What exactly do pressure and temperature do to the molar Gibbs energies of phases?

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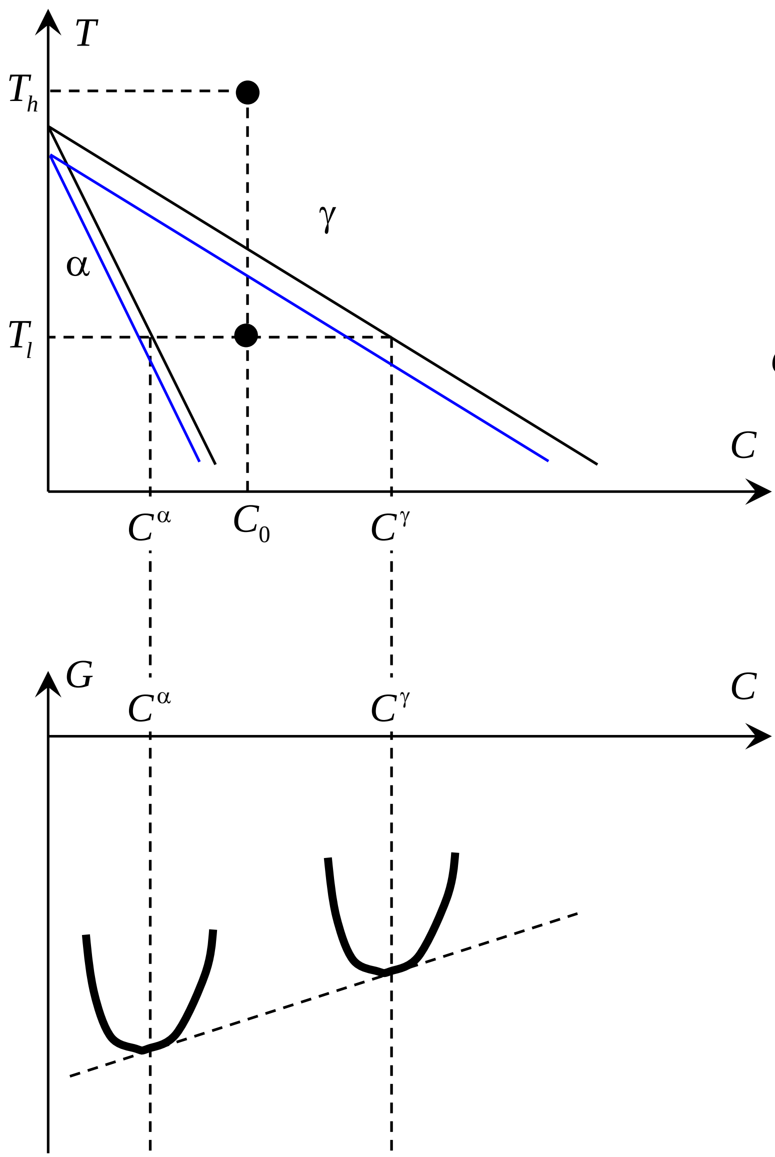
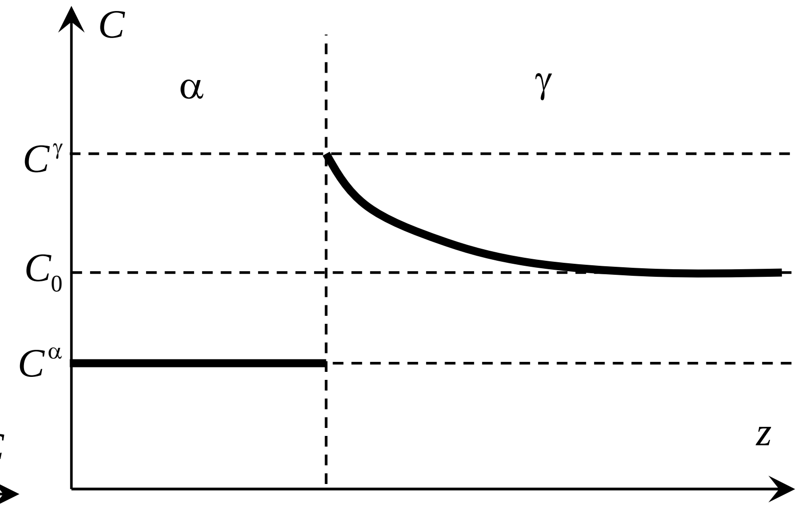
*713
3T04
3A03

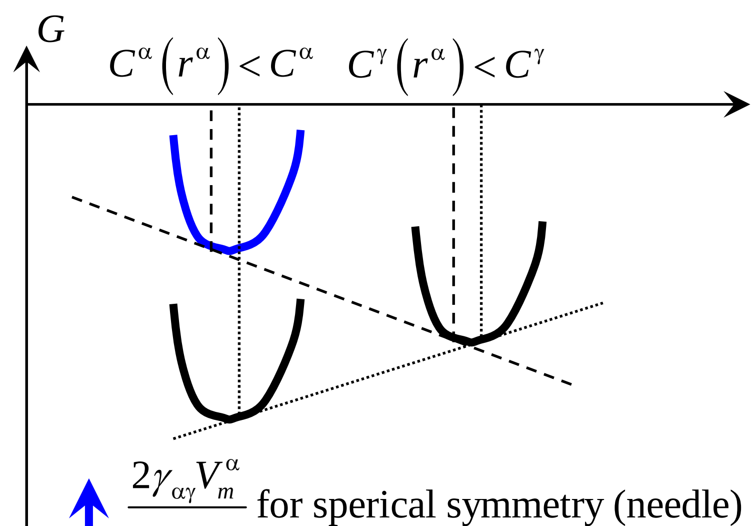
Let us start with the influence of pressure

