

# Thermal Equilibrium

## Basics

- **Thermal equilibrium** is a central concept in [thermodynamics](#). It describes the unique state of an ensemble of particles (i.e. the atoms of a crystal) that the system assumes by itself sooner or later (and later can mean really, really late) for a given set of intrinsic parameters (e.g., temperature, pressure, [chemical potential](#)) and extrinsic parameters (e.g., volume, entropy, number of particles).
  - The state of the system is unambiguously described by a state function which is called a **thermodynamic potential** and there are several thermodynamic potentials that can be used for a system description.
  - Whereas in principle **any** thermodynamic potential can be used for **any** situation (because they are related by a so-called **Legendre transformation**); it is useful to use specific thermodynamic potentials for specific systems.
- Depending on the kind of "contact" between the system under consideration and the environment (e.g. totally isolated, energy flow permitted, particle flow permitted, and so on), typical situations are:
  - **Constant volume  $V$ , temperature  $T$ , and number of particles  $N$ .**
    - The proper thermodynamic potential is the **free energy  $F(V, T, N)$**  (sometimes called **Helmholtz energy**).
  - **Constant pressure  $p$ , constant temperature  $T$ , and constant particle (= atom) number  $N$** 
    - This is the situation typical for a crystal. The appropriate thermodynamic potential is the **free enthalpy  $G(p, T, N)$**  (sometimes called **Gibbs energy**).
  - The **free enthalpy** (defined as  **$G = H - TS$** ) with  **$H$  = enthalpy** of the system and  **$S$  = entropy** is thus the most important thermodynamic potential when considering defects.
    - Thermal equilibrium for this case then simply means a state with an (absolute) minimum of the free enthalpy of the crystal.