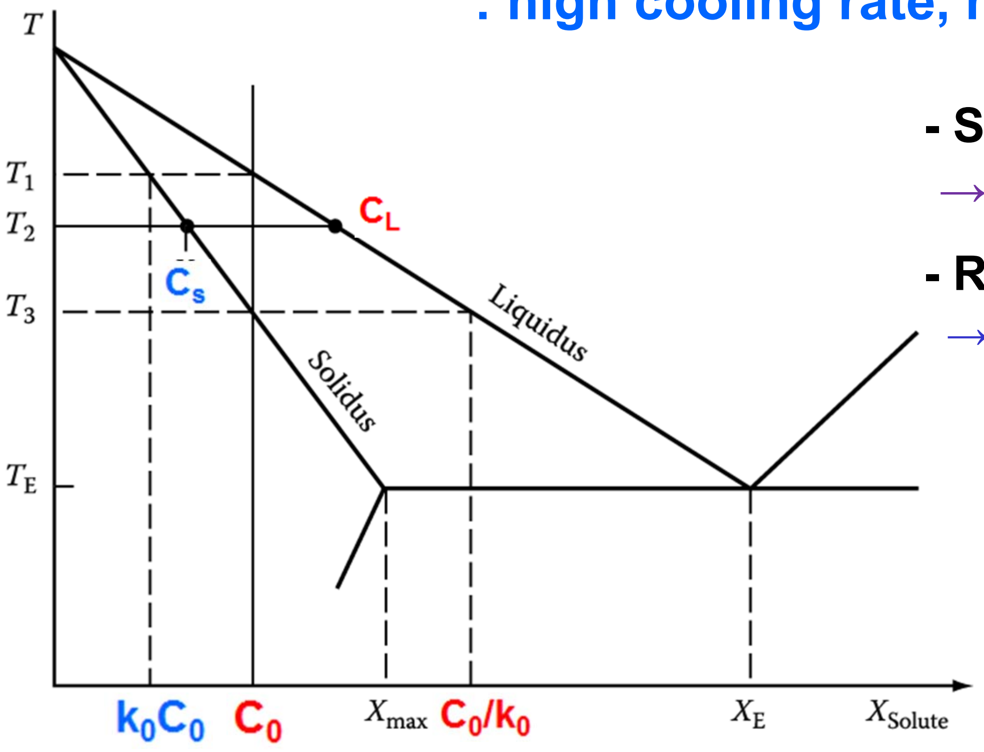
→ not change as the interface moves to the right

→ If composition of solid=C_0, "steady state condition"

Fig. 5.6. Distribution of solute during uniaxial solidification

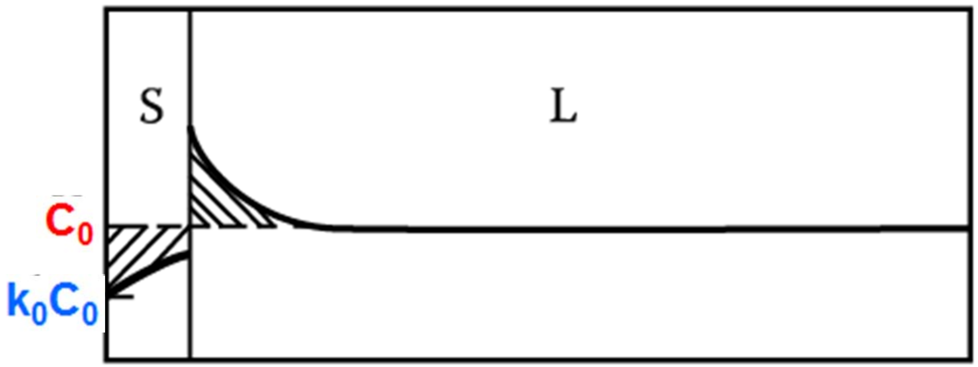
2) No Diffusion on Solid, Diffusional Mixing in the Liquid

: high cooling rate, no stirring→ diffusion



- Solute rejected from solid
  → diffuse into liquid with limitation
- Rapid build up solute in front of the solid
  → rapid increase in the comp. of solid forming (initial transient)
  - if it solidifies at a const. rate, *v*, then a steady state is finally obtained at T_3
  - liquid : C_0/k_0, solid: C_0

local equil. at S/L interface



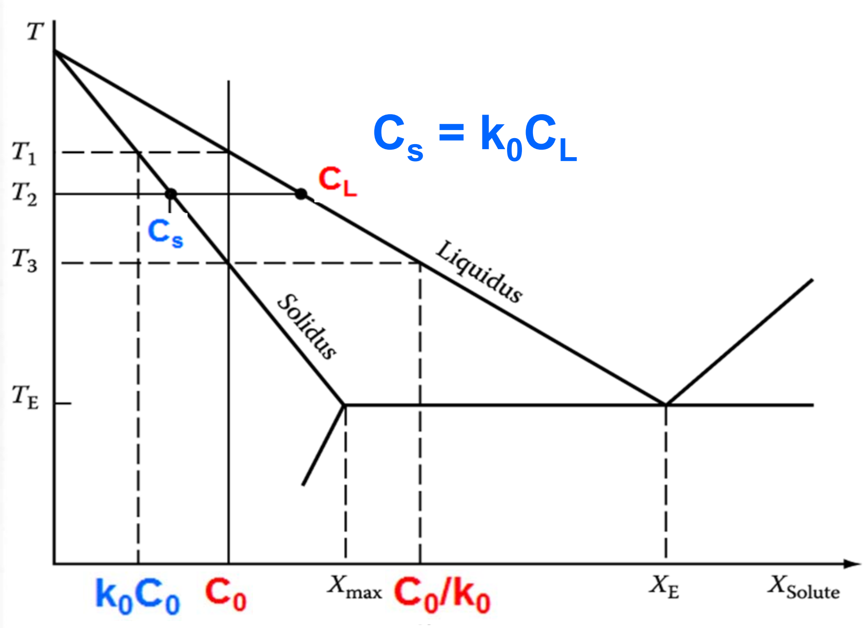
Composition profile at $T_2 < T_{S/L} < T_3$?

Steady-state profile at T_3? at T_E or below ?

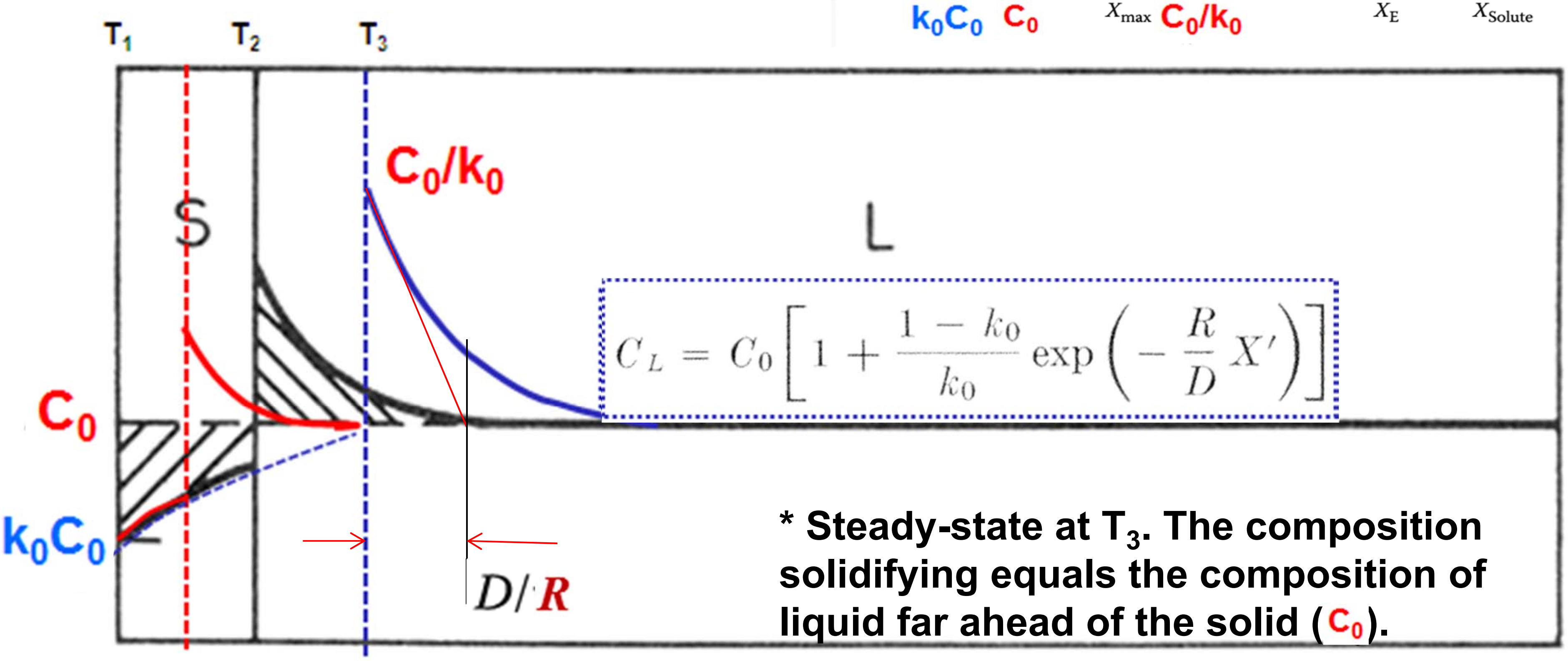
"Alloy solidification"

- Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid



Interface temperature



$$C_L = C_0\left[1+\frac{1-k_0}{k_0}\exp\left(-\frac{R}{D}X'\right)\right]$$

* Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (C_0).

No Diffusion on Solid, Diffusional Mixing in the Liquid

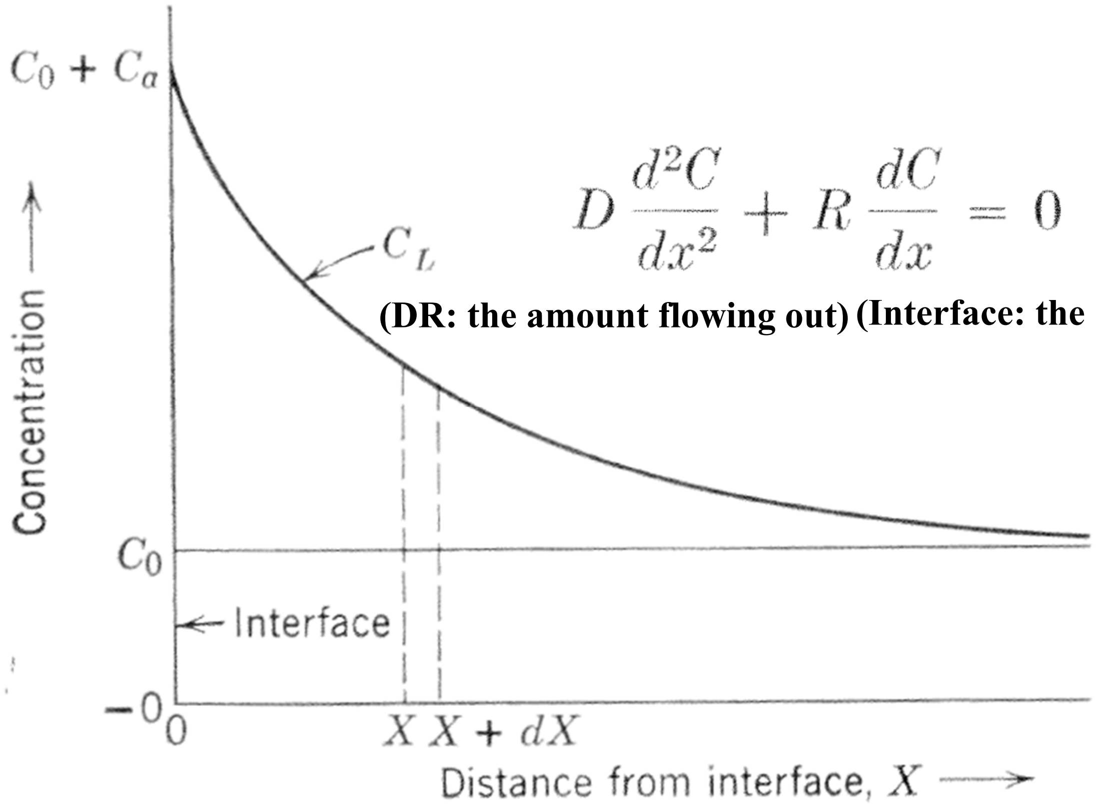
① During steady-state growth,

(Interface →liquid: Diffusion rate)

Rate at which solute diffuses down the concentration gradient away from the interface

= Rate at which solute is rejected from the solidifying liquid

(Solid→Liquid from solidification: solute rejecting rate)



$$D\frac{d^2C}{dx^2} + R\frac{dC}{dx} = 0$$

(DR: the amount flowing out) **(Interface: the amount flowing in)**

Fig. 5.7. Steady state diffusion of solute. (From Ref. 3.)

No Diffusion on Solid, Diffusional Mixing in the Liquid

① During steady-state growth,

(Interface →liquid: Diffusion rate)

Rate at which solute diffuses down the concentration gradient away from the interface
= Rate at which solute is rejected from the solidifying liquid

(Solid→Liquid from solidification: solute rejecting rate)

Set up the equation.

$$J = DC_L' = \mathbf{R}(C_L - C_S)$$

$$J = -D\frac{\partial C_L}{\partial x} = \mathbf{R}\boxed{(C_L - C_S)}$$

(Solidification rate of alloy: <u>excess solute control</u>)

$$\Updownarrow$$

$$K_S T_S' = K_L T_L' + v\boxed{L_V}$$

(Solidification rate of pure metal: <u>latent heat control</u>, 10^4 times faster than that of alloy)

Solve this equation.

$C_S = C_0 \quad for \quad all \quad x \geq 0$

$$\frac{dC_L}{C_L - C_0} = -\frac{\mathbf{R}}{D}dx$$

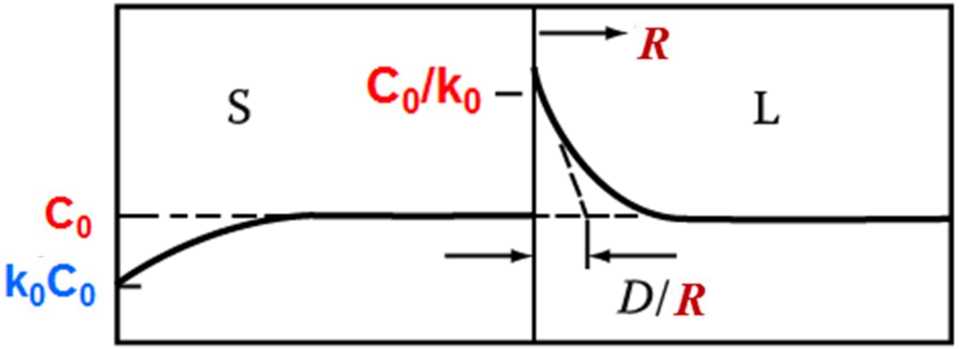
$$\ln(C_L - C_0) = -\frac{\mathbf{R}}{D}x + c$$

$x = 0; C_L = C_0/k_0$

$$c = \ln\left(\frac{C_0}{k_0} - C_0\right)$$

$$\ln \frac{C_L - C_0}{C_0\left(\frac{1}{k_0}-1\right)} = -\frac{R}{D}x$$

$$C_L - C_0 = C_0\left(\frac{1-k_0}{k_0}\right)e^{-\frac{R}{D}x}$$



If $C_S=C_0$,

$$\boxed{C_L = C_0\left[1+\frac{1-k_0}{k_0}\exp\left(-\frac{R}{D}X'\right)\right]} \Leftarrow C_L = C_a\exp\left(-\frac{R}{D}X'\right) + C_0$$

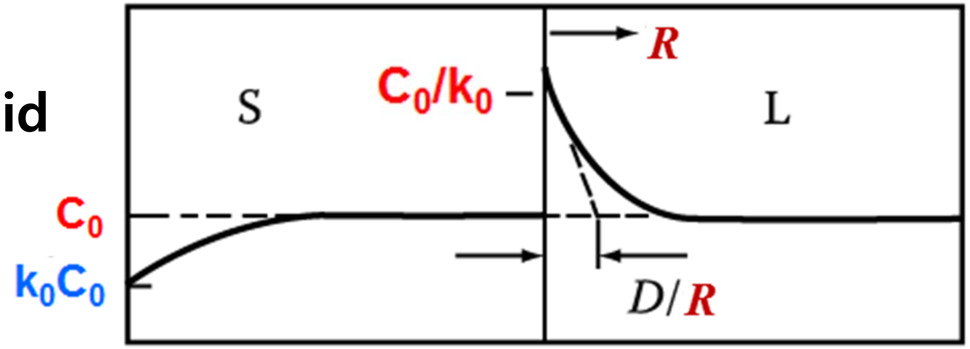
(X'= distance from the interface at which the concentration is C_L)

(C_L decreases exponentially from C_0/k_0 at x=0, the interface, to C_0 at large distances from the interface. The concentration profile has a characteristic width of D/R.)

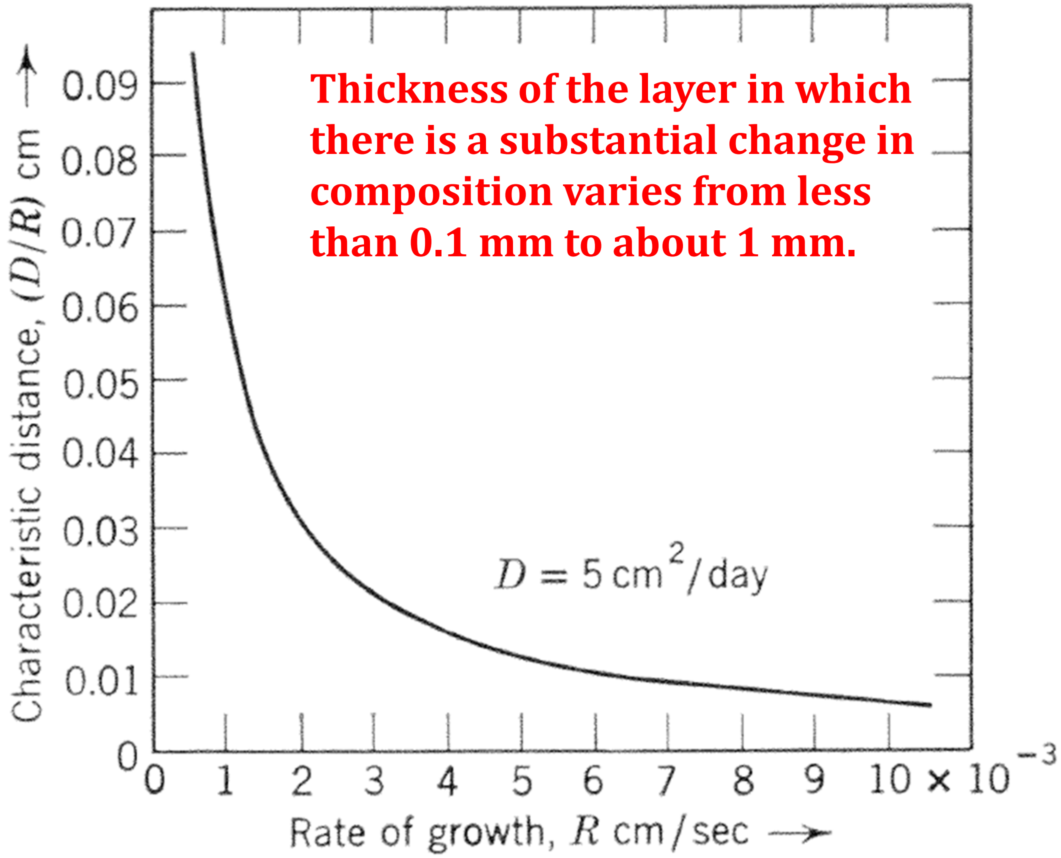
- Liquid distribution: "characteristic distance" given by D/R; that is, the distance in which the excess concentration falls to 1/e of its initial value.

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

During steady-state growth,



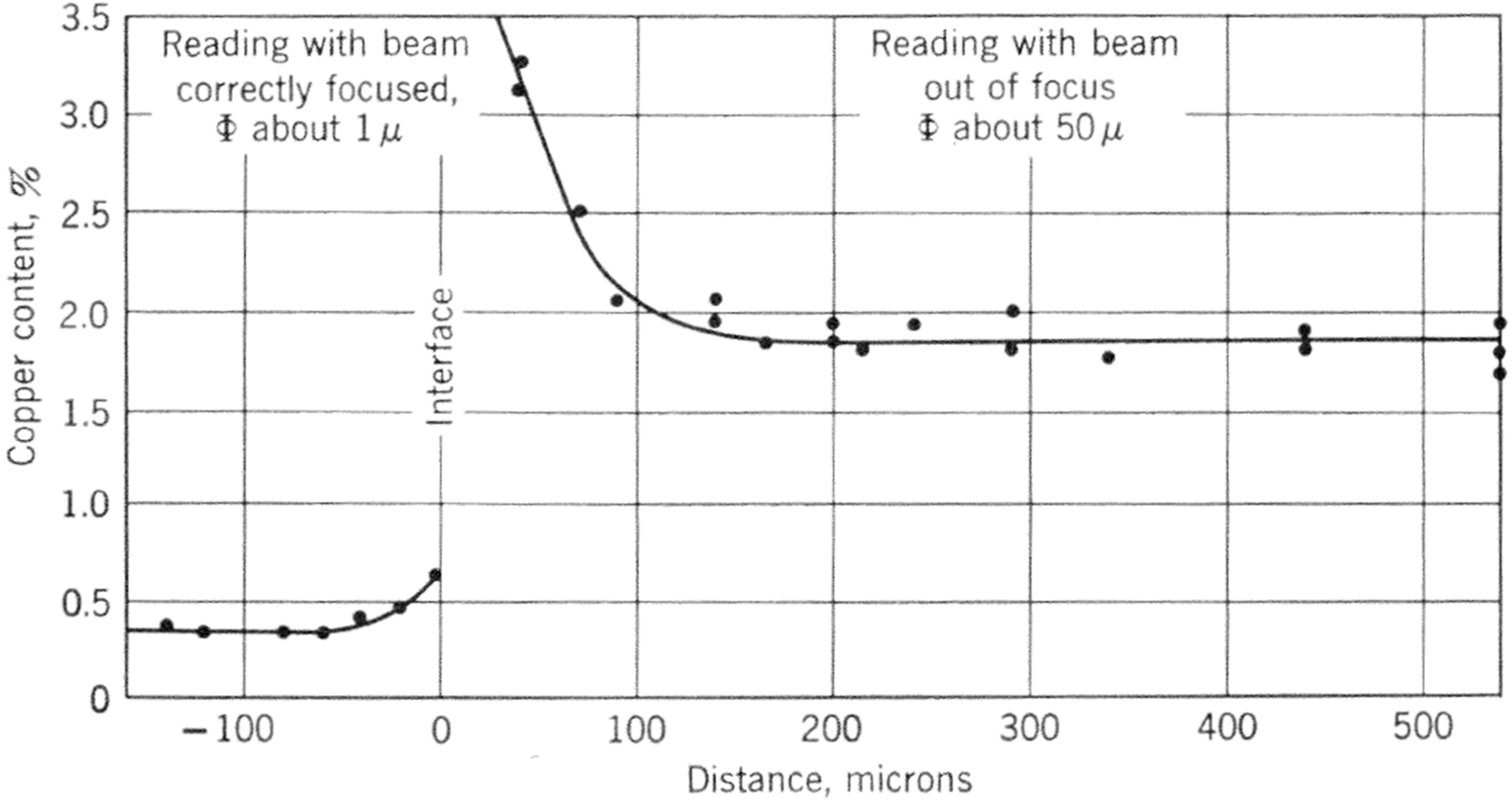
*** For all liquid metals, *D*, 5×10^{-5} cm^2/sec or 5 cm^2/day, is within a factor of ten.**



Thickness of the layer in which there is a substantial change in composition varies from less than 0.1 mm to about 1 mm.

