

Learning and understanding thermodynamics: a struggle against obviousness

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Outline

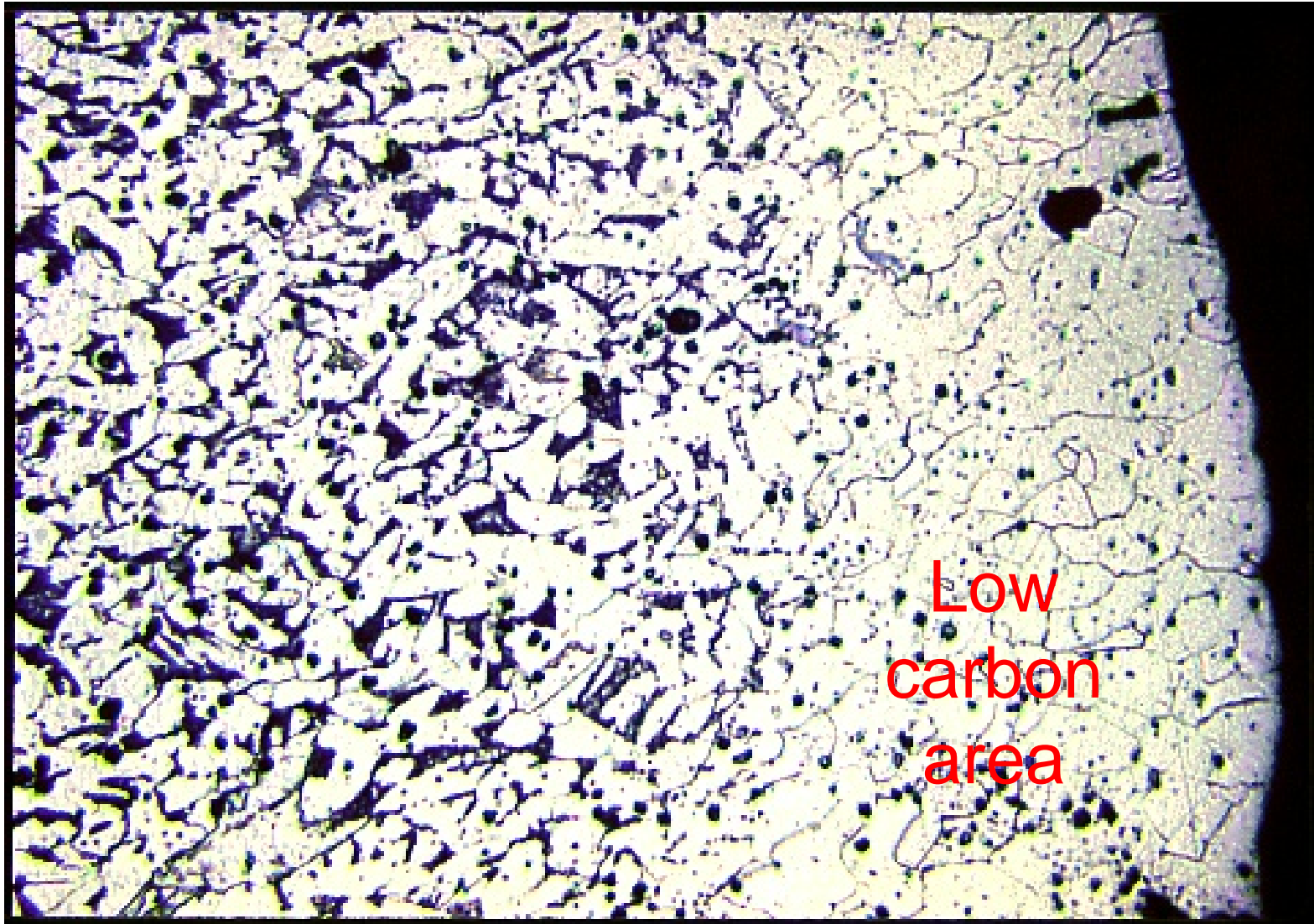
- Decarburization: let us warm up
- Maximal temperature of adiabatic combustion: do we calculate it correctly?
- Influence of pressure on the molar Gibbs energies: what does P do to $G(x)$?
- A choice of a reference frame in the compound energy formalism: is it unique?
- An advice: stay alert, be critical
- MSE: we are waiting for you

Combustion: a source of heat



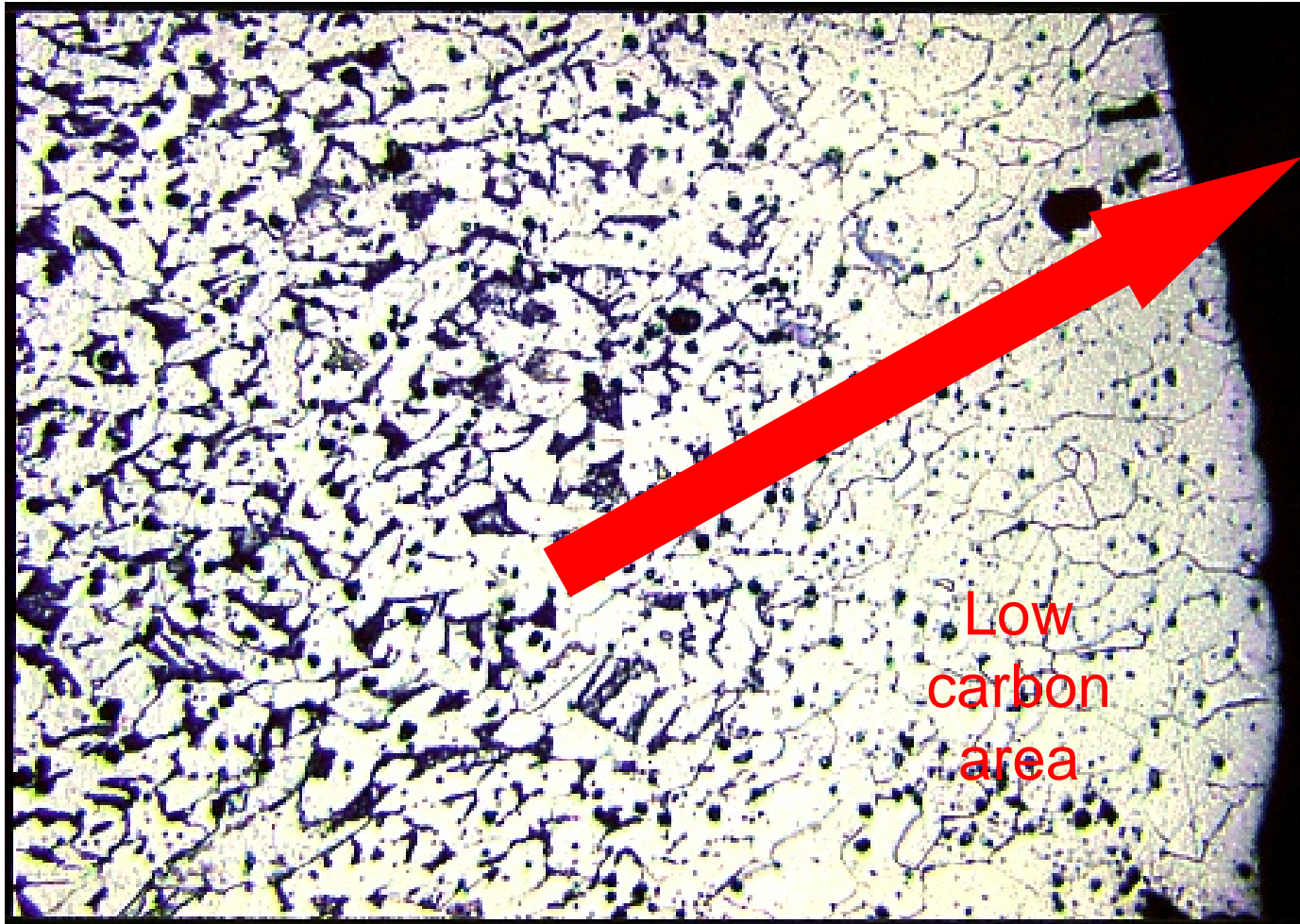
Component	Wt. %
C	0.4
Mn	0.7
Si	1.5
Cr	0.7
V	0.2

Decarburization

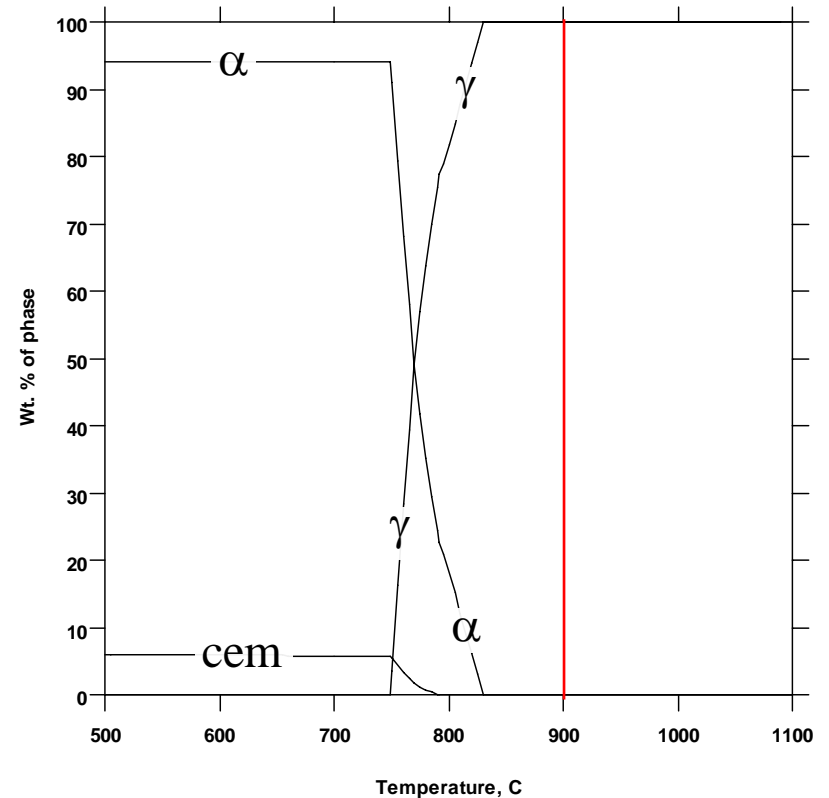
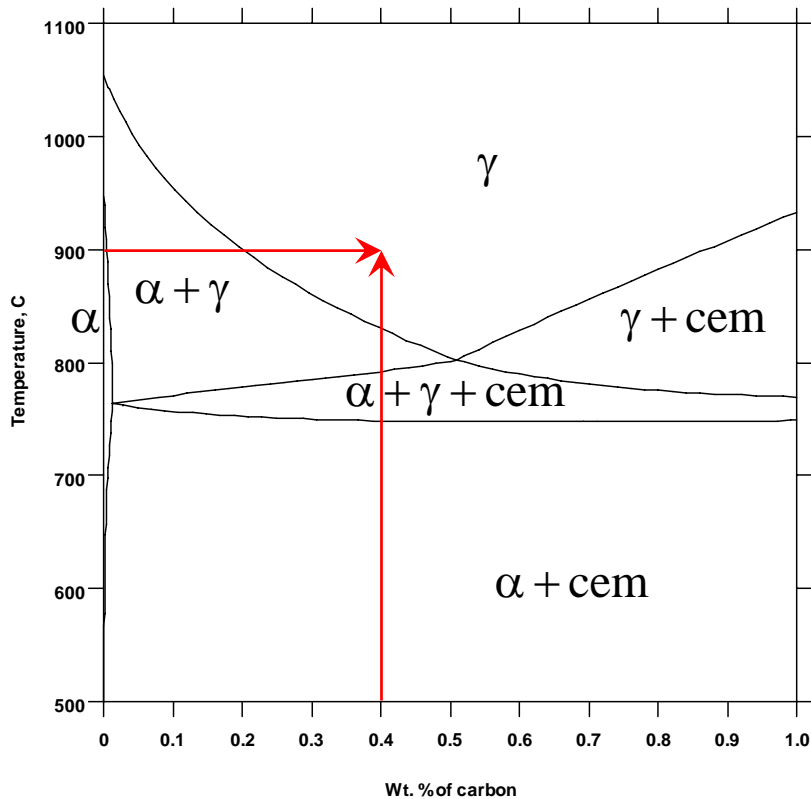


What causes the misfortune?

$$\mu_{\text{C}}^{\text{gas}} < \mu_{\text{C}}^{\text{steel}} \text{ or, equivalently, } a_{\text{C}}^{\text{gas}} < a_{\text{C}}^{\text{steel}}$$



Austenitization: interior and near-surface region behave differently

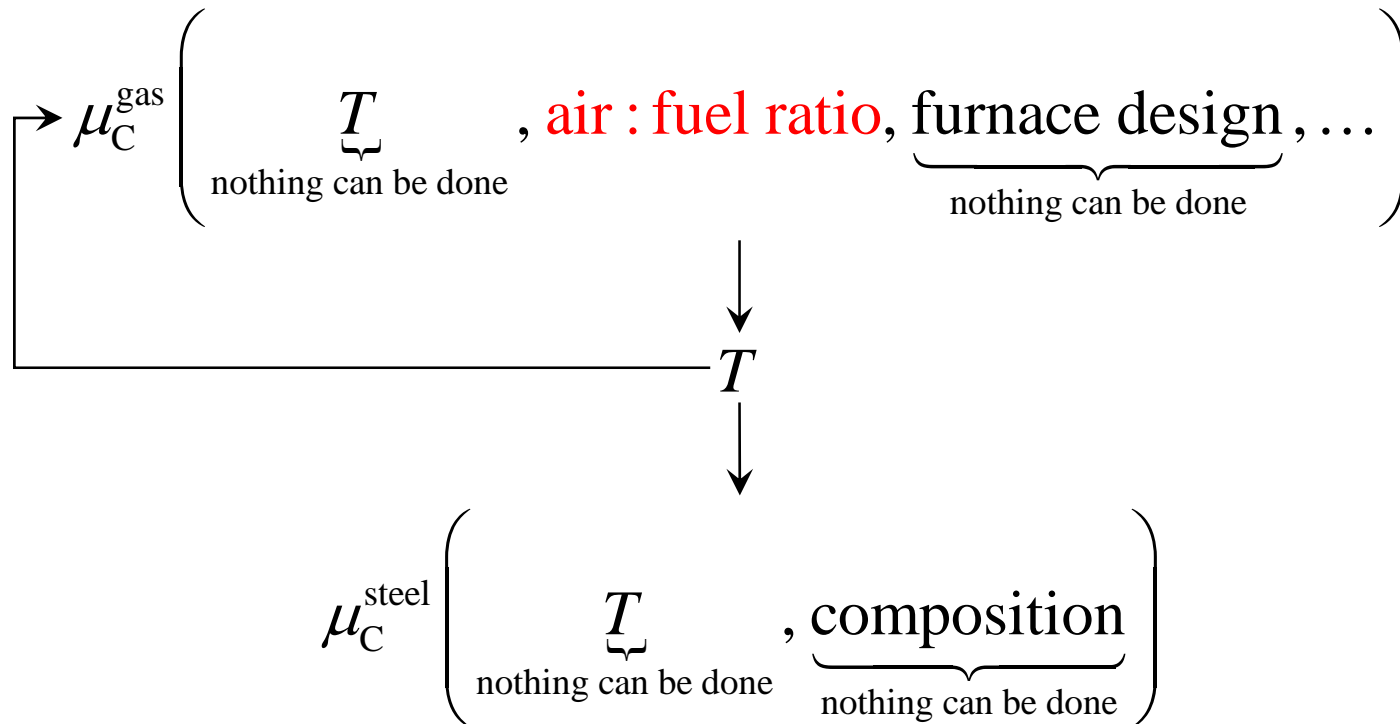


How can decarburization be suppressed or eliminated?

