

**A vague discomfort at the thought of the chemical potential is still characteristic of a physics education. This intellectual gap is due to the obscurity of the writings of J. Willard Gibbs who discovered and understood the matter 100 years ago.**

**C. Kittel**; Preface to his book: Introduction to Solid State Physics

## The chemical potential

### Names and Meanings

- This module is registered in the "advanced" part, despite the fact that the chemical potential belongs to basic thermodynamics. The reason is that people with a mostly *physical background* (like me) may often have learned exciting things like Bose-Einstein condensations and the Liouville theorem in their thermodynamics courses, but not overly much about chemical potentials and chemical equilibrium.
- First we will address, somewhat whimsically, a certain problem related to the name "*Chemical potential*". It is, in the view of many (including professors and students), a slightly unfortunate name for the quantity  $\partial G / \partial n_i$ ; meaning the partial derivative of the free enthalpy with respect to the particle sort  $i$  and all other variables kept constant (See a pure [thermodynamic script](#) as well).
  - In other words, the "chemical potential  $\mu$ " is a measure of how much the [free enthalpy](#) (or the free energy) of a system *changes* (by  $dG_i$ ) if you add or remove a number  $dn_i$  particles of the particle species  $i$  while keeping the number of the other particles (and the temperature  $T$  and the pressure  $p$ ) constant:

$$dG_i = \frac{\partial G}{\partial n_i} \cdot dn_i$$

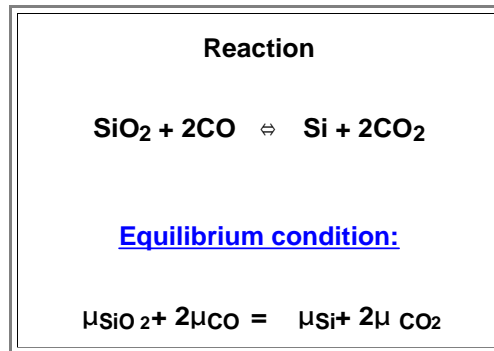
- Since particle numbers are pure numbers free of dimensions, the *unit of the chemical potential is that of an energy*, which justifies the name somewhat.
- However, the particles considered in the context of general thermodynamics do not have to be only atoms or molecules (i.e. the objects of chemistry). They can be electrons, holes, or anything else that can be identified and numbered. In considering e.g., the equilibrium between electrons and holes in semiconductors, physically minded people do not feel that this involves chemistry. Moreover, they feel since electrons and holes are Fermions, classical thermodynamics as expressed in the chemical potential or the mass actions law, might not be the right way to go at it. The "chemical potential" of the electrons, however, is still a major parameter of the system (to the annoyance of the solid state physicists - they therefore usually call it "**Fermi energy**").
- A better name, perhaps, would help. How about "particle potential"? But such a name would not be too good either. Because now there is the danger of mixing-up the *thermodynamic Potential  $G$*  of the particles, and the "*Particle Potential*", which is a partial derivative of  $G$  – not to mention the common electrostatic or gravitational potential. Now, [what exactly is a potential?](#) Use the link to refresh your memory!
  - The Gibbs energy  $G$ , e.g., may be viewed as a thermodynamic potential because it really is a "true" potential. Not only does it satisfy the basic conditions that its value is independent of the integration path (i.e. it does not matter how you got there), but it is also measured in units of energy and its minima (i.e.  $dG = 0$ ) denote stable (or metastable) equilibrium.
  - The chemical potential meets the first two criteria, albeit the second one only barely. This is so because if you define it relative to the particle *concentration* and not the number (which would be equally valid), you end up with an energy *density* and not an energy.
  - The last condition, however, *is not true* for the chemical potential. Its minima do not necessarily signify equilibrium; the equilibrium conditions if several particles are involved are rather

$$\sum_i \mu_i = 0$$

- [Below](#) is a detailed derivation for this.

Lets try a different approach. In a formal way, the particle numbers are *general coordinates* of the free enthalpy for the system under consideration. Since the partial derivatives of thermodynamic potentials with respect to the generalized coordinates can be viewed as **generalized forces** (in direct and meaningful analogy to the gravitational potential), the chemical potentials could just as well be seen as *chemical forces*.