Fig. 5.8. Thickness of diffusion zone as a function of temperature

Fig. 5.9. distribution of copper in an aluminum copper alloy quenched during solidification



- **Experimental confirmation of the existance of the enriched layer in contact with an advancing S/L interface → By Kohn and Philibert, observation of electron microprobe to examine the distribution of Cu enriched layer in Al-Cu alloy**
- **Qualitative agreement: OK but Quantitative agreement: No**
- **Why? 1) No planar interface/ 2) assumption of linear solute transport ~ not satisfied**

No Diffusion on Solid, Diffusional Mixing in the Liquid

② Initial Transient

(a) First solid to form from C_0 liquid: k_0C_0

→ Steady state condition, in which the concentrations of L and S at the interface are C_0/k_0 and C_0, will not be reached until the solidification has proceed far enough for a substantial amount of solute to have been rejected.

(b) Two shaded area (deficit of solute in solid, excess in liquid, compared with C_0) ~ "equal"

(c) Tiller et al: C_S = as a function of the distance

$$\boxed{C_S = C_0\left\{(1-k_0)\left[1-\exp\left(-k_0\frac{R}{D}X\right)\right]+k_0\right\}}$$

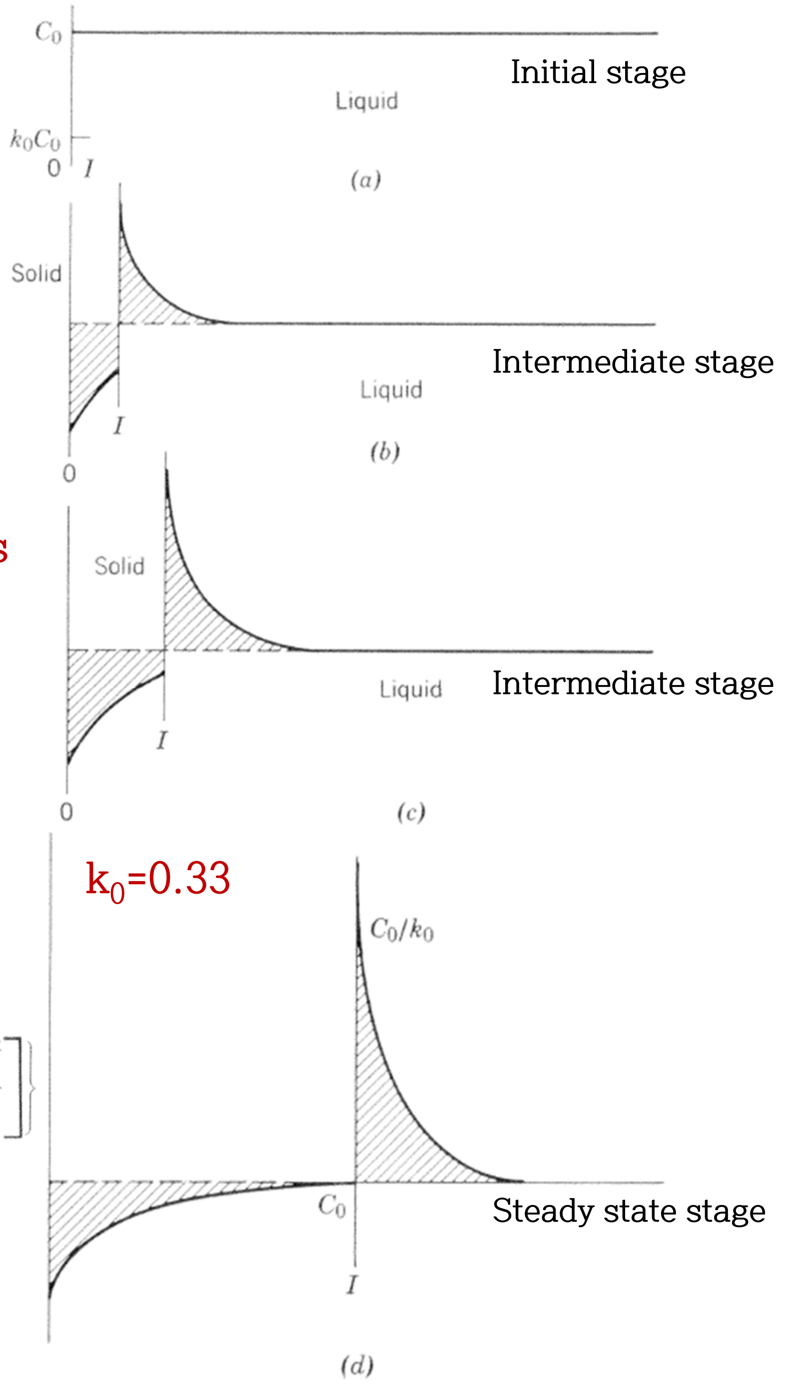
(exp. Approach not quite correct, and that an exact solution is)

$$\frac{C_S}{C_0} = \frac{1}{2}\left\{1+\operatorname{erf}\sqrt{(R/2D)X}+(2k_0-1)\exp\left[-k_0(1-k_0)\frac{R}{D}X\right]\operatorname{erf}\left[\frac{(2k_0-1)\sqrt{(R/D)X}}{2}\right]\right\}$$

∗ C_S values calculated by these two methods → "similar"

∗ Characteristic distance $\boxed{X_c = \frac{D}{k_0R}\ \mathrm{cm}}$

Fig. 5.10. distribution of solute during initial transient.



2) No Diffusion on Solid, Diffusional Mixing in the Liquid

③ Terminal Transient

(a) Steady state condition: No hindrance of solute diffusion & R remain constant. But, former condition ceases when the boundary of the liquid is approached (Figure 5.11.)

(b) Concentration of solid = C_0 ↑ (∵ excess solute must all appear in the terminal region)

(c) Characteristic distance for the diffusion zone (initial transient= D/k_0R, steady state condition = D/R) → terminal transient zone occupies a shorter distance, by a factor k_0 , than the initial zone (concentration change in terminal transient zone_Chapter 8)

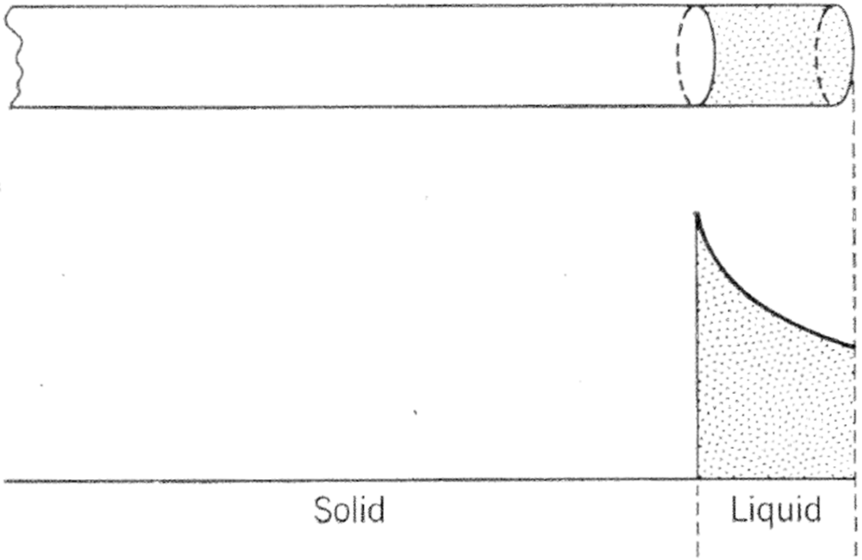


Fig. 5.11. distribution of solute during terminal transient.

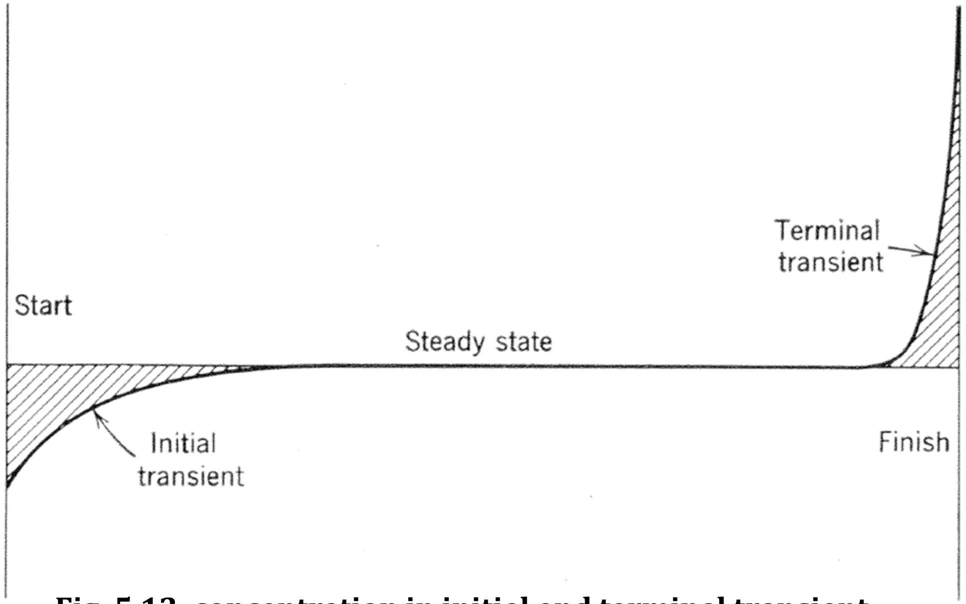
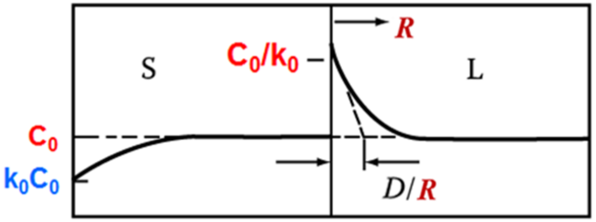
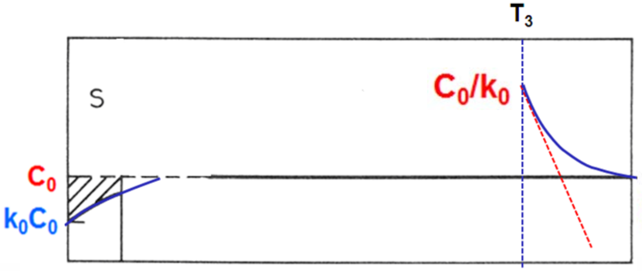


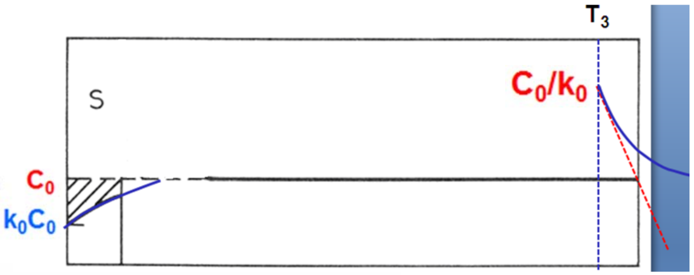
Fig. 5.12. concentration in initial and terminal transient.

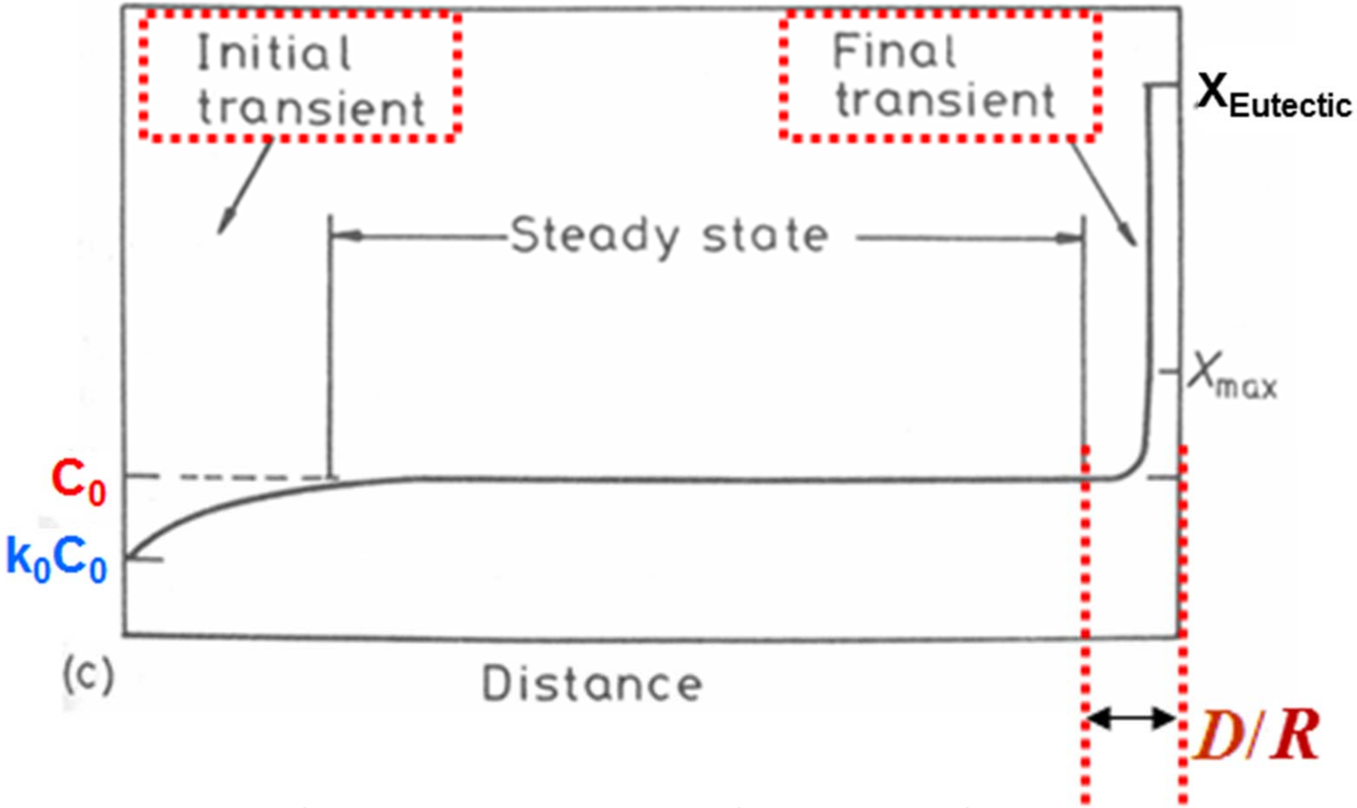
"Alloy solidification" - Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid



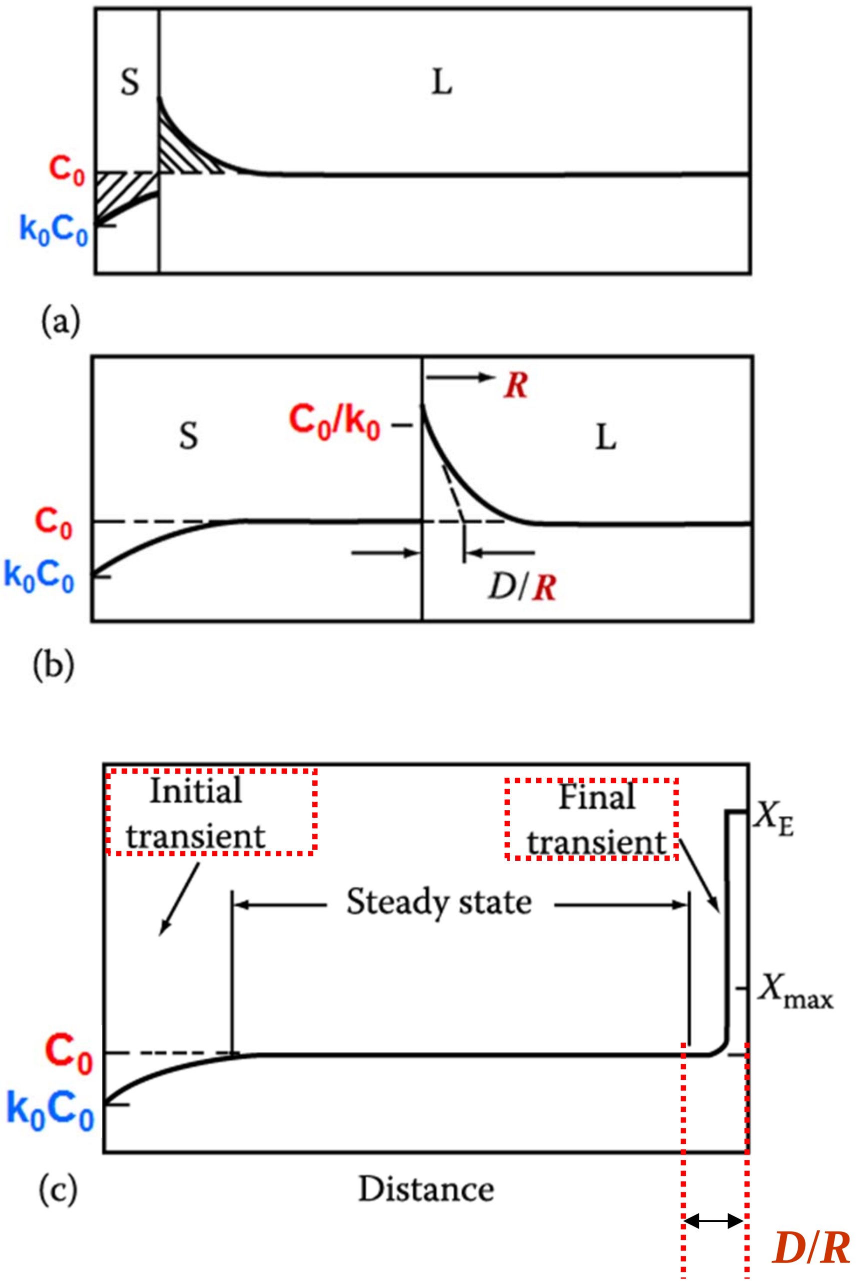






When the solid/liquid interface is within ~D/R of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation.

2) No Diffusion on Solid, Diffusional Mixing in the Liquid



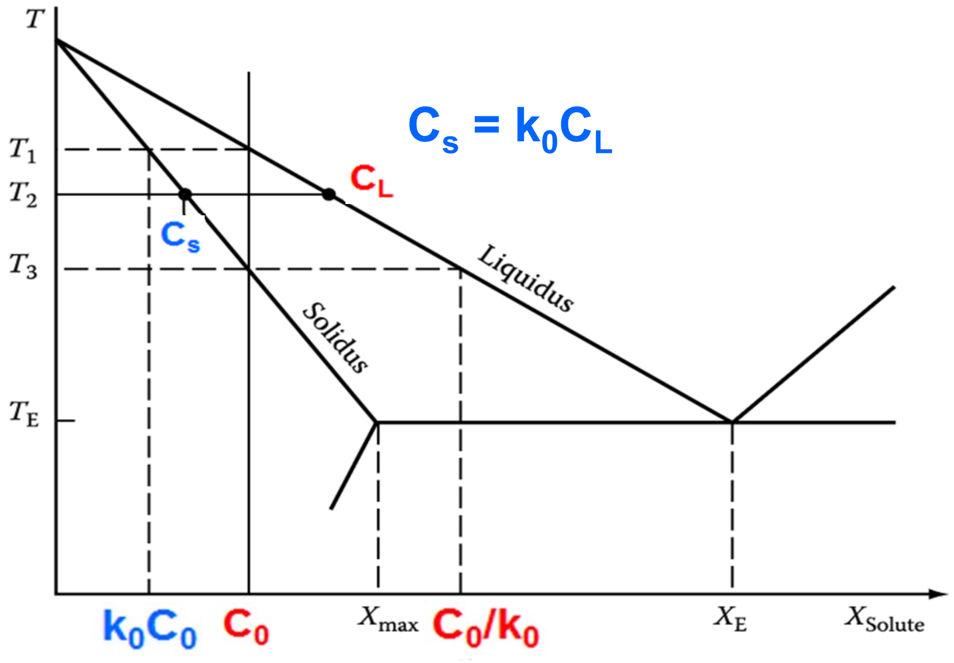


Fig. Planar front solidification of alloy C_0 in upper figure assuming no diffusion in solid and no stirring in the liquid.

(a) Composition profile when S/L temperature is between T_2 and T_3 in upper figure.

(b) Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (C_0).

(c) Composition profile at T_E and below, showing the final transient.

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

④ Change of speed

(a) When R~const., excess solute ahead of the interface = the area under the diffusion curve
→ characteristic distance D/R & solidification rate ~ 1/R

∴ The solid that is formed immediately after a change of speed must have a concentration that differs from C_0.

(b) If R ↑, D/R ↓, the amount of Solute ↓, the solid must have a higher concentration during the transition from steady state at lower R to steady state at higher R.

(C) If R ↓, solid concentration is less than C_0 as shown in Fig. 5.13.

