

# Internal Energy, Enthalpy, Entropy, Free Energy, and Free Enthalpy

## A Thermodynamics Primer

### General Remarks and State Functions

## Basics

Let's face it: Thermodynamics is not easy! *It is not possible to learn it by just reading through this module.*

- However, if you fought your way through thermodynamics proper at least once, and thus are able to look at it from a distance without getting totally confused by the "details" (which you don't have to know anymore, but must be able to understand when they come up), it's not so difficult either.
- It gets even easier by restricting ourselves to solids which means that most of the time we don't have to worry about the *pressure*  $p$  anymore – it is simply constant. We nevertheless specify it here for the sake of general validity.

In this primer we will review the most important issues necessary for understanding defects, including defects in semiconductors. In order to stay simple, we must "cut corners". This means:

- We will usually not show the functional relationships by showing the variables. We thus simply write  $G$  for the free enthalpy, and not  $G(T, p, n_i)$ , showing that  $G$  is a function of the temperature  $T$ , the pressure  $p$  and the particle numbers  $n_i$ .
- In the same spirit, we will omit the indexes showing what stays constant for partial derivations, i.e. we write for the chemical potential  $\mu_i$  of the particle sort  $i$  the simple form

$$\frac{\partial G}{\partial n_i} = \mu_i$$

- In full splendor it should be

$$\frac{\partial G(T, p, n_j)}{\partial n_i} \Big|_{p, T, n_{j \neq i}} = \mu_i(T, p, n_j)$$

- We also are sloppy about standards.  $n_i$  may refer to particle numbers *or* concentrations; in the latter case **particles/cm<sup>3</sup>** or **mol/cm<sup>3</sup>** - you must know what is meant from the context. You are also supposed to know that if [Boltzmann's constant k comes up](#) in an equation, we are working with properties per particle, whereas the gas constant  $R$  signifies properties per mol.

This, admittedly, is dangerous. But multi-indexed quantities are confusing (and not easily written in HTML, anyway)! Let's stay simple and refer to complications whenever they come up.

If we restrict ourselves to crystals, it is rather easy to consider the concepts behind the all-important thermodynamic quantities **Internal Energy, Enthalpy, Entropy, Free Energy** and **Free Enthalpy**. We start with the *internal energy*  $U$  of a crystal.

- Neglecting *external* energies (e.g. the gravitational potential) and *internal energies that never change* (e.g. the energy of the inner electrons), we are essentially left with the internal energy  $U$  being contained in the *vibrations of the crystal atoms* (or molecules), which express themselves in the *temperature  $T$  of the system* according to

$$U = \frac{1}{2} \cdot f \cdot kT$$

- With  $U$  = average energy per atom,  $f$  = degree of freedoms for "investing" energy in an atom ( $f = 6$  for crystals;  $3$  for the kinetic energy in  $v_x, v_y, v_z$ , and  $3$  for the potential energy at  $(x, y, z)$ );  $k$  = Boltzmann's constant and  $T$  = (absolute) temperature

The *(macro)state of the system* is thus given by the number of atoms  $N$ , the pressure  $p$  and the temperature  $T$ . Knowing these numbers is all there is to know about the system *on a macroscopic base*.

- We can change the state of the system by adding or removing heat  $Q$ , putting mechanical work  $W$  into the system or taking it out, and by changing the number of atoms (or more generally, particles) by some  $\Delta N$ .
- Since at this point we keep the number of atoms in our crystal constant, we only have to consider  $Q$  and  $W$  if we change the state. The following basic equations (a formulation of the [1st law of thermodynamics](#)) ([german link](#)) holds

$$dU = dQ - dW$$

- With the changes written in differential form. Note that the regular "d" is not the sign for (partial) derivatives (that would be  $\partial$ ) but for "delta".  $dU$ , e.g., stands for **total change of U**. Note that *sometimes* the **d** indicates a [total differential](#) (e.g. in the case of  $dU$ ), sometimes it does not (e.g. in the case of  $dQ$  or  $dW$ ).
- If we reserve the letter "d" for total differentials only, the equation above actually should have been written as  $dU = \delta Q - \delta W$  but we will not be that rigid here.
- Any mechanical work must change the volume (something must move); for the normal conditions encountered with crystals where the pressure stays constant it can always be expressed as

