REVIEW OF ENGINEERING THERMODYNAMICS

Gibbs energy

G = H – TS;   G: Gibbs Energy, H: Enthalpy, S: Entropy

1. For pure elements or pure compounds (Al, O_2, Al_2O_3, etc.)

$$G_T^o = H_T^o - TS_T^o$$

$$H_T^o = \Delta H_{298\,K}^o + \int_{298\,K}^{T} C_p \, dT \qquad S_T^o = S_{298\,K}^o + \int_{298\,K}^{T} \frac{C_p}{T} \, dT$$

$: C_p = a + bT + cT^{-2} + dT\ln T + \cdots$
is known (measurable)

enthalpy of compound at 298 K with reference to pure stable elemental species
At 298 K, 1 atm ($H_{0K}^o \neq 0$, unknown)

standard entropy at 298 K
($S_{0K}^o = 0$)

Standard state for H : $\Delta H_{298K}^o = 0$
for all stable elements at 1atm and 298K.
Fe(bcc), Fe(fcc), Fe(l), H₂O(l), H₂O(g), H₂(g), O₂(g), O(g), CaO, FeO, C(s), CO₂, CO,.

* In FactSage compound databases, ΔH_{298K}^o, $S_{298\,K}^o$, C_p are stored
→ Absolute Gibbs Energy of compounds relative to elemental species.

Gibbs energy

2. Chemical reaction between pure compounds (No solutions)

$$nA + mB = A_nB_m$$

$$\Delta G_{rxn} = G^o_{A_nB_m} - (nG^o_A + mG^o_B)$$

$$= \Delta H^o_{rxn} - T\Delta S^o_{rxn}$$

In many thermodynamics books, ΔH^o_{rxn}, S^o_{rxn} are given.
These values are not absolute values, but dependent on each chemical reaction.
→ In FactSage, therefore, absolute Gibbs energy of each species (relative to elemental species) is stored. Then, the reaction Gibbs energy for any reaction can be automatically calculated from the Gibbs energy of each species.

Gibbs energy

3. Chemical reaction involving gas

$$nA + mO_2(g) = A_nO_{2m}$$

$$\Delta G_{rxn} = G^o_{A_nO_{2m}} - (nG^o_A + mG_{O_2})$$
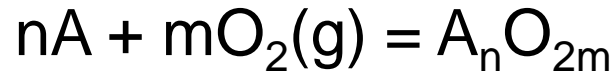
$$G_i = G^o_i + RT \ln P_i$$

for ideal gas species i

$$= \Delta G^o - mRT \ln P_{O_2}$$

At Equilibrium $\quad \Delta G_{rxn} = 0$

$$\therefore \Delta G^o = -RT \ln\left(\frac{1}{P_{O_2}{}^m}\right)$$

Gibbs energy

3. Chemical reaction involving gas (continued)

In general, for aA + bB(g) = cC + dD(g)

At equilibrium

$$\Delta G^o = -RT \ln(\frac{P_D^d}{P_B^b})$$

$$\boxed{\Delta G^o = -RT \ln K}$$

K: Equilibrium constant

FactSage Reaction module can give this kind of answer quickly. *Reaction module is only for stoichiometric species (No solutions are involved in the Reaction module calculation)*
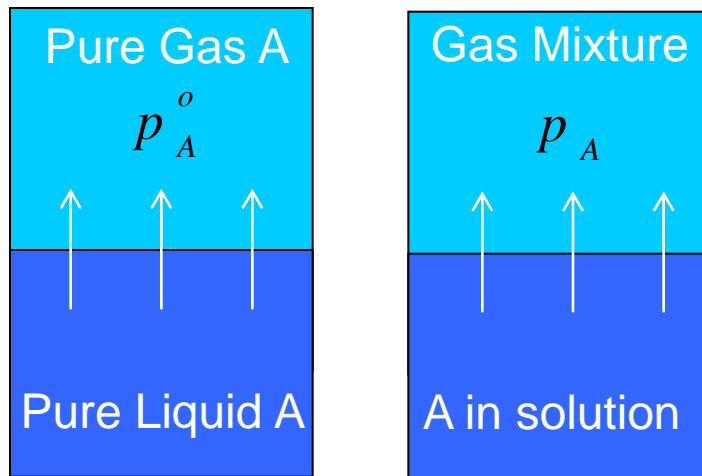
Gibbs energy

4. Chemical reaction involving solid or liquid solutions

$$G_{i(in\ so\ln)} = G^o_{i(pure)} + RT\ \ln(a_i)$$

a: activity

change of Gibbs energy of i in solution by interacting with surrounding species

Definition of activity

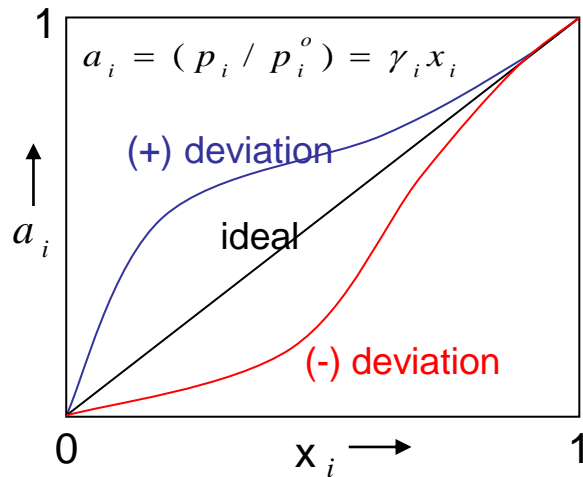| Pure Gas A p^o_A	Gas Mixture p_A
Pure Liquid A	A in solution

$$a_A = \frac{P_A}{P^o_A} = \gamma_A x_A$$

$\therefore a_A$ is the activity of species A in solution: higher activity means a higher chance of evaporating.

