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CT Chapter 1
Basic Thermodynamics

1.1 First law of thermodynamics

States that energy can be neither created nor destroyed

Concerns *changes* in the internal energy – not the absolute value

If the system receives an amount of heat dQ and if an amount of work dW is performed on the system, then the internal energy has increased by $dQ+dW$ i.e. $dU=dQ+dW$

We consider only pressure-volume work, i.e. $dW=-PdV$

$$\boxed{dU = dQ - PdV}$$

1.1 First law of thermodynamics

$dU = dQ - PdV$

Under constant volume (i.e. $dV=0$): $\mathbf{dQ = dU}$

Under constant pressure (rewrite):

$$dQ = dU + PdV$$

$$dQ = dU + PdV + VdP - VdP = dU + d(PV) - VdP$$

$$dQ = d(U + PV) - VdP = dH$$

i.e. $\mathbf{dQ=dH}$

where we have introduced **enthalpy**, $H=U+PV$

In thermodynamics we cannot distinguish between heat and work
- they are just different ways to transfer energy

1.2 Second law of thermodynamics

Introduces the quantity entropy, *S*. It requires that a process or reaction occurring spontaneously inside a system must increase *S* of the system if there is no heat exchange with the surroundings.

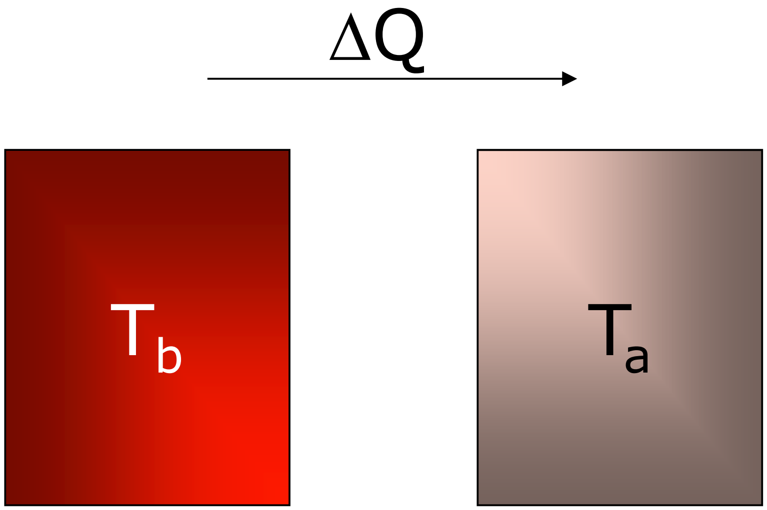
$d_{ip}S > 0$ for spontaneous **internal processes**

An internal process will be infinitely slow at $d_{ip}S = 0$ and may be regarded as a reversible process

A heat exchange itself will change the entropy by dQ/T

Total change of *S*: $dS = \frac{dQ}{T} + d_{ip}S > \frac{dQ}{T}$

1.2 Second law of thermodynamics



Heat only goes spontaneously from high to low temperature

$$\Delta S_{tot} = -\frac{\Delta Q}{T_b} + \frac{\Delta Q}{T_a} = \frac{\Delta Q(T_b - T_a)}{T_a T_b} > 0 \text{ where } T_b > T_a$$

Entropy produced!

1.3 Combined law

1st law $dU = dQ - PdV$

2nd law rewritten $TdS = dQ + Td_{ip}S$

Combined law $TdS = dU + PdV + Td_{ip}S$

Rewrite $-Td_{ip}S = dU + PdV - TdS = d(U + PV - ST) - VdP + SdT$

Introduce $G = U + PV - TS$

Rewrite $dG = VdP - SdT - Td_{ip}S < VdP - SdT$

At constant *P* and *T*: $dG = -Td_{ip}S < 0$

since $d_{ip}S$ always positive

or $-dG = Td_{ip}S > 0$

1.4 Driving force and dissipation

Equilibrium condition

$$(\partial G/\partial\xi)_{P,T}=0$$

$G=G(P,T,\xi)$ (ξ is the extent of the internal process)

The slope, the rate of decrease of *G* may be regarded as the **driving force**, ***D***.

$$D=-(\partial G/\partial\xi)_{T,P}=Td_{ip}S/d\xi$$

Identify *D* with $Td_{ip}S/d\xi$ i.e. $Td_{ip}S=Dd\xi$ in previous eqs.

$$\boxed{dG=VdP-SdT-Dd\xi}$$

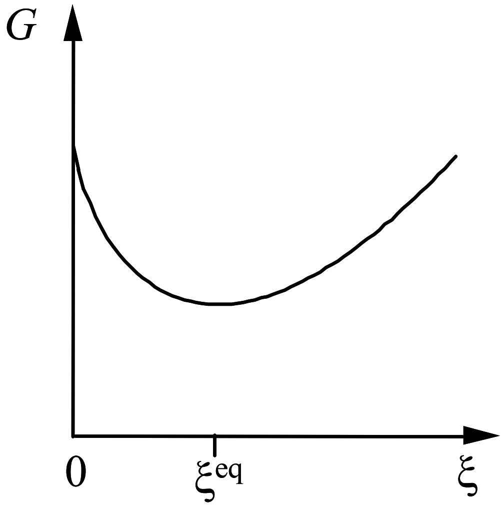


FIG.1.1.