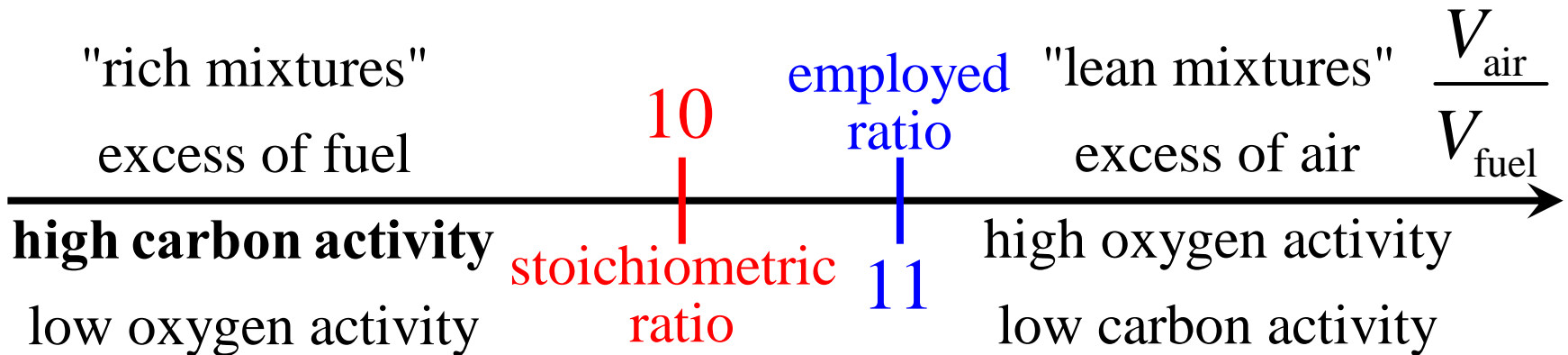
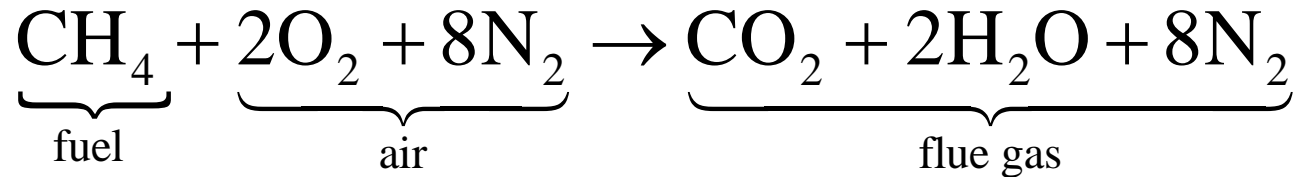
- Kinetics (induction heating: seconds instead of minutes)
- Chemistry (heating in vacuum: an absence of mediators such as H_2O , CO_2 , H_2)
- Thermodynamics

Can the adversity be avoided?

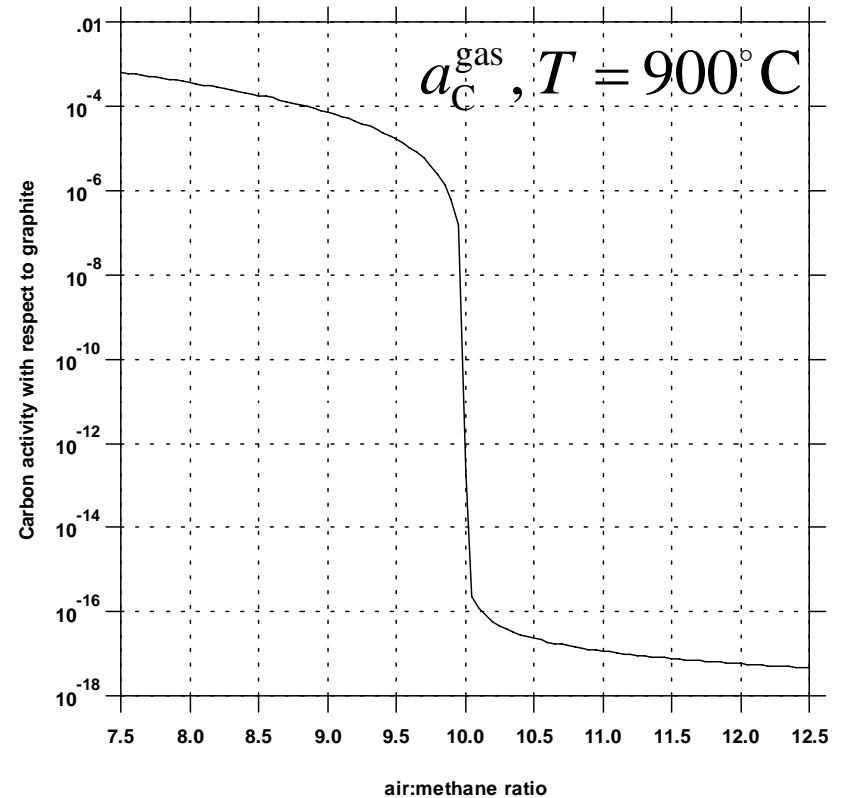
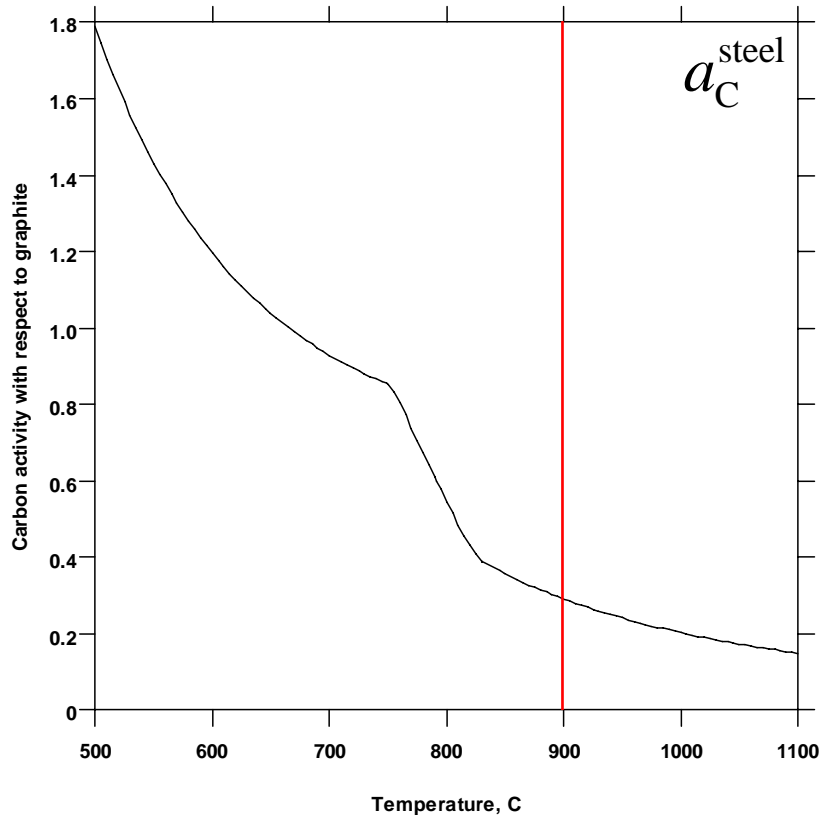
$$\mu_C^{\text{gas}} < \mu_C^{\text{steel}}$$



Terminology (fuel-dependent)

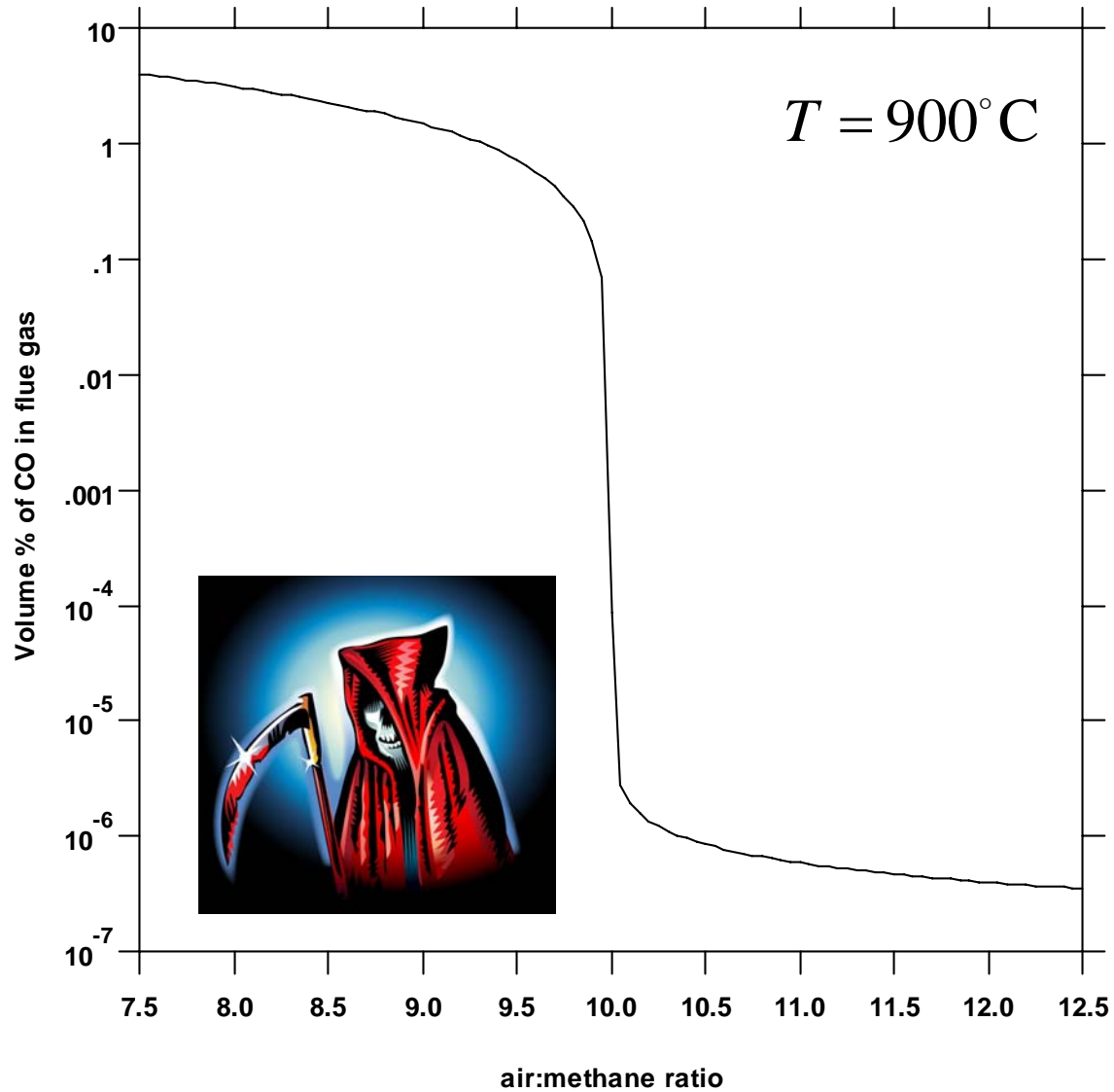


Can decarburization be defeated by changing the air:fuel ratio?



Thermodynamic verdict: no way!

Another reason prohibiting low ratios



Temperature of adiabatic reaction between hydrogen and oxygen

1. Take 0.5 mole of $\text{O}_2(\text{g})$ and 1 moles of $\text{H}_2(\text{g})$ at 25°C and $P = 1 \text{ atm}$. By definition, $H^\circ = 0$.
2. Make 1 mole of $\text{H}_2\text{O}(\text{g})$ at 25°C and put $\Delta_f H^\circ_{298}$ released into a heat reservoir.
3. Maintain $P = 1 \text{ atm}$ and use **all** energy stored in the reservoir for heating 1 mole of gaseous H_2O .
4. Ask yourself a question: do I know how to calculate T_{max} ?

Of course you know, but just in case...

$$\int_{298}^{T_{\max}} C_p^\circ(\tau) d\tau = \underbrace{\Delta_f H_{298}^\circ}_{\text{energy in reservoir}}$$

heating from 298 K
to unknown T_{\max}

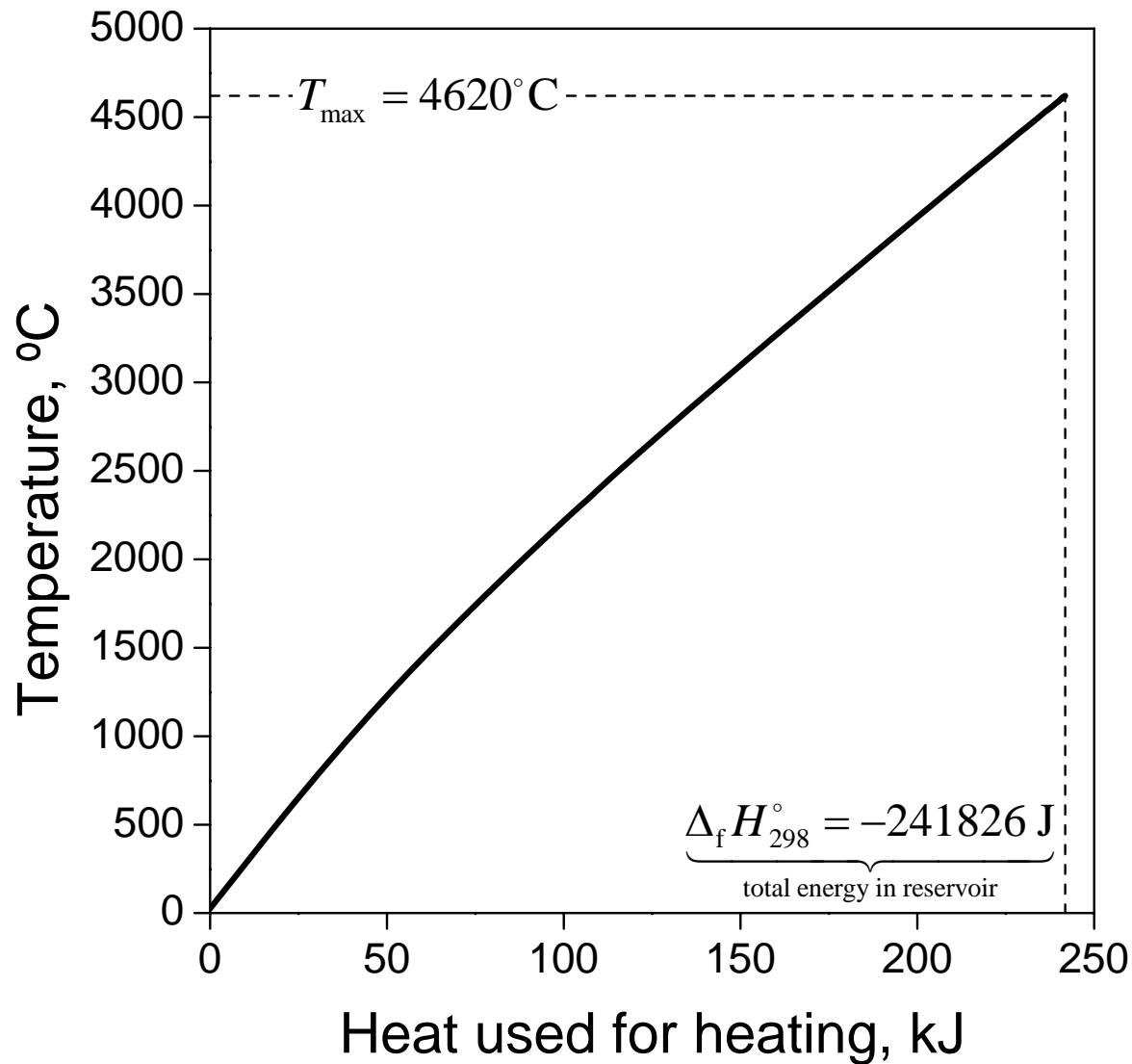
Kelly's expression

$$C_p^\circ(T) = a + bT + \frac{c}{T^2} + dT^2$$

Non-linear equation
Boring, but simple

T_{\max}

$T_{\max} = 4620^{\circ}\text{C}$: an erroneous result



What happens at this temperature?

