



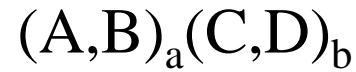
**ROYAL INSTITUTE  
OF TECHNOLOGY**

# CT Chapter 2

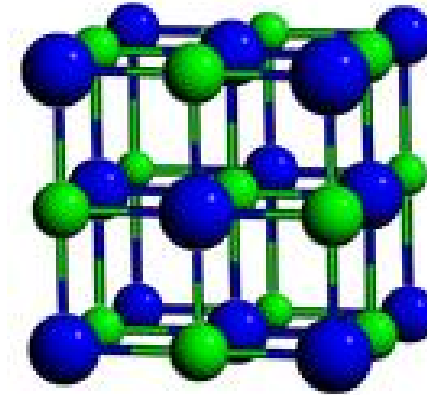
## Solution models

## 2.1 Constitution and constituents

sublattices  
constitution



stoichiometric coefficients



constituents (e.g. A and B on sublattice 1)

site fractions  $y_j$  ( $y_A + y_B = 1$  and  $y_C + y_D = 1$ )

associates (e.g. AB,  $A_2B$ )

species (e.g. A, B, AB,  $A^{+2}$ )

## 2.2 Ideal solutions and related non-ideal solutions

**Substitutional solution** = all components can substitute for each other

Physical mixing of the components contributes to the molar entropy by  $-R \sum x_i \ln x_i$  if the mixing is random (and with  $-TS = +RT \sum x_i \ln x_i$  to the molar Gibbs energy).

Chemical potential is given by  $\mu_i = {}^oG_i + RT \ln x_i$  which is the **ideal solution model**

${}^oG_i$  is the molar Gibbs energy of pure  $i$  in the same solution phase at current  $P$  &  $T$  and is sometimes called the **end-members** of the solution.