1.4 Driving force and dissipation

Equilibrium condition

$$D = -(\partial G / \partial \xi)_{T,P} = T d_{ip} S / d\xi$$

For a phase transformation between two states, α –> β, one obtains by integration

$D = -\Delta G_m$ where $\Delta G_m = G_m^\beta - G_m^\alpha$

1.4 Driving force and dissipation

Internal process

What is an internal process?

Everything that happens spontaneously inside a system as the system approaches equilibrium, i.e. processes that are not ”directly controllable”.

Example: solidification of a supercooled liquid.

1.4 Driving force and dissipation

Internal process – Example 1

Imagine for instance isothermal solidification of a pure supercooled liquid metal. The only thing that changes during the process is the amounts of solid and liquid metal. Let ξ denote the number of moles of solid metal, *n(solid).*

External variable = can be directly controlled during an experiment
Internal variable = property of the system that adjusts as equilibrium is approached and cannot be directly controlled from the outside

1.4 Driving force and dissipation

Internal process – Example 1

The combined law: $\boxed{dG = VdP - SdT - Dd\xi}$

During the solidification *P* and *T* are constant

and we get $D = -dG/d\xi = -\Delta G/\Delta\xi = -\Delta G/\Delta N^{sol}$

The process:

$liquid \rightarrow solid \quad \Delta G = G^{sol} - G^{liq}$

and the **driving force**:

$\mathbf{D} = (G^{liq} - G^{sol})/\Delta N^{sol} = G_m^{liq} - G_m^{sol}$

1.4 Driving force and dissipation

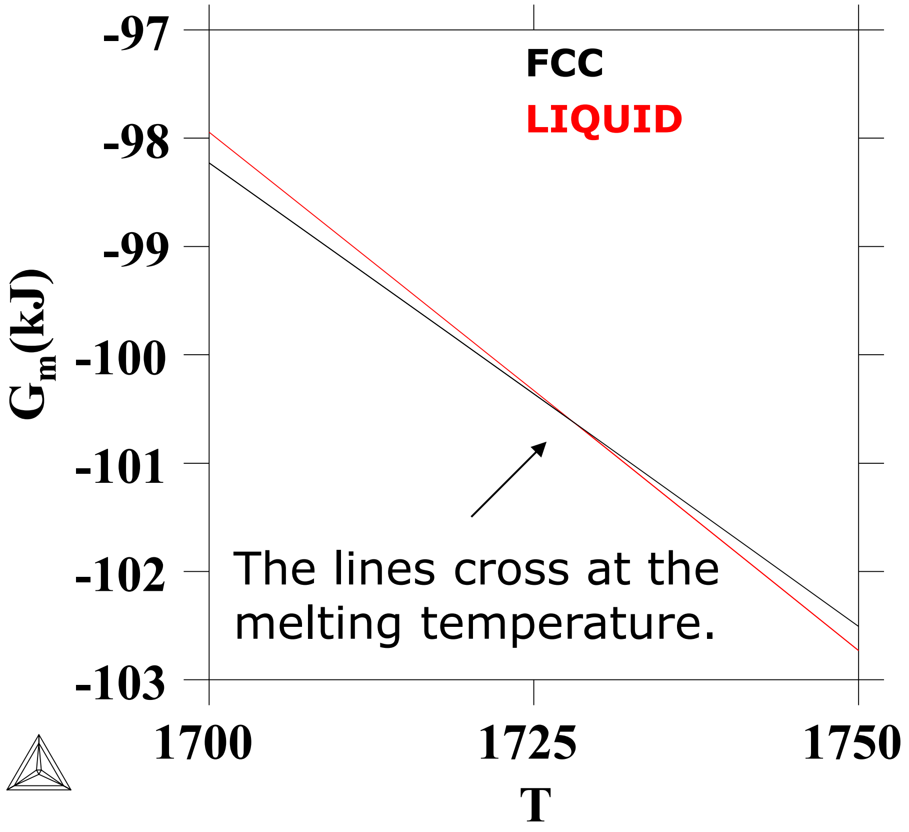
Internal process – Example 1

Here an example where G_m for solid and liquid Ni have been calculated.