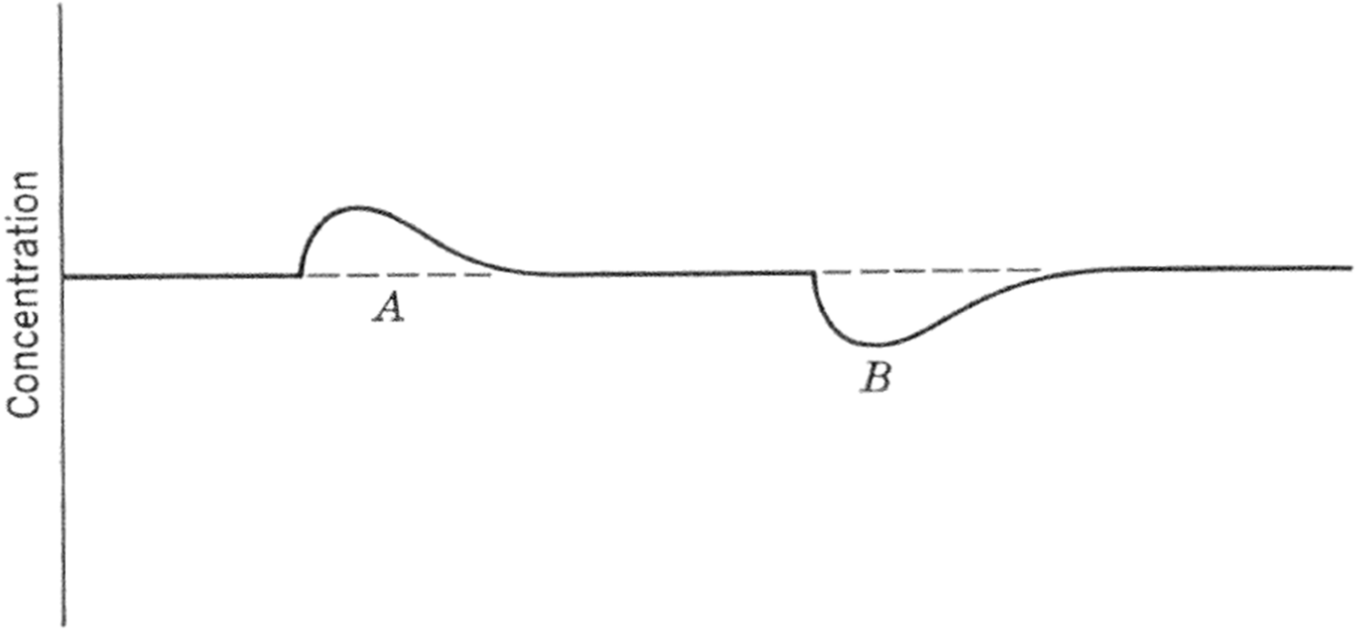


Fig. 5.13. solute distribution following changes in speed of solidification (A) Increase; (B) Decrease.

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

⑤ Effect of curvature of the interface

(a) Steady state condition ($C_s=C_0$, $T_I=T_S$) is valid only if the interface is planar.

(b) If it is convex (center of curvature in the solid), then the solute is not conserved within a cylindrical volume of the solidifying liquid (see Fig. 5.14)

→ Solute concentration is less than C_0 / Liquid concentration adjacent to the interface is less than $C_0/k_{0.}$/ Temp. of Interface is above the solidius temp. for the original liquid.

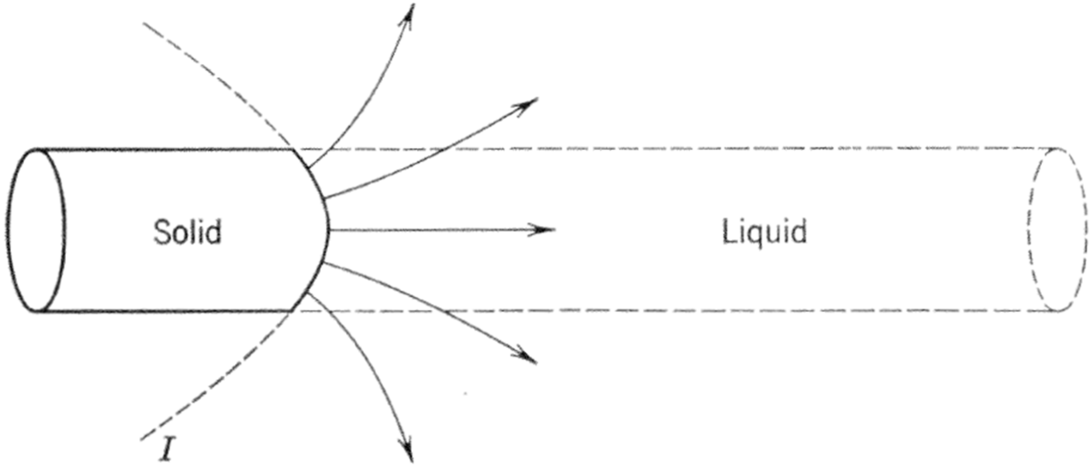


Fig. 5.14. Solute diffusion ahead of a convex interface

(c) If concave, (1) Solid concentration > C_0

(2) solidify at a temp. below that of the initial solidus

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

⑥ Influence of liquid fluid motion: Convection

(a) Assumption of mixing by only diffusion ~ not realistic → ∵ a liquid in which ΔT exist is likely to be subject to convection.

(b) Only case for no convection → density gradient in the liquid is everywhere vertical

(c) If (1) in addition to density gradient caused by ΔT,
(2) density gradients resulting from compositional variation caused by rejection of solute, the problem of achieving a completely non-convection system becomes even more difficult.

(d) It is therefore necessary to consider the extent to which convection, resulting from density gradients that arise from non-uniformity of temperature or of composition, will affect the redistribution of solute during solidification. →”Effect of mixing by fluid motion”

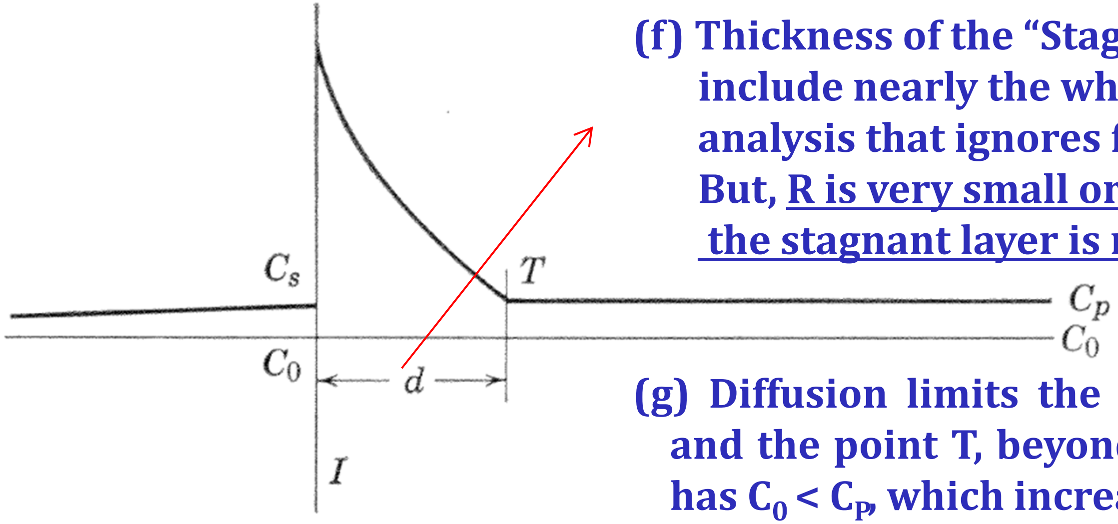


Fig. 5.15. Effect of stirring on the diffusion zone.

(f) Thickness of the “Stagnant” layer is sufficient to include nearly the whole of the diffusion zone, the analysis that ignores fluid motion is valid.
But, R is very small or liquid motion is more violent, the stagnant layer is not thick enough.

(g) Diffusion limits the motion of solute btw interface and the point T, beyond which the liquid is mixed and has $C_0 < C_P$, which increases as solidification process.

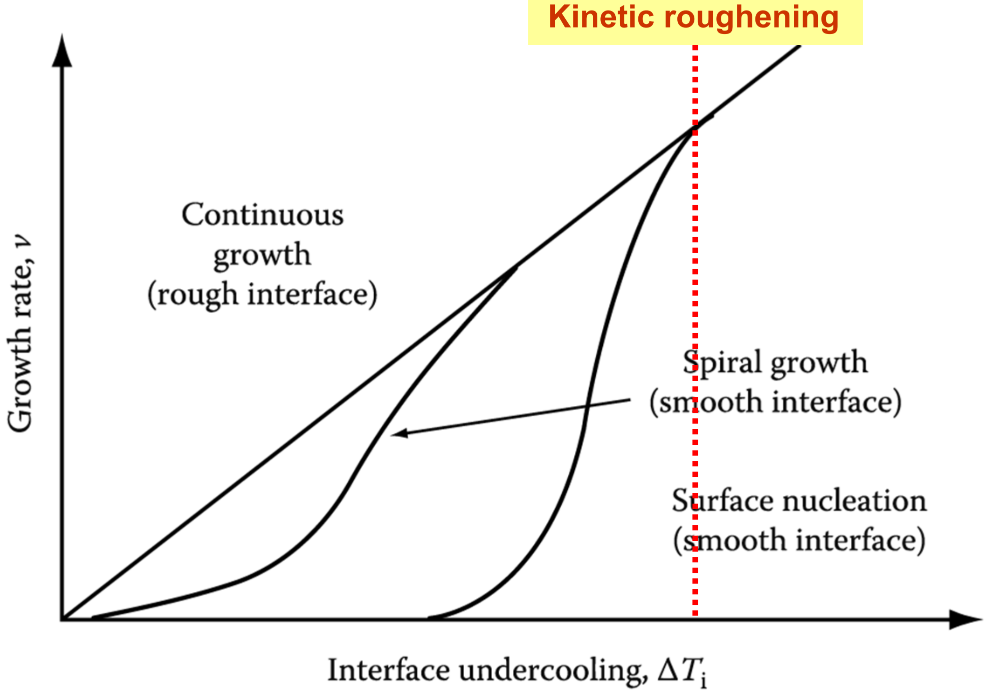
Solidification: Liquid ⟶ Solid

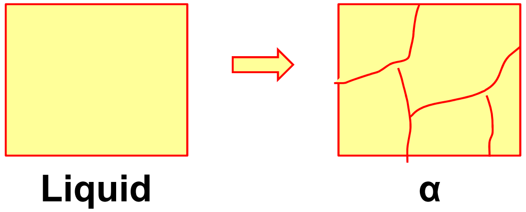
1) Pure Metals: Nucleation and Growth (thermally activated process)

a) homogeneous Nucleation or Heterogeneous Nucleation

- Undercooling ΔT
- Interfacial energy
  γ_{SL} / $S(\theta)$ wetting angle

b) Growth of solid





No compositional change during solidification

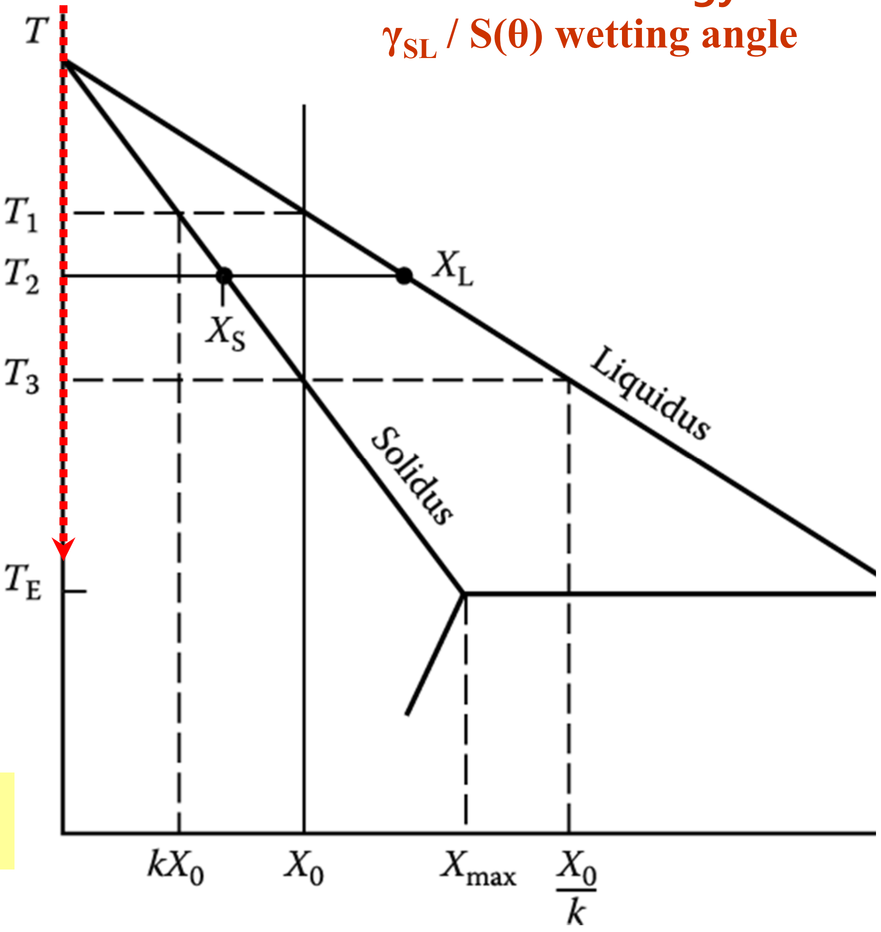


Fig. 4.19 A hypothetical phase diagram.

Chapter 5. Redistribution of solute during solidification

“Alloy solidification”

1. Solidification of single-phase alloys

- **Three limiting cases**

1) Equilibrium Solidification: perfect mixing in solid and liquid

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

3) No Diffusion in Solid, Perfect Mixing in Liquid

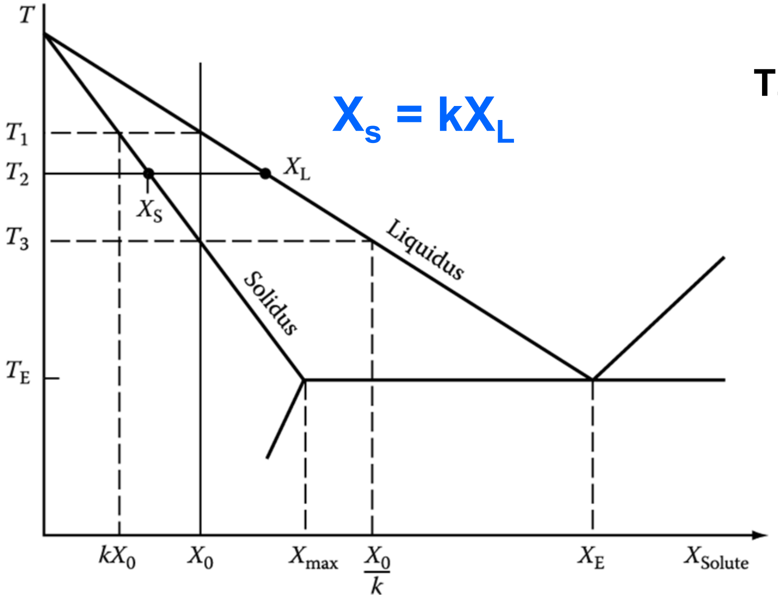
- Planar S/L interface → unidirectional solidification

- Superheated liquid

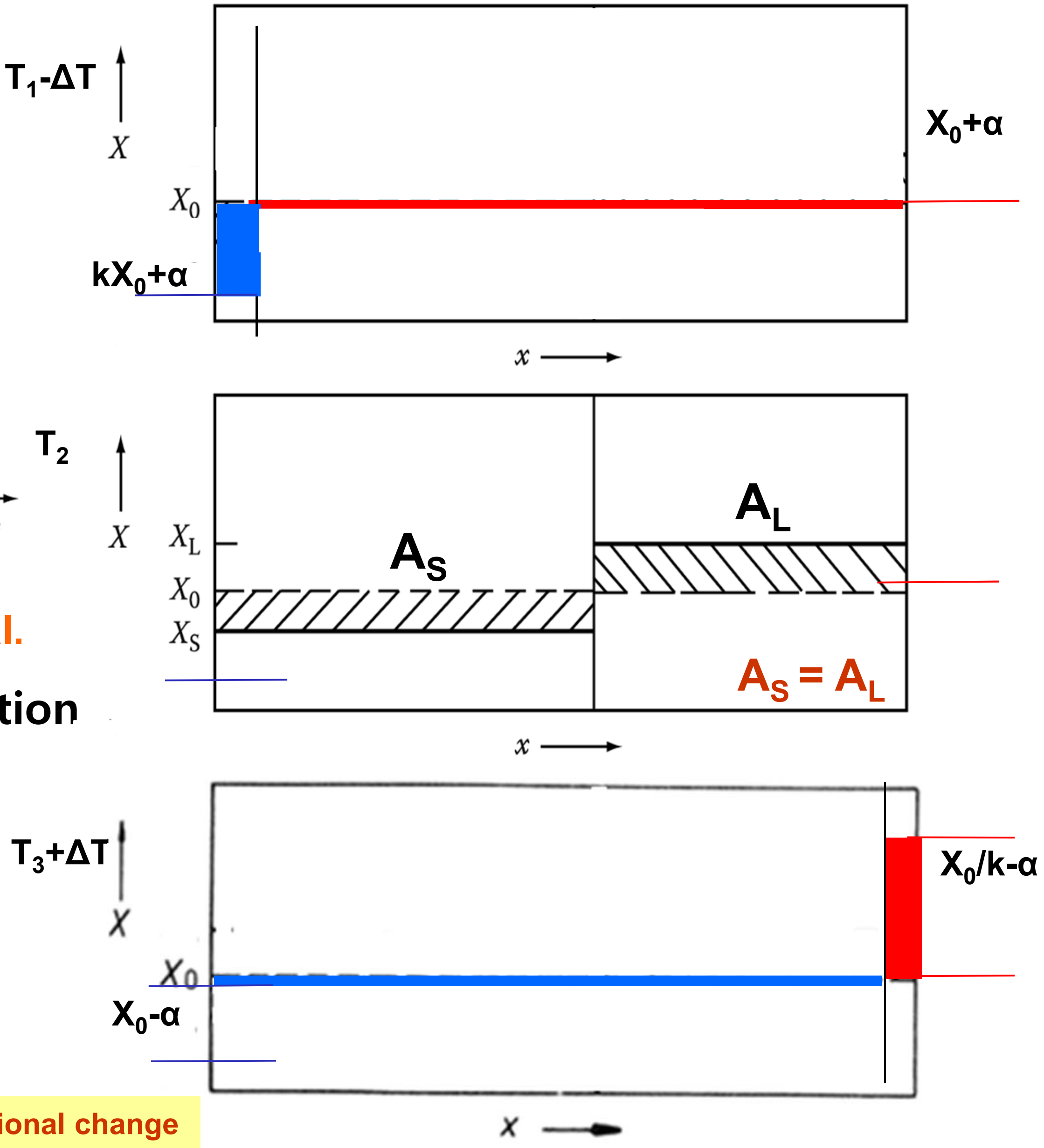
- Cellular and Dendritic Solidification

- Constitutional Supercooling

1) Equilibrium Solidification : perfect mixing in solid and liquid



$X_s = kX_L$



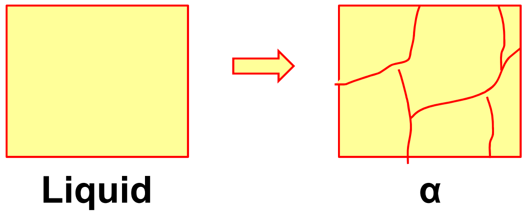
$A_S = A_L$

Conservation of solute requires the two shaded areas to be equal.

* Equilibrium solute concentration

$kX_0 \leq X_s \leq X_0$

$X_0 \leq X_L \leq X_0/k < X_E$



Compositional change during solidification

2) Mixing in the liquid by diffusion only: No diffusion in the solid

* 1) Equilibrium Solidification ⇔ Opposite extreme of perfect mixing in solid and liquid (solute or solvent) does not move → no mixing in either the solid or the liquid → L→S without composition change:“diffusionless solidification” of this kind may take place locally when the liquid is sufficiently supercooled. = “polymorphic transformation”

* 2) For example, $D_S << D_L$

(D_S ignored, D_L~normally_all diffusion in the liquid is to the interface)

In the case of Equilibrium solidification

V (speed of advance of interface)= very slow ↔

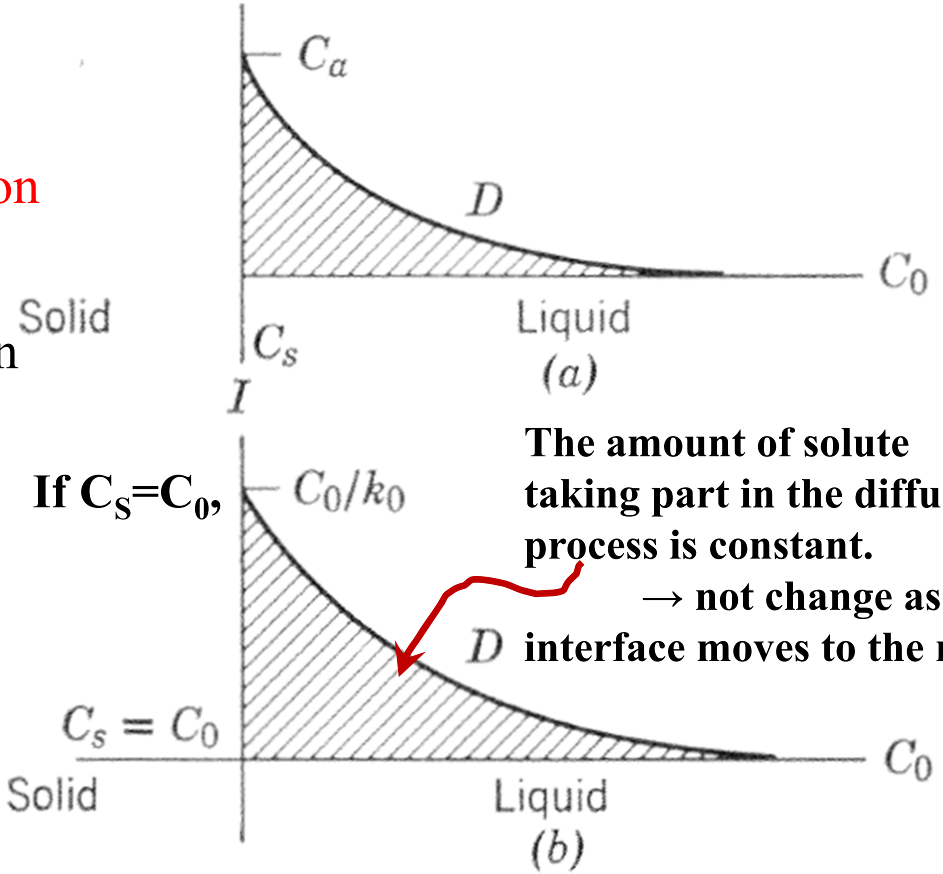
but in this case $V_{interface}$ = ***R*** **cm/sec**

$C_S/C_a = k_0$

C_0**_initial composition of liquid**

$k_E = C_S/C_0$

Here, C_a=solute concentration in the liquid at the interface



If $C_S=C_0$,

The amount of solute taking part in the diffusion process is constant.