## 2.2 Ideal solutions and related non-ideal solutions

### Binary solution

The molar Gibbs energy of the solution

$$G_m = \sum x_i \mu_i = \sum x_i {}^\circ G_i + RT \sum x_i \ln x_i$$

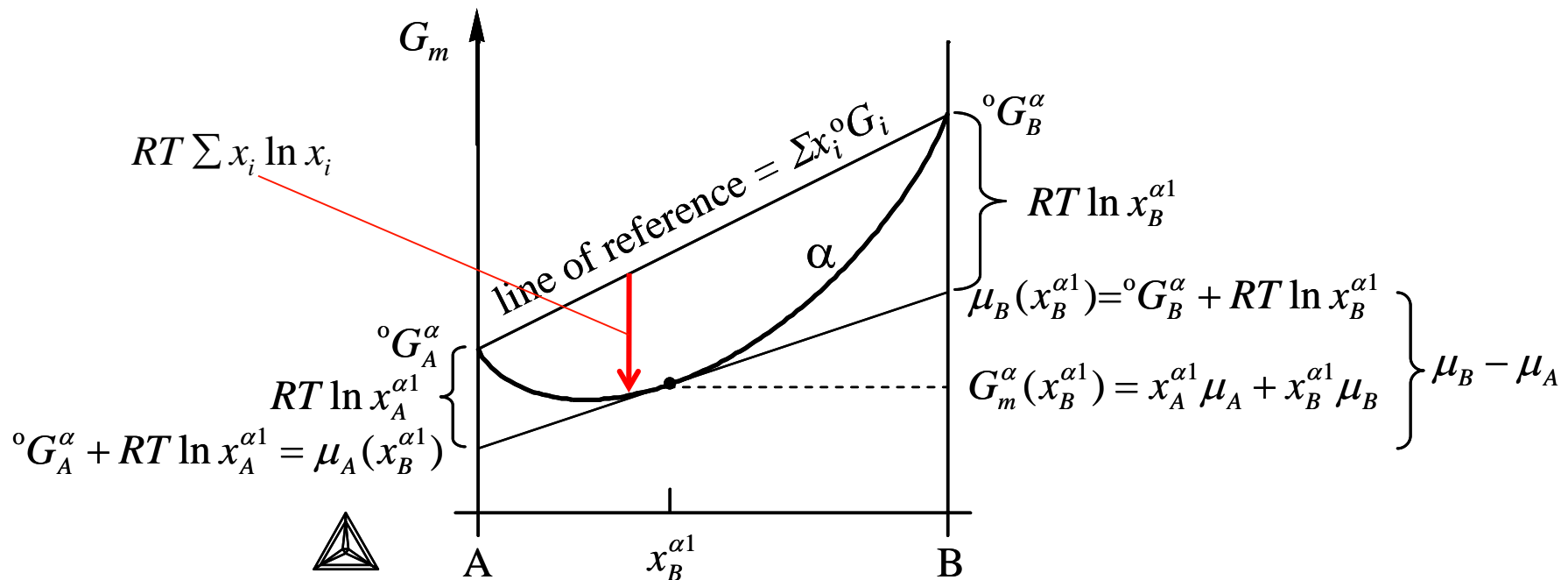


FIG. 2.1

## 2.2 Ideal solutions and related non-ideal solutions

### Ternary solution

The plane of reference is given by  $\sum x_i {}^oG_i$

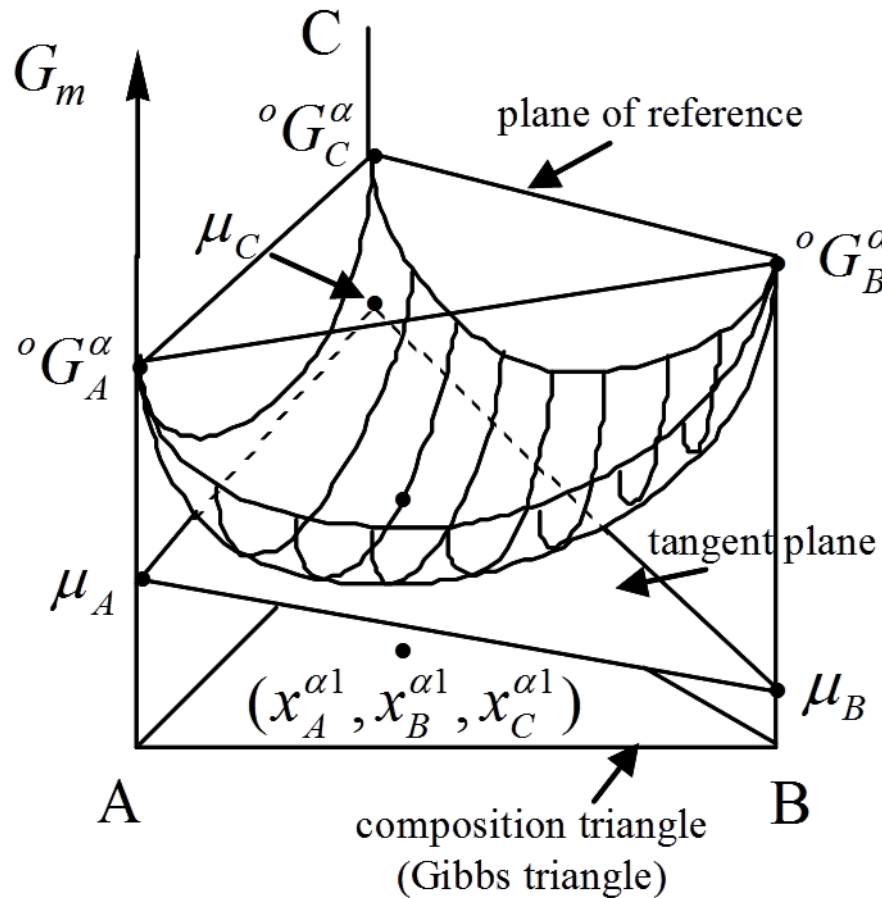


FIG. 2.2

## 2.2 Ideal solutions and related non-ideal solutions

### Deviation from ideal behaviour

A so-called **excess term**,  ${}^E G_m$ , is added to the molar Gibbs energy to model deviation from ideality.

${}^E G_m$  depends on the composition but must be zero at the pure elements (or end-members of the solution)

$$G_m^\alpha = \sum x_i^\alpha \mu_i = \sum x_i^\alpha {}^o G_i^\alpha + RT \sum x_i^\alpha \ln x_i^\alpha + {}^E G_m^\alpha$$

$$\mu_i^\alpha = {}^o G_i^\alpha + RT \ln x_i^\alpha + {}^E G_i^\alpha$$



partial excess Gibbs energy

## 2.3 Chemical activity and activity coefficient

### Chemical activity

Replace  $x_B$  in the ideal solution with activity, it is defined by its relation to chemical potential:

$$\mu_B = {}^oG_B + RT \ln a_B$$

If  ${}^oG_B$  is chosen as pure B for the same phase then the solution is ideal if  $a_B = x_B$

## 2.3 Chemical activity and activity coefficient

### Activity coefficient

For real solutions one may introduce an activity coefficient  $a_B = f_B x_B$ .  $f_B$  usually varies with composition.

Comparing with the excess term we get

$$\mu_B = {}^oG_B^\alpha + RT \ln a_B^\alpha =$$

$${}^oG_B^\alpha + RT \ln f_B^\alpha + RT \ln x_B^\alpha = {}^oG_B^\alpha + RT \ln x_B^\alpha + {}^E G_B^\alpha$$

and

$$RT \ln f_B = {}^E G_B^\alpha \quad \text{i.e.} \quad f_B \equiv \exp({}^E G_B^\alpha / RT)$$



## 2.3 Chemical activity and activity coefficient

### Change of reference state and lattice stability

Essential to use common reference for chemical potentials. Changing from a local reference state to a global e.g. SER we get:

$$\Delta^{ref} G_m^\alpha \equiv G_m^\alpha - \sum x_i^\alpha G_i^{ref} = \Delta G_m^\alpha + \sum x_i^\alpha ({}^o G_i^{local} - G_i^{ref})$$

Comparing the activity of B in two different solution phases, the reference is usually  ${}^o G_B^\alpha$  and  ${}^o G_B^\beta$ . The common reference is usually taken as the most stable state, say  $\alpha$ .

The difference  ${}^o G_B^\alpha - {}^o G_B^\beta$  is the so called **lattice stability**.

## 2.4 Excess Gibbs energy

The simplest approach for the excess Gibbs energy term for a binary system is

$${}^E G_m^\alpha = L x_A^\alpha x_B^\alpha$$

and if  $L$  is constant the solution is called **regular**.