Solidification: liq → fcc

$$D = G_m^{liq} - G_m^{fcc}$$

i.e. positive below T_m and negative above

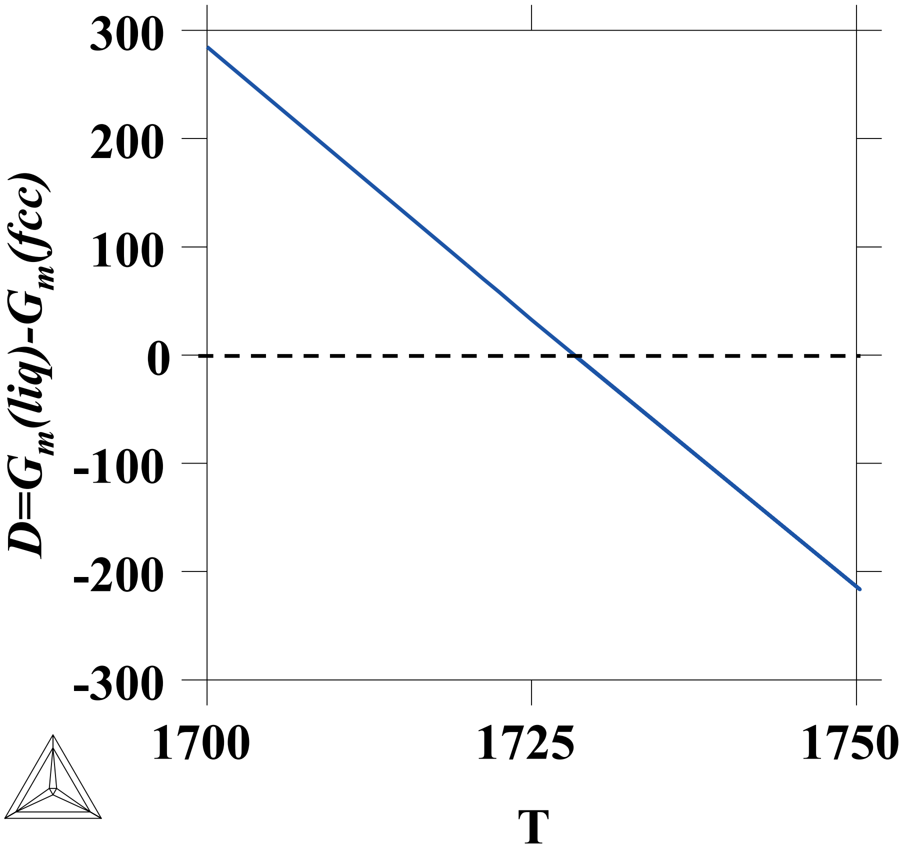


The lines cross at the melting temperature.

1.4 Driving force and dissipation

Internal process – Example 1

Here same calculation but with D on the y-axis.

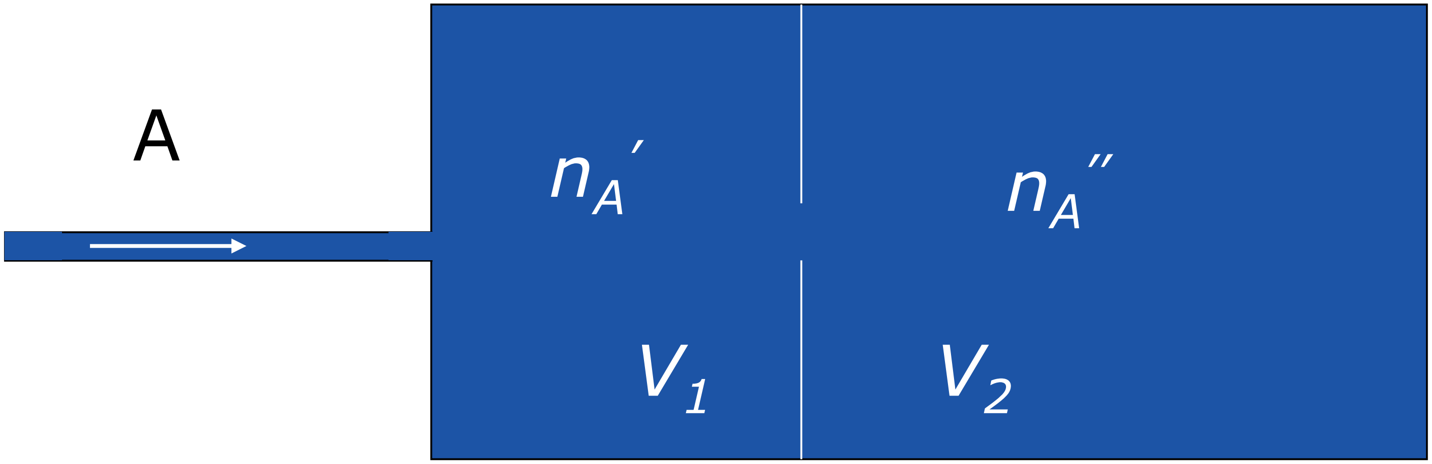


1.4 Driving force and dissipation

Internal process – Example 2

T, V_1 and V_2 are fixed.

Suppose we blow in n_A moles of component A, what are then the equilibrium content of $n_A{}'$ and $n_A{}''$?



External variables are T, V_1, V_2 and n_A and the internal variables are $n_A{}'$ and $n_A{}''$.

1.4 Driving force and dissipation

Internal process – Example 2

The internal variable n_A' and n_A'' are not independent:

$n_A = n_A' + n_A''$

We introduce: $\xi = n_A'$ and get $n_A'' = n_A - \xi$

At equilibrium: $P' = P''$

The gas law, $PV = nRT$, gives

$$P' = \xi RT/V_1 = P'' = (n_A - \xi)RT/V_2$$

$$\xi/V_1 = (n_A - \xi)/V_2 \rightarrow \xi = n_A/(1+V_2/V_1)$$

1.4 Driving force and dissipation

Reversible process and frozen process

$$dG = VdP - SdT - Dd\xi$$

An internal process occurring under D=0 would not produce any entropy or dissipate any Gibbs energy and it would be infinitely slow (sometimes called a reversible process – does not exist)

For a frozen-in process $d\xi$ = 0

In both cases: $dG = VdP - SdT$

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1.5 Variable composition

Consider systems where also the content may change by exchange of matter with the surroundings, then the combined law becomes:

$$dG = VdP - SdT + \sum \mu_i dN_i - Dd\xi$$

$$V = (\partial G / \partial P)_{T,N_i,\xi} \qquad S = -(\partial G / \partial T)_{P,N_i,\xi}$$

$$\boxed{\mu_k = (\partial G / \partial N_k)_{P,T,N_j,\xi}} \qquad D = -(\partial G / \partial \xi)_{P,T,N_i}$$