$$dW = p \cdot dV$$

This term  $pdV$  is cumbersome as long as only situations involving crystals under constant pressure are considered. We thus introduce a *new state function* called enthalpy  $H$  and define it as

$$H = U + pV$$

- If we again change the state of the system by adding or subtracting heat  $Q$  and mechanical work  $W$ , we now obtain for the total *change in enthalpy*  $dH$

$$dH = dU + pdV + Vdp$$

- With  $Vdp = 0$ , because the pressure  $p$  is constant, and  $dU = dQ - pdV$  we obtain

$$dH = dQ$$

- This is a simple relation always best suited for systems under constant pressure and also clarifying why we tend to think of enthalpy as **heat**.
- $dH$  is a measure of the energy needed to form a substance in a given state, it is occasionally also called the **heat of formation** (always referring to the difference between two states).
- Of course, not much happens if the substance is just heated a bit but does not change its chemical nature – let's say we look at a mixture of  $H_2$  and  $O_2$  which we heat up a bit. All the fun comes from chemical reactions (or phase changes) – in our example it would be the formation of  $H_2O$  in a somewhat violent fashion.

It was thought that the sign of  $dH$  would indicate if a reaction should or should not occur. A negative sign would mean that the reaction would transfer energy to the surroundings and thus could easily happen, whereas a positive sign would tell us that energy would have to be pumped into the system – nothing would happen by itself.

- It's not that simple! While this point of view was true enough for relatively large  $dH$  (let's say  $> 100$  kcal/mol), the criterion often does not work for smaller changes of  $dH$ .
- The reason, of course, is that we neglected the change of the **entropy S** of the system,  $dS$ , that occurs parallel to  $dH$ .

*Purely mechanical systems* (consisting of non-interacting mass points) would be in equilibrium for the lowest possible internal energy, i.e. for a minimum in their potential energy and no movement – just lying still at the lowest possible point. *But thermodynamic systems* consisting of many interacting particles and some externally fixed condition (e.g. a constant temperature), are in equilibrium if the *best possible balance between a small energy and a large entropy is achieved!*

- We just take that as an article of faith (or law of nature) at this point.
- Often, both quantities are opposed to each other: High entropies mean high energies and vice versa. The entropy part becomes more important at high temperatures, and the thermodynamic potential which has to be minimized for systems under constant pressure, is the **free enthalpy G** (also called **Gibbs energy**). It is defined as

$$G = H - T \cdot S$$

- With  $S = \text{entropy} = dQ_{\text{rev}}/T$  in classical thermodynamics (the suffix "rev" refers to reversible processes).
- If you have a system with constant volume (and variable pressure), the best suited state function is the **free energy F** (also called **Helmholtz energy**). It is defined as

$$F = U - T \cdot S$$

Before turning to the entropy, a word to the choice of state functions. We now already have four:  $U$ ,  $H$ ,  $G$ ,  $F$  – but for a given system, there is only *one* state. Two things are important in this context:

- State functions, by definition, must describe the state of a system no matter how this state developed – they must, in other words, meet all the requirements for potentials and thus are **thermodynamic potentials**. We have not proved if this is the case for  $U$ ,  $H$ ,  $G$ ,  $F$  – turn to the [potential module](#) for some input to this question – but they really are potentials.
- Any* state function or thermodynamic potential can be used to describe *any* system (always for equilibrium, of course), but for a given system some are more convenient than others. The most convenient (and thus important) one for crystals (usually under constant pressure) is the free enthalpy.

