

2017 Spring

“Calculation and Applications Phase Equilibria”

Principles Solidification

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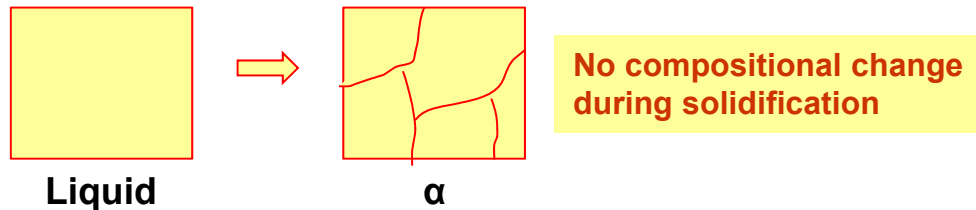
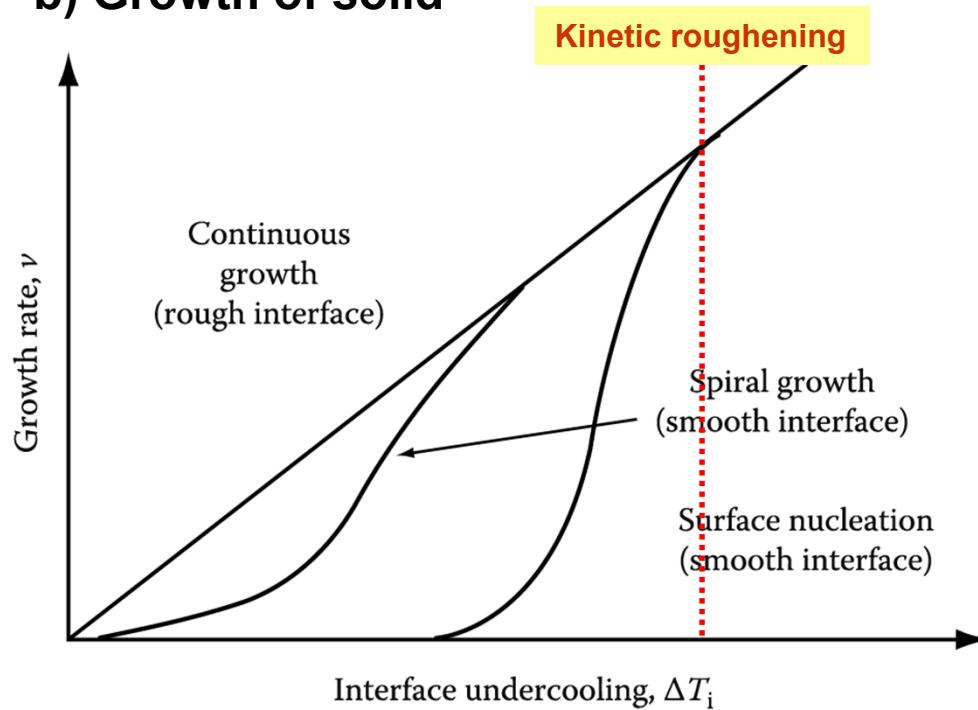
Office hours: by appointment

Solidification: Liquid \longrightarrow Solid

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

a) homogeneous Nucleation or Heterogeneous Nucleation • Undercooling ΔT

b) Growth of solid



• Interfacial energy γ_{SL} / $S(\theta)$ wetting angle

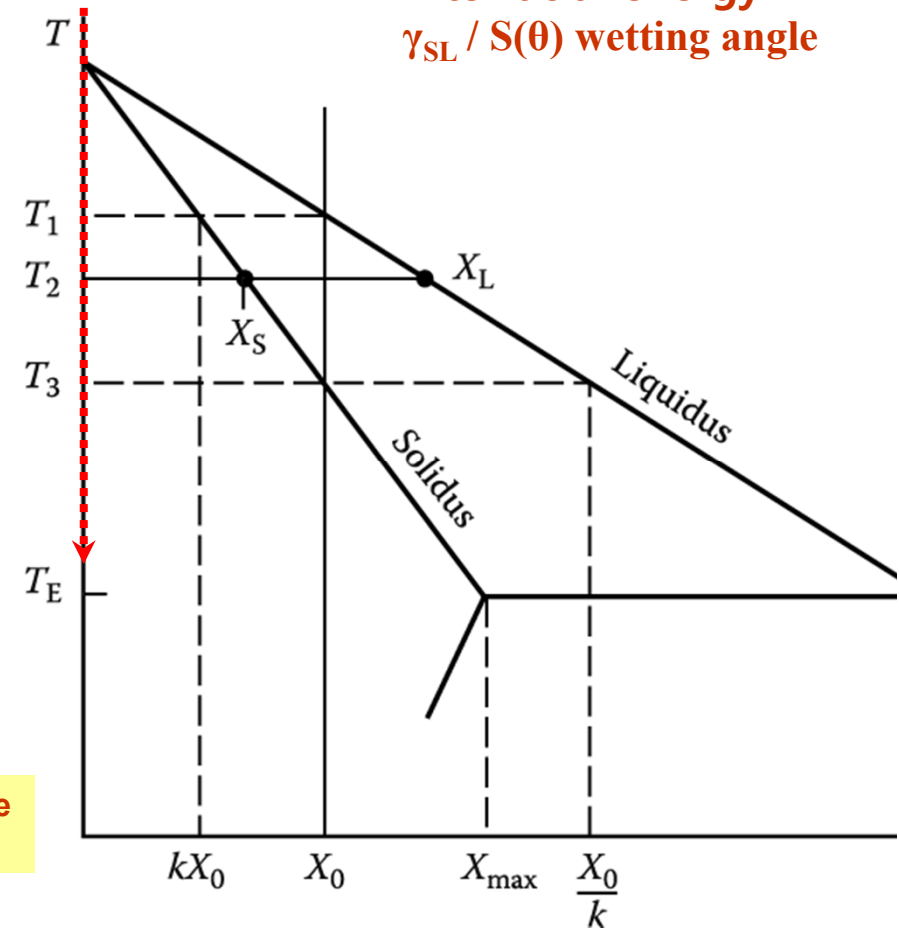


Fig. 4.19 A hypothetical phase diagram.

"Alloy solidification"

1. Solidification of single-phase alloys

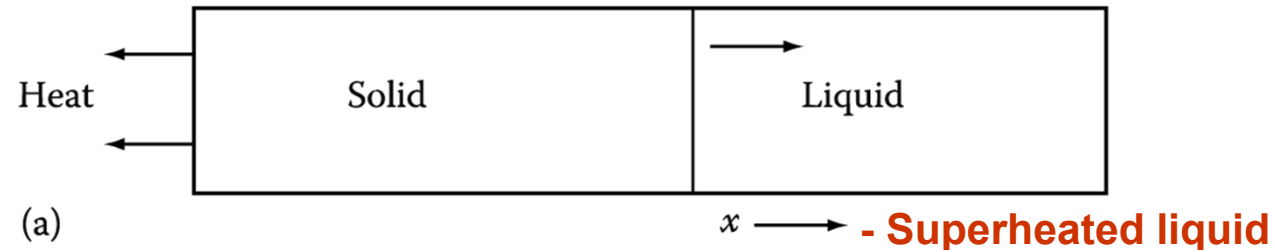
- Three limiting cases

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

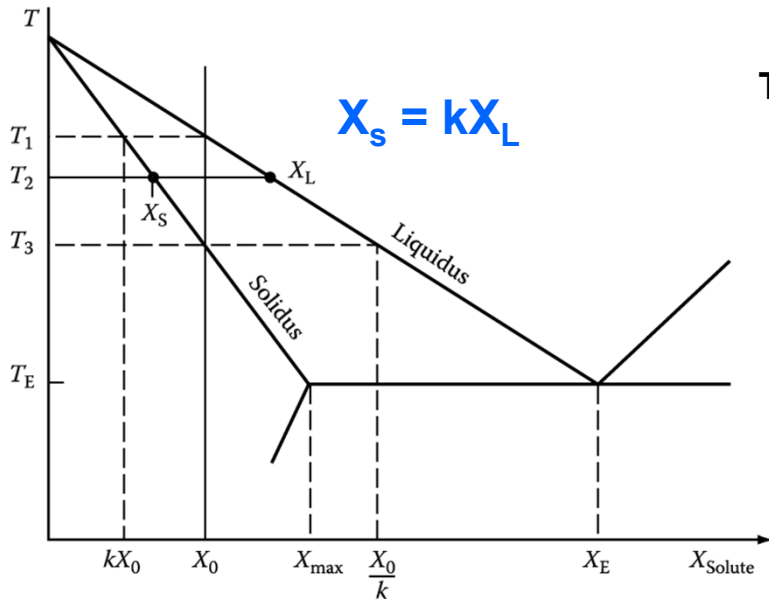
- Planar S/L interface → unidirectional solidification



- Cellular and Dendritic Solidification

- Supercooled liquid

1) Equilibrium Solidification : perfect mixing in solid and liquid

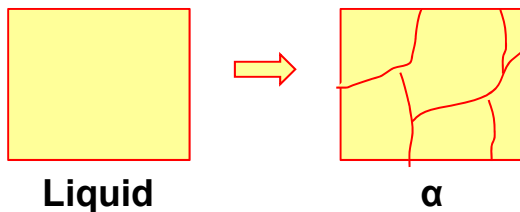


Conservation of solute requires the two shaded areas to be equal.

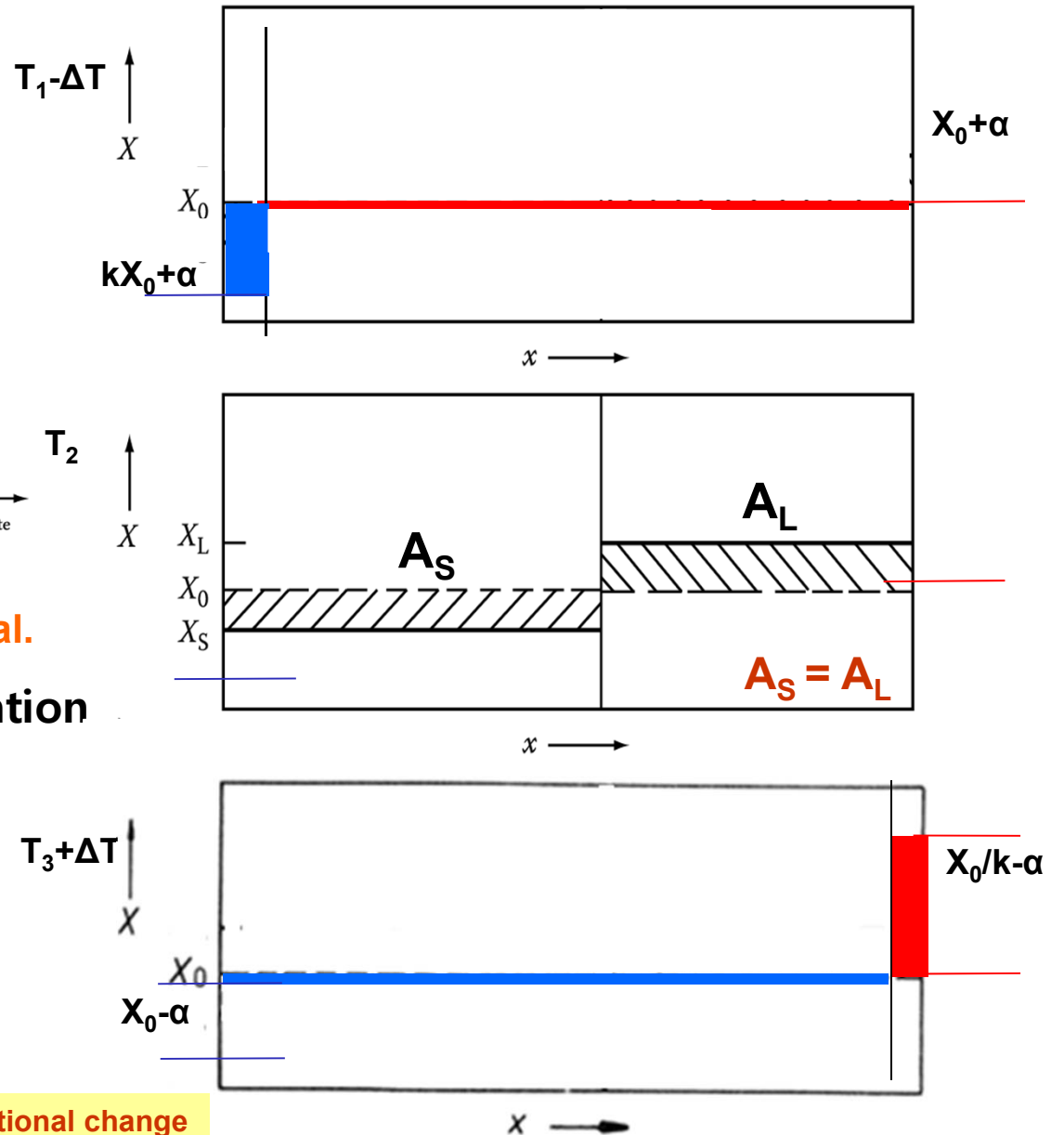
* Equilibrium solute concentration

$$kX_0 \leq X_S \leq X_0$$

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



Compositional change during solidification



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

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

* 2) For example, $D_S \ll D_L$
(D_S ignored, $D_L \sim$ normally all diffusion in the liquid is to the interface)

