2018 Fall

Advanced Solidification

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Contents for previous class

Chapter 2

Solidification as an Atomic Process

*** Solid versus Liquid**

*** Free surface (solid/vapor interface)?**

*** Solid /Liquid Interfaces**

*** Broken bond model → calculation of the E of solid/ liquid interface**

c. The difference between crystals and liquids

1) their behavior when subjected to stress

Liquid

Shape change as response to any shear stress

↔

Crystal

Elastically deformed

2) Volume change

vibration **2/3kT, ν** **Latent heat** **2/3kT, ν**

→ **relocation of the atom in positions with higher potential E**

Liquid

Less close packed (or more "open") structure

↔ **ΔV**

Crystal

Close-packed or nearly close packed structure

→ **"+" : all metals except gallium and bismuth**

("borderline" case for classification as metals)

→ **"-" : Silicon and germanium**

d. Quasi-chemical approach

Page 25

* Solid: force between pairs of atoms

→ vaporize: break all “pairwise” bonds

For, example: Copper (Cu)

Vaporization | **Melting**

Heat of vaporization 80 Kcal/mole vs Heat of fusion 3.1 Kcal/mole

⟷

25 times → 1/25 broken

Melting: each bond is replaced by one with 4 percent less E,

although bond energy of liquid is changed by the positions.

→ Heat of fusion during melting: need to generate weaker liquid bonds

Q: Free surface (solid/vapor interface)?

(a) E_{SV} vs γ ?

Extra energy per atom on surface

Interfacial free energy

- The measured γ values for pure metals near the melting temperature (γ_{SV})

$E_{SV} = 3\,\varepsilon/2 = 0.25\,L_S/N_a$ ⇨ $\gamma_{SV} = 0.15\,L_S/N_a$ J / surface atom

(¼ of L_s/N_a) (∵ surface free E averaged over many surface plane, S effect at high T)

(b) Equilibrium shape: Wulff surface

: Polyhedron with the largest facets having the lowest interfacial free energy

$$\sum_{i=1}^{n} A_i \gamma_j = Minimum$$

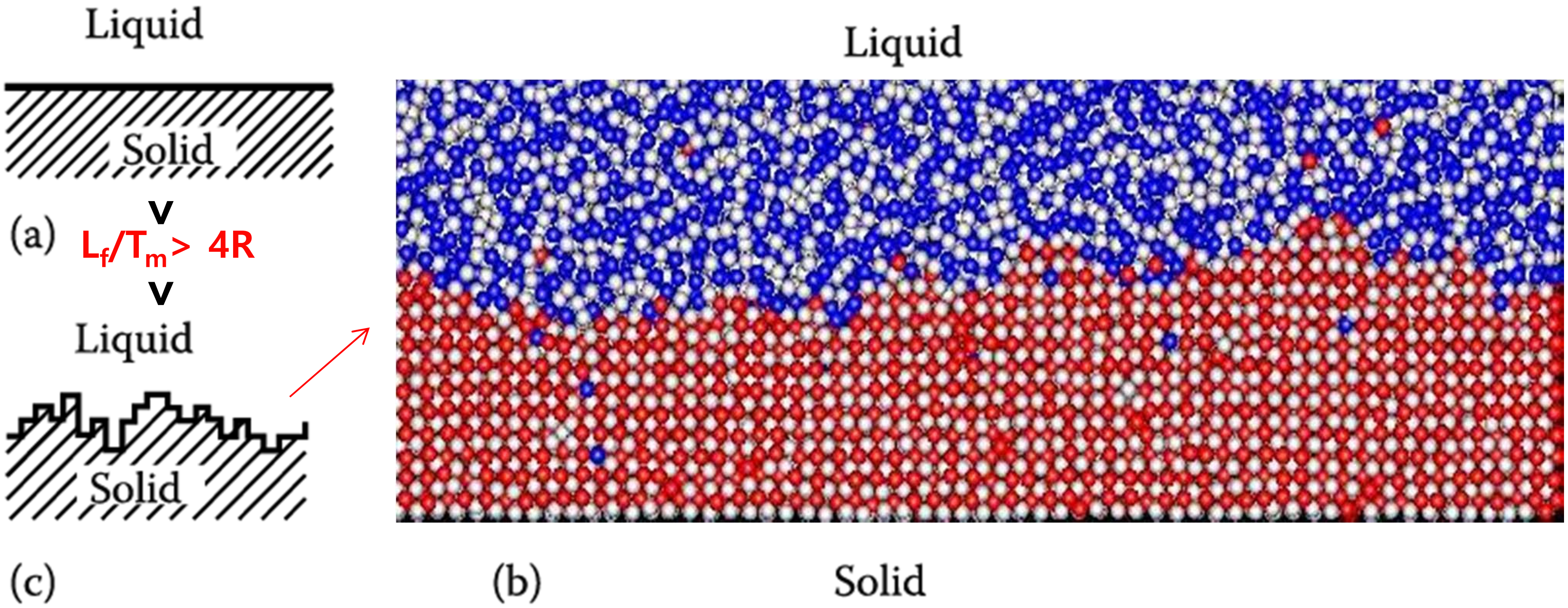
* Solid /Liquid Interfaces

: consequences for the structure and energy of the interface

Faceted interface **Rather narrow transition zone** approximately one atom layer thick

Smooth ~ same as solid/vapor interfaces, i.e., atomically flat close-packed interface

: some intermetallic compounds, elements such as Si, Ge, Sb, and most nonmetals



v

$L_f/T_m > 4R$

v

Fig. 3. 63 Solid/liquid interfaces: (a) atomically smooth, (b) and (c) atomically rough, or diffuse interfaces.

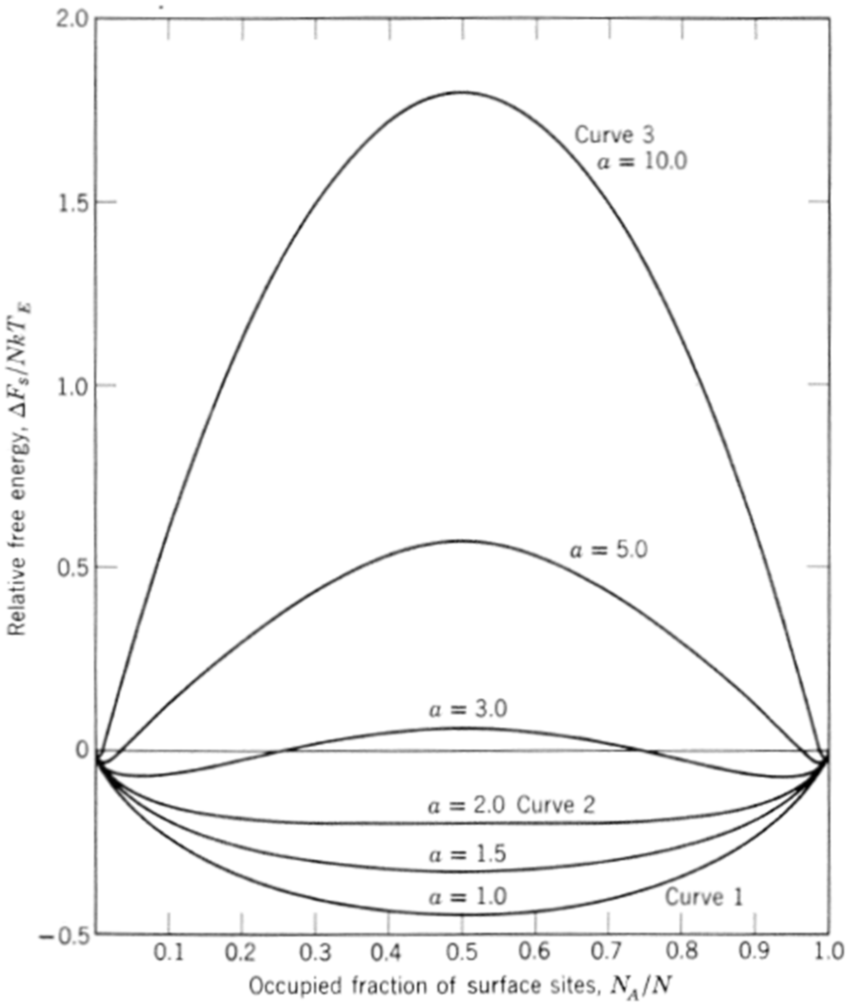
Diffusion interface (non-faceted) **Rather wide transition zone** over several atom layers

: most metals, L_f/T_m ~ R (gas constant) ~automatically **"rough" & diffuse interface**

$$\boxed{\frac{F_s}{NkT_E} = \frac{\alpha N_A(1-N_A)}{N^2} - \ln N(N-N_A) - \frac{N_A}{N}\ln\frac{N-N_A}{N_A}}$$

where

$$\underline{\alpha = \left(\frac{L_0}{kT_E}\right)\left(\frac{\eta_1}{v}\right)}$$



Variation of free energy of interface with fraction of sites filled.

(a) **Minimum of free E at $N_A/N=0.5$ for all values of α less than about 2**

→ **rough interface: stable**

→ **50 percent of the sites being filled**

→ **locally filled → "multilayer"**

(b) **2 minima of free E, one at very small value of N_A/N and the other for a value close to unity for all higher values**

→ **very few sites are filled on a complete layer or almost all sites are filled.**

→ **smooth interface: stable**

* **Parameter α controls the structure of the equilibrium interface.**

a) **L_0/kT_E~ depends on the material, the crystal structure, and on the nature of the adjoining phase**

b) **η_1/v~ depends on the face**

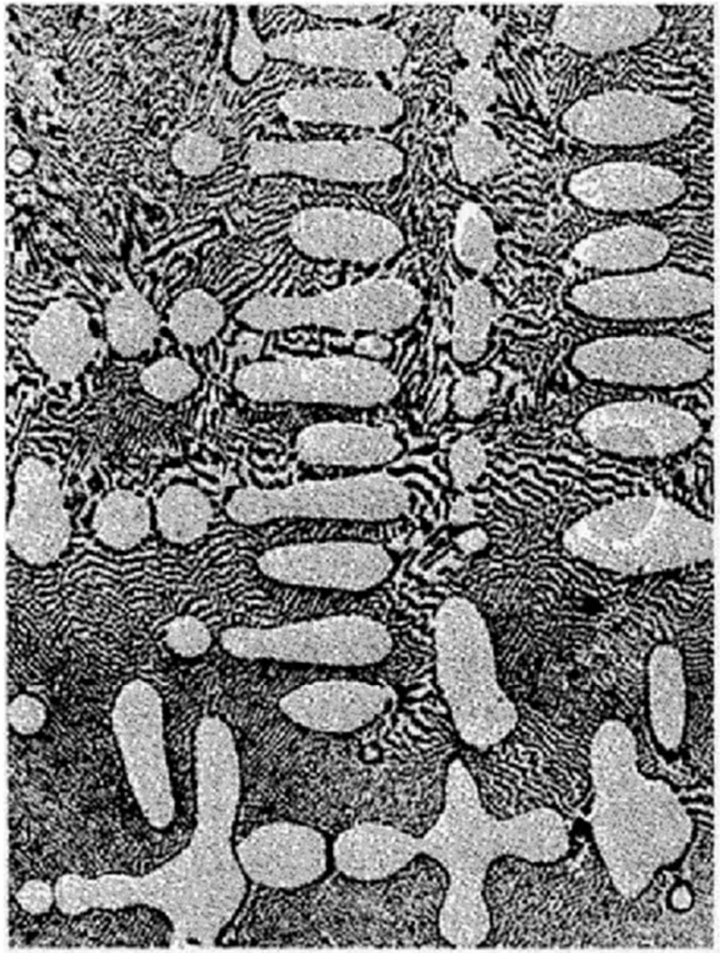
L_0/kT_E ~ less than 2 for all metals, for equilibrium between melt and crystal: typically, 1.2

Since η_1/v ~ necessarily less than 0.5

α melt-crystal interface < α vaper-crystal interface

Ice: α of basal plane > 2/ but α of all other plane should be rough.

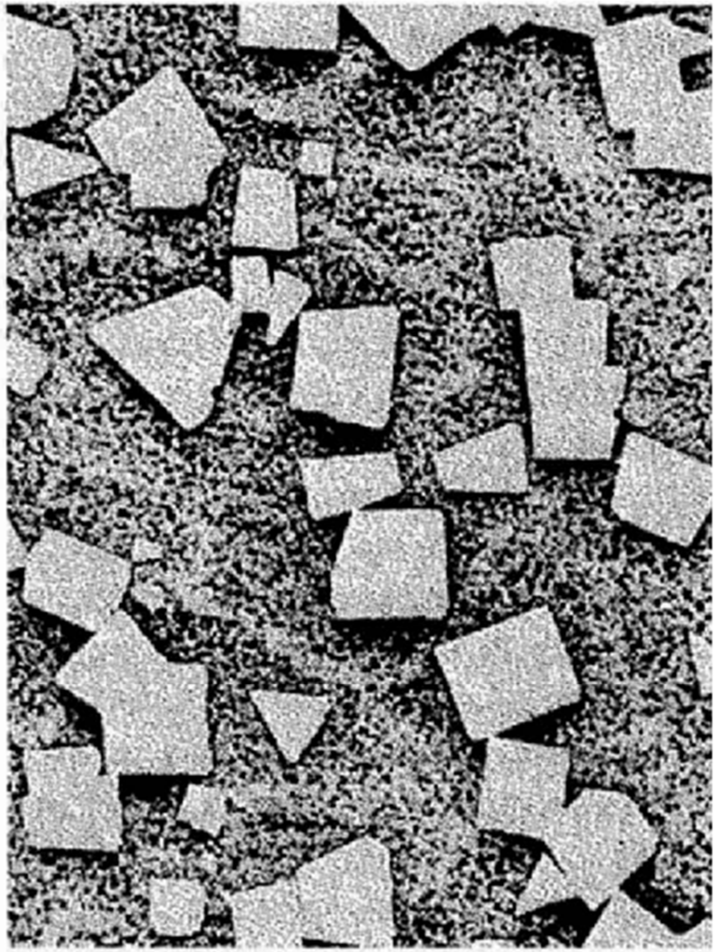
Primary Ag dendrite
in Cu-Ag eutectic matrix



(a) Non-faceted

- Free E ~do not vary with crystallographic orientation
- γ-plot ~ spherical

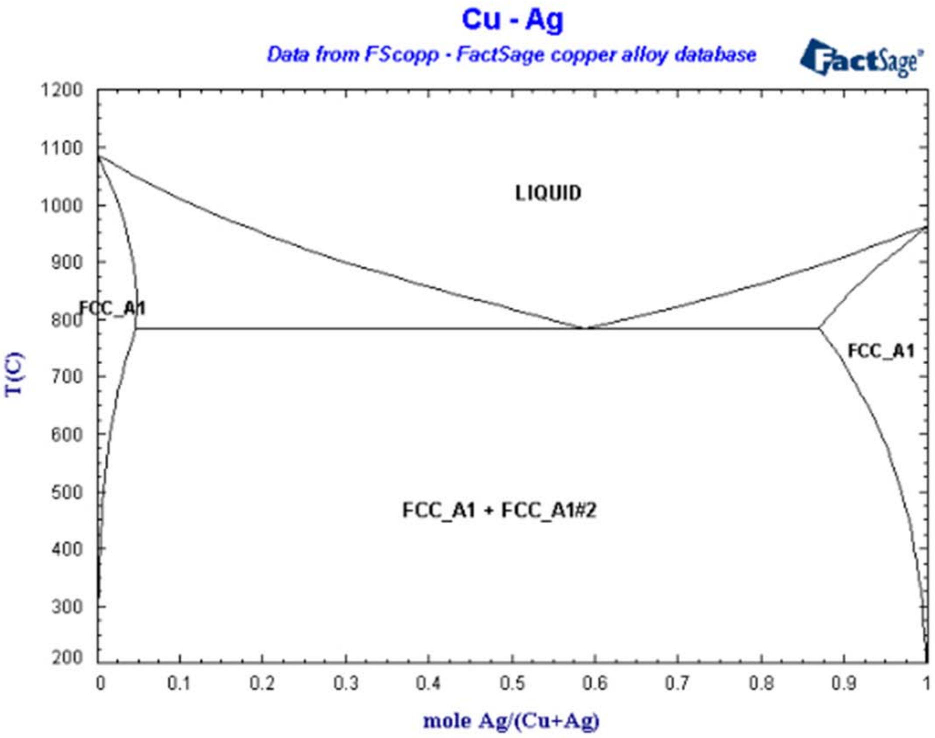
β′-SnSb intermetallic compound
in Sn(Sb) solid solution



(b) Faceted

- Strong crystallographic effects
- Solidify with low-index close-packed facets

Primary Ag dendrite
in Cu-Ag eutectic matrix



β′-SnSb intermetallic compound
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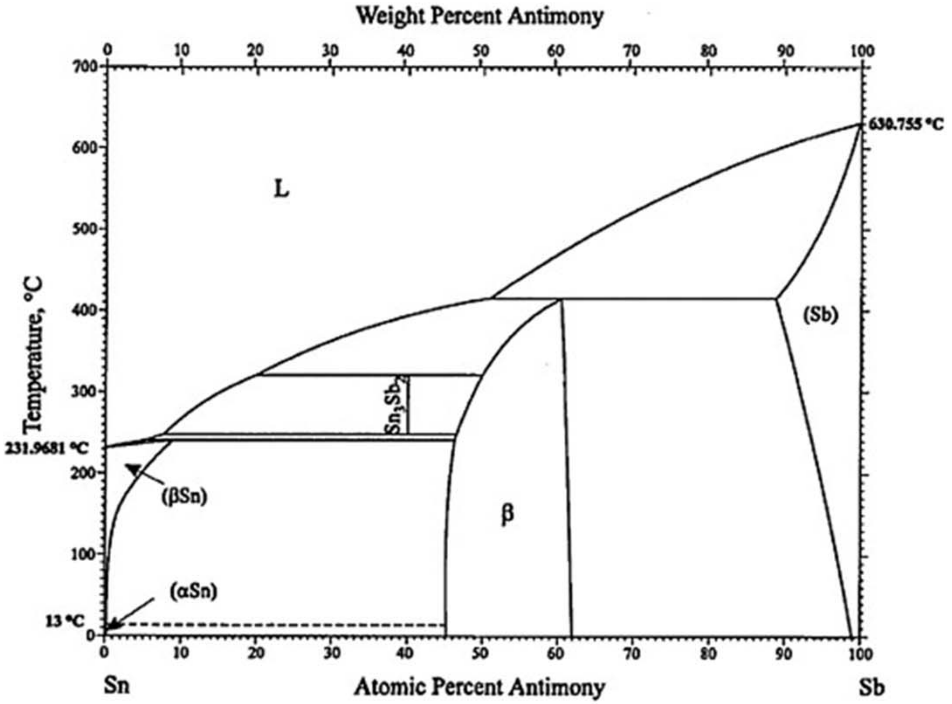
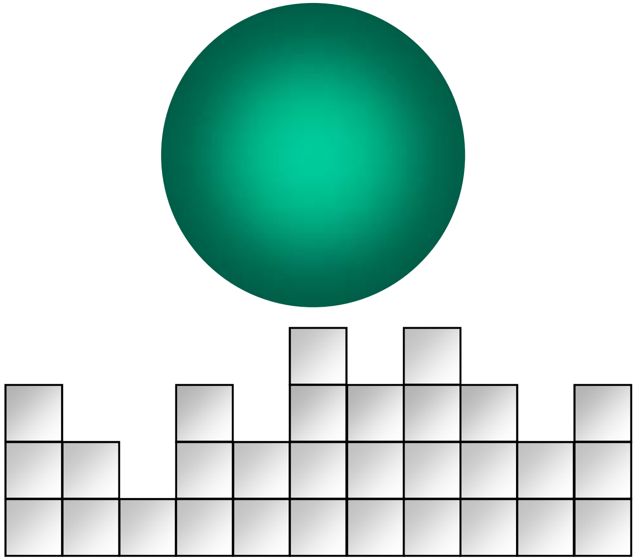
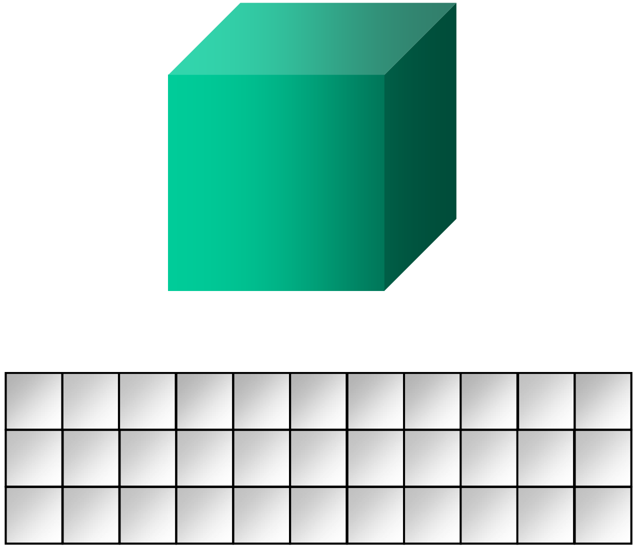


Equilibrium Shape and Interface Structure on an Atomic Scale



atomically-disordered

Ex) metallic systems



atomically-flat

nonmetals

Apply thermodynamics to this fact and derive more information.