Output from POLY-3, equilibrium = 1, label A0 , database: SSUB3

Conditions:

N(H2)=1, N(O2)=0.5, T=4893.29, P=1E5

DEGREES OF FREEDOM 0

Temperature 4893.29 K (4620.14 C), Pressure 1.000000E+05

Number of moles of components 1.50000E+00, Mass in grams 1.80148E+01

Total Gibbs energy -1.87698E+06, Enthalpy 9.34464E+05, Volume 1.18691E+00

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
H2	1.0000E+00	6.6667E-01	1.7999E-12	-1.1003E+06	SER
O2	5.0000E-01	3.3333E-01	2.6171E-17	-1.5534E+06	SER

GAS Status ENTERED Driving force 0.0000E+00

Moles 1.5000E+00, Mass 1.8015E+01, Volume fraction 1.0000E+00 Mole fractions:

H2 6.66667E-01 O2 3.33333E-01

Constitution:

H	6.47172E-01	H1O1	1.20372E-02	H1O2	8.06924E-07
O	3.24793E-01	O2	2.81954E-03	O3	5.47919E-09
H2	1.28658E-02	H2O1	3.11755E-04	H2O2	1.44469E-09

A dramatic difference

Output from POLY-3, equilibrium = 1, label A0 , database: SSUB3

Conditions:

P=1E5, N(H2)=1, N(O2)=0.5, H=0

DEGREES OF FREEDOM 0

Temperature 3077.91 K (2804.76 C), Pressure 1.000000E+05

Number of moles of components 1.50000E+00, Mass in grams 1.80148E+01

Total Gibbs energy -1.01149E+06, Enthalpy 4.40821E-10, Volume 3.10200E-01

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
H2	1.0000E+00	6.6667E-01	1.2037E-10	-5.8452E+05	SER
O2	5.0000E-01	3.3333E-01	3.2235E-15	-8.5394E+05	SER

GAS Status ENTERED Driving force 0.0000E+00

Moles 1.5000E+00, Mass 1.8015E+01, Volume fraction 1.0000E+00 Mole fractions:

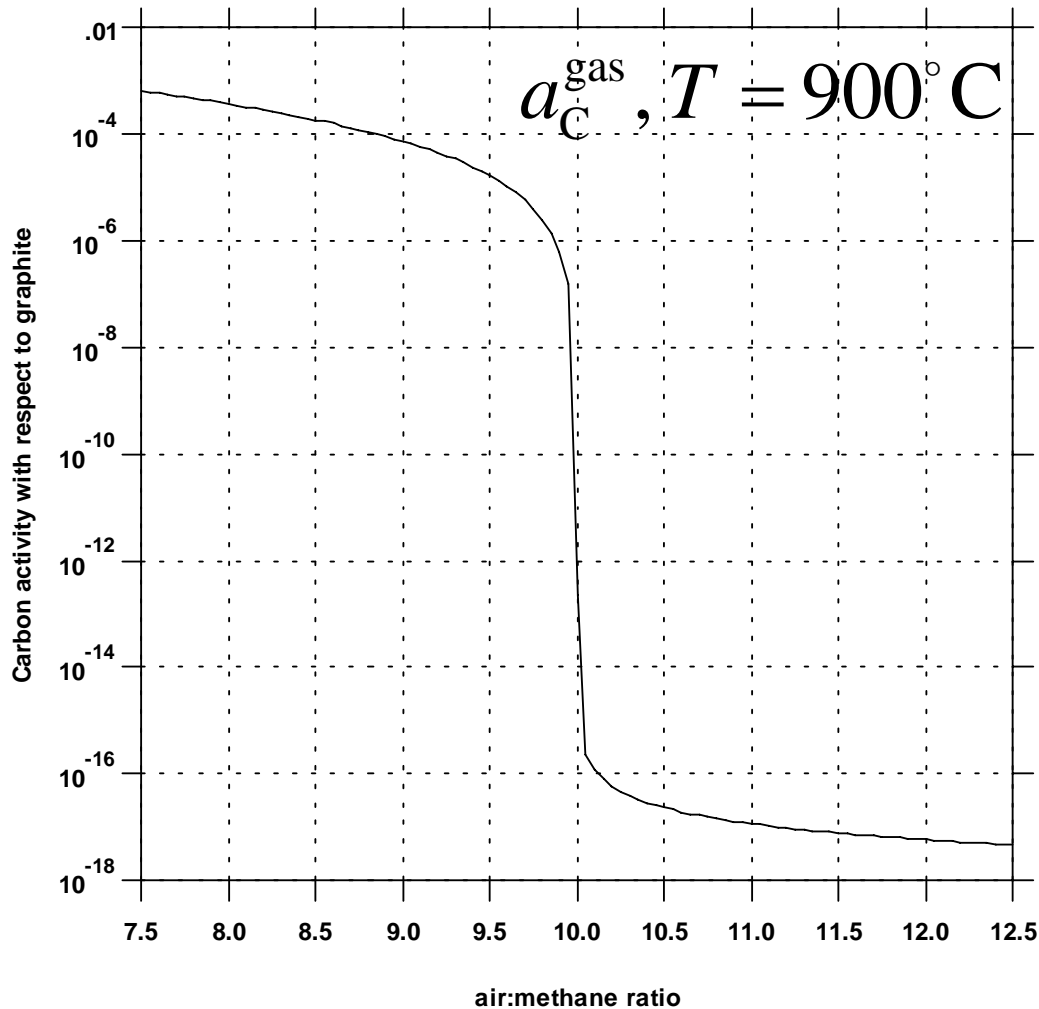
H2 6.66667E-01 O2 3.33333E-01

Constitution:

H2O1	5.85041E-01	H	7.70546E-02	H1O2	4.50911E-05
H2	1.48661E-01	O2	5.06614E-02	H2O2	2.49697E-06
H1O1	1.05477E-01	O	3.30571E-02	O3	1.90507E-08

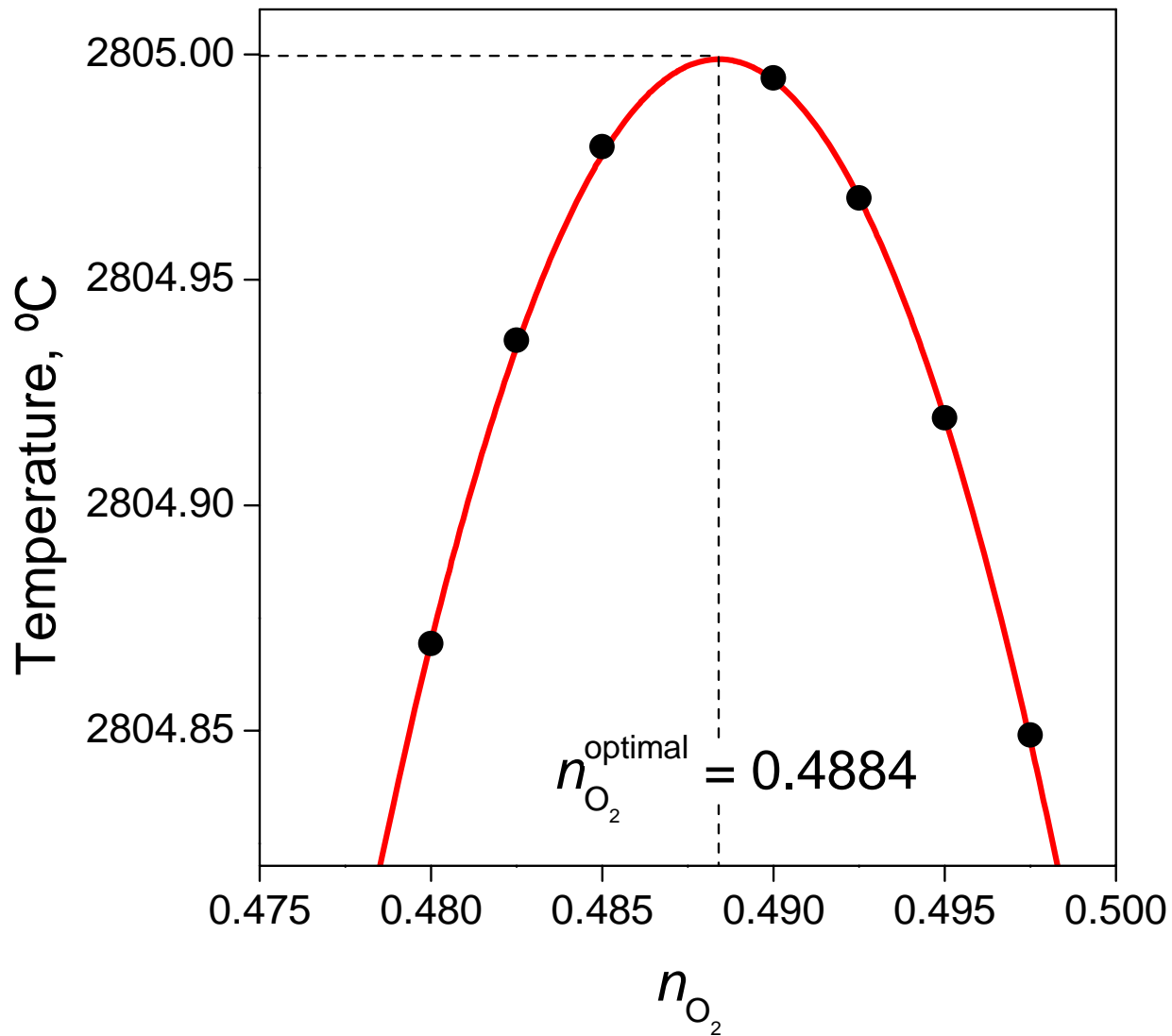
$$\underbrace{T_{\max} = 4620^{\circ}\text{C}}_{\text{only H}_2\text{O is considered}} \rightarrow \underbrace{T_{\max} = 2805^{\circ}\text{C}}_{\text{all species are considered}}$$

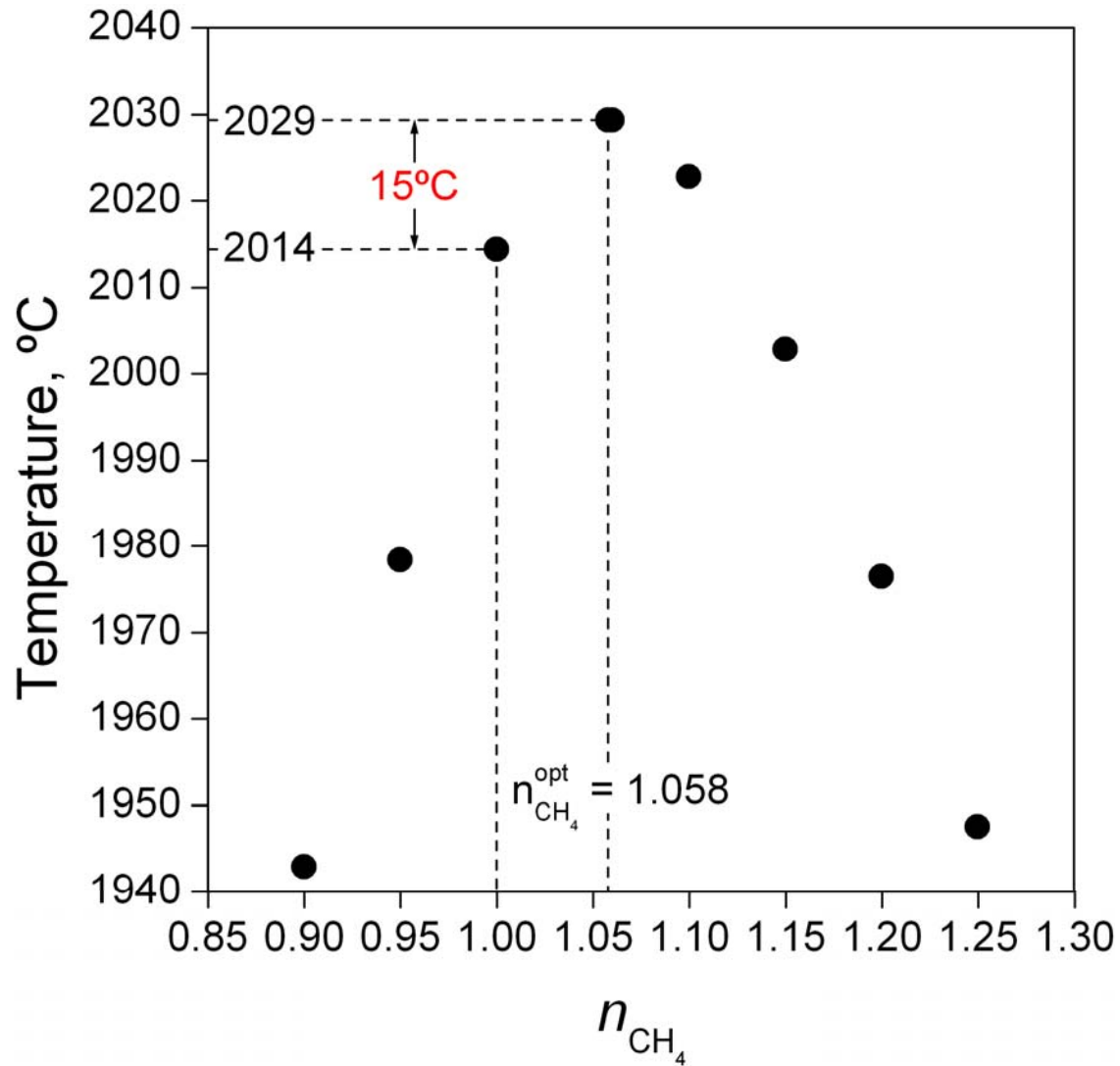
A less obvious fault in our calculations



$$\left(\frac{\partial^2 a_C^{\text{gas}}}{\partial \text{ratio}^2} \right)_{\text{ratio}=10} \stackrel{?}{=} 0$$

Who said that 2:1 was the best ratio?





Fuel & oxidizer? Yes, but ratio as well!