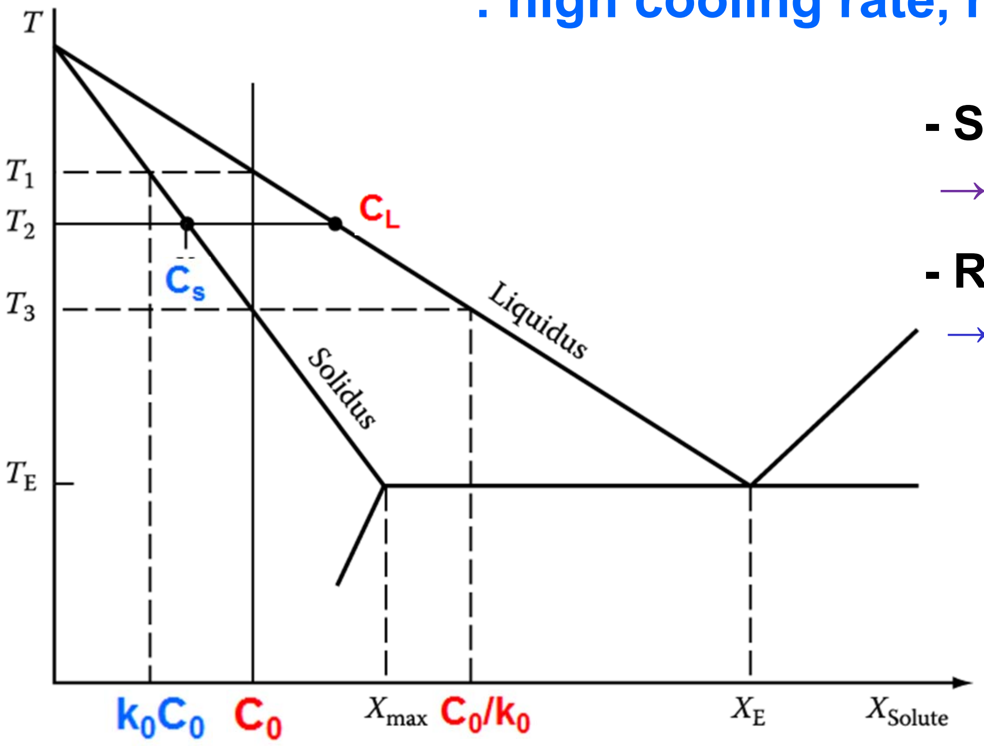
→ not change as the interface moves to the right

→ If composition of solid=C_0, “steady state condition”

Fig. 5.6. Distribution of solute during uniaxial solidification

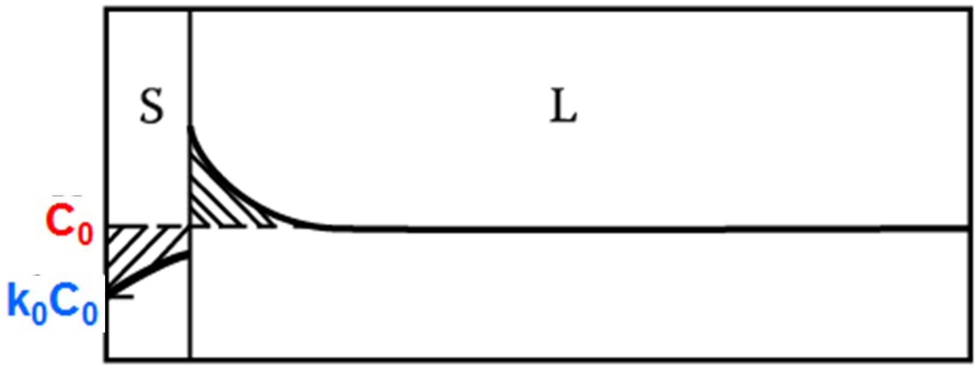
2) No Diffusion on Solid, Diffusional Mixing in the Liquid

: high cooling rate, no stirring → diffusion



- Solute rejected from solid
  → diffuse into liquid with limitation
- Rapid build up solute in front of the solid
  → rapid increase in the comp. of solid forming (initial transient)
  - if it solidifies at a const. rate, *v*, then a steady state is finally obtained at T_3
  - liquid : C_0/k_0, solid: C_0

local equil. at S/L interface



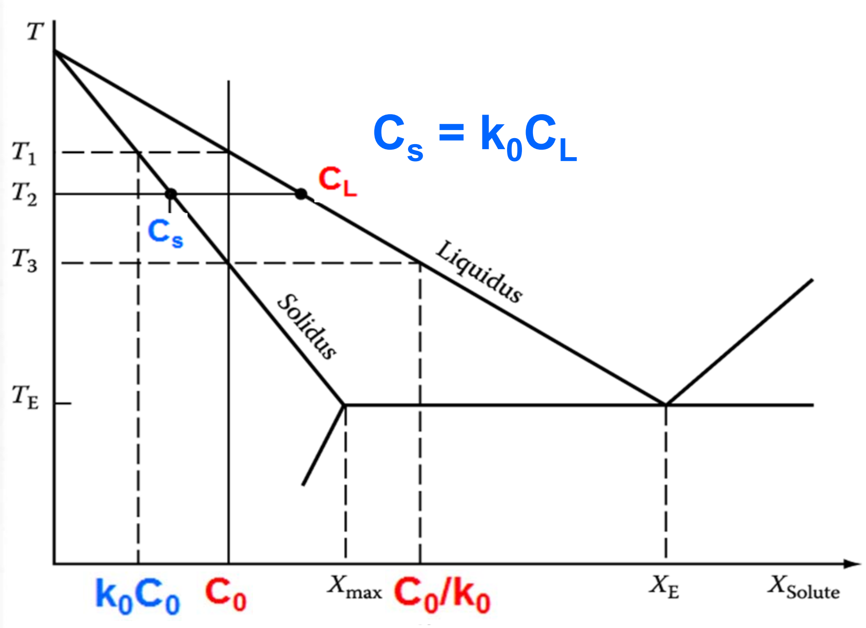
Composition profile at $T_2 < T_{S/L} < T_3$?

Steady-state profile at T_3?
at T_E or below ?

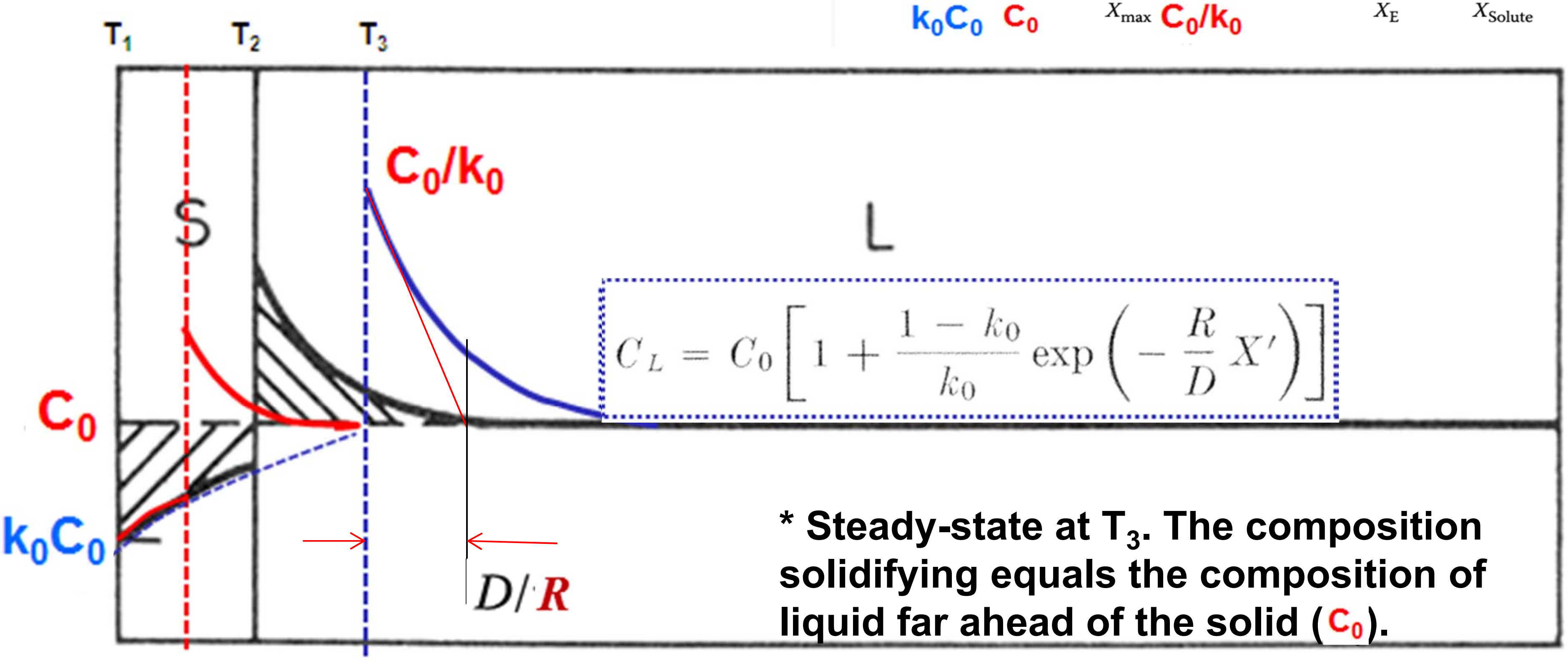
"Alloy solidification"

- Solidification of single-phase alloys

* No Diffusion on Solid,
Diffusional Mixing in the Liquid



Interface temperature

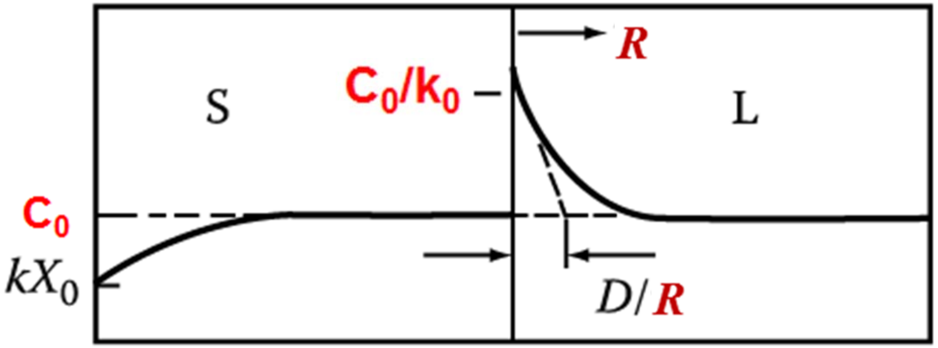


$$C_L = C_0\left[1+\frac{1-k_0}{k_0}\exp\left(-\frac{R}{D}X'\right)\right]$$

* Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (C_0).

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

① **During steady-state growth,**



(Interface →liquid: Diffusion rate)

Rate at which solute diffuses down the concentration gradient away from the interface

= Rate at which solute is rejected from the solidifying liquid

(Solid→Liquid from solidification: solute rejecting rate)

If $C_S=C_0$,

$$\boxed{C_L = C_0\left[1 + \frac{1-k_0}{k_0}\exp\left(-\frac{R}{D}X'\right)\right]} \Leftarrow C_L = C_a \exp\left(-\frac{R}{D}X'\right) + C_0$$

(X'= distance from the interface at which the concentration is C_L)

(C_L decreases exponentially from C_0/k_0 at x=0, the interface, to C_0 at large distances from the interface. The concentration profile has a characteristic width of D/R.)

- Liquid distribution: "characteristic distance" given by D/R; that is, the distance in which the excess concentration falls to 1/e of its initial value.

No Diffusion on Solid, Diffusional Mixing in the Liquid

② Initial Transient

(a) First solid to form from C_0 liquid: k_0C_0

→ Steady state condition, in which the concentrations of L and S at the interface are C_0/k_0 and C_0, will not be reached until the solidification has proceed far enough for a substantial amount of solute to have been rejected.

(b) Two shaded area (deficit of solute in solid, excess in liquid, compared with C_0) ~ “equal”

(c) Tiller et al: C_S = as a function of the distance

$$C_S = C_0\left\{(1-k_0)\left[1-\exp\left(-k_0\frac{R}{D}X\right)\right]+k_0\right\}$$

(exp. Approach not quite correct, and that an exact solution is)

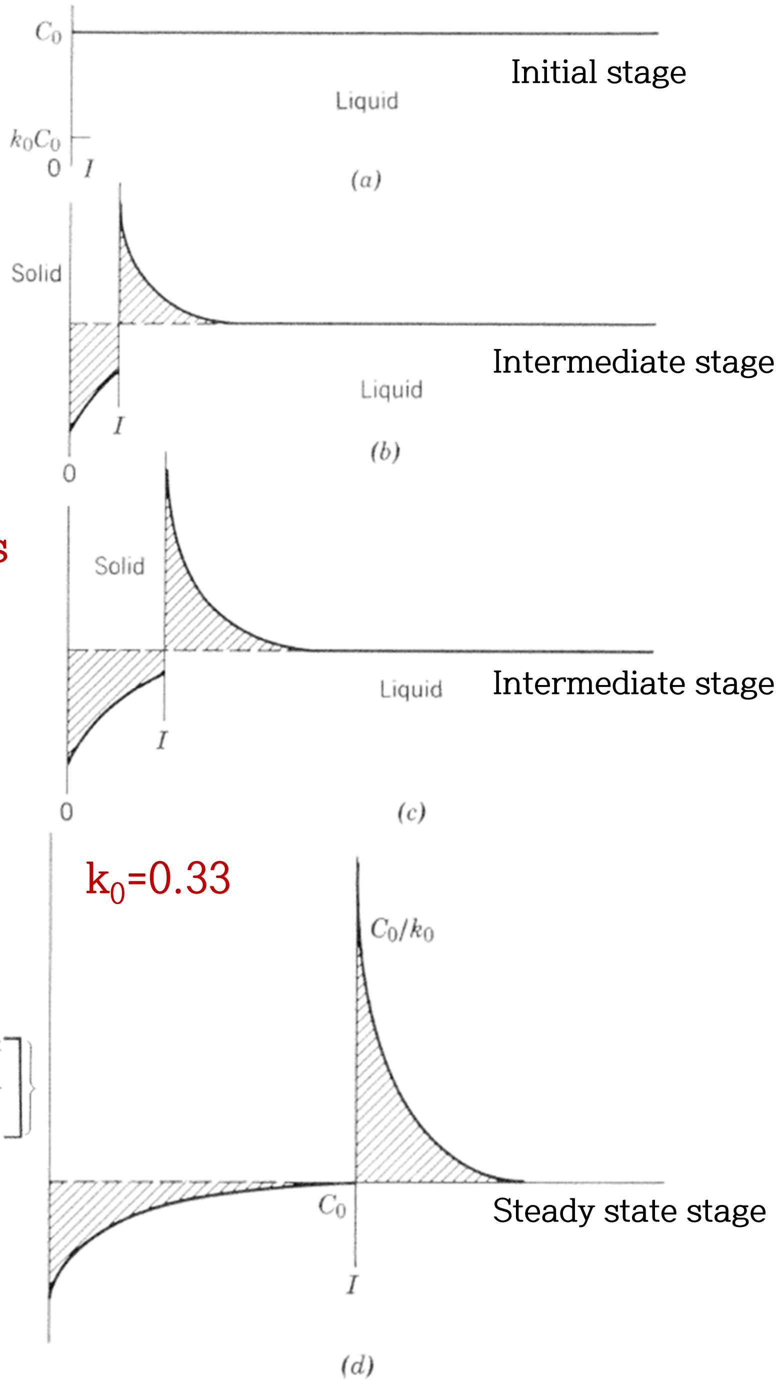
$$\frac{C_S}{C_0}=\frac{1}{2}\left\{1+\operatorname{erf}\sqrt{(R/2D)X}+(2k_0-1)\exp\left[-k_0(1-k_0)\frac{R}{D}X\right]\operatorname{erf}\left[\frac{(2k_0-1)\sqrt{(R/D)X}}{2}\right]\right\}$$

* C_S values calculated by these two methods → “similar”

* Characteristic distance

$$X_c=\frac{D}{k_0R}\text{ cm}$$

Fig. 5.10. distribution of solute during initial transient.



2) No Diffusion on Solid, Diffusional Mixing in the Liquid

③ Terminal Transient

(a) Steady state condition: No hindrance of solute diffusion & *R* remain constant. But, former condition ceases when the boundary of the liquid is approached (Figure 5.11.)

(b) Concentration of solid = C_0 ↑ (∵ excess solute must all appear in the terminal region)

(c) Characteristic distance for the diffusion zone (initial transient= D/k_0R, steady state condition = D/R) → terminal transient zone occupies a shorter distance, by a factor k_0 , than the initial zone (concentration change in terminal transient zone_Chapter 8)

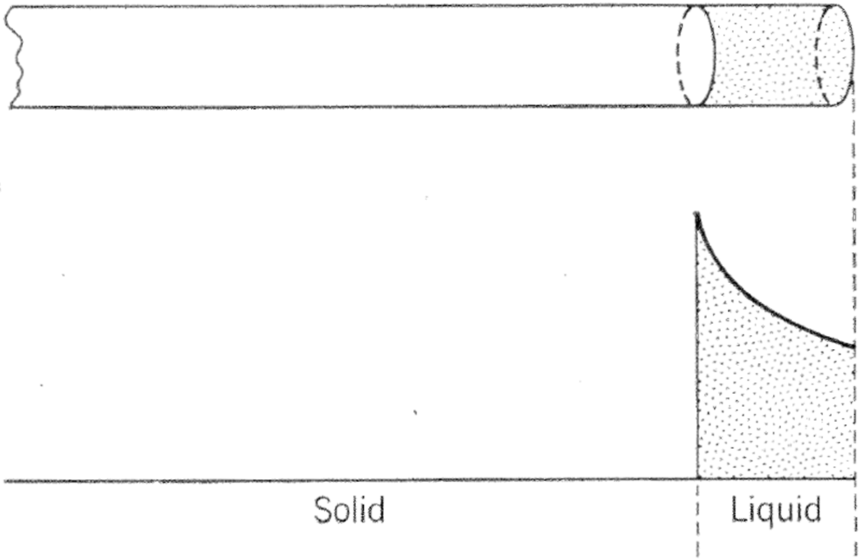


Fig. 5.11. distribution of solute during terminal transient.

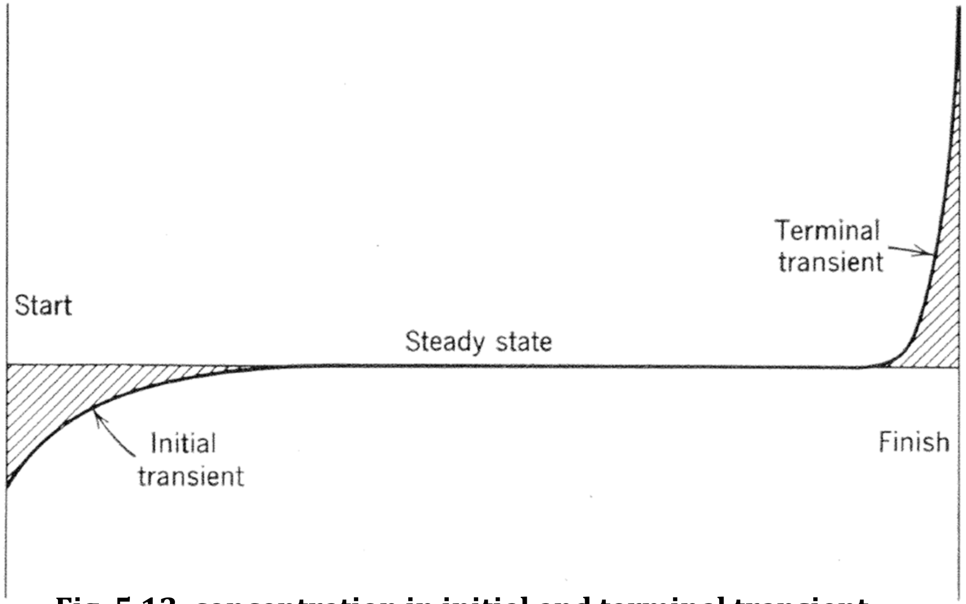
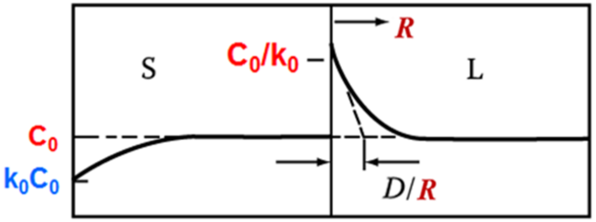
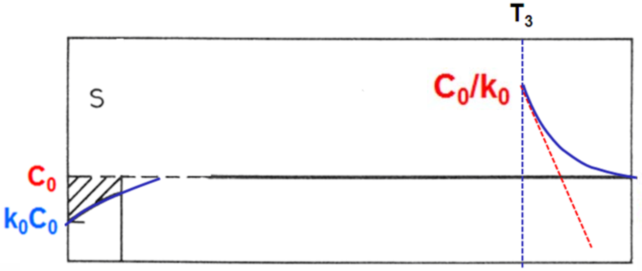


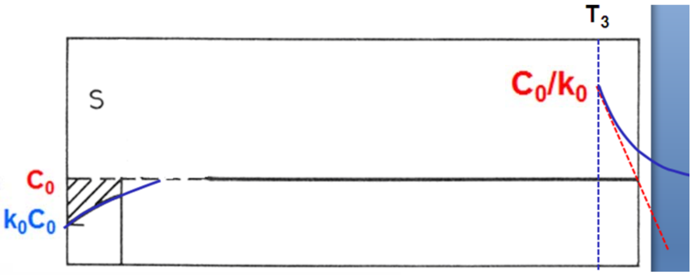
Fig. 5.12. concentration in initial and terminal transient.