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Gibbs energy

4. Chemical reaction involving solid or liquid solutions

Activity

$$a_i = (p_i / p_i^o) = \gamma_i x_i$$

(graph with axes a_i vs x_i, showing (+) deviation, ideal, and (-) deviation curves, ranging 0 to 1)

(+) deviation: repulsion between i and other species
→ $a_i > x_i$: more active chemical reaction of i

(-) deviation: attraction between i and other species
→ $a_i < x_i$: less active chemical reaction of i

In general, for aA + bB(g) = cC + dD(g)

$$\Delta G_{rxn} = \sum G_{products} - \sum G_{reactants}$$

At Equilibrium

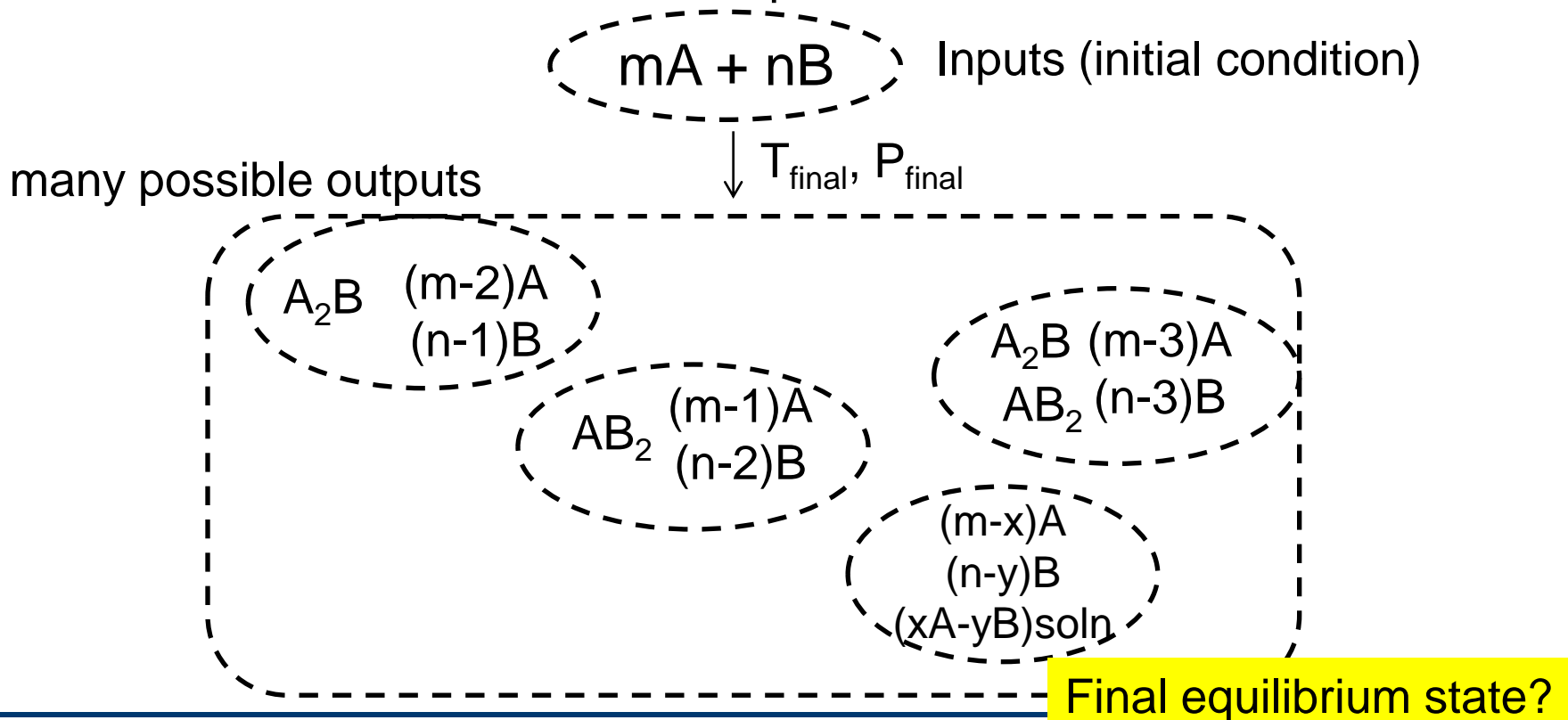$$\Delta G^o = -RT \ln\left(\frac{a_C^c P_D^d}{a_A^a P_B^b} \right)$$

* FactSage solution databases contain model parameters to calculate
$G_i → a_i$

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Gibbs energy minimization

In most thermodynamics texts, one calculates equilibrium conditions

$$\Delta G_{rxn} = 0 \longrightarrow \Delta G^o = -RT \ln K_{eq}$$

In real calculations, we want to know the direction of reaction and the final products

mA + nB   Inputs (initial condition)

$\downarrow T_{final}, P_{final}$

many possible outputs

A_2B (m-2)A (n-1)B

AB_2 (m-1)A (n-2)B

A_2B (m-3)A AB_2 (n-3)B

(m-x)A (n-y)B (xA-yB)soln

Final equilibrium state?

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Gibbs energy minimization

(continued)

→ We have to find out which phase assemblage is most stable at given T_f and P_f for a given mass balance (inputs).

→ Gibbs energy minimization routine. (ChemSage, Solgas-mix, etc.) The most stable phase assemblage is the one with the lowest Gibbs energy.
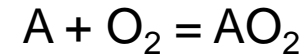
In FactSage
i)   Input amounts
ii)   Select all possible product phases (solid compounds, solid solutions, liquid solutions, gases)
iii) Set T_{final} and P_{final}
iv)   Calculation (Gibbs energy minimization routine)
v)   Equilibrium phase assemblage calculated

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Ellingham diagrams

(A)
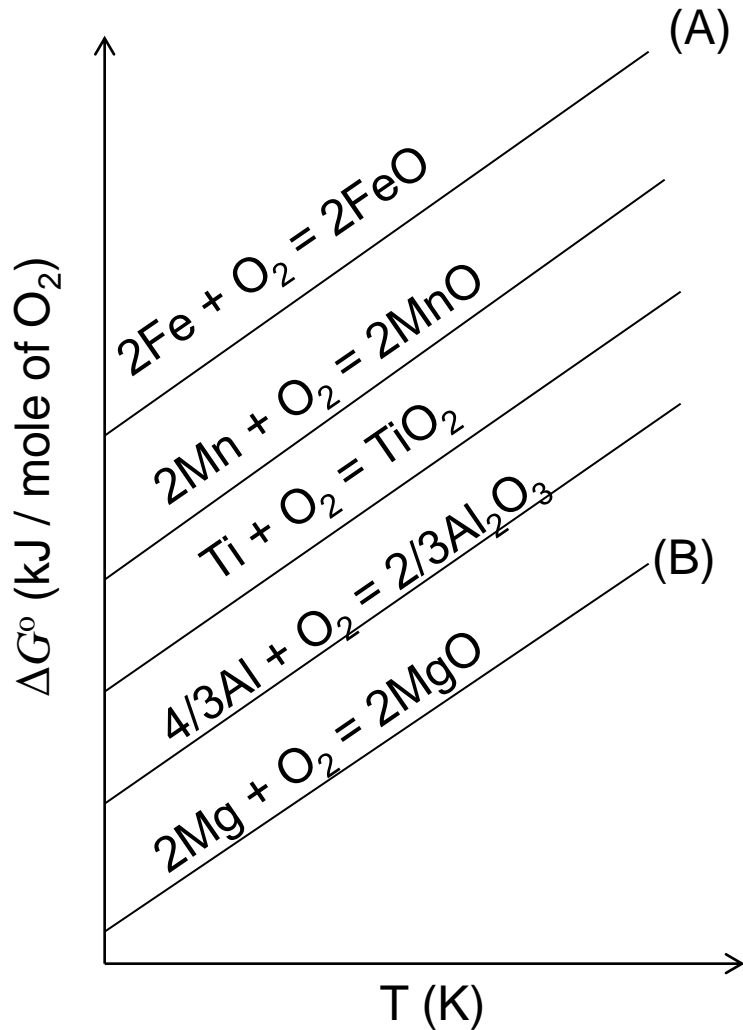
- Collection of ΔG^o values for oxidation reactions