### Entropy - Statistical Consideration

The key question is:

## What is entropy?

- There is a classical answer, but here we only use the statistical definition where *entropy is the measure of the "probability"  $w$  of a given macrostate*, or, essentially the same thing, *the number  $P$  of microstates possible for the given macrostate*.
- Not too helpful: What is a **microstate** or a **macrostate**? Or the **probability of a macrostate**?
- Well, *any* particular arrangement of atoms (or more generally, particles) where we look only on *average quantities* is a *macrostate*, while any *individual arrangement* defining the properties (e.g. location and momentary velocity) of all the particles for a given macrostate is a *microstate*.
- In other words, and somewhat simplified: For a microstate it matters what individual particles do, for the macrostate it does not.
- The difference between microstates and macrostates is best illustrated for a gas in a closed container: We can define many possible macrostates, e.g.
  - 1. All molecules are in the left half of the container.
  - 2. 70 % of the molecules are in the left half of the container, 30 % in the right half.
  - 3. Equal (average) distribution of the molecules.
 and all these macrostates (plus many more) could have exactly the same internal energy  $U$  (or  $H$ ).
- However, the *probability* of experimentally finding one or the other of those macrostates is very different. The probabilities of the macrostates 1. and 2. are certainly much much smaller than the probability of macrostate No. 3.
- For all the possible macrostates, the *state function* tells us which one will be realized (= is most probable) in thermal equilibrium.

How do we calculate the probability of a macrostate? Let's see:

- For every possible macrostate we can think of, there are many microstates to realize it. Its exactly like playing dice: Let's assume you have 3 dice. A macrostate would be some possible number you may throw; e.g. 9. The corresponding microstates are the possible combinations of the individual dice. For throwing 9 we have

Dice	1. Poss.	2. Poss.	3. Poss.	....
1	1	1	1	
2	1	2	3	
3	7	6	5	

- and so on. You get the picture.

The *probability* for such a macrostate would be the number of microstates divided by the number of all possible combinations of the dice (which is a constant). We can see off-hand that the macrostates "3" and "18" are the most unlikely ones, having only one microstate at their disposal, while 9, 10, or 12 are more likely to occur.

● Now we know what *the number of possible ways to generate the same macrostate* means and why the "probability"  $w$  of a given macrostate is "almost" the same thing.

▶ An example just as easy as playing dice, comes from our friend, the vacancy. We simply ask: How many ways  $P$  (= *microstates*) are there to arrange  $n$  vacancies (= *macrostate*) in a crystal of  $N$  atoms?

● When we figure that out, we can use the equilibrium condition to select the most likely macrostate and this gives us the number of vacancies in equilibrium.

▶ The fundamental point now is that just knowing the internal energy  $U$  of a system with a constant volume and temperature is not good enough to tell us what the equilibrium configuration will be because *we* could think of many macrostates with the same  $U$  (and mother nature, to be sure, can come up with lots more).

● That's why just minimizing  $U$  (or  $H$ ) is not good enough, we have to minimize  $F = U - TS$  or  $G = H - TS$  to find the equilibrium configuration of the system, and for that we have to know the entropy, because we now can interpret these formulas:

● Of all the many *macrostates* possible for a given  $U$  (or  $H$ ) the one with the *largest entropy* at the given temperature will be the one that the system will adopt

▶ Obviously, we need to be able to calculate the entropy of a certain macrostate and this is done by employing the statistical definition of the entropy  $S$ , the famous **Boltzmann entropy equation** (*german link*):

$$S = k \cdot \ln w$$

or

$$S = k \cdot \ln P$$

With  $w$  = probability of a macrostate and  $P$  = number of microstates for a macrostate.

▶ If you feel that the ambiguity with respect to taking  $w$  or  $P$  is a bit puzzling - that's because it is! You should consult [the link](#) to see that at least it is nothing to worry about. Whatever you chose to work with, the results you will get in the end will be the same.

● Entropy  $S$ , by the way, is *not a state function* ( $TS$  would be one).

▶ We used the statistical definition of entropy and the minimization of the free enthalpy in [chapter 2.1](#); and in an [exercise module](#) it can be seen in detail how to apply it to derive the formula for the vacancy concentration