A common polynomial for the excess term is the Redlich-Kister polynomial

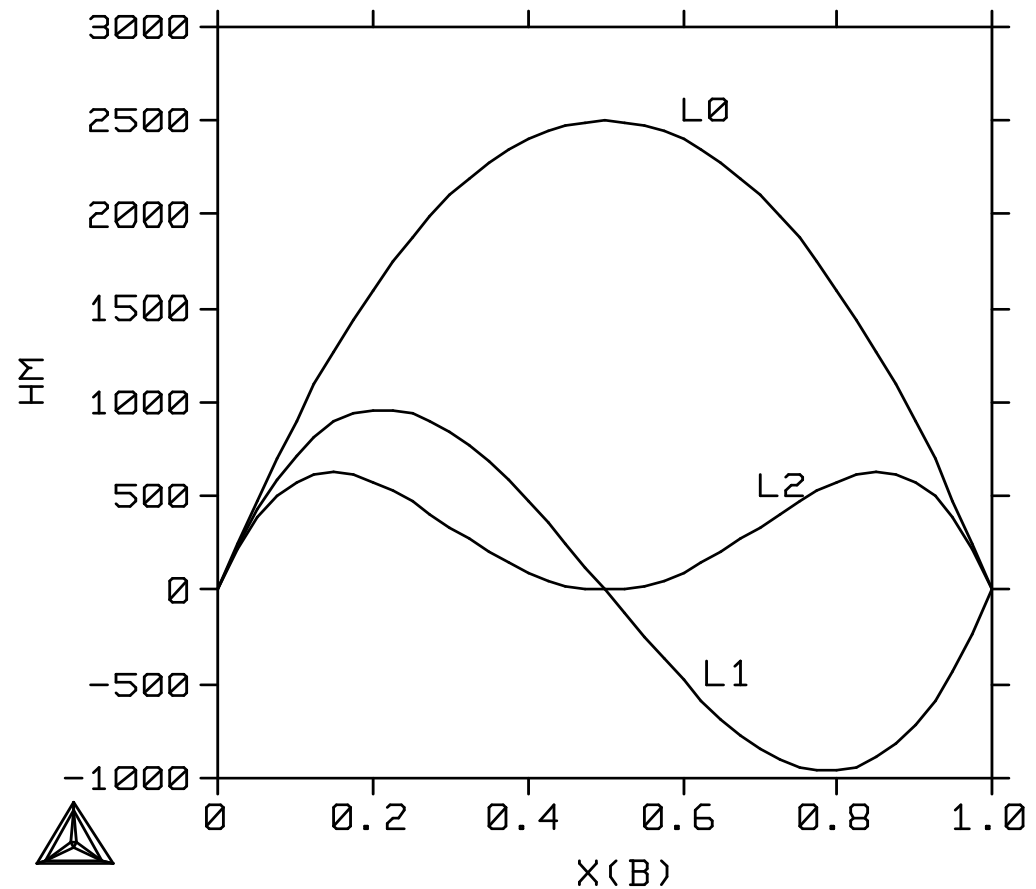
$$L = {}^0L + (x_A^\alpha - x_B^\alpha) {}^1L + (x_A^\alpha - x_B^\alpha)^2 {}^2L..$$

Other types of polynomials are possible but all are identical in the binary case. However, they will differ in ternary extrapolations and therefore the most symmetrical is preferred

## 2.4 Excess Gibbs energy

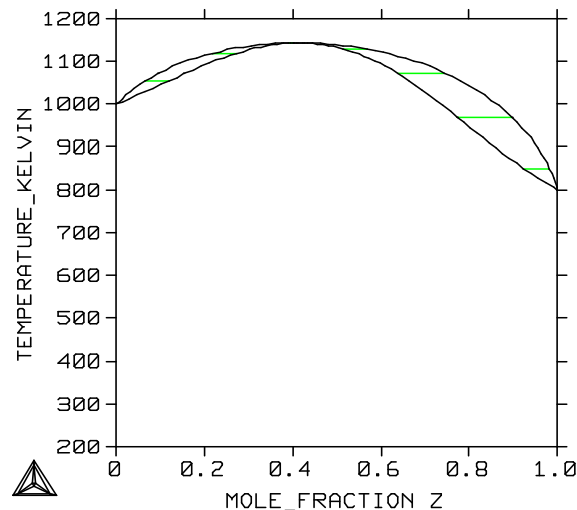
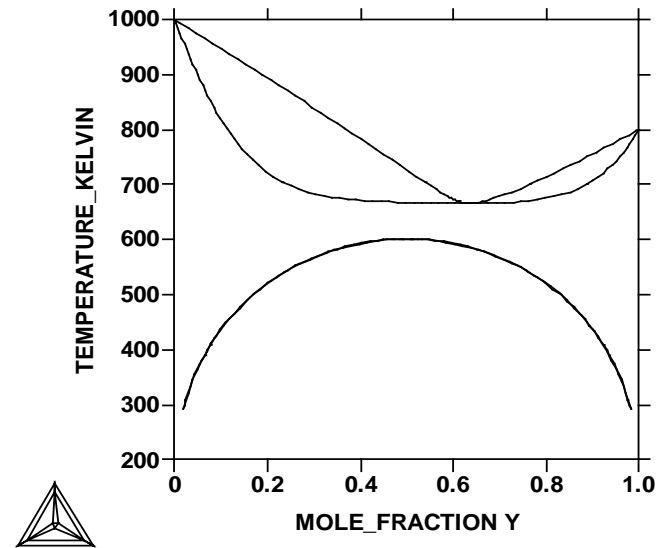
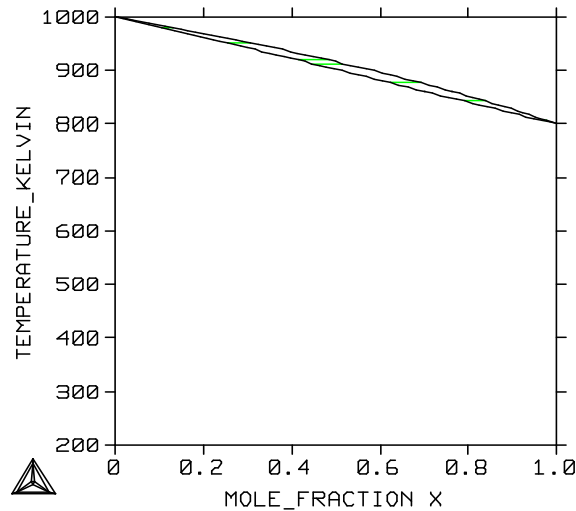
### Redlich-Kister polynomials

The contribution to the excess enthalpy as a function of composition for the first three coefficients of the R-K series, all with the same value, 10000 J/mol.