$$mA + O_2 = A_mO_2 \text{ (reference: 1 mol of } O_2)$$

- Only consider pure compounds.
  (No solutions are considered.)

ΔG^o (kJ / mole of O_2)

$2Fe + O_2 = 2FeO$

$2Mn + O_2 = 2MnO$

$Ti + O_2 = TiO_2$

$4/3Al + O_2 = 2/3Al_2O_3$

(B)

$2Mg + O_2 = 2MgO$

T (K)

$$A + O_2 = AO_2$$

$$\Delta G = \Delta G^o + RT \ln \frac{(a_{AO_2})}{(a_A)(p_{O_2})} \quad , (\Delta G = 0 : Equilibrium)$$
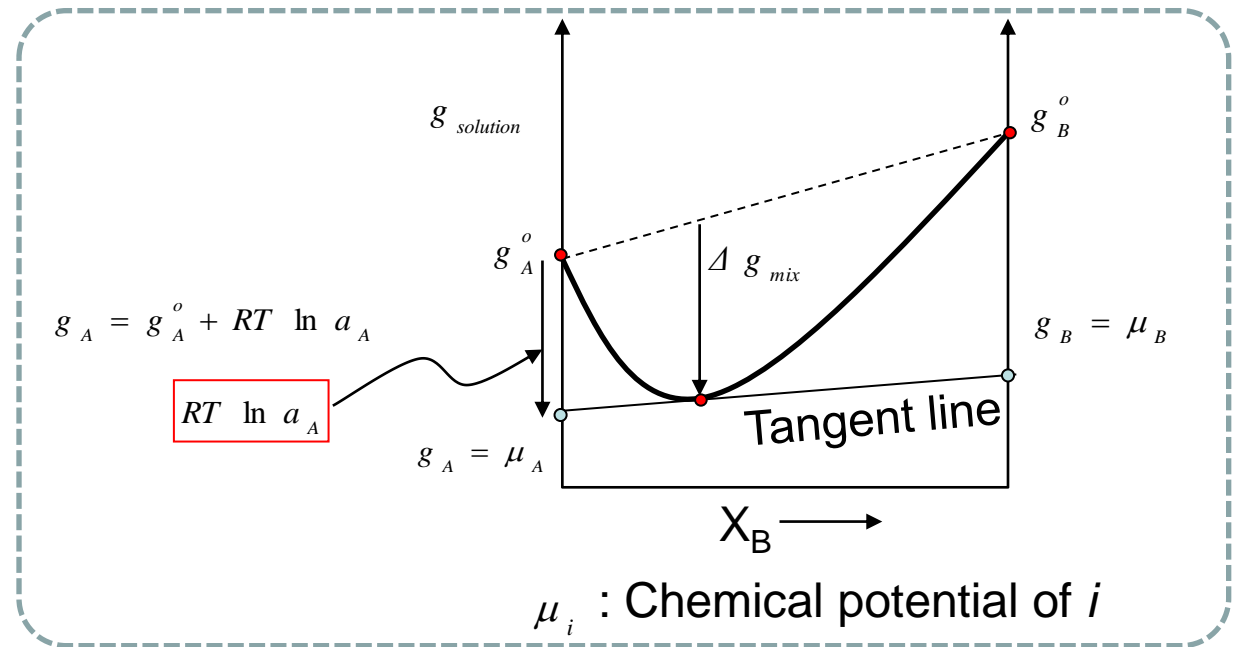
$$\Delta G^o = RT \ln p_{O_2}$$

$$\Delta G^o = (R \ln p_{O_2}) \times T$$

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Solution thermodynamics

A-B solution, (Solid or liquid solution)

$$G_{solution(molar)} = \sum x_i g_i$$

$$g_i = g_i^o + RT \ln a_i \quad \textbf{g}_i\textbf{: partial molar Gibbs energy of } i \textbf{ in solution}$$

$g_{solution}$

g_B^o

g_A^o

Δg_{mix}

$g_A = g_A^o + RT \ln a_A$

$g_B = \mu_B$

$RT \ln a_A$

Tangent line

$g_A = \mu_A$

$X_B \longrightarrow$

μ_i : Chemical potential of i

$$= (x_A g_A^o + x_B g_B^o) + RT (x_A \ln a_A + x_B \ln a_B)$$

Solution thermodynamics

A-B solution, (Solid or liquid solution)

$$G_{soln(molar)} = (x_A g_A^o + x_B g_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

$$a_i = x_i \gamma_i$$

1. Ideal solution: $\gamma_A = 1, \gamma_B = 1$

$$G_{soln(molar)} = (x_A g_A^o + x_B g_B^o) + RT(x_A \ln x_A + x_B \ln x_B)$$

2. Regular solution: $RT \ln \gamma_A = \Omega_{AB} x_B^2$ **Ω: Regular solution parameter**

$$G_{soln(molar)} = (x_A g_A^o + x_B g_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + \Omega_{AB} x_A x_B$$

Solution thermodynamics

A-B solution, (Solid or liquid solution)

$$G_{soln(molar)} = (x_A g_A^o + x_B g_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