In the case of Equilibrium solidification

V (speed of advance of interface) = very slow \Leftrightarrow

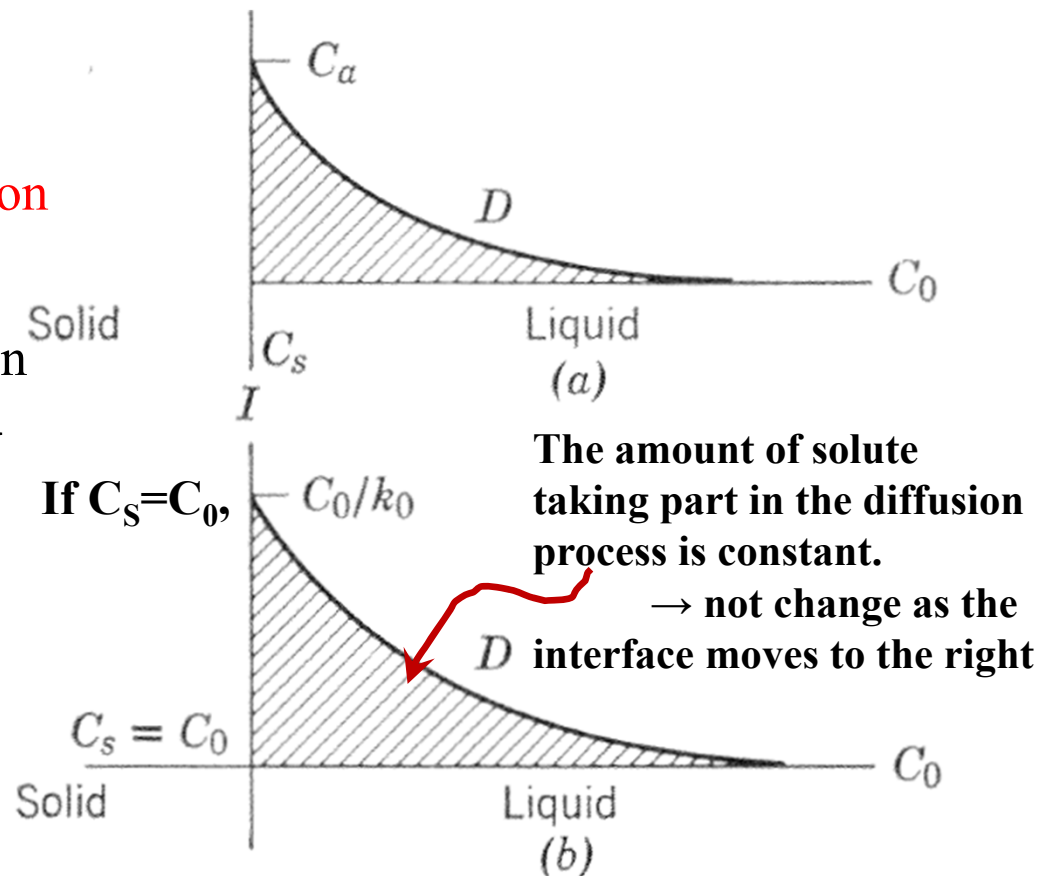
but in this case $V_{\text{interface}} = R$ cm/sec

$$C_S/C_a = k_0$$

C_0 initial composition of liquid

$$k_E = C_S/C_0$$

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

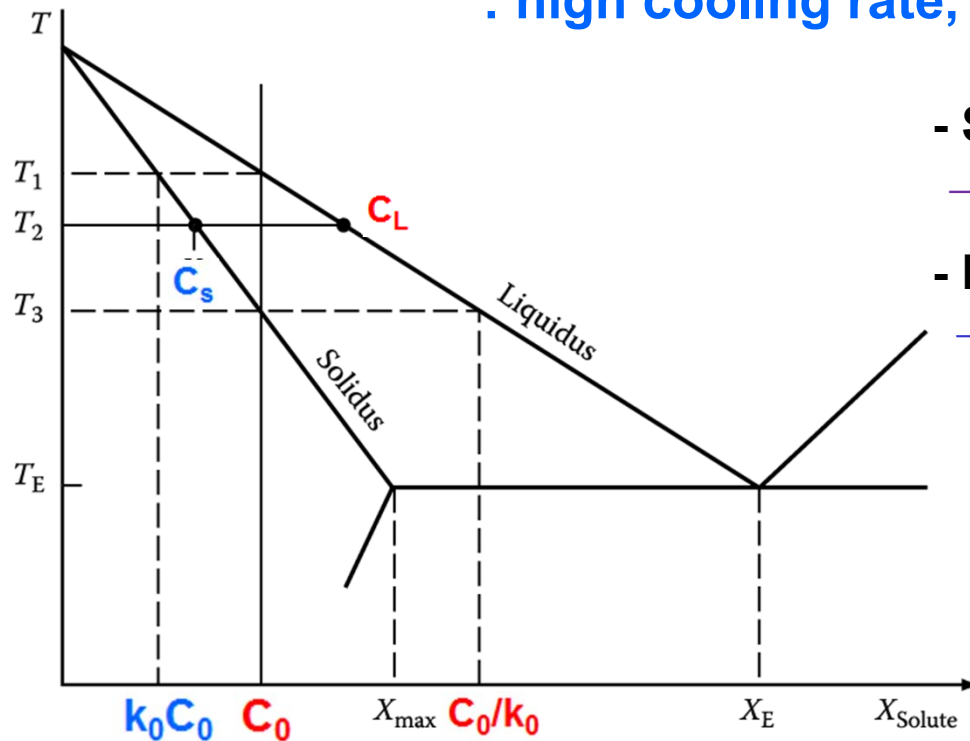


\rightarrow **If composition of solid = C_0 , “steady state condition”**

Fig. 5.6. Distribution of solute during uniaxial solidification

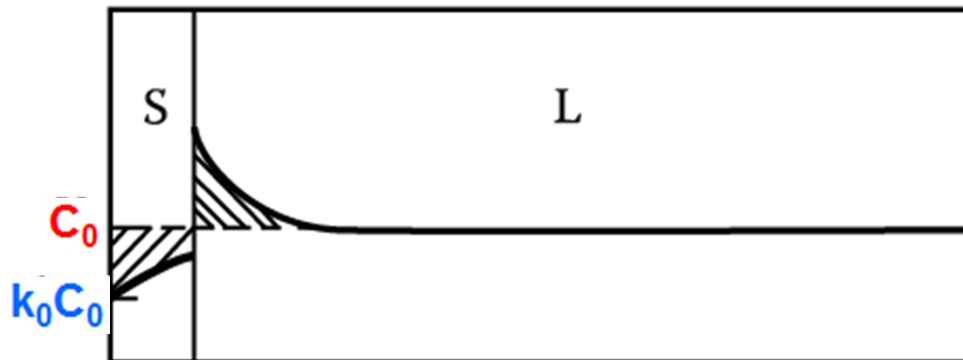
2) No Diffusion on Solid, Diffusional Mixing in the Liquid

: 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



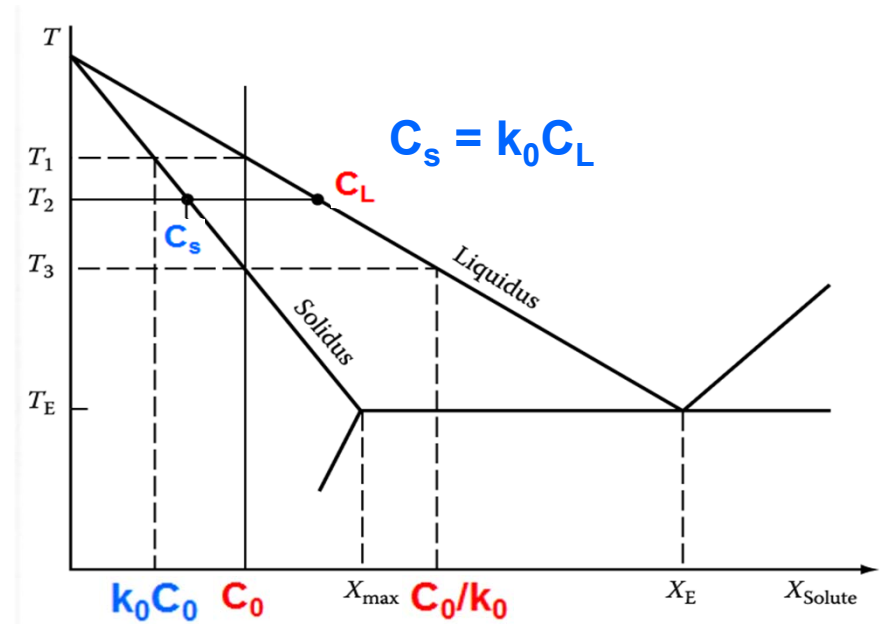
Composition profile
at $T_2 < T_{S/L} < T_3$?

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

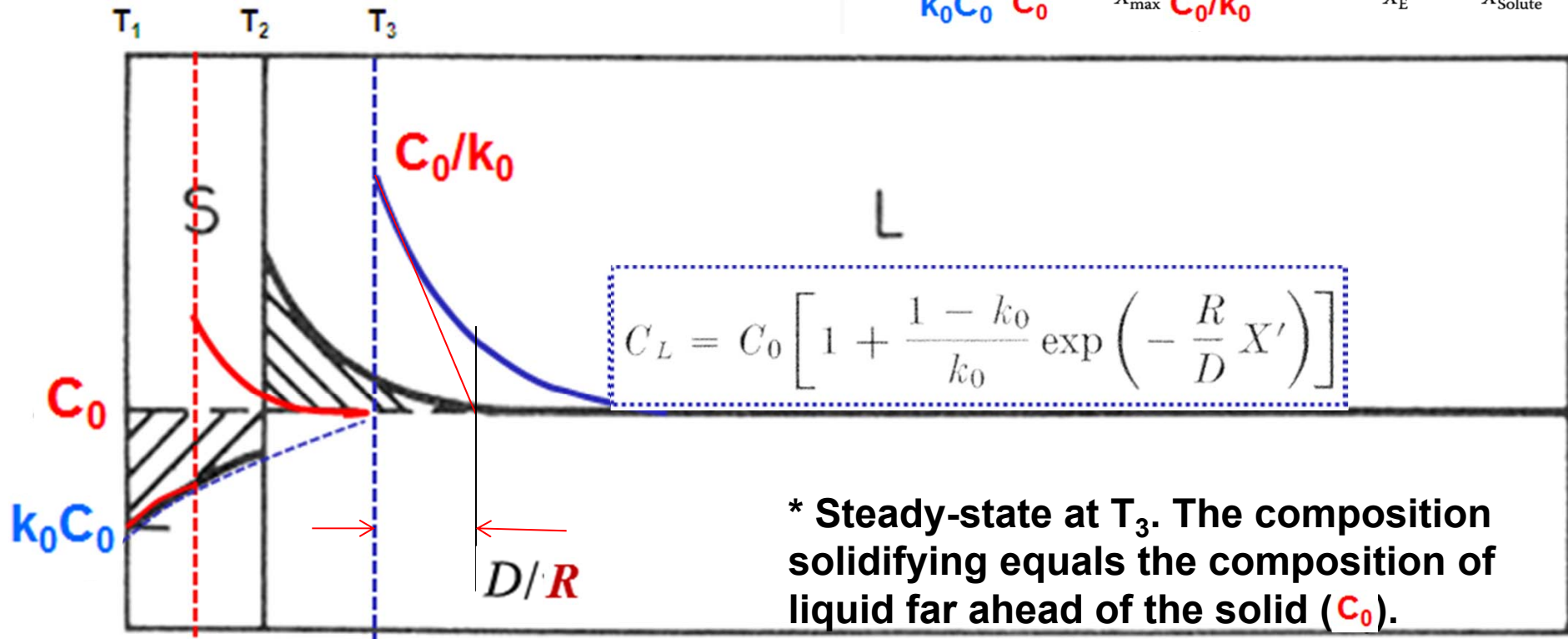
“Alloy solidification”

- Solidification of single-phase alloys

* No Diffusion on Solid,
Diffusional Mixing in the Liquid

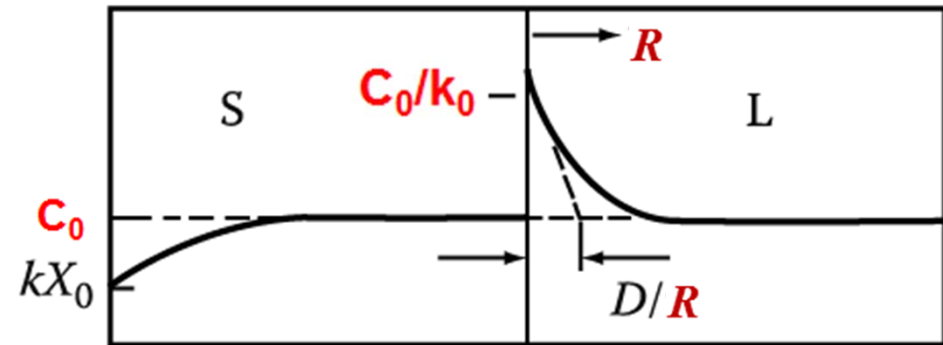


Interface temperature



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 $C_S = C_0$,

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

(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: $k_0 C_0$

→ 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)

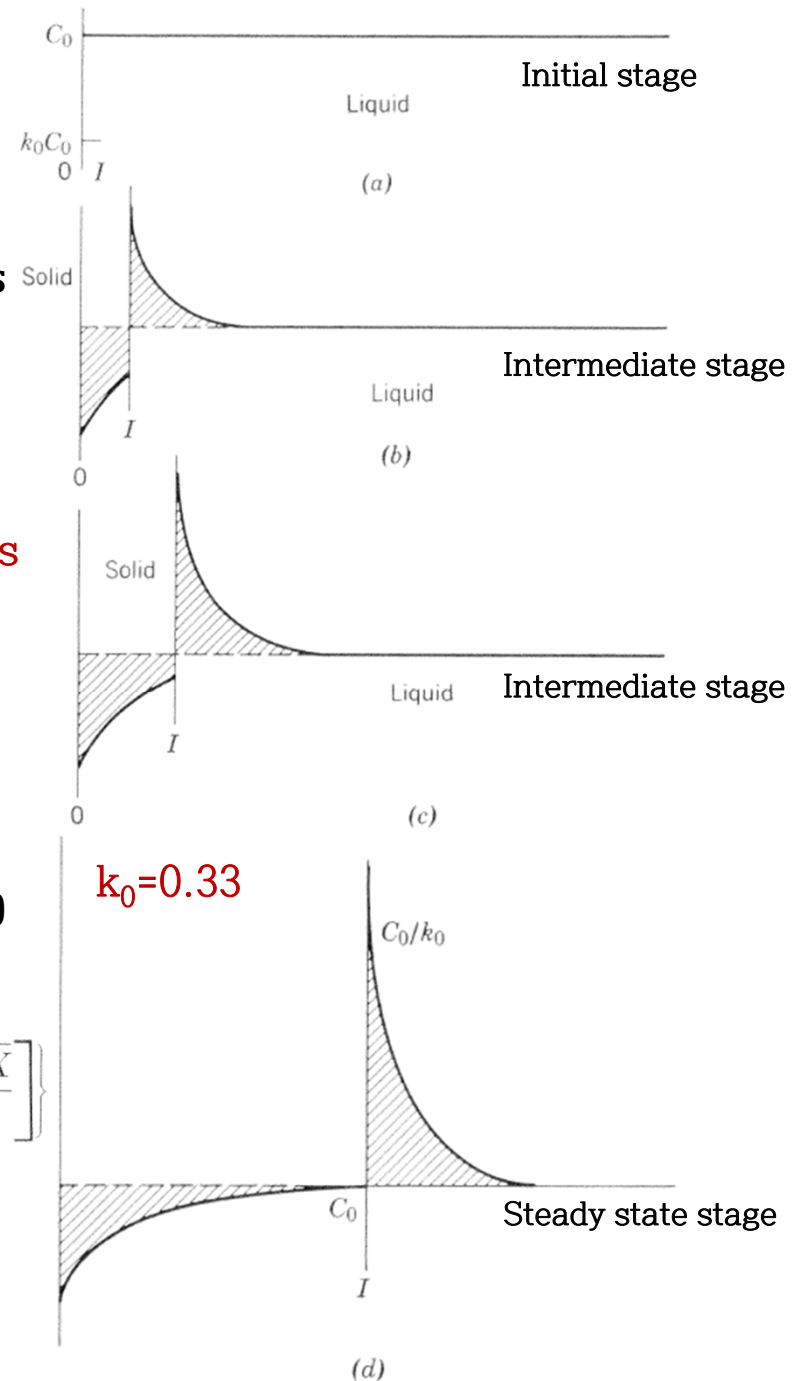
$$\frac{C_S}{C_0} = \frac{1}{2} \left\{ 1 + \operatorname{erf} \sqrt{(R/2D)X} + (2k_0 - 1) \exp \left[-k_0(1 - k_0) \frac{R}{D} X \right] \operatorname{erf} \left[\frac{(2k_0 - 1)\sqrt{(R/D)X}}{2} \right] \right\}$$

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

* Characteristic distance

$$X_c = \frac{D}{k_0 R} \text{ cm}$$

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 = $C_0 \uparrow$ (\because 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) \rightarrow terminal transient zone occupies **a shorter distance, by a factor k_0 , than the initial zone** (concentration change in terminal transient zone_Chapter 8)

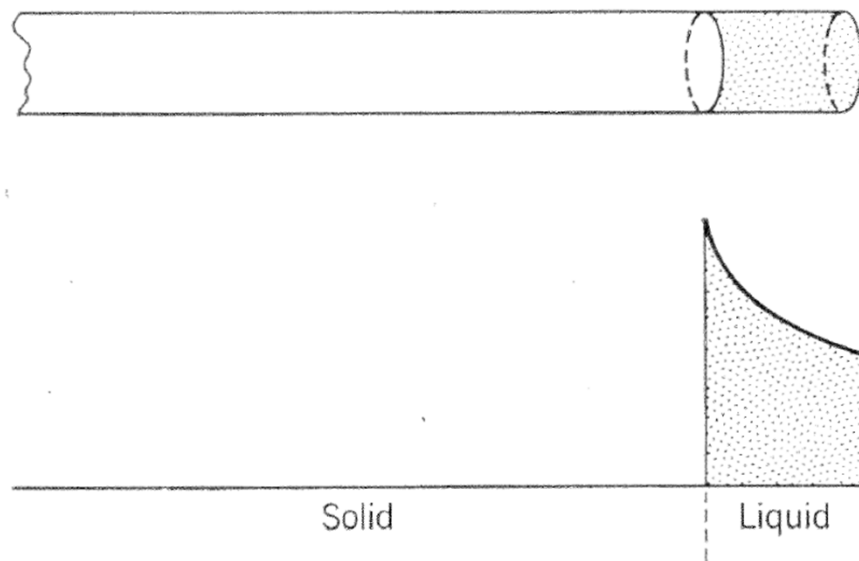


Fig. 5.11. distribution of solute during terminal transient.