Entropy-dominant

weak bonding energy

stable at high T

←

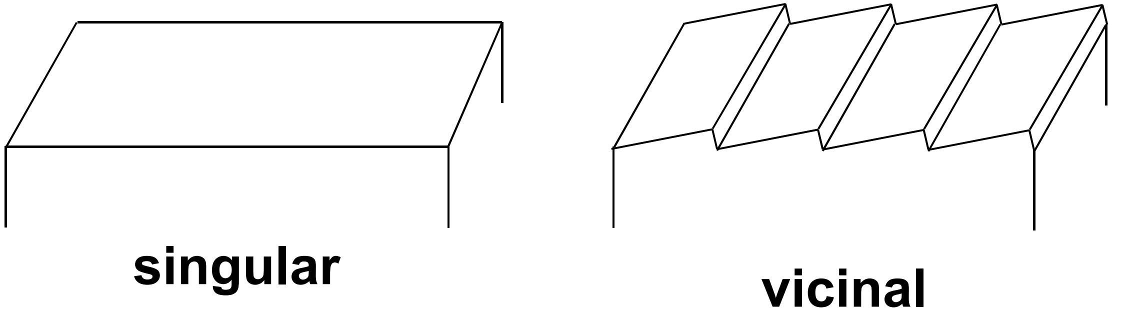
Enthalpy-dominant

strong bonding energy

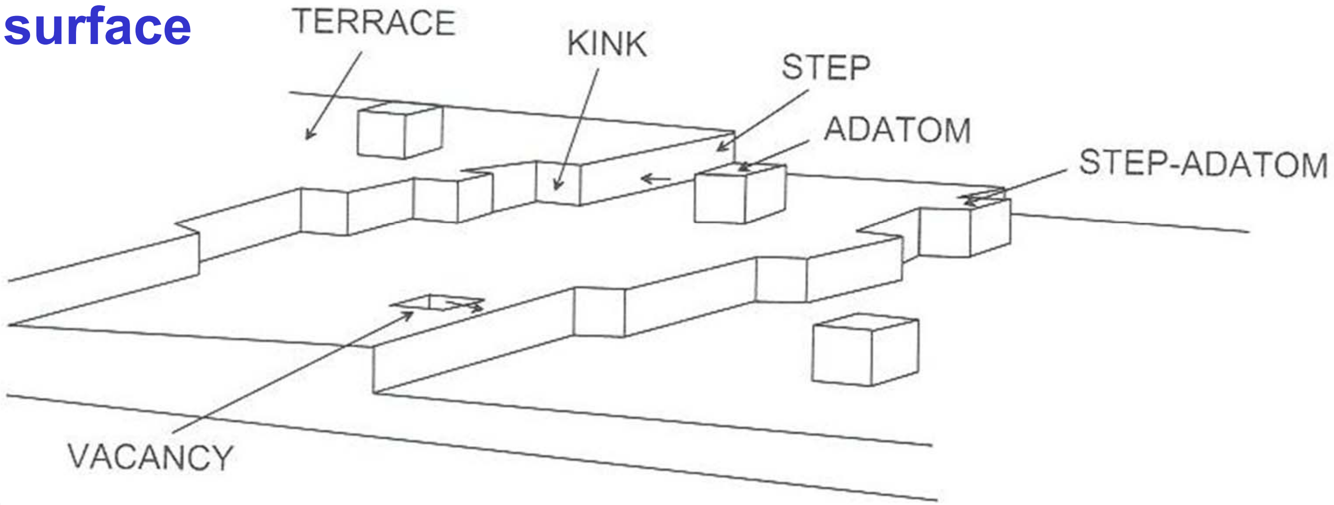
stable at low T

Atomic View

Ideal Surfaces



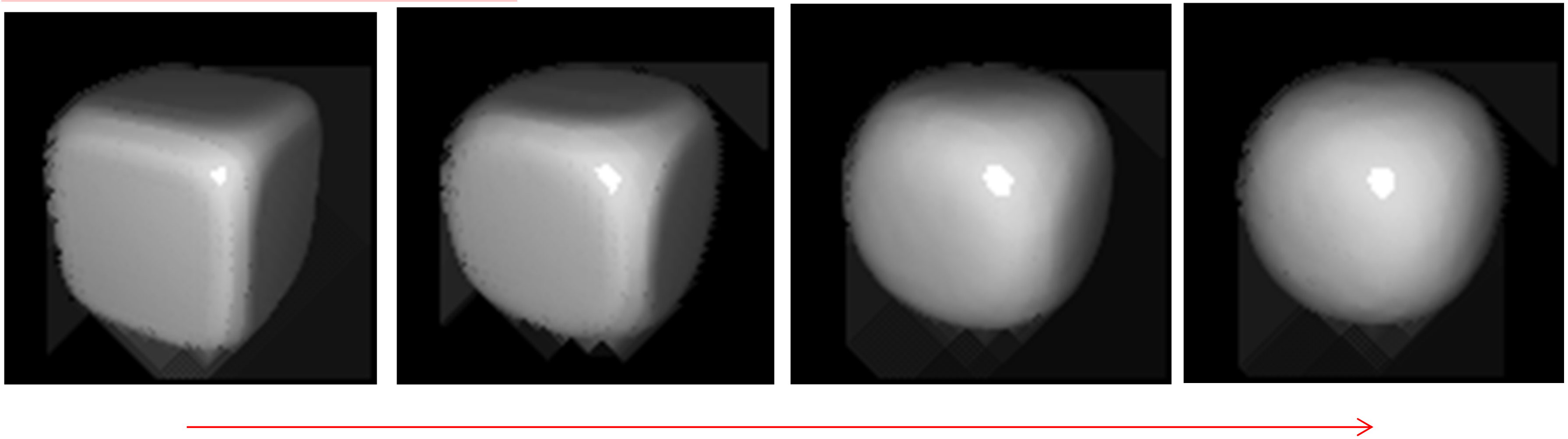
More realistic surface



- Realistic surfaces of crystals typically look like this at low temperature
- At sufficiently high temperature, the structure becomes atomically rough

(Thermal Roughening)

Thermal Roughening



singular (smooth) interface

rough interface

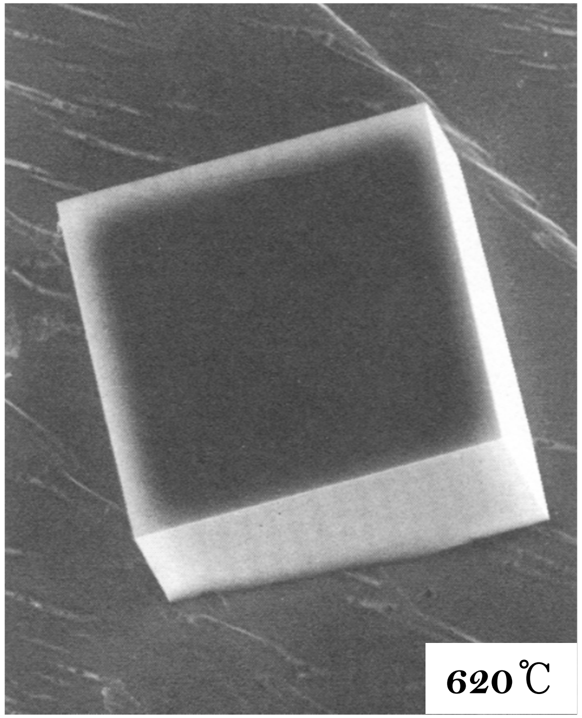
Enthalpy-dominant

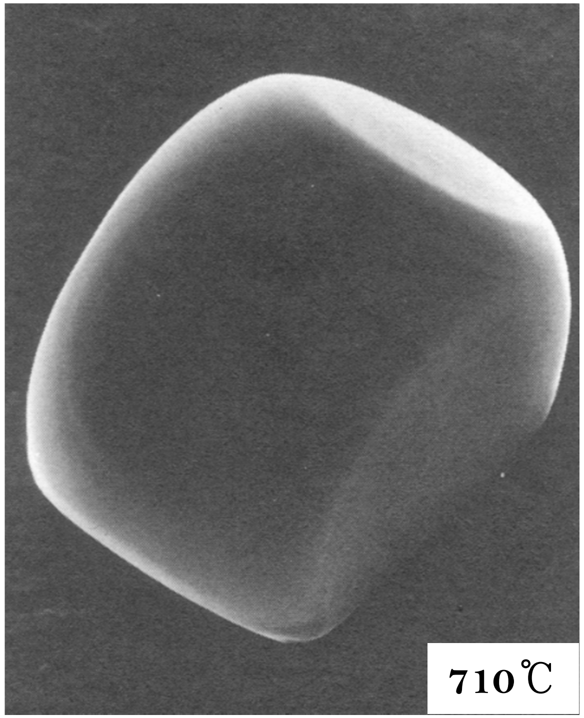
Entropy-dominant

Heating up to the roughening transition.

✓ Equilibrium shape of NaCl crystal

Thermal Roughening





J.C. Heyraud, J.J. Metois, J. Crystal Growth , 84, 503 (1987)

Compare the kinetic barrier for atomic attachment.

Which has a low growth barrier?

Contents for today's class I

* Melting vs. Freezing at equilibrium temperature, T_E

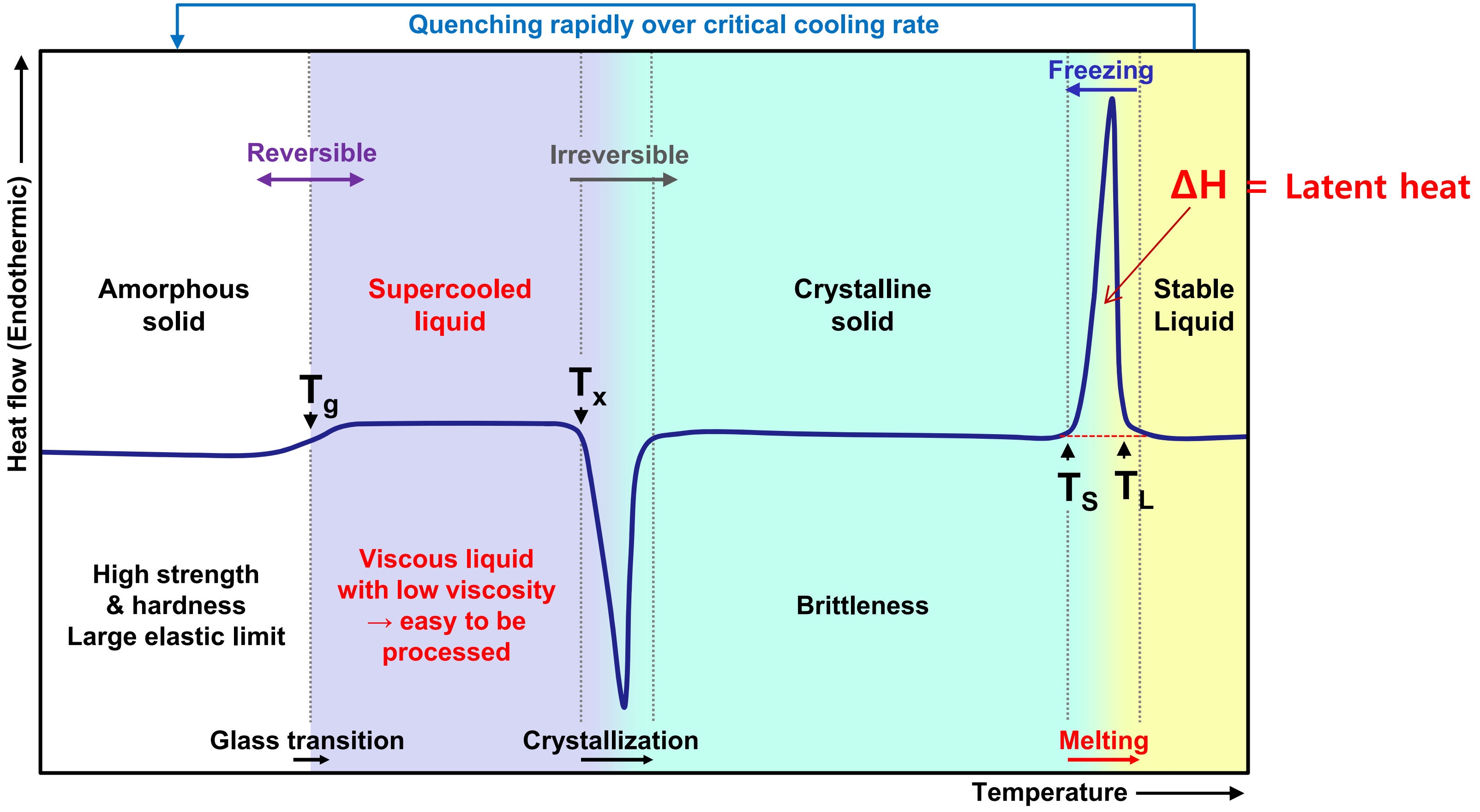
Net rate, $\overline{R}$ = difference between R_M and R_F

$$= N_L A_F G_F \nu_L \exp(-Q_F/RT) - N_S A_M G_M \nu_S \exp(-Q_M/RT)$$

* Process of Crystal Growth

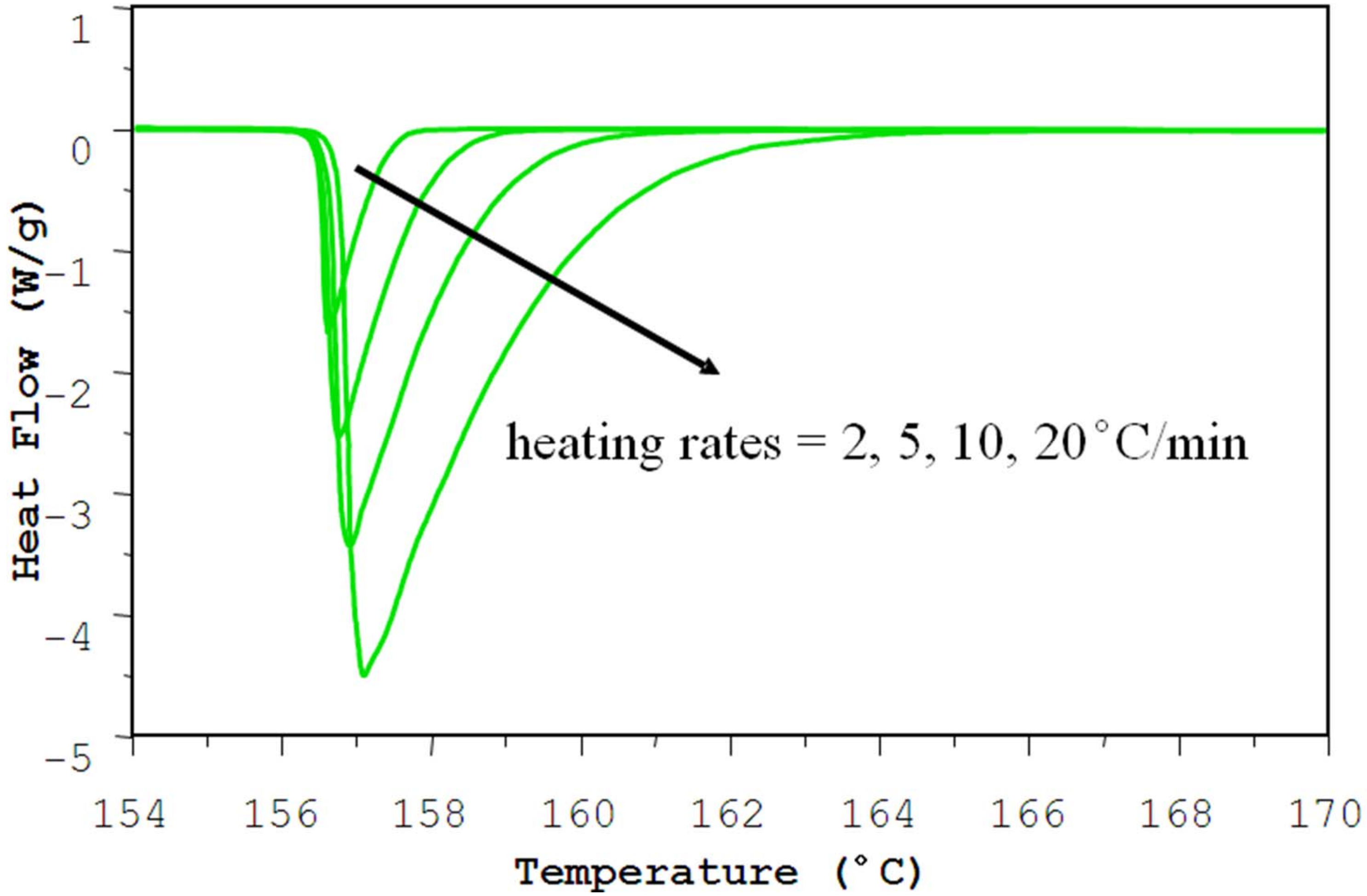
2.3 Equilibrium between a Pure Metal and Its Melt