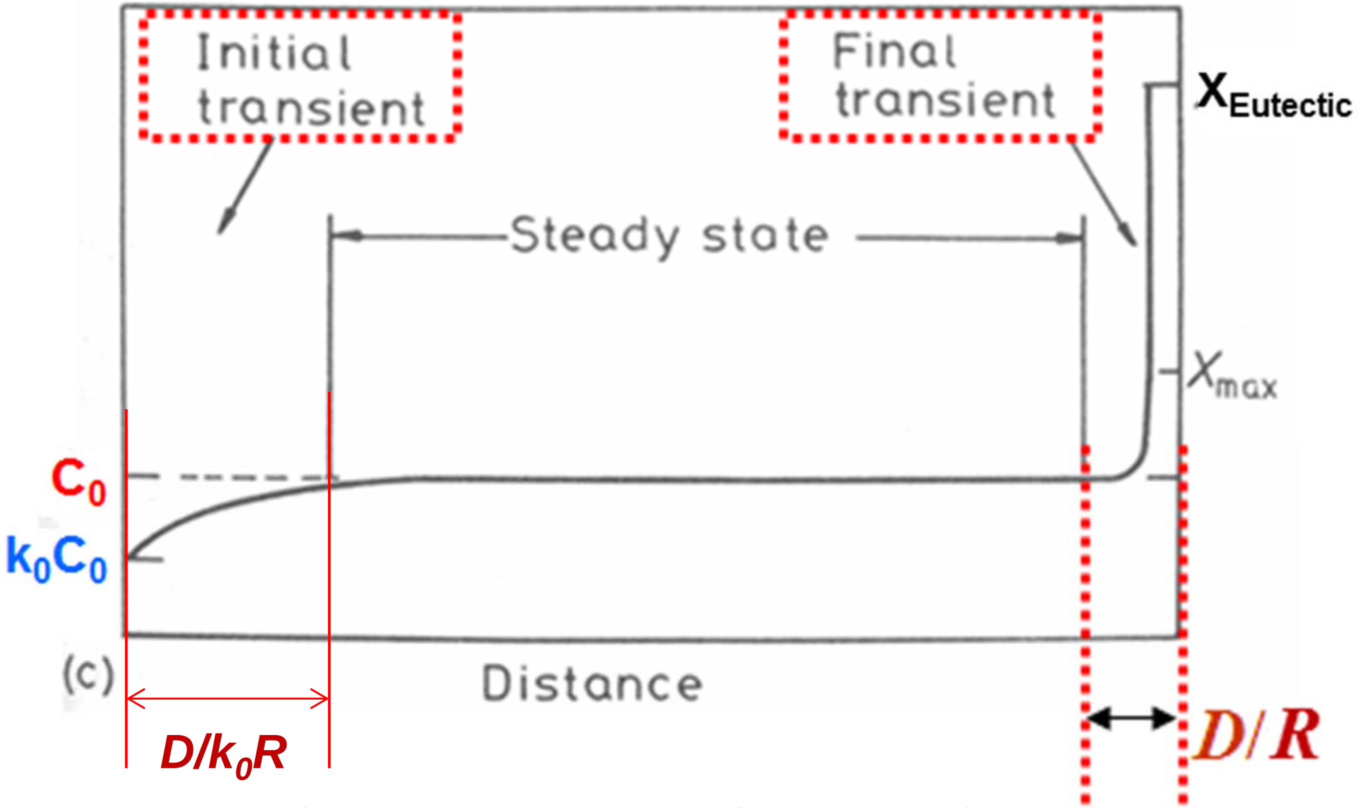
“Alloy solidification” - Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid



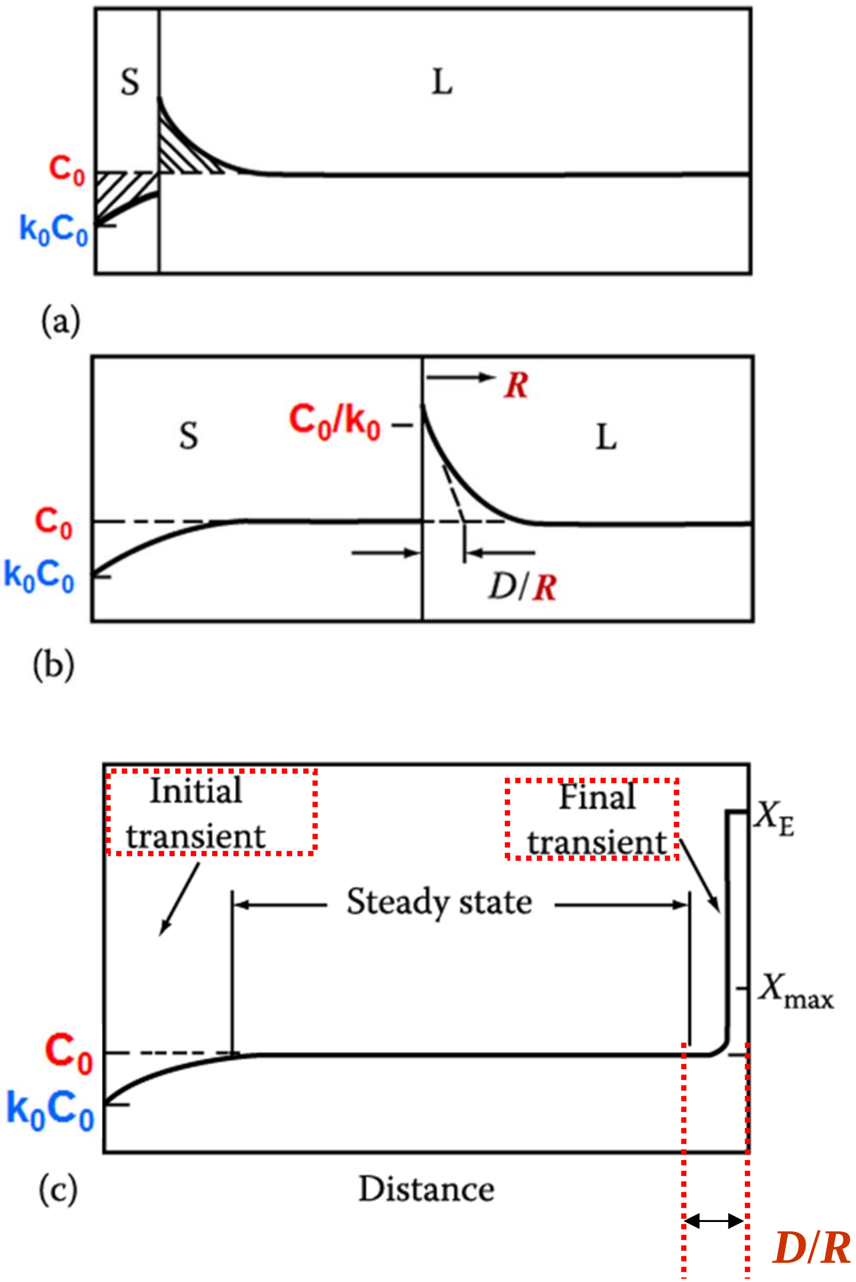






When the solid/liquid interface is within ~D/R of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation.

2) No Diffusion on Solid, Diffusional Mixing in the Liquid



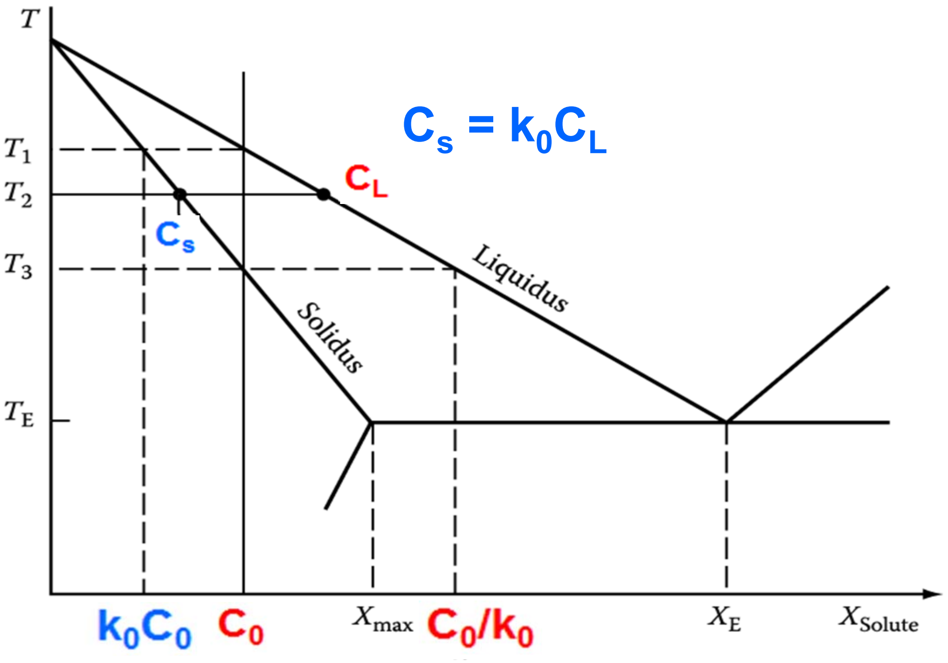


Fig. Planar front solidification of alloy C_0 in upper figure assuming no diffusion in solid and no stirring in the liquid.

(a) Composition profile when S/L temperature is between T_2 and T_3 in upper figure.

(b) Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (C_0).

(c) Composition profile at T_E and below, showing the final transient.

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

④ Change of speed

(a) When R~const, excess solute ahead of the interface = the area under the diffusion curve
→ characteristic distance D/R & solidification rate ~ 1/R

∴ The solid that is formed immediately after a change of speed must have a concentration that differs from C_0.

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(C) If R ↓, solid concentration is less than C_0 as shown in Fig. 5.13.

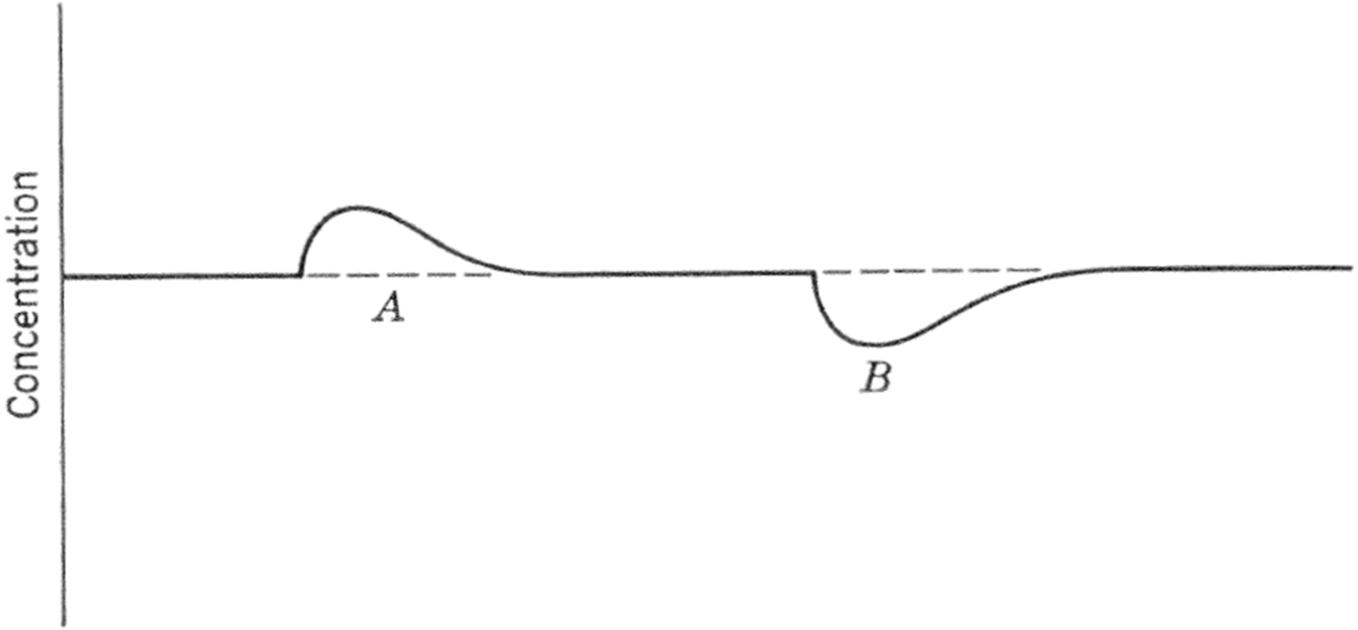

Fig. 5.13. solute distribution following changes in speed of solidification (A) Increase; (B) Decrease.

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⑤ Effect of curvature of the interface

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(b) If it is convex (center of curvature in the solid), then the solute is not conserved within a cylindrical volume of the solidifying liquid (see Fig. 5.14)

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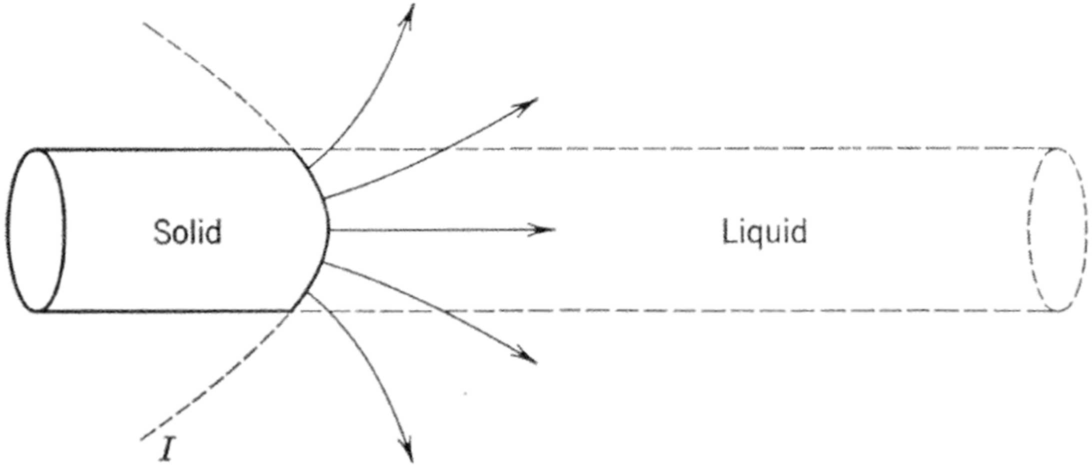

Fig. 5.14. Solute diffusion ahead of a convex interface

(c) If concave, (1) Solid concentration > C_0

(2) solidify at a temp. below that of the initial solidus

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

⑥ Influence of liquid fluid motion: Convection

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(b) Only case for no convection → density gradient in the liquid is everywhere vertical

(c) If (1) in addition to density gradient caused by ΔT,
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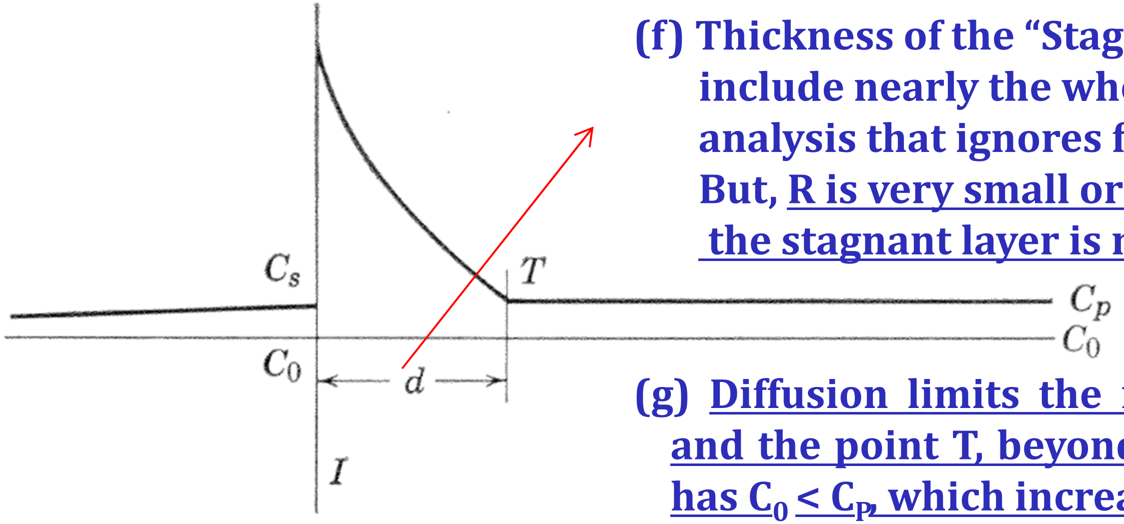


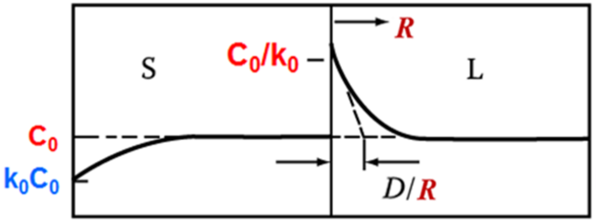
Fig. 5.15. Effect of stirring on the diffusion zone.

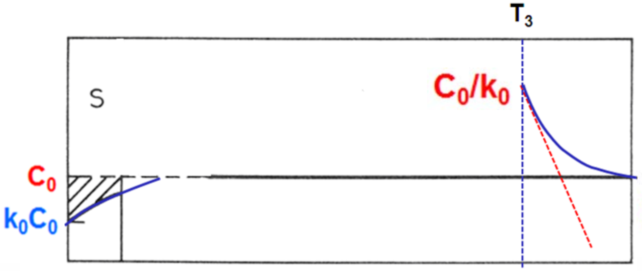
(f) Thickness of the "Stagnant" layer is sufficient to include nearly the whole of the diffusion zone, the analysis that ignores fluid motion is valid.
But, R is very small or liquid motion is more violent, the stagnant layer is not thick enough.

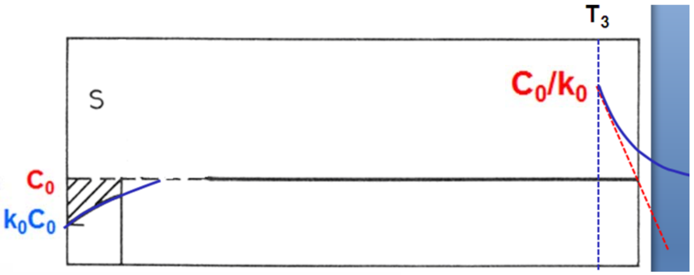
(g) Diffusion limits the motion of solute btw interface and the point T, beyond which the liquid is mixed and has $C_0 < C_P$, which increases as solidification process.

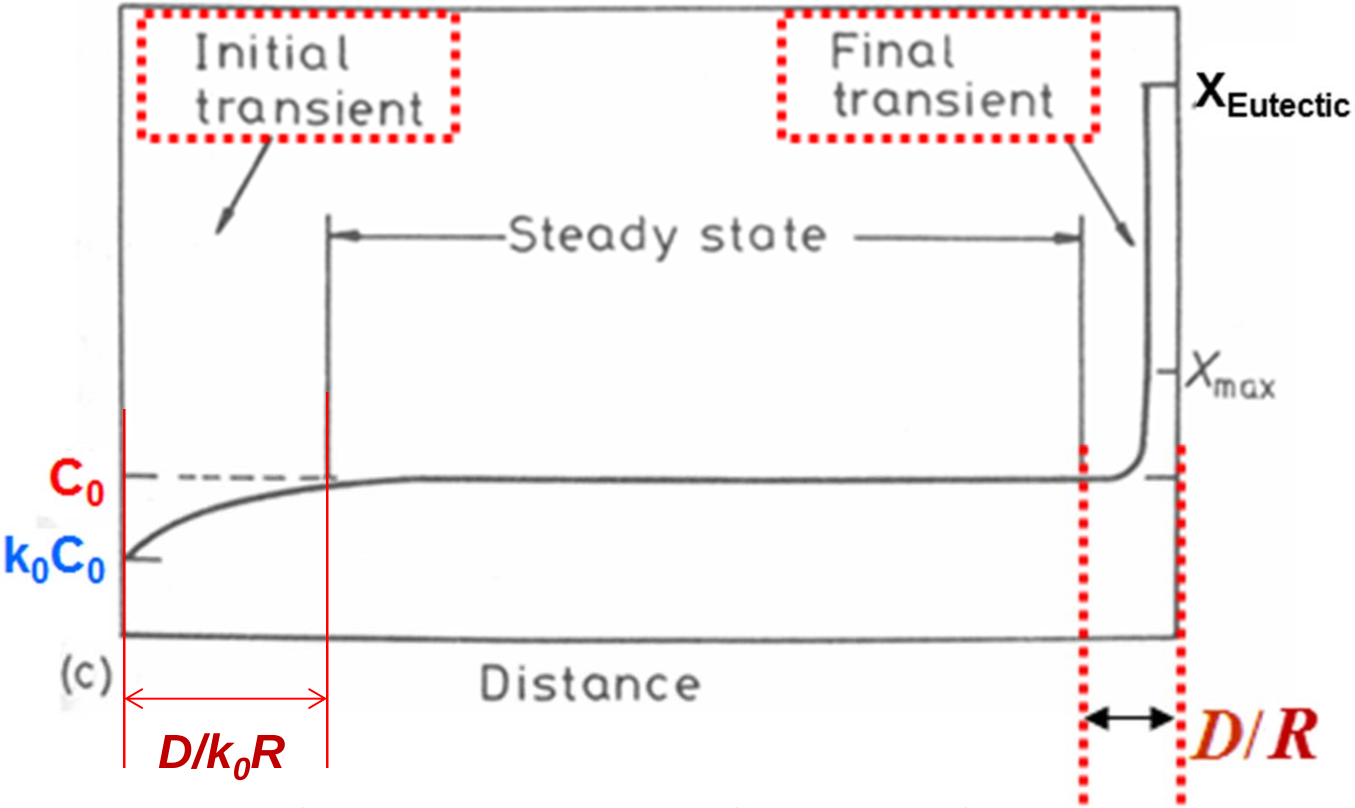
“Alloy solidification” - Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid









When the solid/liquid interface is within ~D/R of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation.