I taught many thermodynamics-related
courses



Shewmon “Transformations in metals”

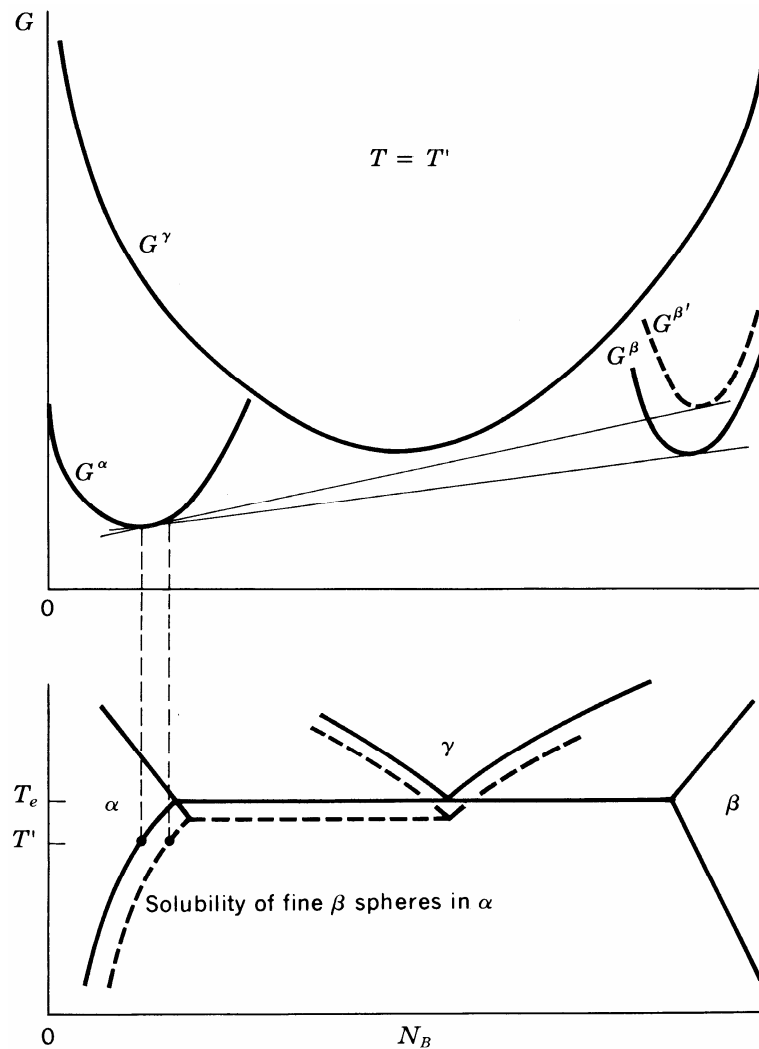


figure 4-10. Free-energy diagram and phase diagram indicating change in solubility of β , and eutectoid temperature when β is present as fine spheres (labeled β').

Porter, Easterling “Phase transformations in metals and alloys”

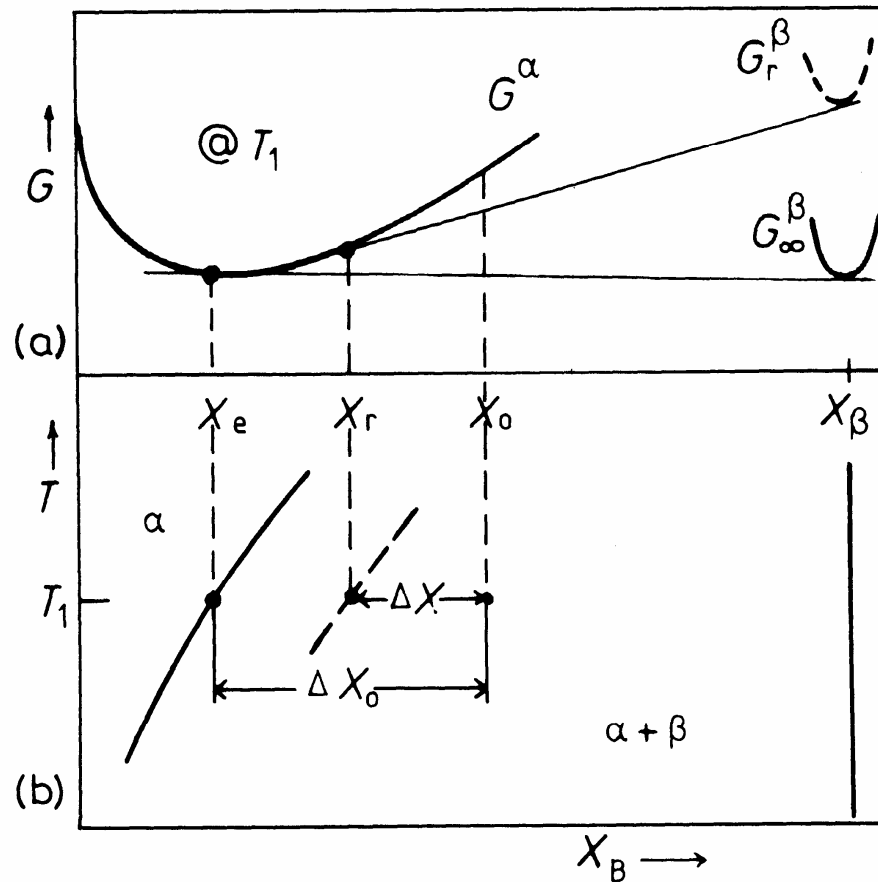


Fig. 5.20 The Gibbs-Thomson effect. (a) Free energy curves at T_1 . (b) Corresponding phase diagram.

Hillert “Applications of Gibbs energy-composition diagrams”

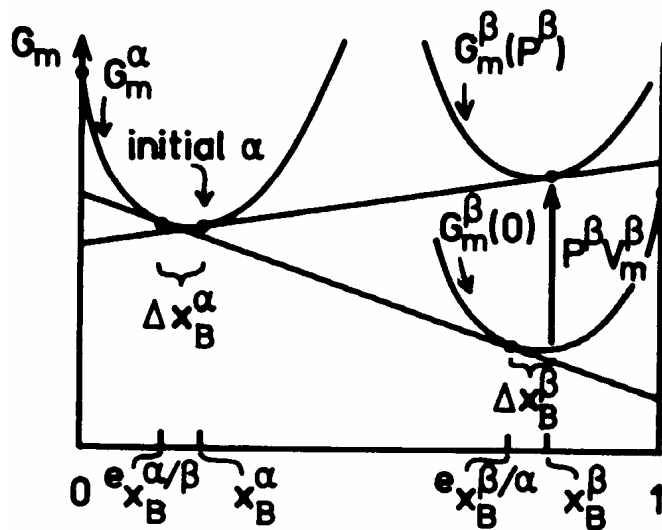


Fig. 27. Change in compositions when a pressure is applied to one of the phases in a two-phase equilibrium.

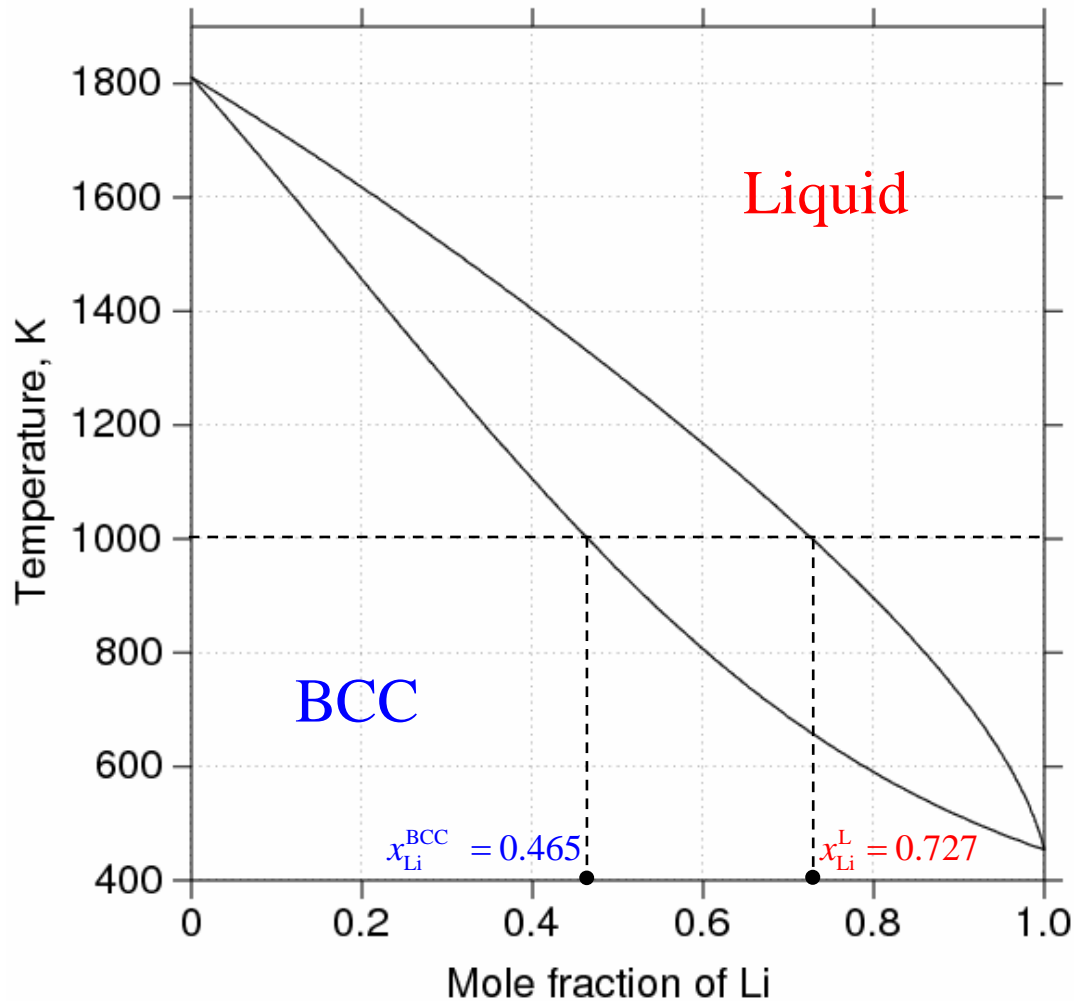
Rationale

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

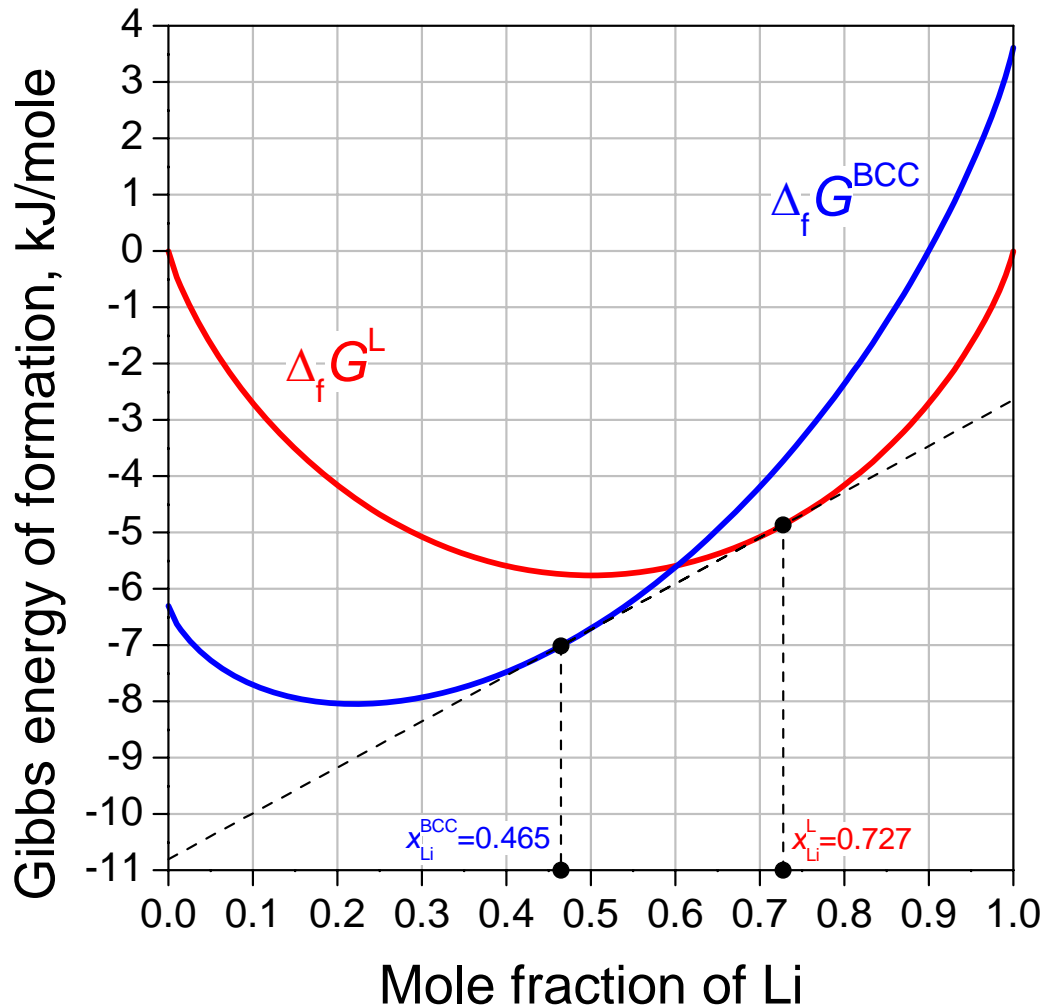


If P increases, then G moves **upward**

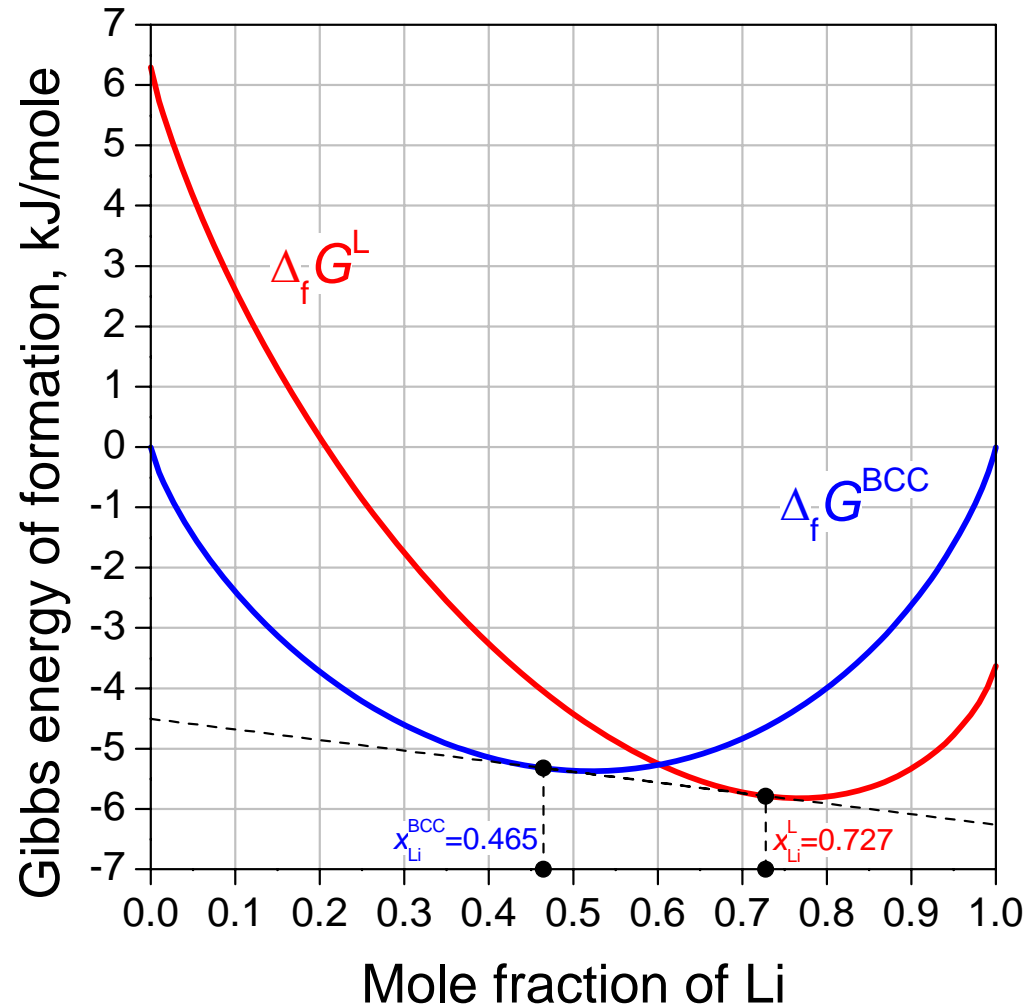
Liquid/BCC equilibrium in the Fe–Li system