## 2.4 Excess Gibbs energy

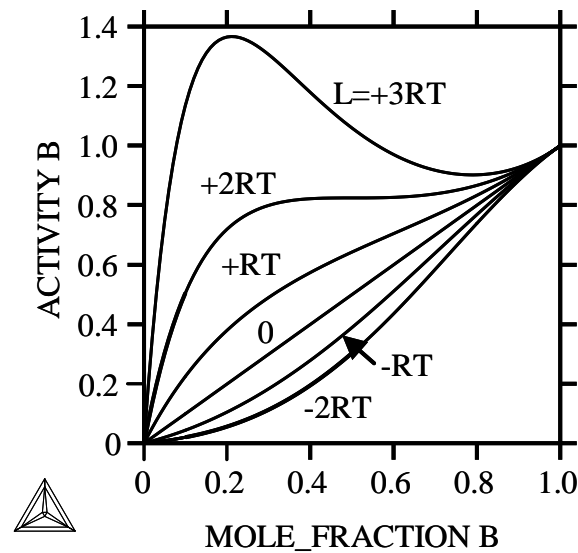
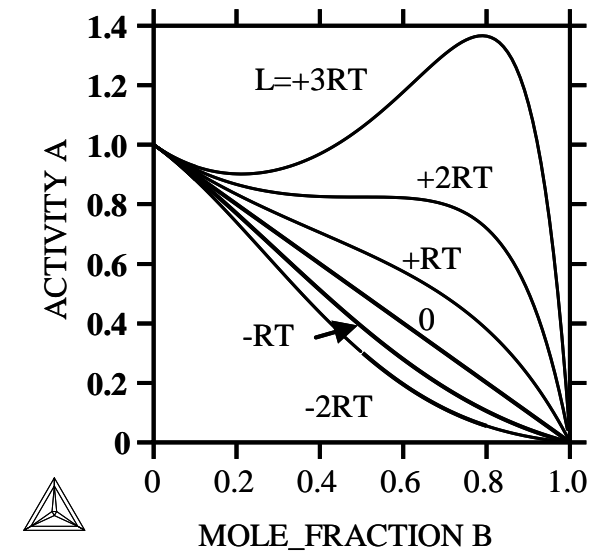
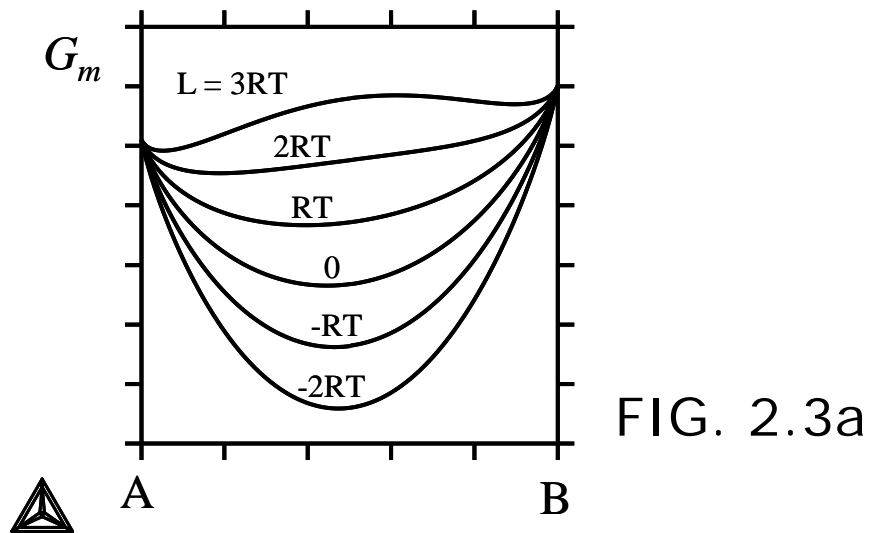
### Example: Effect of Excess term on the phase diagram



Ideal interaction in the liquid and the following interaction in the solid:

0 (top left), +10000 J/mol (above) and -10000 J/mol (left)