a) Melting vs. Freezing at equilibrium temperature, T_E



< Schematic DSC (Differential Scanning Calorimeter) Trace of Metallic Glasses >

Effect of Heating Rate on Indium Melting Temperature



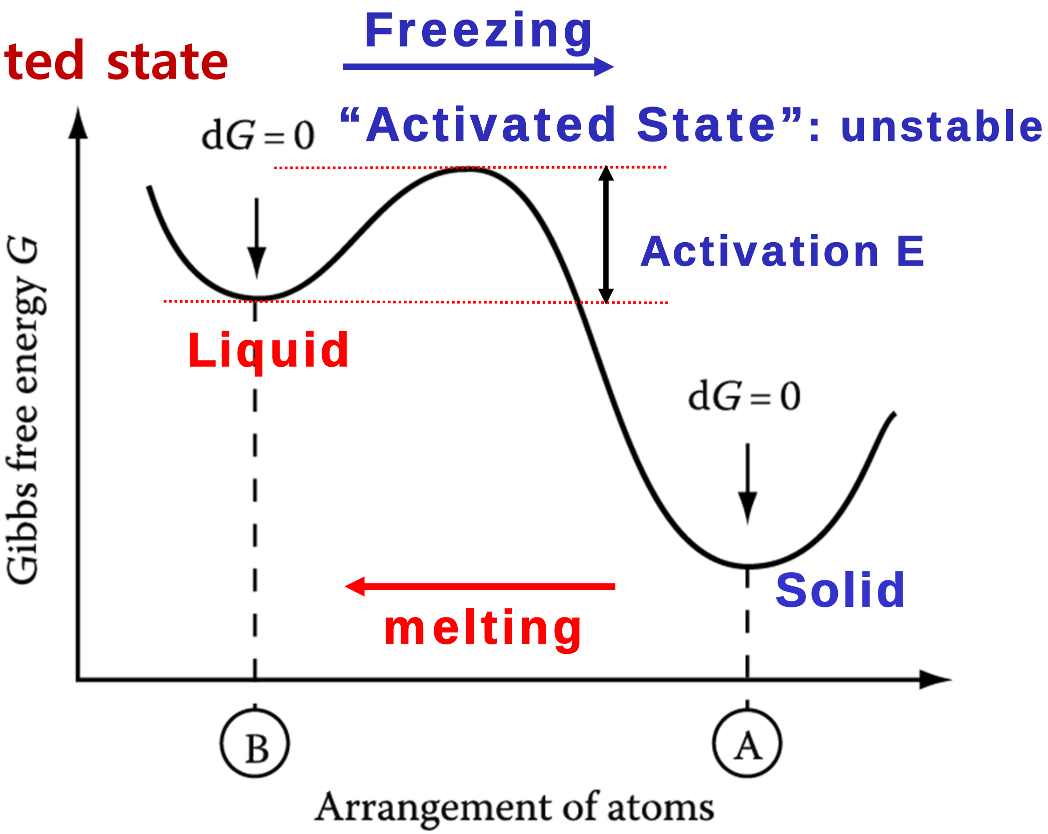
(b) Rate of melting or freezing

$\propto$ rate at which latent heat is supplied or removed

(c) Net rate, $\overline{R}$ = difference in the rates of melting and freezing

In order to calculate these rates, it is necessary to make some **assumptions**

① **Existence of Activated state**



< Solid to Liquid Phase Transformation at T_E >

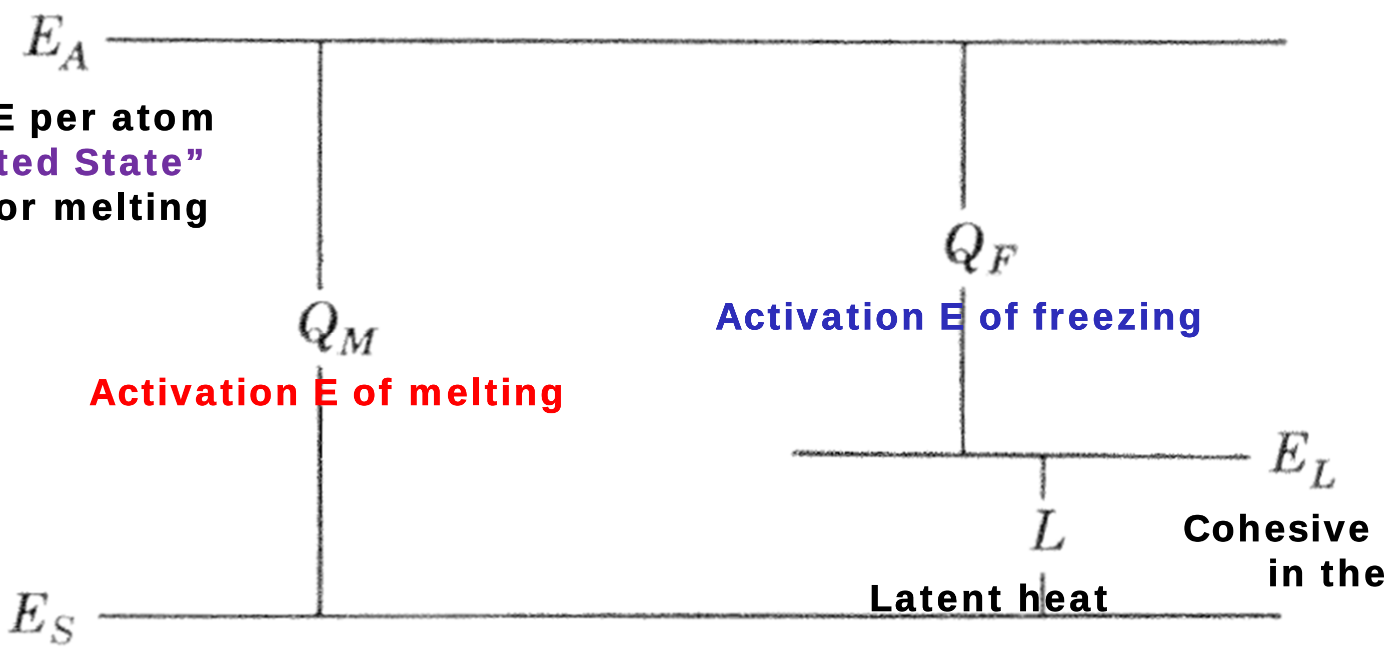
② **Energy differences at all sites at "Repeat step" of the solid-liquid interface ~ constant ("latent heat per atom")**

~ neglect high energy site (i.e., site with low coordination #)

(c) Net rate, $\overline{R}$ = difference in the rates of melting and freezing

① E condition: Sufficient E up to the activated state

< Energies and activation energies for melting and freezing>



Cohesive E per atom
in "Activated State"
~ min. E for melting

Activation E of freezing

Activation E of melting

Cohesive E per atom
in the Liquid

Latent heat

Cohesive E per atom
in the Solid

ν_S	frequency of atomic vibration	ν_L
$\nu_S \exp(-Q_M/RT)$	# of successive vibration times for melting and for freezing	$\nu_L \exp(-Q_F/RT)$

(c) Net rate, $\overline{R}$ = difference in the rates of melting and freezing

② Geometric factor $G_M \longleftrightarrow G_F$

: Proportion of atoms with sufficient energy to escape interface to normal direction

③ Accommodation coefficient $A_M \longleftrightarrow A_F$

: Proportion of suitable site for each process at the surface of the other phase

$A_M G_M \nu_S \exp(-Q_M/RT)$	# of times per second that all Three conditions are satisfied	$A_F G_F \nu_L \exp(-Q_F/RT)$
N_S	Atoms per unit area of the solid and liquid	N_L

The number of crossing unit area per second

Melting $R_M = N_S A_M G_M \nu_S \exp(-Q_M/RT)$

Freezing $R_F = N_L A_F G_F \nu_L \exp(-Q_F/RT)$

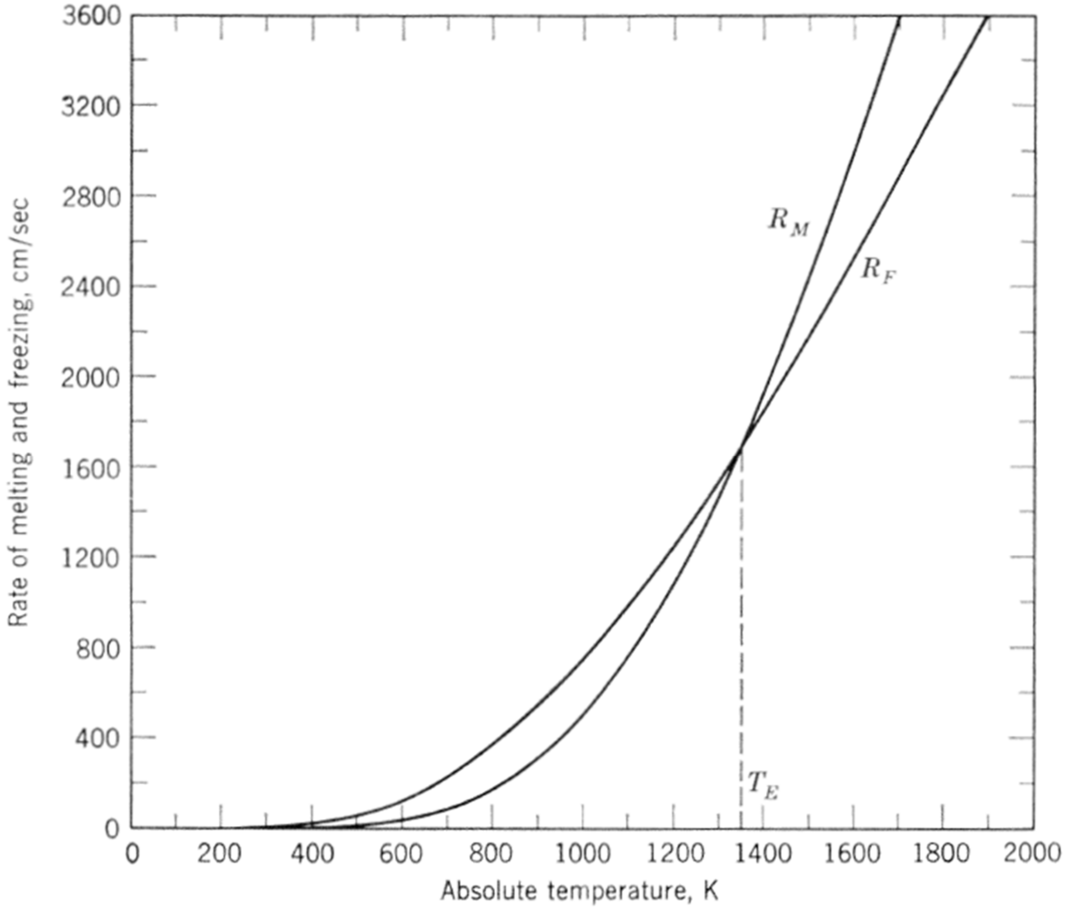
: 2 process ("melting" and "freezing") are regarded as occurring simultaneously and independently.

* **Rates of melting and freezing, R_M and R_F vary with temperature.**

1) The curve of R_M rises more rapidly than that for R_F ($\because Q_M > Q_F$)

2) R_M becomes larger than R_F ($\because A_M > A_F$ & $Q_M > Q_F$)

$R_M = R_F$ at equilibrium temperature, T_E

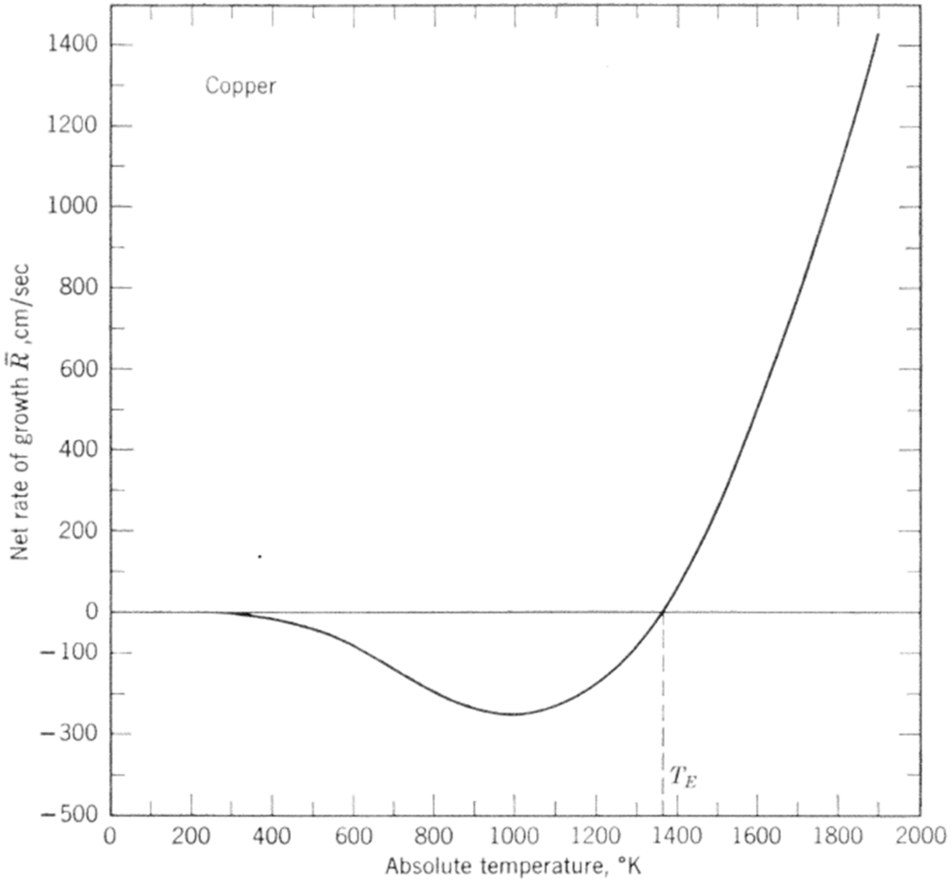


< Variation of the rates of the melting and freezing processes for copper with temperature>

(c) Net rate, $\overline{R}$ = difference between R_M and R_F

$$= N_L A_F G_F \nu_L \exp(-Q_F/RT) - N_S A_M G_M \nu_S \exp(-Q_M/RT)$$

Parameter in this equation depend on the substance under consideration.
For example, Ns and A_F vary with the crystallographic orientation of the interface.
→ Although T_E is probably the same for all surface orientations of a given substance, the value of $\overline{R}$ for a given departure from equilibrium is certainly not constant.



< Net rate of the melting and freezing as a function of temperature for copper>

at equilibrium temperature, T_E, $R_M = R_F$

$$N_S A_M G_M \nu_S \exp\left(-Q_M/RT_E\right) = N_L A_F G_F \nu_L \exp\left(-Q_F/RT_E\right)$$

or

$$\exp\left(\frac{Q_M - Q_F}{RT_E}\right) = \frac{A_M G_M N_S \nu_S}{A_F G_F N_L \nu_L}$$

but

$$Q_M - Q_F = L$$

hence

$$\frac{L}{RT_E} = \ln \frac{A_M G_M N_S \nu_S}{A_F G_F N_L \nu_L}$$

In the case of a plane solid-liquid interface, **$G_F \approx G_M$, $N_L \approx N_S$, and $\nu_L = \nu_S$**

$$\boxed{\frac{L}{RT_E} = \ln \frac{A_M}{A_F}}$$

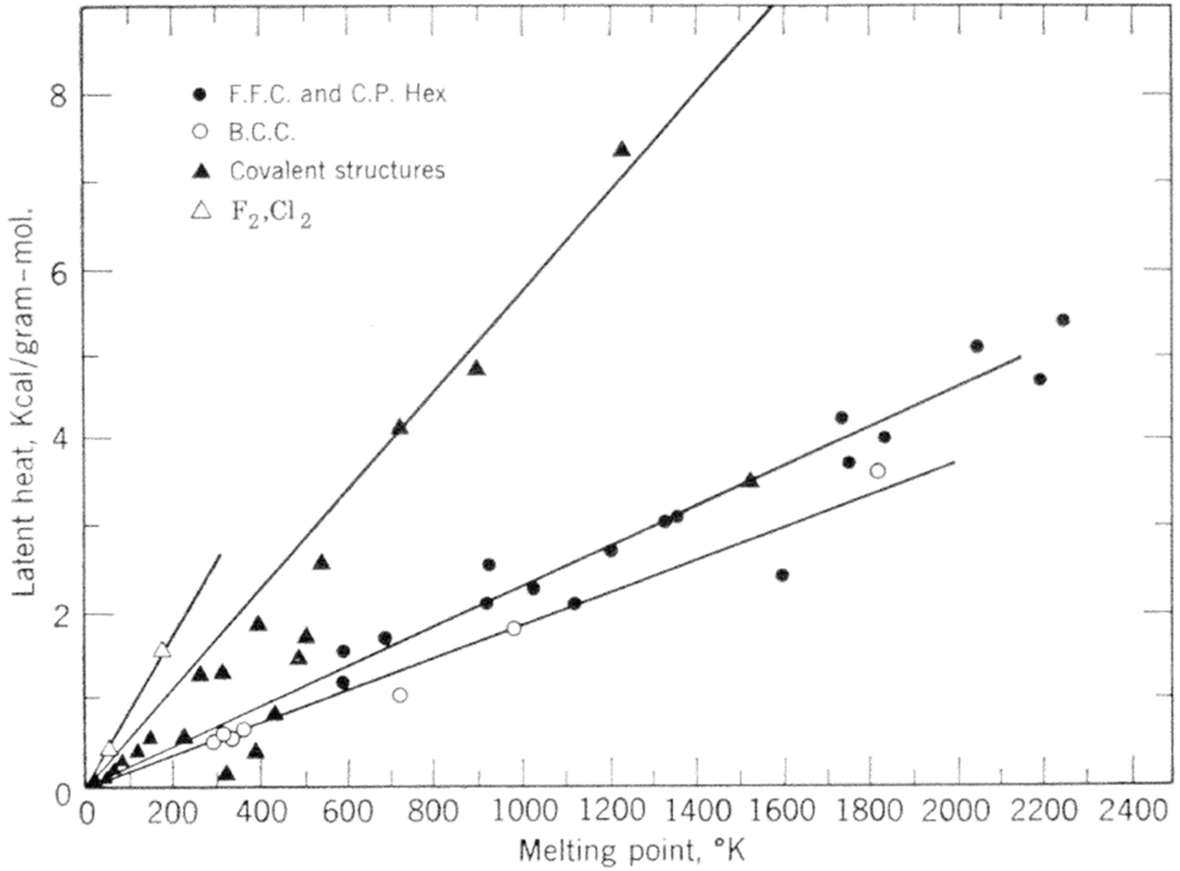
a) $T_E \propto L$ (latent heat) and depends on two accommodation coefficient

b) $A_M \sim 1$ for all liquid, A_F depends on crystal structure

$$\boxed{\frac{L}{RT_E} = \ln\frac{A_M}{A_F}}$$

b) A_M ~ 1 for all liquid, A_F depends on crystal structure

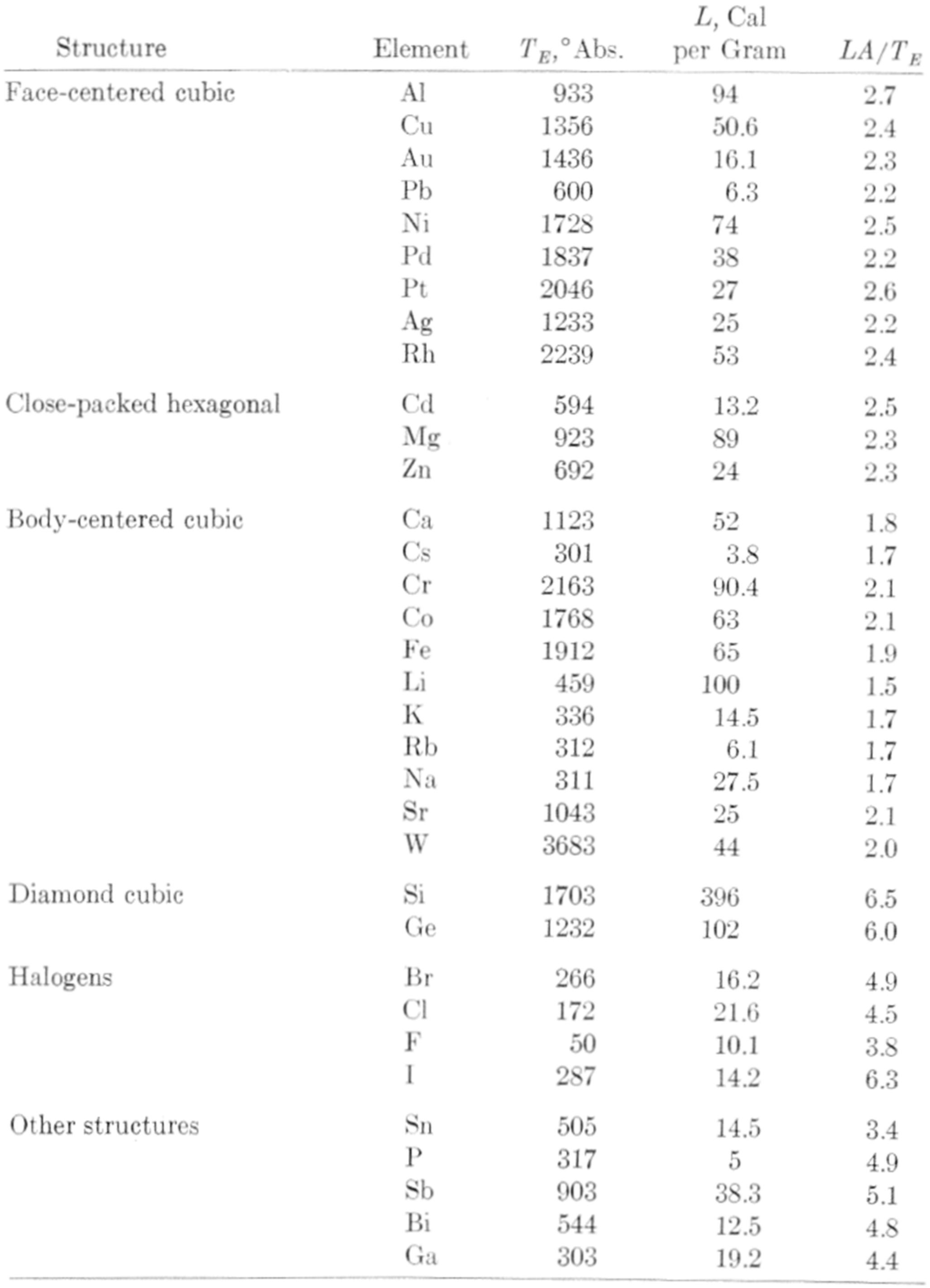
- **Metallic structure** (FCC, C.P.H, and BCC, “less localized bonding”) ~ good relationship compared with the structures which are covalently bonded (“specific directional bonds”).
- **Molecular liquid such as F_2, Cl_2 ~ extra condition for A_F**
  (∵ molecule must be correctly oriented in order to be accommodated.)