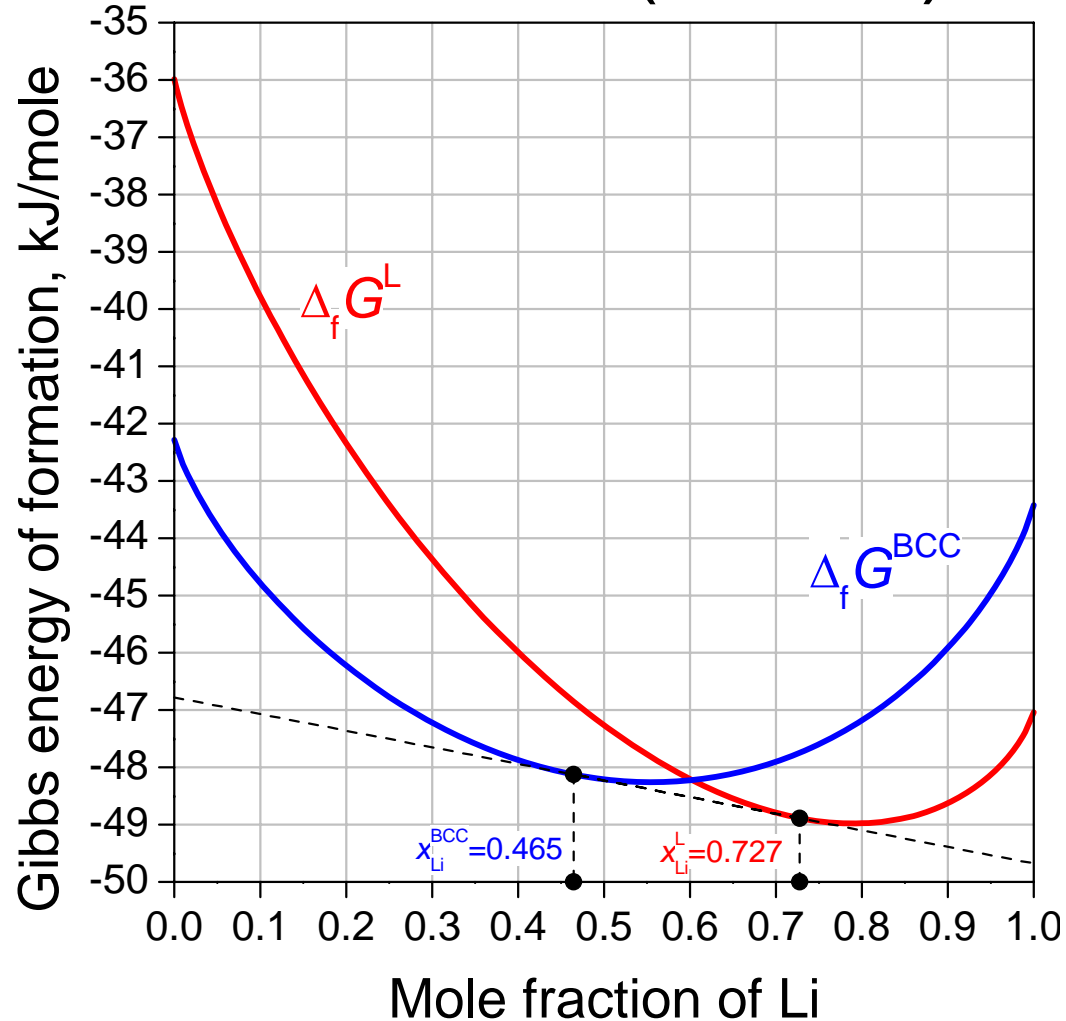
$T = 1000$ K, reference states are pure liquid Fe and pure liquid Li



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



$T = 1000$ K, “standard element references” (SGTE)

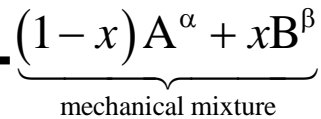


Not G per se, but $\Delta_f G$!

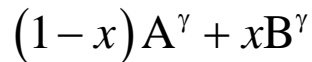
$$\left(\frac{\partial G}{\partial P} \right)_T = \underbrace{V}_{\text{always positive}}$$

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

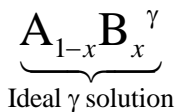
Let us make a phase γ from pure components



$$\Delta^{\text{st}}G = (1-x)\Delta_{\text{tr}}G_A^{0\alpha \rightarrow \gamma} + x\Delta_{\text{tr}}G_B^{0\beta \rightarrow \gamma}$$

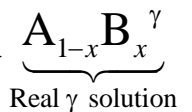


$$\Delta^{\text{id}}G = RT[(1-x)\ln(1-x) + x\ln x]$$



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

$$\Delta_{\text{f}}G$$



Reference states are pure **liquid** components

$$\Delta G^L = (1-x) \underbrace{\Delta_{\text{tr}} G_A^{0L \rightarrow L}}_{\equiv 0} + x \underbrace{\Delta_{\text{tr}} G_B^{0L \rightarrow L}}_{\equiv 0} + \underbrace{\Delta^{\text{id}} G^L}_{\neq f(P)} + \underbrace{\Delta^{\text{ex}} G^L}_{\neq f(P)}$$

$$\Delta G^\alpha = (1-x) \Delta_{\text{tr}} G_A^{0L \rightarrow \alpha} + x \Delta_{\text{tr}} G_B^{0L \rightarrow \alpha} + \underbrace{\Delta^{\text{id}} G^\alpha}_{\neq f(P)} + \underbrace{\Delta^{\text{ex}} G^\alpha}_{\neq f(P)}$$

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

$$\begin{aligned} \left(\frac{\partial \Delta G^\alpha}{\partial P} \right)_T &= (1-x) \left(\frac{\partial \Delta_{\text{tr}} G_A^{0L \rightarrow \alpha}}{\partial P} \right)_T + x \left(\frac{\partial \Delta_{\text{tr}} G_B^{0L \rightarrow \alpha}}{\partial P} \right)_T \\ &= (1-x) \underbrace{\left(V_A^\alpha - V_A^L \right)}_{\text{usually negative}} + x \underbrace{\left(V_B^\alpha - V_B^L \right)}_{\text{usually negative}} < 0 \end{aligned}$$

$$V_m = \frac{A}{\rho}$$

Why “usually”? Because there are rare exceptions such as H₂O, Bi, Sb, cast iron

What does this mean?!



ΔG^L does **not** change its position

ΔG^α shifts **downward** by $\left[(1-x)(V_A^L - V_A^\alpha) + x(V_B^L - V_B^\alpha) \right] \times P$

The solid phase α is stabilized by pressure applied

Now reference states are pure **solid** components

$$\Delta G^L = (1-x)\Delta_{\text{tr}}G_A^{0\alpha\rightarrow L} + x\Delta_{\text{tr}}G_B^{0\alpha\rightarrow L} + \underbrace{\Delta^{\text{id}}G^L}_{\neq f(P)} + \underbrace{\Delta^{\text{ex}}G^L}_{\neq f(P)}$$

$$\Delta G^\alpha = (1-x)\underbrace{\Delta_{\text{tr}}G_A^{0\alpha\rightarrow\alpha}}_{\equiv 0} + x\underbrace{\Delta_{\text{tr}}G_B^{0\alpha\rightarrow\alpha}}_{\equiv 0} + \underbrace{\Delta^{\text{id}}G^\alpha}_{\neq f(P)} + \underbrace{\Delta^{\text{ex}}G^\alpha}_{\neq f(P)}$$

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

$$\begin{aligned} \left(\frac{\partial\Delta G^L}{\partial P}\right)_T &= (1-x)\left(\frac{\partial\Delta_{\text{tr}}G_A^{0\alpha\rightarrow L}}{\partial P}\right)_T + x\left(\frac{\partial\Delta_{\text{tr}}G_B^{0\alpha\rightarrow L}}{\partial P}\right)_T \\ &= (1-x)\underbrace{(V_A^L - V_A^\alpha)}_{\text{usually positive}} + x\underbrace{(V_B^L - V_B^\alpha)}_{\text{usually positive}} > 0 \end{aligned}$$

$$V_m = \frac{A}{\rho}$$

What's going on?!



ΔG^α does **not** change its position

ΔG^L shifts **upward** by $\left[(1-x)(V_A^L - V_A^\alpha) + x(V_B^L - V_B^\alpha) \right] \times P$

The liquid phase is **de**stabilized by pressure applied

Reference states are pure **liquid** components

ΔG^L does **not** change its position,

ΔG^α shifts **downward** by

$$\underbrace{\left[(1-x)(V_A^L - V_A^\alpha) + x(V_B^L - V_B^\alpha) \right]}_{\text{our result}} \times P$$

ΔG^α does **not** change its position,

ΔG^L shifts **upward** by

$$\left[(1-x)(V_A^L - V_A^\alpha) + x(V_B^L - V_B^\alpha) \right] \times P$$

In terms of relative positions, these 3 situations are **identical**

$$\Delta G^\alpha \text{ shifts } \mathbf{upward} \text{ by } \left[(1-x)V_A^\alpha + xV_B^\alpha \right] \times P$$

$$\Delta G^L \text{ shifts } \mathbf{upward} \text{ by } \left[(1-x)V_A^L + xV_B^L \right] \times P$$

Reference states are pure **solid** components

ΔG^α does **not** change its position,

ΔG^L shifts **upward** by

$$\underbrace{\left[(1-x)(V_A^L - V_A^\alpha) + x(V_B^L - V_B^\alpha) \right]}_{\text{our result}} \times P$$

ΔG^L does **not** change its position,

ΔG^α shifts **downward** by

$$\left[(1-x)(V_A^L - V_A^\alpha) + x(V_B^L - V_B^\alpha) \right] \times P$$

In terms of relative positions, these 3 situations are **identical**

$$\Delta G^\alpha \text{ shifts } \mathbf{upward} \text{ by } \left[(1-x)V_A^\alpha + xV_B^\alpha \right] \times P$$

$$\Delta G^L \text{ shifts } \mathbf{upward} \text{ by } \left[(1-x)V_A^L + xV_B^L \right] \times P$$

Shewmon “Transformations in metals”

4-6 Consider a system in which four phases exist with a $G(N_B)$ diagram as shown in Fig. 4-13. Show the phase diagram that results if the free energy of the α , β , and γ phases decreases relative to that of the liquid as the temperature is decreased. Do this by first showing the $G(N_B)$ diagram for several lower temperatures.

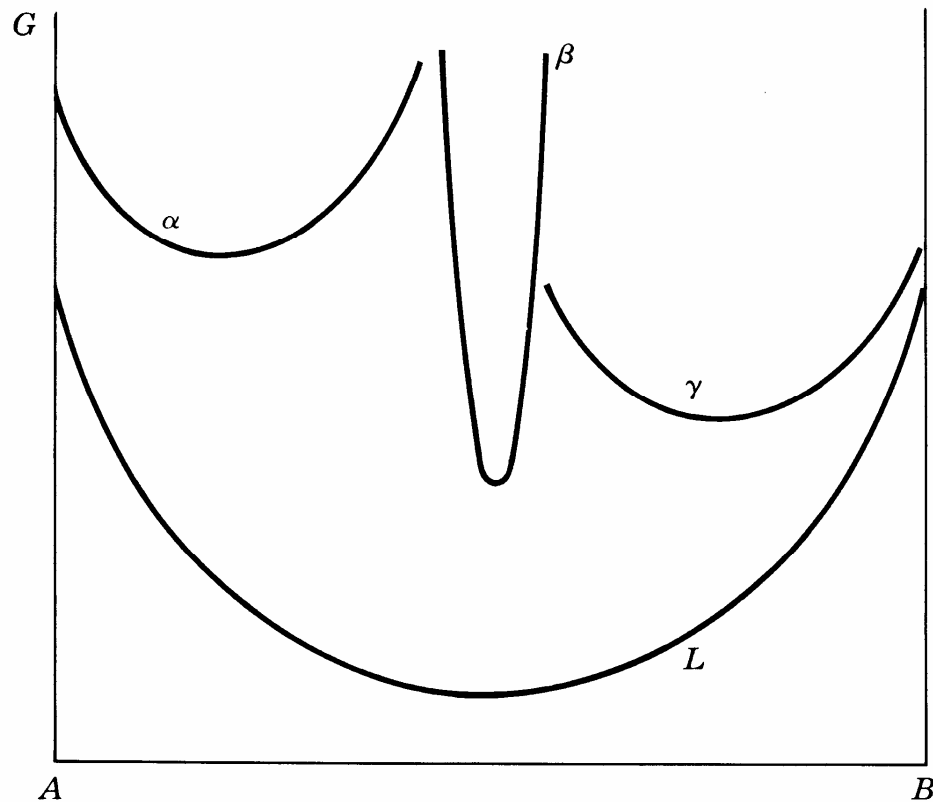
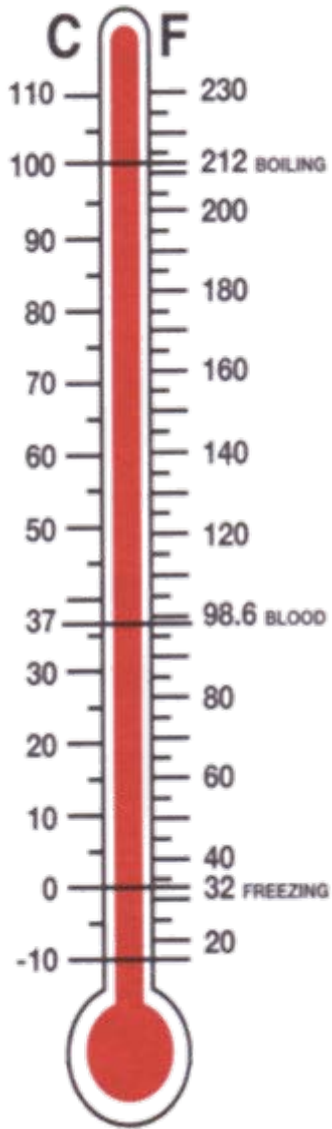


figure 4-13

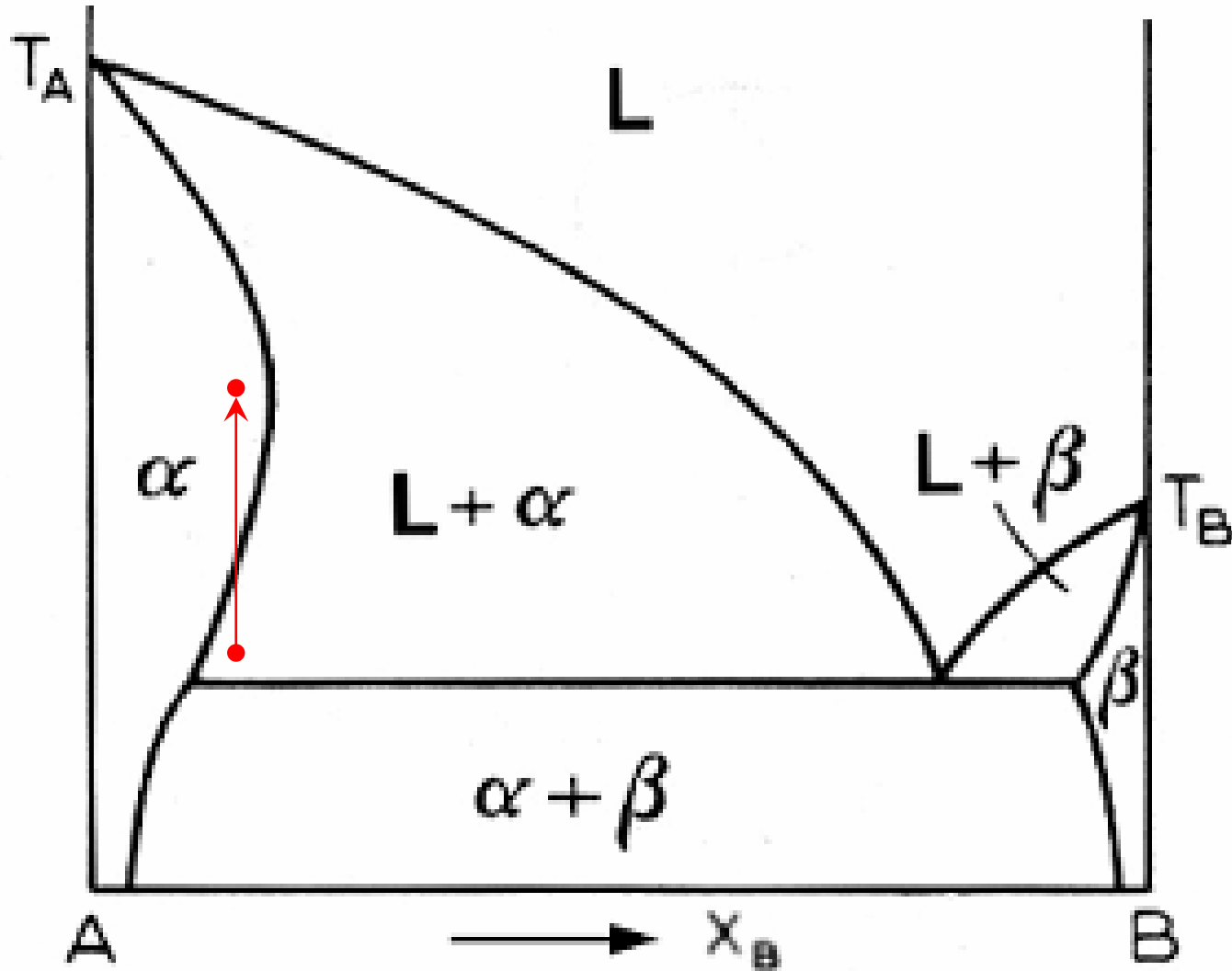
Home task: not G , but $\Delta_f G$!