This influence is not of a scholastic interest only





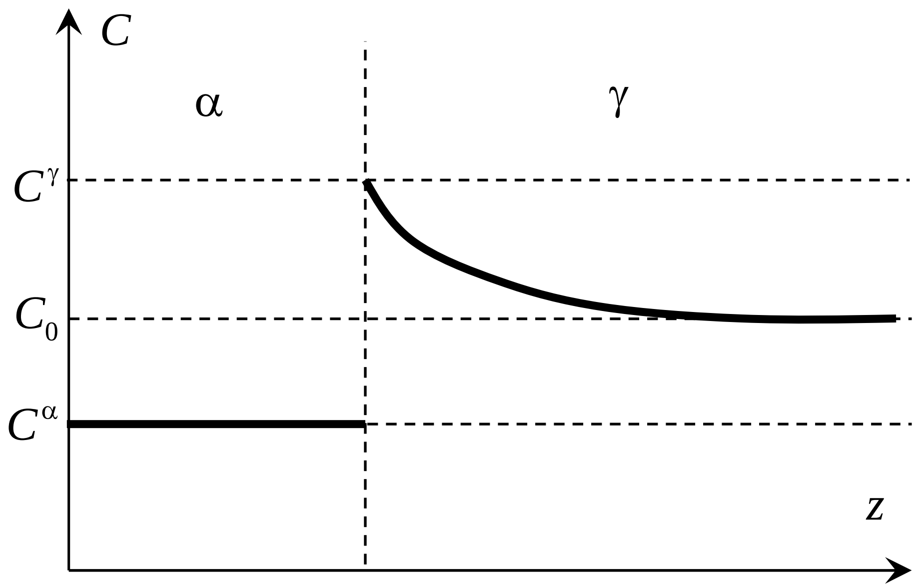
A planar α/γ interface



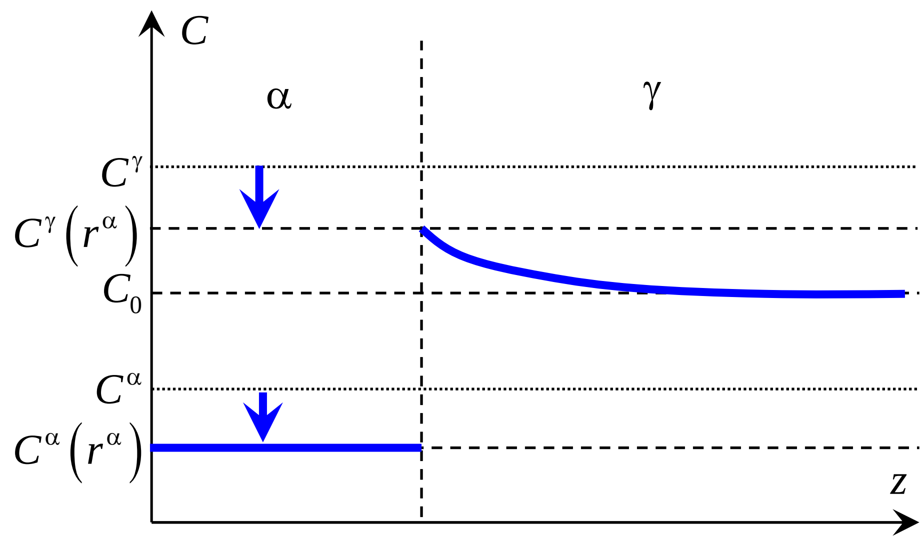
$\frac{2\gamma_{\alpha\gamma}V_m^\alpha}{r}$ for sperical symmetry (needle)

$\frac{\gamma_{\alpha\gamma}V_m^\alpha}{r}$ for cylindrical symmetry (plate)

A definition of a critical radius



$r^{\alpha} = \infty$



$r_{\text{critical}} < r^{\alpha} < \infty$

$$C^{\gamma}\left(r_{\text{critical}}\right) = C_0$$

Shewmon “Transformations in metals”, Page 151

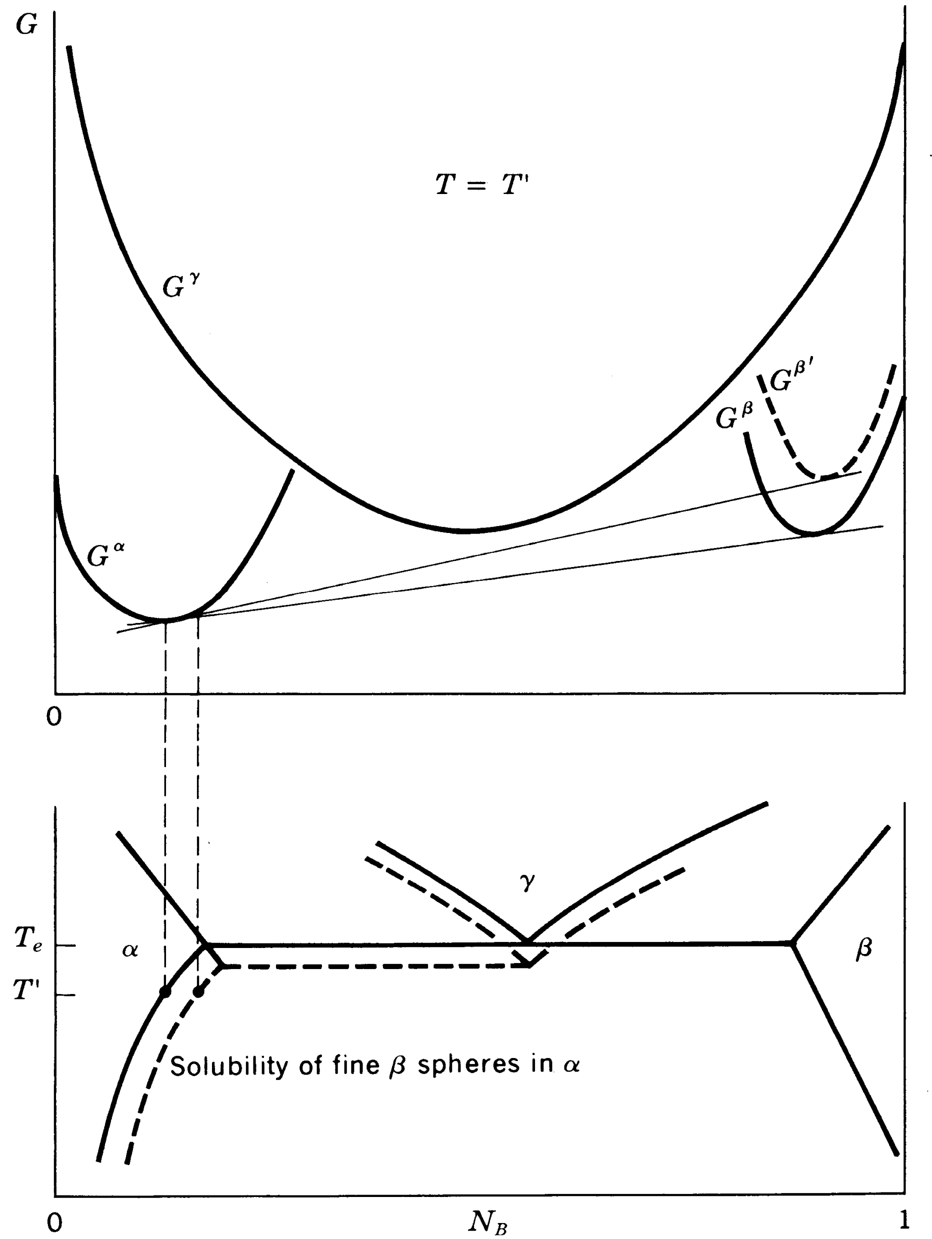


figure 4-10. *Free-energy diagram and phase diagram indicating change in solubility of β, and eutectoid temperature when β is present as fine spheres (labeled β′).*