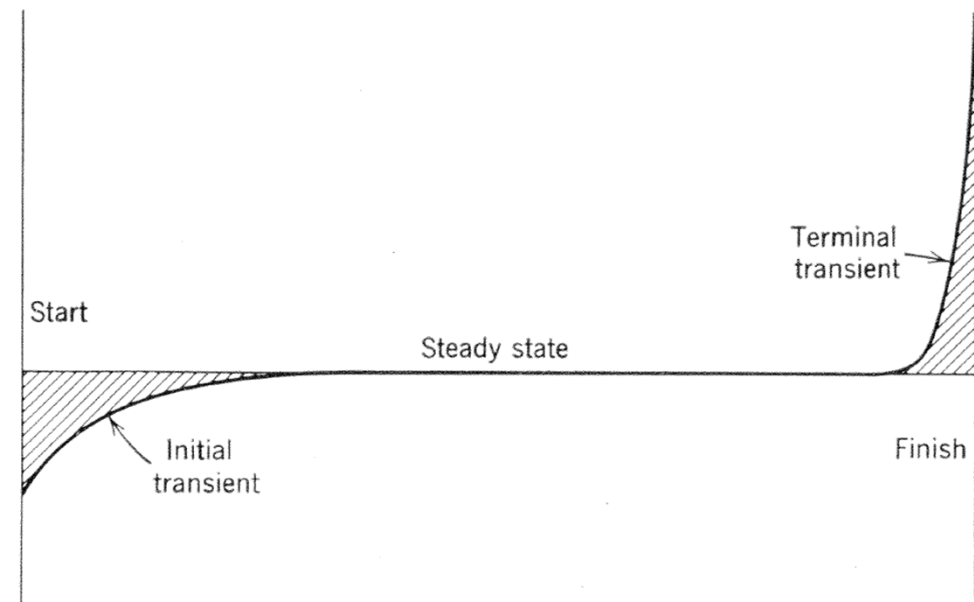
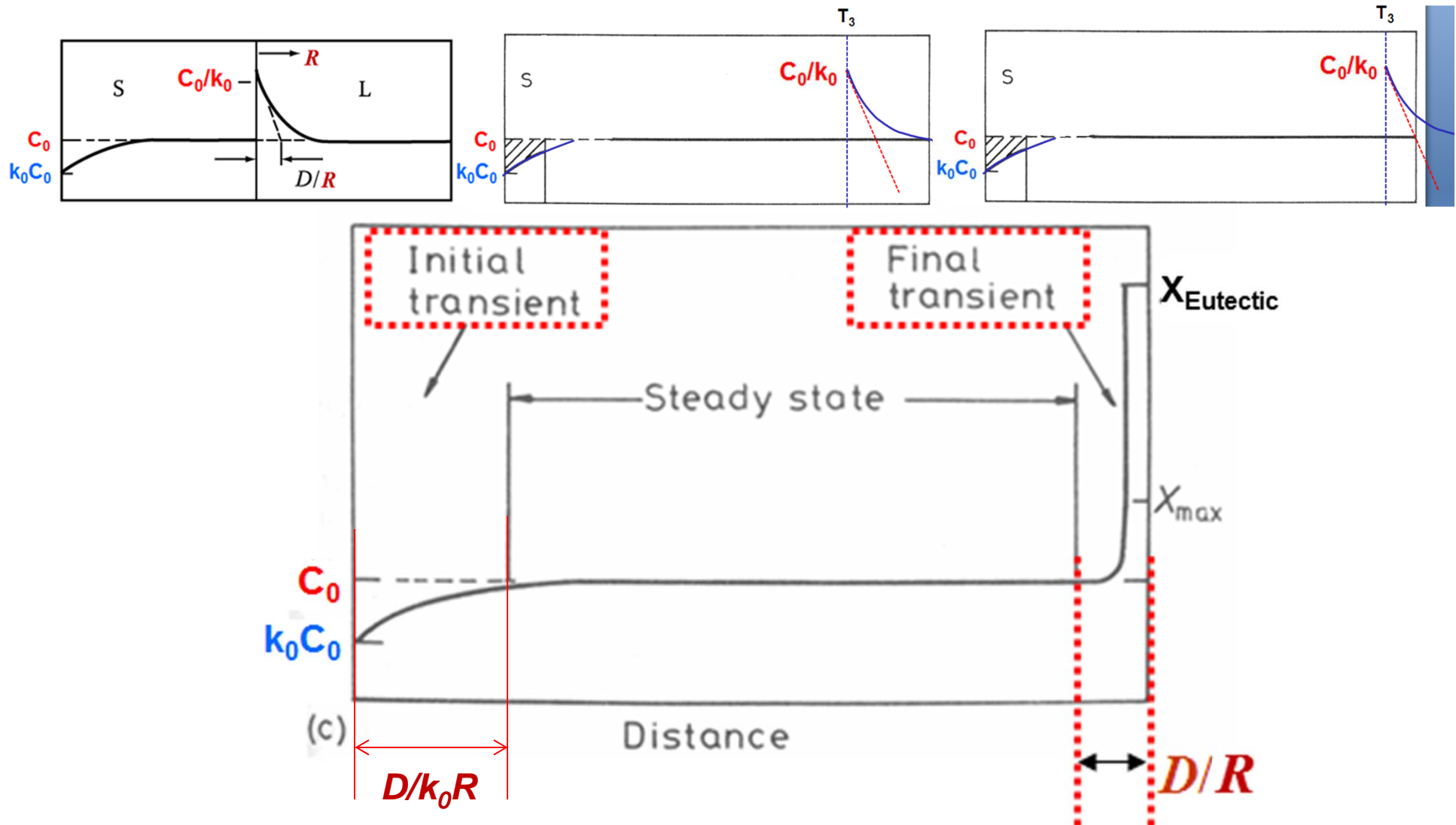


Fig. 5.12. concentration in initial and terminal transient.

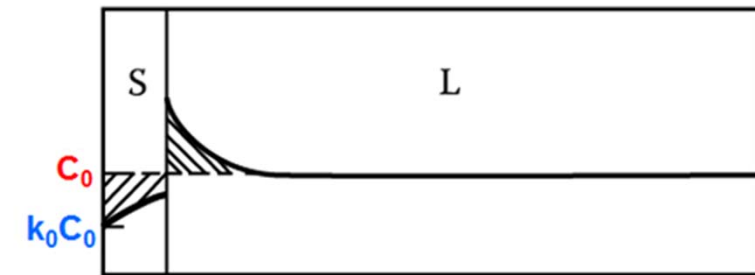
"Alloy solidification" - Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid

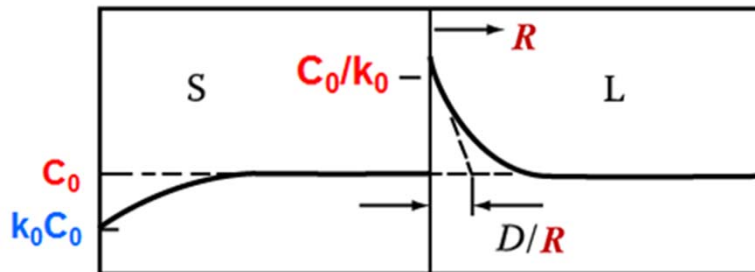


When the solid/liquid interface is within $\sim D/R$ of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation.

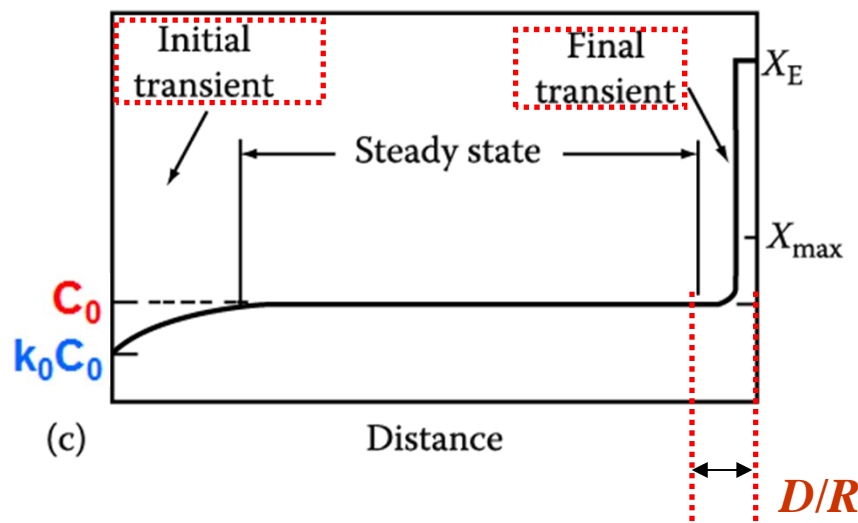
2) No Diffusion on Solid, Diffusional Mixing in the Liquid



(a)



(b)



(c)

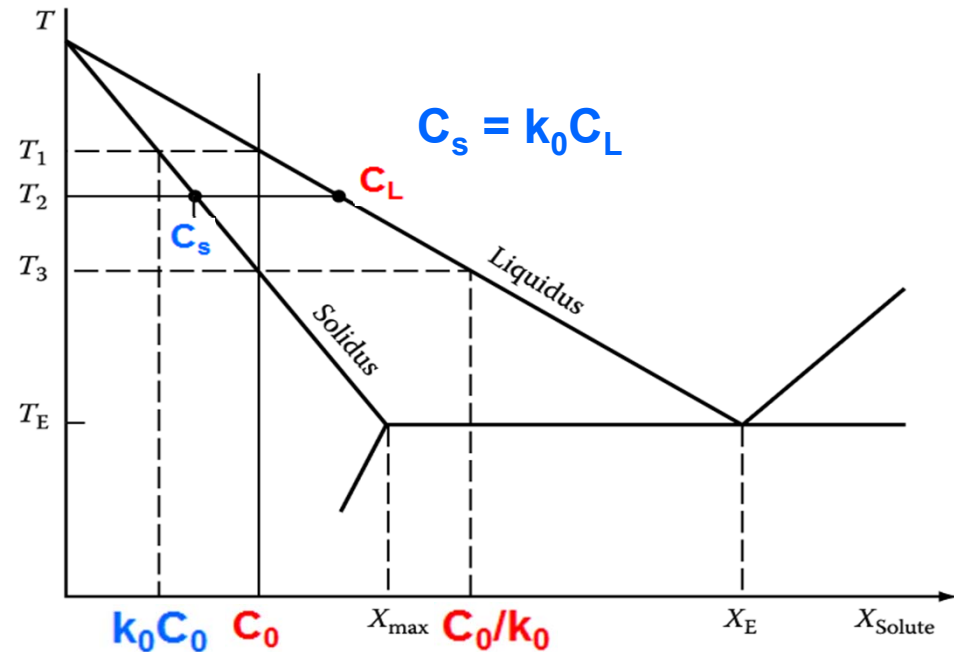


Fig. Planar front solidification of alloy C_0 in upper figure assuming no diffusion in solid and no stirring in the liquid.

- (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 $R \sim \text{const}$, excess solute ahead of the interface = the area under the diffusion curve
→ characteristic distance D/R & solidification rate $\sim 1/R$

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

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

(c) If $R \downarrow$, solid concentration is less than C_0 as shown in Fig. 5.13.

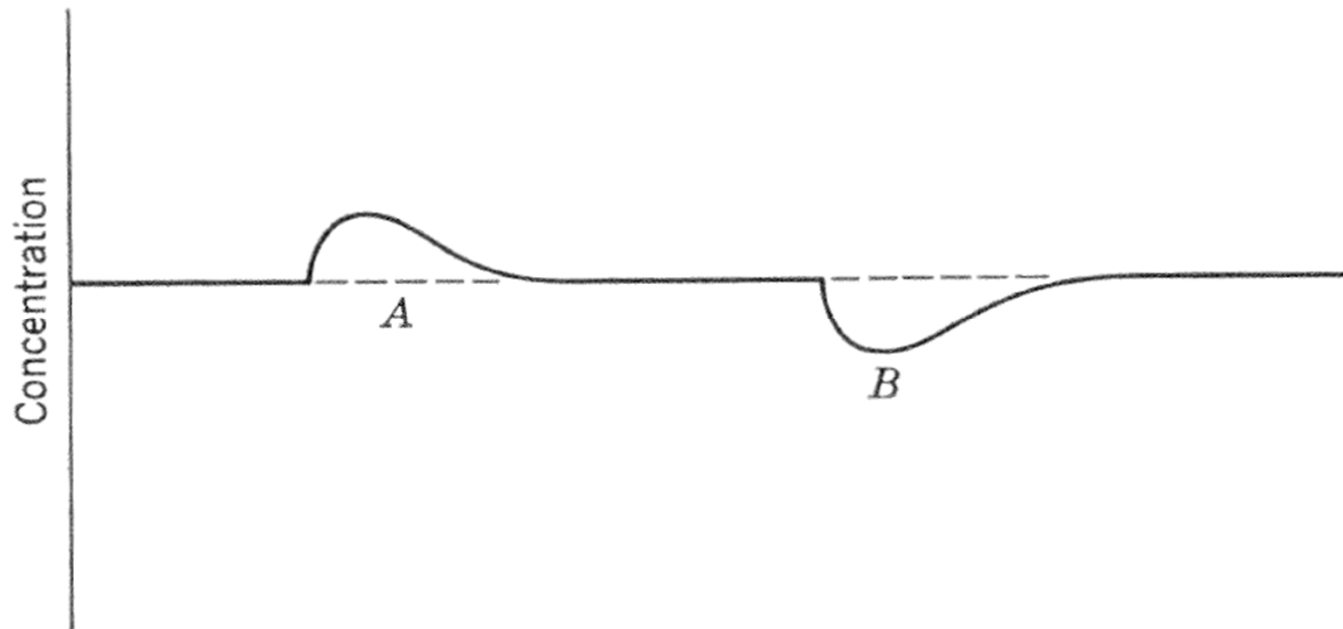


Fig. 5.13. solute distribution following changes in speed of solidification (A) Increase; (B) Decrease.