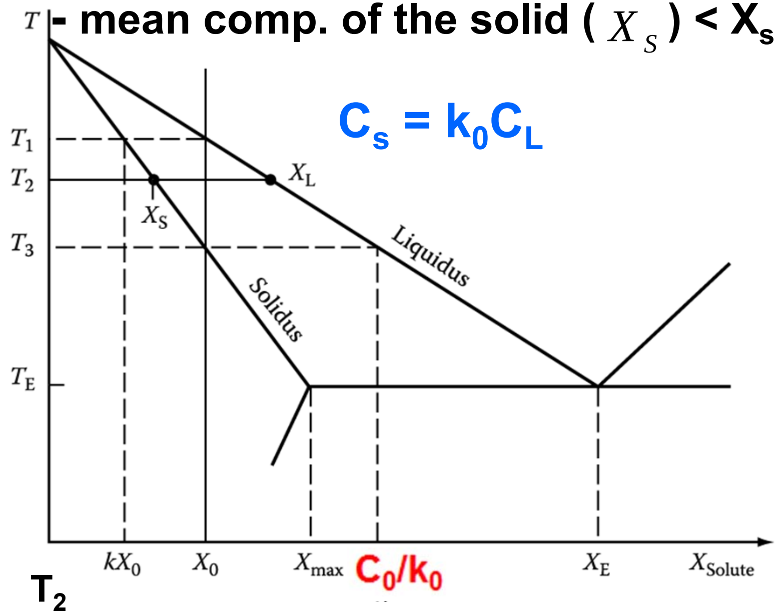
3) No Diffusion in Solid, Perfect Mixing in Liquid

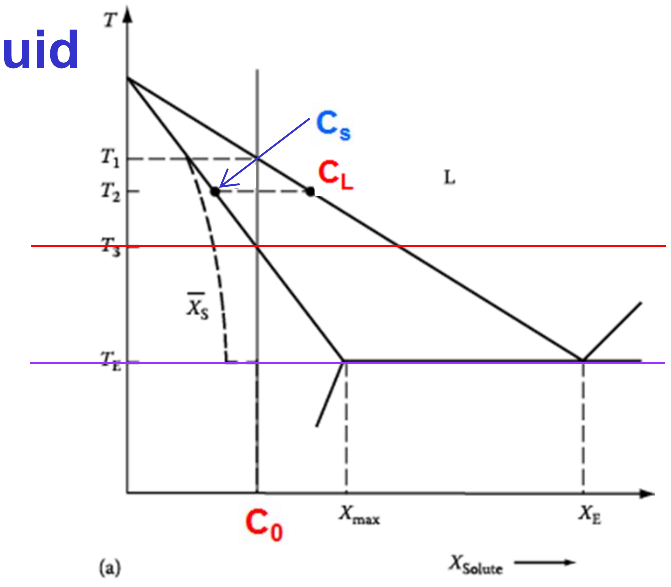
: high cooling rate, efficient stirring

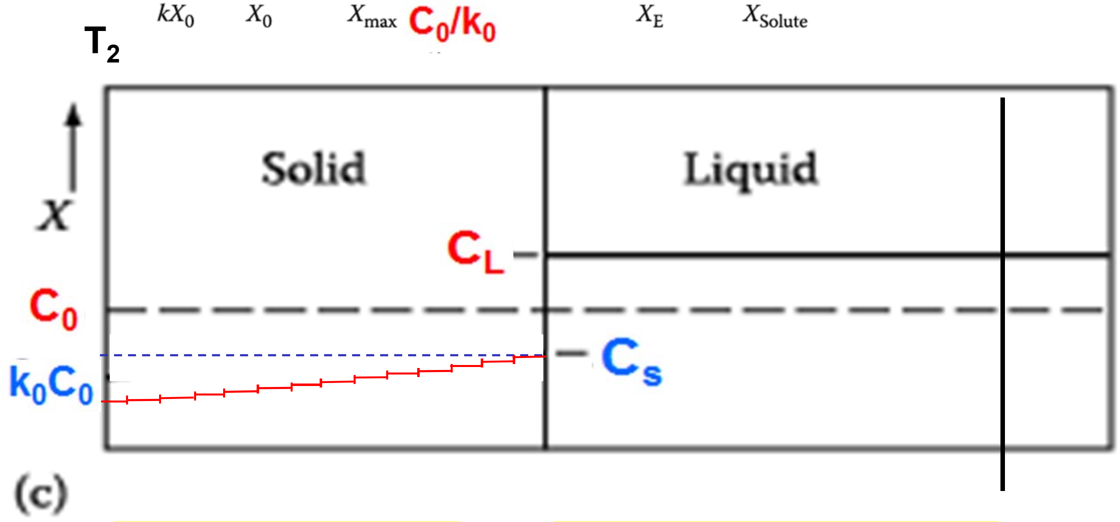
- Separate layers of solid retain their original compositions

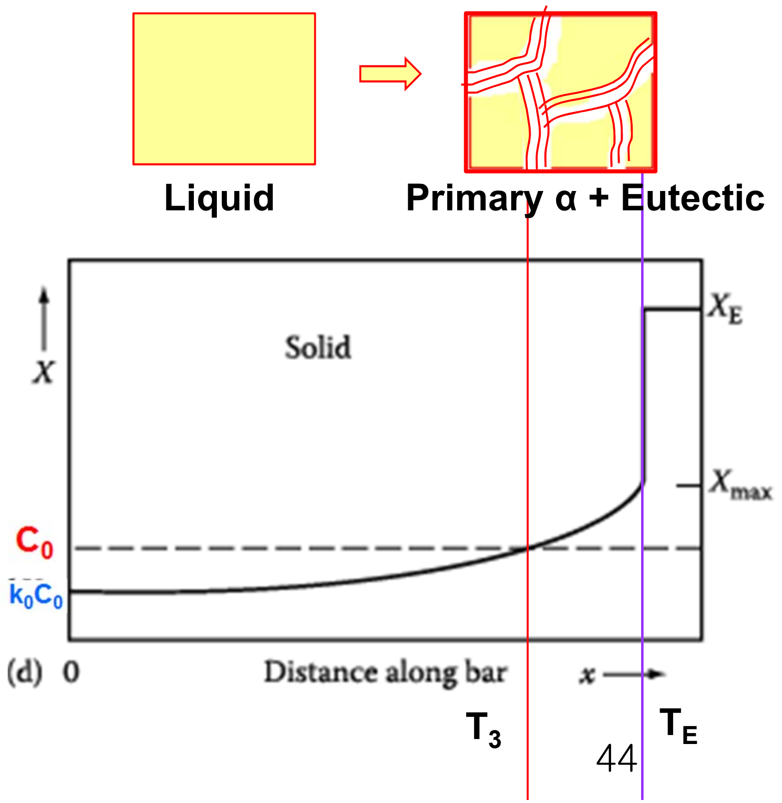
- mean comp. of the solid ($\overline{X}_S$) < X_s

$C_s = k_0C_L$









solid → $\overline{X}_s$ < C_s

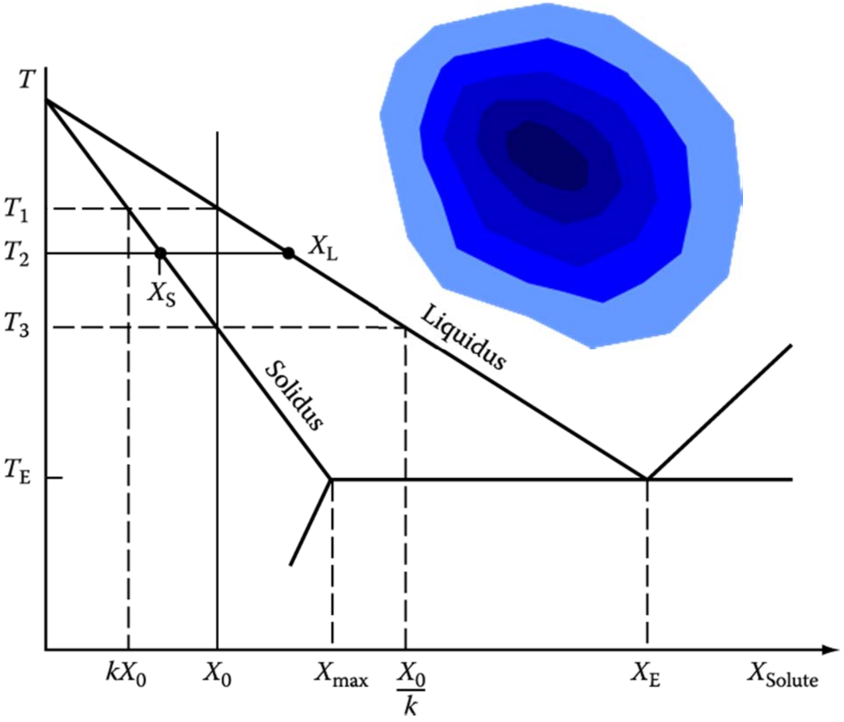
liquid > C_0/k_0 → X_E

Mass balance: non-equilibrium lever rule (coring structure)

When cooled by dT from any arbitrary T, determine the followings.

solute ejected into the liquid = ?

→ solute increase in the liquid



Ignore the difference in molar volume between the solid and liquid.

f_s: volume fraction solidified

solute ejected into the liquid=? → **proportional to what?** **df_s** **$(C_L - C_S)$**

solute increase in the liquid=? → **proportional to what?** **$(1-f_s)$** **dC_L**

$$(C_L - C_S)df_S = (1-f_S)dC_L$$

Solve this equation.

when $f_S = 0 \rightarrow C_S, C_L$?

$C_S = k_0C_0$ and $C_L = C_0$

Initial conditions

$$\int_0^{f_S} \frac{df_S}{1-f_S} = \int_{C_0}^{C_L} \frac{dC_L}{C_L - C_S} = \int_{C_0}^{C_L} \frac{dC_L}{C_L - kC_L} = \int_{C_0}^{C_L} \frac{dC_L}{C_L(1-k)}$$

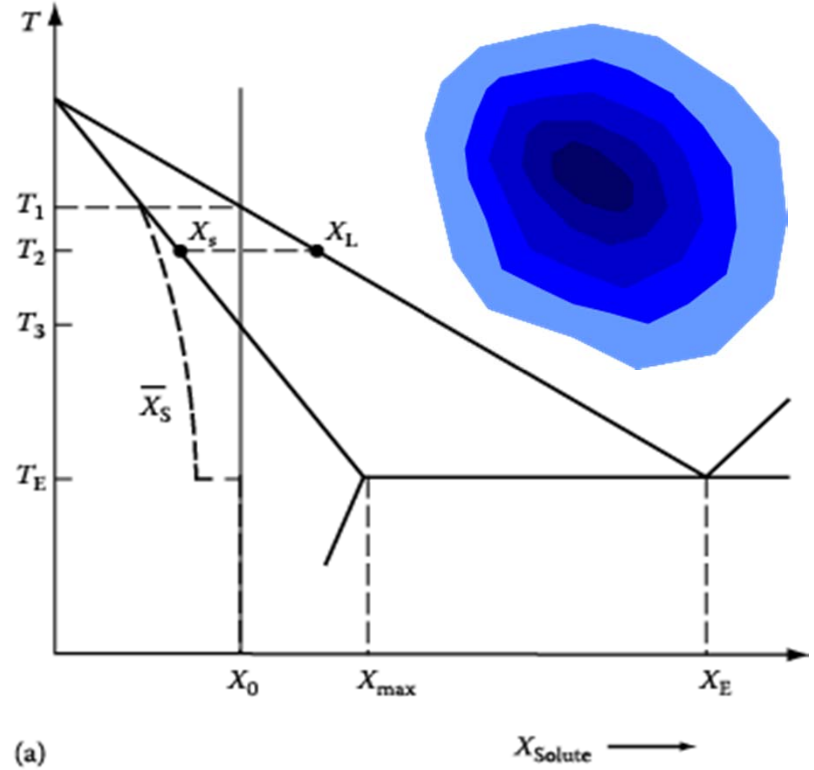
$$\int_0^{f_S} (1-k)(-1)\,d\ln(1-f_S) = \int_{C_0}^{C_L} d\ln C_L$$

$$\ln\frac{C_L}{C_0} = (k-1)\ln(1-f_S)$$

$$\therefore\ C_L = C_0 f_L^{(k-1)}$$

$$C_S = kC_0(1-f_S)^{(k-1)}$$

: non-equilibrium lever rule (Scheil equation)



→ quite generally applicable even for nonplanar solid/liquid interfaces provided here, the liquid composition is uniform and that the Gibbs-Thomson effect is negligible.

If k<1: predicts that if no diff. in solid, some eutectic always exist to solidify.

3) Complete or partial mixing of liquid: no diffusion in solid

: high cooling rate, efficient stirring

(a) Variation of C_S/C_0 with g (f_s) is shown in Fig. 5.16 for values of k_E from 0.01 **to** 5.

(b) There is no steady state region!
→ rejected solute : mix with liquid & whole of the liquid is changed continuously.

(c) Solidification speed does not appear explicitly
→ k_E depends on the speed.

∴ a) very low speed: $k_E = k_0$,
if speed ↑, diffusion zone ~ more important

& $k_E \rightarrow 1$ (steady state region of "diffusion controlled" case)

(d) Calculation of the value, k_E :
→ Why? d = thickness of boundary layer through solute diffusion

Value of d is limited by the velocity of the liquid parallel to the interface, & depends on the velocity of liquid.

10^{-3} cm < d < 10^{-1} cm

Very vigorous stirring Natural convention

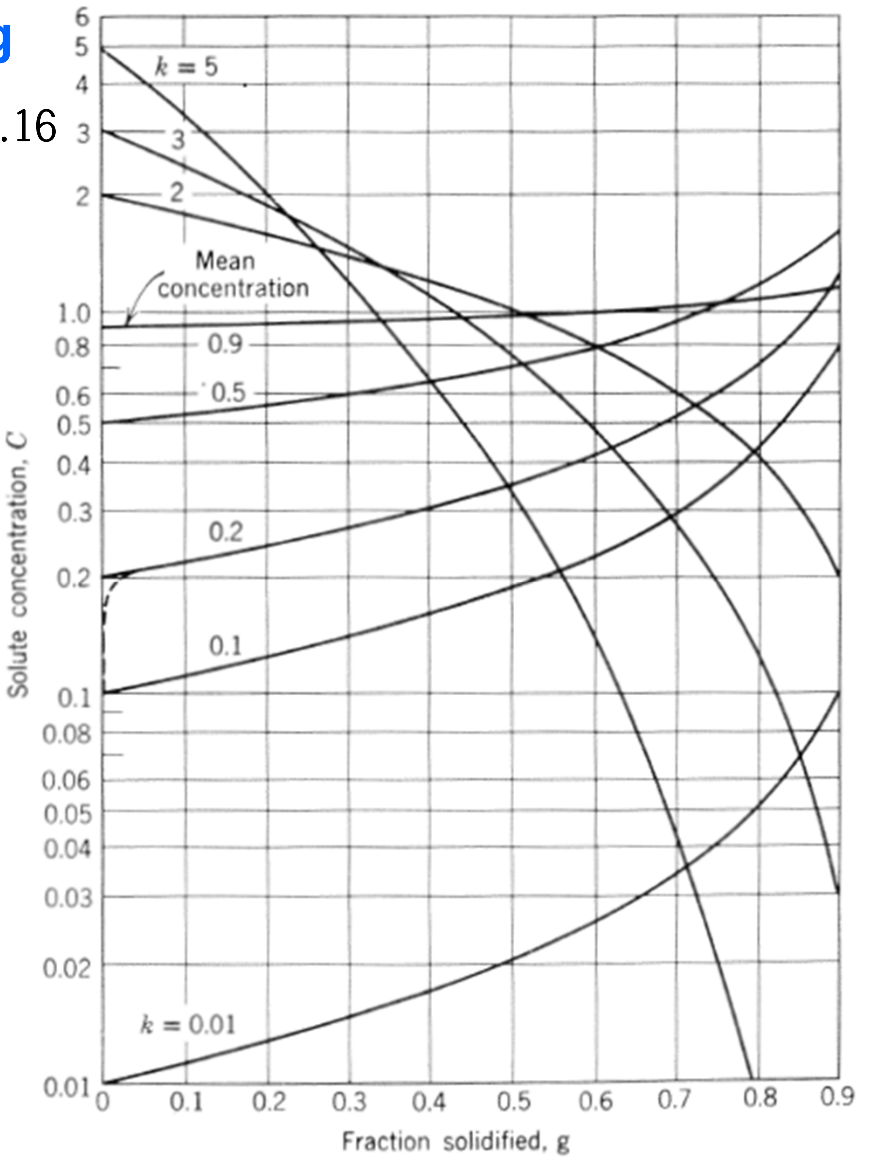


Fig. 5.16. Curves for normal freezing (liquid completely mixed at all times). C_0 is 1 for all curves.

3) Complete or partial mixing of liquid: no diffusion in solid

: high cooling rate, efficient stirring

(e) $k_0 \le k_E \le 1$

Process is so slow or the mixing so effective that the whole of the liquid had the same composition.

⇔

Bulk liquid ~ C_0 composition due to no mixing

(f) If effectiveness of mixing is increased,

$k_E \rightarrow k_0$ **/ R ↓ / d ↓ / D ↑**

R → Rd/D

(actual growth velocity) (normalized growth velocity)

$$k_E = \frac{k_0}{k_0 + (1-k_0)\exp\left(-\frac{Rd}{D}\right)}$$

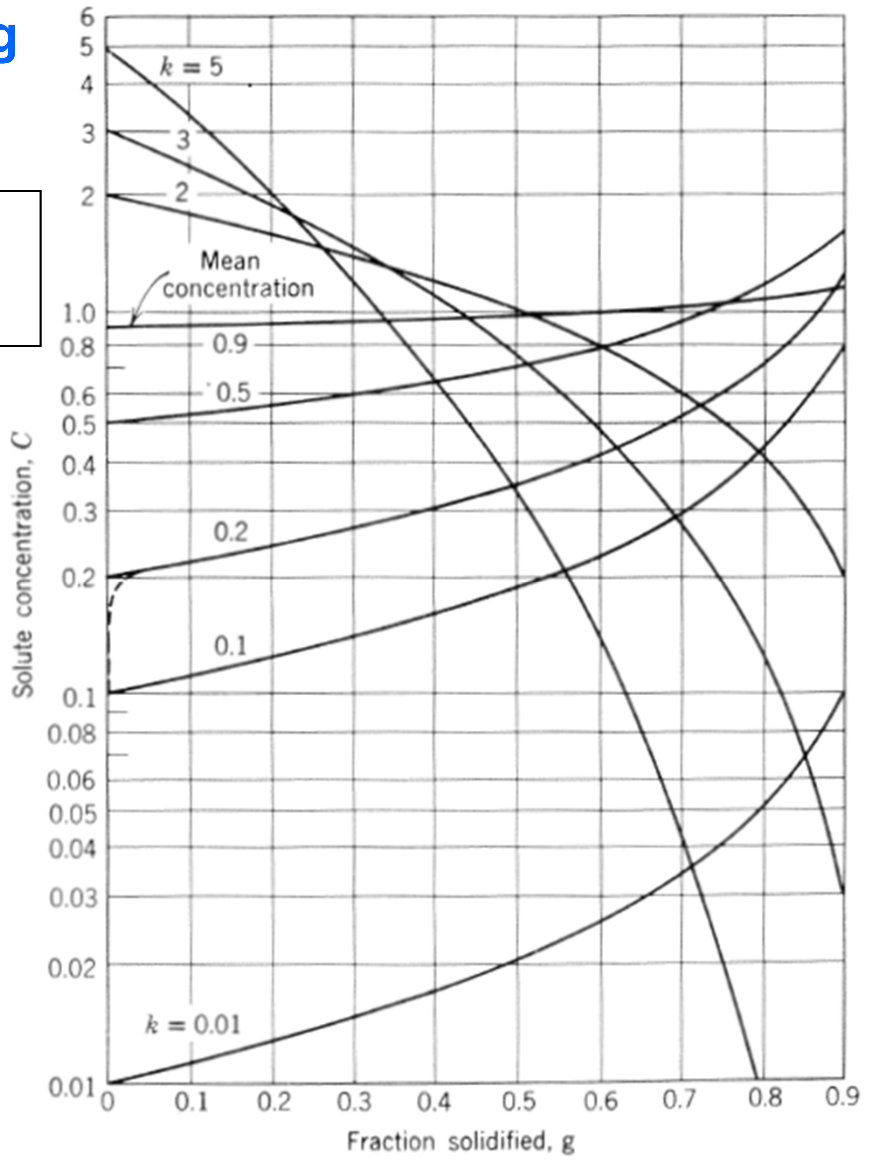


Fig. 5.16. Curves for normal freezing (liquid completely mixed at all times). C_0 is 1 for all curves.

$$k_E = \frac{k_0}{k_0 + (1 - k_0)\exp\left(-\frac{Rd}{D}\right)}$$

- Fig. 5.17 shows how k_E varies with normalized growth velocity (Rd/D) for values of k_0 from 0.1 to 0.9.

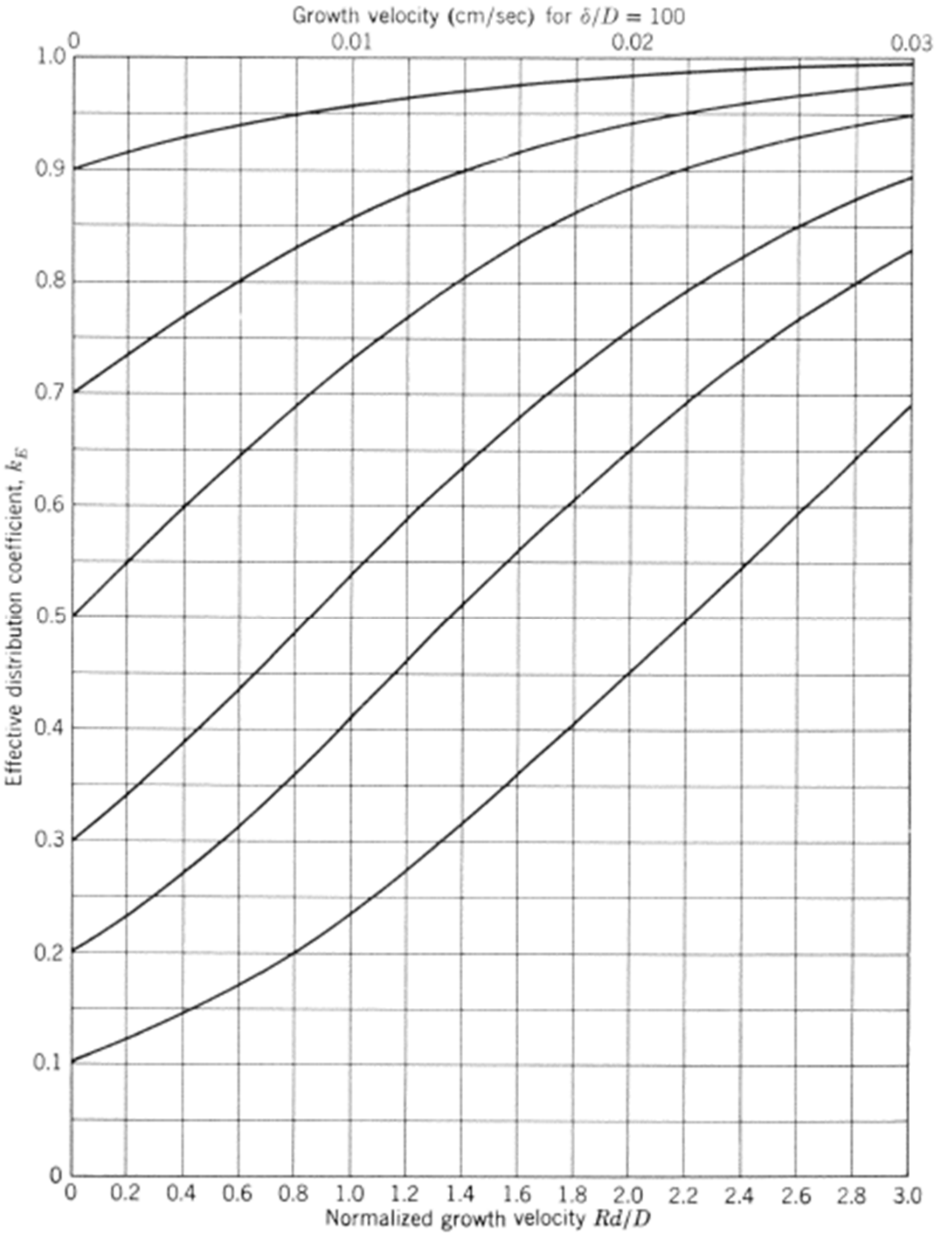


Fig. 5.17. Dependence of effective distribution coefficient on normalized growth velocity (From Ref. 9, p. 14)

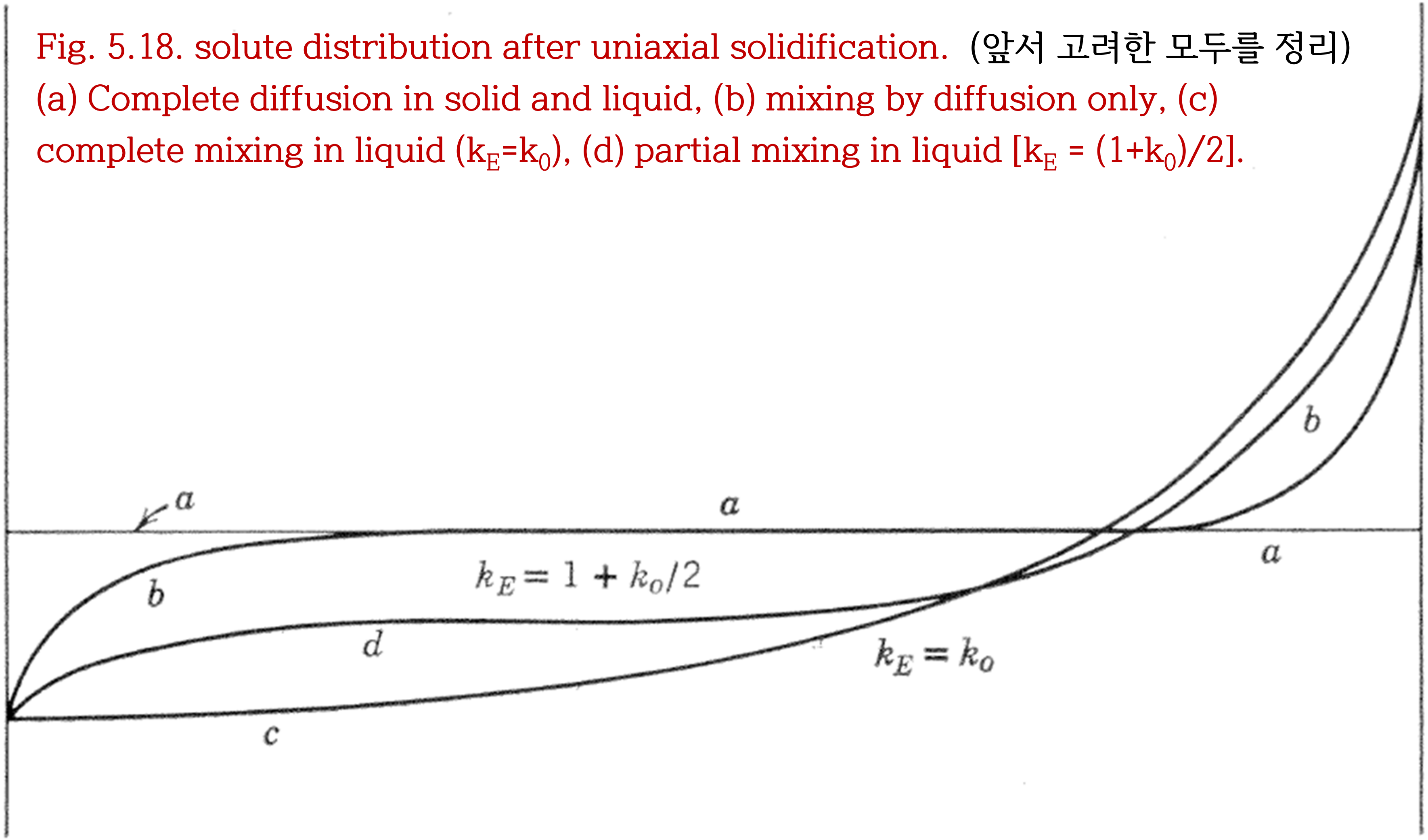


Fig. 5.18. solute distribution after uniaxial solidification. (앞서 고려한 모두를 정리)
(a) Complete diffusion in solid and liquid, (b) mixing by diffusion only, (c) complete mixing in liquid (k_E=k_0), (d) partial mixing in liquid [k_E = $(1+k_0)/2$].