Porter, Easterling “Phase transformations in metals and alloys”, Page 285

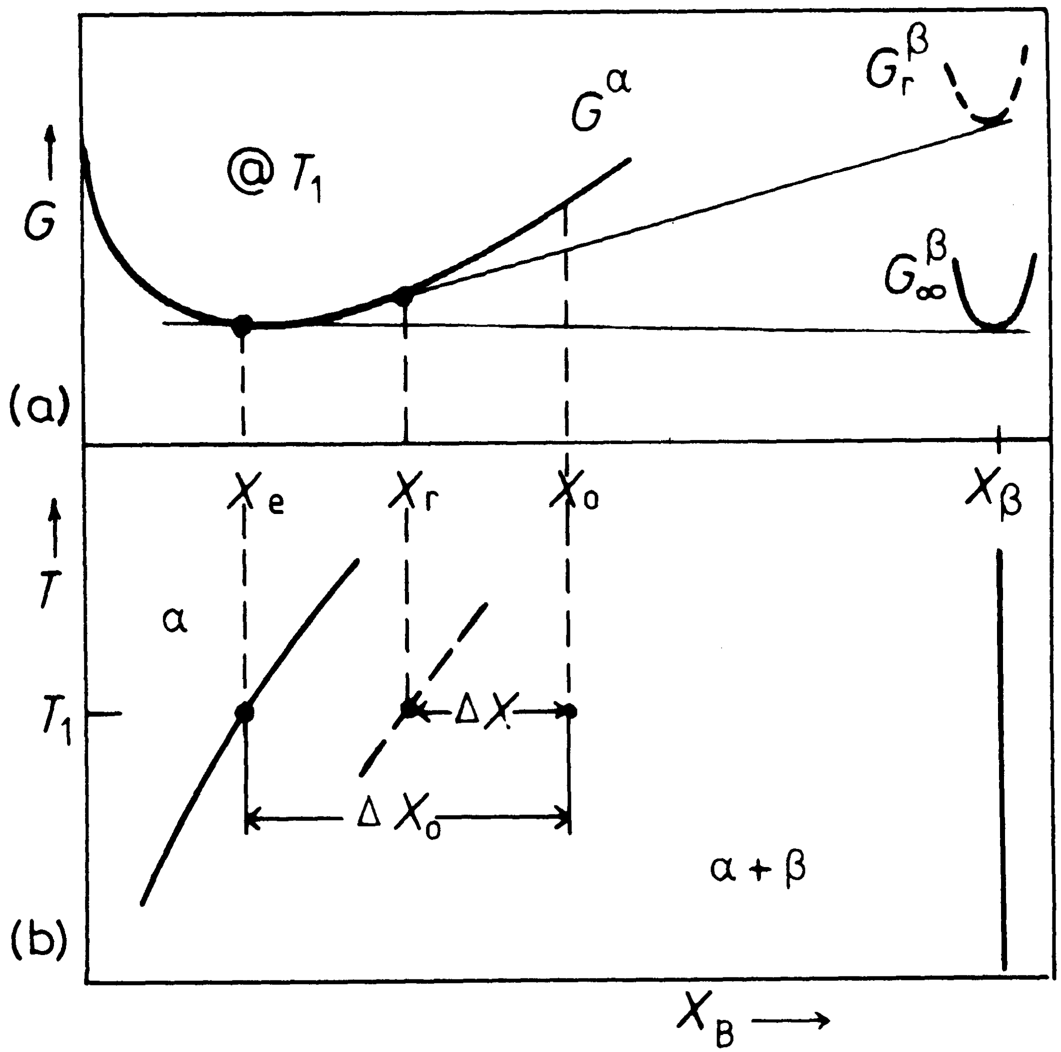


Fig. 5.20 The Gibbs-Thomson effect. (a) Free energy curves at T_1. (b) Corresponding phase diagram.

Hillert "Applications of Gibbs energy-composition diagrams" in "Lectures on the theory of phase transformations", Page 21

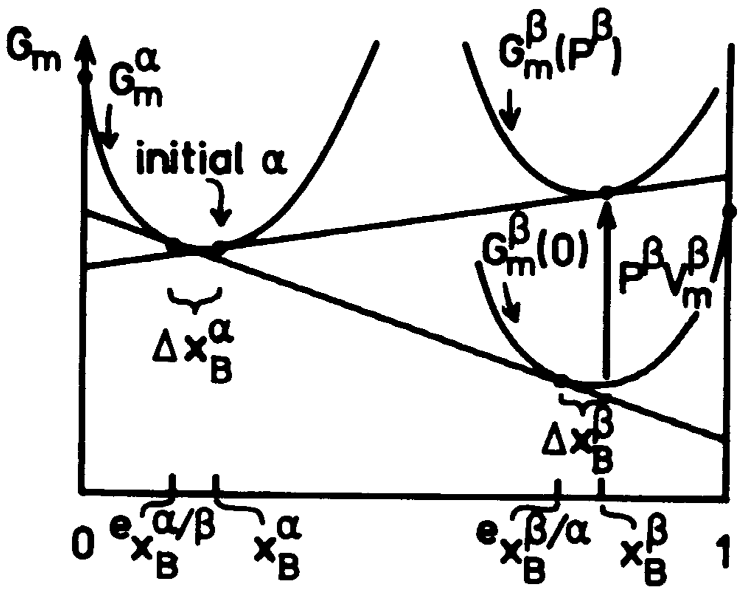


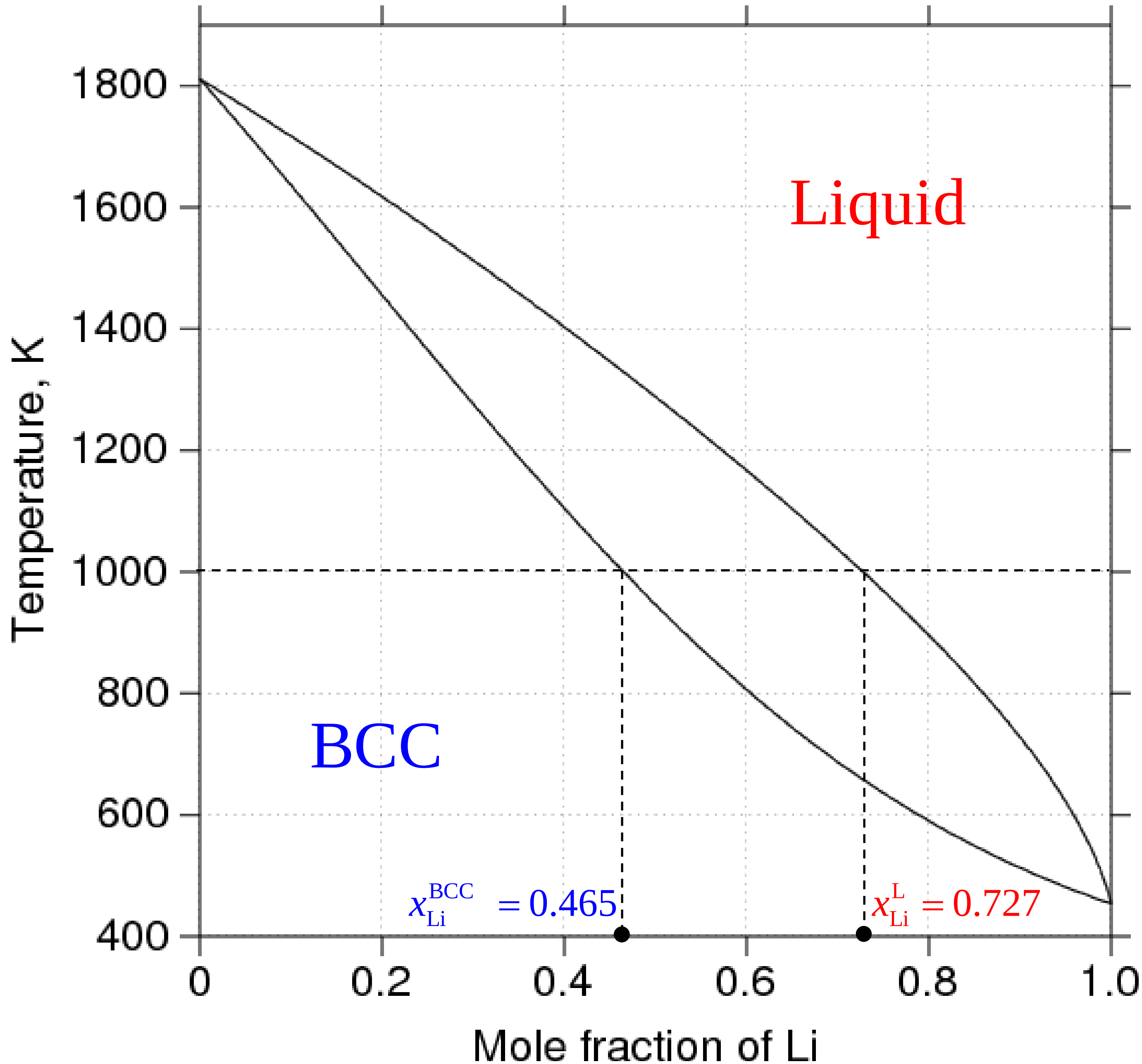
Fig. 27. Change in compositions when a pressure is applied to one of the phases in a two-phase equilibrium.

