Mass Action Law

## General Remarks

This module is registered in the "advanced" part, because it uses the concept of the chemical potential also developed in the advanced part.

- We use a rather general derivation, but do not go too deep into the details.

The mass action law is usually taught in high school chemistry, so we know what we want to find: We look at some chemical reaction, e.g.

$$2H_2 + O_2 \Leftrightarrow 2H_2O$$
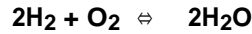
The mass action law, as we know it, than asserts that the concentrations of the particles (= molecules in this case) in equilibrium can be written as

$$\frac{[H_2]^2 \cdot [O_2]}{[H_2O]^2} = K(T, p)$$

- With **K =** reaction constant.

- Or in words: The product of the concentration of the reaction partners with all concentrations always taken *to the power of their stoichiometric factors*, equals a constant **K** which has a numerical value that depends on the temperature and pressure. The constant **K** is called **reaction constant**.

This statement, however, includes already a *generalization* and a *convention*:

- There can be any number of particles reacting or resulting from the reaction, and we always bring the *results of the reaction*, (in the example the H_2O), to the *right side* of the equation and assign a *negative value to its stoichiometric factors* - the reaction products thus end up in the *denominator* of the concentration products. We mostly use *integers* for the stoichiometric factors, but that is not de rigeur.

- An alternative way of writing the reaction equations that shows the "minus" sign more clearly, is

$$2H_2 + O_2 - 2H_2O = 0$$
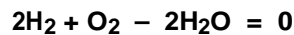
- The mass action law is deceptively simple, it is however not so trivial to derive it from thermodynamics *including a value for the reaction constant*, and it is often quite tricky to use for real cases!

We will now give a standard derivation; an alternative way is given in another module.

Standard Derivation Using the Chemical Potential

First we define arbitrary reactions of any kind by the equation

$$\nu_1 \cdot A_1 + \nu_2 \cdot A_2 + ... + \nu_f \cdot A_f = \nu_g \cdot A_g + \nu_{g+1} \cdot A_{g+1} + ... + \nu_i \cdot A_i$$

- The A_x denote the particles (or reactions partners involved) - atoms, ions, molecules, vacancies, electrons, holes, .. - we want to be very general at this point. The corresponding stoichiometric factors are the ν_x, and they are usually (but not always) integers. Bringing the *products of the reaction* to the left side of the equation *which gives their stoichiometric factors a negative sign*, leads to the simple version

$$\sum_1^i \nu_i \cdot A_i = 0$$

Chemical reactions as written down in standard notation always inherently assume that we have exactly the right amount of the chemicals (or, as we prefer to call it, particles) that are needed.

- The reaction above, for our example, thus takes *two* mols of H_2 ($= A_1$) for *every* mol of O_2 ($= A_2$); or in our lingo, *two* H_2 particles (= molecules in this case) for *one* O_2 particle., yielding *two* H_2O ($= A_3$) particles.

- We have $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = -2$.

Real life is different. You mix *some* number of H_2 particles with *some* number of O_2 particles, and after the reaction you have *some* number of all three particles involved (with one number probably being very low, or ideally zero, if the most scarce particle was completely used up in the reaction).

- In deriving the mass action law, we have to allow for this by allowing arbitrary starting concentrations c_i^0 of the particles involved including, if we wish, some concentration of the reaction products even before a reaction took place - nobody keeps us from filling some water into the container with H_2 and O_2 before we start the reaction.

We want to get a statement about the *concentration of the particles in equilibrium* for an *arbitrary mix of concentrations at the start of the reaction in non-equilibrium*; for ease of writing we denote the equilibrium concentration of the component *i* with c_i; the concentration at the start than is c_i^0, and an arbitrary concentration is C_i.

- The various c_i may be the number of mols, the absolute number of particles, or the concentration relative to some fixed value - it doesn't matter as long as the same definition is used throughout.

- As pointed out above, it is important to realize, that the c_i^0 can have any initial values whatsoever - you always can throw into a closed container whatever you want - but the dC_i; the *changes in the concentrations*, are tied to each other via the reaction equation.

- If you produce one mol of H_2O from any initial quantity of H_2 and O_2; you will have reduced the H_2 concentration by **1 mol** and the O_2 concentration by **0,5** mol - the dC_i thus are *not independent*.

The whole mixture of stuff - at whatever composition, i.e. for the whole range of the C_i - will have some free enthalpy $G(C_i, p, T)$.

- The important question is: For which concentration values of the various particles, do we have equilibrium and thus the minimum of *G*?

- In other words: For what conditions is **d*G* = 0**?

- Lets write it down. With $G = G(C_i, p, T)$ we have for **dG**

$$dG = \frac{\partial G}{\partial C_1} \cdot dC_1 + \frac{\partial G}{\partial C_2} \cdot dC_1 + ... + \frac{\partial G}{\partial C_i} \cdot dC_i + \frac{\partial G}{\partial T} \cdot dT + \frac{\partial G}{\partial p} \cdot dp$$

- The $(\partial G/\partial C_i)$ by definition are the chemical potentials μ_i of the particle sort *x* in the mixture, and the two last terms are simply **= 0** if we look at it at constant pressure and temperature. For equilibrium.this leaves us with

$$dG = \sum_{1}^{i} \mu_i \cdot dC_i = 0$$

Now comes a decisive step. We know that our dC_i are tied somehow, but how?