< Relationship between latent heat and melting point>

Table 2.1. Values of LA/T_E for elements.

LA is Latent Heat times
Atomic Weight



Structure	Element	T_E, °Abs.	L, Cal per Gram	LA/T_E
Face-centered cubic	Al	933	94	2.7
	Cu	1356	50.6	2.4
	Au	1436	16.1	2.3
	Pb	600	6.3	2.2
	Ni	1728	74	2.5
	Pd	1837	38	2.2
	Pt	2046	27	2.6
	Ag	1233	25	2.2
	Rh	2239	53	2.4
Close-packed hexagonal	Cd	594	13.2	2.5
	Mg	923	89	2.3
	Zn	692	24	2.3
Body-centered cubic	Ca	1123	52	1.8
	Cs	301	3.8	1.7
	Cr	2163	90.4	2.1
	Co	1768	63	2.1
	Fe	1912	65	1.9
	Li	459	100	1.5
	K	336	14.5	1.7
	Rb	312	6.1	1.7
	Na	311	27.5	1.7
	Sr	1043	25	2.1
	W	3683	44	2.0
Diamond cubic	Si	1703	396	6.5
	Ge	1232	102	6.0
Halogens	Br	266	16.2	4.9
	Cl	172	21.6	4.5
	F	50	10.1	3.8
	I	287	14.2	6.3
Other structures	Sn	505	14.5	3.4
	P	317	5	4.9
	Sb	903	38.3	5.1
	Bi	544	12.5	4.8
	Ga	303	19.2	4.4

*** The expression of T_E does not include E_A, but it may be estimated as follow.**

$$\boxed{\frac{L}{RT_E} = \ln\frac{A_M}{A_F}}$$

- **Latent heat** and $\mathbf{T_E}$ ~ can be determined at equilibrium
- The actual value of $\mathbf{A_M}$ and $\mathbf{A_F}$ ~ cannot be calculated from measurements

  But, **the ratio of the accommodation coefficients can be found!!**

Based on the definition of the accommodation coefficient, $\mathbf{A_M}$ and $\mathbf{A_F} \le 1$

for melting

$$\boxed{\frac{L}{RT_E} = \ln\frac{A_M}{A_F}} \quad ➡ \quad \mathbf{A_M/A_F = \exp\,(L/RT_E)}$$

a) Upper limit of $\mathbf{A_F}$: putting $\mathbf{A_M} = 1$ $A_F < \dfrac{1}{\exp\,(L/RT)} = \dfrac{1}{3.16} = 0.32$

b) Lower limit of $\mathbf{A_F}$

A mass of metal solidifies (as used, for example, in the calibration of a thermocouple) is not sensitive to ordinary variations in the rate of solidification.

For example, Freezing point of a metal sample in the form of a cylinder 6 cm in dia.

Solidification time: 10 min. → $\Delta T_E \le 1/10°$

➡ $d\bar{R}/dT \le 1/\ 20$ cm/sec/degree

The value of $d\bar{R}/dT$ is computed as follows:

$$\bar{R} = N_S A_M G_M \nu_S \exp\left(-Q_M/RT\right) - N_L A_F G_F \nu_L \exp\left(-Q_F/RT\right)$$

whence

$$\frac{d\bar{R}}{dT} = N_S A_M G_M \nu_S \frac{Q_M}{RT_E{}^2} \exp\left(\frac{-Q_M}{RT_E}\right) - N_L A_F G_F L \frac{Q_F}{RT_E{}^2} \exp\left(\frac{-Q_F}{RT_E}\right)$$

substituting $A_M/A_F = 3.16$, and assuming for copper that

$$G_M = G_F = \frac{1}{6}, \quad \nu_S = \nu_L = 2.8 \times 10^{13}\ \text{sec}^{-1}, \quad N_S = \frac{(3 \times 10^{-8})^3}{\sqrt{2}}$$

$$\frac{Q_M}{RT_E} = 2.65, \quad \frac{L}{RT_E} = 1.5, \quad T_E = 1356^\circ$$

Activation E of melting **Latent heat**

then

$$\frac{Q_F}{RT_E} = 1.15$$

then $$\boxed{(d\bar{R}/dT)_{T=T_E} = 8.4 A_M \ \text{cm/sec/degree}}$$

adopt $d\bar{R}/dT \leq 1/\ 20$ cm/sec/degree

➡ lower limit of A_F for copper ~ 0.002

If the relationship between $\bar{R}$ & T were determined experimentally, the absolute values of the accommodation coefficients and the activation energies could be found.

Orrok and Chalmers: measure ΔT directly during rapid melting of a lead crystal

$\Delta \mathbf{T}_\mathbf{E} \leq 1/10^\circ$ for a rate $\overline{R}$ of 1 cm/sec ➡ $d\overline{R}/dT \geq 10$ cm/sec/deg

If this value of $d\overline{R}/dT = 10$ is inserted in the equation above,
a value of 0.3 is found for $\mathbf{A}_F$, which is close to the upper lime of $\mathbf{A}_F$.

"Not clear yet" ~ $\mathbf{A}_F = 0.3$ for all sites ⟷ $\mathbf{A}_F = 0.3$ for limited possible sites

These analysis has some limitation because;

a) Contradictory assumption 1: all sites which atoms can leave the surface of the solid require equal energies, equal to the latent heat of fusion.

➡ Some of the atoms have higher E, and therefore require less activation E.

b) Contradictory assumption 2: all atoms at the surface can reach the activated state by acquiring thermal energy $\mathbf{Q}_M$.

➡ Some of the atoms can reach the activated state with thermal energies that are much lower than $\mathbf{Q}_M$, some as low as $\mathbf{Q}_M - L/2$ for atoms with only three crystal neighbors.

Thus, it is not to be expected that the equations derived above are quantitative accurate. They do, nevertheless, give **a useful physical insight into the processes of melting and solidification**, and in particular into the significance of T_E, *melting point, and freezing point.*

2.4 The Process of Crystal Growth

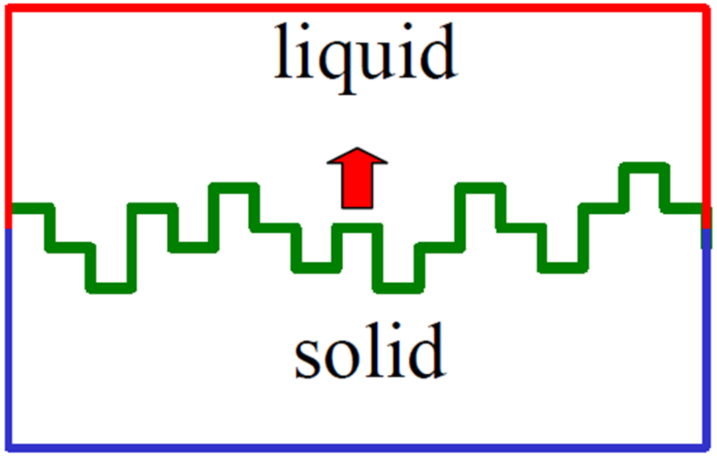
: The next step after the nucleation is growth.

Q: What kinds of Growth in a pure solid exist?

Two types of solid-liquid interface

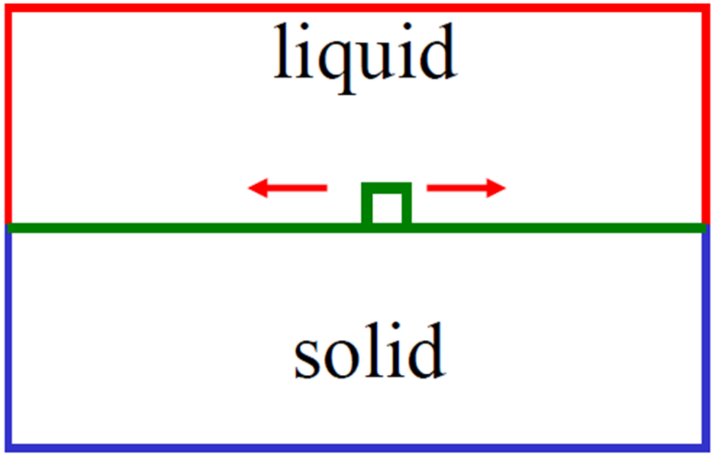
a) Continuous growth

: Atomically rough or diffuse interface



b) Lateral growth

: Atomically flat of sharply defined interface



2.4 The Process of Crystal Growth

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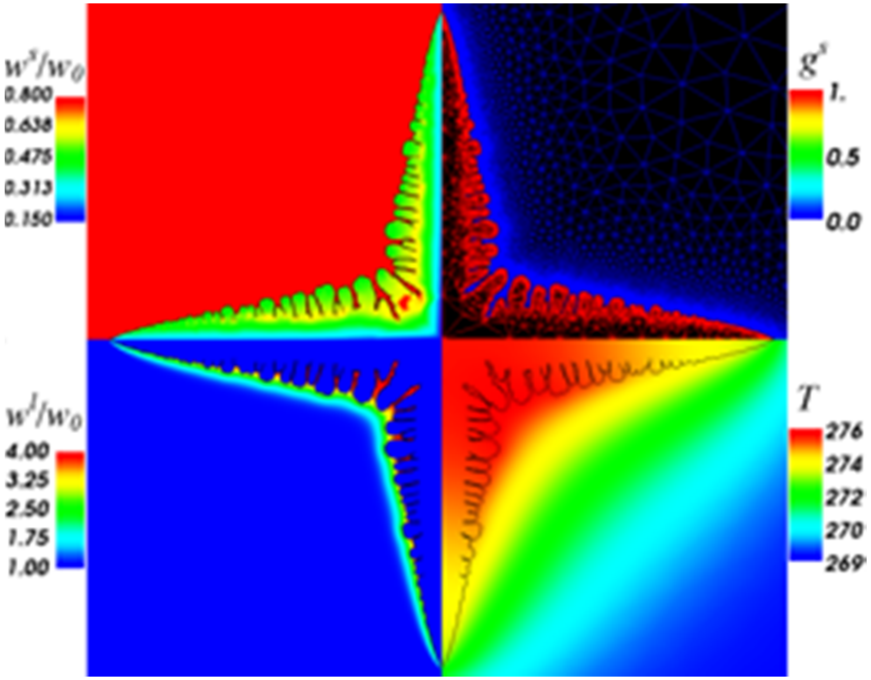
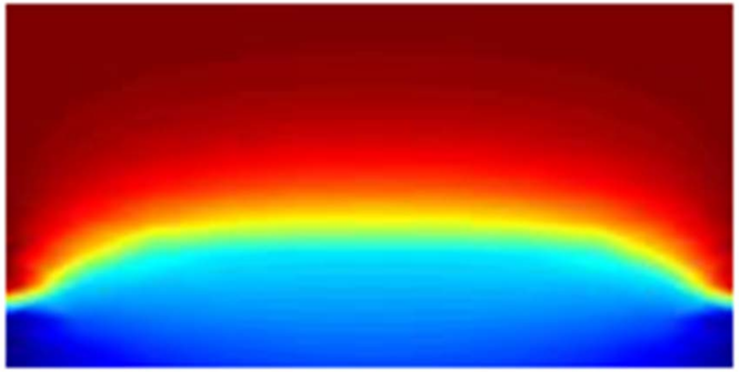
b) Lateral growth

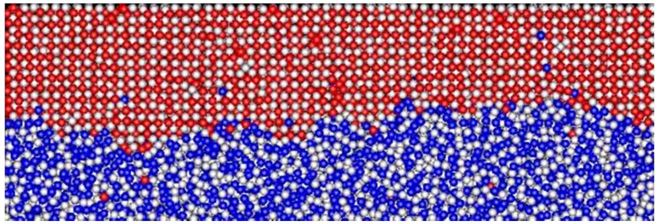
: Atomically flat of sharply defined interface





a) Continuous growth

The migration of a rough solid/liquid interface can be treated in a similar way to the migration of a random high angle grain boundary.

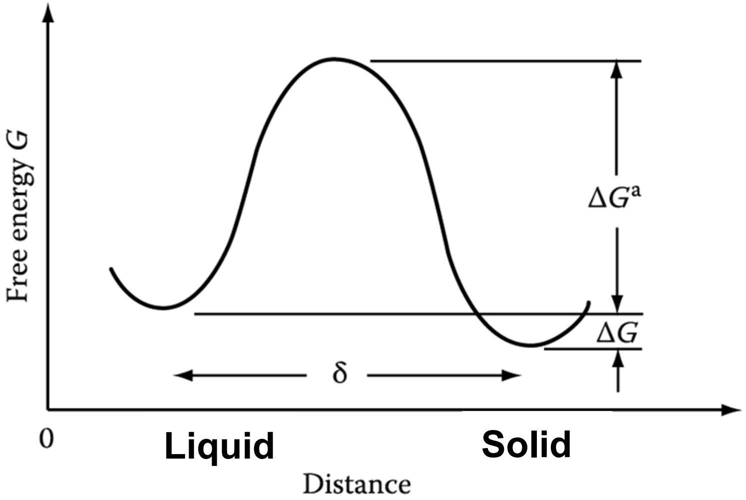


- Driving force for solidification

$$\boxed{\Delta G = \frac{L}{T_m}\Delta T_i}$$

L: latent heat of melting

ΔT_i : undercooling of the interface



- Net rate of solidification

$$\boxed{\overline{R} = k_1\Delta T_i}$$

k_1: properties of boundary mobility

Reference (eq. 3.21) $v = M \cdot \Delta G / V_m$

The rate of the continuous growth (typical for metals) is usually a "diffusion controlled process".

- Pure metal grow at a rate controlled by heat transfer to the interfacial region.
- Alloy grow at a rate controlled by solute diffusion.

b) Lateral growth

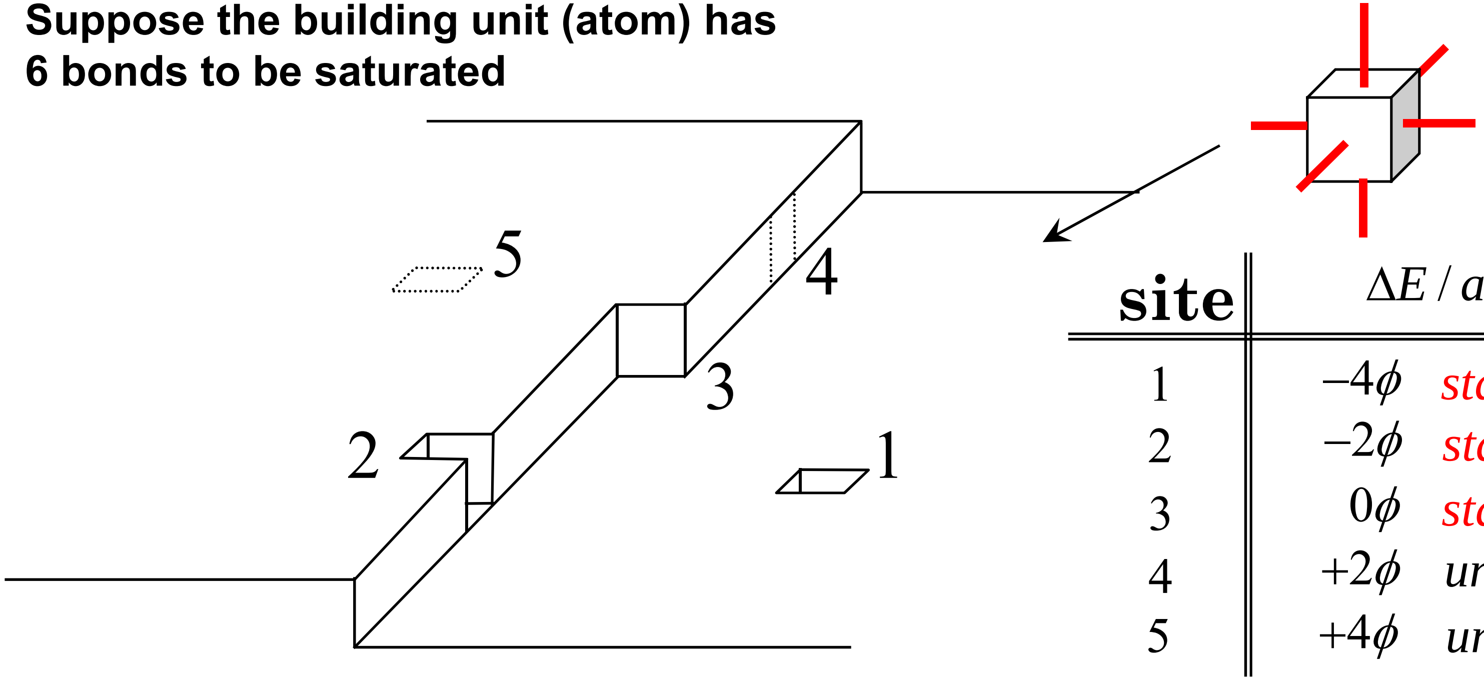
- Materials with a high entropy of melting (~high T_m) prefer to form atomically smooth, closed-packed interfaces.
- For this type of interface the minimum free energy also corresponds to the minimum internal energy, i.e. a minimum number of broken ‘solid’ bonds.

Two ways in which ledges and jogs (kinks) can be provided.

① Surface (2-D) nucleation ② Spiral growth

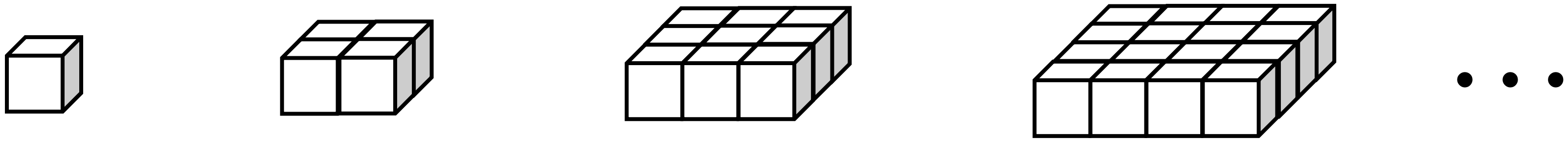
Condition for Atomic Attachment

Suppose the building unit (atom) has
6 bonds to be saturated



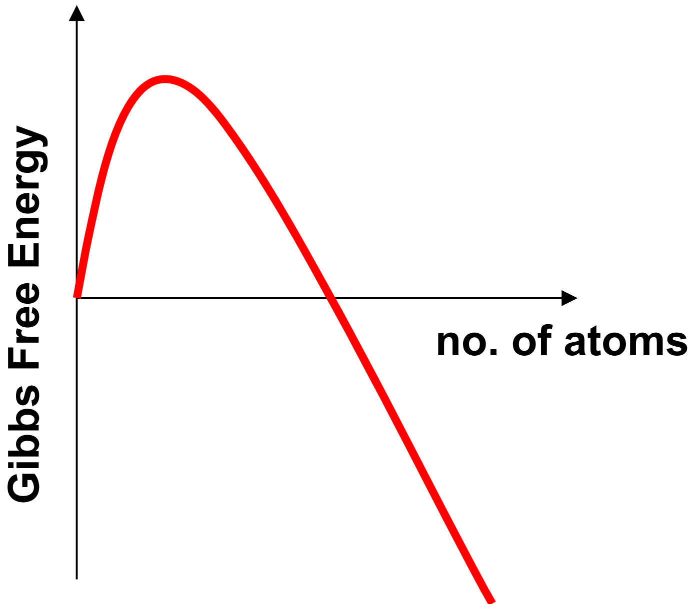
site	ΔE / atom			
1	-4ϕ	*stable*		
2	-2ϕ	*stable*		
3	0ϕ	*stable*	:	*kink*
4	$+2\phi$	*unstable*		
5	$+4\phi$	*unstable*		

How many unsaturated bonds are there if they are epitaxial to the underneath atomic layer?