Rationale

$$\left(\frac{\partial G}{\partial P}\right)_T = \underbrace{V}_{\text{Always positive}}$$

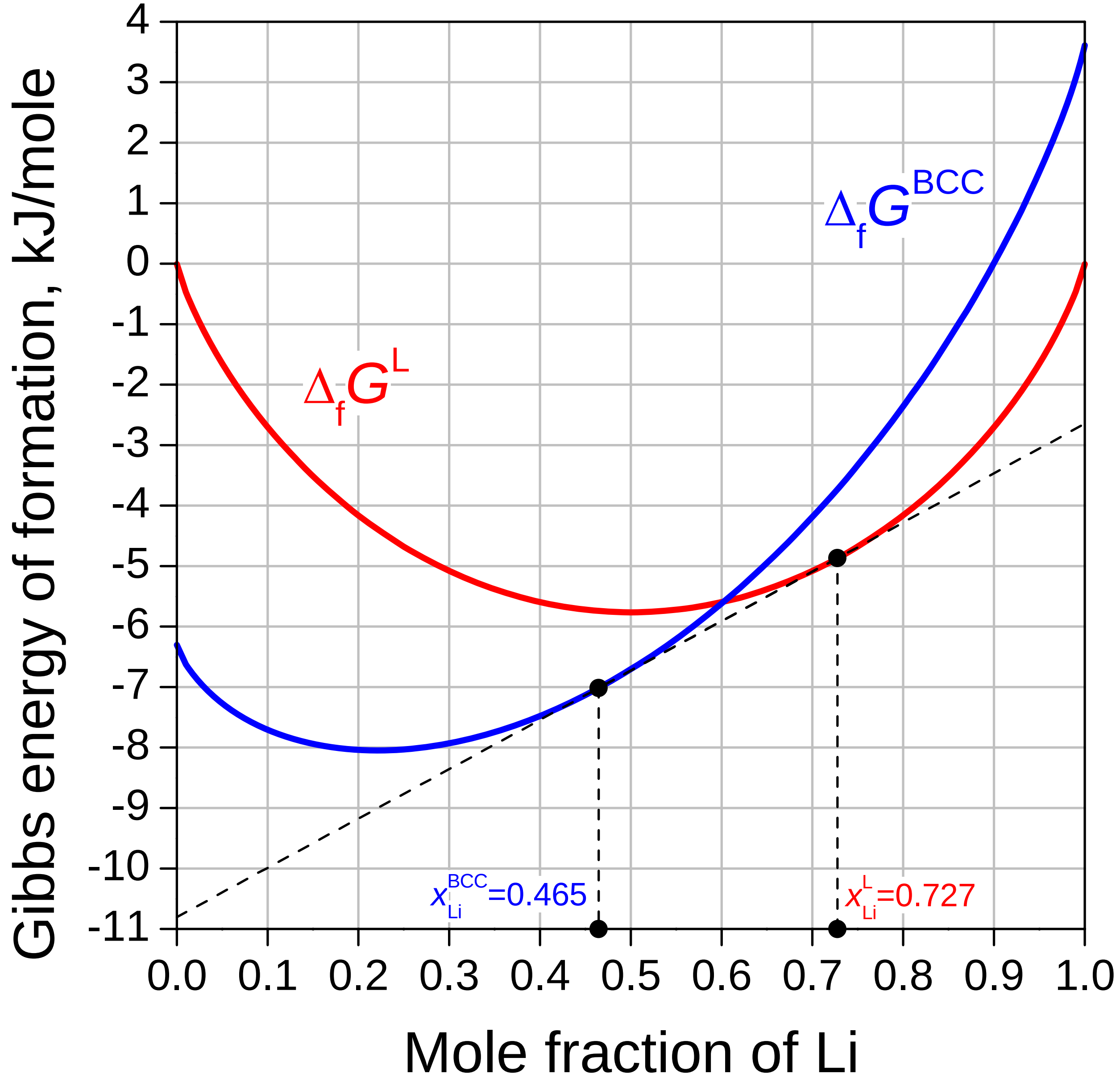
Liquid/BCC equilibrium in the Fe–Li system