- To see this, we "wiggle" the system a little and react some particles, changing the concentrations a little bit. As a measure of this change we introduce a "**reaction coordinate**" $d\xi$; a somewhat artificial, but useful quantity (without a unit).

- The changes in the concentrations of the various particles of our system then must be proportional to $d\xi$ *and the proportionality constants are the stoichiometric indices* ν_i. Think about it! However you wiggle - if the concentration of O_2 changes some, the concentration of H_2 will change twice as much.

- In other words, or better yet, in math, we have

$$dC_i = \nu_i \cdot d\xi$$

Substituting that into the equation for **d*G*** from above, we obtain

$$dG = \sum_{1}^{i} \mu_i \cdot \nu_i \cdot d\xi = d\xi \cdot \sum_{1}^{i} \mu_i \cdot \nu_i = 0$$

- Since $d\xi$ is some arbitrary number, the sum term must be zero by itself and we have as **equilibrium condition**

$$\sum_{1}^{i} \mu_i \cdot \nu_i = 0$$

● This looks (hopefully) familiar. It is the equilibrium condition we had before for particles not reacting with each other when we looked at the meaning of the chemical potential.

▶ Now all we have to do is to take the "master equation" for the chemical potential so beloved by the more chemically minded, and plug it into the equilibrium condition for our reactions.

● In order to stay within our particle scheme, we use k instead of R and the activity A_i of the component i instead of its concentration C_i. Feel free to read "*activity*" as "*somewhat corrected concentration*" if you are unfamiliar or uncomfortable with activities. We have

$$\mu_i = \mu_i^0 + kT \cdot \ln A_i$$

● And, since we are treating equilibrium, the activity A_i now is the equilibrium activity a_i (= concentration c_i if everything would be "ideal") instead of the arbitrary concentration C_i because we are treating equilibrium now by definition.

● Inserting this formula in the equilibrium condition from above (and omitting the index "i" at the sum symbol for ease of writing) yields

$$\sum (\nu_i \cdot \mu_i^0) + kT \cdot \sum (\nu_i \cdot \ln a_i) = 0$$

▶ Going through the mathematical motions now is easy.

● Expressing the sum of $\ln$'s as the $\ln$ of the products of the arguments, and rearranging a bit gives

$$\ln \prod (a_i)^{\nu_i} = - \frac{1}{kT} \cdot \sum \mu_i^0 \cdot \nu_i = - \frac{1}{kT} \cdot \Delta G^0$$

● Because $\sum \nu_i \cdot \mu_i^0$ is just the sum over all standard reaction enthalpies involved, which we call ΔG^0.

▶ The product on the right hand side is just a fancy way to write down one part of the mass action law, it would give exactly what we formulated for the case of $2H_2 + O_2 \Leftrightarrow H_2 + O$ from above. Putting everything in the exponent finally yields the mass action law:

$$\prod (a_i)^{\nu_i} = \exp - \frac{G^0}{kT} = K^{-1} = \text{(Reaction Constant)}^{-1}$$

● It doesn't matter much, but it is standard to write K^{-1}. In other words, put the products of the reaction in the nominator to get K.

▶ There seems to be a bit of magic involved: We started with arbitrary amounts of components, let them react an arbitrary amount (we even defined a new quantity, the reaction coordinate ξ) - and none of this shows up in the final formula! There are certainly some questions.

● What's left are only equilibrium concentrations (or activities) - what happened to the starting concentrations?

● Can't we derive the mass action law then without introducing quantities that seem not to be needed?

▶ Some short answers:

● At some point, we essentially switched to changes (= derivatives) of prime quantities - and everything not changing is now gone. It is still there, however, if we do real calculations because then we need more information - the mass action law, after all, is just *one* equation for *several* unknown concentrations.

● There probably is a more direct way to get the mass action law that does not involve the somehow superfluous reaction coordinate. However - I do not know it and I'm in good company. Several text books I consulted do not know a better way either. Still, try the link for some alternatives.

▶ Lets go back to our original question and mix arbitrary amounts of whatever and than let the buggers react. What will we get, throwing in the reaction equation and possibly some reaction enthalpies?

- The mass action law now gives us *one* relation between the equilibrium concentration, but not the absolute amounts. There are, after all, just as many unknowns for the equilibrium concentrations as you have components, and you need more than one equation to nail everything down.
- Additionally, the way we have spelled out the mass action law here also has a number of pitfalls; if you want to really use it, you must know a bit more, in particular about conventions that must be strictly adhered to.

All that is essentially beyond the scope of this "Defect" lecture, but for the hell of it, a few more modules intertwining mass action law and chemical potentials were made; they are accessible via the following links.

- Pitfalls and extensions of the mass action law
- Some standard (chemical) examples of applying mass action law
- Alternative derivations of the mass action law
- Some defects in ionic crystal related applications of the mass action law

Appendix: Some Necessary Math

This appendix contains one of the necessary mathematical transformations used above to refresh your memory

$$\Sigma \ln (c_i)^{V_i} = \ln(c_1)^{V_1} + \ln(c_2)^{V_2} + ... = \ln\{(c_1)^{V_1} \cdot (c_2)^{V_2} ... \} = \ln \prod (c_i)^{V_i}$$