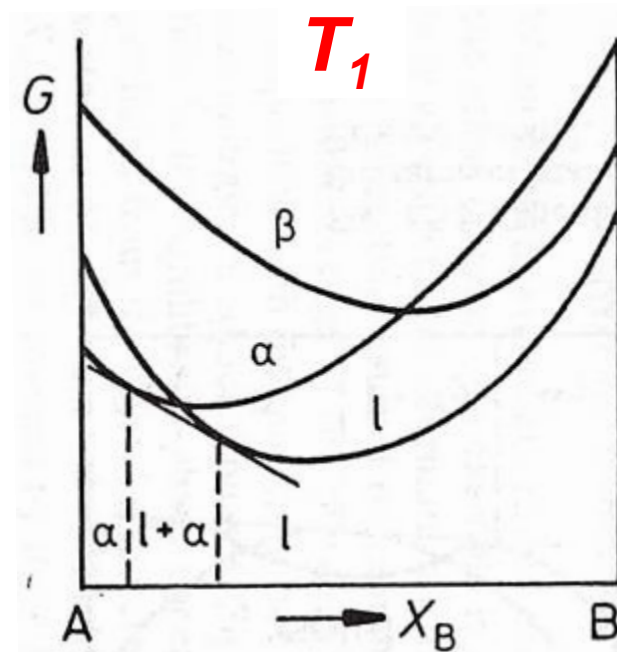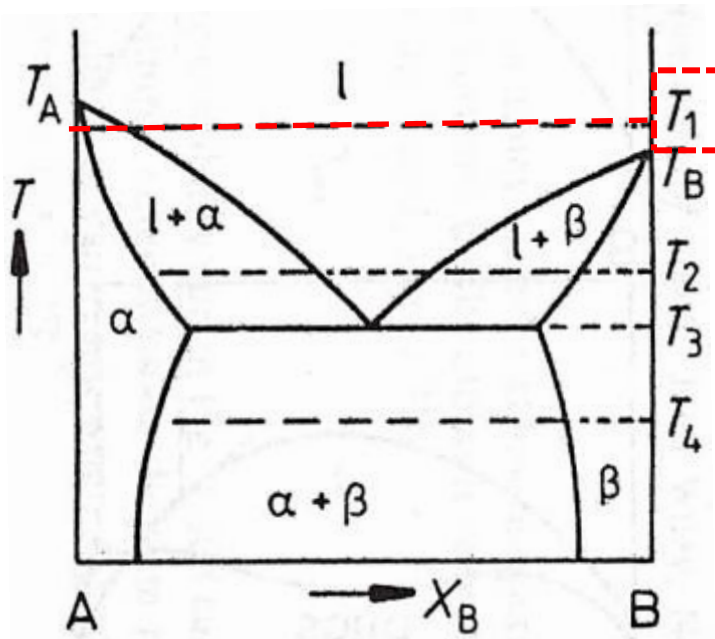**3. General solution:** $\quad \gamma_A = f(x,T) \qquad a_A = \gamma_A x_A$

$$G_{soln(molar)} = (x_A g_A^o + x_B g_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex}$$

"Polynomial model": $\quad G^{ex} = \sum_{i,j \geq 1} \omega_{AB}^{ij} x_A^i x_B^j = RT(X_A \ln \gamma_A + X_B \ln \gamma_B)$

* FactSage supports many complex solution models. Solution databases (FToxid, FTSalt, ...) contain optimized model parameters reproducing Gibbs energies of solutions.

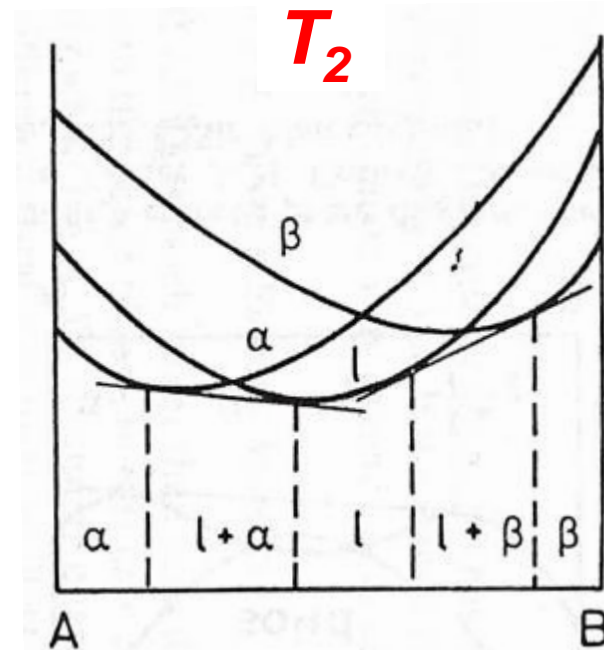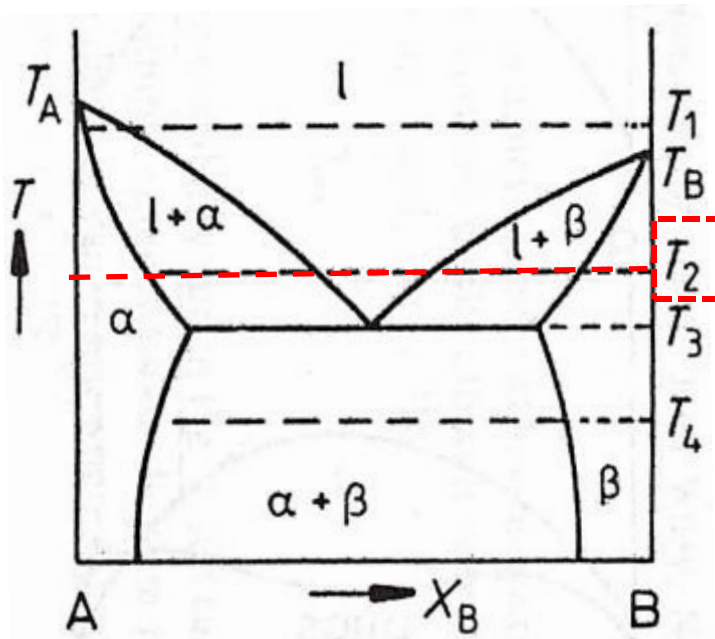# Gibbs Energy and Phase Diagrams

→ A phase diagram shows graphically the minimum Gibbs energy assemblages of a system.