If no internal entropy production, we get

$$dG = VdP - SdT + \sum \mu_i dN_i$$

and if P, T and N_j are constant

$$\mu_k = (\partial G / \partial N_k)_{P,T,N_j}$$

1.5 Variable composition

External variables and potentials

μ_k is the **partial Gibbs energy** of component k

P, T, μ_k, V, S, N_i are all **external variables**

P, T, μ_k are also **potentials** as they must have uniform values in the whole system at equilibrium

Specifically, μ_k is the **chemical potential** of k

1.5 Variable composition

Chemical potential

Using $x_k \equiv N_k / \Sigma N_i = N_k / N$ we can get

$$dG = VdP - SdT + (\Sigma \mu_i x_i)dN - Dd\xi$$

Consider a large amount of homogenous matter with uniform *P*, *T* and composition and let the system be a very small volume of it. Extend its limits gradually i.e. integrate

$$G = (\Sigma \mu_i x_i)N = \Sigma \mu_i N_i$$

the molar Gibbs energy is defined as

$$G_m \equiv G / N = \Sigma \mu_i x_i$$

1.5 Variable Composition

Definition of chemical potential illustrated

Definition: $\boxed{\mu_k = (\partial G / \partial N_k)_{P,T,N_j}}$

Binary case: $\mu_B = (\partial G / \partial N_B)_{P,T,N_A}$

$$G_B \equiv \mu_B = G_m + x_A \frac{dG_m}{dx_B}$$

$$G_A \equiv \mu_A = G_m - x_B \frac{dG_m}{dx_B}$$

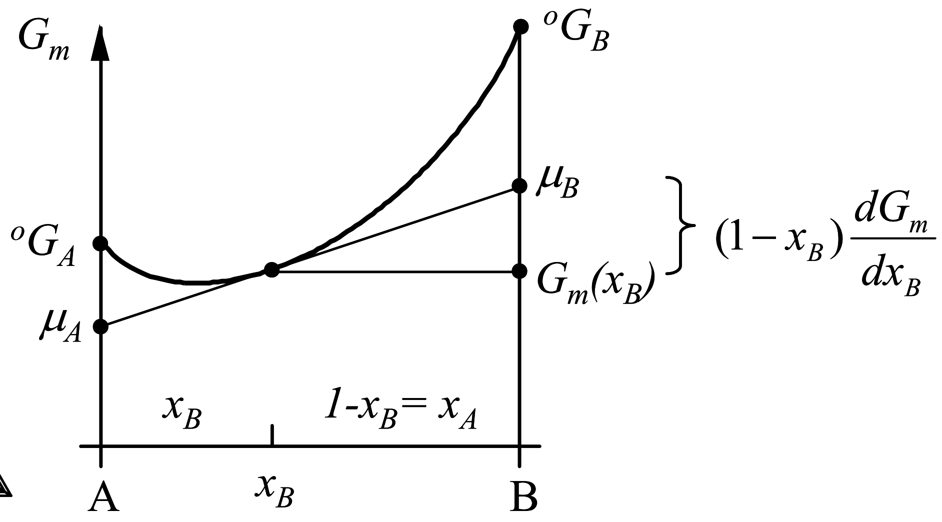


FIG.1.2.

1.6 Expressing chemical potentials through the molar Gibbs energy

Binary system

We may derive the following equation for the slope of the tangent in Fig.1.2:

$$\mu_B - \mu_A =$$

$$G_m + x_A\left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right) - G_m - x_B\left(\frac{\partial G_m}{\partial x_A} - \frac{\partial G_m}{\partial x_B}\right) =$$

$$\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A} = \frac{dG_m}{dx_B}$$

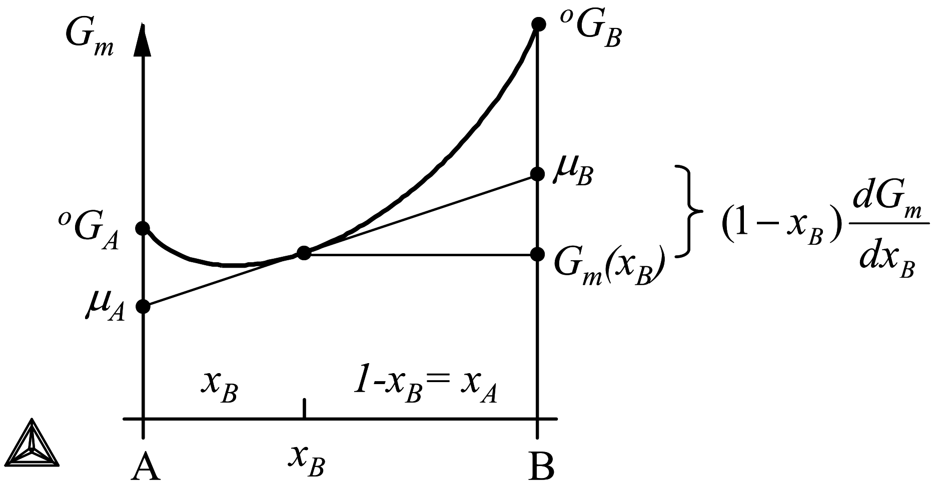


FIG.1.2

1.6 Expressing chemical potentials through the molar Gibbs energy

Multicomponent system

Chemical potential of B

$$G_B \equiv \mu_B = G_m + \frac{\partial G_m}{\partial x_B} - \sum x_i \frac{\partial G_m}{\partial x_i}$$

may also be regarded as the **partial** molar Gibbs energy of component B.