Thermo-Calc + COST 507 database

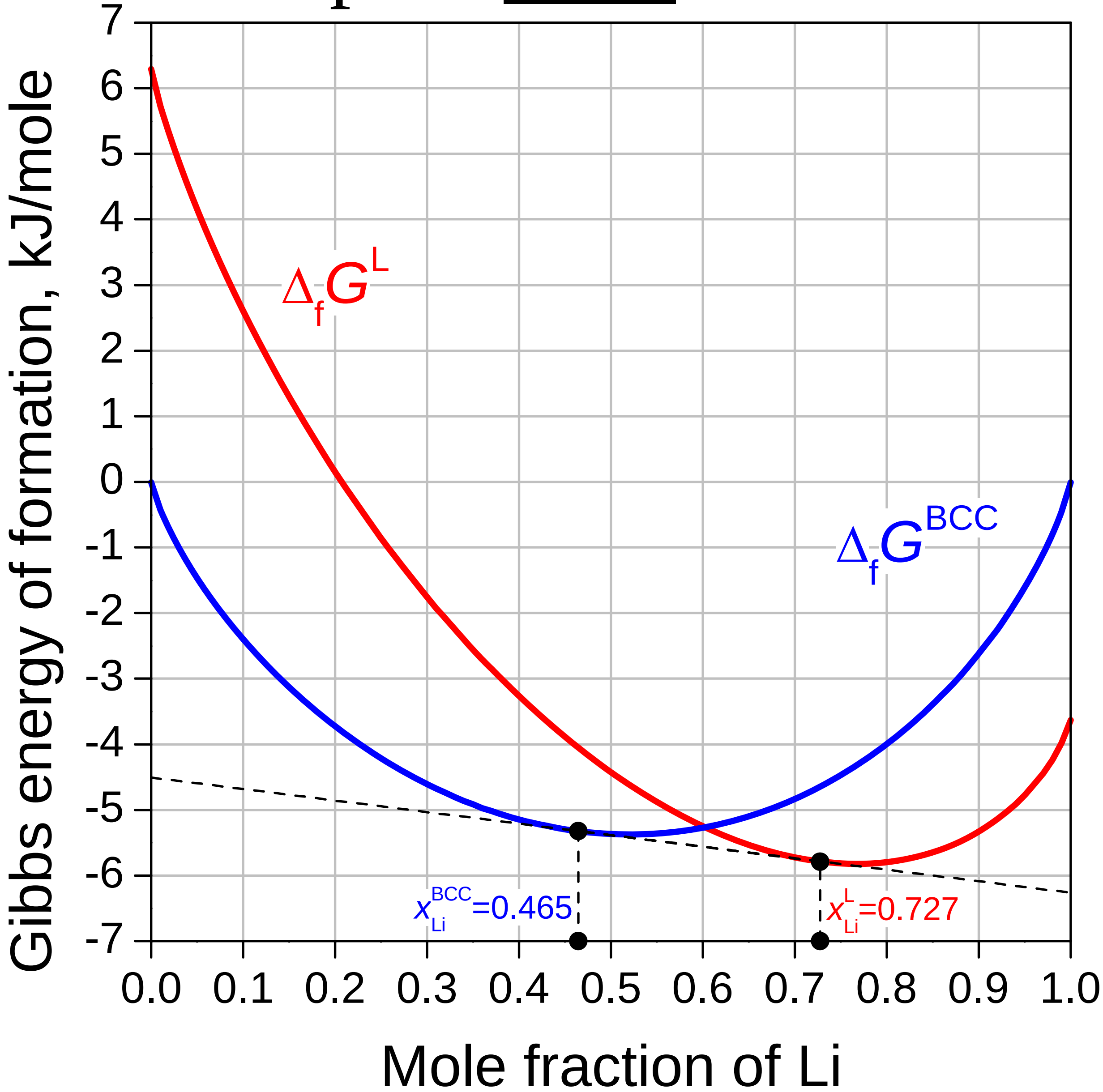


T = 1000 K, reference states are pure <u>liquid</u> Fe and pure <u>liquid</u> Li

Thermo-Calc + COST 507 database



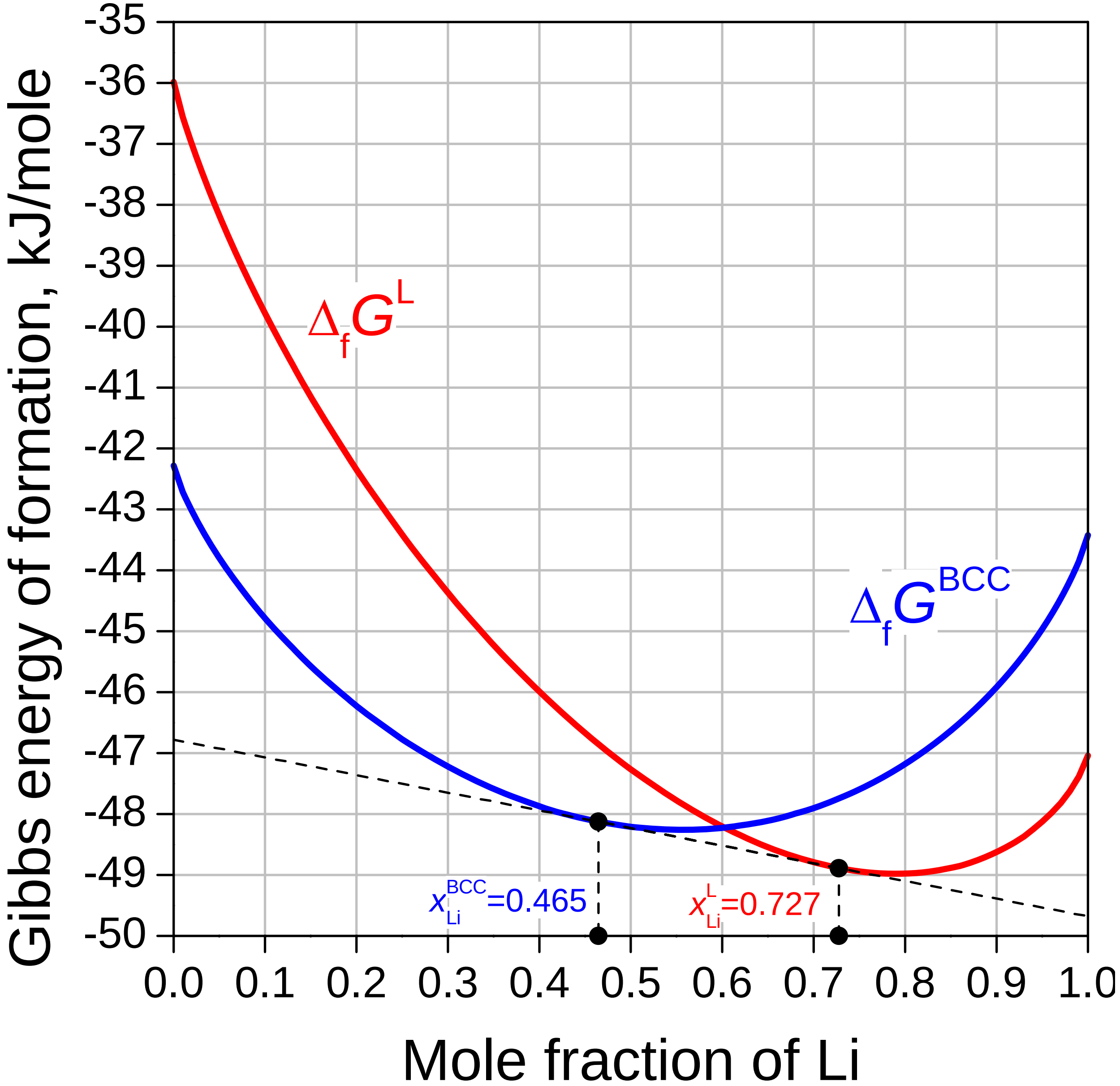
T = 1000 K, reference states are pure BCC Fe and pure BCC Li



Thermo-Calc + COST 507 database

T = 1000 K, the so-called "standard element references" are used

Thermo-Calc + COST 507 database



Not G per se, but $\Delta_f G$!

$$\left(\frac{\partial G}{\partial P}\right)_T = \underbrace{V}_{\text{Always positive}}$$

$$\left(\frac{\partial \Delta_f G}{\partial P}\right)_T = \underbrace{\Delta_f V}_{?}$$

Let us make a phase γ from pure components

$$\left(1-x\right)\mathrm{A}^{\alpha}+x\mathrm{B}^{\beta}$$

$$\left(1-x\right)\Delta_{\mathrm{tr}}G_{\mathrm{A}}^{0\,\alpha\rightarrow\gamma}+x\Delta_{\mathrm{tr}}G_{\mathrm{B}}^{0\,\beta\rightarrow\gamma}$$

$$\left(1-x\right)\mathrm{A}^{\gamma}+x\mathrm{B}^{\gamma}$$

$$RT\left[\left(1-x\right)\ln\left(1-x\right)+x\ln x\right]$$

$$\underbrace{\mathrm{A}_{1-x}\mathrm{B}_{x}{}^{\gamma}}_{\text{Ideal } \gamma \text{ solution}}$$

$$\Delta_{\mathrm{f}}G$$

$$\Delta^{\mathrm{ex}}G$$

$$\underbrace{\mathrm{A}_{1-x}\mathrm{B}_{x}{}^{\gamma}}_{\text{Real } \gamma \text{ solution}}$$