$+4\phi/\,atom$	$+8\phi/\,4\ atoms$	$+12\phi/\,9\ atoms$	$+16\phi/\,16\ atoms$
Δf = -kTln(P/P$_e$)	4Δf	9Δf	16Δf
$+4\phi/\,atom$	$+2\phi/\,atom$	$+\frac{4}{3}\phi/\,atom$	$+1\phi/\,atom$
ΔE/atom	ΔE/atom	ΔE/atom	ΔE/atom

Draw the plot showing how the free energy varies with the number of atoms in the presence of supersaturation (driving force) for growth.



→ 2-Dimensional Nucleation ①

- **If large # of atoms form a disc-shaped layer,**

→ self-stabilized and continue to grow.

- **Δ*T* becomes large, r* ↓.**

- $\overline{R} \infty \exp\,(-k_2/\Delta T_i)$

② Spiral growth: Growth by Screw Dislocation

Crystals grown with a low supersaturation were always found to have a 'growth spirals' on the growing surfaces.

- **addition of atoms to the ledge cause it to rotate around the axis of screw dislocation**
- **If atoms add at an equal rate to all points along the step, the angular velocity of the step will be initially greatest nearest to the dislocation core.**
- **the spiral tightens until it reaches a minimum radius of r***
- $\overline{R} = k_3(\Delta T_i)^2$

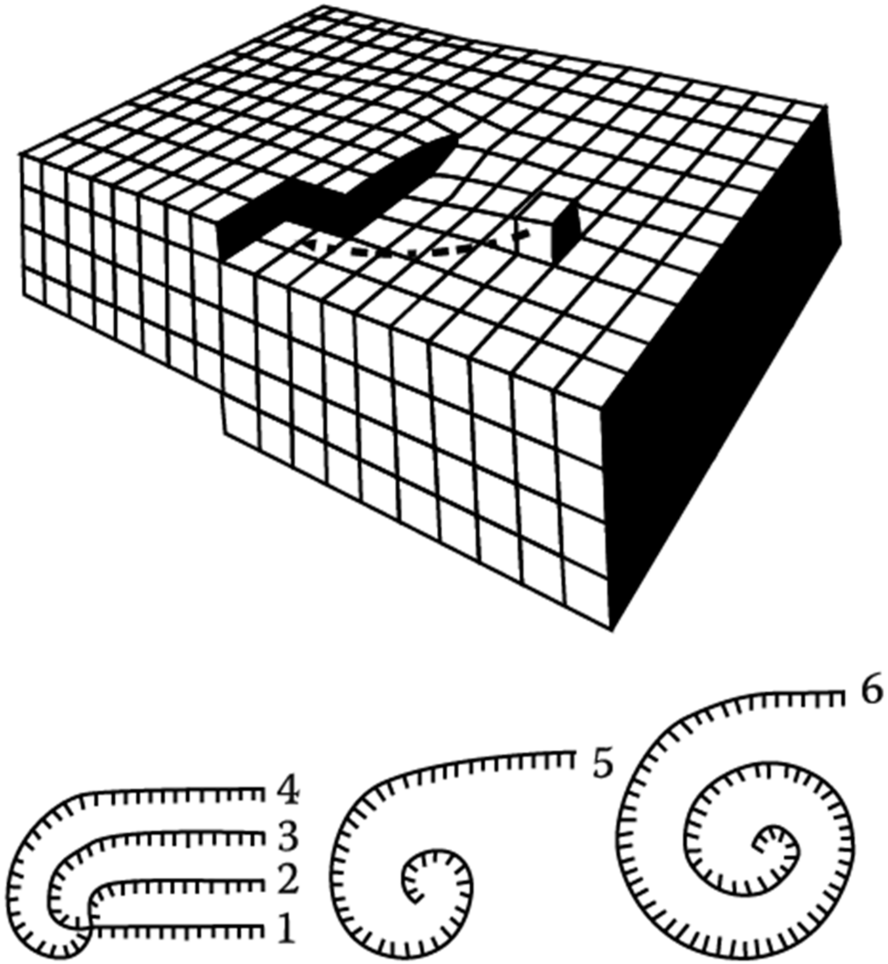
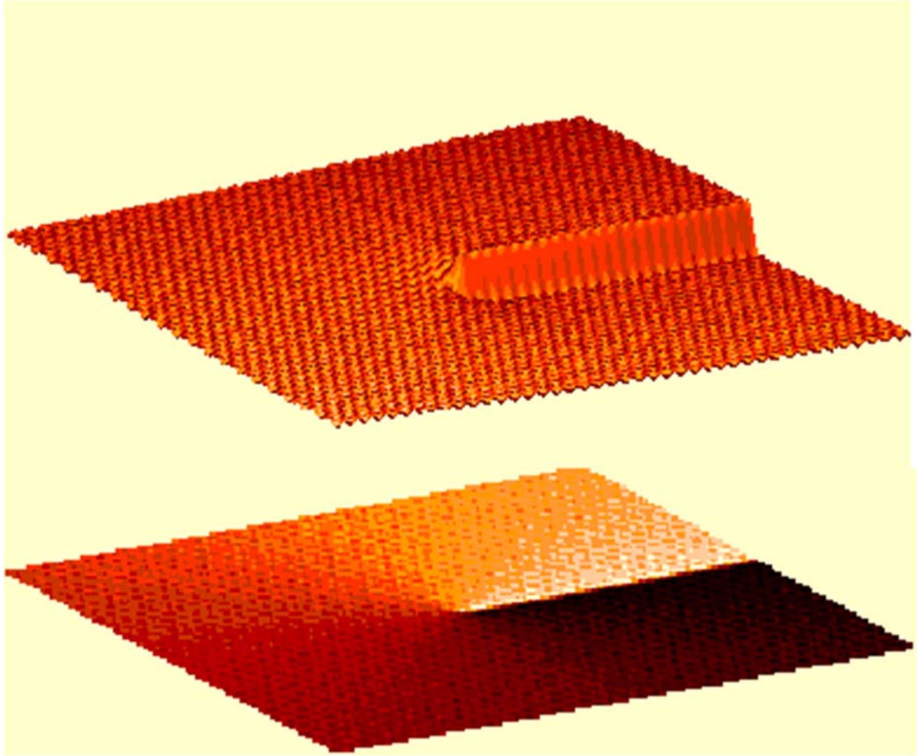


Fig. 4. 13 Spiral growth. (a) A screw dislocation terminating in the solid/liquid interface showing the associated ledge. Addition of atoms at the ledge causes it to rotate with an angular velocity decreasing away from the dislocation core so that a growth spiral develops as shown in (b).

Growth by Screw Dislocation



Burton, Cabrera and Frank (BCF, 1948) elaborated the spiral growth mechanism, assuming steps are atomically disordered...

Their interpretation successfully explained the growth velocity of crystals as long as the assumption is valid…

③ Growth from twin boundary → "feather crystal" under small ΔT

- **another permanent source of steps like spiral growth**

  → not monoatomic height ledge but macro ledge

Kinetic Roughening

Rough interface - Ideal Growth → diffusion-controlled → dendritic growth

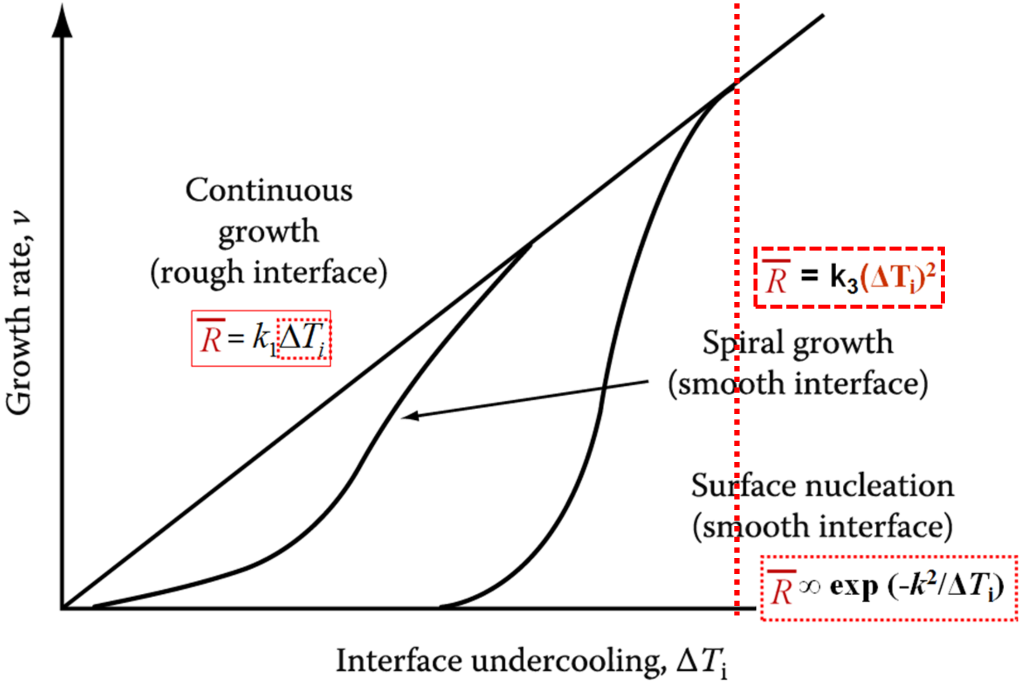
Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

Small ΔT → "feather" type of growth ⟷ Large ΔT → cellular/dendritic growth

The growth rate of the singular interface cannot be higher than ideal growth rate.

When the growth rate of the singular Interface is high enough, it follows the ideal growth rate like a rough interface.

→ kinetic roughening



Contents for today's class II

* **Melting vs. Freezing at equilibrium temperature, T_E**

→ **Solid-Liquid Equilibrium in Alloys**

*** Two-Phase Equilibrium**

→ **Binary phase diagrams**

2.5 Solid-Liquid Equilibrium in Alloys

* Kinetic description of pure substance

Melting $R_M = N_S A_M G_M \nu_S \exp(-Q_M/RT)$

Freezing $R_F = N_L A_F G_F \nu_L \exp(-Q_F/RT)$

* Kinetic description of alloys

More than one chemical element,

i component

C_S^i C_L^i Molar fraction concentration

If melting and freezing are determined by the same expression as before (pure substance),

a) Rate for each species ∝ atomic concentration in the phase from which it moves

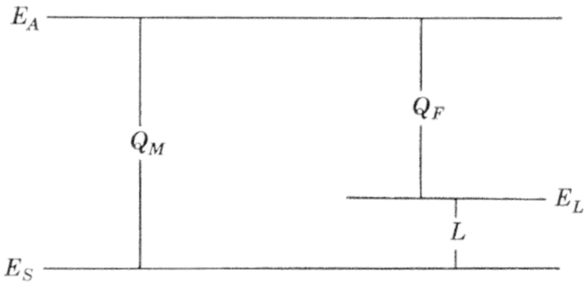
b) Concentration in the surface layer of each phase is identical which that in the interior.

c) Values of Q_M ∝ different for different species

(∵ solute atom tightly bound than the solvent atom in a crystal)

d) Q_F ~ same for all the species present

(not strictly true, but qualitative usefulness of the conclusions)



Then, for the species i,

Melting $R_M^{\,i} = N_S^{\,i} C_S^{\,i} A_M^{\,i} G_M^{\,i} \nu_S^{\,i} \exp\left(-Q_M^{\,i}/RT\right)$

Freezing $R_F^{\,i} = N_L^{\,i} C_L^{\,i} A_F^{\,i} G_F^{\,i} \nu_L^{\,i} \exp\left(-Q_F^{\,i}/RT\right)$

* **Equilibrium condition for each component** ($R_M^{\,i} = R_F^{\,i}$) **is given by,**

$$\boxed{\frac{C_S{}^i N_S{}^i A_M{}^i G_M{}^i \nu_S{}^i}{C_L{}^i N_L{}^i A_F{}^i G_F{}^i \nu_L{}^i} = \exp\left[\frac{(Q_M{}^i - Q_F{}^i)}{RT}\right]}$$

* **If Q, A, G, & ν are independent of concentration, the general expression become,**

$$n\,\frac{C_S{}^i}{C_L{}^i} = \frac{L^i}{R}\left(\frac{1}{T} - \frac{1}{T_E{}^i}\right)$$

(A form of Clausisus clapeyron equation)

$T_E^{\,i}$ **: Equil. Temp. for pure component** ***i*** **/ T: Temp. for solution**

For dilute solutions of B in A; $C_S^A \rightarrow 1$, $C_L^A \rightarrow 1$, and $T \rightarrow T_E^A$

then $\ln (C_S^A / C_L^A) \rightarrow (C_L^B - C_L^A)$ calling $\Delta T_E^i = T_E^i - T$,

$$\frac{L^A}{R(T_E^A)^2} = \frac{C_L^B}{\Delta T_A} - \frac{C_S^B}{\Delta T_A}$$

(A form of vant' Hoff relationship)

: giving the difference in slop of the liquidus and solidus lines
at zero concentration for any binary alloy in terms of
the latent heat of fusion (L) and the melting point of solvent phase (T_E^A)

Van't Hoff equation relates the change in the equilibrium constant, K_{eq}, of a chemical reaction to the change in temperature , T, given the standard enthalpy change ΔH, for the process. The equation has been widely utilized to explore the changes in state functions in the thermodynamic system.

- Two-Phase Equilibrium

1) Simple Phase Diagrams

Assumption: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.
(3) $T_m(A) > T_m(B)$

$$\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0$$

$$\mathrm{d}G^s = V^s\,\mathrm{d}P - S^s\,\mathrm{d}T + \mu^s_{\mathrm{A}}\,\mathrm{d}X^s_{\mathrm{A}} + \mu^s_{\mathrm{B}}\,\mathrm{d}X^s_{\mathrm{B}}$$
$$\mathrm{d}G^l = V^l\,\mathrm{d}P - S^l\,\mathrm{d}T + \mu^l_{\mathrm{A}}\,\mathrm{d}X^l_{\mathrm{A}} + \mu^l_{\mathrm{B}}\,\mathrm{d}X^l_{\mathrm{B}}.$$

At equilibrium

$$\mathrm{d}G^s = \mathrm{d}G^l, \quad \mu^s_{\mathrm{A}} = \mu^l_{\mathrm{A}} \quad \text{and} \quad \mu^s_{\mathrm{B}} = \mu^l_{\mathrm{B}}.$$

At constant P

$$-(S^s - S^l)\,\mathrm{d}T = (\mu_{\mathrm{A}} - \mu_{\mathrm{B}})(\mathrm{d}X^l_{\mathrm{A}} - \mathrm{d}X^s_{\mathrm{A}}).$$

Differentiating with respect to X_{A},

$$(S^s - S^l)\frac{\mathrm{d}T}{\mathrm{d}X_{\mathrm{A}}} = (\mu_{\mathrm{A}} - \mu_{\mathrm{B}})\left(\frac{\mathrm{d}X^s_{\mathrm{A}}}{\mathrm{d}X_{\mathrm{A}}} - \frac{\mathrm{d}X^l_{\mathrm{A}}}{\mathrm{d}X_{\mathrm{A}}}\right). \qquad (102)$$

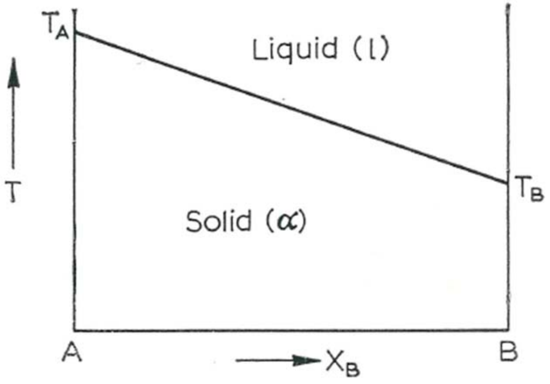


Fig. 22.

If the boundary between liquid and solid were as shown in Fig. 22, then $X^s_{\mathrm{A}} = X^l_{\mathrm{A}}$ (the liquid and solid would have the same composition when in equilibrium at a point on the line $T_{\mathrm{A}}T_{\mathrm{B}}$).
From eqn. (102)

$$(S^s - S^l)\frac{\mathrm{d}T}{\mathrm{d}X_{\mathrm{A}}} = 0.$$

From eqn. (102)

$$(S^s - S^l)\frac{\mathrm{d}T}{\mathrm{d}X_A} = 0.$$

Since $S^s \neq S^l$, then $\mathrm{d}T/\mathrm{d}X_A = 0$. Thus the condition $X_A^s = X_A^l$ is only associated with $\mathrm{d}T/\mathrm{d}X_A = 0$, *i.e.* with a minimum or a maximum in the line $T_A T_B$ of Fig. 22. Except for this particular case therefore $X_A^s \neq X_A^l$. There is a difference between the composition of the liquid and solid phase in the general case.

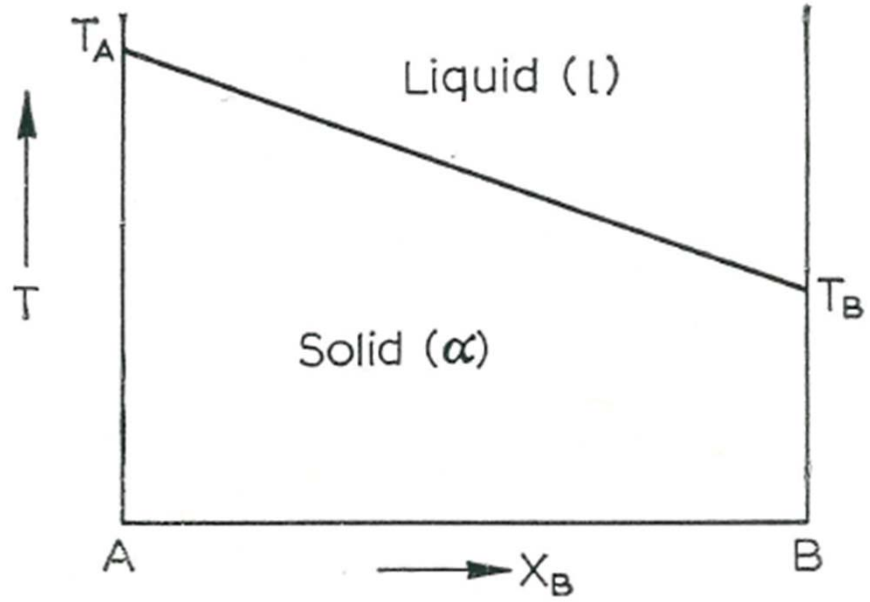
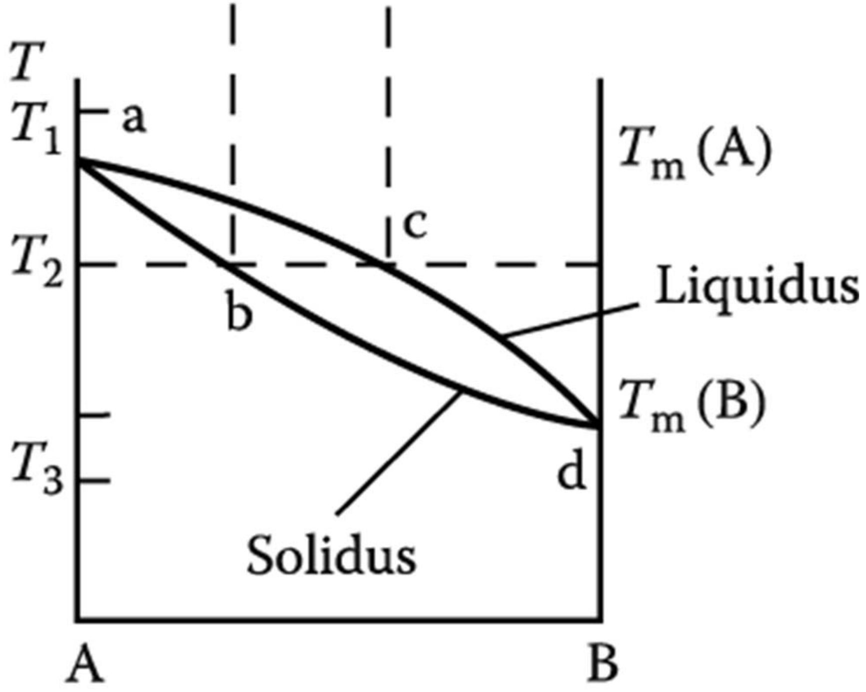


Fig. 22.