Porter, D.A., and Easterling, K.E., Phase Transformation in Metals and Alloys, 2nd Ed. CHAMAN & HALL (1992)
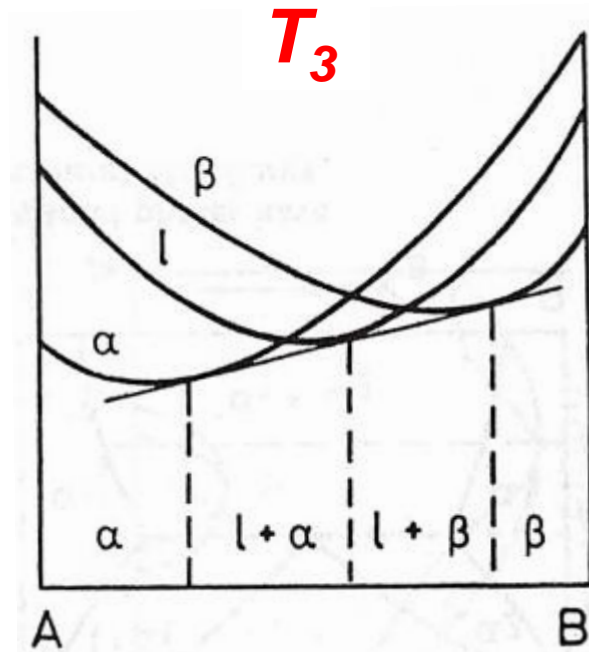
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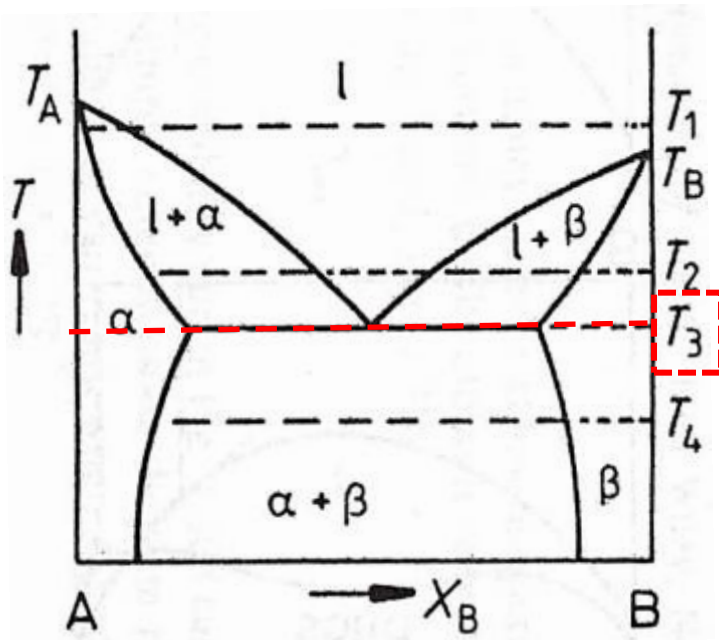
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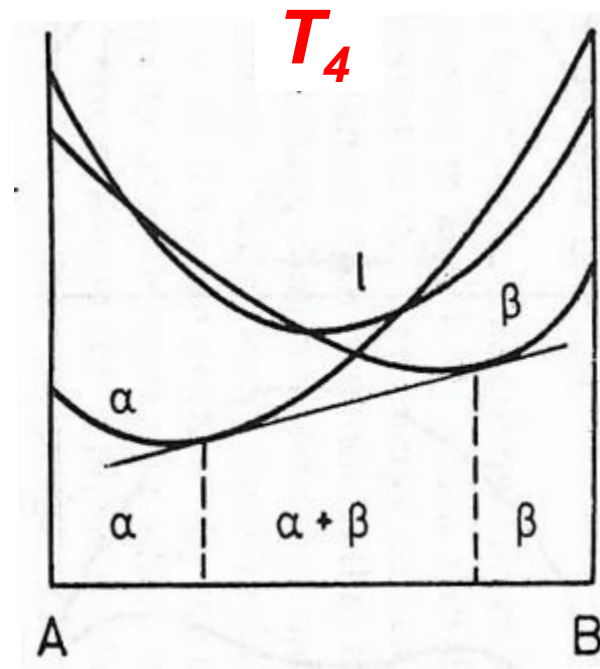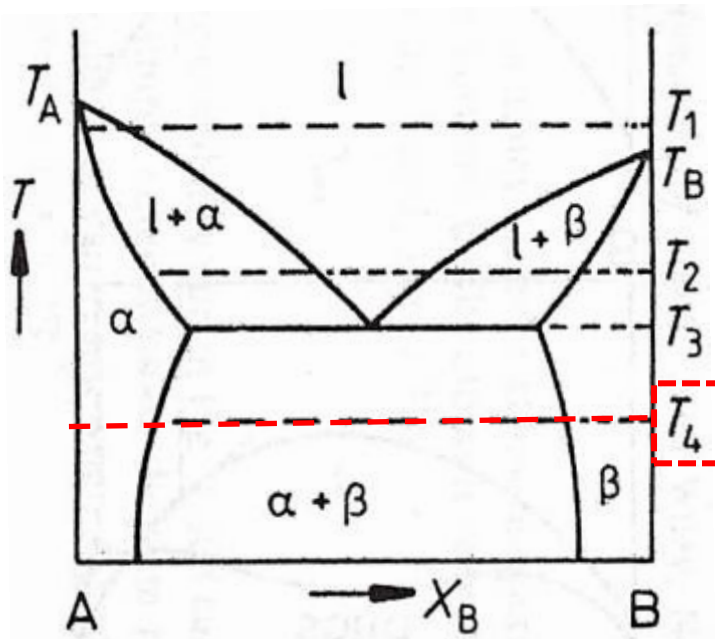
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Thermodynamic Database Development: FactSage

Pure compounds

$$G^o_T = H^o_T - TS^o_T$$

$$H^o_T = \Delta H^o_{298\ K} + \int_{298\ K}^{T} C_p\, dT$$

$$S^o_T = S^o_{298\ K} + \int_{298\ K}^{T} \frac{C_p}{T}\, dT \qquad S^o_{298\ K} = \int_{0\ K}^{298\ K} \frac{C_p}{T}\, dT$$

- ➤ Calorimetry
- ➤ emf
- ➤ Knudsen cell
- ➤ Vapor pressure

Solution

$$G^{ex} = \sum_{i,\,j \geq 1} \omega^{ij}_{AB}\, x^i_A\, x^j_B$$

- ➤ emf (activity)
- ➤ Knudsen cell (activity)
- ➤ Vapor pressure (activity)
- ➤ Solution calorimetry (enthalpy)
- ➤ Phase diagrams