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

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

Retrograde solubility



Making an excusable mistake

Steel contains 0.4 wt.% of C

$$A_{\text{C}} = 12.011 \text{ g/mole}$$

$$A_{\text{Fe}} = 55.847 \text{ g/mole}$$

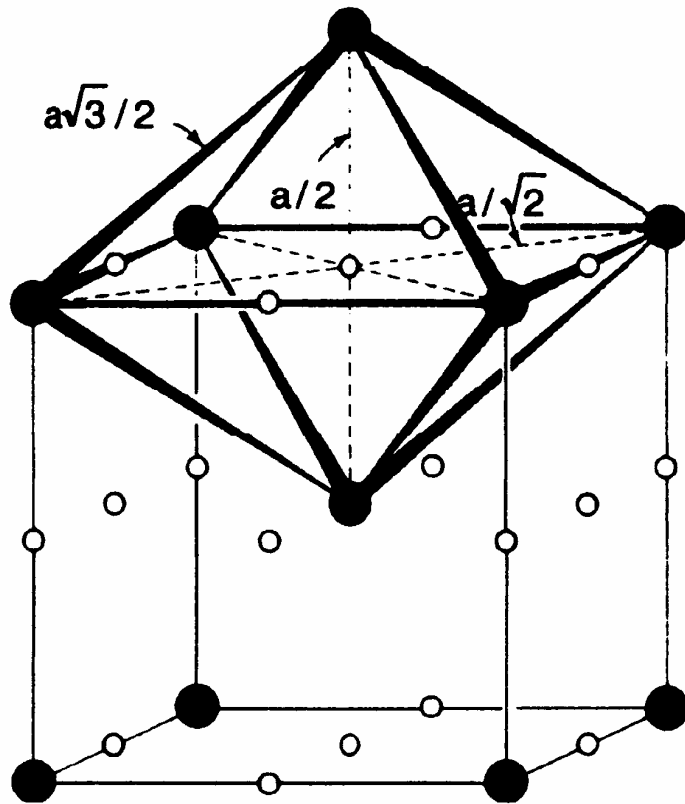
$$x_{\text{C}} \approx 0.0183$$



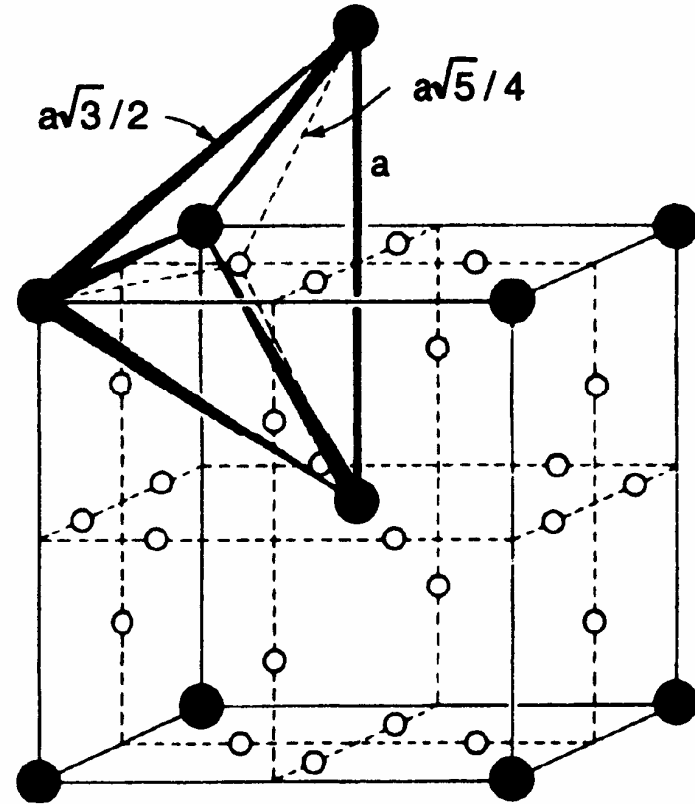
$$S^{\text{conf}} = -R(0.9817 \ln 0.9817 + 0.0183 \ln 0.0183) \approx 0.761 \frac{\text{J}}{\text{K} \times \text{mole}}$$

a wrong result

α -Fe (ferrite) and δ -Fe

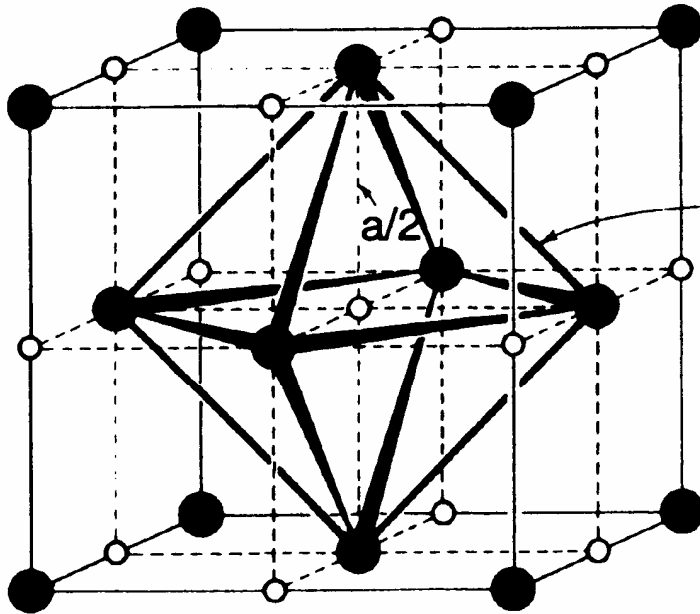


- metal-Atom
- atom in octahedral interstice

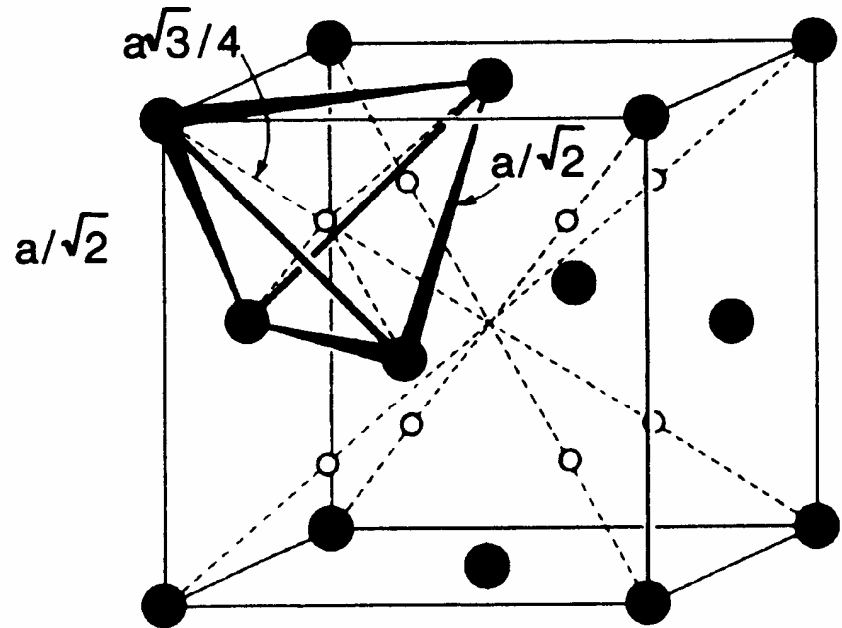


- metal-Atom
- atom in tetrahedral interstice

γ -Fe (austenite)

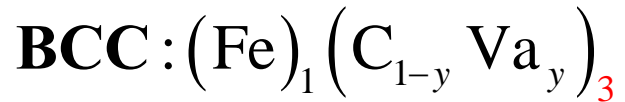


- metal atom
- atom in octahedral interstice



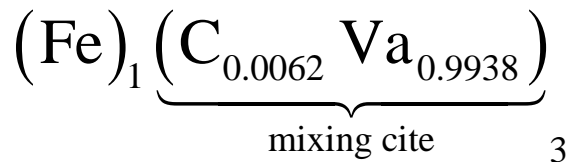
- metal atom
- atom in tetrahedral interstice

Correcting the mistake

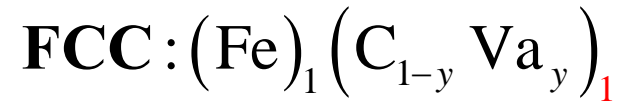


$$x_C = \frac{3(1-y)}{1+3(1-y)} = \frac{3-3y}{4-3y}$$

$$x_C = 0.0183$$

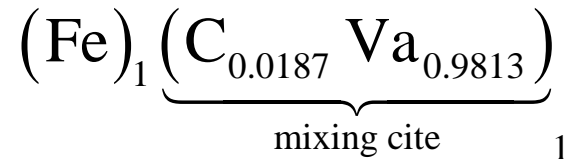


$$S_{\text{conf}}^{\text{BCC}} = 0.926 \text{ instead of } 0.761$$



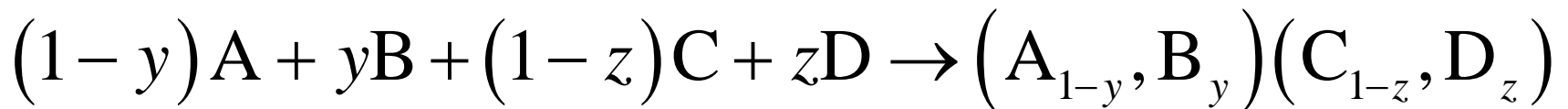
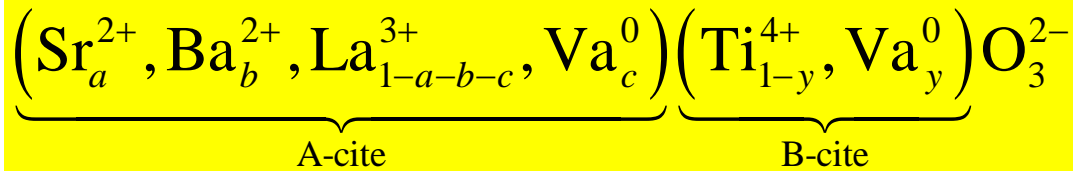
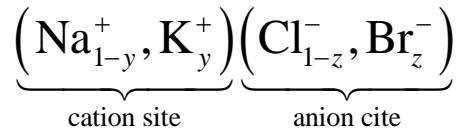
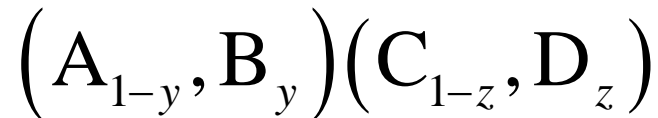
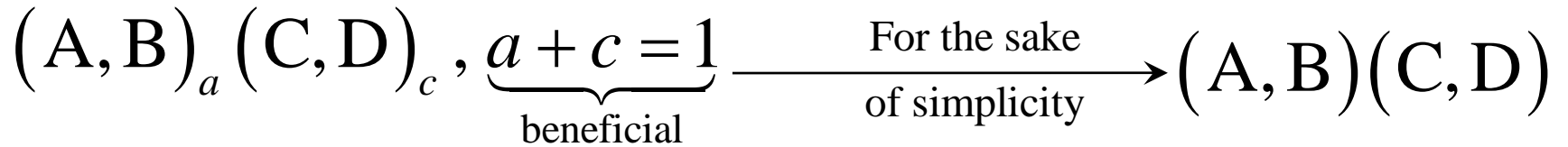
$$x_C = \frac{1-y}{1+(1-y)} = \frac{1-y}{2-y}$$