Generally we can express any partial molar quantity:

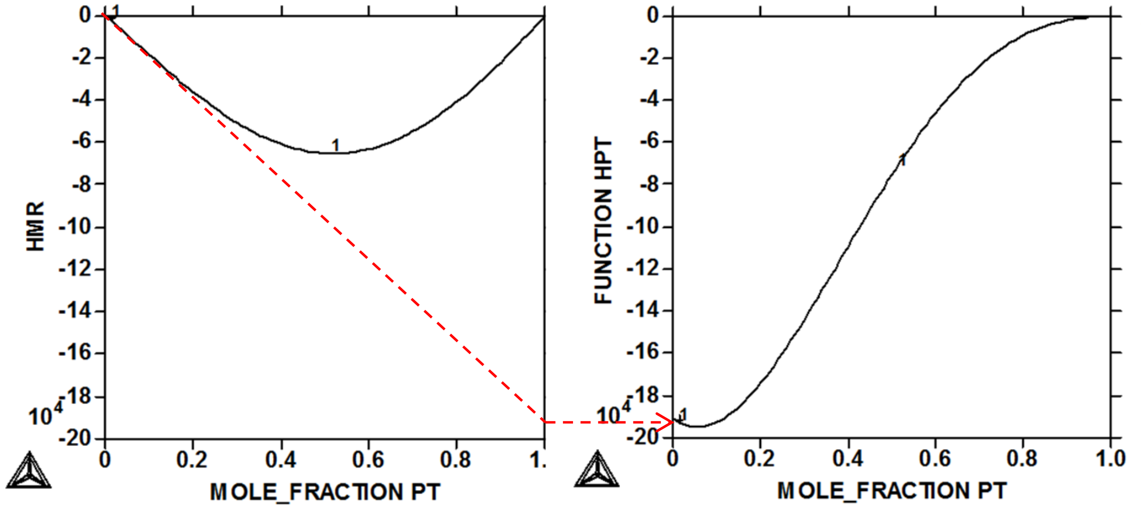
$$A_k \equiv \left(\frac{\partial A}{\partial N_k} \right)_{P,T,N_j} = A_m + \frac{\partial A_m}{\partial x_B} - \sum x_i \frac{\partial A_m}{\partial x_i}$$

e.g. if *A* is exchanged with *H* we get the partial enthalpy of component k usually called **heat of solution** of component k

1.6 Expressing chemical potentials through the molar Gibbs energy

Heat of solution – Example 1

Enthalpy versus mole fraction Pt in an Fe-Pt fcc solution at 700 K



Reference phase for both components is fcc.
Enthalpy of solution may be calculated as

$$H_{Pt} = H_m + x_{Fe}\frac{dH_m}{dx_{Pt}}$$

or

$$H_{Pt} = \left(\frac{\partial H}{\partial N_{Pt}}\right)_{P,T,N_{Fe}}$$

1.6 Expressing chemical potentials through the molar Gibbs energy

Two phase equilibrium – common tangent construction

Phases at equilibrium must have the same values for T, P and all chemical potentials.

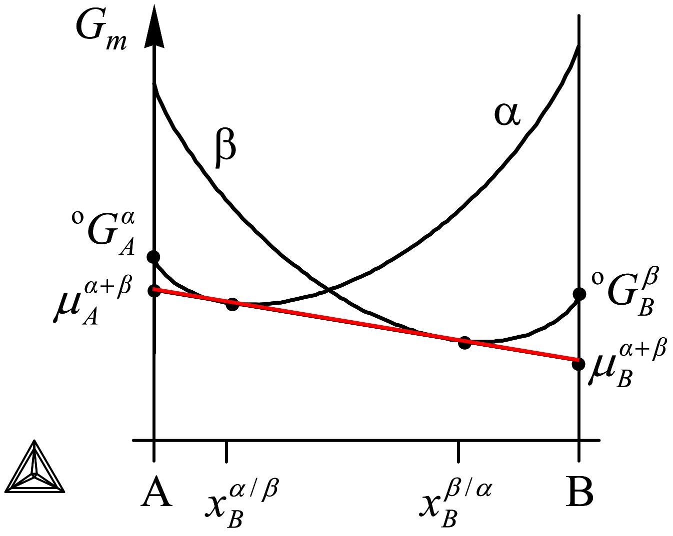


FIG.1.3.

1.6 Expressing chemical potentials through the molar Gibbs energy

Stoichiometric phase, φ

Here the tangents can be drawn arbitrarily i.e. the chemical potentials are not define for such a phase alone.

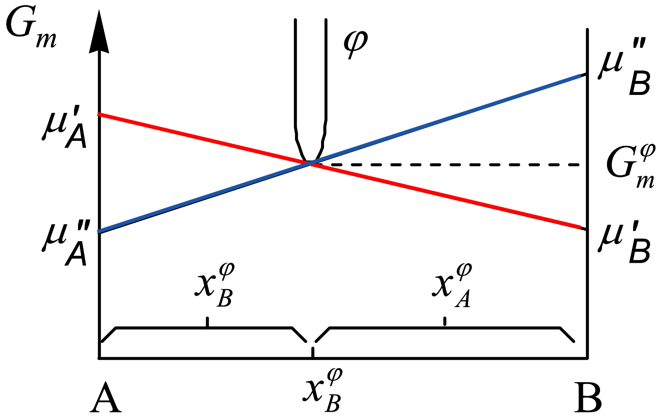


FIG.1.4.