- The equilibrium conditions are then immediately clear: The sum of the forces must be zero. If there is only one particle in the system (e.g. vacancies in a crystal), equilibrium exists if there is no "chemical force", i.e.  $\mu_{\text{vac}} = \partial G / \partial n_{\text{V}} = 0$ . If there are more particles that are coupled by some reaction equation, the left-hand sum of the chemical potentials (times the number of particles involved) must be equal to the right hand sum. An example:



- Think of a beam balance and you get the drift.

This suggests yet another name: "**Particle force**" or "**Particle change force**". Of course, now we would have a force being measured in terms of energy - not too nice either, but maybe something has to give?

- Unfortunately, there is another drawback. If we look at currents (electrical or otherwise), i.e. at *non-equilibrium* conditions, the driving forces for currents very generally can be identified with the gradients of the chemical potentials (which still may be defined even under *global* non-equilibrium as long as we have *local* equilibrium). Now we would have a force being the derivative of a force - and that is not too clear either. In this context a potential would be a much better name.

So - *forget it!*  $\partial G / \partial n_i$  is called, and will be called "*chemical potential of the particle sort i*". But by now, you know what it means. Still, if you feel uncomfortable with the name "Chemical Potential" in the context of looking at non-chemical stuff, e.g. the behavior of electrons, use your own name while thinking about it, keep in mind what it means, but do write down "*chemical potential*".

### The Burden of History: Gases and Fugacity

The good part about the chemical potential is its simplicity - after you have dug through the usual thermodynamical calculations. It is especially easy to obtain for (ideal) gases.

- An ideal gas is a system of particles *of any kind whatsoever* that obeys the equation  $p \cdot V = N \cdot R \cdot T$  with  $N =$  Number of mols in the system; or  $p \cdot V = n \cdot k \cdot T$  with  $n =$  Number of particles in the system.

- Lets go through this quickly (haha), because we are not really interested in gases, but only want to remember the nomenclature and the way to go at it.

From regular thermodynamics we get a lot of relations between the partial derivatives of state functions and therefore also for the chemical potential, e.g.

$\frac{\partial \mu_i}{\partial p} = V_i$
$\frac{\partial \mu_i}{\partial T} = - S_i$

- with the proper quantities kept constant and with care as to the use of absolute or molar values*

From these equations we obtain for the chemical potential of a pure ideal gas, i.e. a system consisting only of one kind of component - a bunch of  $\text{O}_2$  molecules in a container, or a *bunch of vacancies in a crystal*:

$$\mu_{\text{ideal gas}}(p, T) = \mu_{\text{ideal gas}}^0 + RT \cdot \ln \frac{p}{p^0}$$

Now wait a minute! In the case of vacancies, we seem to have *two* components - the vacancies and the crystal, not to mention that considering vacancies as an ideal gas seems to be stretching the concept a bit.

- Well - yes, there is the crystal, but for the real gas there is the vacuum in which the particles move. As long as the "container" of the ideal gas particles does not do anything, we may ignore it (if we don't, math will do it for us as soon as we write down equations like the [mass action law](#) or others that tell us what happens inside the "container").
- So get used to the idea of treating point defects like an ideal gas for a start!

What is  $\mu^0$  ideal gas? It is called something like "*the standard chemical potential for the pure phase*". Let's look at what it means from *two* points of view.

- First**, if we stay with the vacancy example, i.e. we consider an ideal gas of vacancies, the pressure is given by  $pV = n \cdot kT$  with  $n$ =number of vacancies in the crystal, or  $p = n \cdot kT/V$ . Likewise,  $p^0$ , the pressure at some reference state, can be written as  $p^0 = NkT/V^0$  with  $N$ = number of vacancies at the reference state and  $V^0$  volume of the system at the reference state.
- Rewriting the chemical potential of our vacancies for  $n$  gives (in 3 easy steps)

$$\frac{p}{p^0} = \frac{n \cdot k \cdot T \cdot V^0}{N \cdot k \cdot T \cdot V} = \exp \frac{\mu_V - \mu_V^0}{RT}$$

- Since the volume of the crystal will not change much no matter at what state you look, we have  $(V^0/V) \approx 1$ . Moreover, in equilibrium [we demand](#)  $\mu_V = 0$ . This leaves us with

$$\frac{n}{N} = \exp - \frac{\mu_V^0}{RT}$$

- And this looks very familiar! If we chose the standard state to be  $N$ = number of atoms of the crystal=number of sites for vacancies,  $\mu_V^0$  must be the energy of forming one mol of vacancies and that is simply the formation energy measured in **kJ/mol**. If you like electron volts, simply replace **R** by **k**.
- In other words, the standard reference state is very important, but also a bit trivial. You can choose whatever you like, but there are *smart* choices and *not so smart choices*. Best to stick with the conventions - they usually are smart choices and you can use the numbers given in books and tables without conversion to some other system.