$$x_C = 0.0183$$

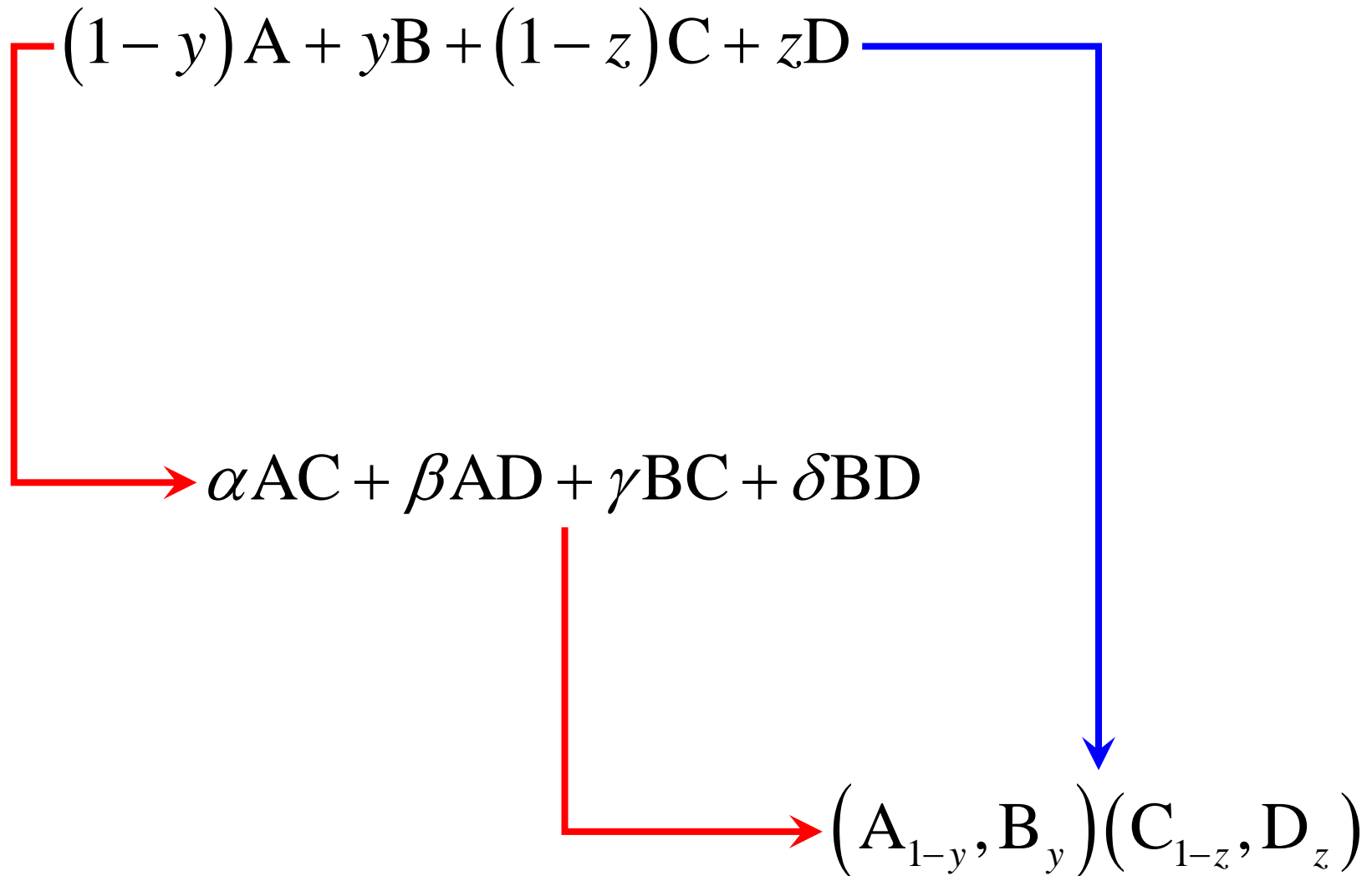


$$S_{\text{conf}}^{\text{FCC}} = 0.758 \text{ instead of } 0.761$$

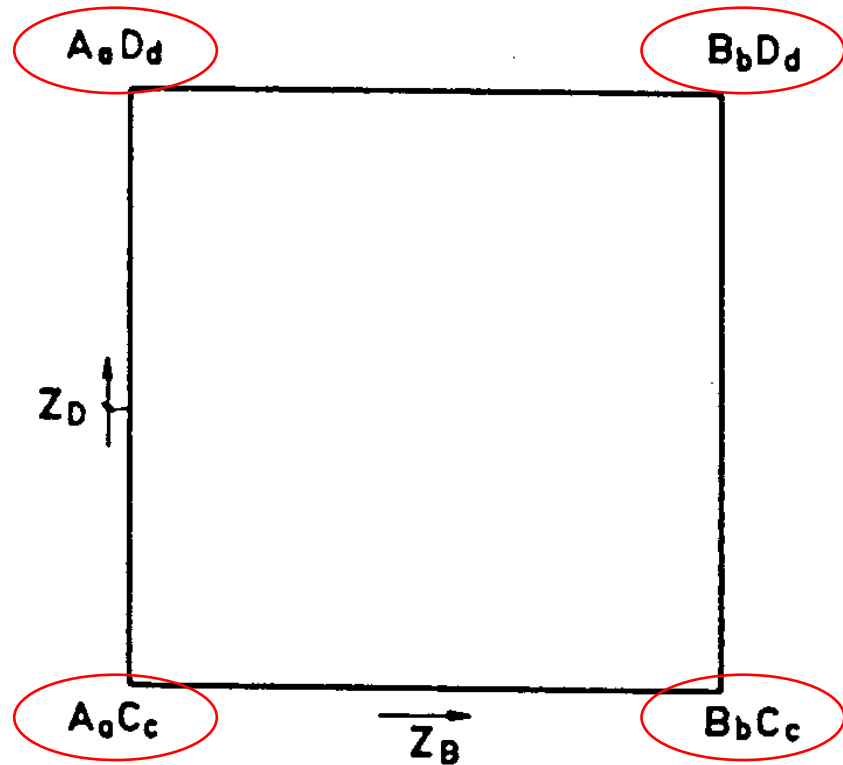
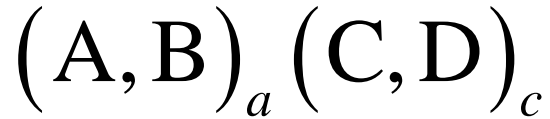
Sublattice model (CEF)



Another way to synthesize the phase



Playing field



Compounds
a.k.a.
end-members

Fig. 1. Representation of composition in a quaternary system where the components mix with each other, two and two.

Hillert's suggestion was based on a powerful KISS principle

$$\alpha AC + \beta AD + \gamma BC + \delta BD \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

$$(1-y)(1-z)AC + (1-y)zAD$$

$$+ y(1-z)BC + yzBD \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

$$\mathbf{A} \quad (1-y)(1-z) + (1-y)z$$

$$= \cancel{1-z} - y + \cancel{yz} + \cancel{z} - \cancel{yz} = 1 - y$$

Reference surface, not reference line or plane or hyperplane

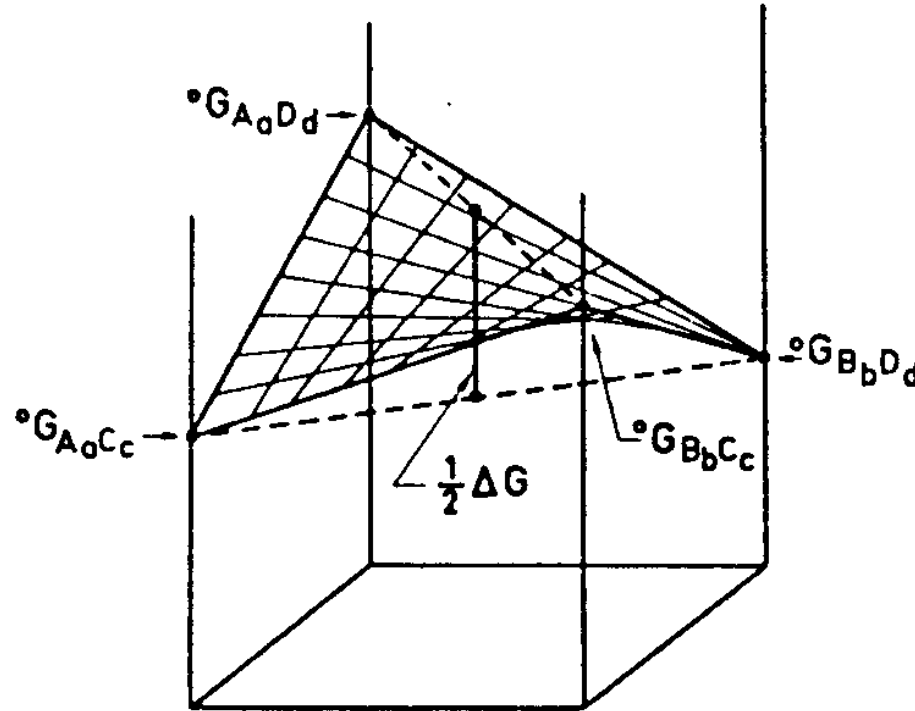


Fig. 2. Suggested surface of reference for the free energy in a quaternary system where the components mix with each other two and two.

What's about uniqueness?

$$\alpha AC + \beta AD + \gamma BC + \delta BD \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

$$\left\{ \begin{array}{l} \mathbf{A} \quad \alpha + \beta = 1 - y \\ \mathbf{B} \quad \gamma + \delta = y \\ \mathbf{C} \quad \alpha + \gamma = 1 - z \\ \mathbf{D} \quad \beta + \delta = z \end{array} \right.$$

$$\begin{array}{l}
 1 \begin{pmatrix} 1 & 1 & 0 & 0 \end{pmatrix} \\
 2 \begin{pmatrix} 0 & 0 & 1 & 1 \end{pmatrix} \\
 3 \begin{pmatrix} 1 & 0 & 1 & 0 \end{pmatrix} \\
 4 \begin{pmatrix} 0 & 1 & 0 & 1 \end{pmatrix}
 \end{array}$$

$$\begin{array}{l}
 1 - 3 = (0 \quad 1 \quad -1 \quad 0) \\
 (0 \quad 1 \quad -1 \quad 0) + 2 = \underbrace{(0 \quad 1 \quad 0 \quad 1)}_4
 \end{array}$$

$$\text{rank} = 3$$

$$4 - 3 = 1$$

Hillert's choice was the simplest and most convenient one

Tikhonov regularization

$$\begin{cases} x_1 + x_2 = 1 \\ x_1 + x_2 = 1 \end{cases}$$

$$\underbrace{\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}}_A \underbrace{\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}}_x = \underbrace{\begin{pmatrix} 1 \\ 1 \end{pmatrix}}_b$$

$$\|A\mathbf{x} - \mathbf{b}\|^2 \rightarrow \min \quad \mathbf{x} = (A^T A)^{-1} A^T \mathbf{b}$$

But what if A is ill-conditioned or singular?

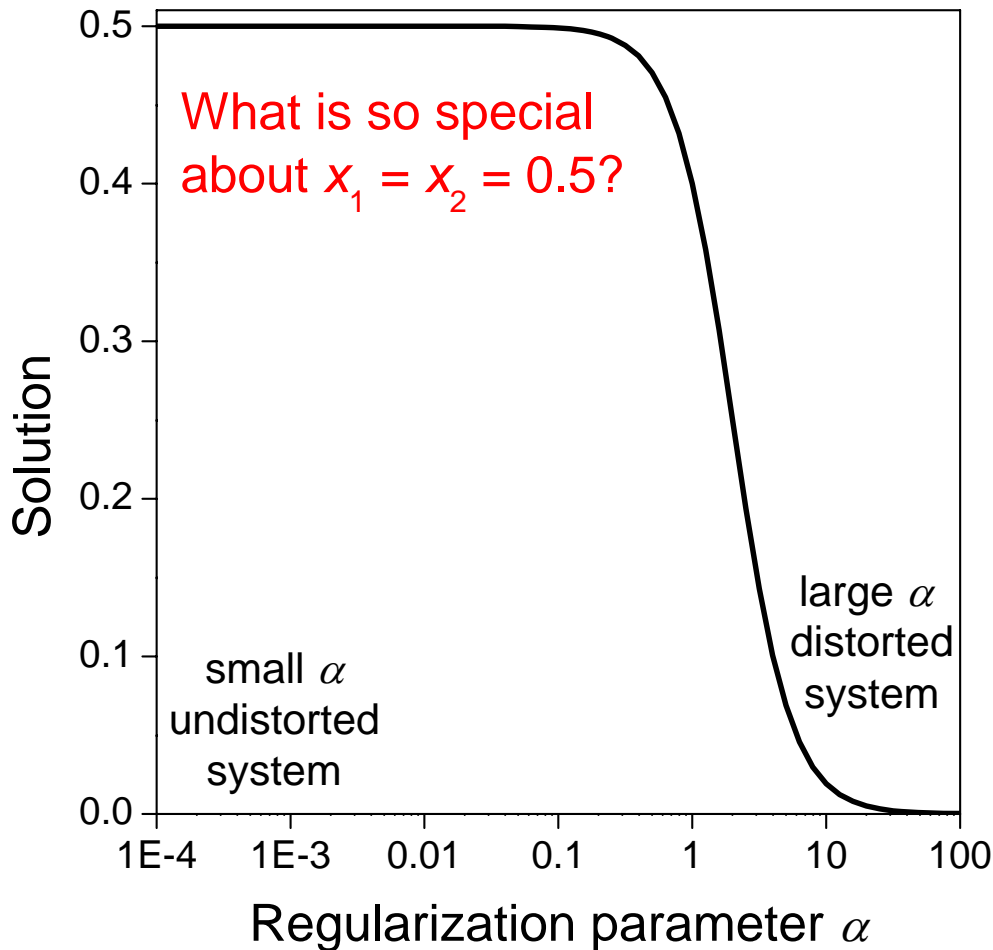
$$\|A\mathbf{x} - \mathbf{b}\|^2 + \|\mathbf{\Gamma}\mathbf{x}\|^2 \rightarrow \min, \quad \mathbf{\Gamma} = \underbrace{\alpha}_{\text{regularization parameter}} \times \underbrace{\mathbf{I}}_{\text{identity matrix}}$$

$$\mathbf{x}(\alpha) = (A^T A + \mathbf{\Gamma}^T \mathbf{\Gamma})^{-1} A^T \mathbf{b}$$

How does it work?

$$\begin{cases} x_1 + x_2 = 1 \\ x_1 + x_2 = 1 \end{cases}$$

$$\mathbf{x}(\alpha) = (A^T A + \Gamma^T \Gamma)^{-1} A^T \mathbf{b}$$



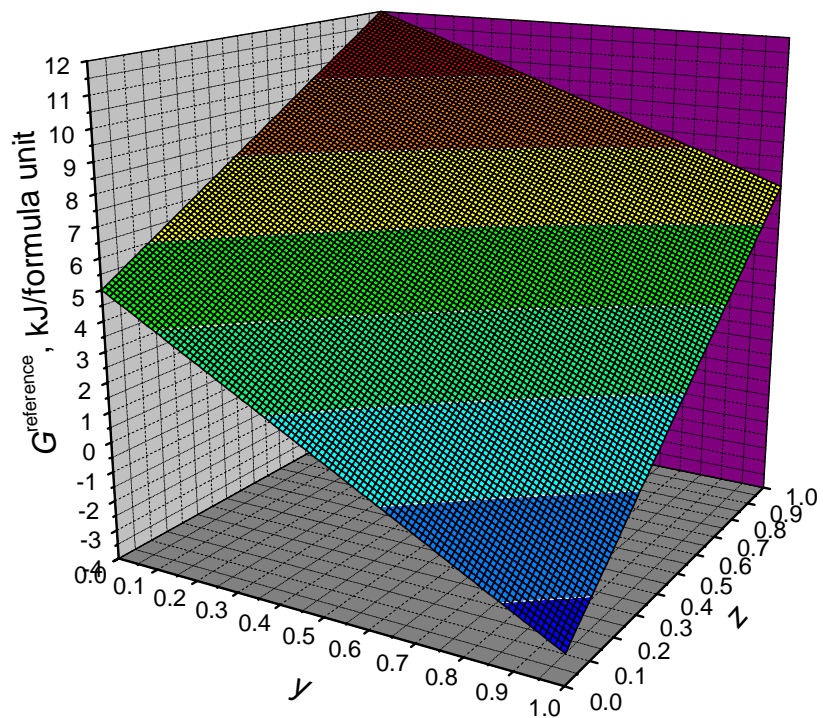
$$\begin{cases} x_1 + x_2 = 1 \\ x_1 + x_2 = 1 \\ x_1^2 + x_2^2 \rightarrow \min \end{cases}$$

Let us choose a particular solution
possessing the minimal norm

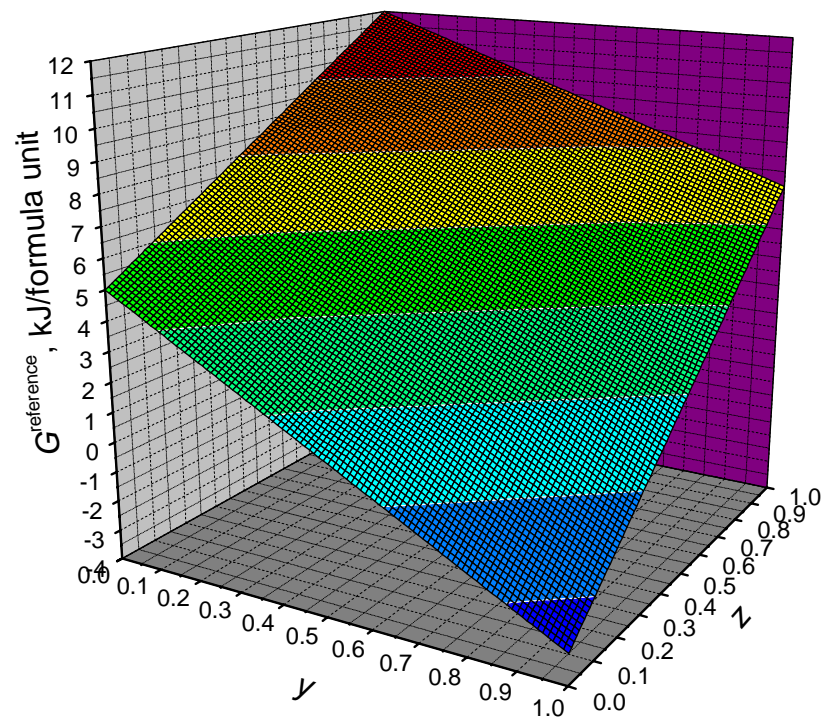
$$\alpha AC + \beta AD + \gamma BC + \delta BD \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

$$\left\{ \begin{array}{l} \alpha + \beta = 1 - y \\ \gamma + \delta = y \\ \alpha + \gamma = 1 - z \\ \beta + \delta = z \\ \alpha^2 + \beta^2 + \gamma^2 + \delta^2 \rightarrow \min \\ \alpha \geq 0, \beta \geq 0, \gamma \geq 0, \delta \geq 0 \end{array} \right.$$