(f)

* **Consider the free energy curves for liquid and α phase at a temperature T, where $T_A>T>T_B$. The standard states are pure *solid* A and pure *liquid* B at temperature T. → Derive the free energy curves for the liquid and α phases.**

1) Free energy curve for the liquid phase

For an ideal solution with a reaction

$$X_A \text{ moles of liquid A} + X_B \text{ moles of liquid B} = 1 \text{ mole liquid solution}$$

$$\boxed{\Delta G_m = RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l)} \tag{61}$$

But the standard state for A is pure solid A. To obtain the free energy change, ΔG_m^l, for the formation of the liquid solution, we must allow for the conversion of X_A moles of solid A into X_A moles of liquid A, *i.e.*

$$X_A \text{ moles solid A} = X_A \text{ moles liquid A}$$

$$\boxed{\Delta G = X_A^l \Delta G_A}$$

where ΔG_A is the difference in free energy between liquid and solid A (the free energy of fusion of A).

Hence for the reaction

$$X_A \text{ moles of solid A} + X_B \text{ moles of liquid B} = 1 \text{ mole liquid solution}$$

$$\boxed{\Delta G_m^l = X_A^l \Delta G_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).}$$

2) Free energy curve for α phase

For an ideal solid solution formed according to the equation

X_A moles of solid A + X_B moles of solid B = 1 mole α solid solution

$$\boxed{\Delta G_m = RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).}$$

Since the standard state for B is pure *liquid* B, allowance must be made for the free energy change on transforming X_B moles of liquid B to X_B moles of solid B, *i.e.*

$$\boxed{\Delta G = -X_B^s \Delta G_B}$$

where ΔG_B is the difference in free energy between liquid and solid B. It is a negative quantity since the liquid phase is the more stable at temperature T.

For the reaction

X_A moles of solid A + X_B moles of liquid B = 1 mole α solid solution

$$\boxed{\Delta G_m^s = -X_B^s \Delta G_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).}$$

At temperature T the chemical potential of component B is identical in the α and liquid phases. Therefore

$$\boxed{\frac{\partial \Delta G_m^s}{\partial X_B} = \frac{\partial \Delta G_m^l}{\partial X_B}}$$

$$\frac{\partial \Delta G_m^s}{\partial X_B} = -\Delta G_B + RT \ln \frac{X_B^s}{X_A^s} \quad \text{and} \quad \frac{\partial \Delta G_m^l}{\partial X_B} = -\Delta G_A + RT \ln \frac{X_B^l}{X_A^l}.$$

Therefore

$$\Delta G_A - \Delta G_B = RT\left(\ln \frac{X_B^l}{X_A^l} - \ln \frac{X_B^s}{X_A^s}\right)$$

or,

$$\Delta G_A - \Delta G_B = RT\left(\ln \frac{X_A^s}{X_A^l} - \ln \frac{X_B^s}{X_B^l}\right).$$

We can relate ΔG_A and ΔG_B to ΔH_A and ΔH_B, T_A and T_B, *i.e.* to the respective molar heats of fusion of pure A and B, and their melting points. For example, for component B at T_B:

$$\Delta G_B = \Delta H_B - T_B \Delta S_B = 0$$

or,

$$\boxed{\Delta S_B = \frac{\Delta H_B}{T_B}.}$$

At a temperature T,

$$\Delta G_B = \Delta H_B - T\Delta S_B \neq 0.$$

Therefore

$$\Delta G_{\mathrm{B}} = \Delta H_{\mathrm{B}} - T\,\frac{\Delta H_{\mathrm{B}}}{T_{\mathrm{B}}}$$

$$\boxed{= \Delta H_{\mathrm{B}}\left(1 - \frac{T}{T_{\mathrm{B}}}\right).}$$

Substituting,

$$\Delta H_{\mathrm{A}}\left(1 - \frac{T}{T_{\mathrm{A}}}\right) - \Delta H_{\mathrm{B}}\left(1 - \frac{T}{T_{\mathrm{B}}}\right) = RT\left(\ln\frac{X_{\mathrm{A}}^{s}}{X_{\mathrm{A}}^{l}} - \ln\frac{X_{\mathrm{B}}^{s}}{X_{\mathrm{B}}^{l}}\right)$$

or,

$$\ln\frac{X_{\mathrm{A}}^{s}}{X_{\mathrm{A}}^{l}} - \ln\frac{X_{\mathrm{B}}^{s}}{X_{\mathrm{B}}^{l}} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}}\right) - \frac{\Delta H_{\mathrm{B}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}}\right).$$

As the temperature approaches T_{A} the quantities X_{A}^{s} and X_{A}^{l} will approach unity, and $1/T$ will approach $1/T_{\mathrm{A}}$.

Hence near T_{A}:

$$\boxed{\ln\frac{X_{\mathrm{B}}^{s}}{X_{\mathrm{B}}^{l}} = \frac{\Delta H_{\mathrm{B}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}}\right).} \tag{103}$$

Similarly, if the temperature approaches T_{B}, $X_{\mathrm{B}}^{s} \simeq X_{\mathrm{B}}^{l} \rightarrow 1$ and $1/T \rightarrow 1/T_{\mathrm{B}}$. Near T_{B}:

$$\boxed{\ln\frac{X_{\mathrm{A}}^{s}}{X_{\mathrm{A}}^{l}} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}}\right).} \tag{104}$$

Knowing ΔH_{A}, ΔH_{B}, T_{A} and T_{B}, the above two equations can be used to determine the compositions of co-existing phases at a series of temperatures, T, between T_{A} and T_{B}. → **Fig. 23*f***

Referring to Fig. 23f, if A is regarded as the solvent, for very dilute solutions of B in A we can write

$$X_{\mathrm{A}} \to 1 \quad \text{and} \quad -\ln X_{\mathrm{A}} \simeq X_{\mathrm{B}}.$$

In terms of eqn. (104):

$$X_{\mathrm{A}}^{l} - X_{\mathrm{A}}^{s} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{T_{\mathrm{A}} - T}{T T_{\mathrm{A}}}\right).$$

Since $X_{\mathrm{A}}^{l} = 1 - X_{\mathrm{B}}^{l}$ and $X_{\mathrm{A}}^{s} = 1 - X_{\mathrm{B}}^{s}$

$$X_{\mathrm{B}}^{s} - X_{\mathrm{B}}^{l} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{T_{\mathrm{A}} - T}{T T_{\mathrm{A}}}\right). \tag{105}$$

As T approaches T_{A} (in dilute solutions of B in solvent A), the denominator on the right-hand side of eqn. (105) can be written RT_{A}^{2}. Therefore

$$X_{\mathrm{B}}^{s} - X_{\mathrm{B}}^{l} = \frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}^{2}}(T_{\mathrm{A}} - T) \tag{106}$$

or,

$$\left(\frac{\mathrm{d}X_{\mathrm{B}}^{s}}{\mathrm{d}T} - \frac{\mathrm{d}X_{\mathrm{B}}^{l}}{\mathrm{d}T}\right)_{T = T_{\mathrm{A}}} = \frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}^{2}}. \tag{107}$$

Equations (106) and (107) are referred to as the Van't Hoff relation. They give the depression of the freezing point for a liquid solution in equilibrium with a solid solution. The difference in initial slopes of the solidus and liquidus curves, the slopes at $T = T_{\mathrm{A}}$ and $X_{\mathrm{A}} = 1$, are dependent on the latent heat of fusion of pure A (ΔH_{A}) but independent of the nature of the solute.

Assumption: a solute atom in a crystal requires either more or less energy to reach its active state than the atoms of the solvent.

* If less, it is easier for solute atoms to “melt ” than for solvent atoms, while it is equally easy for both to “freeze”,

Thus, equilibrium will be established when there are fewer solute atoms in the solid than in the liquid. → Figure 27 (a)

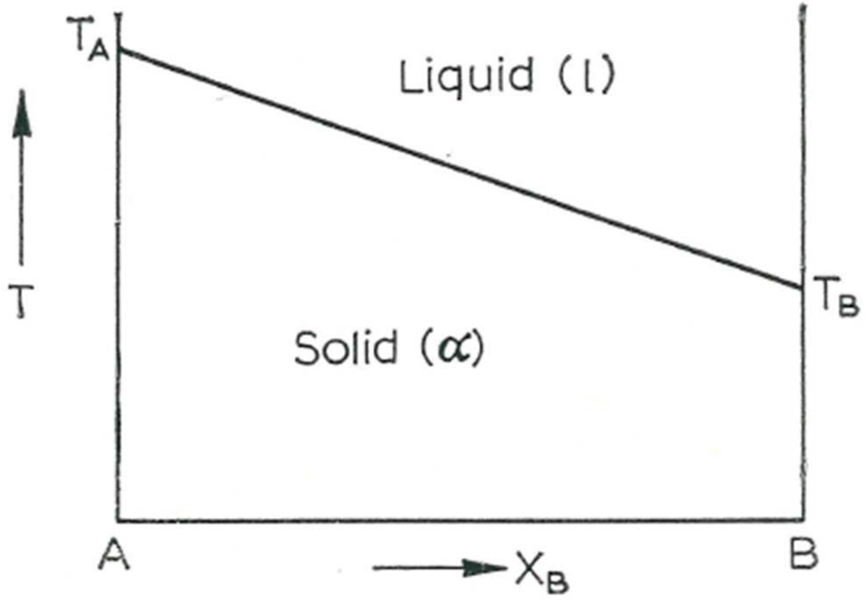
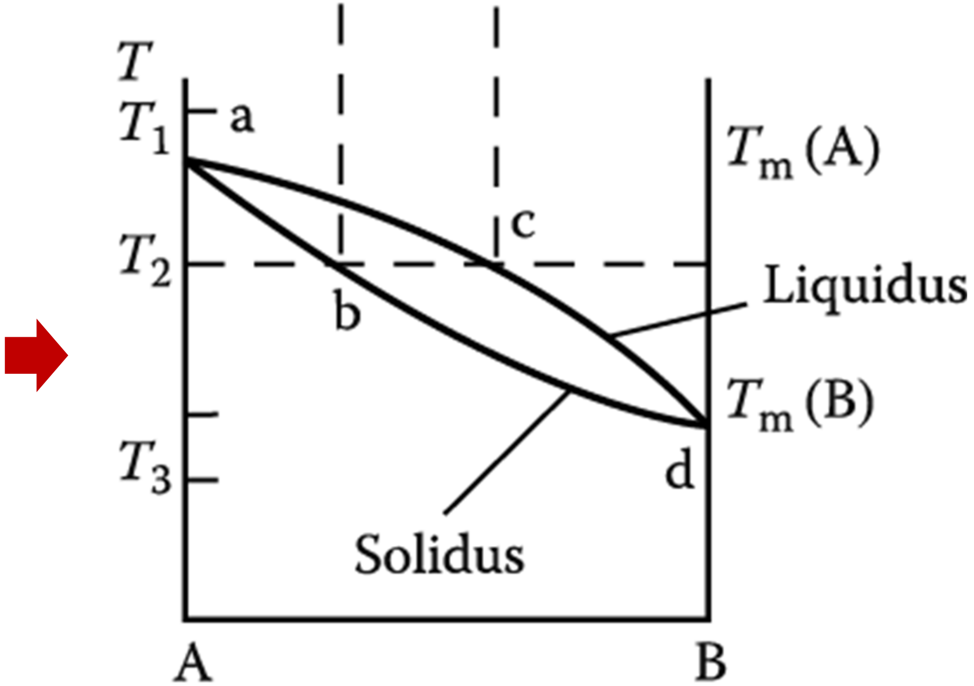


Fig. 22.



(f)

* The rates of both processes ~ solvent concentration

In case of alloys

1) Rate in liquid < Rate in solid (∵ $X_B^{Solid} < X_B^{Liquid}$),

2) the presence of the solute slows down the "freezing" process of the solvent more than the "melting" process _Thus, $T_E \rightarrow T_E'$

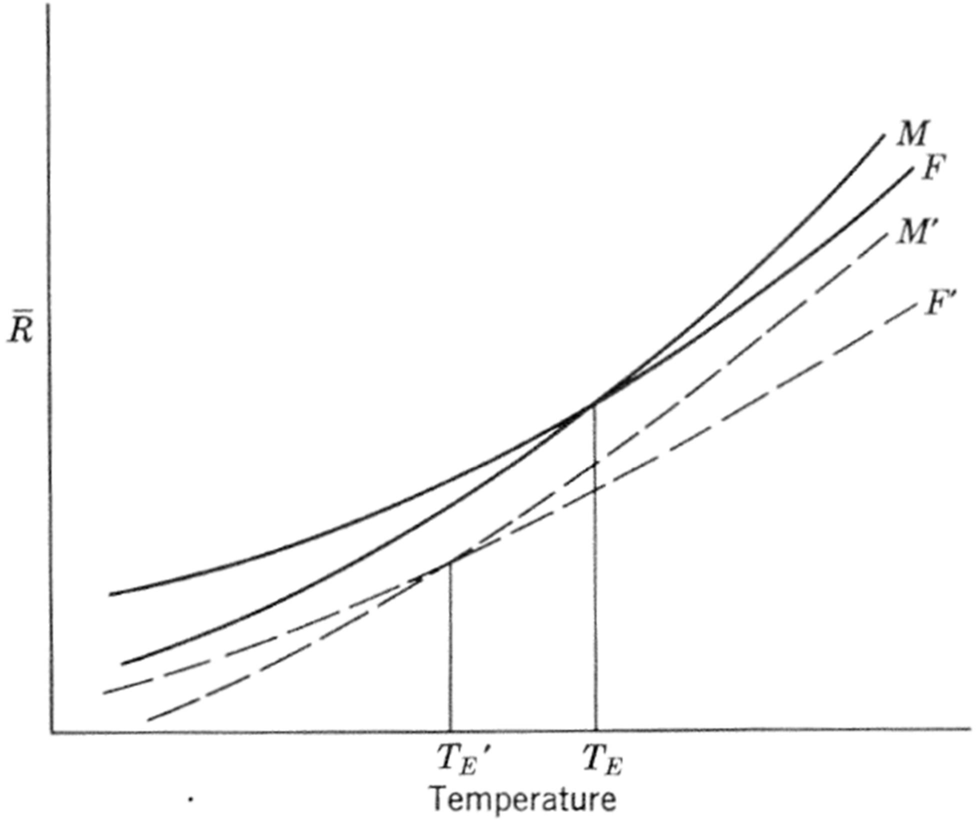
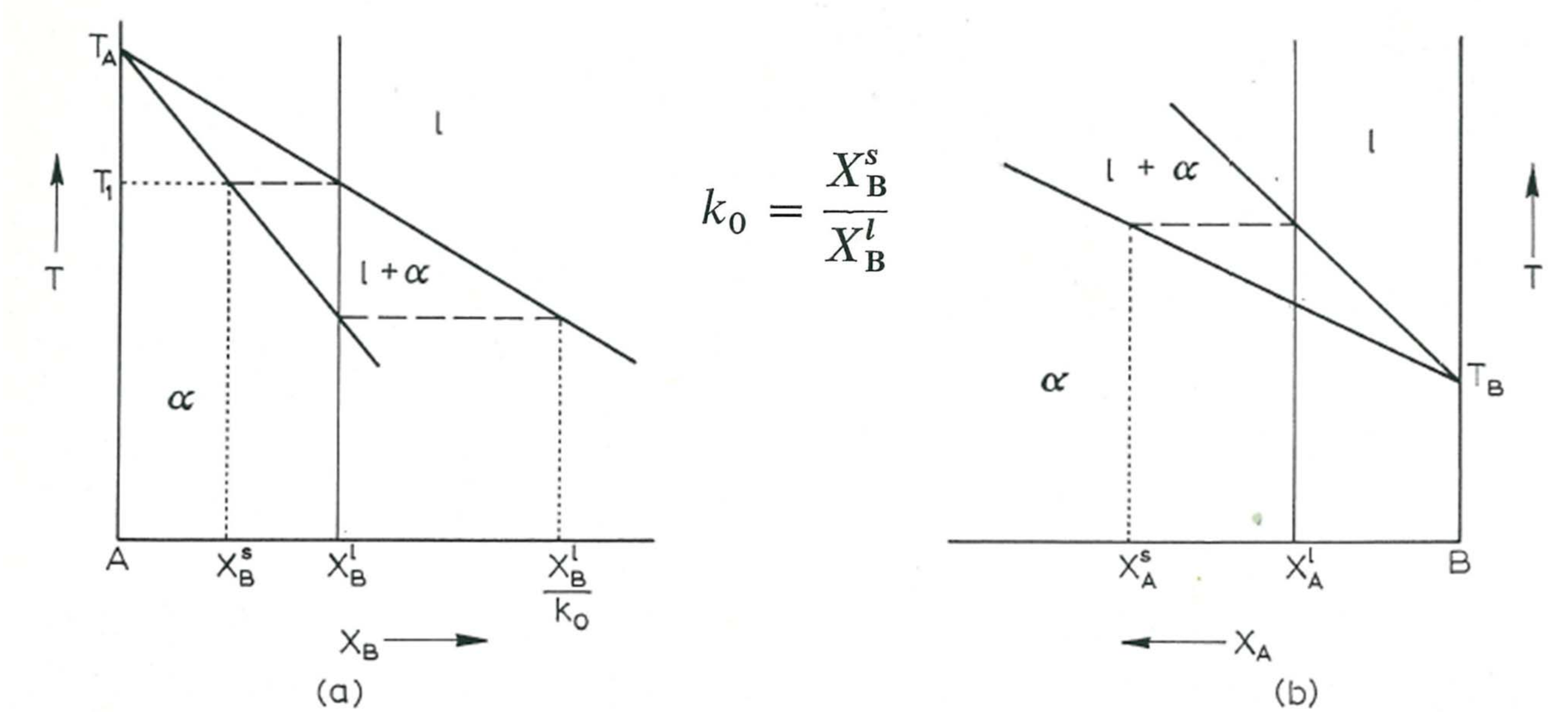


Fig. 2.11. Effect of a solute on the equilibrium temperature.