Now the *second* point of view.

- Since the chemical potential is an energy (with many properties very similar to the better known gravitational or electrostatic potential energy), there is no unique choice of its zero point. All that counts are *changes*, i.e.  $\mu_i(\text{state } x) - \mu_i(\text{state } 0)$ .
- For  $\mu_i(\text{state } 0)$  we write  $\mu_i^0$  and call it standard potential.

So far so good. But what about the chemical potential of some stuff (always particles) in a *mixture* with other particles? To start easy, let's take a mixture of ideal gases -  $O_2$  with  $N_2$ , vacancies and interstitials (both uncharged, so there is negligible interaction).

- We want the chemical potential  $\mu_i^{\text{mix}}(p, T)$  of the component  $i$  in a mixture of ideal gases as a function of the temperature and the (total) pressure. We first need the quantities "*mole fraction*" and "*partial pressure*" to describe a mixture.
- The **mole fraction**  $x_i$  is simply the amount of phase  $i$  (measured in mols or particle numbers) divided by the sum of the amounts of all phases.
- The **partial pressure**  $p_i$  of gas number  $i$  in a mixture of gases is simply the pressure that gas number  $i$  would have if you take all the other gases away and let it occupy the available volume. It follows that the total pressure  $p = \sum_i p_i$  and  $p_i/p = x_i$  (for ideal gases).

With that we obtain for the chemical potential  $\mu_i$  of the component  $i$  in a mixture of ideal gases

$$\mu_i^{\text{mix}}(p, T) = \mu_i^{\text{pure}}(p, T) + RT \cdot \ln \frac{p_i}{p}$$

- With  $p_i$ =partial pressure of component  $i$  and  $p$ = actual pressure= $\sum p_i$
- In words:* The chemical potential of gas number  $i$  in a mixture of gases at a certain temperature  $T$  and pressure  $p$  is equal to the chemical potential of this gas in the pure phase at  $p$  and  $T$  plus  $RT \cdot \ln x_i$ . *But note that  $x_i < 1$  for all cases* and thus  $RT \cdot \ln x_i < 0$ .
- Gases like to mix! It lowers their chemical potentials and thus their free enthalpy.

Now comes a big (and, to the eye of a physicist), somewhat confusing trick:

- We call  $\mu_i^{\text{pure}}(p, T)$  now the *standard state* and write it  $\mu_i^0$  which is only the same thing as our old  $\mu_i^0$  as long as  $p=p^0$ , or, in the vacancy example above,  $N=N_0$ =**Lohschmidts** number (=number of particles in a mol). Again, you are free in your choices of standard states - use it wisely!

Considering this, we obtain a kind of "*master equation*" for the chemical potential of the component  $i$  in some mixture of ideal gases:

$$\mu_i^{\text{id}}(p, T) = \mu_i^0 + RT \cdot \ln \frac{p_i}{p}$$

The **ln** term simply contains the entropy of mixing; otherwise, when we mix two gases, we would only add up the enthalpy/energy contained in the two pure components before the mixing.

- This is one way of writing down the chemical potential *for a mixture of gases*. Again note that whenever we see the **Gas constant**  $R$  instead of the Boltzmann constant  $k$ , you know that you are dealing with amounts that are taken *per mol* of a substance instead of per particle.

Again, what exactly is  $\mu_i^0$  now? Nothing but the reference for the energy scale, but nevertheless a quantity of prime importance, called the "*standard potential of component i*" ( the superscript "0" always refers to the "standard" reference frame; in the case of gases mostly to atmospheric pressure and room temperature). It is also called **standard reaction enthalpy** and gives the change in the total free enthalpy at *standard conditions* if you wiggle the concentration of particle  $i$  a bit via

$$\Delta G^0 = \mu_i^0 \cdot \Delta n_i$$

In other words:  $\mu_i^0 = \Delta G^0 / \Delta n_i$  or  $\mu_i^0$ = the increase in enthalpy (or sloppily, energy) if you add a unit of the particles under consideration to the particles already in place.