Comparison

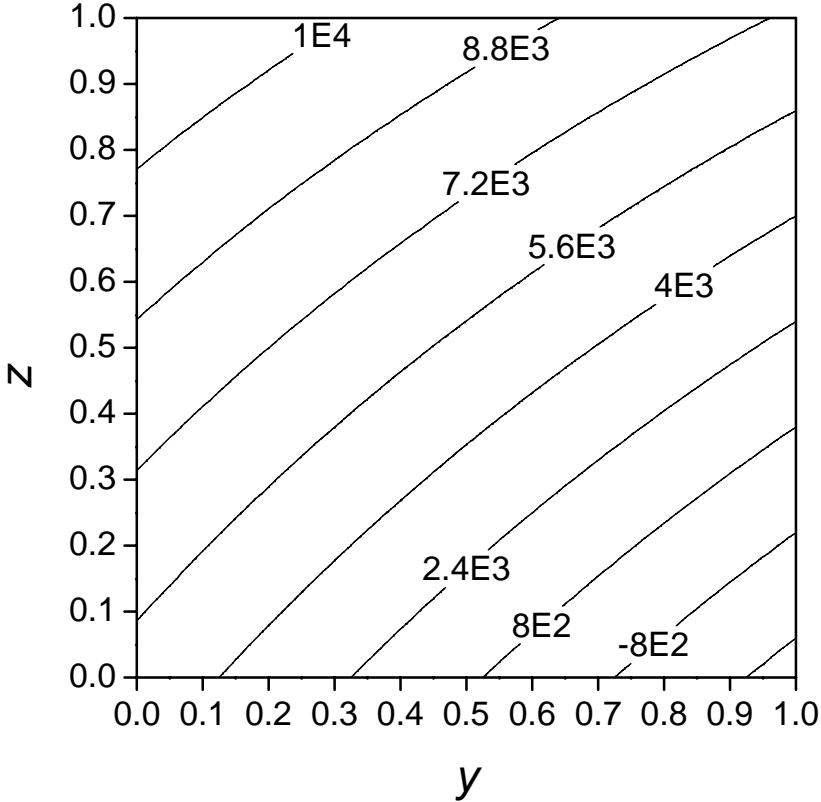


Hillert

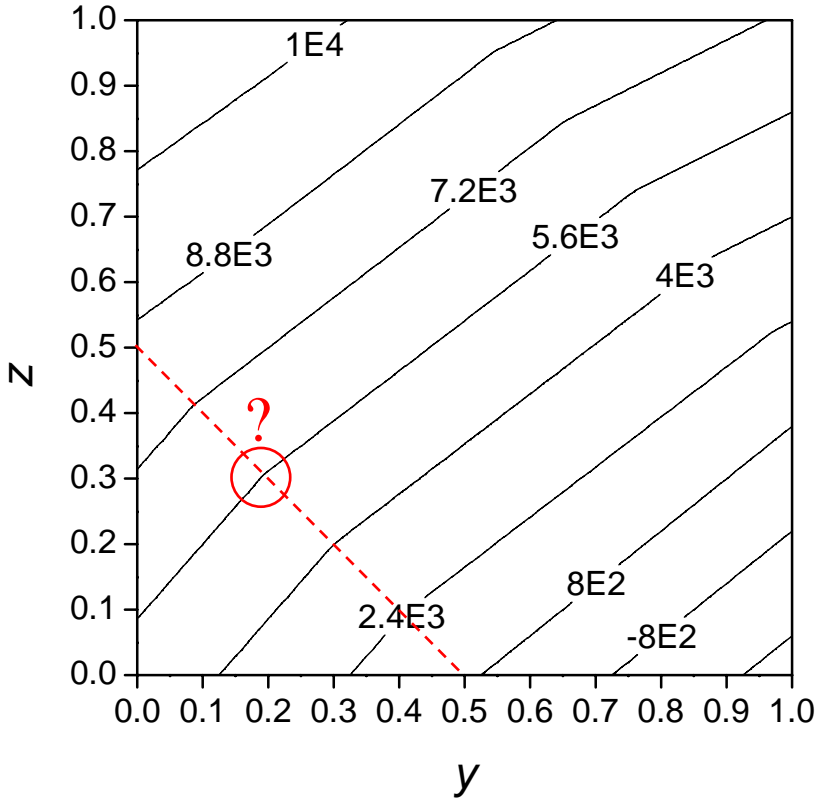


Euclid

Comparison



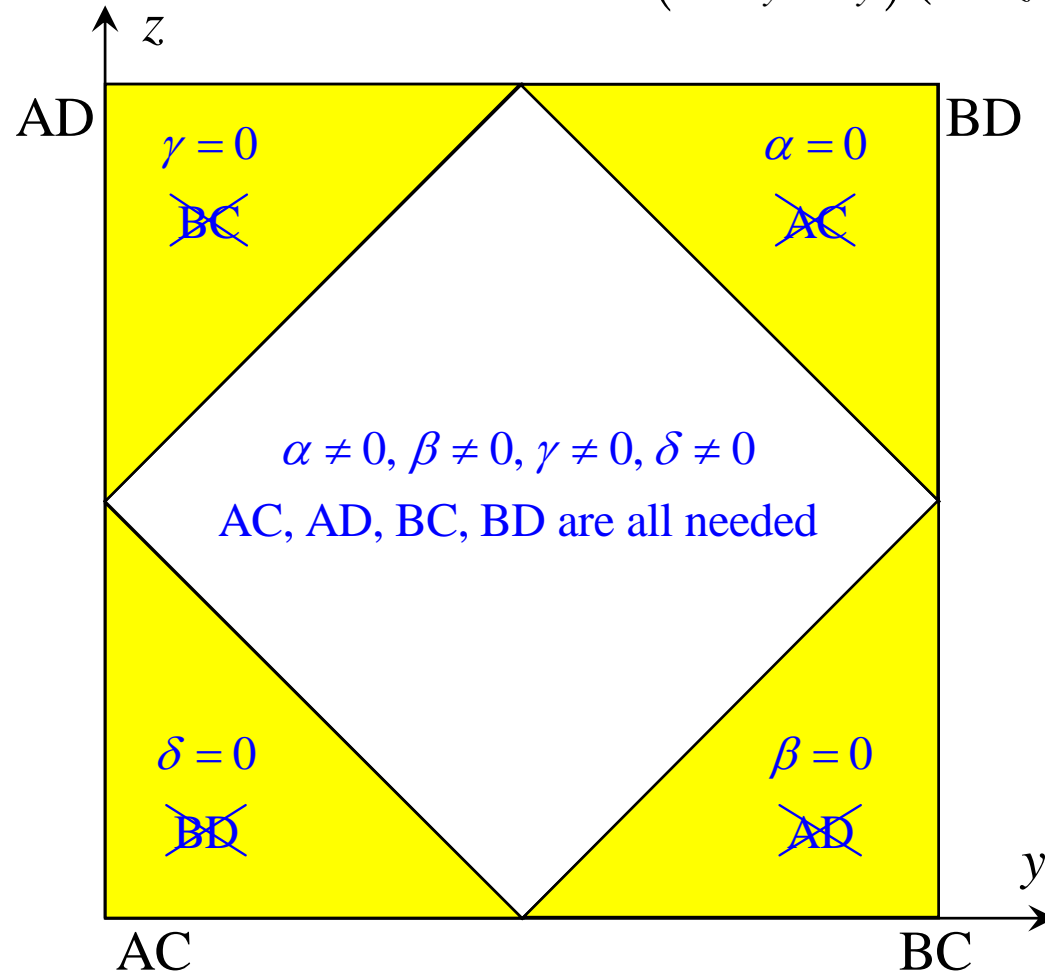
Hillert



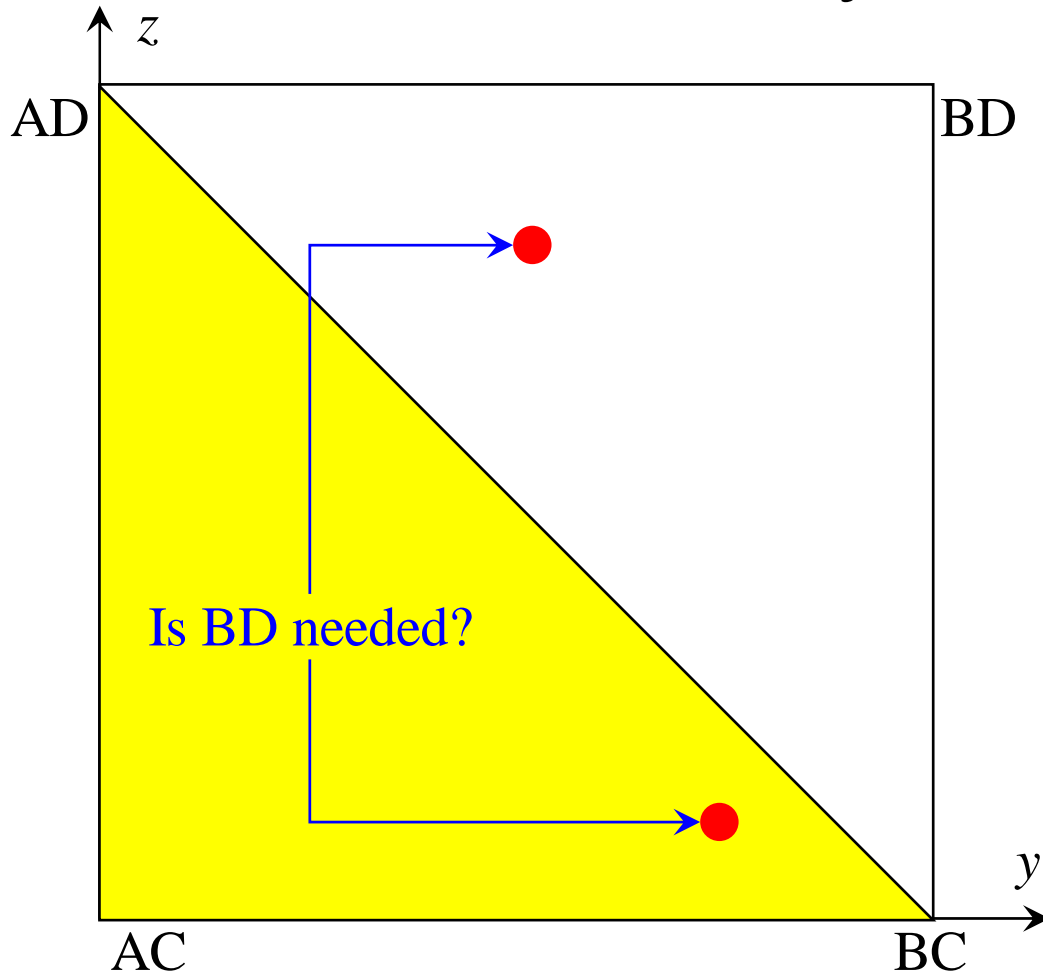
Euclid

An interesting “side effect”

$$\alpha AC + \beta AD + \gamma BC + \delta BD \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

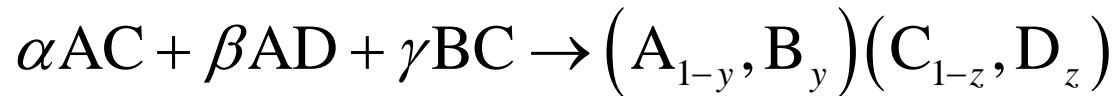


Are all end-members always needed?



$$\alpha AC + \beta AD + \gamma BC + \underbrace{\delta BD}_{?} \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

Only three compounds are required



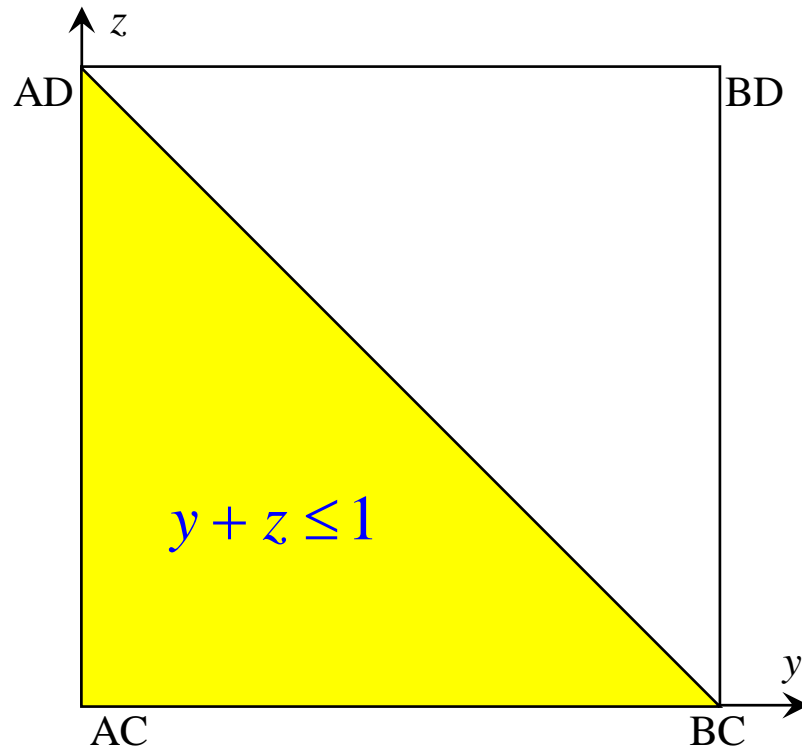
$$\left\{ \begin{array}{l} \mathbf{A} \quad \alpha + \beta = 1 - y \\ \mathbf{B} \quad \gamma = y \\ \mathbf{C} \quad \alpha + \gamma = 1 - z \\ \mathbf{D} \quad \beta = z \end{array} \right.$$



Non-negativity condition

$$(1 - y - z)AC + zAD + yBC \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

$$1 - y - z \geq 0 \Rightarrow y + z \leq 1$$



Another particular solution

$$\alpha AC + \beta AD + \gamma BC + \delta BD \rightarrow (A_{1-y}, B_y)(C_{1-z}, D_z)$$

$$\left\{ \begin{array}{l} \alpha + \beta = 1 - y \\ \gamma + \delta = y \\ \alpha + \gamma = 1 - z \\ \beta + \delta = z \\ \alpha^2 + \beta^2 + \gamma^2 + \delta^2 \rightarrow \min \\ \alpha \geq 0, \beta \geq 0, \gamma \geq 0, \delta \geq 0 \end{array} \right.$$

$$\left\{ \begin{array}{l} \alpha + \beta = 1 - y \\ \gamma + \delta = y \\ \alpha + \gamma = 1 - z \\ \beta + \delta = z \\ \min(\alpha, \beta, \gamma, \delta) \rightarrow \min \\ \alpha \geq 0, \beta \geq 0, \gamma \geq 0, \delta \geq 0 \end{array} \right.$$

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