Dilute Solutions
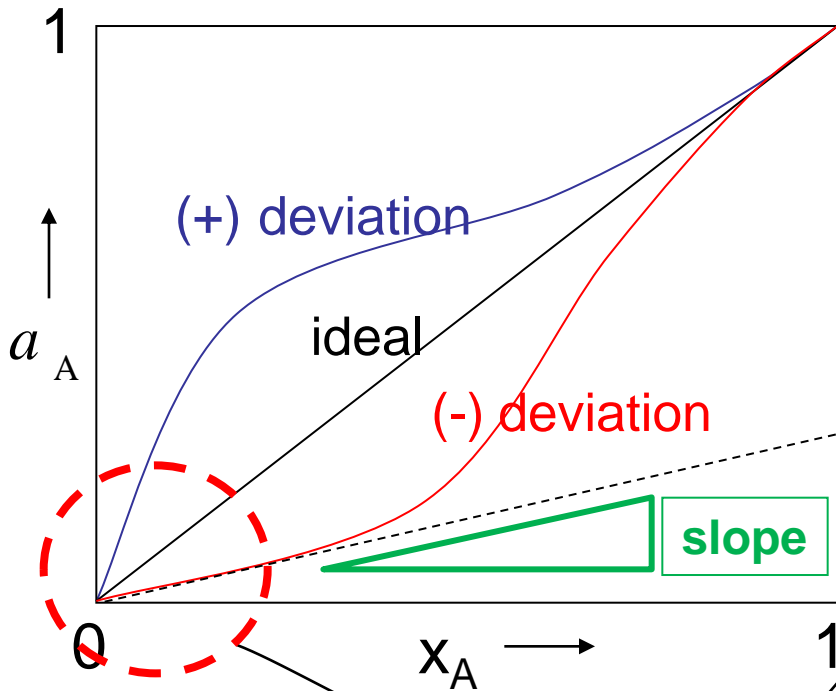
$a_A = \gamma_A^o x_A$: Henry's law

$\gamma_A = \gamma_A^o$

Constant slope

Henrian activity coefficient

* In FactSage, you cannot see the Henrian activity coefficient (in general, activity coefficient) value directly, but if you calculate the activity in the Equilib module in the very dilute composition region, you can calculate the Henrian activity coefficient using this relationship.

Dilute Solution

Most refining processes involve impurity elements (dilute solutes)
→ Henrian activity is important

For example, Al-deoxidation process in steelmaking,

$$2\,\underline{Al} + 3\,\underline{O} = Al_2O_3\,(s)$$
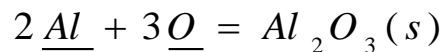
$$\Delta G^o = -RT\,\ln\frac{(a_{Al_2O_3})}{(a_{Al}^2)\,(a_O^3)} = -RT\,\ln\frac{(a_{Al_2O_3})}{(\gamma_{Al}^o\,X_{Al}^2)\,(\gamma_O^o\,X_O^3)}$$

γ_{Al}^o is the Henrian activity coefficient of Al in pure liquid Fe

Now, if we have other elements in Fe such as <u>O, Mn, C,</u> etc.
there is interaction between Al and these elements.

→ Change of γ_{Al} from γ_{Al}^o : interaction coefficients

$$\ln\gamma_{Al} = \ln\gamma_{Al}^o + \varepsilon_{Al}^{Al}\,x_{Al} + \varepsilon_{Al}^{O}\,x_O + \varepsilon_{Al}^{C}\,x_C + \dots$$

* FactSage FTmisc-FeLQ database contains these Henrian activity coefficients and interaction parameters for liquid steel.

Change of Standard State

Gibbs Energy

$g^o_{i(wt.\%)}$

$g^o_{i(H)}$

$g^o_{i(R)}$

$RT \ln a_{i(H)}$ $RT \ln a_{i(wt\%)}$

$RT \ln a_{i(R)}$

$\bar{g}_i(\bar{g}_i)$

Change of standard state is like temperature scales, K, oC (that is, just the zero point of $\ln a_i$ is changed).
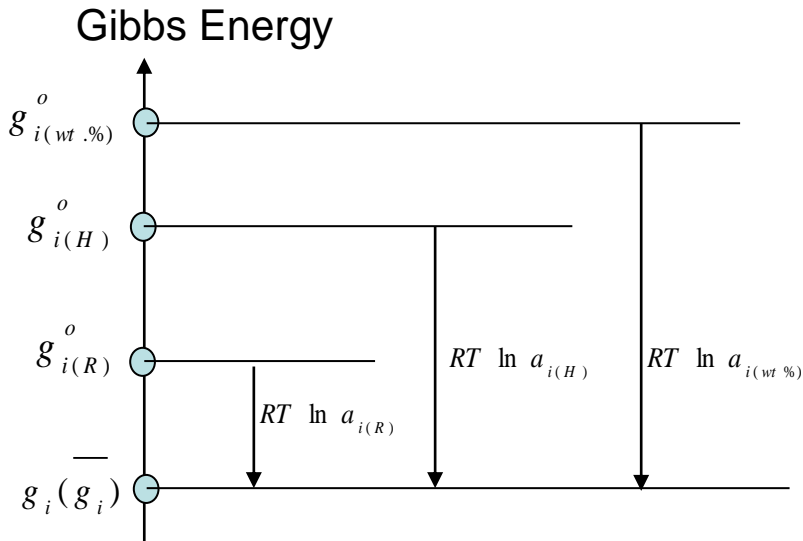
Change of standard state is like temperature scales, K, °C (that is, just the zero point of $\ln a_i$ is changed).

$$\bar{G}_i = G^o_{i(R)} + RT \ln a_{i(R)} = G^o_{i(H)} + RT \ln a_{i(H)}$$

$$= G^o_{i(wt.\%)} + RT \ln a_{i(wt.\%)}$$

➢ Raoultian standard state → Henrian standard state

$$\Delta G^o_{i(R \to H)} = RT \ln \gamma^o_i \qquad a_{i(H)} = f_i x_i$$

$$\ln f_i = \varepsilon^i_i x_i + \varepsilon^j_i x_j + \varepsilon^k_i x_k + ...$$

➢ Raoultian standard state → 1 wt.% standard state

$$\Delta G^o_{i(R \to wt\%)} = RT \ln \left(\frac{\gamma^o_i M_{Bulk}}{100 M_i} \right) \quad a_{i(wt.\%)} = f_i [wt\% i]$$

$$\log f_i = e^i_i [wt\% i] + e^j_i [wt\% j] + e^k_i [wt\% k] + ...$$

FactSage doesn't provide standard state conversions. Users must do the conversions using the formulae above.

