

The state of such a system is determined by 'Potentials' analogous to the potential energy of the block (which is determined by the centre of gravity (CG) of the block). These potentials are the **Thermodynamic Potentials** (A thermodynamic potential is a Scalar Potential to represent the thermodynamic state of the system).

The relevant potential depends on the 'parameters' which are being held constant and the parameters which are allowed to change. More technically these are the **State/Thermodynamic Variables** (A state variable is a precisely measurable physical property which characterizes the state of the system- It does not matter as to how the system reached that state). **Pressure (P), Volume (V), Temperature (T), Entropy (S)** are examples of state variables.

There are 4 important potentials (in some sense of equal stature). These are: **Internal Energy, Enthalpy, Gibbs Free Energy**

Intensive properties are those which are independent of the size of the system

➤ P, T

Extensive Properties are dependent on the quantity of material

➤ V, E, H, S, G

Gibb's free energy, G can be expressed as $G = H - TS$

- H – enthalpy (J/mol) , T – temperature in K, S – entropy (J/mol.K)

Further $H = E + PV$

- E – Internal energy (J/mol), P – Pressure (N/m²) , V – Volume (m³/mol)

In the solid state, the term PV is in general very small (in the temperature and pressure range we consider) and can be neglected.

On the other hand, internal energy of metals is in the order of kJ/mol. So PV term is less than even 1%.

Internal energy has two components:

- Potential energy , which depends on atomic bonds and
- Kinetic energy , which depends on the vibration of atoms at their lattice position

The relation can be rewritten as $H = G + TS$

- H measures the total energy of the body
- TS measures the useless energy that is the energy which can't be spent for any work or transformation.

From previous studies, we understand that system can attain minimum free energy by decreasing enthalpy and/or increasing entropy.

That means $dH \leq 0$ and/or $dS \geq 0$ since $dH - TdS \leq 0$

One component can have different stable phases at different temperature and pressure ranges, for example, solid, liquid and the gas phase.

One phase is said to be stable, when it has lower free energy compared to other phases in a particular range of temperature and pressure.

Let us consider constant pressure.

To compare the stability of different phases in a particular range of temperatures, we need to calculate the free energy of the phases with respect to temperature.

To determine Gibb's free energy at a particular temperature, we need to determine H and S. Similarly it can be calculated at every temperature to gain knowledge on the change in free energy with temperature.

From previous studies

$$dG = VdP - SdT$$

$$G^l = G^s \rightarrow \Delta G = 0$$

consider: $S \rightarrow L$

$$dG^S = V^S dT - S^S dT$$

$$dG^L = V^L dT - S^L dT$$

$$(V^S - V^L)dP = (S^S - S^L)dT$$

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} = \frac{V^S - V^L}{S^S - S^L}$$

$\frac{dT}{dP}$ = *The rate of change of transformation temperature as a function of pressure*

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}$$

Is known as Clausius-Clapeyron

The equation (previous page) can also write

We know $\Delta G = \Delta H - T\Delta S$

At equilibrium $\Delta G = 0$ i.e., $\Delta H - T\Delta S = 0$, $\Delta S = \frac{\Delta H}{T}$

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

Is also known as Clausius-Clapeyron equation

At the equilibrium melting temperature T_m the free energies of solid and liquid are equal, i.e., $\Delta G = 0$. Consequently

$$\Delta G = \Delta H - T_m \Delta S = 0$$

And therefore at T_m

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m}$$

This is known as the entropy of fusion. It is observed experimentally that the entropy of fusion is a constant $\approx R$ (8.3 J/mol · K) for most metals (Richard's rule).

For small undercoolings (ΔT) the difference in the specific heats of the liquid and solid ($C_p^L - C_p^S$) can be ignored.

Combining equations 1 and 2 thus gives

$$\Delta G \cong L - T \frac{L}{T_m}$$

i.e., for small ΔT

$$\Delta G \cong \frac{L\Delta T}{T_m}$$

Previously we are considered one element only. Now we consider interaction between two elements. This is not straightforward since elements can interact differently and thermodynamic parameters may change accordingly.