## 2.4 Excess Gibbs energy



## 2.4 Excess Gibbs energy

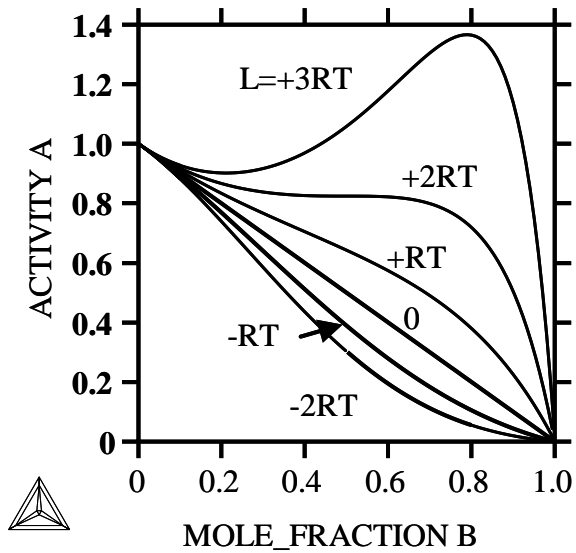


FIG. 2.6

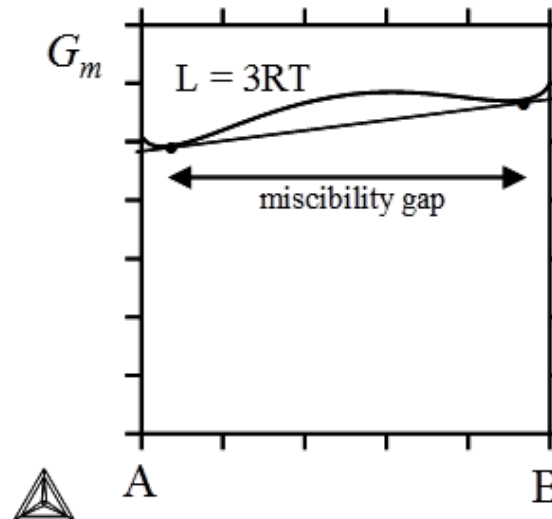


FIG. 2.8

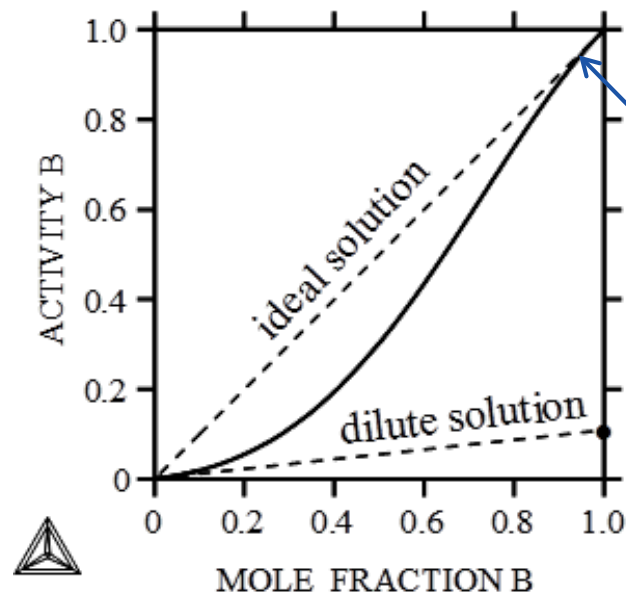
## 2.5 Dilute solutions

### Raoult's law

Let us consider a particular  $\alpha$  solution that behaves as a regular solution and has a negative regular solution parameter. For high B content  $a_B^\alpha - x_B^\alpha$  and we get

$$\mu_B \cong {}^o G_B^\alpha + RT \ln x_B^\alpha + 0$$

$$a_B^\alpha = x_B^\alpha f_B^\alpha \cong x_B^\alpha e^0 = x_B^\alpha$$



Raoult's law

FIG. 2.5

## 2.5 Dilute solutions

### Henry's law

For low B content we get

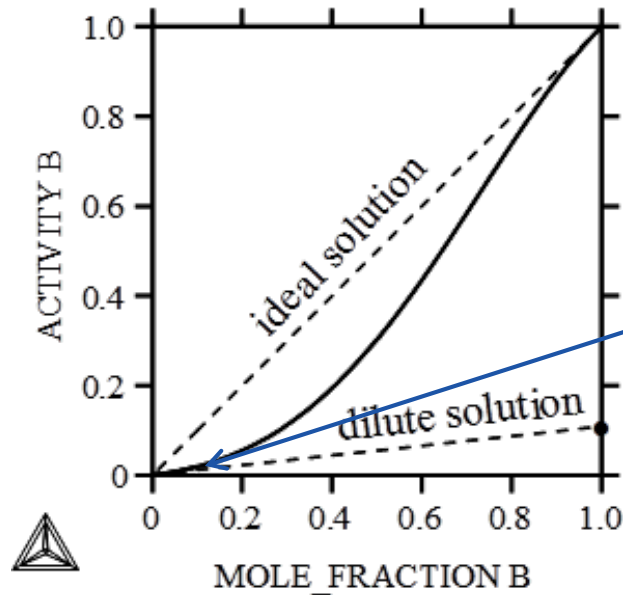
$$x_B^\alpha \rightarrow 0 \quad x_A^\alpha \rightarrow 1$$

$$\mu_B - {}^oG_B^\alpha = RT \ln a_B^\alpha = RT \ln x_B^\alpha + {}^E G_B^\alpha$$

$$= RT \ln x_B^\alpha + RT \ln f_B^\alpha = RT \ln x_B^\alpha + L(x_A^\alpha)^2 \cong RT \ln x_B^\alpha + L$$



FIG. 2.5



At  $x_B^\alpha = 1$

$$\mu_B - {}^oG_B^\alpha = 0 + L = RT \ln a_B^\alpha$$

$$a_B^\alpha = \exp(L / RT)$$

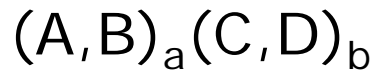
Henry's law

$$\leftarrow \exp[{}^E G_B(x_B \rightarrow 0) / RT] = \exp(L / RT)$$



## 2.6 Phases with sublattices

When lattice sites are not equivalent they are divided in different sublattices e.g.