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 solidus temp. for the original liquid.**

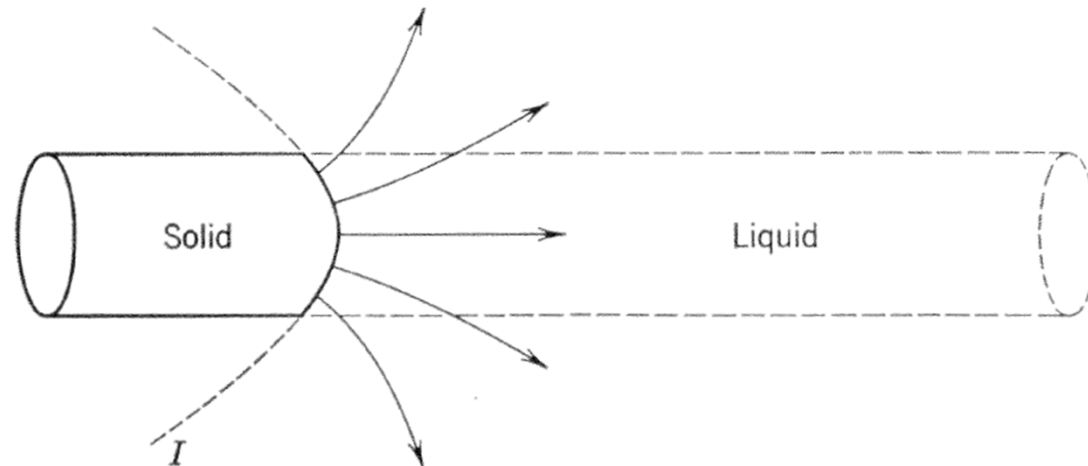


Fig. 5.14. Solute diffusion ahead of a convex interface

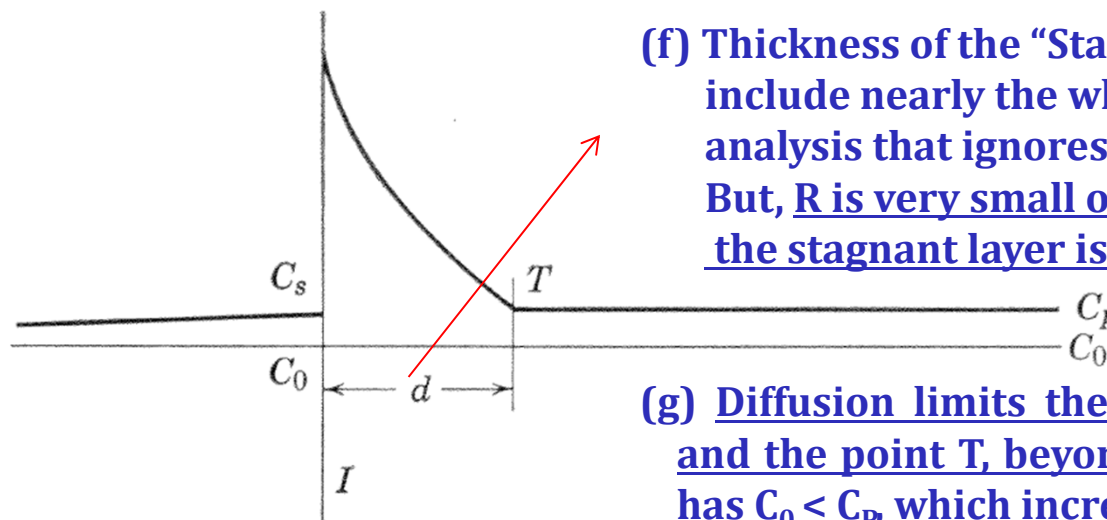
(c) **If concave**, (1) Solid concentration $> C_0$

(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"



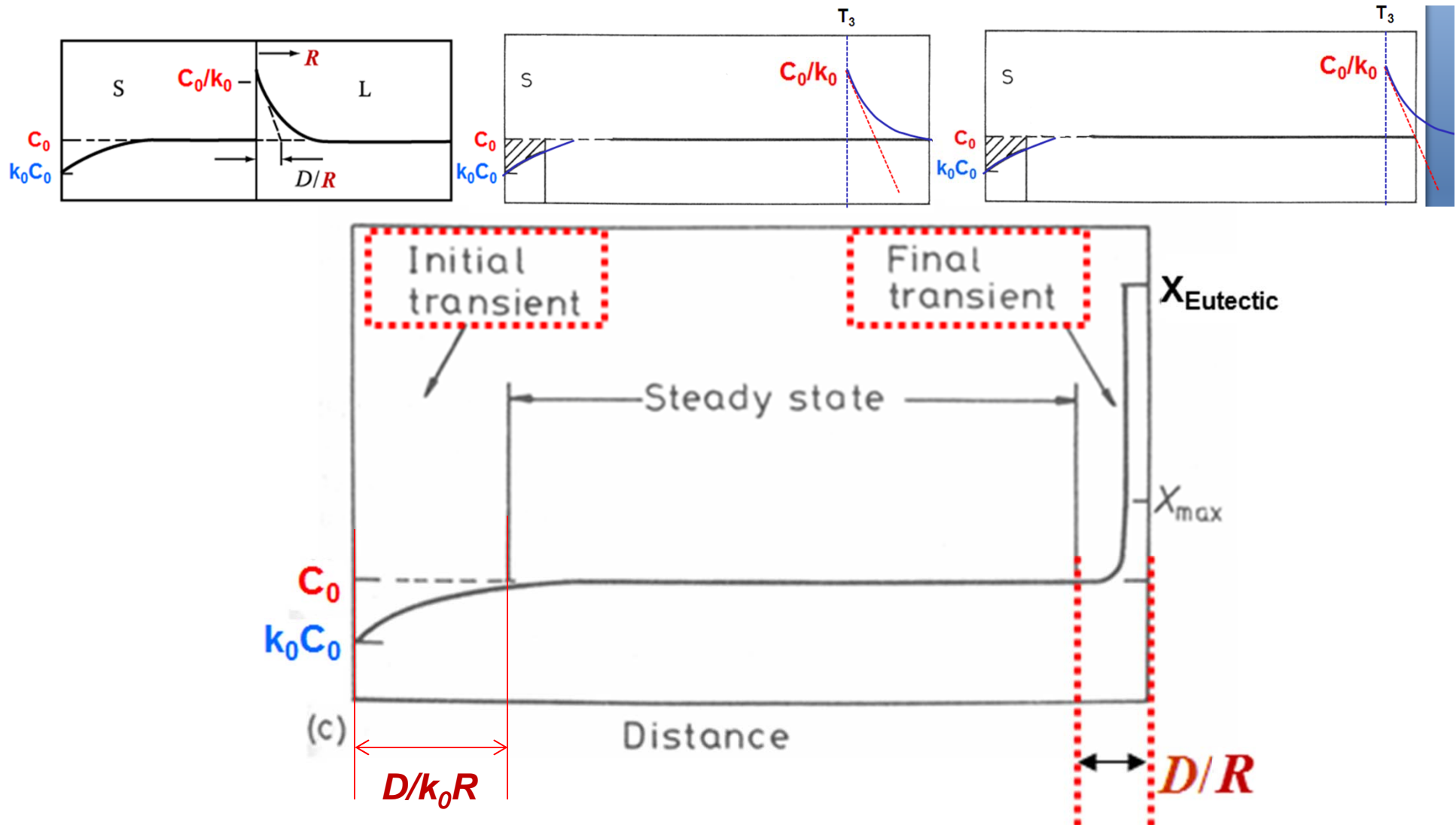
(f) Thickness of the "Stagnant" layer is sufficient to include nearly the whole of the diffusion zone, the analysis that ignores fluid motion is valid. But, R is very small or liquid motion is more violent, the stagnant layer is not thick enough.

(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.

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

"Alloy solidification" - Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid

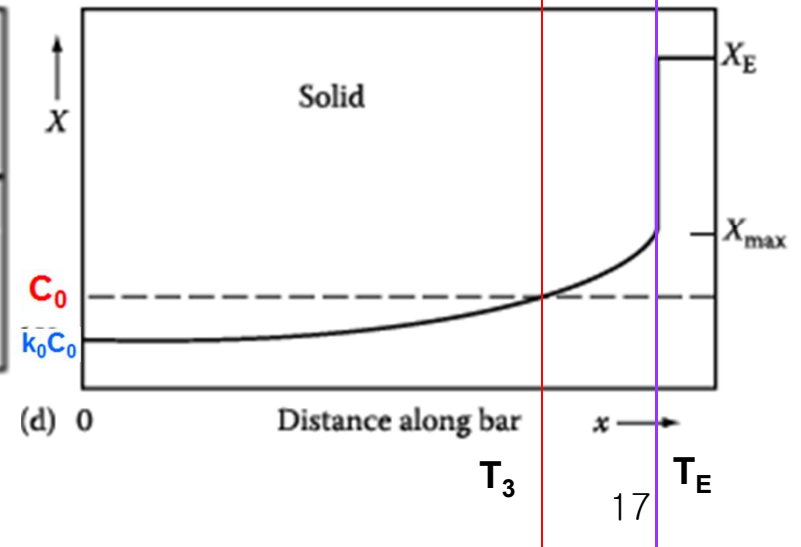
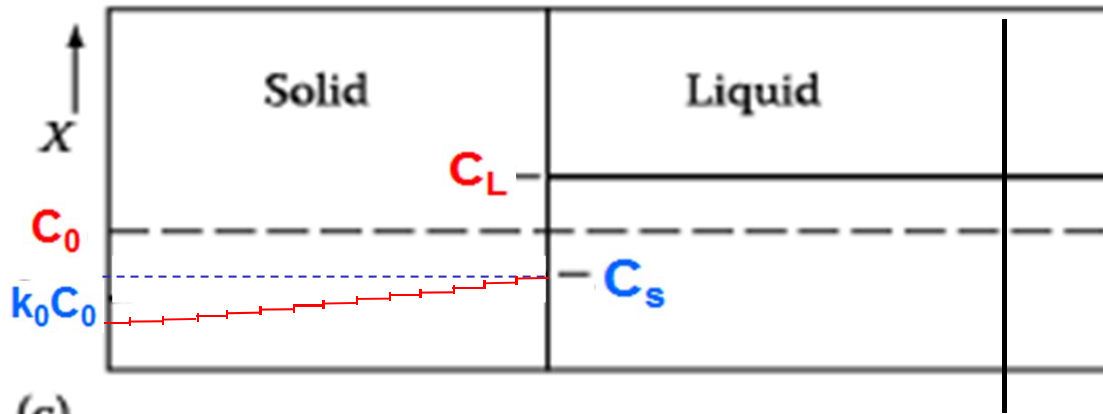
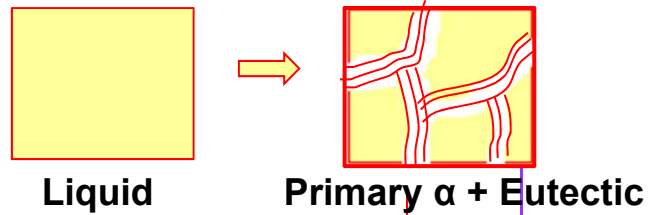
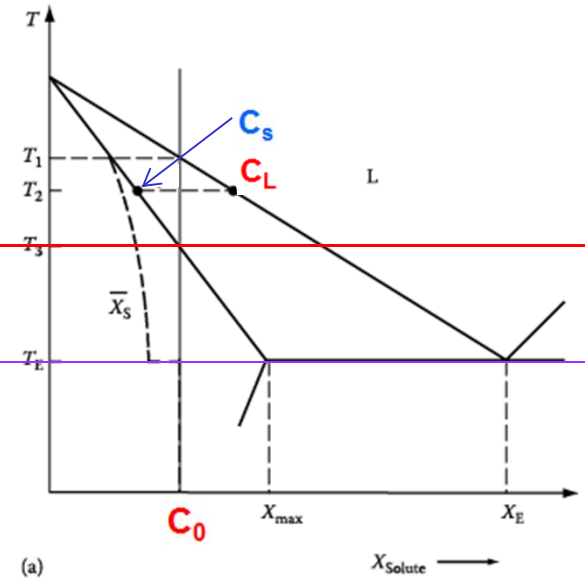
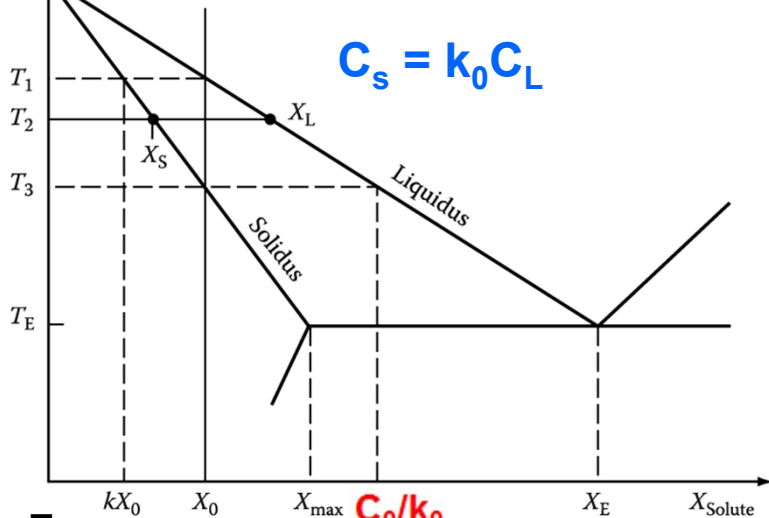


When the solid/liquid interface is within $\sim D/R$ of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation.

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 (\bar{X}_S) < X_S



$solid \rightarrow \bar{X}_S < C_s$

$liquid > C_0/k_0 \rightarrow X_E$

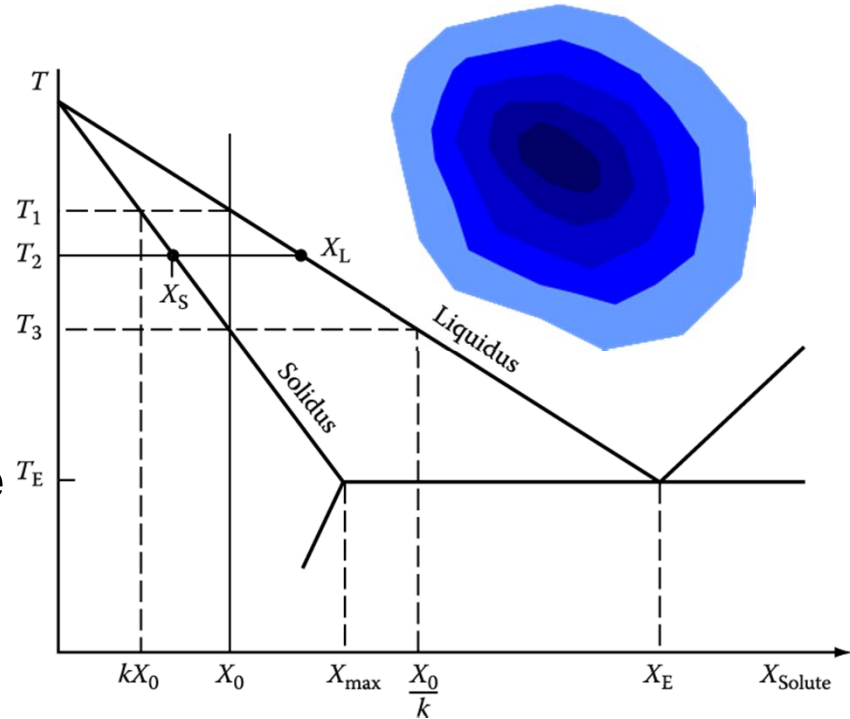
Mass balance: non-equilibrium lever rule (coring structure)

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=?
 solute increase in the liquid=?