Gibbs energy of reaction

$$\Delta G_{reaction} = (\Sigma n_i g_i)_{products} - (\Sigma n_i g_i)_{reactants}$$

$$g_i = g_i^o + RT \ln a_i$$

Activity of i
Standard state should be checked carefully
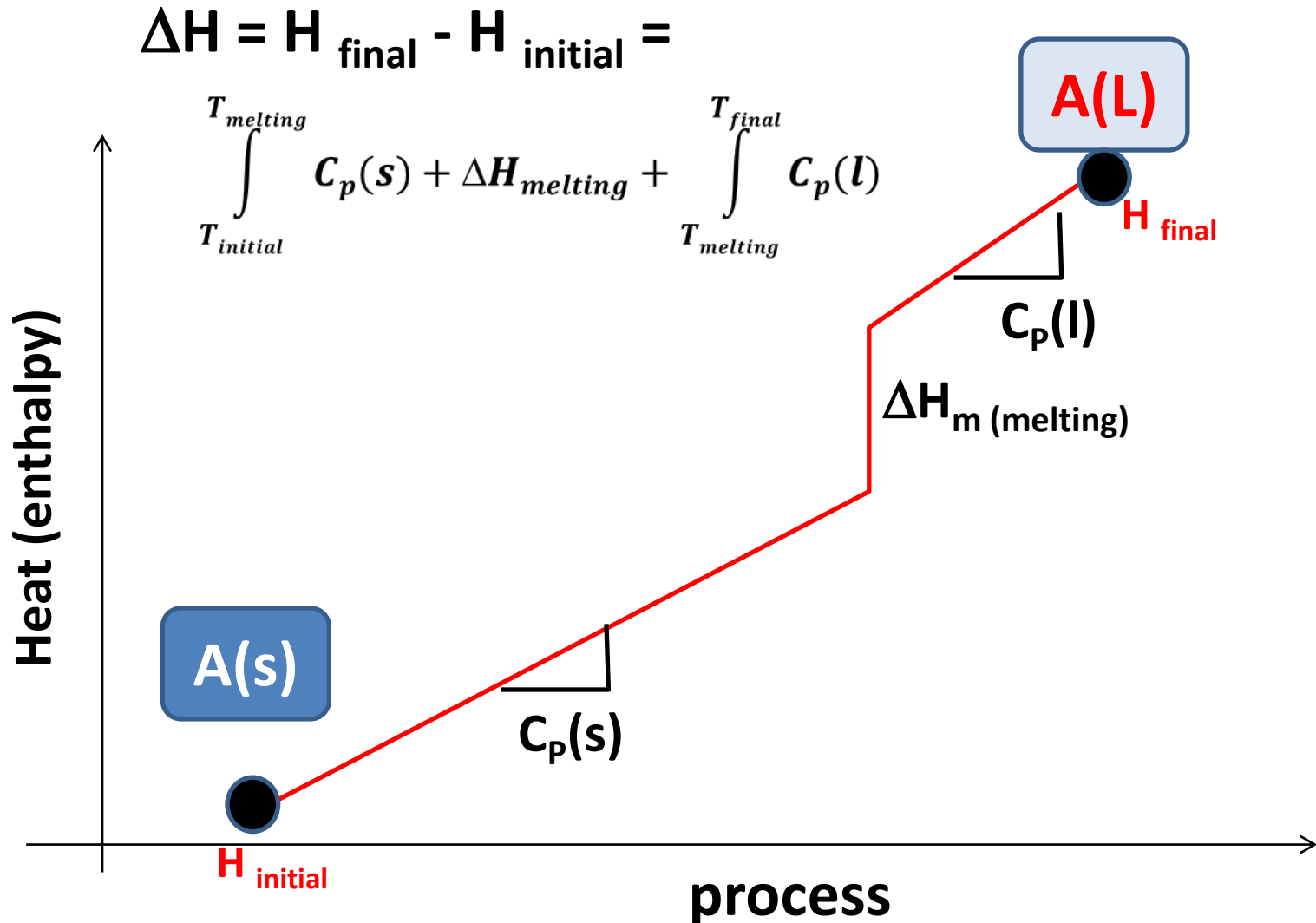
When the reactants or products are
- Pure species (not in a solution): activity = 1
- Species in solution: requires an activity value (can be calculated from FactSage)

No direct way to do this type of calculation in FactSage.
In FactSage, $\Delta G_{reaction}^o$ (between pure species) can be calculated from the Reaction module, and the activity of each solution species in the reactants or products can be calculated using the Equilib module. Then, using the above formula, we can calculate $\Delta G_{reaction}$

Heat evolution calculation

$$\Delta H = H_{\text{final}} - H_{\text{initial}} =$$

$$\int\limits_{T_{initial}}^{T_{melting}} C_p(s) + \Delta H_{melting} + \int\limits_{T_{melting}}^{T_{final}} C_p(l)$$

A(L)

H_{final}

$C_P(l)$

$\Delta H_{m \text{ (melting)}}$

Heat (enthalpy)

A(s)