1.7 Gibbs-Duhem relation

Different possiblities (pairs) for the chemical potentials in Fig. 1.4. Can express the molar Gibbs energy of φ using any pairs and the relation

$$G_m^\varphi = \Sigma \mu_i^\varphi x_i^\varphi = \mu_A^\varphi x_A^\varphi + \mu_B^\varphi x_B^\varphi$$

and since the x_i:s and G_m are **constants** we get

$$dG_m^\varphi = x_A^\varphi d\mu_A^\varphi + x_B^\varphi d\mu_B^\varphi = 0$$

Can be proven that it holds also for solution phases with small compositional variations. The general form is

$$\sum x_i \, d\mu_i - V_m dP + S_m dT = 0$$

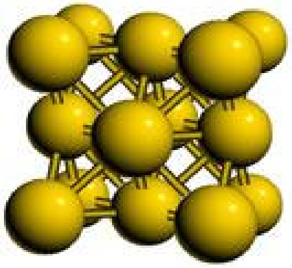
1.8 Phases

Phases
- are often denoted by a Greek letter e.g. α, β, γ.
- are identified by their structure (not composition)
- may be
  - stoichiometric i.e. fixed composition e.g. Al_2O_3, CaO
  - line compounds e.g. Al_2O_3 – Fe_2O_3
  - solution phases e.g. fcc, liquid

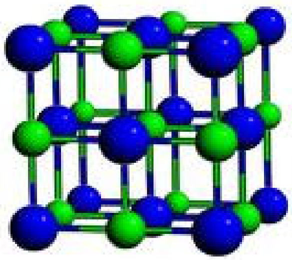
In thermodynamic databases phases usually have generic phase names, named by their structure e.g. FCC_A1, BCC_A2, BCC_B2.

Crystallographic data

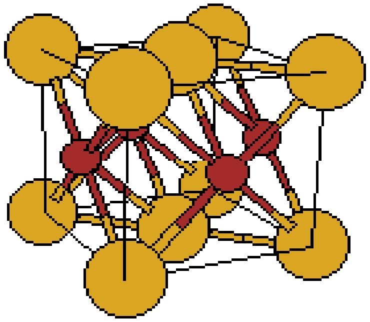
A1



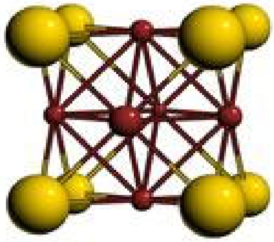
B1



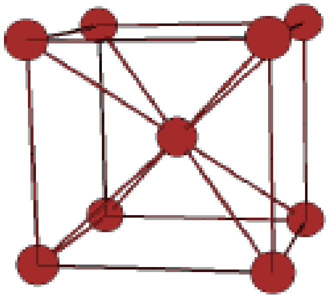
L1$_0$



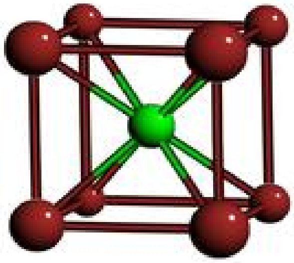
L1$_2$



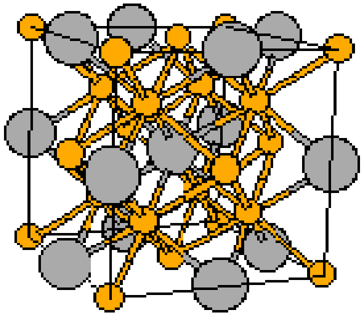
A2



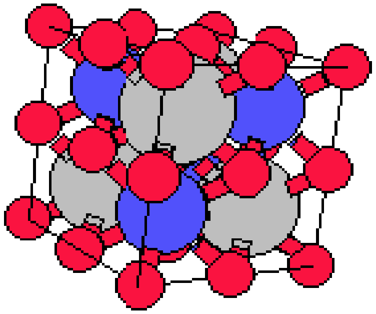
B2



D0$_3$



L2$_1$



1.9 Gibbs phase rule

In Gibbs-Duhem relation

$$\sum x_i \, d\mu_i - V_m dP + S_m dT = 0$$

there are c+2 terms (c =# of independent components), each term consisting of one **extensive** quantity and one **potential**. The two quantitites in a pair are **conjugate variables**.

In a one phase system we may vary the potentials in c+2-1 ways since G-D gives a relation between the potentials.

In a system with p phases we get the variance, v, (or degrees of freedom): **v = c + 2 - p**

1.9 Gibbs phase rule

Example

Gibbs phase rule was derived for potentials and can thus only be applied to phase diagrams with potential axes, e.g. *P* vs *T* or *T* vs μ_i or as below, T vs activity:

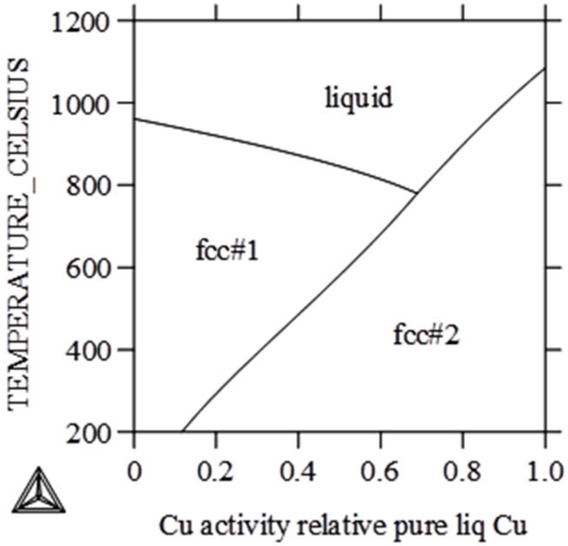


FIG 1.5.