Reference states are pure liquid components

$$\Delta G^{\mathrm{L}} = (1-x)\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\mathrm{L}\to\mathrm{L}}}_{\equiv 0} + x\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\mathrm{L}\to\mathrm{L}}}_{\equiv 0} + \underbrace{\Delta^{\mathrm{id}} G^{\mathrm{L}}}_{\neq f(P)} + \underbrace{\Delta^{\mathrm{ex}} G^{\mathrm{L}}}_{\neq f(P)}$$

$$\Delta G^{\alpha} = (1-x)\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\mathrm{L}\to\alpha} + x\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\mathrm{L}\to\alpha} + \underbrace{\Delta^{\mathrm{id}} G^{\alpha}}_{\neq f(P)} + \underbrace{\Delta^{\mathrm{ex}} G^{\alpha}}_{\neq f(P)}$$

$$\left(\frac{\partial \Delta G^{\mathrm{L}}}{\partial P}\right)_T = 0$$

$$\left(\frac{\partial \Delta G^{\alpha}}{\partial P}\right)_T = (1-x)\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\mathrm{L}\to\alpha}}{\partial P}\right)_T + x\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\mathrm{L}\to\alpha}}{\partial P}\right)_T$$

$$= (1-x)\underbrace{\left(V_{\mathrm{A}}^{\alpha} - V_{\mathrm{A}}^{\mathrm{L}}\right)}_{\text{Usually negative}} + x\underbrace{\left(V_{\mathrm{B}}^{\alpha} - V_{\mathrm{B}}^{\mathrm{L}}\right)}_{\text{Usually negative}} < 0$$

Why “usually”? Because there are rare exceptions such as H_2O, Bi, Sb

What does this mean?

ΔG^{L} does not change its position

ΔG^{α} shifts downward by $(1-x)\left(V_{\mathrm{A}}^{\alpha}-V_{\mathrm{A}}^{\mathrm{L}}\right)+x\left(V_{\mathrm{B}}^{\alpha}-V_{\mathrm{B}}^{\mathrm{L}}\right)$

The α phase is stabilized by pressure applied

Reference states are pure solid components

$$\Delta G^{\mathrm{L}} = (1-x)\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\alpha\to\mathrm{L}} + x\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\alpha\to\mathrm{L}} + \underbrace{\Delta^{\mathrm{id}} G^{\mathrm{L}}}_{\neq f(P)} + \underbrace{\Delta^{\mathrm{ex}} G^{\mathrm{L}}}_{\neq f(P)}$$

$$\Delta G^{\alpha} = (1-x)\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\alpha\to\alpha}}_{\equiv 0} + x\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\alpha\to\alpha}}_{\equiv 0} + \underbrace{\Delta^{\mathrm{id}} G^{\alpha}}_{\neq f(P)} + \underbrace{\Delta^{\mathrm{ex}} G^{\alpha}}_{\neq f(P)}$$

$$\left(\frac{\partial \Delta G^{\alpha}}{\partial P}\right)_T = 0$$

$$\left(\frac{\partial \Delta G^{\mathrm{L}}}{\partial P}\right)_T = (1-x)\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\alpha\to\mathrm{L}}}{\partial P}\right)_T + x\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\alpha\to\mathrm{L}}}{\partial P}\right)_T$$

$$= (1-x)\underbrace{\left(V_{\mathrm{A}}^{\mathrm{L}} - V_{\mathrm{A}}^{\alpha}\right)}_{\text{Usually positive}} + x\underbrace{\left(V_{\mathrm{B}}^{\mathrm{L}} - V_{\mathrm{B}}^{\alpha}\right)}_{\text{Usually positive}} > 0$$

What does this mean?

ΔG^{α} does not change its position

ΔG^{L} shifts upward by $(1-x)\left(V_A^{L}-V_A^{\alpha}\right)+x\left(V_B^{L}-V_B^{\alpha}\right)$

The liquid phase is destabilized by pressure applied

Reference states are pure liquid components

ΔG^{L} does not change its position,

ΔG^{α} shifts downward by

$$\underbrace{(1-x)\left(V_{\mathrm{A}}^{\alpha}-V_{\mathrm{A}}^{\mathrm{L}}\right)+x\left(V_{\mathrm{B}}^{\alpha}-V_{\mathrm{B}}^{\mathrm{L}}\right)}_{\text{The result of our derivations}}$$

ΔG^{α} does not change its position,

ΔG^{L} shifts upward by

$$(1-x)\left(V_{\mathrm{A}}^{\mathrm{L}}-V_{\mathrm{A}}^{\alpha}\right)+x\left(V_{\mathrm{B}}^{\mathrm{L}}-V_{\mathrm{B}}^{\alpha}\right)$$

Identical in terms of phase stabilities!

ΔG^{α} shifts upward by $(1-x)V_{\mathrm{A}}^{\alpha}+xV_{\mathrm{B}}^{\alpha}$,

ΔG^{L} shifts upward by $(1-x)V_{\mathrm{A}}^{\mathrm{L}}+xV_{\mathrm{B}}^{\mathrm{L}}$

Reference states are pure solid components

ΔG^{α} does not change its position,

ΔG^{L} shifts upward by

$$\underbrace{(1-x)\left(V_A^L - V_A^{\alpha}\right) + x\left(V_B^L - V_B^{\alpha}\right)}_{\text{The result of our derivations}}$$

ΔG^{L} does not change its position,

ΔG^{α} shifts downward by

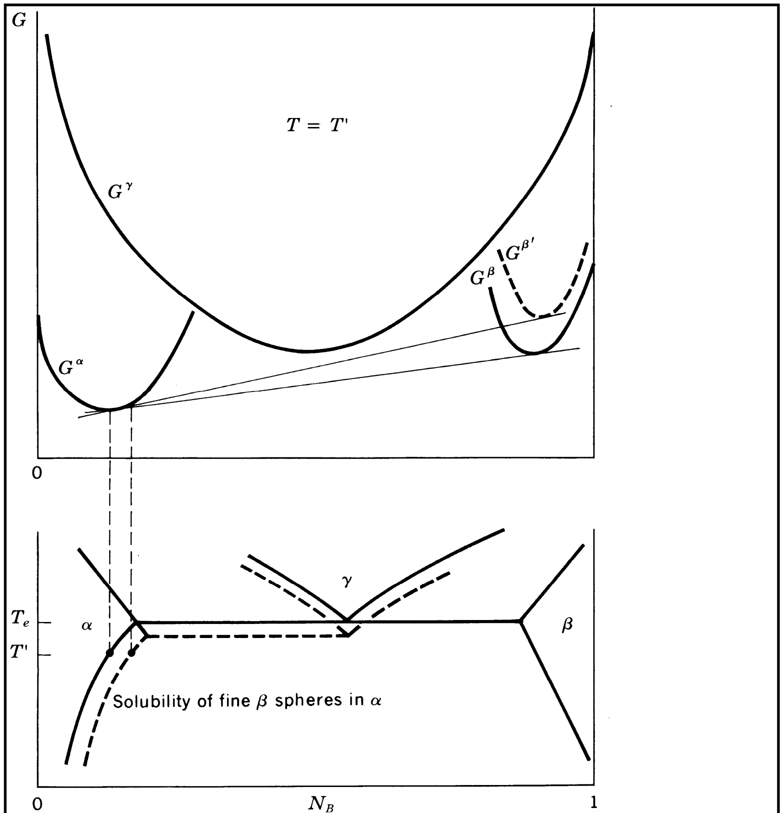
$$(1-x)\left(V_A^{\alpha} - V_A^{L}\right) + x\left(V_B^{\alpha} - V_B^{L}\right)$$

Identical in terms of phase stabilities!