→ proportional to what?
 → proportional to what?

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

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

Solve this equation.

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

$$C_S = k_0 C_0 \text{ and } C_L = C_0$$

Initial conditions

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

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

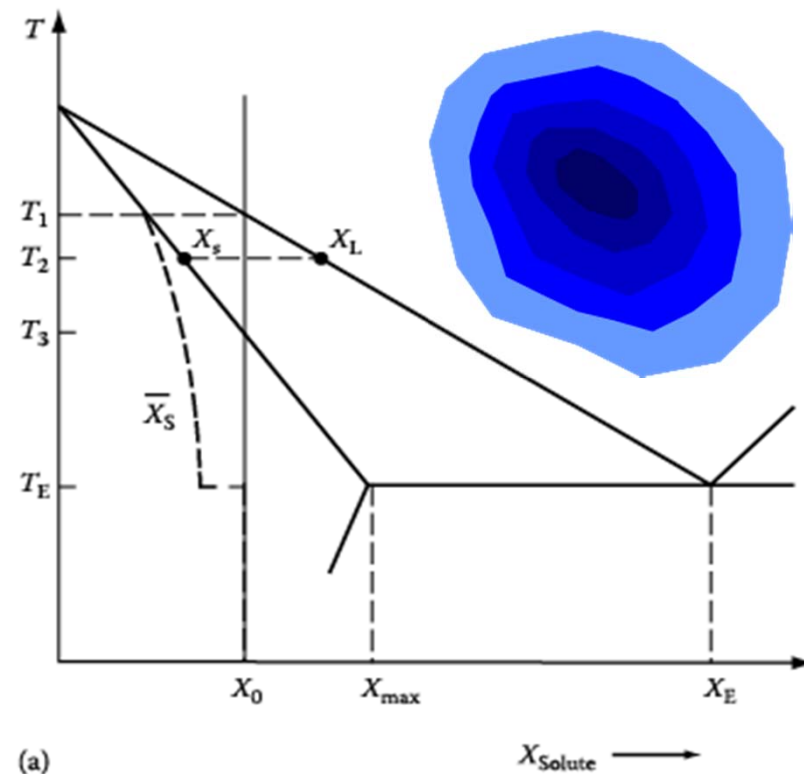
$$\ln \frac{C_L}{C_0} = (k-1) \ln(1-f_S)$$

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

$$C_S = k C_0 (1-f_S)^{(k-1)}$$

**: 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.

$$10^{-3} \text{ cm} < d < 10^{-1} \text{ cm}$$

Very vigorous stirring Natural convention

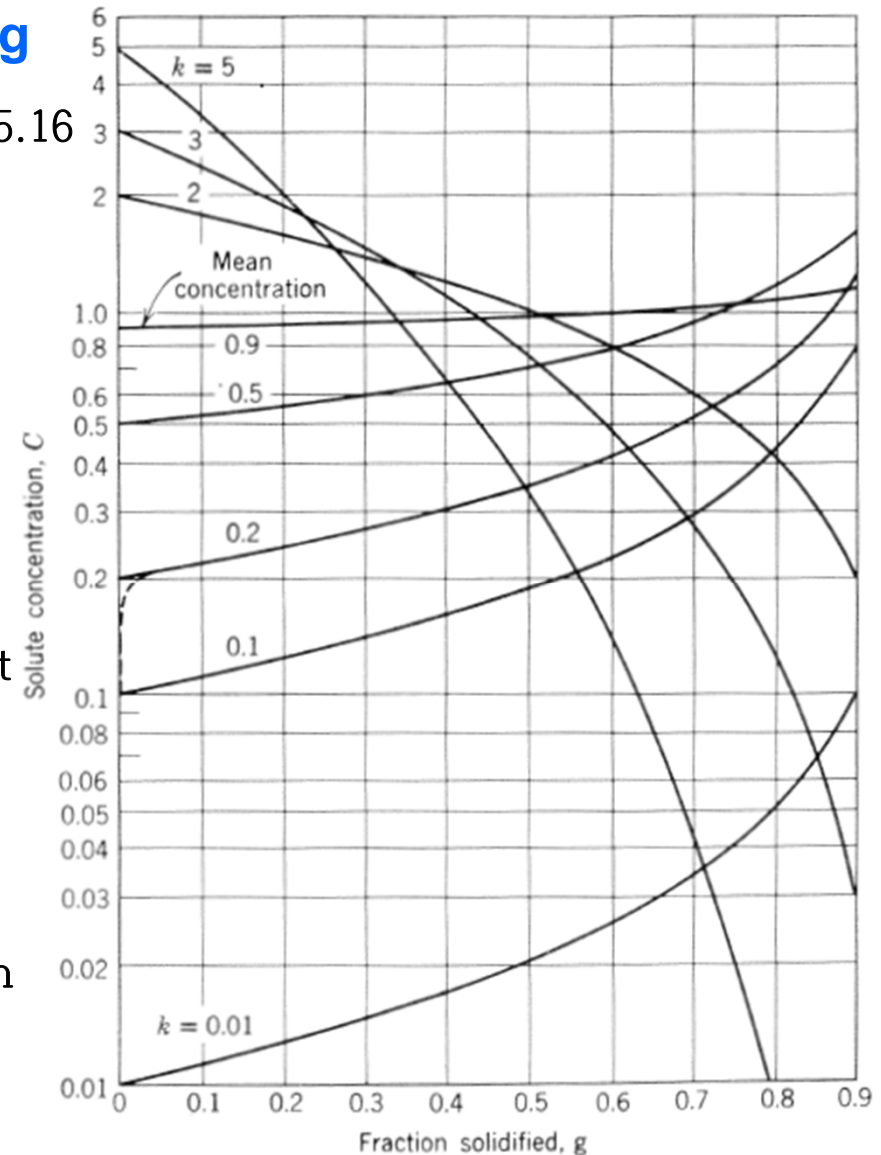


Fig. 5.16. Curves for normal freezing (liquid completely mixed at all times). C_0 is 1 for all curves.

3) Complete or partial mixing of liquid: no diffusion in solid : high cooling rate, efficient stirring

(e)

$$k_0 \leq k_E \leq 1$$

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



Bulk liquid $\sim C_0$ composition due to no mixing

(f) If effectiveness of mixing is increased,

$$k_E \rightarrow k_0 / R \downarrow / d \downarrow / D \uparrow$$

$$R \rightarrow Rd/D$$

(actual growth velocity) (normalized growth velocity)

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

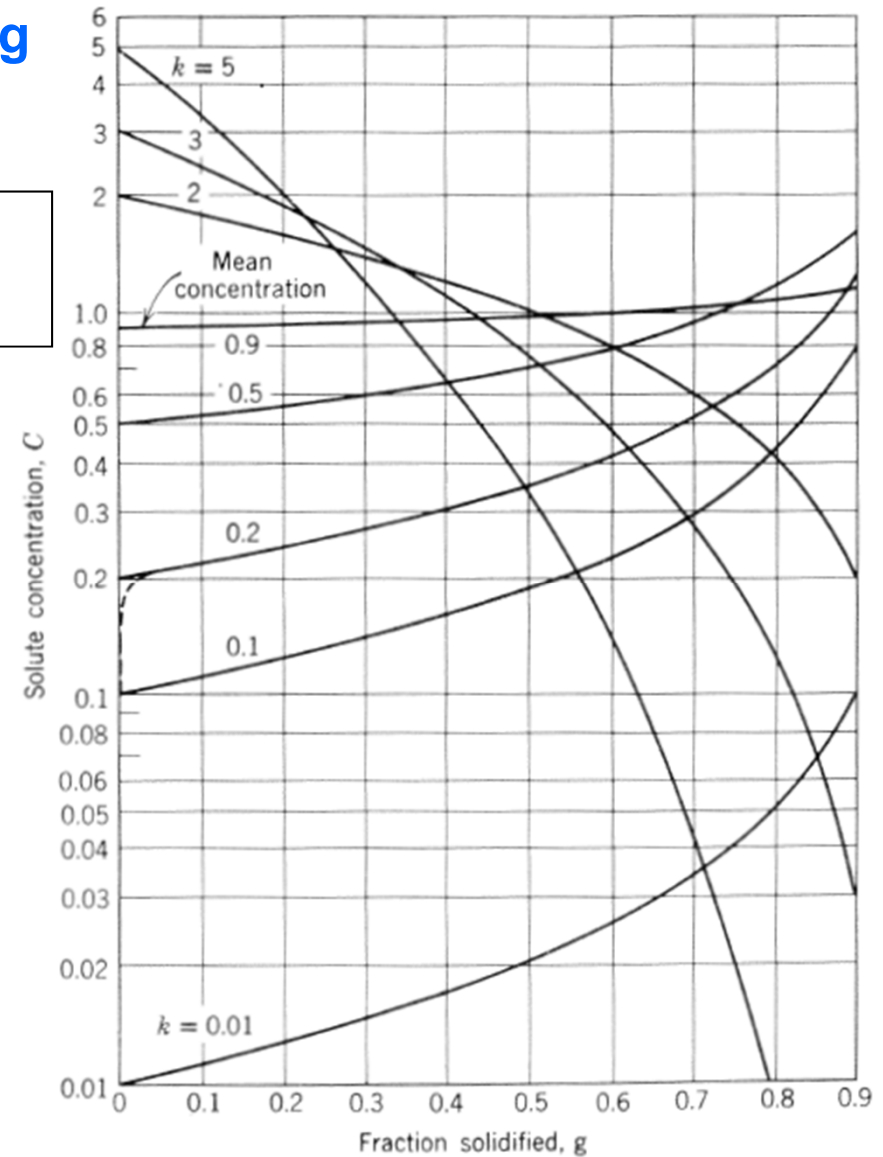


Fig. 5.16. Curves for normal freezing (liquid completely mixed at all times). C_0 is 1 for all curves.

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

- 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.

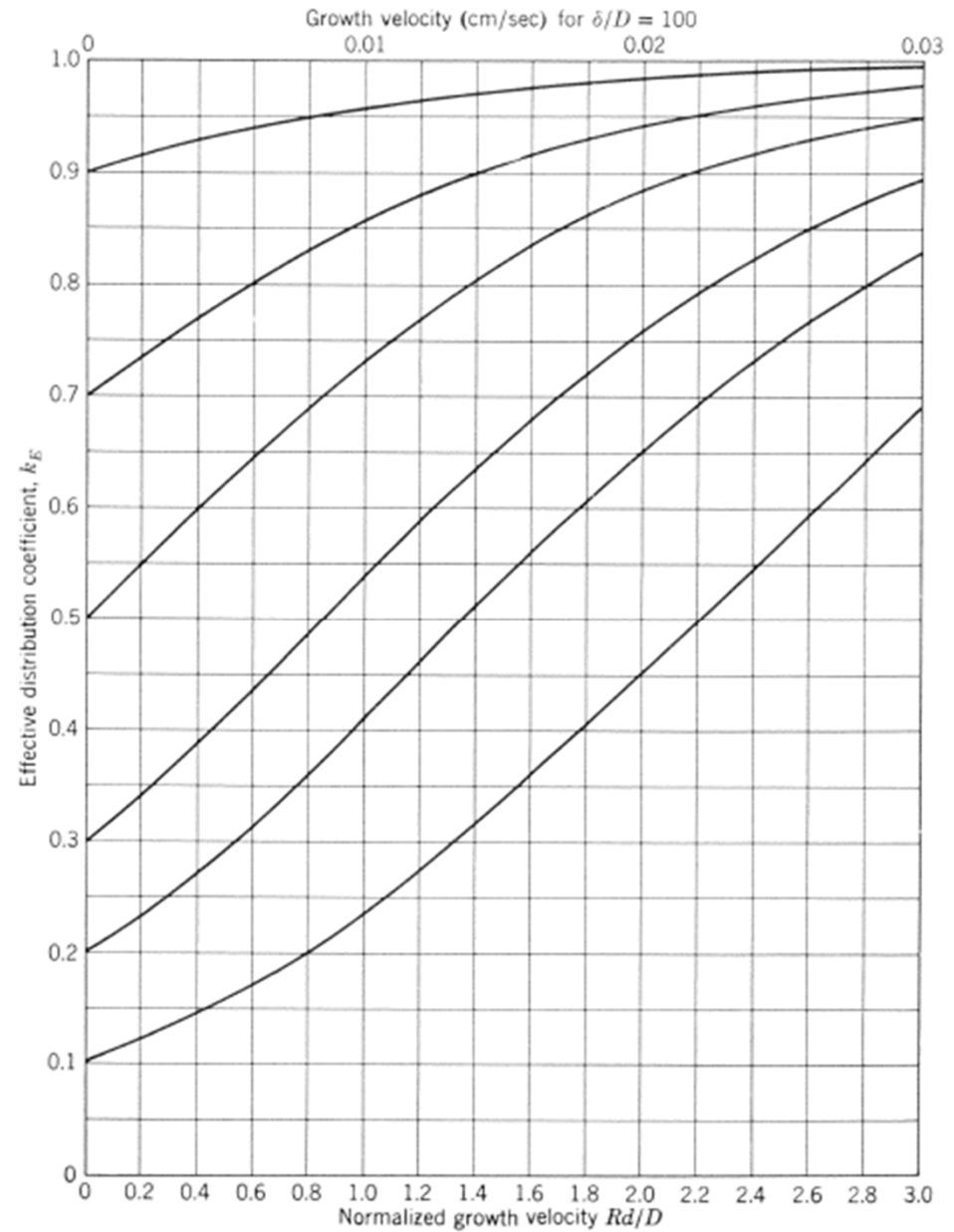
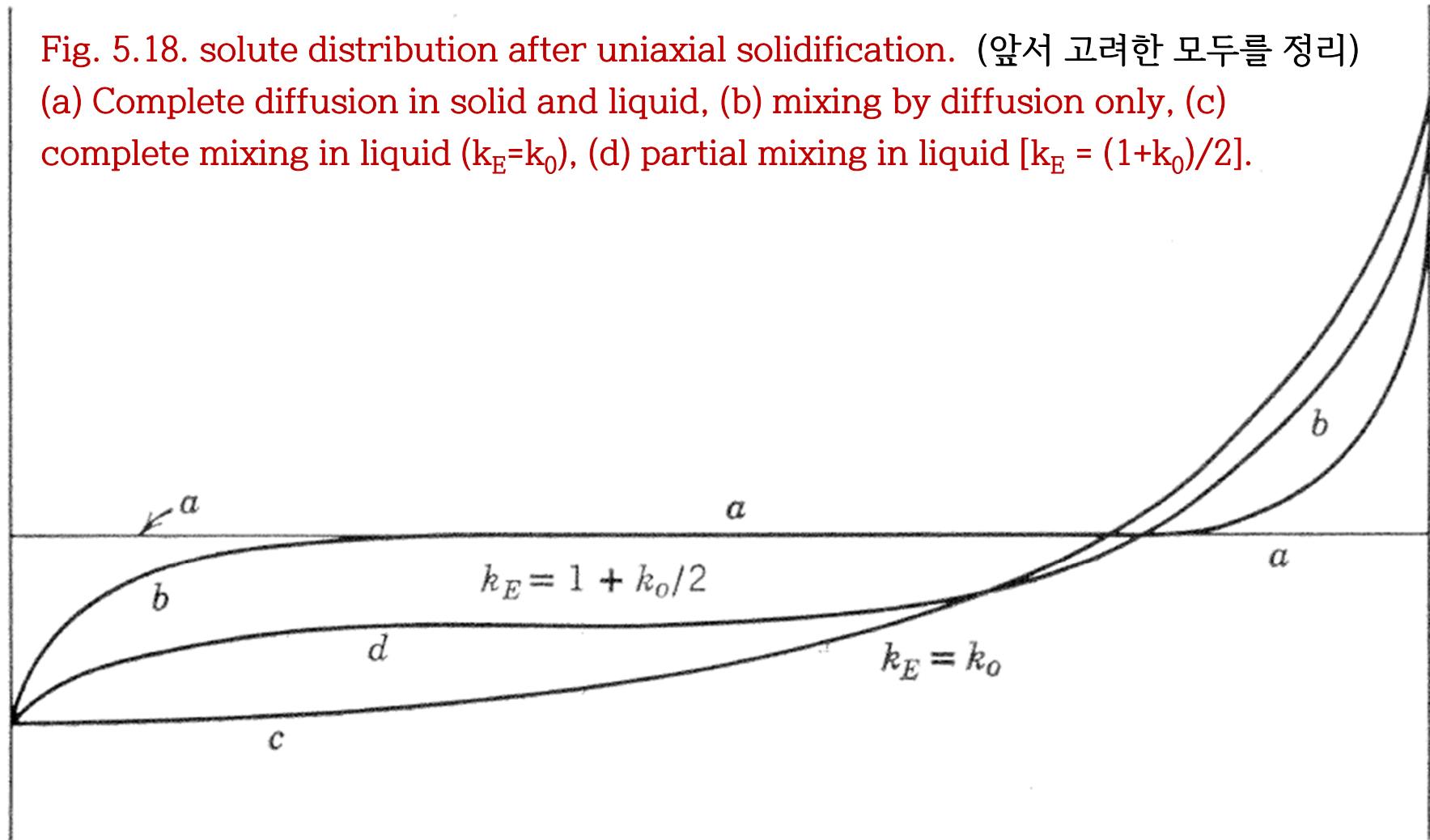