Ag-Cu system at constant P.

c=2

v = c+1- p (c+1 since P const.)

p=1: v = 2 + 1 – 1 = 2 (area)

p=2: v = 2 + 1 – 2 = 1 (line)

p=3: v = 2 + 1 – 3 = 0 (point)

1.10 Introduction of new components

Sometimes convenient to use other components than the elements and **at equilibrium** we have

$$\mu_{A_aB_b} = a\mu_A + b\mu_B$$

For the H-O system we might want H_2O

$$\mu_{H_2O} = 2\mu_H + \mu_O$$

or expressed differently

$$\mu_{H_2O} = \mu_{H_2} + 0.5\mu_{O_2}$$

1.10 Introduction of new components

For the reaction $H_2 + 0.5O_2 \rightarrow H_2O$ we have, **before equilibrium** has been established, a driving force, *D*

$$D = \mu_{H_2} + 0.5\mu_{O_2} - \mu_{H_2O}$$

Any new set of components may be used, but the number of independent components never changes.

1.11 Gibbs energy of formation

The change of the molar Gibbs energy when one mole of phase φ is formed from the correct amounts of A and B. A and B are insoluble in one another.

$$\Delta G_m = G_m^\varphi - x_A^\varphi \mu_A - x_B^\varphi \mu_B = G_m^\varphi - x_A^\varphi {}^oG_A^\alpha - x_B^\varphi {}^oG_B^\beta$$

The driving force, $D = -\Delta G_m$, is here positive.

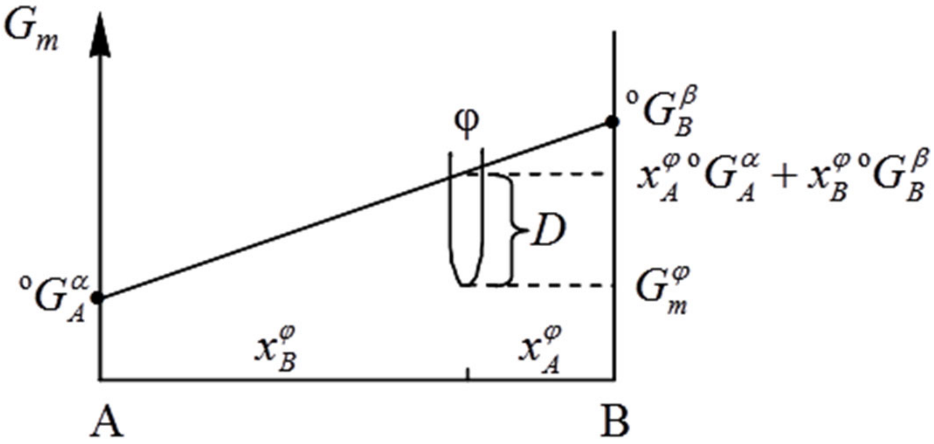


FIG 1.6.

1.11 Gibbs energy of formation

Standard Gibbs energy of formation

A compound is usually give as A_aB_b and Gibbs energy is given per mole of **formula units**

$$G^{\varphi}_{A_aB_b} = (a+b)G^{\varphi}_m$$

and the change per formula unit becomes

$$\Delta_f {}^{o}G^{\varphi}_{A_aB_b} = {}^{o}G^{\varphi}_{A_aB_b} - a\,{}^{o}G^{\alpha}_{A} - b\,{}^{o}G^{\beta}_{B} = -(a+b)D$$

o denotes **pure component** (i.e. pure element or stoichiometric compound)

$\Delta_f {}^{o}G^{\varphi}_{A_aB_b}$ is the **standard Gibbs energy of formation** of φ if pure α and β have been chosen as the standard states for A and B, respectively, at the same *P* and *T*.

1.11 Gibbs energy of formation

Precipitation from a solution phase

When φ precipitates from a solution phase the maximum driving force is obtained with a parallel tangent construction

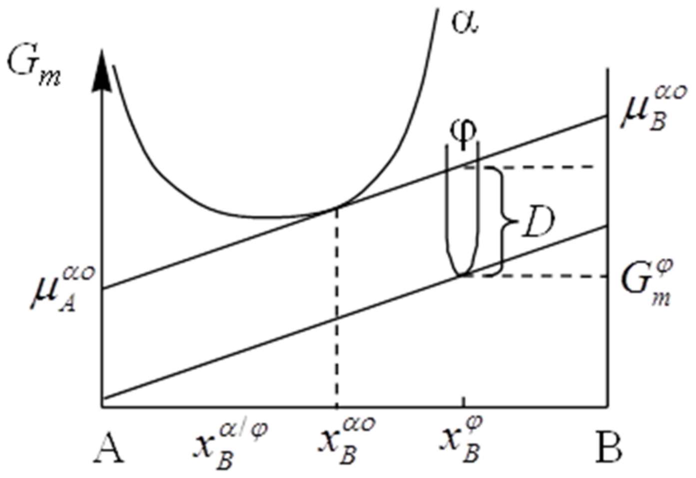


FIG 1.7a.