End-members:  $A_aC_b$ ,  $A_aD_b$ ,  $B_aC_b$ ,  $B_aD_b$

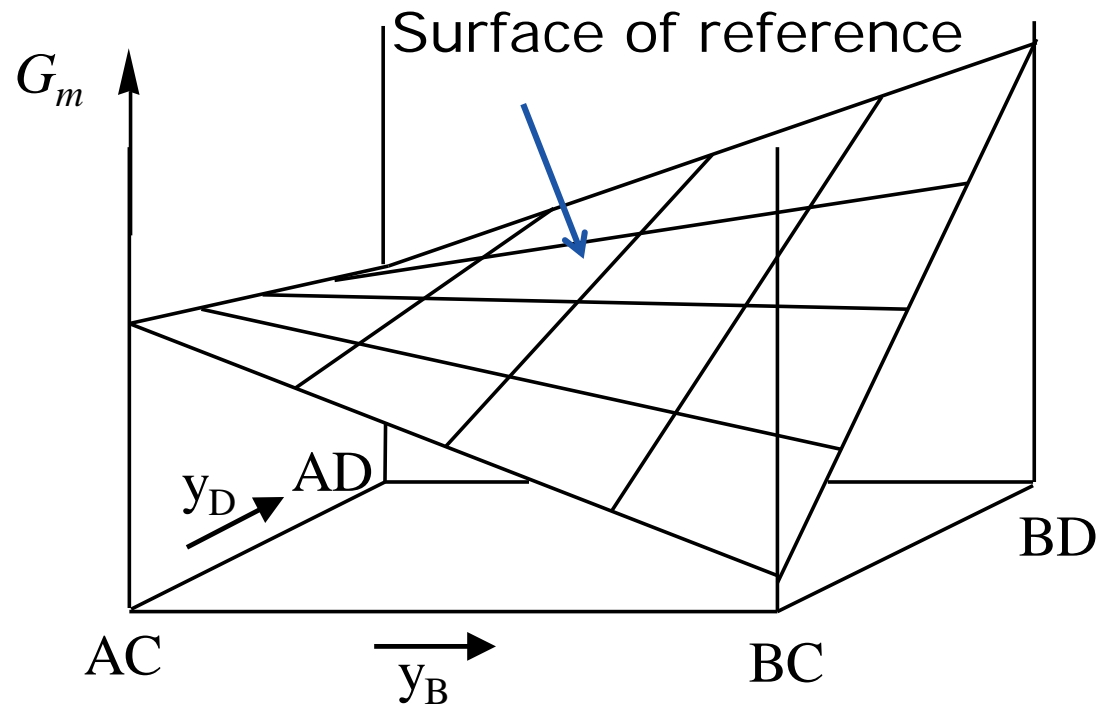


FIG. 2.6

## 2.6 Phases with sublattices

Site fractions,  $y_i$ , are used to express the Gibbs energy for one mole of formula units

$$G_m = \sum \sum y_i' y_j'' G_{i_a j_b} + aRT \sum y_i' \ln y_i' + bRT \sum y_j'' \ln y_j''$$

they are related to the mole fractions as

$$y_C'' = \frac{N_C}{N_C + N_D} = \frac{(a/b)N_C}{N_A + N_B} = \frac{(a/b)x_C}{x_A + x_B}$$

with the  $(A,B)_a(C,D)_b$  model as example

### Ideal Compound Energy Model



since ideal mixing on each sublattice and no excess term

## 2.6 Phases with sublattices

### Chemical potential when stoichiometric constraint

Chemical potential of the elements cannot be defined for such a phase alone. Instead the chemical potential of the end-member can be obtained, e.g.

$$\mu_{A_a C_b} = {}^o G_{A_a C_b} + y_B' y_D'' \Delta^o G_{A_a C_b + B_a D_b} + aRT \ln y_A' + bRT \ln y_C''$$

where  $\Delta^o G_{A_a C_b + B_a D_b} = {}^o G_{A_a D_b} + {}^o G_{B_a C_b} - {}^o G_{A_a C_b} - {}^o G_{B_a D_b}$

and is called the **standard Gibbs energy of reaction** of the reciprocal reaction  $A_a C_b + B_a D_b \rightarrow A_a D_b + B_a C_b$

One can show that  $\mu_{A_a C_b} + \mu_{B_a D_b} = \mu_{A_a D_b} + \mu_{B_a C_b}$

(Obvious!)

## 2.6 Phases with sublattices

### Stoichiometric constraint

Reciprocal system and due to Gibbs-Duhem it behaves like a ternary!

Only three of the chemical potentials of the four elements are independent in a reciprocal system

$$a\mu_A = \mu_{A_aD_b} - b\mu_D$$

$$a\mu_B = \mu_{B_aD_b} - b\mu_D$$

$$b\mu_C = \mu_{A_aC_b} - \mu_{A_aD_b} + b\mu_D$$

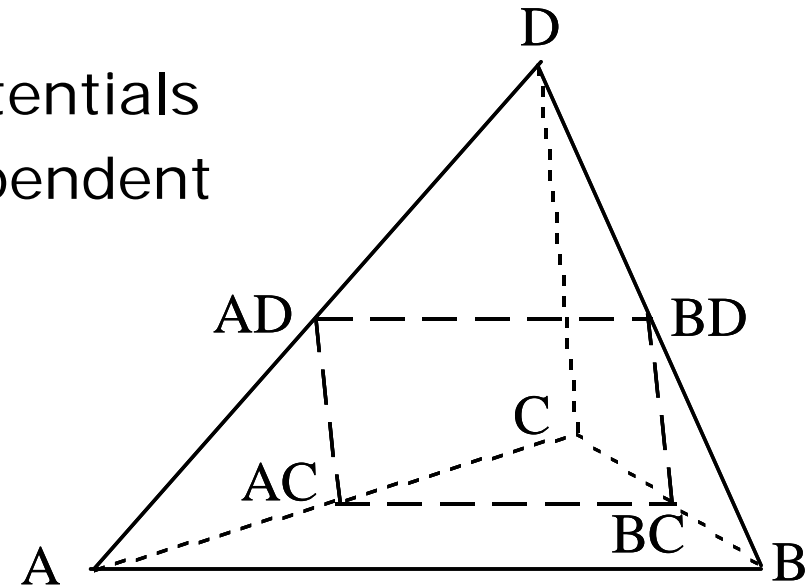


FIG. 2.4

where  $\mu_D$  is regarded as reference (e.g. oxygen)

## 2.6 Phases with sublattices

### Stoichiometric constraint

If we instead have e.g.  $(A,B)_a(A,C,D)_b$

i.e.

if (at least) one element can dissolve in all sublattices  
then the chemical potentials of all elements may be  
evaluated since  $\mu_{A:A}$  is equal to the chemical potential  
of A with  ${}^oG_{A:A}$  as reference, related to  $G_A^{ref}$  if  
 ${}^oG_{A:A} - (a+b)G_A^{ref}$  is known.

## 2.7 Interstitial solutions

Let us regard D as Va and C as interstitials:



The end-members  $A_aD_b$  and  $B_bD_b$  would then be pure A and B!