ΔG^{α} shifts upward by $(1-x)V_A^{\alpha} + xV_B^{\alpha}$,

ΔG^{L} shifts upward by $(1-x)V_A^{L} + xV_B^{L}$

Aha!



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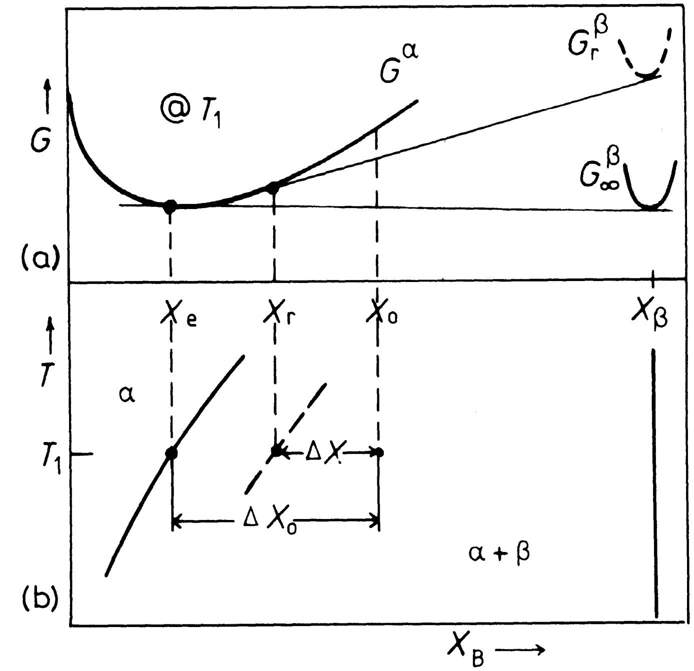

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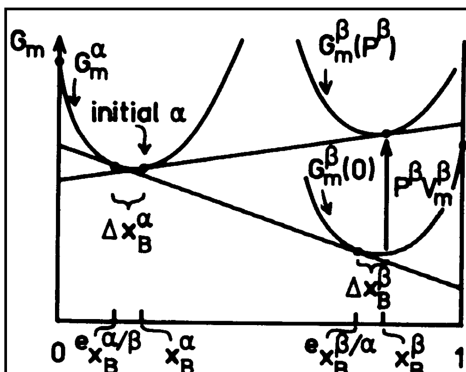
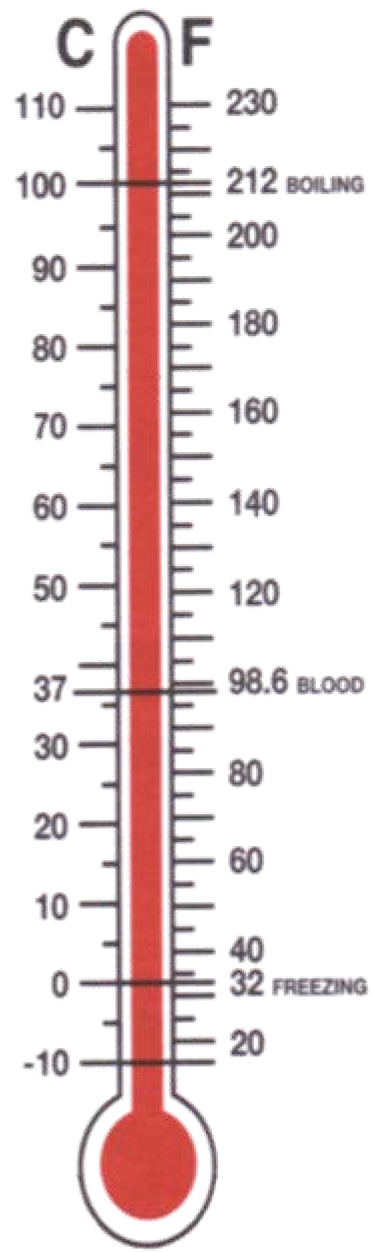
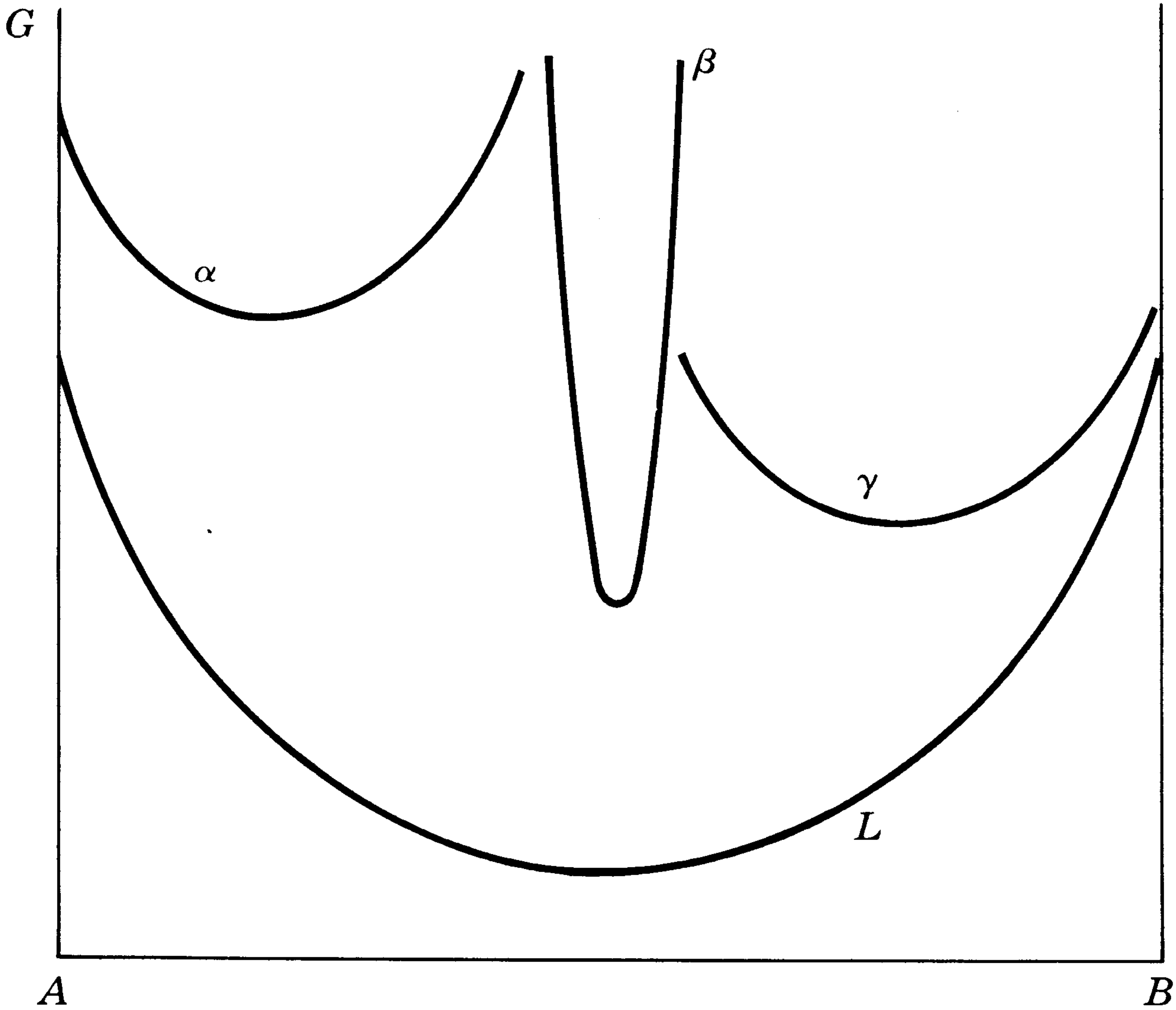


Fig. 27. Change in compositions when a pressure is applied to one of the phases in a two-phase equilibrium.