* Comments: Solidus temperature of an alloy

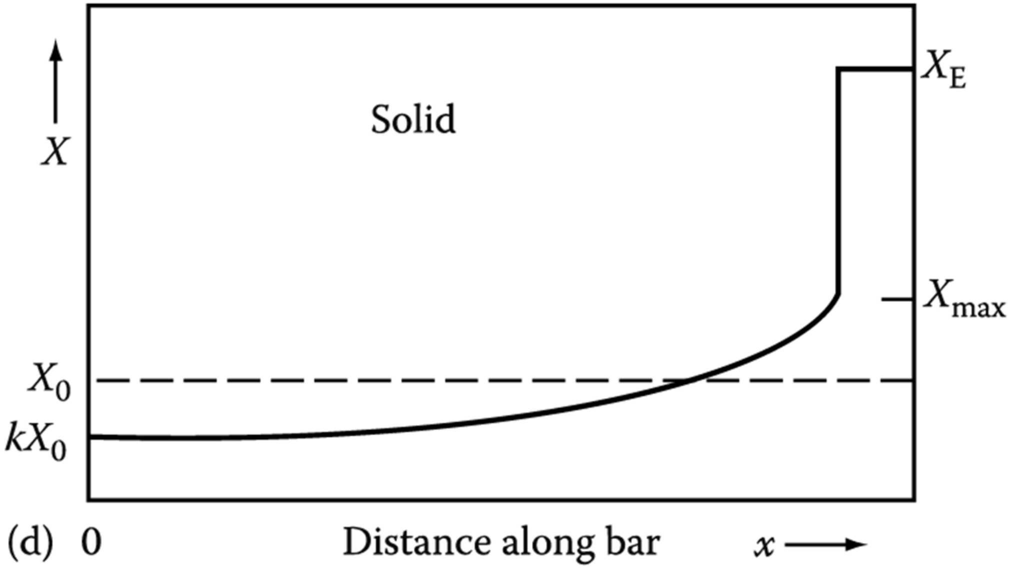
T_L: Solidification start → supercooling → T_L (recalesence)→ T_S: Solidification finish

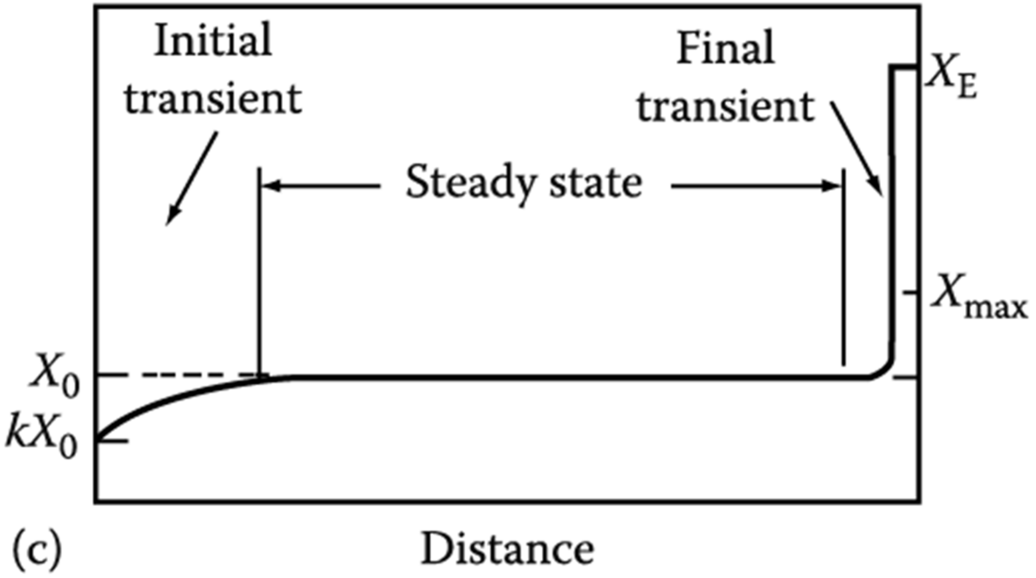
Phase diagram → determined from cooling curve ∴ T_L satisfactory, T_S large errors

When a single-phase solid is formed, the last liquid always solidifies at a temperature below the solidus for the original liquid (of composition C_0) some times by a large amount→ Please check “Zone refining”.

Concentration profiles in practice

: exhibit features between two cases





➡ **Zone Refining**

5.4 Zone Refining

: A crystal growing from a solution usually rejects either the solute or the solvent → **“Purifying Crystalline”**

(a) Distribution coefficient of any solute, k_0 ~ very small ($< 10^{-6}$)

→ Importance of R/ d/ D ↓ → Purity ↑ by multi-stage process

(b) Distribution coefficient k_0 ~close to 1,

→ Purity ↑ by multi-stage process

→ possible, but not practical

∴ Each successive stage would provide less material of high purity.

Zone melting or Zone refining – W.G. Pfann Invention ~ various extension and modifications (see Pfann’s book: Zone melting, John Wiley & Sons New York, 1958)

Ring heater

The form of a bar
& Held in suitable
container

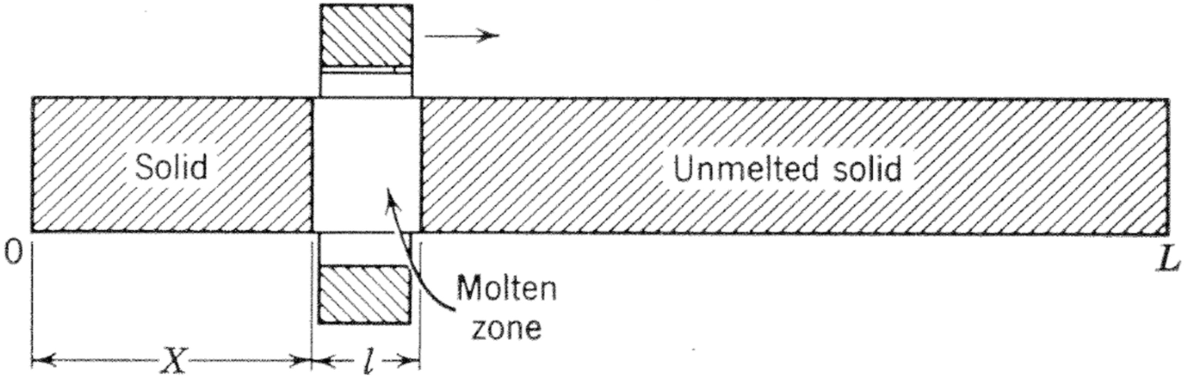
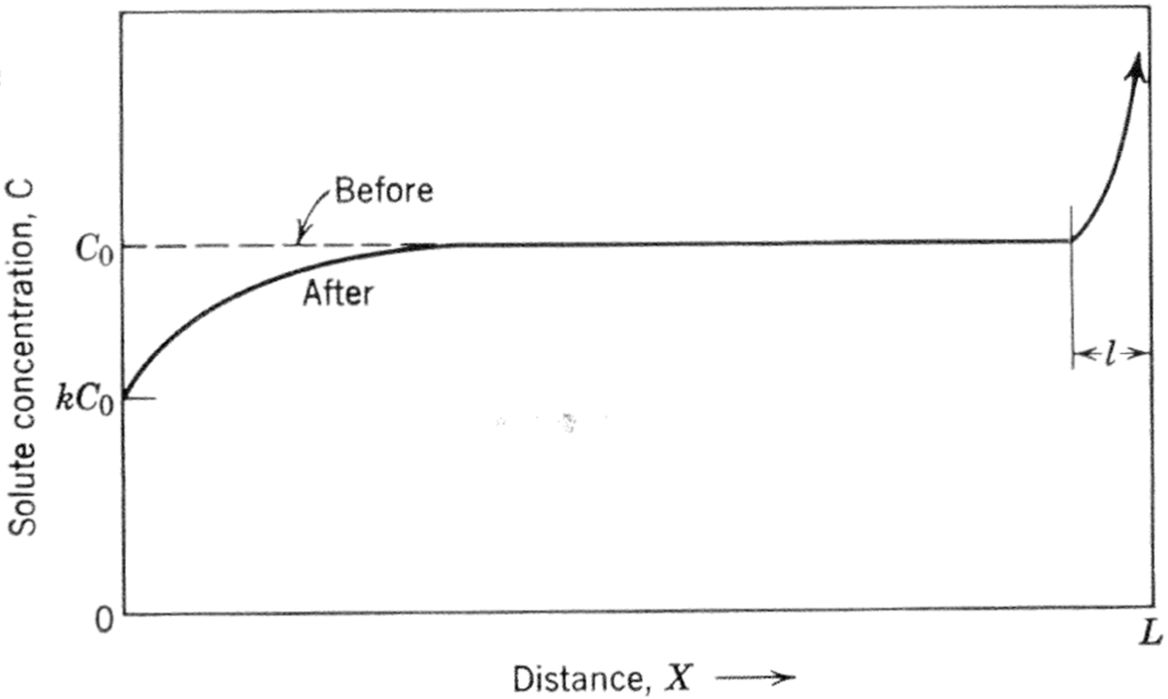


Fig. 5.19. Zone melting, schematic. (From Ref. 9, p. 24.)

(a) Fig. 5.20. Distribution of solute after passage of one molten zone; initial concentration C_0. (From Ref.9, p. 25)



* Concentration distribution :
except terminal transient region

$$\frac{C_s}{C_0} = 1 - (1 - k_E) \exp\left(-\frac{k_E X}{l}\right)$$

(b) Concentration gradients after multi-pass in the same direction as first:

further transfer of solute from left to right

(c) Effect of k_E on purification:

low k_E (left) : small # of pass → **large decrease of** solute concentration
$k_E \sim 1$ (next page): requires a very large # to produce a comparable effect

① $k_E = 0.1$

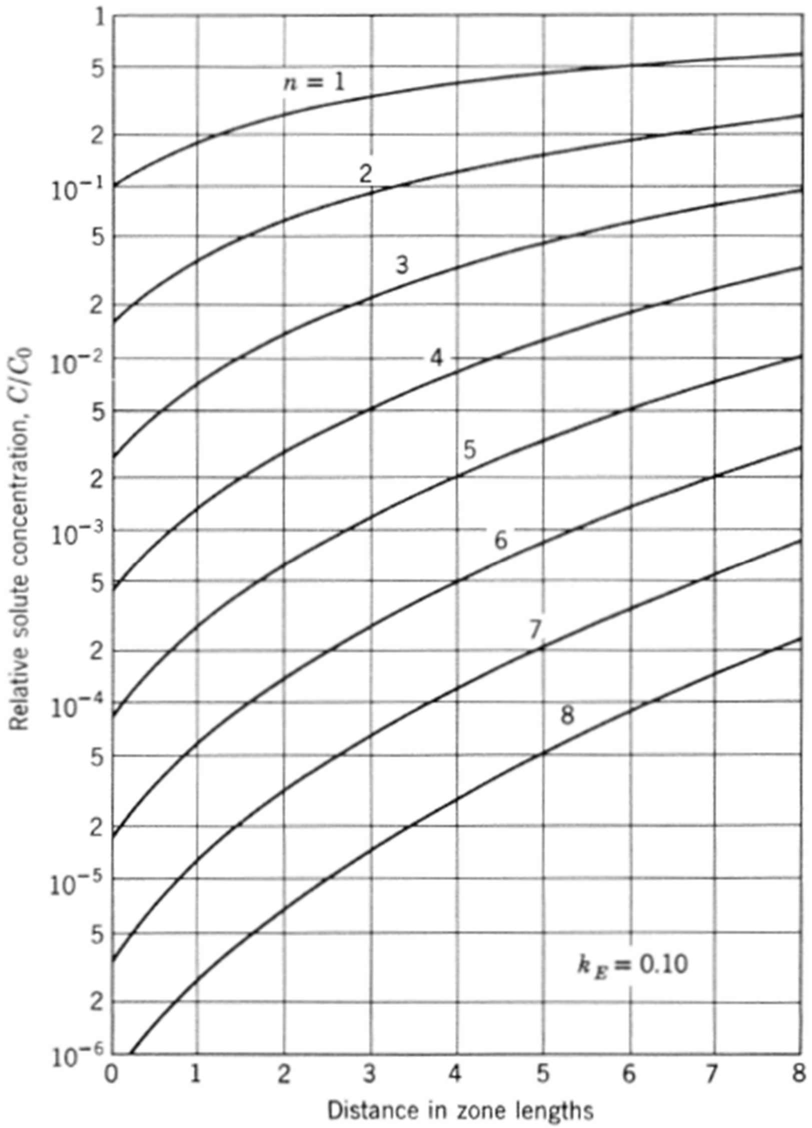


Fig. 5.22. Solute concentration after n zones for $k_E = 0.1$.

② $k_E = 0.25$

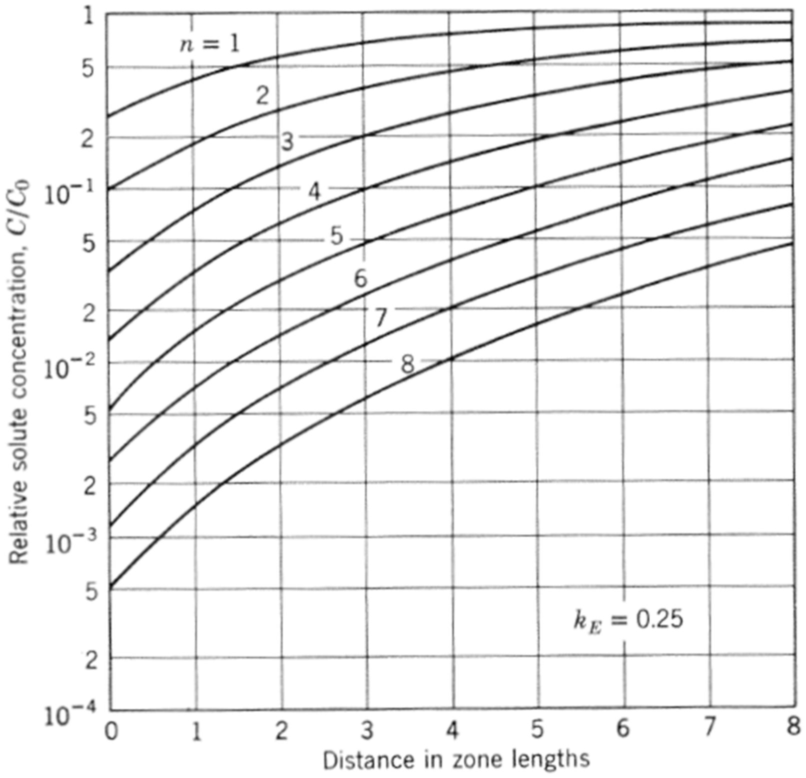


Fig. 5.21. Solute concentration against distance (in zone lengths) after passage of n zones

(c) Effect of k_E on purification:

low k_E (left) : small # of pass → **large decrease of** solute concentration
$k_E \sim 1$: requires a very large # to produce a comparable effect

③ $k_E = 0.9524$

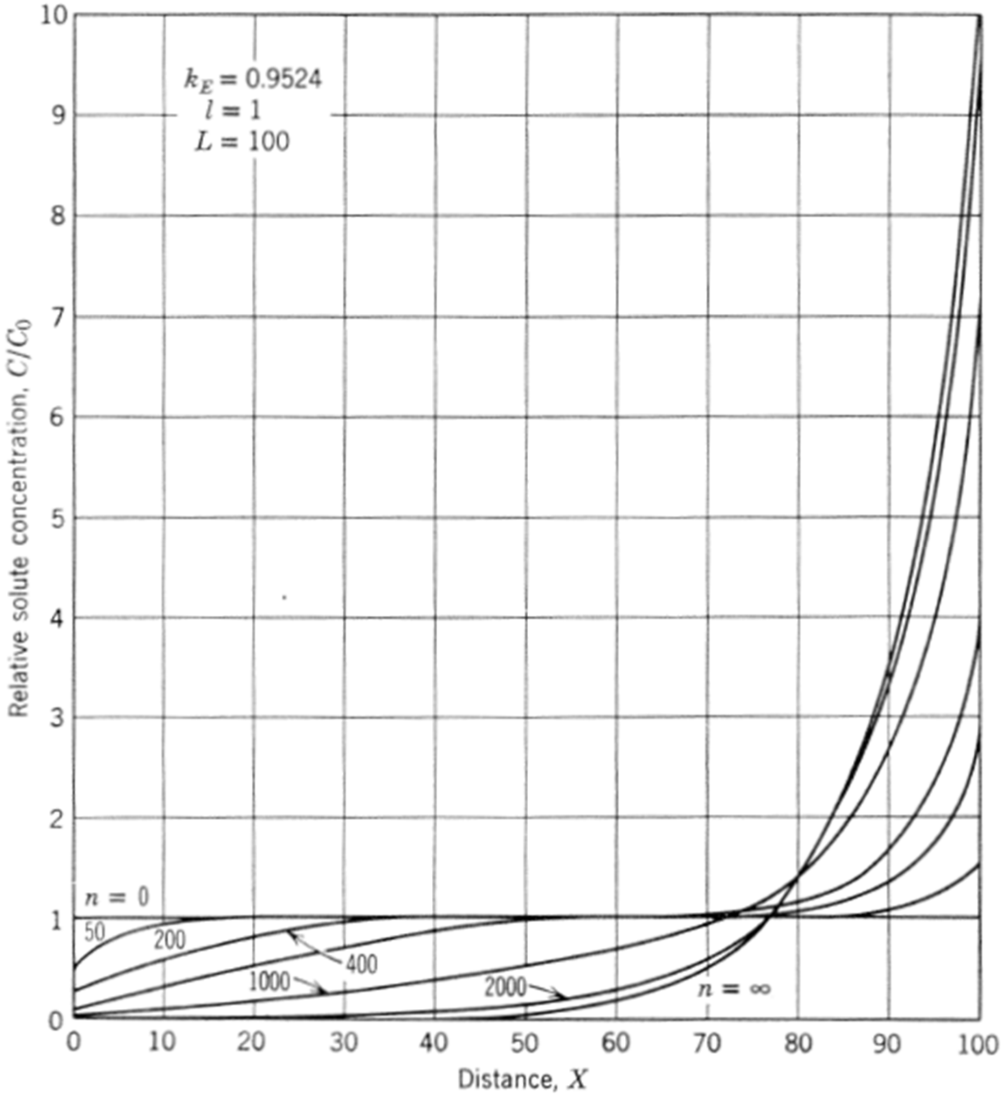
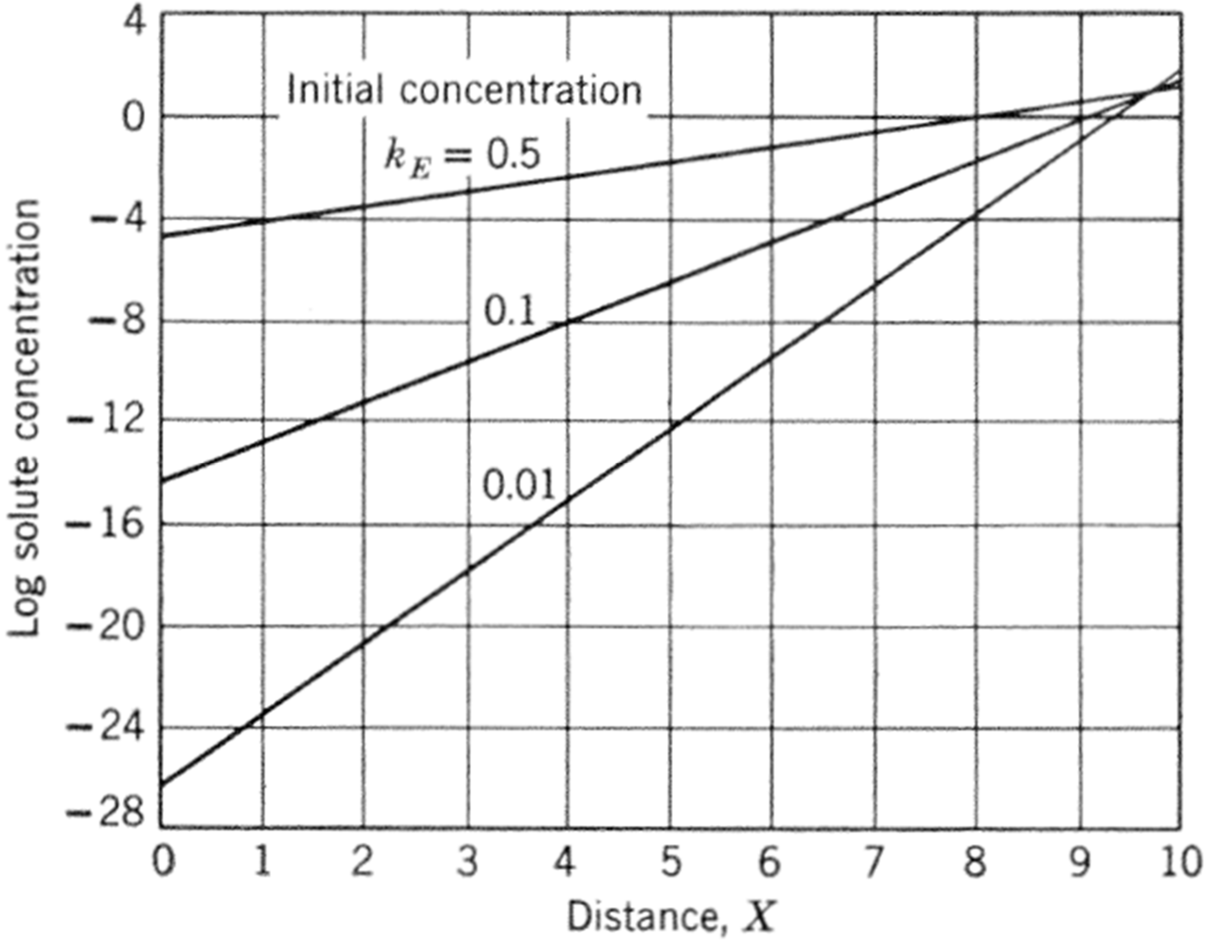


Fig. 5.23. Solute concentration for $k_E = 0.95$.