$C_P(s)$

H_{initial}

process

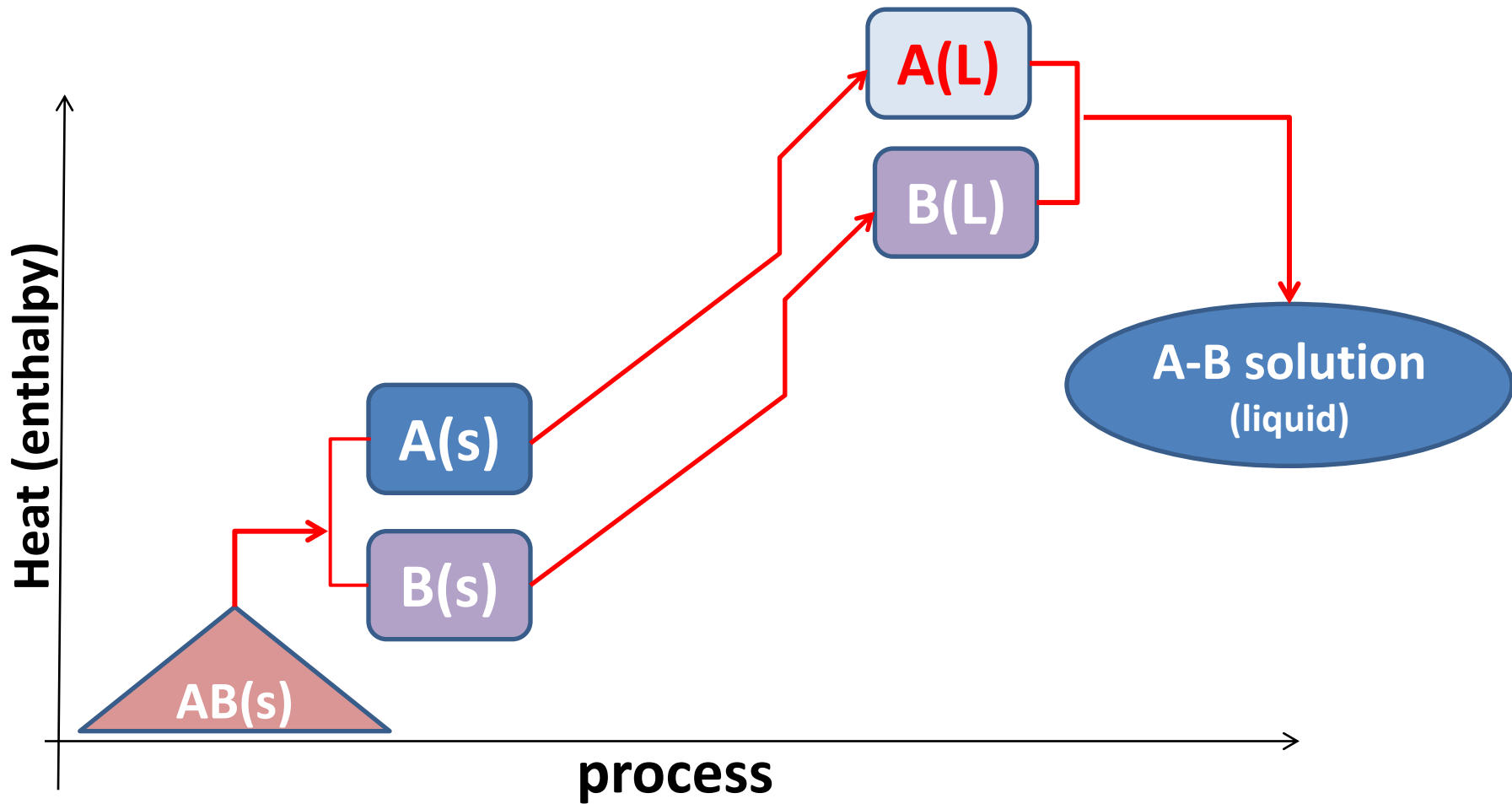# Heat evolution calculation

ΔH_f = heat of formation (or reaction)
from A(s) + B(s) to AB(s)
(typically negative value)

Heat (enthalpy)

A(s)

B(s)

ΔH_f

AB(s)

Negative ΔH means "generation of heat"

process
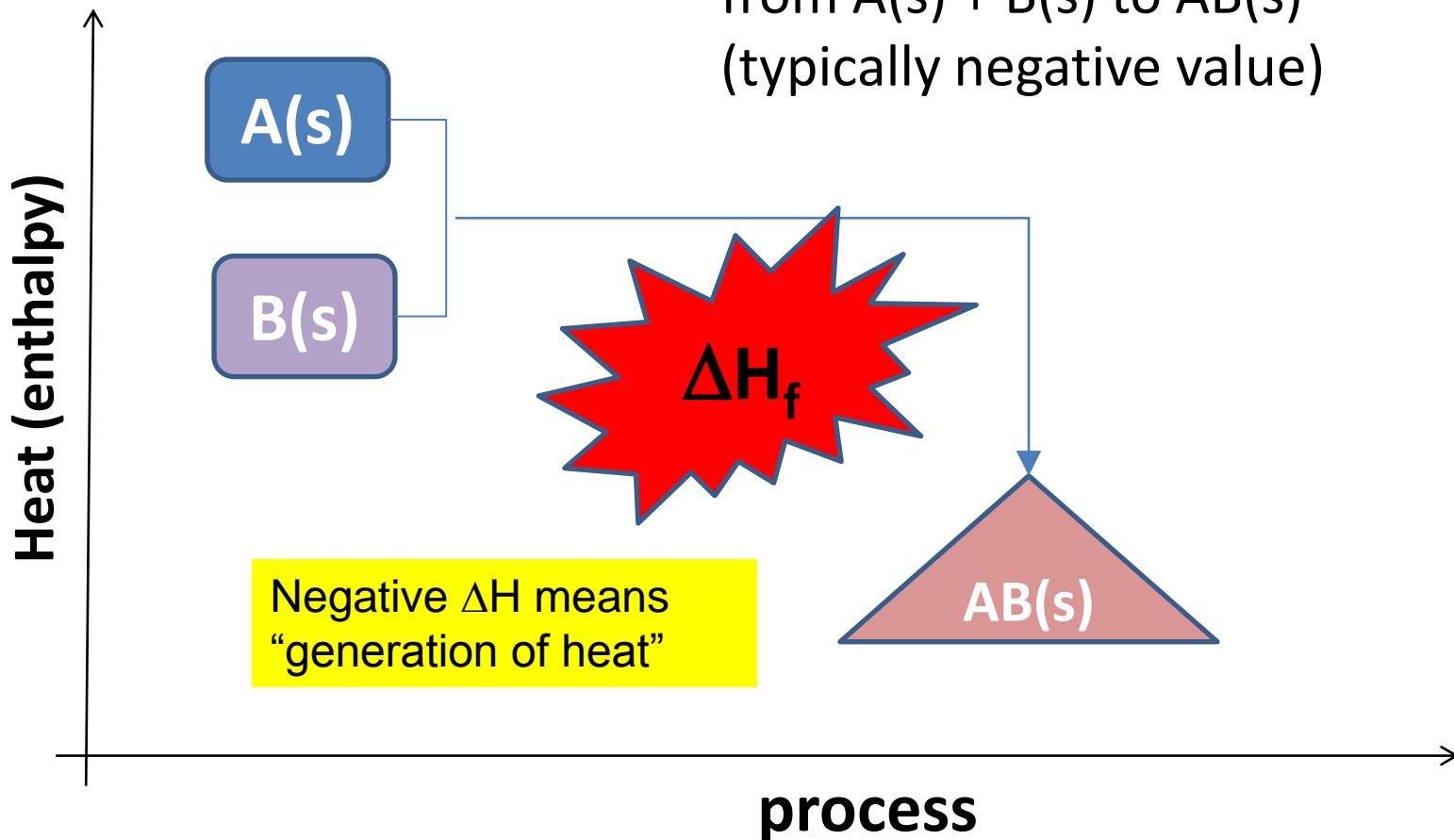
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Heat evolution calculation

In FactSage, the $H_{initial}$ and H_{final} are directly calculated because the H of each phase is calculated from the thermodynamic equations (database) of each solid or liquid phase. **It is important to select proper initial and final materials states and temperatures**

Heat evolution calculation

- Many industrial processes require mass and heat balance calculations. FactSage can provide a very easy way to do such calculations. For example, the following calculation would take several hours or days (or more) manually, but it takes less than 1 minute with the FactSage Equilib module.

$CaCO_3$ (25°C)

Fe-C ingot (500°C)

+

Fe-Mn-Si melt (1600°C)

Heat loss

Final products temperature pressure