Now about the influence of temperature



Shewmon “Transformations in metals”, Page 154



Rationale

$$\left(\frac{\partial G}{\partial T}\right)_P = \underbrace{-S}_{\text{Always negative}}$$

Not G, but $\Delta_f G$!

$$\left(\frac{\partial G}{\partial T}\right)_P = \underbrace{-S}_{\text{Always negative}}$$

$$\left(\frac{\partial \Delta_f G}{\partial T}\right)_P = \underbrace{-\Delta_f S}_{?}$$

Reference states are pure liquid components

$$\Delta G^{\mathrm{L}} = (1-x)\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\mathrm{L}\to\mathrm{L}}}_{\equiv 0} + x\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\mathrm{L}\to\mathrm{L}}}_{\equiv 0} + \Delta^{\mathrm{id}} G^{\mathrm{L}} + \underbrace{\Delta^{\mathrm{ex}} G^{\mathrm{L}}}_{\neq f(T)}$$

$$\Delta G^{\alpha} = (1-x)\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\mathrm{L}\to\alpha} + x\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\mathrm{L}\to\alpha} + \Delta^{\mathrm{id}} G^{\alpha} + \underbrace{\Delta^{\mathrm{ex}} G^{\alpha}}_{\neq f(T)}$$

$$\left(\frac{\partial \Delta G^{\mathrm{L}}}{\partial T}\right)_P = -\Delta^{\mathrm{id}} S^{\mathrm{L}}$$

$$\left(\frac{\partial \Delta G^{\alpha}}{\partial T}\right)_P = (1-x)\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\mathrm{L}\to\alpha}}{\partial T}\right)_P + x\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\mathrm{L}\to\alpha}}{\partial T}\right)_P - \Delta^{\mathrm{id}} S^{\alpha}$$

$$= \underbrace{-(1-x)\underbrace{\left(S_{\mathrm{A}}^{\alpha} - S_{\mathrm{A}}^{\mathrm{L}}\right)}_{\text{Always negative}} - x\underbrace{\left(S_{\mathrm{B}}^{\alpha} - S_{\mathrm{B}}^{\mathrm{L}}\right)}_{\text{Always Negative}}}_{\text{Always positive}} - \Delta^{\mathrm{id}} S^{\alpha} > \left(\frac{\partial \Delta G^{\mathrm{L}}}{\partial T}\right)_P$$

What does this mean?

With respect to ΔG^{L},

ΔG^{α} shifts upward by

$$\underbrace{(1-x)\left(S_{\mathrm{A}}^{\mathrm{L}}-S_{\mathrm{A}}^{\alpha}\right)+x\left(S_{\mathrm{B}}^{\mathrm{L}}-S_{\mathrm{B}}^{\alpha}\right)}_{\text{The result of our derivations}}$$

With respect to ΔG^{α},

ΔG^{L} shifts downward by

$$(1-x)\left(S_{\mathrm{A}}^{\alpha}-S_{\mathrm{A}}^{\mathrm{L}}\right)+x\left(S_{\mathrm{B}}^{\alpha}-S_{\mathrm{B}}^{\mathrm{L}}\right)$$

Identical in terms of phase stabilities!

ΔG^{α} shifts downward by $-(1-x)S_{\mathrm{A}}^{\alpha}-xS_{\mathrm{B}}^{\alpha}$,

ΔG^{L} shifts downward by $-(1-x)S_{\mathrm{A}}^{\mathrm{L}}-xS_{\mathrm{B}}^{\mathrm{L}}$

Reference states are pure solid components

$$\Delta G^{\mathrm{L}} = (1-x)\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\alpha\to\mathrm{L}} + x\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\alpha\to\mathrm{L}} + \Delta^{\mathrm{id}} G^{\mathrm{L}} + \underbrace{\Delta^{\mathrm{ex}} G^{\mathrm{L}}}_{\neq f(T)}$$

$$\Delta G^{\alpha} = (1-x)\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\alpha\to\alpha}}_{\equiv 0} + x\underbrace{\Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\alpha\to\alpha}}_{\equiv 0} + \Delta^{\mathrm{id}} G^{\alpha} + \underbrace{\Delta^{\mathrm{ex}} G^{\alpha}}_{\neq f(T)}$$

$$\left(\frac{\partial \Delta G^{\alpha}}{\partial T}\right)_P = -\Delta^{\mathrm{id}} S^{\alpha}$$

$$\left(\frac{\partial \Delta G^{\mathrm{L}}}{\partial T}\right)_P = (1-x)\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{A}}^{0\,\alpha\to\mathrm{L}}}{\partial T}\right)_P + x\left(\frac{\partial \Delta_{\mathrm{tr}} G_{\mathrm{B}}^{0\,\alpha\to\mathrm{L}}}{\partial T}\right)_P - \Delta^{\mathrm{id}} S^{\mathrm{L}}$$

$$= \underbrace{-(1-x)\underbrace{\left(S_{\mathrm{A}}^{\mathrm{L}} - S_{\mathrm{A}}^{\alpha}\right)}_{\text{Always positive}} - x\underbrace{\left(S_{\mathrm{B}}^{\mathrm{L}} - S_{\mathrm{B}}^{\alpha}\right)}_{\text{Always positive}}}_{\text{Always negative}} - \Delta^{\mathrm{id}} S^{\mathrm{L}} < \left(\frac{\partial \Delta G^{\alpha}}{\partial T}\right)_P$$

What does this mean?

With respect to ΔG^{α},

ΔG^{L} shifts downward by

$$\underbrace{(1-x)\left(S_{\mathrm{A}}^{\alpha}-S_{\mathrm{A}}^{\mathrm{L}}\right)+x\left(S_{\mathrm{B}}^{\alpha}-S_{\mathrm{B}}^{\mathrm{L}}\right)}_{\text{The result of our derivations}}$$

With respect to ΔG^{L},

ΔG^{α} shifts upward by

$$(1-x)\left(S_{\mathrm{A}}^{\mathrm{L}}-S_{\mathrm{A}}^{\alpha}\right)+x\left(S_{\mathrm{B}}^{\mathrm{L}}-S_{\mathrm{B}}^{\alpha}\right)$$

Identical in terms of phase stabilities!

ΔG^{α} shifts downward by $-(1-x)S_{\mathrm{A}}^{\alpha}-xS_{\mathrm{B}}^{\alpha}$,

ΔG^{L} shifts downward by $-(1-x)S_{\mathrm{A}}^{\mathrm{L}}-xS_{\mathrm{B}}^{\mathrm{L}}$

Conclusions

- "The Gibbs energy of a phase" actually means "The Gibbs energy of formation of the phase".
- A choice of reference states is important when such quantities as enthalpies, activities or chemical potentials are calculated, but it is immaterial in terms of relative phase stabilities.
- Be critical, do not be a conformist!