**Example:** bcc  $(Fe,Cr)_1(C,Va)_3$  where  $Fe_1Va_3$  and  $Cr_1Va_3$  would be pure bcc-Fe and bcc-Cr respectively

## 2.8 The ideal gas model

For a monatomic species the ideal gas model predicts:

$$\mu_J = K_J + RT \ln P_J$$

$P_J$  is regarded as the partial pressure of species  $J$  but is actually defined as  $y_J P$  where  $y_J$  is the fraction of  $J$  relative all other species in the gas and  $P$  is the total pressure. We may write:

$$\mu_J = K_J + RT \ln P + RT \ln y_J$$

## 2.8 The ideal gas model

$K_j + RT \ln P$  depends strongly on pressure compared to  ${}^{\circ}G_j$  for a condensed phase. For a gas species one usually defines the pure species at a  $P$  of 1 bar as the reference at the current  $T$  i.e. the **standard state**.

$$\mu_j = {}^{\circ}G_j(1\text{bar}, T) + RT \ln P_j$$

the **partial pressure must then be expressed in bar**. We usually omit 1 bar,  $T$  and write

$$\mu_j = {}^{\circ}G_j + RT \ln P_j$$

and  ${}^{\circ}$  for a gas then means that the species is in pure gaseous form at 1 bar and the current  $T$ .



## 2.8 The ideal gas model

For a diatomic gas species we get:  $\mu_{J_2} = {}^oG_{J_2} + RT \ln P_{J_2}$   
at equilibrium we have

$$\mu_{J_2} = 2\mu_J$$

and we can evaluate  $\mu_J = 0.5({}^oG_{J_2} + RT \ln P_{J_2})$

and also the equilibrium value of  $P_J$  from  $P_{J_2}$

$$P_J^2 = P_{J_2} \exp[({}^oG_{J_2} - 2{}^oG_J) / RT]$$

## 2.8 The ideal gas model

For the gaseous elements, H, N and O, the diatomic species is much more abundant than the monatomic species, i.e.  $H_2$ ,  $N_2$  and  $O_2$ , and in those cases these species are used as reference, i.e.  $0.5^\circ G_{J_2}$  is used as reference for species  $J$ .

In such cases  $P_{J_2}$  is the partial pressure in an imagined atmosphere **where  $J$  and  $J_2$  are in equilibrium.**

## 2.8 The ideal gas model

### Example – gas in database


GAS

CONSTITUENTS: O, O2, O3

$$G(\text{GAS}, \text{O}; 0) - H_{298}(1/2\_MOLE\_O2(\text{GAS}), \text{O}; 0) = +F13634T + R \cdot T \cdot \ln(1E-05 \cdot P)$$

$$G(\text{GAS}, \text{O}_2; 0) - 2 H_{298}(1/2\_MOLE\_O2(\text{GAS}), \text{O}; 0) = +F14003T + R \cdot T \cdot \ln(1E-05 \cdot P)$$

$$G(\text{GAS}, \text{O}_3; 0) - 3 H_{298}(1/2\_MOLE\_O2(\text{GAS}), \text{O}; 0) = +F14300T + R \cdot T \cdot \ln(1E-05 \cdot P)$$



$$P = 1 \text{ bar} = 1E5 \text{ Pa} \rightarrow \ln(1E-05 \cdot P) = 0$$

## 2.8 The ideal gas model

### Example – gas in database

SYMBOL	STATUS	VALUE / FUNCTION
4 F14003T	20000000	$298.15 < T < 900.00:$ $-6960.69252 - 51.1831473 * T - 22.25862 * T * \ln(T) - .01023867 * T^{**2} + 1.339947E-06 * T^{**3} - 76749.55 * T^{**(-1)}$ $900.00 < T < 3700.00:$ $-13136.0172 + 24.743296 * T - 33.55726 * T * \ln(T) - .0012348985 * T^{**2} + 1.66943333E-08 * T^{**3} + 539886 * T^{**(-1)}$ $3700.00 < T < 9600.00:$ $+14154.6461 - 51.4854586 * T - 24.47978 * T * \ln(T) - .002634759 * T^{**2} + 6.01544333E-08 * T^{**3} - 15120935 * T^{**(-1)}$ $9600.00 < T < 18500.00:$ $-314316.628 + 515.068037 * T - 87.56143 * T * \ln(T) + .0025787245 * T^{**2} - 1.878765E-08 * T^{**3} + 2.9052515E+08 * T^{**(-1)}$ $18500.00 < T < 20000.00:$ $-108797.175 + 288.483019 * T - 63.737 * T * \ln(T) + .0014375 * T^{**2} - 9E-09 * T^{**3} + .25153895 * T^{**(-1)}$

## 2.9 Vapour pressure

Even solid elements may have a vapour pressure, usually very small. The standard state for the gas would be based on the solid state at 1 bar and the current T.

The chemical potential of the monatomic species in the gas would be

$$\mu_M = {}^oG_M^{gas} + RT \ln P_M \pm G_M^{std} = G_M^{std} + \Delta_f {}^oG_M^{gas} + RT \ln P_M$$

$$P_M = \exp[(\mu_M - G_M^{std} - \Delta_f {}^oG_M^{gas}) / RT]$$

where  $\Delta_f {}^oG_M^{gas} = {}^oG_M^{gas} - G_M^{std}$

and similarly

$$P_{M_2} = \exp[(\mu_{M_2} - 2G_M^{std} - \Delta_f {}^oG_{M_2}^{gas}) / RT]$$

## 2.10 Thermal vacancies

Thermal vacancies are the empty sites in a solid metal. They are called "thermal" since they increase with T.