Fig. 5.17. Dependence of effective distribution coefficient on normalized growth velocity (From Ref. 9, p. 14)

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

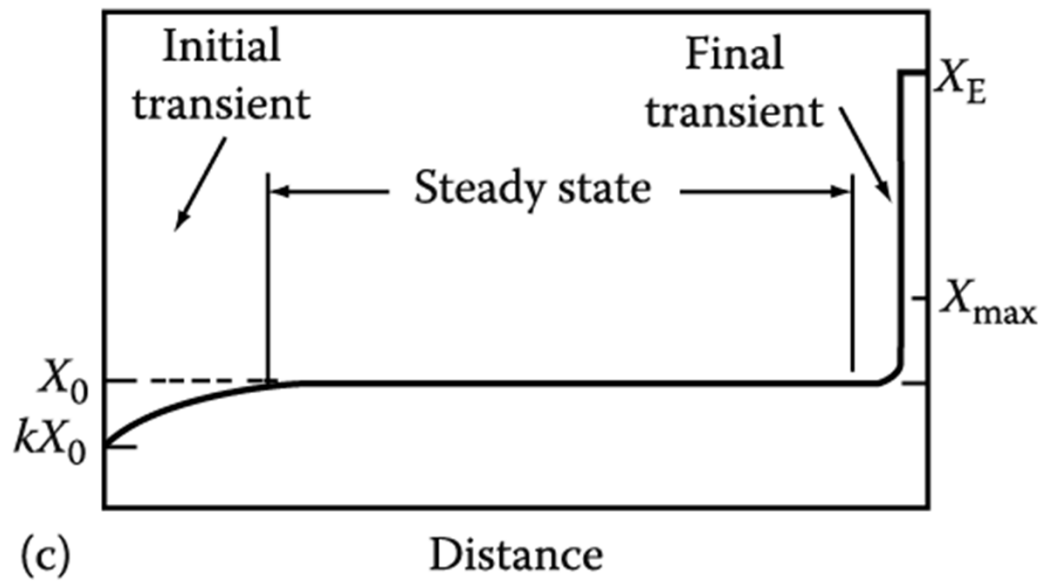
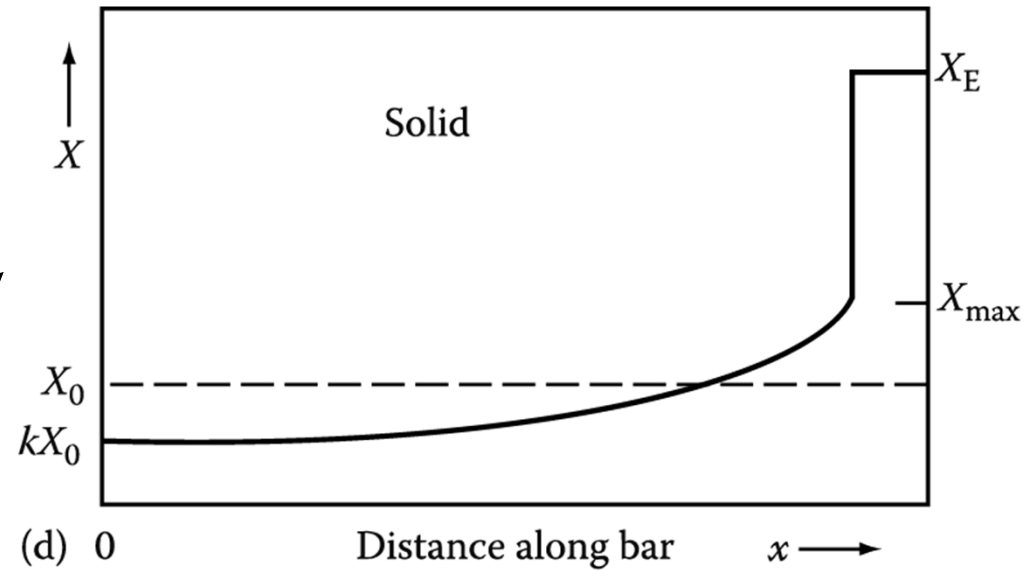
T_L : Solidification start \rightarrow supercooling $\rightarrow T_L$ (recalescence) $\rightarrow T_S$: Solidification finish

Phase diagram \rightarrow determined from cooling curve $\therefore T_L$ 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 \rightarrow 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, $k_0 \sim$ very small ($< 10^{-6}$)
→ Importance of $R/d/D \downarrow$ → Purity \uparrow by multi-stage process

(b) Distribution coefficient $k_0 \sim$ close to 1,
→ Purity \uparrow 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)

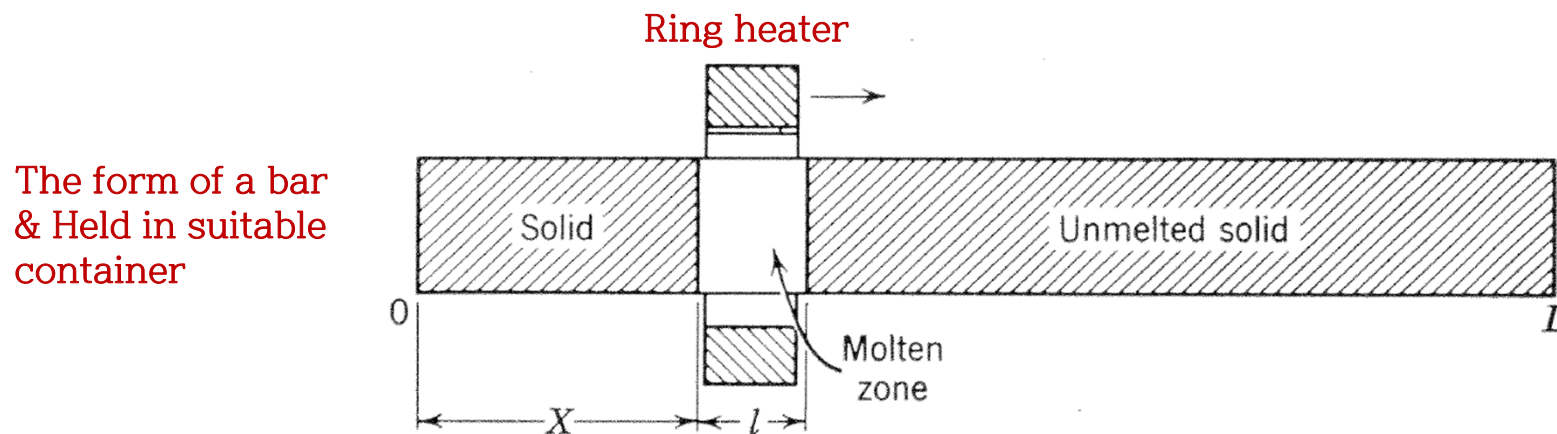
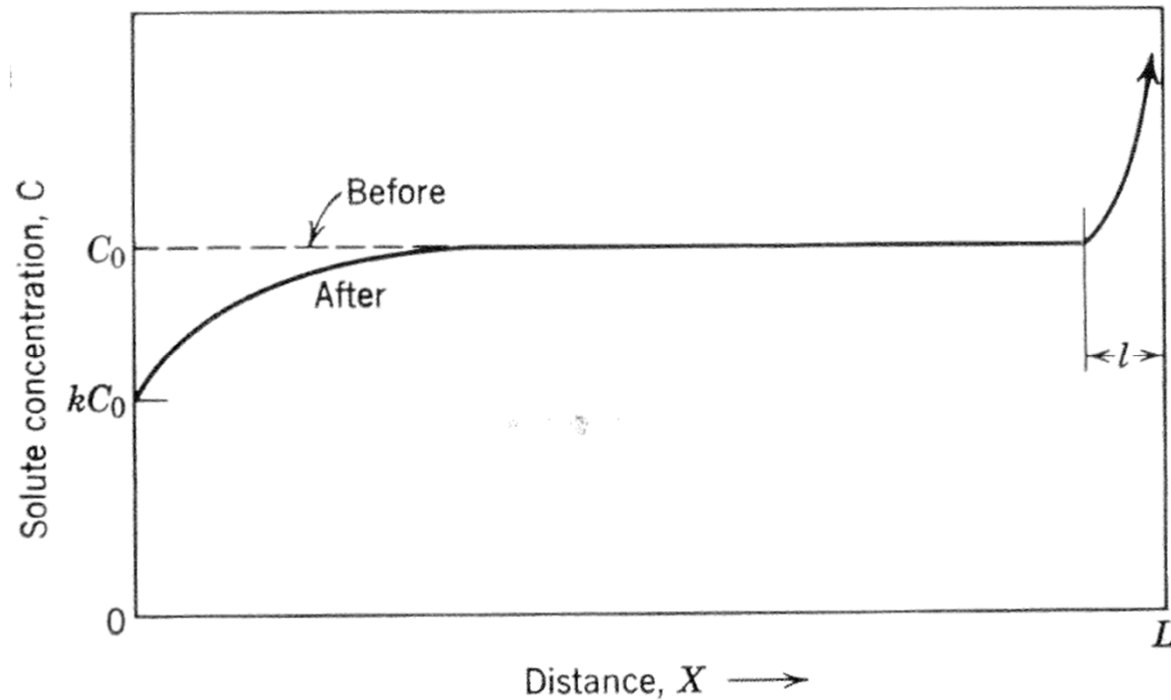


Fig. 5.19. Zone melting, schematic. (From Ref. 9, p. 24.)

- (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 \rightarrow large decrease of solute concentration
 $k_E \sim 1$ (next page): requires a very large # to produce a comparable effect

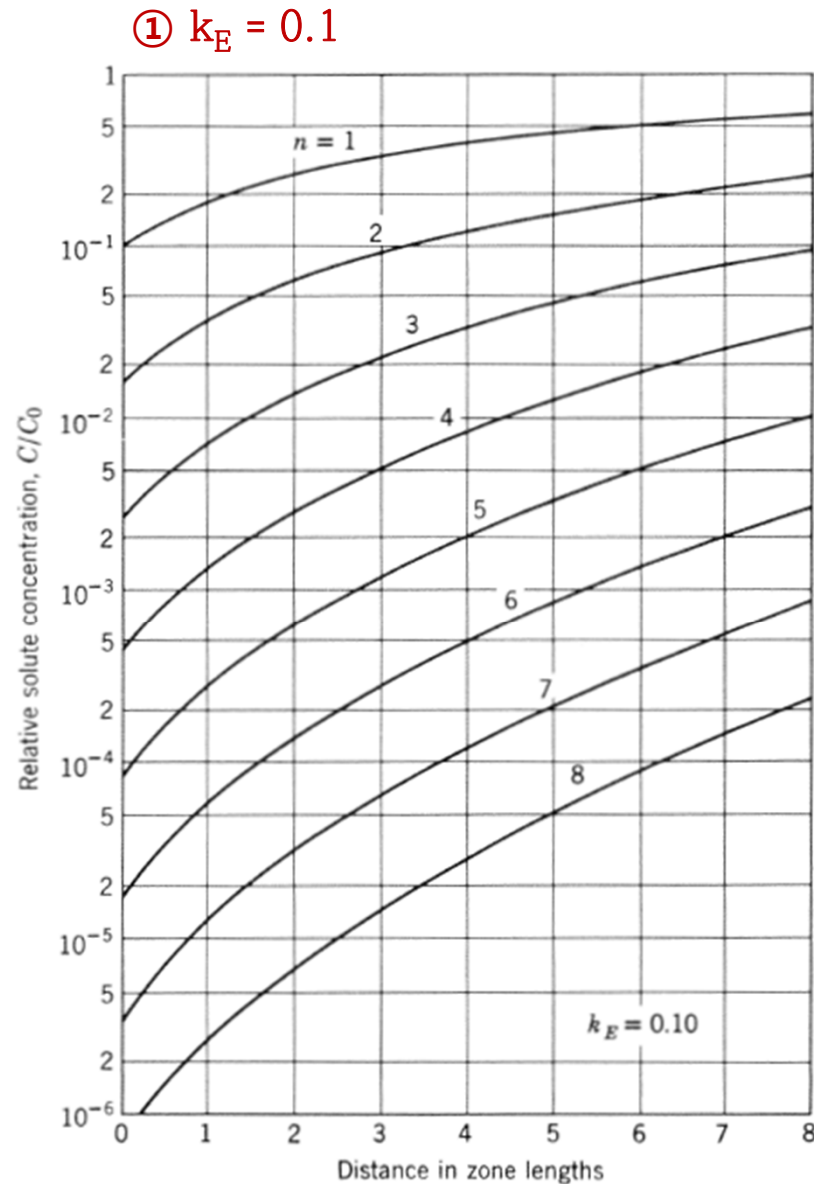


Fig. 5.22. Solute concentration after n zones for $k_E = 0.1$.