*** If more, it is easier for solvent atoms to “melt ” than for solute atoms. Thus, equilibrium will be established when there are fewer solute atoms in the liquid than in the solid. → Figure 27 (b)**

Typical liquidus and solidus curves

Less common than Fig. 27 (a)

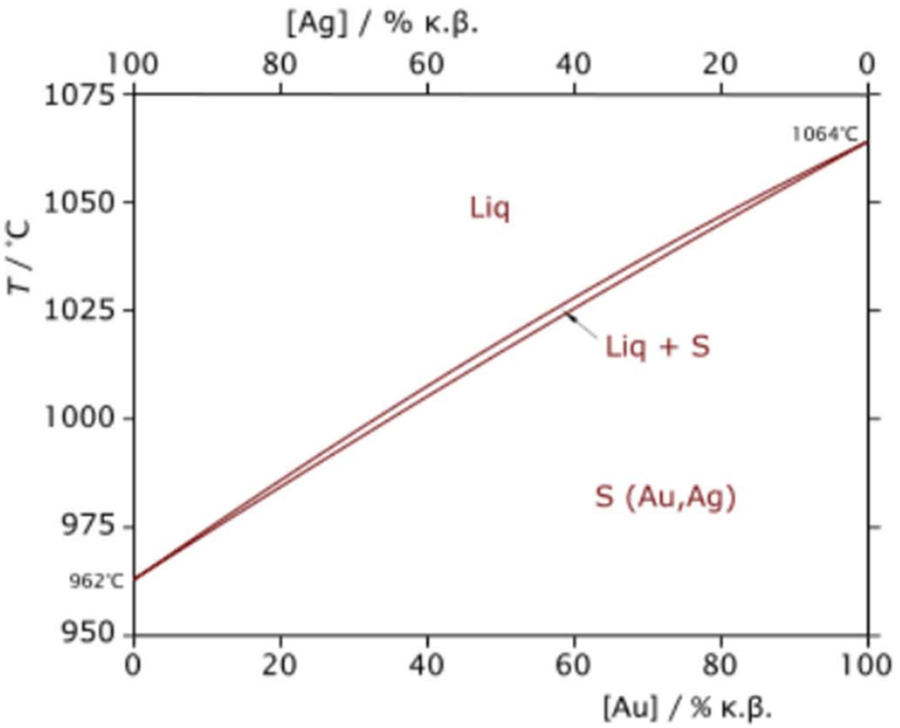


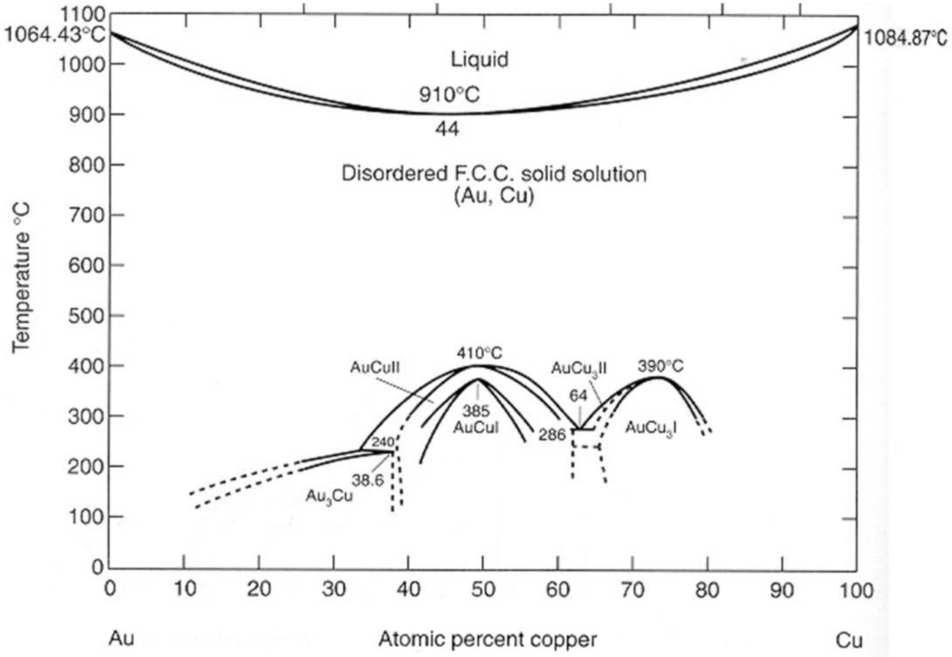
$$k_0 = \frac{X_B^s}{X_B^l}$$

Fig. 27. Part of a phase diagram with (a) $k_0 < 1$, and (b) $k_0 > 1$.

Assumption: both ideal solutions, very dilute solutions → good approximation

Assumption: complete mutual solid solubility





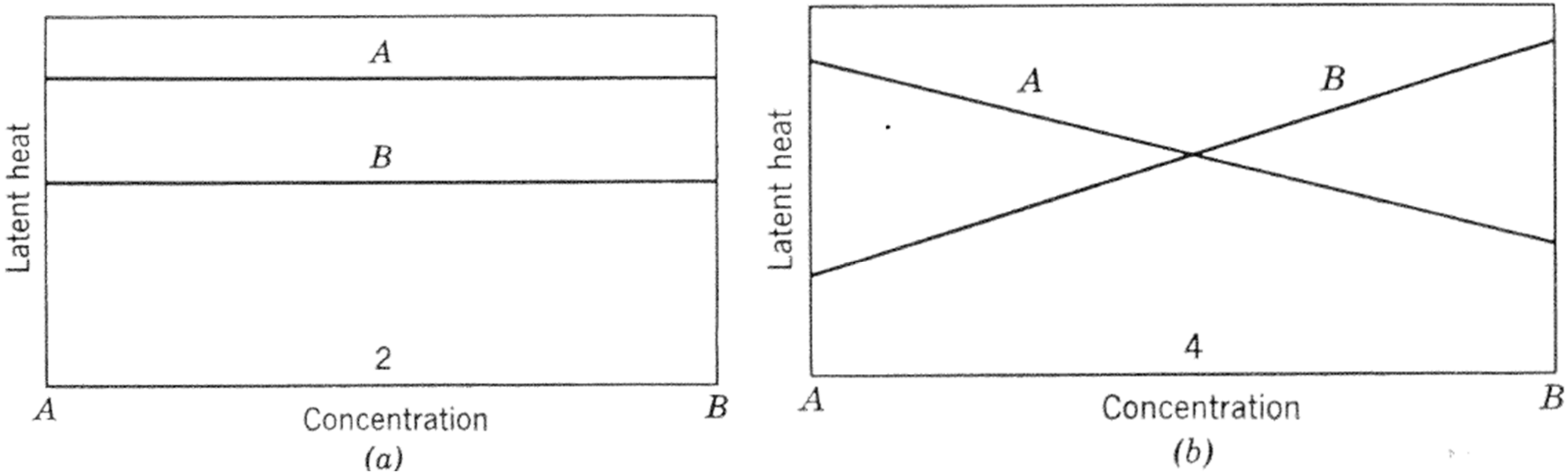


Fig. 2.14. Latent heat-concentration relationships for solid solutions. (From Ref. 24.)

Assumption: limited solid solubility, two different terminal crystal structures

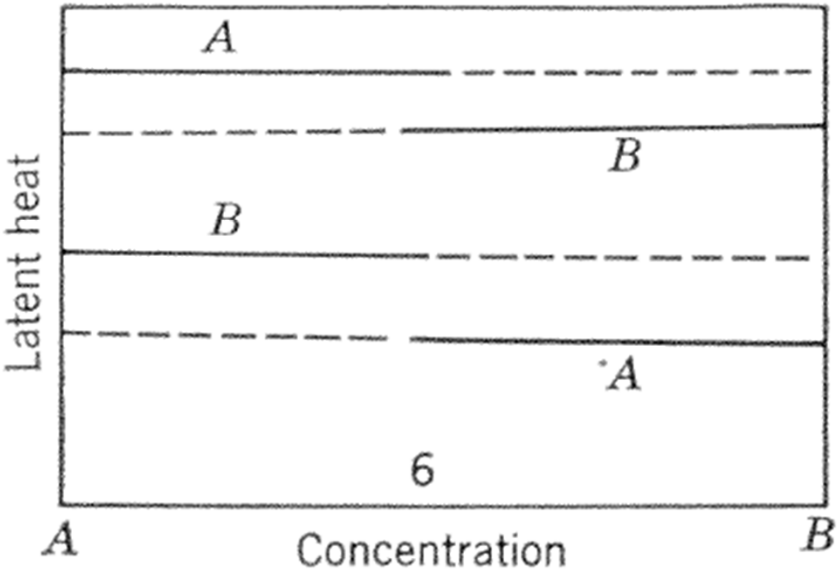


Fig. 2.16. Relationship between latent heat and concentration for an ideal eutectic forming system. (From Ref. 24.)

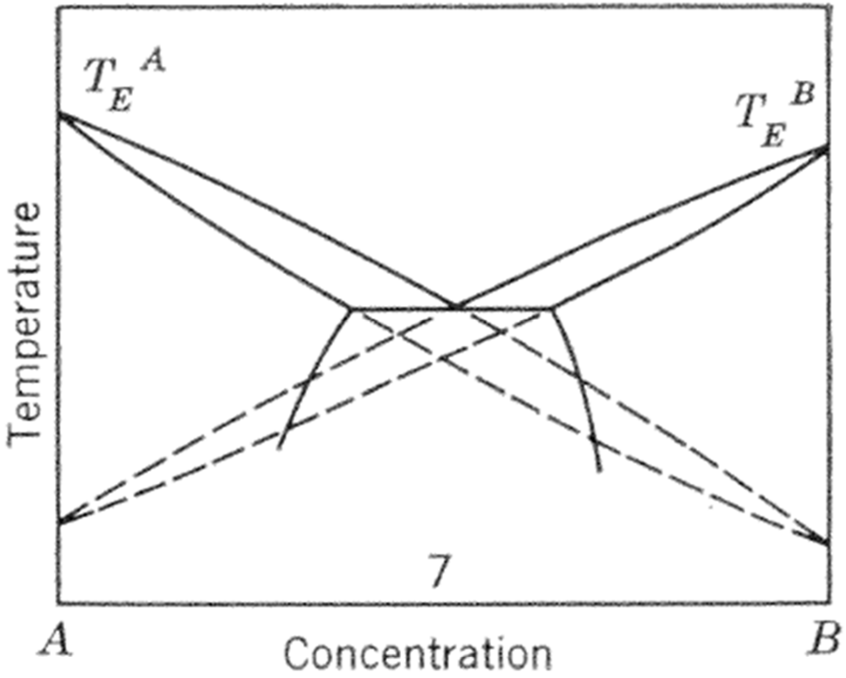


Fig. 2.17. Schematic phase diagram for eutectic forming system. (From Ref. 24.)

1) Simple Phase Diagrams

Assumption: (1) completely miscible in solid and liquid.

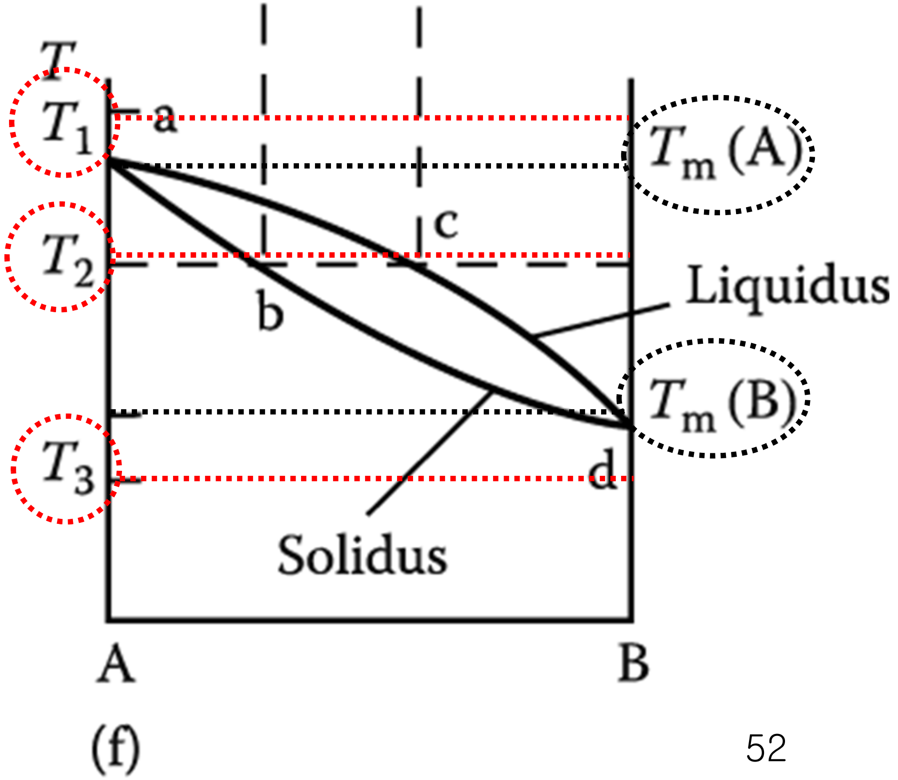
(2) Both are ideal soln.

$\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0$

(3) $T_m(A) > T_m(B)$

(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$

Draw G^L and G^S as a function of composition X_B at T_1, $T_m(A)$, T_2, $T_m(B)$, and T_3.

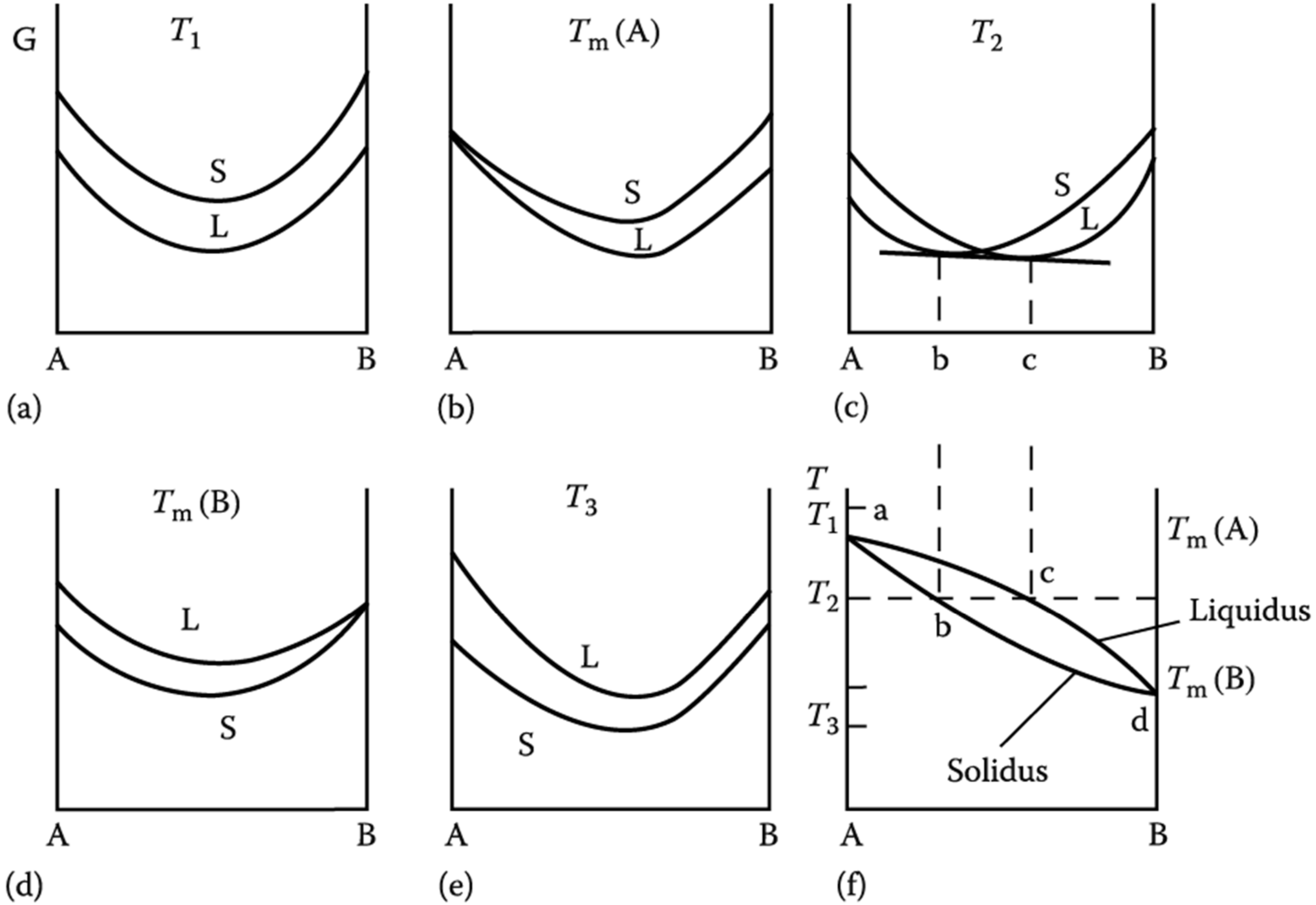


1.5 Binary phase diagrams

1) Simple Phase Diagrams

Assumption:

(1) completely miscible in solid and liquid.
(2) Both are ideal soln.
(3) $T_m(A) > T_m(B)$
(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$



*** Consider actual (or so-called regular) solutions in which** $\Delta H_m \neq 0$, but $\Delta S_m = \Delta S_{m,\mathrm{ideal}}$.

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta G_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

Since

$$\Delta G_A = \Delta H_A - T\Delta S_A$$

then,

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta H_A - X_A^l T\Delta S_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

The free energy curve for the solid phase is:

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta G_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s)$$

or,

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta H_B + X_B^s T\Delta S_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).$$

1) Simple Phase Diagrams

a) Variation of temp.: $G^L > G^s$

b) T ↓ → Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

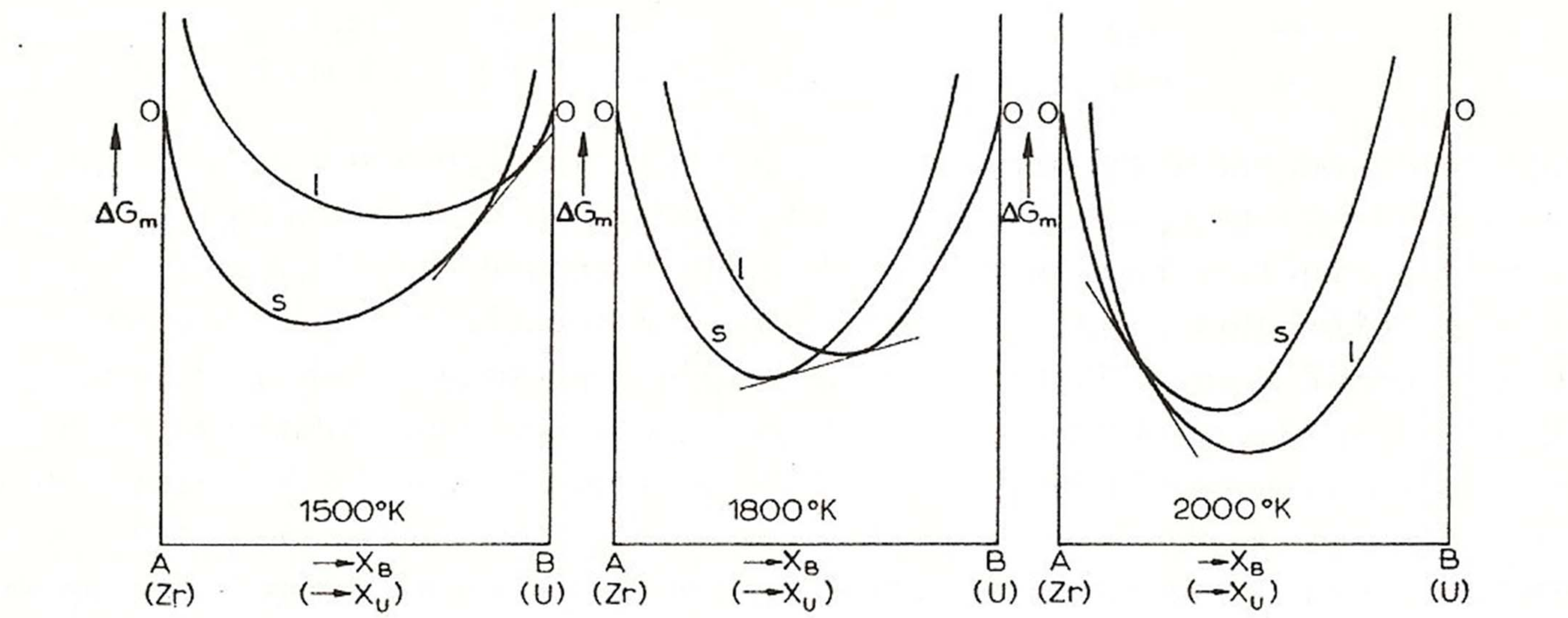


Fig. 26. Free energy curves for liquid and solid phases in the U–Zr system at 1500°, 1800° and 2000 °K.

