

Phase Diagrams

Gibbs Free Energy, Lever Rule

Useful terms

- A phase- a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system
- Components-different elements or chemical compounds which make up the system
- Composition of a phase is described by giving the relative amounts of each component
- Phase transformation-how one or more phases in an alloy change into a new phase(s)

- Porter, Easterling, Sherif-Phase Transformations in Metals and Alloys
- Tilley-Understanding Solids, the Science of Materials

Useful terms

Enthalpy - $H=U+PV$

where H =enthalpy, U =internal energy, P =pressure and V =volume

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy

Also at constant pressure the [heat](#) flow (q) for the process is equal to the change in enthalpy defined by the equation:

$$\Delta H=q$$

Entropy is a measure of how much the energy of atoms and molecules become spread out in a process and can be defined in terms of statistical probabilities or in terms of other thermodynamic quantities

[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Thermodynamics/Energies_and_Potentials/Entropy/Simple_Entropy_Changes_-_Examples](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Thermodynamics/Energies_and_Potentials/Entropy/Simple_Entropy_Changes_-_Examples)

Why do phase transformations occur?

- The state of the alloy is unstable relative to the final state

How is Phase stability measured?

- Thermodynamics
- At constant temperature and pressure, the relative stability of a system is determined by its Gibbs free energy (G)

Gibbs Free Energy

Gibbs free energy, denoted G , combines [enthalpy](#) and [entropy](#) into a single value.

The change in free energy, ΔG , is equal to the sum of the enthalpy plus the product of the temperature and entropy of the system.

ΔG can predict the direction of the chemical reaction under two conditions:

- 1.constant temperature and
- 2.constant pressure.

If ΔG is positive, then the reaction is nonspontaneous (i.e., an the input of external energy is necessary for the reaction to occur)

and if it is negative, then it is spontaneous (occurs without external energy input).

- Gibbs energy was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the “available energy” in a system. His paper published in 1873, “Graphical Methods in the Thermodynamics of Fluids,” outlined how his equation could predict the behavior of systems when they are combined. This quantity is the energy associated with a chemical reaction that can be used to do work, and is the sum of its enthalpy (H) and the product of the temperature and the entropy (S) of the system. This quantity is defined as follows:
 - $G=H-TS(1)$
 - $G=U+PV-TS(2)$

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where

- U is internal energy (SI unit: joule)
- P is pressure (SI unit: pascal)
- V is volume (SI unit: m^3)
- T is temperature (SI unit: kelvin)
- S is entropy (SI unit: joule/kelvin)
- H is the enthalpy (SI unit: joule)

Energy and heat

- The internal energy is the total kinetic energy and potential energy of atoms in the system.
- Kinetic energy comes from atomic vibrations in solids and liquids and from rotational and translational energy in a liquid or gas.
- Potential energy comes from the bonds between the atoms in the system.
- During a transformation the heat absorbed or evolved depends on the change in internal energy but also on the volume of the system.
- At constant pressure the heat change = change in H

Equilibrium

- A system is in equilibrium when it is in the most stable state.
- Due to the laws of thermodynamics, at constant temperature and pressure, a closed system will be in stable equilibrium if it has the lowest possible value of Gibbs free energy.
- $\Delta G=0$
- Stable =Low enthalpy high entropy
- Solids stable at low temperatures
- At high temperatures, liquids and gases become most stable

Metastable equilibrium

- Where there is a local minimum in free energy.
- Graphite is stable, diamond is metastable at room temperature/pressure so diamond will change to graphite in time.