- What do the equations mean? If we use the unit "particle",  $\mu^0$  is exactly the amount of free enthalpy needed to add (or subtract) one particle; usually given in [**eV/particle**] which is [**eV**]. If we use the unit "**mol**", it is the free enthalpy needed to add (or subtract) one mol, usually given in [**kJ/mol**].

So far we have considered rather straight-forward thermodynamics; the difficulties arise if we use the concept of the chemical potential for **non-ideal gases**, for liquids and solids, for mixtures gases liquids and solids, or, as we do, for things like vacancies which are not usually described in those terms anyway. The first step is to consider non-ideal gases:

- If the gas is non-ideal, which means that it has some kind of interaction between its particles, it will obey some **virial equation** (any equation replacing  $p \cdot V = N \cdot R \cdot T$ ). The simplest possible virial equation is  $V = R \cdot T \cdot p + B$  and for this we obtain

$$\mu^{\text{non-id}}(p) = \mu^0 + RT \cdot \ln \frac{p}{p^0} + B \cdot p$$

- For any other virial equation we can derive the corresponding formula for the chemical potential of that particular non-ideal gas. It will always have some extra terms containing the pressure.

However, to make things easy, chemists like to *keep the simple equation* for  $\mu^{\text{id}}$  even in the case of non-ideal gases by *substituting the real pressure  $p$  by a quantity called fugacity  $f$*  chosen in such a way that the correct value for  $\mu^{\text{non-id}}$  results.

- Fugacity and pressure thus are necessarily related and we define

$$f := \varphi \cdot p$$

- The dimensionless number  $\varphi$  can always be calculated from the virial equation applicable to the situation. In our example we have

$$\ln \varphi = \frac{B \cdot p}{RT}$$

As long as we look at gases, there is no problem. Fugacity is a well defined concept, even if needs getting used to. The next step, however, is a bit more problematic.

### Solids and Activities

Now we will turn to solids (and in one fell swoop we also include liquids in this). The good news is that the equation for a mix of ideal gases is equally valid for a mix of **ideal condensed** phases, i.e. **ideal solids**. The bad news is: An ideal solid in analogy to gases, i.e. without any interaction between the atoms, is an **oxymoron** (i.e. a contradiction in itself).

- What then are ideal solids supposed to be? Since we need interactions between the atoms or molecules, we must mean something different from gases. What is meant by "ideal" in this cases is that the interactions between the constituents of the solid are the same, regardless of their nature.
- Now that is certainly not a good approximation for most solids. So we use the same trick as in gases, we replace the mole fraction (which is a concentration)  $x_i$  of the component  $i$  by a quantity that contains the deviation from ideality; that quantity is called "**activity**"  $a_i$ .
- Again, we define the activity  $a_i$  of component  $i$  by

$$a_i := \varphi_i \cdot x_i$$

- With  $\varphi_i$  now carrying the burden of non-ideality.
  - In contrast to gases,  $\varphi_i$  is **not** all that easily calculated, in fact it is almost quite hopeless. You may have to resort to an experiment and measure it.
- In any case, if we use activities instead of concentrations or fugacities (which we treat as special case of activities), we are totally general and obtain for the chemical potentials of whatever component in any mixture:

$$\mu_i = \mu_i^0 + RT \cdot \ln a_i$$

Now, in looking at simple vacancies we already [had the formula](#) for the chemical potential of a vacancy; it read (if you put the various equations given in the link together):

$$\frac{\partial G}{\partial n_V} = 0 \quad G_F - kT \cdot \ln \frac{N}{n} = \mu_V$$

- with  $n/N = n_V$ , the equilibrium concentration of vacancies which we now also may call  $a_V$ , the activity of vacancies, if we want to be totally general.
- We have [k instead of R](#), so we must be considering energies per particle and not per mol - which we did. We therefore do not have a mol fraction but a particle number fraction; but this is identical, anyway. All we have to do to get the activity is to reshuffle the **ln**:

$$\frac{\partial G}{\partial n_V} = \mu_V = G_F + kT \cdot \ln \frac{n}{N} = G_F + kT \cdot \ln a_V$$

Now this is exactly the formula for an ideal gas or solid if we identify the formation enthalpy  $G_F$  of a vacancy with its standard chemical potential  $\mu_0(\text{vacancy})$  - and we [did that already](#), too.