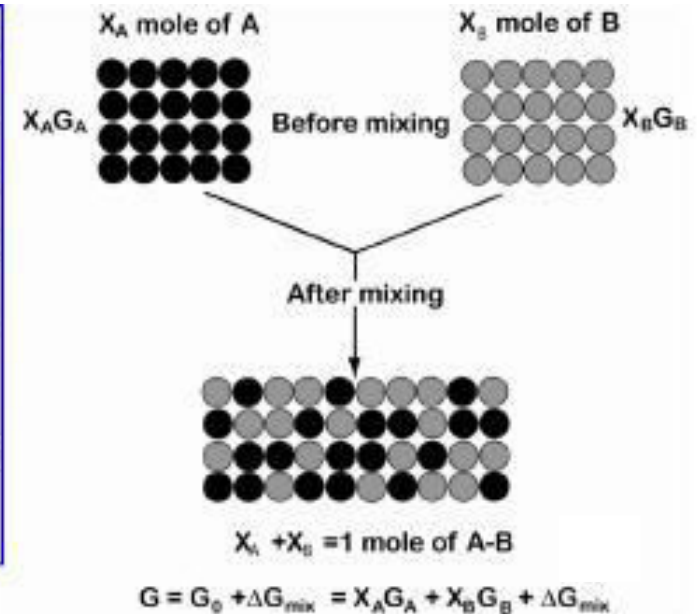
Let us consider a **Binary** system with elements A and B. For our analysis, we consider X_A mole of A and X_B mole of B so that $X_A + X_B = 1$

That means we consider total one mole of the system That further means we consider total number of atoms equal to the Avogadro number, $N_0 (= 6.023 \times 10^{23})$,

$$\text{Where } X_i = \frac{N_i}{N_0} \text{ is the number of atoms of element } i.$$

Unlike single component system, where we determine the change in free energy with temperature, in the binary case we shall find the change in free energy with the change in composition at different constant temperature at a time.

Let us consider the free energy for one mole of element A is G_A and one mole of B is G_B .



So before mixing when kept separately, X_A mole of A and X_B mole of B will have the free energy of $X_A G_A$ and $X_B G_B$ respectively

$$\text{Total free energy before mixing } G_0 = X_A G_A + X_B G_B$$

After mixing there will be change in free energy

$$\text{Total free energy after mixing } G = G_0 + \Delta G_{mix}$$

ΔG_{mix} is the free energy change of the alloy because of mixing

$$\Delta G_{mix} = G - G_0 = H - TS - (H_0 - TS_0) = (H - H_0) - T(S - S_0)$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

So, once we determine the change in free energy because of mixing, we can determine the total free energy after mixing.

Let us first determine, the enthalpy change because of mixing (ΔH_{mix}) and the change in entropy because of mixing (ΔS_{mix})

We take the following assumptions:

- ✓ The molar volume does not change because of mixing
- ✓ Bond energies between the pure elements do not change with the change in composition
- ✓ We neglect the role of other energies.

After mixing, the system can have three different types of bonding, A-A, B-B and A-B

Enthalpy of mixing can be expressed as $\Delta H_{mix} = N_0 Z X_A X_B \Delta \epsilon$

N_0 - Avogadro number, Z = coordination number

The change in internal energy

$$\Delta \epsilon = \epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB})$$

ϵ_{AB} is the bond energy between A and B

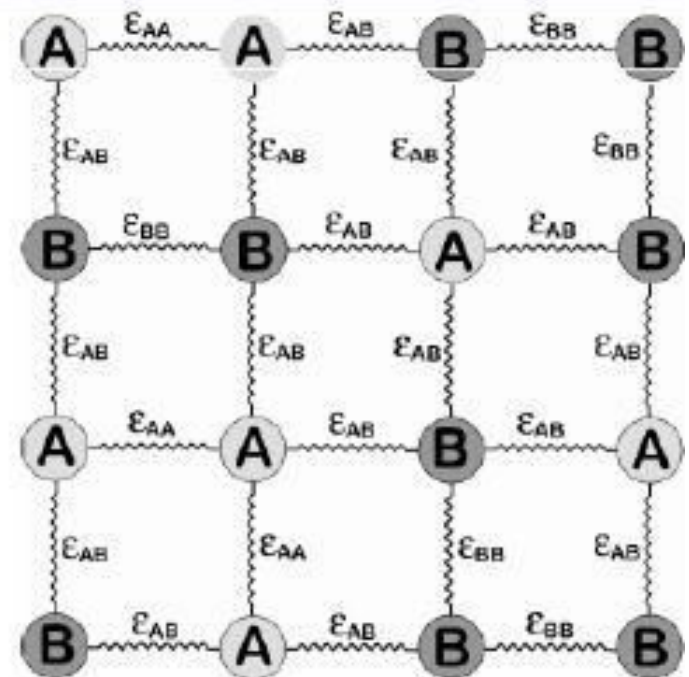
ϵ_{AA} is the bond energy between A and A

ϵ_{BB} is the bond energy between B and B

It can be written as

$$\Delta H_{mix} = \Omega X_A X_B$$

Where $\Omega = N_0 Z \Delta \epsilon$



Situation 1: Enthalpy of mixing is zero

$$\Delta H_{mix} = \Omega X_A X_B = 0$$

That means $\epsilon_{AB} = \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$