$$D = x_A^\varphi \mu_A^{\alpha o} + x_B^\varphi \mu_B^{\alpha o} - G_m^\varphi$$

$$(a+b)D = a(\mu_A^{\alpha o} - {}^oG_A^\alpha) + b(\mu_B^{\alpha o} - {}^oG_B^\beta) - \Delta_f\, {}^oG_{A_aB_b}^\varphi$$

1.11 Gibbs energy of formation

Driving force for the complete process

The driving force decreases as the process proceeds and will reach zero when equilibrium is reached. The *total*, *integrated* or *average* driving force is the total change in molar Gibbs energy between the final state and the initial state

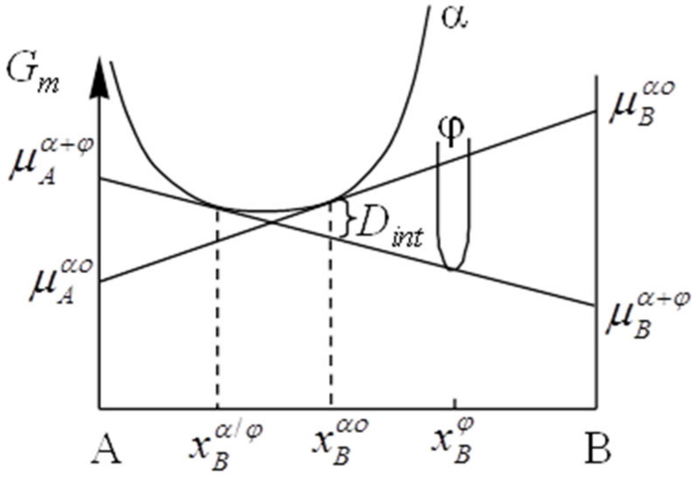


FIG 1.7b.

1.12 Properties of the Gibbs energy function

All thermodynamic properties can be expressed through its Gibbs energy, e.g.

$$V = (\partial G / \partial P)_{T,N_i}$$

$$S = -(\partial G / \partial T)_{P,N_i}$$

$$H \equiv U + PV = G + TS = G - T(\partial G / \partial T)_{P,N_i} = (\partial (G/T) / \partial (1/T))_{P,N_i}$$

1.12 Properties of the Gibbs energy function

Heat capacity

Heat capacity is defined as the capability of a system to receive heat under a given increase of T, dQ/dT

Under constant volume: **$dQ = dU$**

$$C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Under constant pressure: **$dQ=dH$**

$$C_P \equiv \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

1.12 Properties of the Gibbs energy function

Isothermal compressibility and thermal expansion

We can also obtain κ_T and α from Gibbs energy

$$\kappa_T = -(\partial V/\partial P)_{T,N_i}/V = -(\partial^2 G/\partial P^2)_{T,N_i}/(\partial G/\partial P)_{T,N_i}$$

$$\alpha = (\partial V/\partial T)_{P,N_i}/V = (\partial^2 G/\partial T \partial P)_{N_i}/(\partial G/\partial P)_{T,N_i}$$

Such important properties can be determined experimentally and are stored in tables in books.

Nowadays one instead stores $G(P,T,N_i)$ in thermodynamic databases and obtain all quantities discussed above by computer calculations.

1.13 Adiabatic changes

During an **adiabatic** process $dQ = 0$
During a **reversible** process $d\xi = 0$

We may rearrange the second law into

$$dS = dQ/T + d_{ip}S = dQ/T + (1/T)Dd\xi$$

and for an adiabatic reversible process we thus obtain dS = 0, i.e. an **isentropic** process.

1.14 State of reference and standard state

Model-based reference

Chemical potentials of pure components are usually given as ${}^{\mathrm{o}}G_A^{\alpha}$ i.e. molar Gibbs energy of pure (º) A in the same crystal structure as the solution (α). ${}^{\mathrm{o}}G_A^{\alpha}$ is thus the reference state for A in the α-solution. We may call this a **model-based reference**.

Comparing the chemical potential of A in α and β one should remember that μ_A^{α} is unaffected by the choice of reference

$$\mu_A^{\alpha} = {}^{\mathrm{o}}G_A^{\alpha} + f(comp) = {}^{\mathrm{o}}G_A^{std} + ({}^{\mathrm{o}}G_A^{\alpha} - {}^{\mathrm{o}}G_A^{std}) + f(comp)$$

1.14 State of reference and standard state

State of reference

Different choices e.g.

G_k^{NPT} = Gibbs energy of the equilibrium state at 25 ^oC and 1 atm for element k. NPT = Normal *P* and *T*

H_k^{SER}= enthalpy of the equilibrium state at 25 ^oC and 1 bar and entropy at 0 K which by agreement is set to zero, for the element *k*.
SER = Standard Element Reference

1.15 Duhem's theorem

For a closed system, i.e. all N_i are constant, the equilibrium state is uniquely defined by giving P and T (or their conjugate variables) regardless of how many phases are involved. We thus have to give c+2 conditions to define the equilibrium.

1.16 Characteristic state function and Gibbs energy model

The **characteristic state function** for fixed *P*, *T* and N_i is Gibbs energy.

In order to use it we need to know how it varies for all the different phases as function of *P*, *T*, N_i and internal variables

$$G^{\alpha}(P,T,N_i^{\alpha},\xi_1,\xi_2...)$$

Such an analytical expression is regarded as a thermodynamic model from which all thermodynamic information may be obtained.