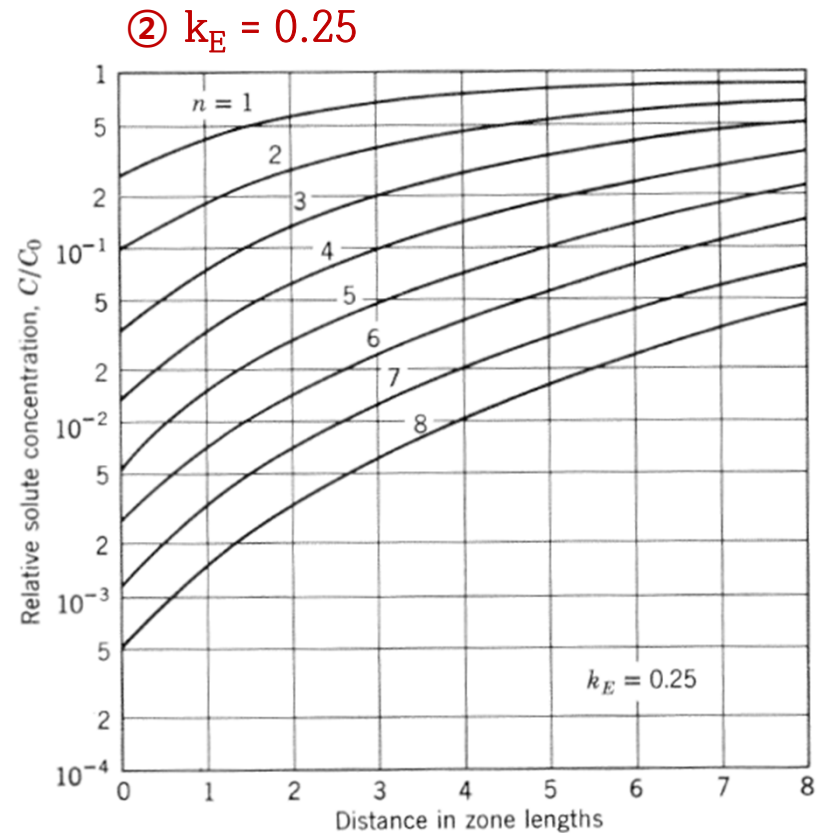


Fig. 5.21. Solute concentration against distance (in zone lengths) after passage of n zones

(c) Effect of k_E on purification: low k_E (left) : small # of pass \rightarrow large decrease of solute concentration
 $k_E \sim 1$: requires a very large # to produce a comparable effect

③ $k_E = 0.9524$

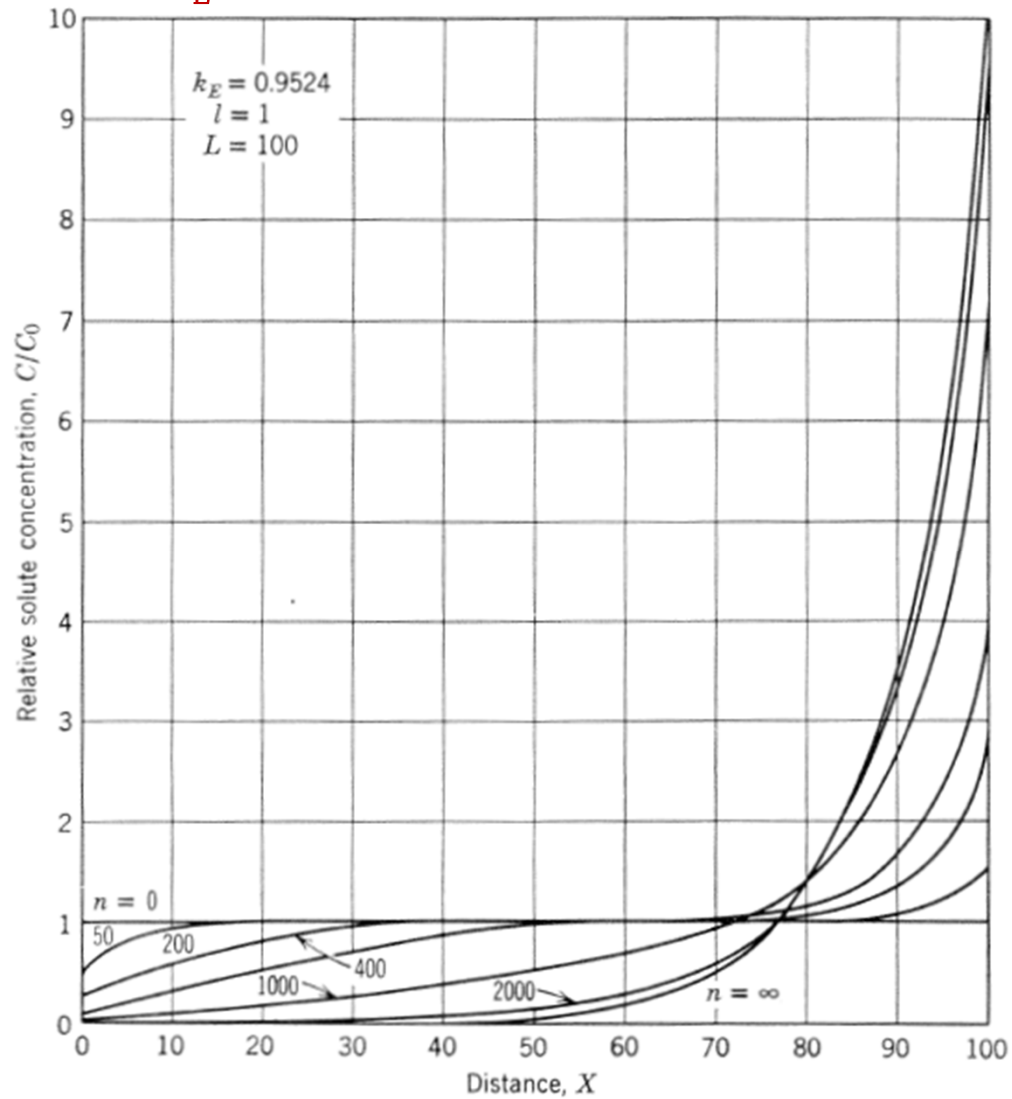
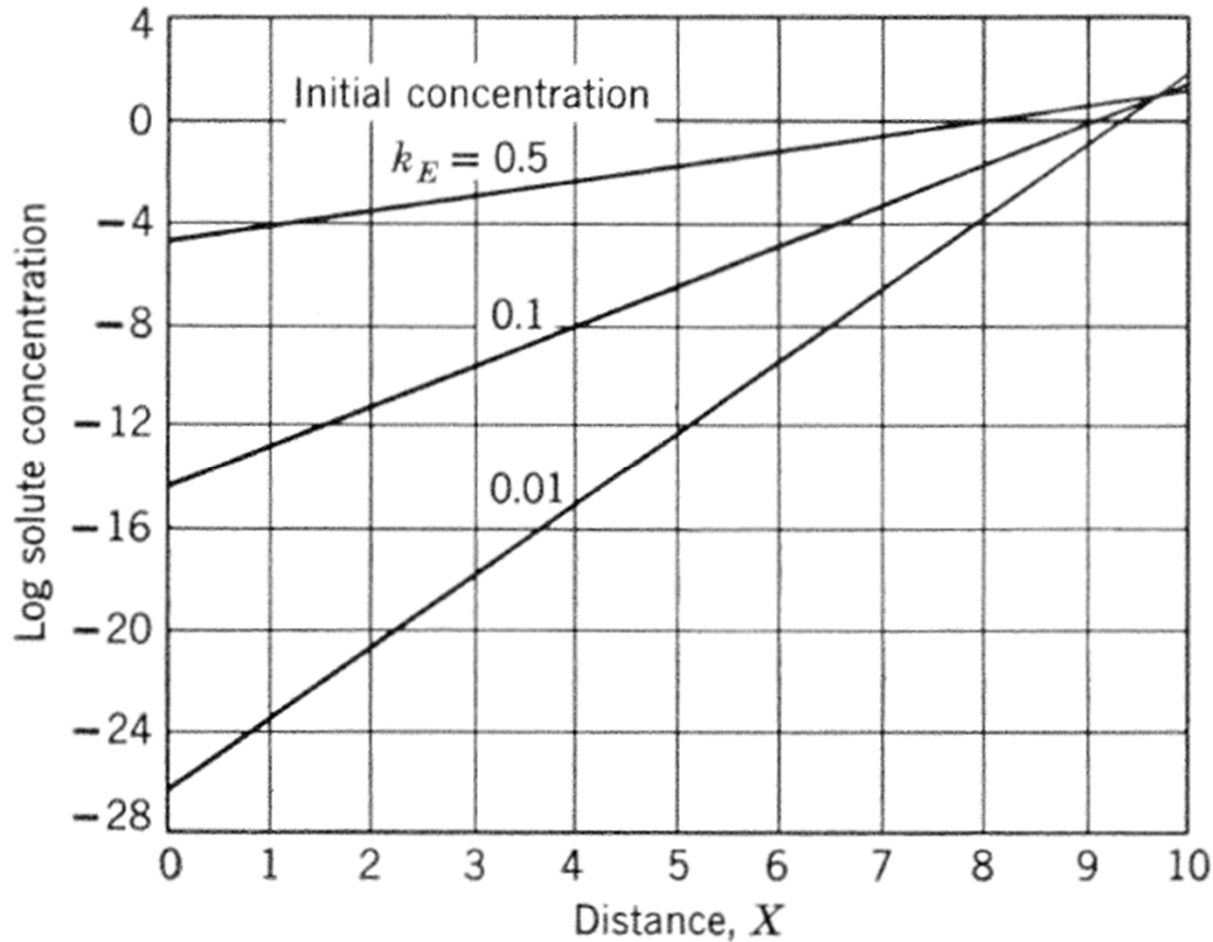


Fig. 5.23. Solute concentration for $k_E = 0.95$.

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)

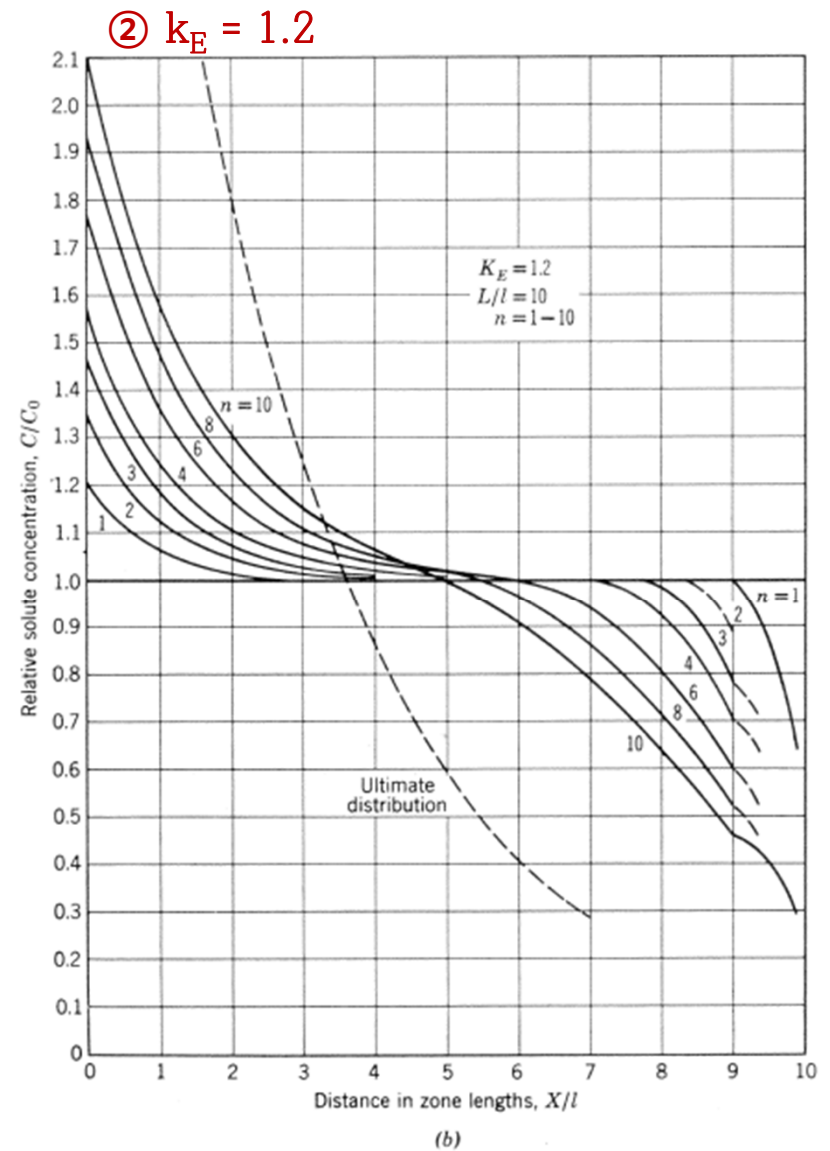
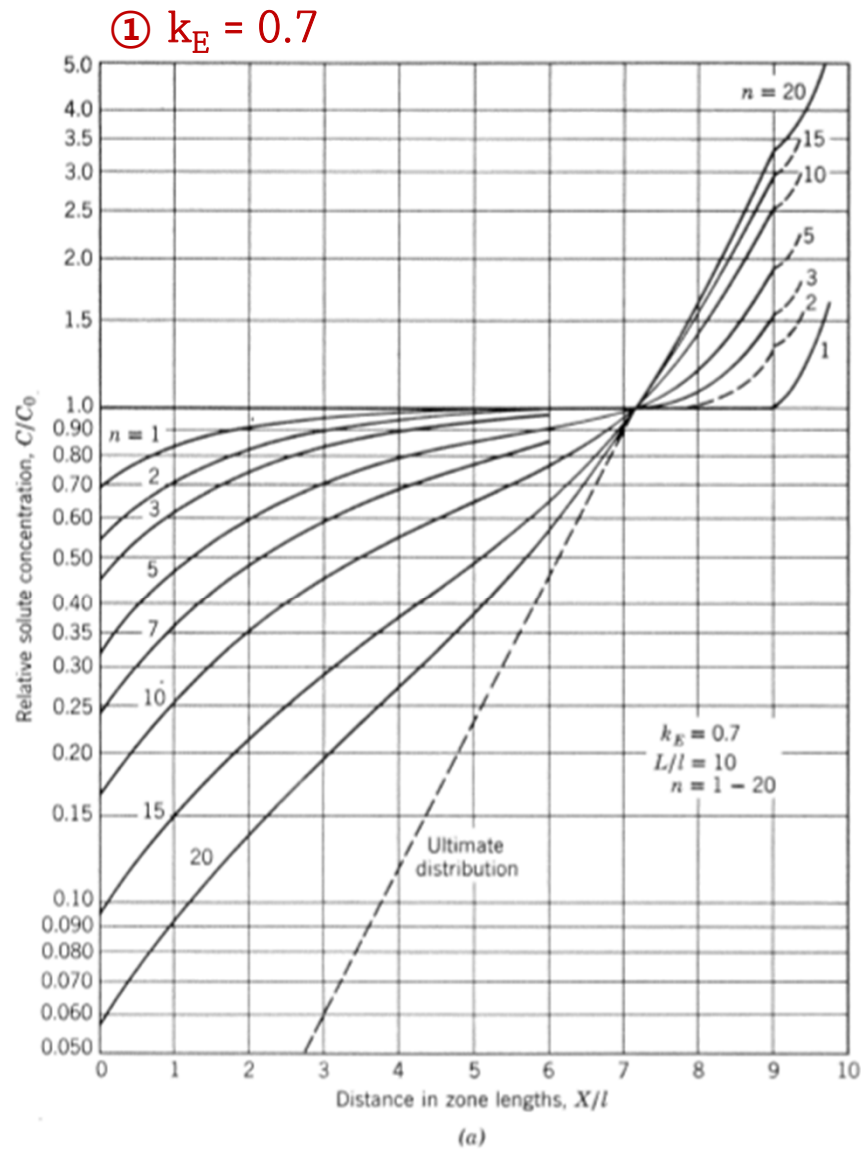


(a) How the ultimate distribution (i.e. when a steady state has been reached) varies with the value of k_E for a bar 10 zones in length.