It was assumed that $\Delta H_m^l = \Delta H_m^s$

1.5 Binary phase diagrams

1) Simple Phase Diagrams

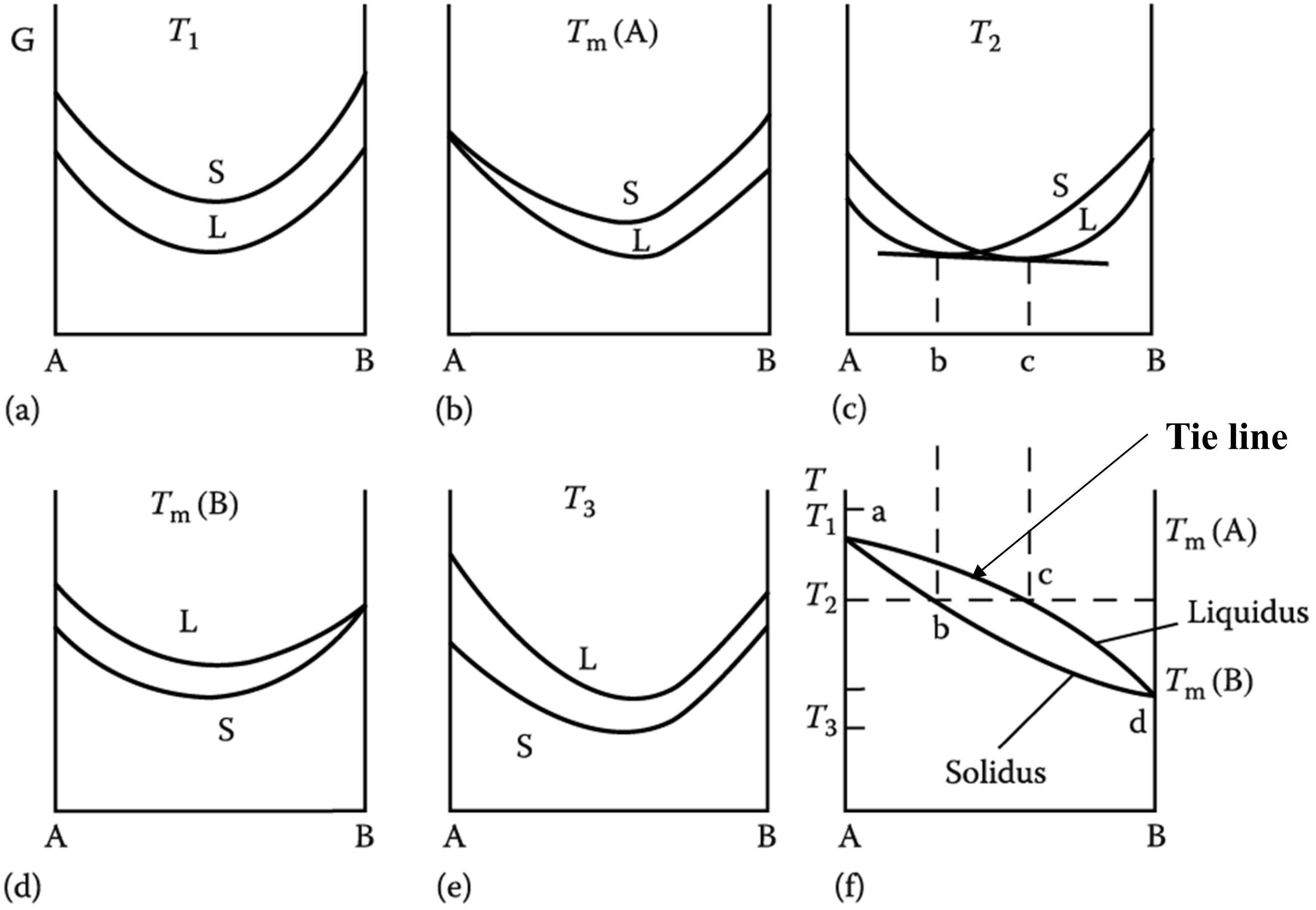
a) Variation of temp.: $G^L > G^s$

b) T ↓ → Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

Assumption:

- (1) completely miscible in solid and liquid.
- (2) Both are ideal soln.
- (3) $T_m(A) > T_m(B)$
- (4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$



Referring to Fig. 23f, if A is regarded as the solvent, for very dilute solutions of B in A we can write

$$X_A \to 1 \quad \text{and} \quad -\ln X_A \simeq X_B.$$

In terms of eqn. (104):

$$X_A^l - X_A^s = \frac{\Delta H_A}{R}\left(\frac{T_A - T}{TT_A}\right).$$

Since $X_A^l = 1 - X_B^l$ and $X_A^s = 1 - X_B^s$

$$X_B^s - X_B^l = \frac{\Delta H_A}{R}\left(\frac{T_A - T}{TT_A}\right). \tag{105}$$

As T approaches T_A (in dilute solutions of B in solvent A), the denominator on the right-hand side of eqn. (105) can be written RT_A^2. Therefore

$$X_B^s - X_B^l = \frac{\Delta H_A}{RT_A^2}(T_A - T) \tag{106}$$

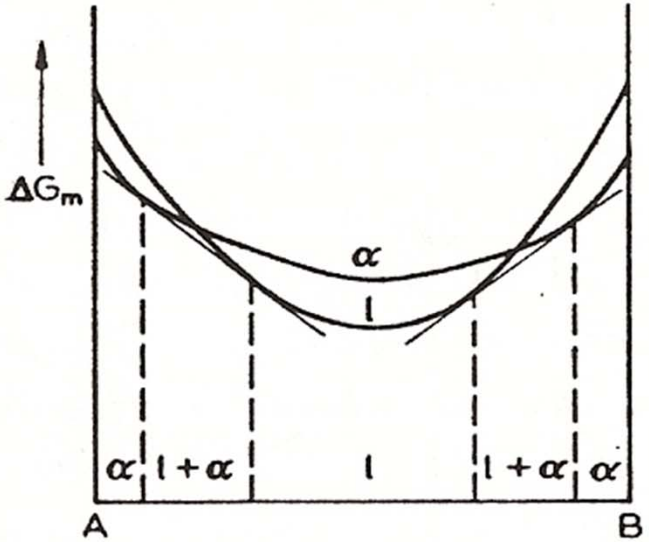
or,

$$\left(\frac{\mathrm{d}X_B^s}{\mathrm{d}T} - \frac{\mathrm{d}X_B^l}{\mathrm{d}T}\right)_{T=T_A} = \frac{\Delta H_A}{RT_A^2}. \tag{107}$$

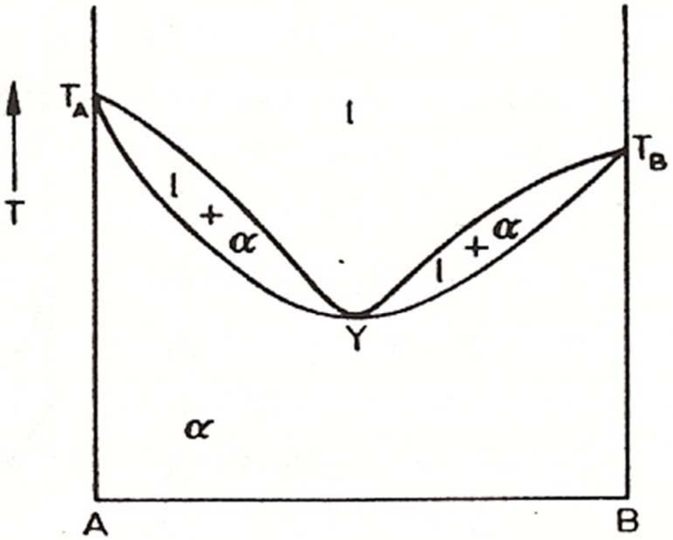
Equations (106) and (107) are referred to as the Van't Hoff relation. They give the depression of the freezing point for a liquid solution in equilibrium with a solid solution. The difference in initial slopes of the solidus and liquidus curves, the slopes at $T = T_A$ and $X_A = 1$, are dependent on the latent heat of fusion of pure A (ΔH_A) but independent of the nature of the solute.

2) Variant of the simple phase diagram

$$\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$$



(a)



(b)

2) Variant of the simple phase diagram

$$\Delta H_{mix} > 0 \quad \Delta H_{mix}^{\alpha} > \Delta H_{mix}^{l}$$

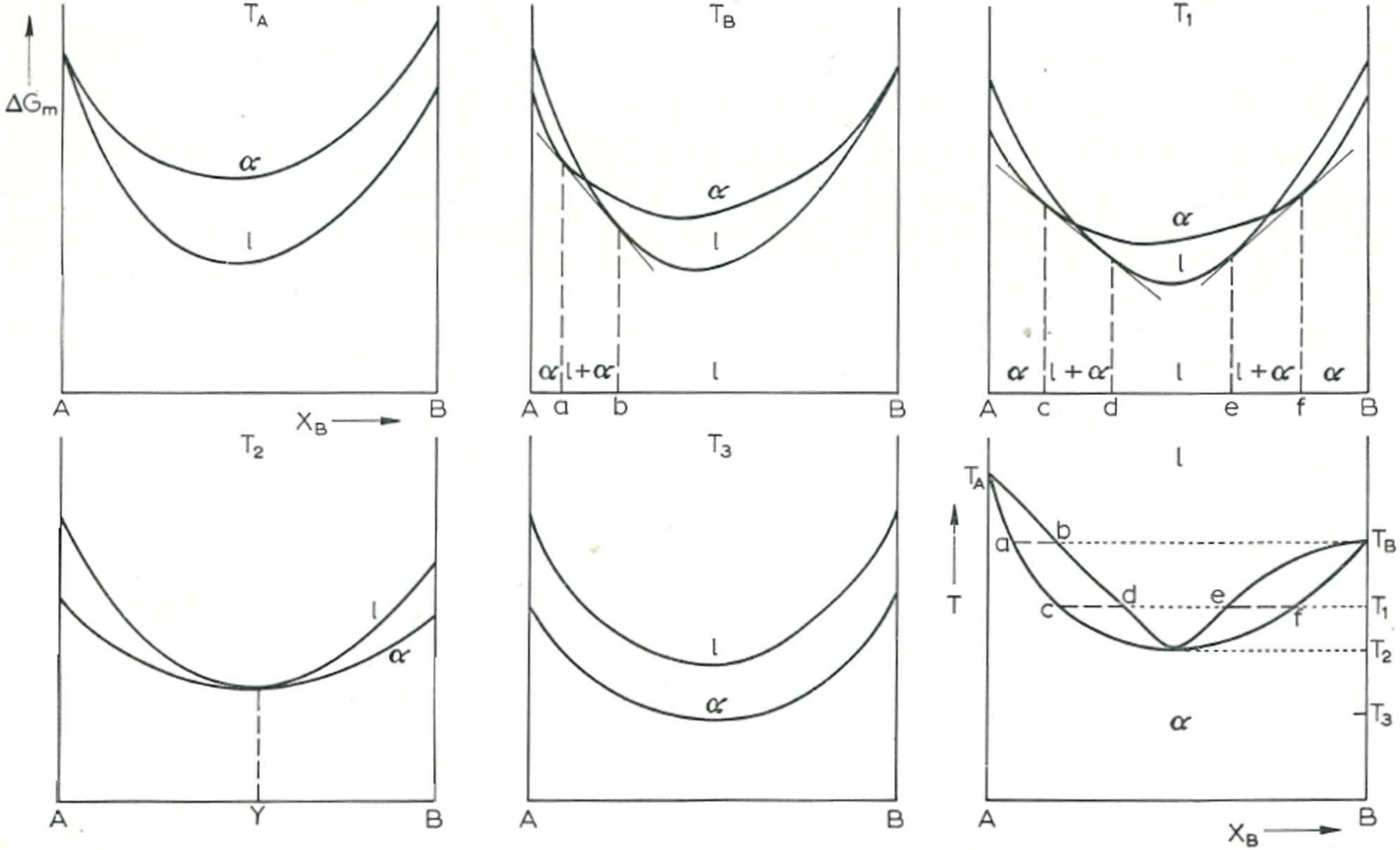
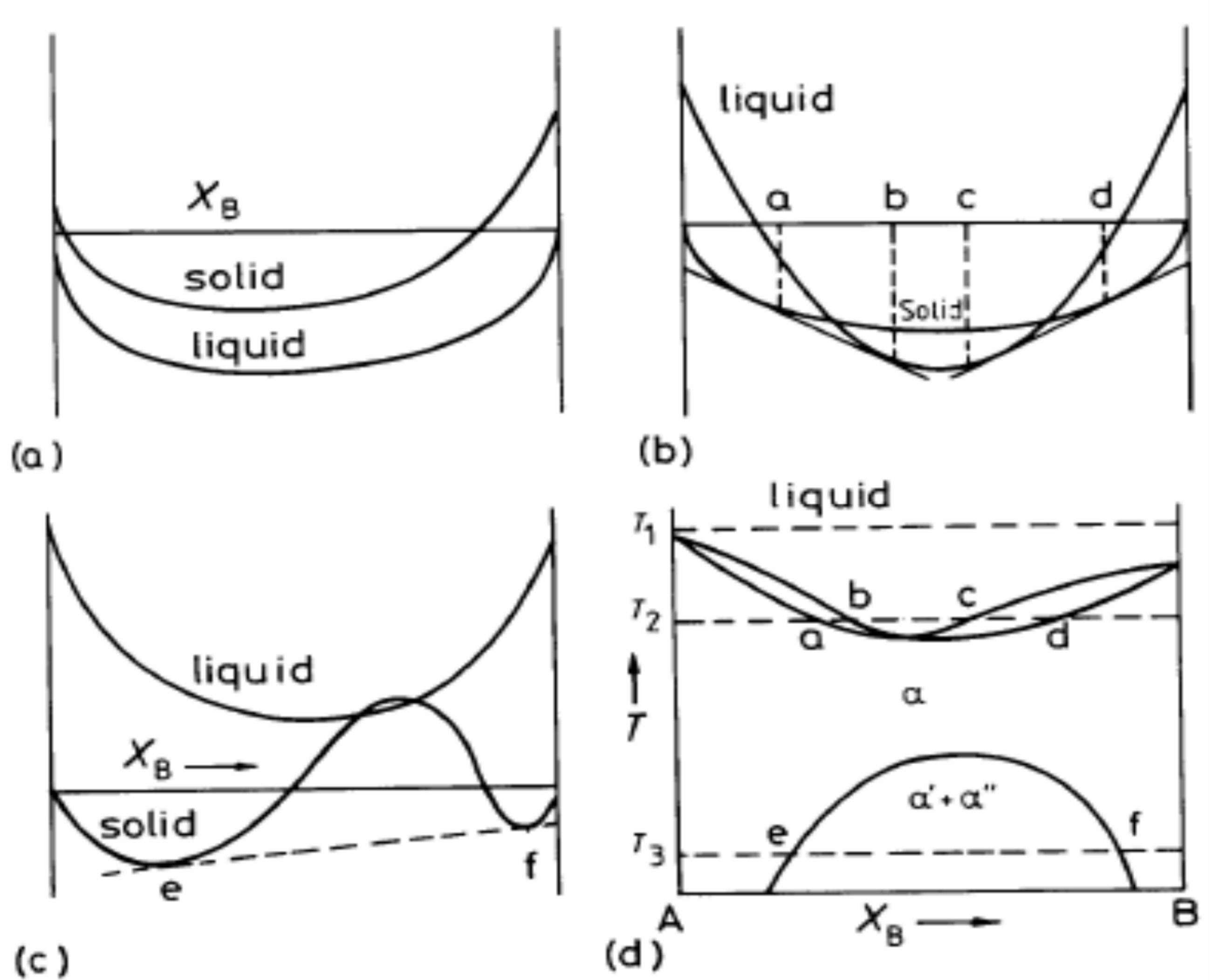


Fig. 30. Derivation of the phase diagram (Fig. 29b) from free energy curves for the liquid and solid phases. $T_A > T_B > T_1 > T_2 > T_3$.

2) Variant of the simple phase diagram

Systems with miscibility gab $\Delta H_{mix} > 0$ $\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$



congruent minima

2) Variant of the simple phase diagram

$\Delta H_{mix} < 0$

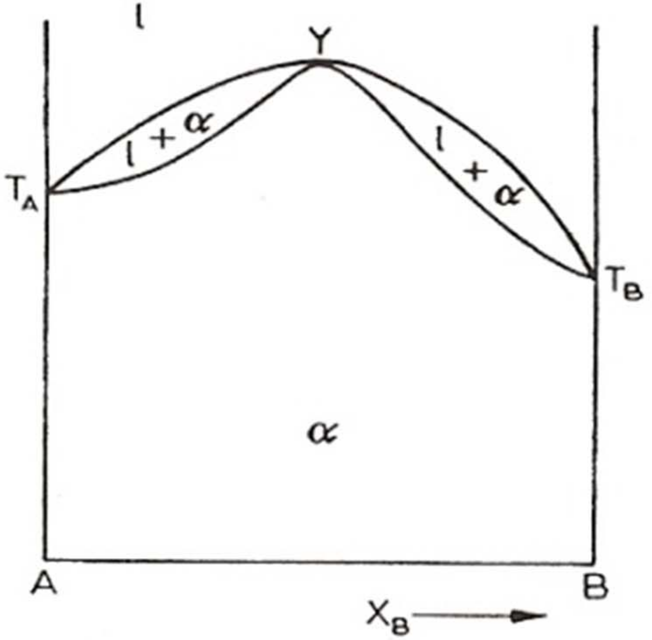


Fig. 32. Phase diagram with a maximum in the liquidus.

$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

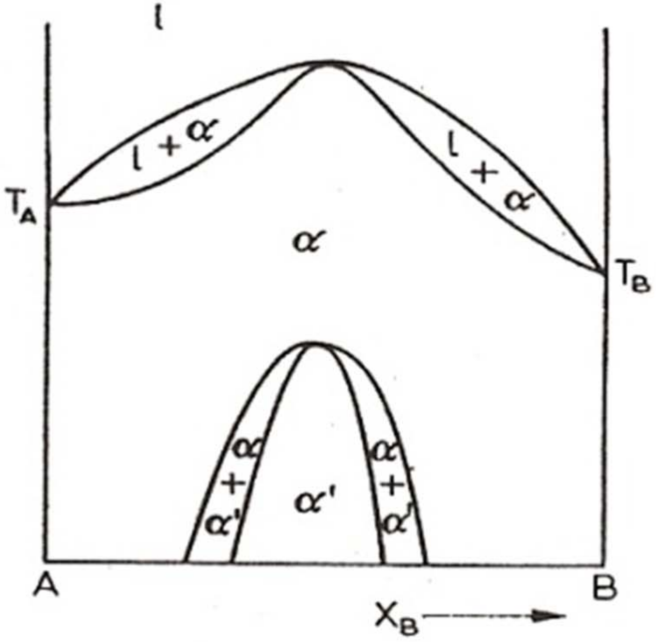


Fig. 33. Appearance of an ordered α′ phase at low temperatures.

Binary phase diagrams

1) Simple Phase Diagrams

Both are ideal soln. → At T change, curvature and width change of G curve by S

2) Systems with miscibility gap

$$\Delta H_{mix}^{L} = 0 \qquad \Delta H_{mix}^{S} > 0$$

At T change, curvature and width change of G curve by S + shape change of curve by H

4) Simple Eutectic Systems

$$\Delta H_{mix}^{L} = 0 \qquad \Delta H_{mix}^{S} >> 0$$

→ miscibility gap extends to the melting temperature.

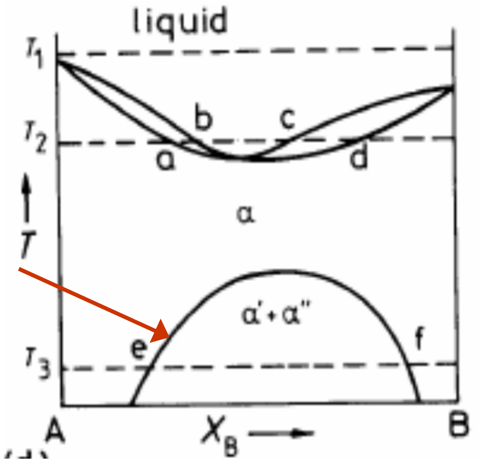
3) Ordered Alloys

$$\Delta H_{mix}^{L} = 0 \qquad \Delta H_{mix}^{S} < 0$$

$\Delta H_{mix} < 0$ → A atoms and B atoms like each other. → Ordered alloy at low T

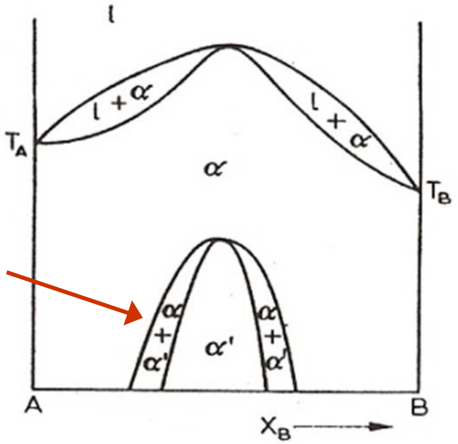
$\Delta H_{mix} << 0$ → The ordered state can extend to the melting temperature.

$$\boxed{\Delta H_{mix}^{\alpha} > \Delta H_{mix}^{l} > 0}$$



miscibility gab

$$\boxed{\Delta H_{mix}^{\alpha} < \Delta H_{mix}^{l} < 0}$$



Ordered phase