$(A, Va)_1$

The system is unary and the amount of Va is thus an internal variable

$$y_{Va}^{eq} = \exp\left[-\left({}^oG_{Va} + L_{AVa} y_A^2\right) / RT\right] \cong \exp\left[-E_{AVa} / RT\right]$$

Since the number of Va is so small we cannot distinguish experimentally between the two terms

## 2.11 Solutions with associates

One type of non-ideal solutions uses associates e.g. molecules to describe the excess term.

For A-B solutions with AB associates (in addition to A and B) we get *per mole of constituents*,

$$G_m(y_1, y_2 \dots) = y_A {}^oG_A + y_B {}^oG_B + y_{AB} {}^oG_{AB} + RT \sum y_i \ln y_i$$

which may be regarded as an ideal solution model for a solution with associates.

We use here site fractions or more correct **constituent fraction** even though there is only one sublattice

## 2.11 Solutions with associates

### Associate Model - Example Cd-Te

We have Cd, Te and also CdTe species (compare to a gas phase with molecules)

$$x_{Cd} = \frac{y_{Cd} + y_{CdTe}}{y_{Cd} + y_{Te} + 2y_{CdTe}}$$

$$x_{Te} = \frac{y_{Te} + y_{CdTe}}{y_{Cd} + y_{Te} + 2y_{CdTe}}$$

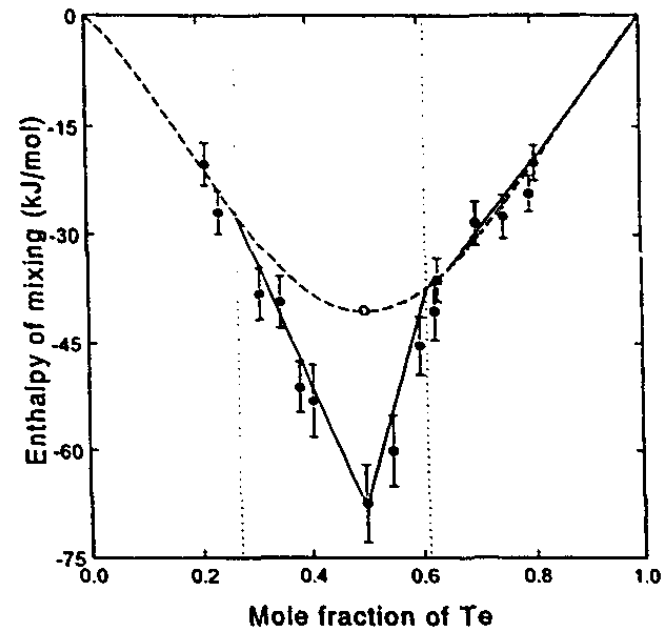


Fig. 4. Molar integral enthalpy of formation of the Cd-Te alloys referring



## 2.11 Solutions with associates

We treat the  $y_j$ :s as  $x_j$ :s which is allowed for frozen-in states or at internal equilibrium:

$$\mu_j = G_m + \frac{\partial G_m}{\partial y_j} - \sum y_i \frac{\partial G_m}{\partial y_i} \cong {}^o G_j + RT \ln y_j$$

At internal equilibrium using  $\mu_{AB} = \mu_A + \mu_B$  and the above eqn. we get

$$\mu_{AB} = {}^o G_{AB} + RT \ln y_{AB}^{eq} = {}^o G_A + RT \ln y_A^{eq} + {}^o G_B + RT \ln y_B^{eq}$$

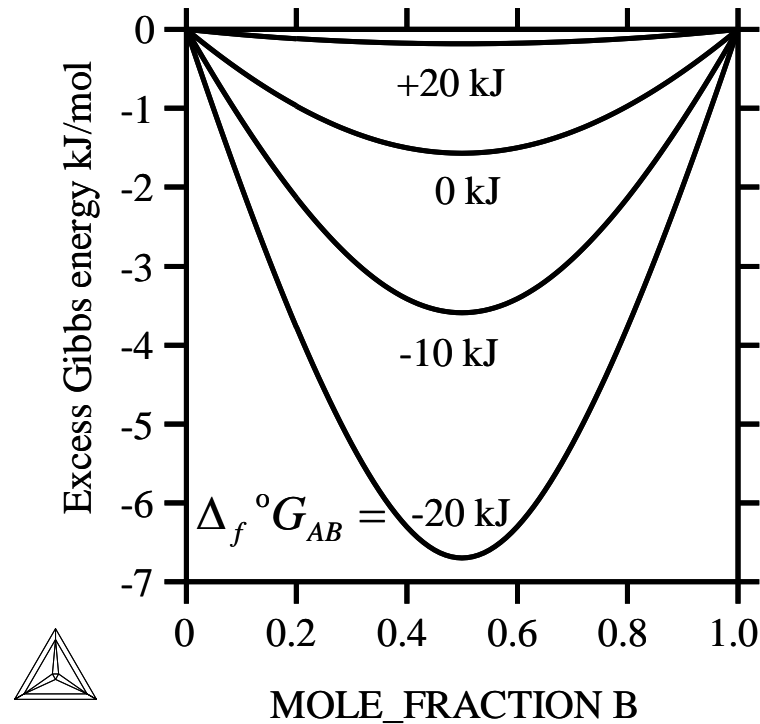
$$\text{and } \frac{y_{AB}^{eq}}{y_A^{eq} y_B^{eq}} = \exp(-\Delta {}^o G_{AB} / RT) = K$$

$$\text{where } \Delta {}^o G_{AB} = {}^o G_{AB} - {}^o G_A - {}^o G_B$$

An example of the **law of mass action** and  $K$  is a temperature dependent coefficient, often called **equilibrium constant**

## 2.11 Solutions with associates

### Excess Gibbs energy due to associates



$${}^E G_m = G_m (\text{associate model}) - G_m (\text{ideal solution model})$$