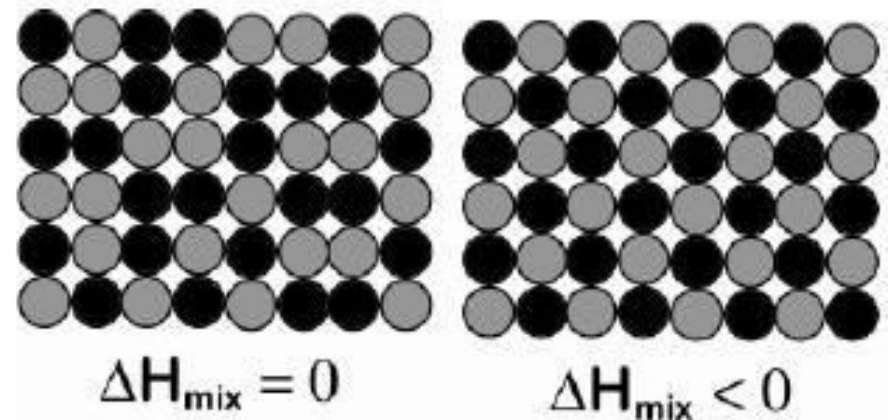
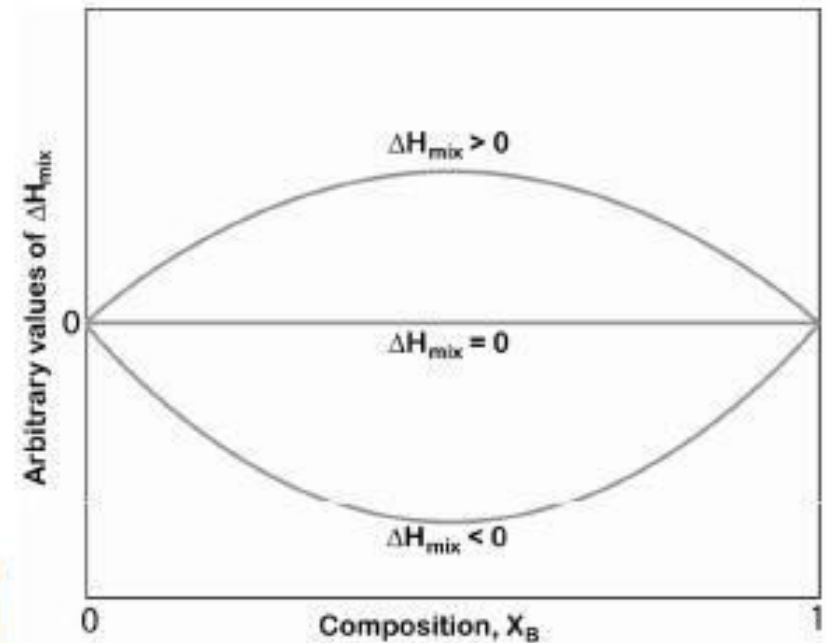
There will be no preference to choose neighboring atoms. Atoms can sit randomly at any lattice points.

Situation 2: Enthalpy of mixing is less than zero

$$\Delta H_{mix} = \Omega X_A X_B < 0$$

That means $\epsilon_{AB} < \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$

Because of transformation internal energy will decrease. That means transformation is exothermic. Atoms will try to maximize A-B bonds.