Replacing the concentration  $n/N$  of the vacancies with the activity of the vacancies is fine - but fortunately, for vacancy concentrations in elemental crystals, there is no difference between concentration and activity, because vacancy concentrations are always small (below  $10^{-4}$ ) - the vacancies are far apart and therefore do not interact very much - *they do behave like an ideal gas!*

The situation, however, may be completely different for point defects in *large concentrations*, e.g. impurity atoms or vacancies and interstitials in ionic crystals.

The latter case is special because the *concentration of intrinsic point defects may depend on the stoichiometry and on impurities*: If there is e.g. a trace of  $\text{Ca}^{++}$  in a  $\text{NaCl}$  crystal, there must be a corresponding concentration of  $\text{Na}$  - vacancies to maintain charge neutrality and this concentration can not only be much larger than the maximum concentration in thermal equilibrium for "perfect" crystals, it will also be constant, i.e. independent of the temperature!

How to use the chemical potentials and activities in this context is described in a series of modules in the "[backbone II](#)" section of chapter 2. Here we will only give one example - equilibrium between phases.

### Chemical Potential and Phase Equilibrium

Consider some substance at constant pressure and temperature, but with *two possible phases*.

An everyday example is water in contact with ice, or any binary substance with a given composition (e.g.  $\text{Pb}$  and  $\text{Sn}$  - solder) at some point at its phase diagram where two phases coexist (consult the module "[phase diagrams](#)"), for that matter.

How many particles will be contained in phase 1 and how many in phase 2? Given  $N$  particles altogether, we will have  $N_1$  particles in phase 1 and  $N_2 = N - N_1$  in phase 2. How large is  $N_1$ ?

Lets look at the free enthalpy of the substance, or better yet, at its change with the particle numbers. In full generality, we have two equations:

$$1. \quad dG(p, T, N_1, N_2) = \frac{\partial G}{\partial T} \cdot dT + \frac{\partial G}{\partial p} \cdot dp + \frac{\partial G}{\partial N_1} \cdot dN_1 + \frac{\partial G}{\partial N_2} \cdot dN_2$$

$$2. \quad N_1 + N_2 = N = \text{const}$$

Since we look at a situation with *constant pressure and temperature*, we have that  $dT = 0 = dp$ .

For equilibrium, we demand  $dG = 0$ . From equ. (2) we get

$$dN_1 = -dN_2$$

Substituting that in equ. (1) yields

$$\frac{\partial G}{\partial N_1} \cdot dN_1 - \frac{\partial G}{\partial N_2} \cdot dN_1 = dG = 0$$

$$\frac{\partial G}{\partial N_1} \cdot dN_1 = \frac{\partial G}{\partial N_2} \cdot dN_1$$

$$\frac{\partial G}{\partial N_1} = \frac{\partial G}{\partial N_2}$$

$$\mu(N_1) = \mu(N_2)$$

*q.e.d.*

What happens if  $\mu(N_1) > \mu(N_2)$ ; i.e. if we have non-equilibrium conditions with  $\mu(N_1)$ , *the chemical potential of the particles in phase 1* being larger than in phase 2?

- We now must change the particle numbers in the phases until equilibrium is achieved.
- So do we have to increase  $N_1$  (at the same time decreasing  $N_2$ ) or should it go the other way around?
- Well, whatever we do, *it must decrease G*, so  $dG$  must be negative if we change the particle numbers the right way. For  $dG$  we had (a few lines above)

$$dG = \frac{\partial G}{\partial N_1} \cdot dN_1 - \frac{\partial G}{\partial N_2} \cdot dN_2$$
$$dG = \mu(N_1) \cdot dN_1 - \mu(N_2) \cdot dN_2$$

- For positive  $dN_1$ , we will have  $dG > 0$  since  $\mu(N_1) > \mu(N_2)$ . This necessarily leads to the general conclusion:
- **$dN_1$  must be  $< 0$**  if the system is to move towards equilibrium.

In words this means: The phase with the larger chemical potential will have to shrink and the phase with the smaller chemical potential will grow until equilibrium is achieved and  $\mu(N_1) = \mu(N_2)$ .

- *This is a very general truth.* Electrons, e.g., move from the phase with the higher chemical potential (than called [Fermi energy](#)) to the phase with the lower one.
- We can also turn it around: Vacancies in supersaturation will tend to move to vacancy agglomerates and increase their size. It follows that the chemical potential of supersaturated single vacancies must be larger than that of vacancies in an agglomerate.

Following up this line of thought leads straight to the [law of mass action](#), which will be dealt with in another module.