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, ²⁹ have distribution coefficients greater than 1 & accumulate 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.

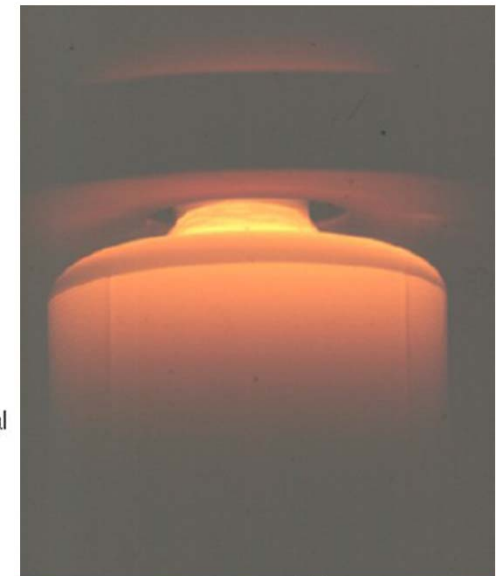
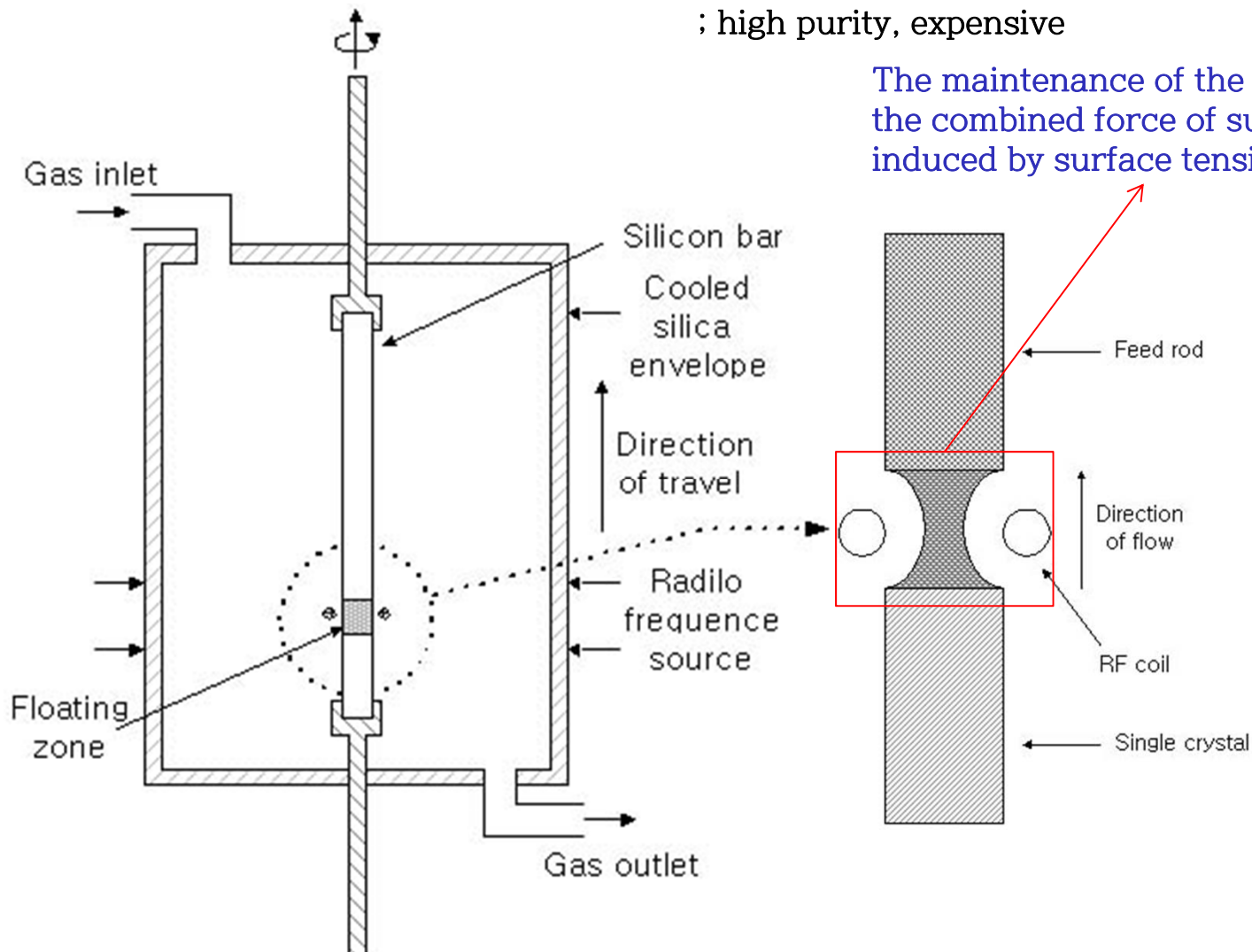


* When purifying through zone refining, metals with high reactivity and high T_m should be carefully considered for contamination especially from containers. → This problem is minimized by using the various floating zone methods described below.

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

; high purity, expensive

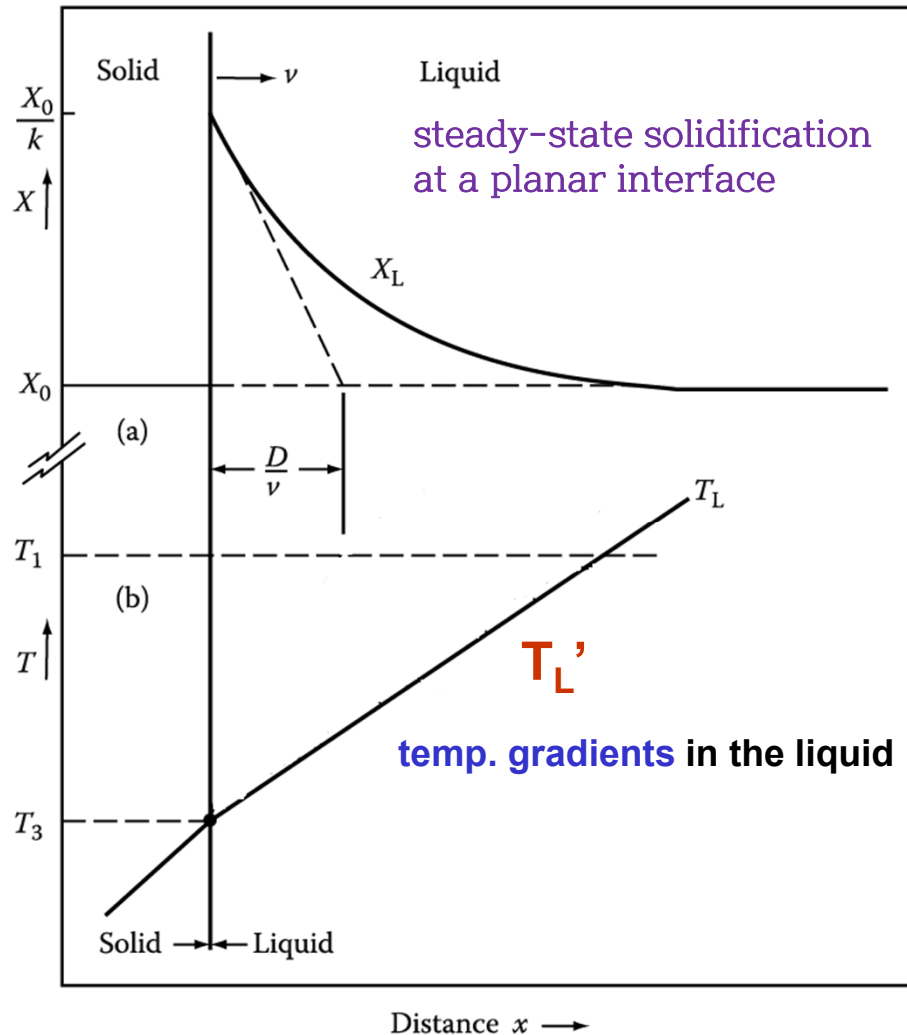
The maintenance of the molten zone is possible by the combined force of surface tension or stress induced by surface tension and electromagnetic.



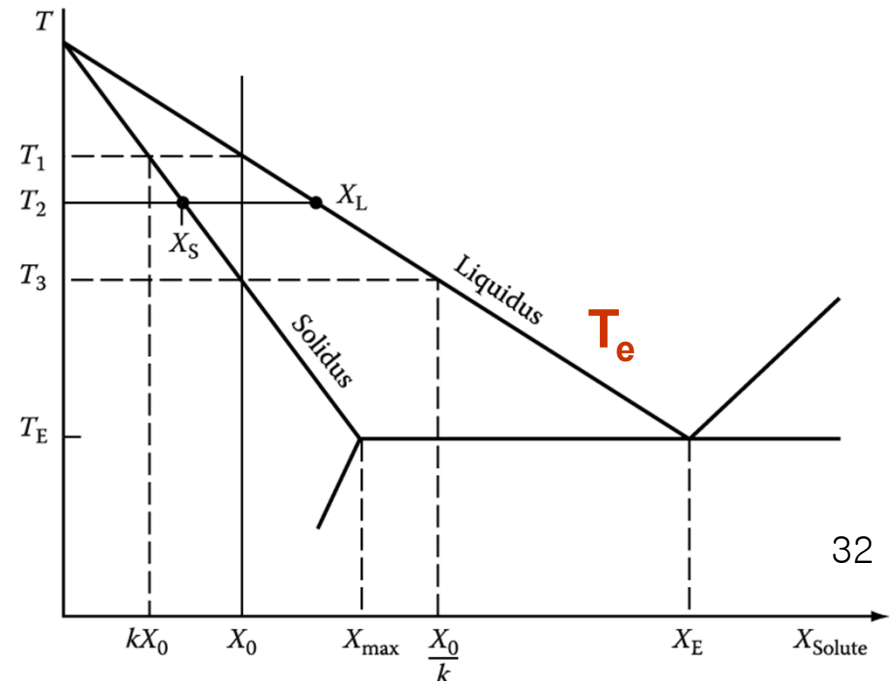
* Cellular and Dendritic Solidification

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.

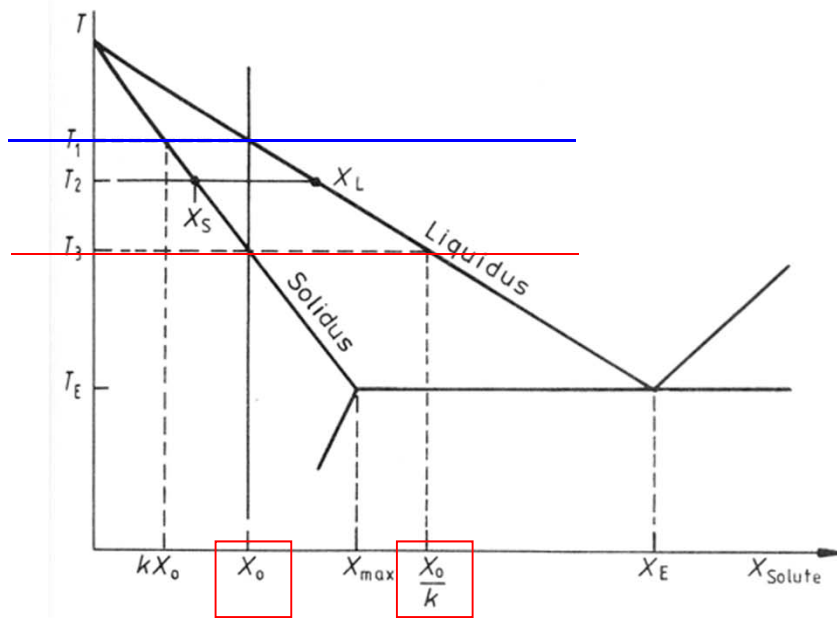


What would be “ T_e ” along the concentration profile ahead of the growth front during steady-state solidification?



* Constitutional Supercooling

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

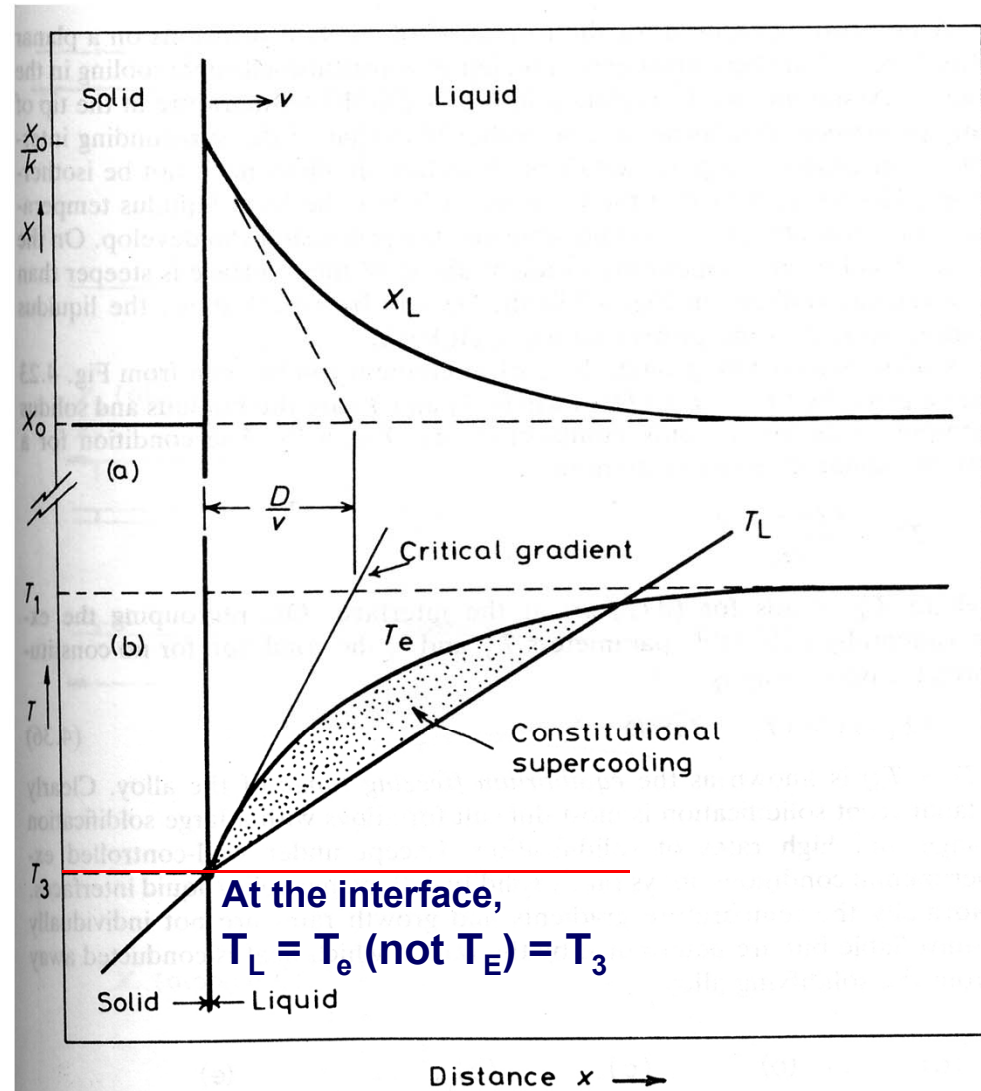


* Actual temperature gradient in Liquid

$$T_L'$$

* equilibrium solidification temp. change

$$T_e$$



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