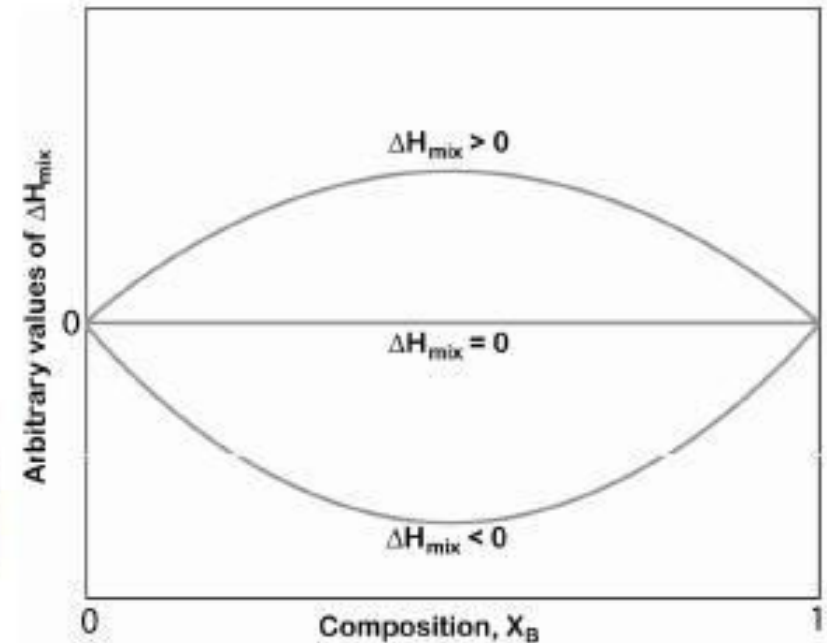


Situation 3: Enthalpy of mixing is greater than zero

$$\Delta H_{mix} = \Omega X_A X_B > 0$$

That means $\epsilon_{AB} > \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$

Because of transformation internal energy will increase. That means transformation is to be endothermic. Atoms will try to maximize A-A and B-B bonds.



If we consider that the number of vacancies is very small then the increase of enthalpy because of formation of vacancies can be written as

$$\Delta H \approx X_V \Delta H_V$$

ΔX_V is the mole fraction of vacancy and
 ΔH_V is the increase in enthalpy because of one mole of vacancies

There will be the change in the pattern of vibration of atoms next to vacancies because of extra free space. The increase in (thermal) entropy because of the extra freedom of vibration can be written as

$$\Delta S_{thermal} = X_V \Delta S_V$$

ΔS_V is the increase in entropy for one mole of vacancies

In both the cases, we are actually assuming linear relationship because of very small concentration of vacancies.

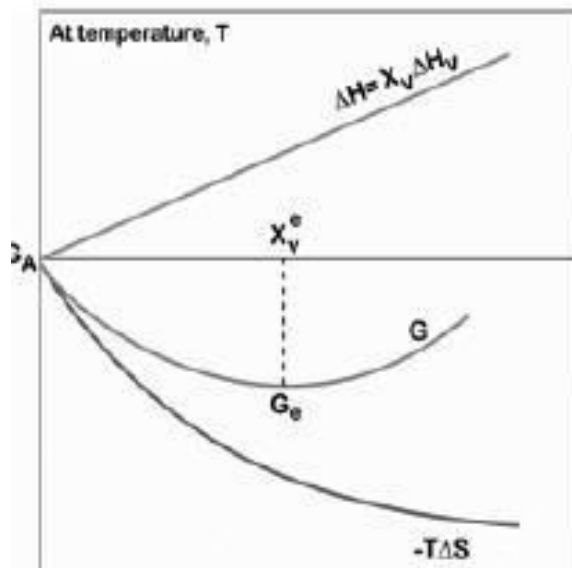
Further there will be change in configurational entropy considering the mixing of A and V and can be expressed as (Note that we are considering $X_A + X_V = 1$)

$$\Delta S_{config} = -R[X_V \ln X_V + X_A \ln X_A] = -R[X_V \ln X_V + (1 - X_V) \ln(1 - X_V)]$$

Total entropy of mixing $\Delta S_{mix} = \Delta S_V X_V - R[X_V \ln X_V + (1 - X_V) \ln(1 - X_V)]$
 (Total contribution from thermal and configurational entropy)

Total free energy in the presence of vacancies

$$\begin{aligned} G &= G_A + \Delta G \\ &= G_A + \Delta H - T\Delta S \\ &= G_A + X_V \Delta H_V - T[\Delta S_V - R[X_V \ln X_V + (1 - X_V) \ln(1 - X_V)]] \end{aligned}$$



Note here that G of element A when vacancies are present decreases. So always there will be vacancies present in materials. Further G decreases to a minimum value and then increases with the further increase in vacancy concentration. So, in equilibrium condition, certain concentration of vacancies will be present, which corresponds to G_e .

Since the slope is zero at the minima, we can find the equilibrium vacancy concentration from

$$\frac{dG}{dX_V} = 0$$

$$\Delta H_V - T\Delta S_V + RT \left[\ln X_V + X_V \cdot \frac{1}{X_V} - \ln(1 - X_V) - (1 - X_V) \cdot \frac{1}{(1 - X_V)} \right] = 0$$

Since the number of vacancies that can be present in the system is very small

$$1 - X_V \approx 1$$

$$\Delta H_V - T\Delta S_V + RT \ln X_V = 0$$

The relation for equilibrium concentration of vacancies can be written as

$$X_V^e = X_V = \exp\left(-\frac{\Delta H_V - T\Delta S_V}{RT}\right) = \exp\left(-\frac{\Delta G_V}{RT}\right)$$

Although there is increase in configurational entropy because of the presence of vacancies, it is not included in the activation energy barrier, ΔG_V .