Figure 5.24 Limiting distribution which is approached after passage of many zones; Length of ingot is 10 zone lengths. (From Ref. 9, p. 41)



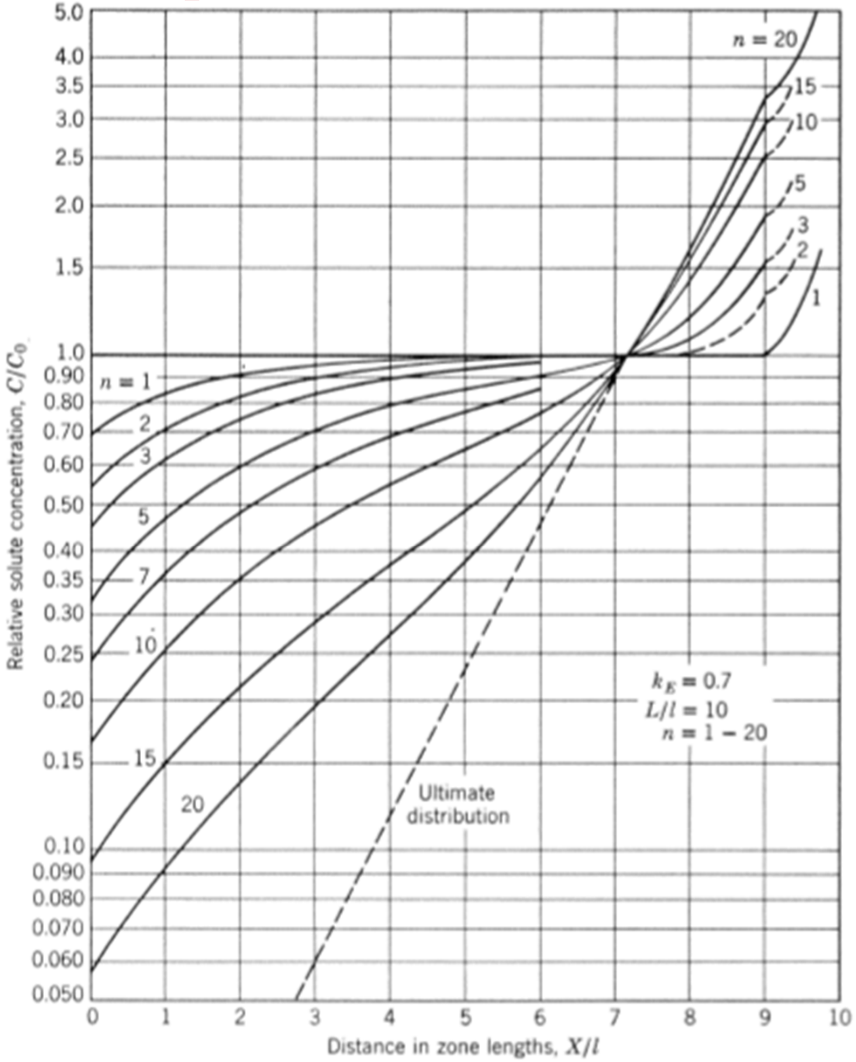
(a) How the ultimate distribution (i.e. when a steady state has been reached) varies with the value of k_E for a bar 10 zones in length.

Assumption : - Impurity to be removed have distribution coefficient less than 1.
- Solutes are rejected by growing crystals and accumulate in the terminal region.

But, (b) some solute are preferentially accepted by growing crystal, and therefore, have distribution coefficients greater than 1& accomulate in the first part to solidify

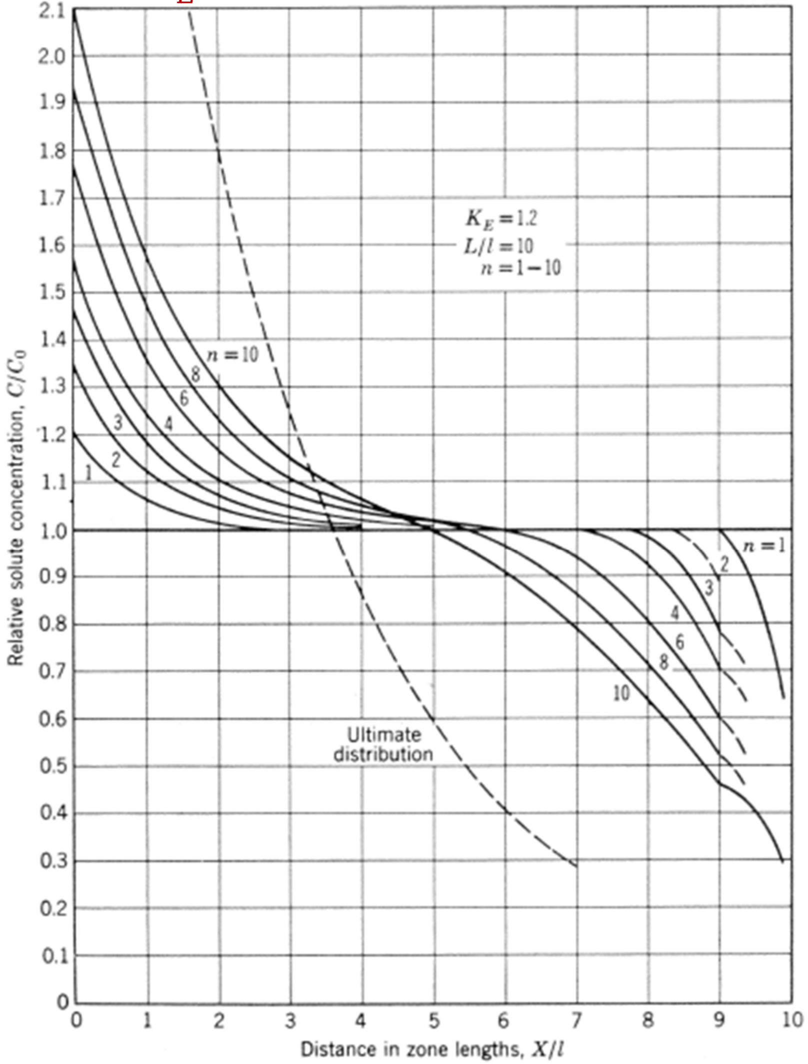
* A comparison of separation obtained with k_E =0.7 and 1.2 is shown in Fig. 5.25, where a bar ten zones in length L/l=10 is subjected to various number of passes.

① k_E = 0.7



(a)

② k_E = 1.2



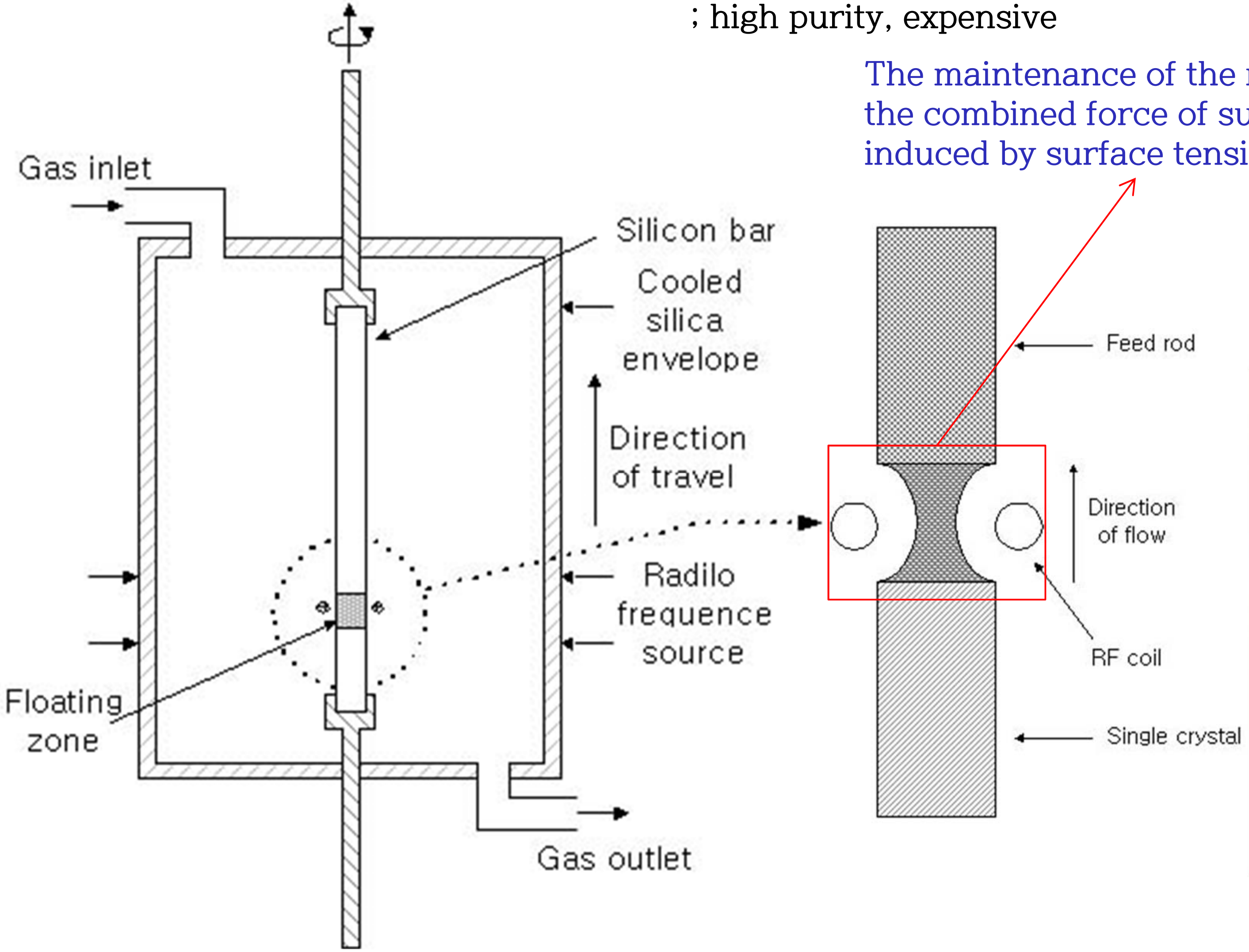
(b)

* When purifying through zone refining, metals with high reactivity and high Tm should be carefully considered for contamination especially from containers.→ This problem is minimized by using the various floating zone methods described below.

Single Crystal Growth: c) Float-zone (FZ) method

; high purity, expensive

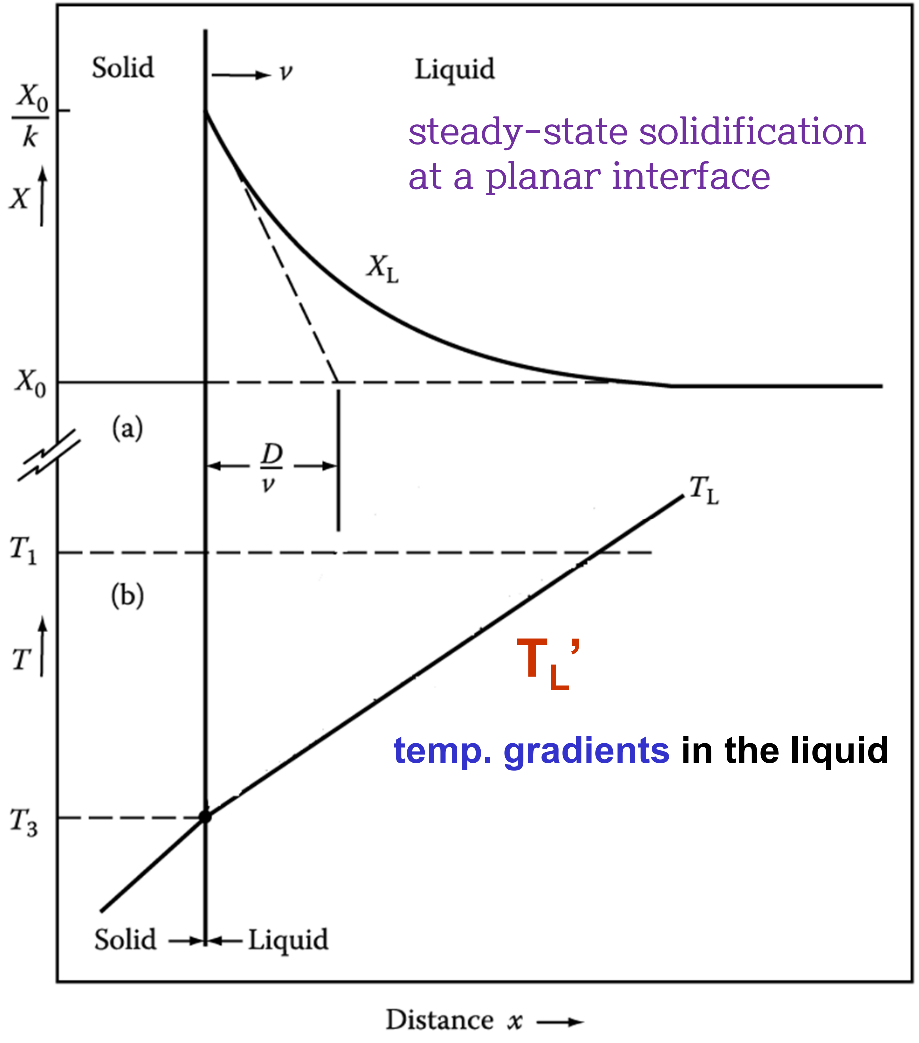
The maintenance of the molten zone is possible by the combined force of surface tension or stress induced by surface tension and electromagnetic.



∗ Cellular and Dendritic Solidification

Fast Solute diffusion similar to the conduction of latent heat in pure metal, possible to break up the planar front into dendrites.

→ complicated, however, by the possibility of temp. gradients in the liquid.

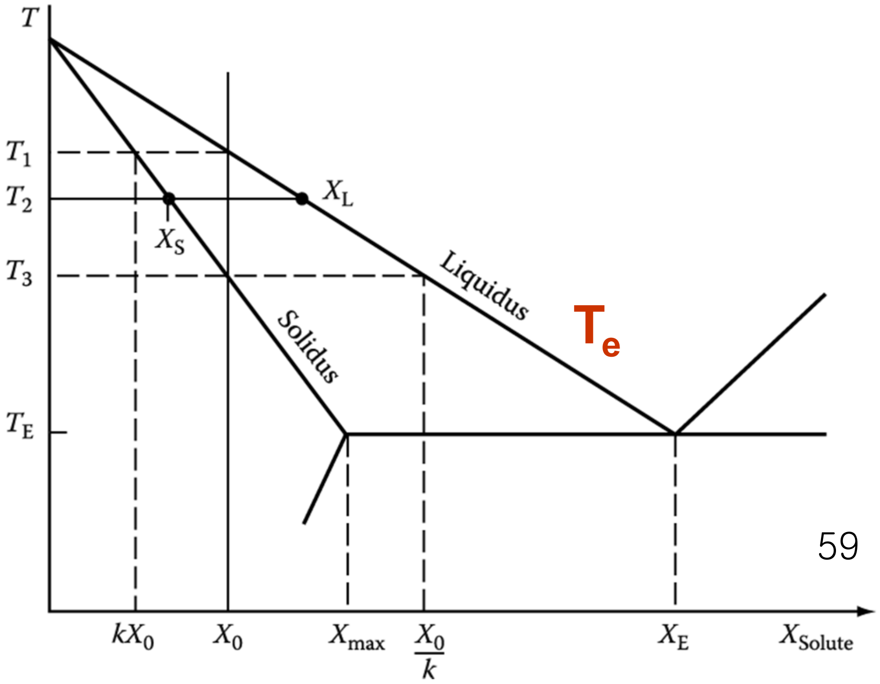


steady-state solidification at a planar interface

T_L'

temp. gradients in the liquid

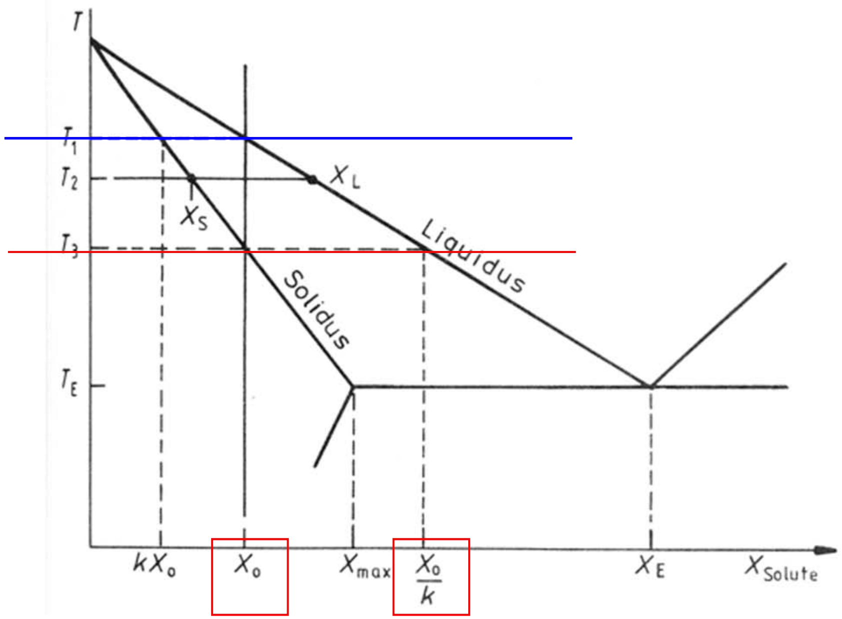
What would be "T_e" along the concentration profile ahead of the growth front during steady-state solidification?



T_e

* Constitutional Supercooling

No Diffusion on Solid, Diffusional Mixing in the Liquid ➡ **Steady State**

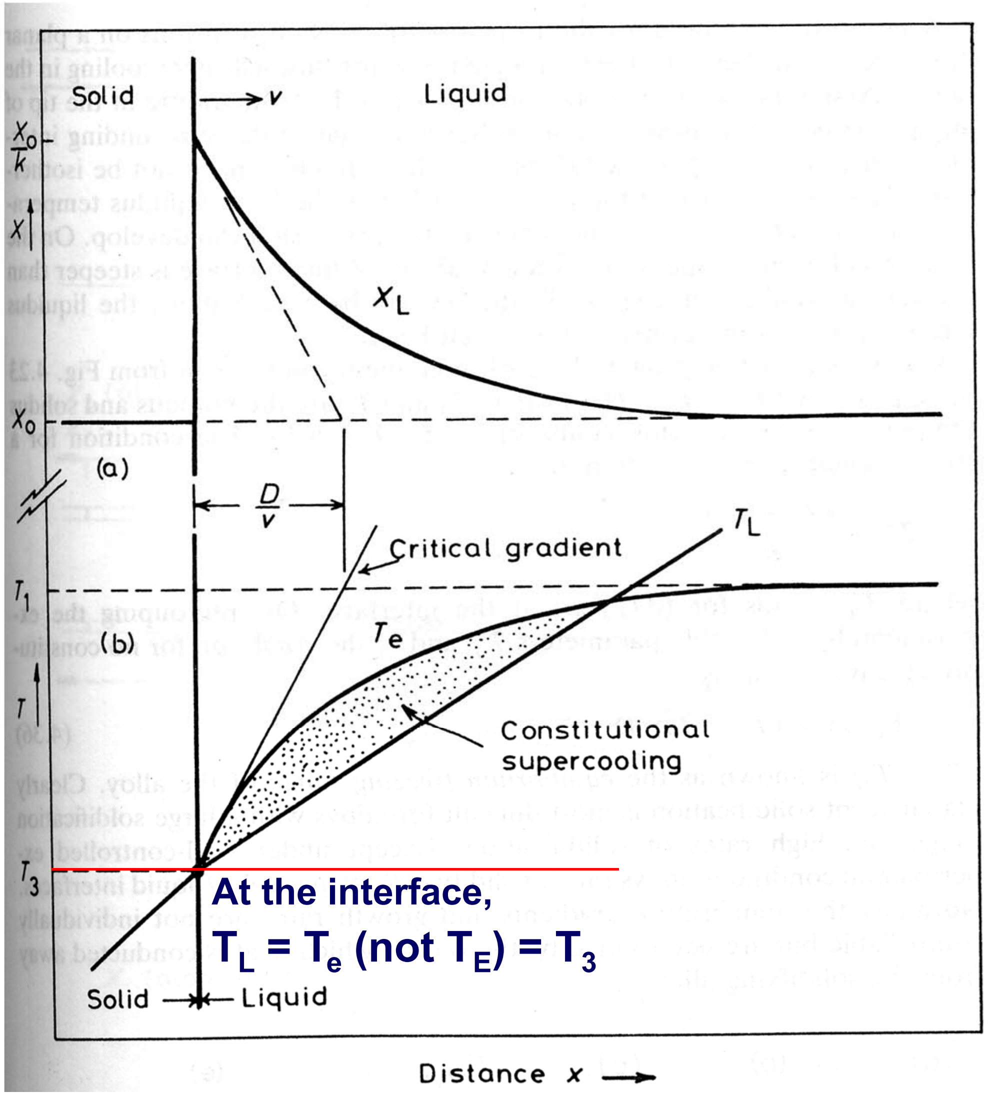


*** Actual temperature gradient in Liquid**

T_L'

*** equilibrium solidification temp. change**

T_e



At the interface,

$T_L = T_e$ (not T_E) $= T_3$

$T_L' > (T_1-T_3)/(D/v)$: **the protrusion melts back** ➡ **Planar interface: stable**