# Pitfalls and Extensions of the Mass Action Law

What is Reacting?

Advanced

Lets look at *ammonia synthesis*, a major chemical breakthrough at the beginning of the **20 th** century, as a pretty simple chemical reaction *between gases* (Remember : In the chemical formalism invoking the mass action law, point defects behave like (ideal) gases).

- The reaction equation that naturally comes to mind is

$$N_2 + 3H_2 \Leftrightarrow 2NH_3$$
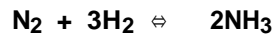
- and the mass action law tells us that

$$\frac{[N_2] \cdot [H_2]^3}{[NH_3]^2} = K_1$$

- With K_1 = reaction constant for this process. We used the square brackets **[..]** as the notation for concentrations, but lets keep in mind that the mass action law in full generality is *formulated for activities or fugacities*!

However, we also could look at the *dissociation of ammonia* - equilibrium entails that some ammonia is formed, some decays; the "$\Leftrightarrow$" sign symbolizes that the reaction can go both ways. So lets write

$$2NH_3 \Leftrightarrow N_2 + 3H_2$$

- The mass action law than gives

$$\frac{[NH_3]^2}{[N_2] \cdot [H_2]^3} = K_2 = \frac{1}{K_1}$$

To make things worse, we could write the two equations also like

$$1/2N_2 + 3/2H_2 \Leftrightarrow NH_3$$

$$\frac{[N_2]^{1/2} \cdot [H_2]^{3/2}}{[NH_3]} = K_3 = (K_1)^{1/2}$$

- and nobody keeps us from using the reaction as a source for hydrogen via

$$2/3NH_3 - 1/3N_2 \Leftrightarrow H_2$$

$$\frac{[NH_3]^{2/3} \cdot [N_2]^{1/3}}{[H_2]} = K_4 = ?$$

And so on. Now *what does it mean ?* What exactly does the mass action law tell us? There are two distinct points in the examples which are important to realize:

- **1.** Only the mass action law *together* with the reaction equation *and* the convention of what we have in the nominator and denominator of the sum of products makes any sense. A reaction constant given as some number (or function of *p* and *T*) by itself is meaningless.

2. The standard chemical potentials μ_i^0 that are contained in the reaction constant (via $\Sigma_i \mu_i^0$) where defined for reacting *one* standard unit, usually **1 mol**. The reaction constant in the mass action law thus is the reaction constant for producing **1** unit, i.e. one mol and thus applies, loosely speaking, to the component with the stoichiometry index **1**.

That was N_2 in the first example. Try it. Rearranging the reaction equation to produce *one mol* of N_2 gives

$$2NH_3 - 3H_2 = N_2$$

$$\frac{[NH_3]^2 \cdot [H_2]^{-3}}{[N_2]} = K_1^{-1}$$
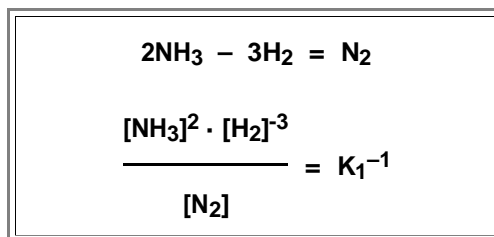
Which is just what we had for the inverse reaction before.

So the right equation for figuring out what it takes to make *one mol NH$_3$* is actually the one with the fractional stoichiometry indexes!

This looks worse than it is. All it takes is to remember the various conventions underlying the mass action law, something you will get used to very quickly in actual work. The next point is the tricky one!

Concentrations Relative to What?

Lets stick with the ammonia synthesis and give the concentrations symbolized by **[..]** a closer look. What we have is a *homogeneous* reaction, i.e. only gases are involved (a *heterogeneous* reaction thus involves that materials in more one kind of state are participating).

We may then express the concentrations as partial pressures, (or, if we want to be totally precise, as fugacities). We thus have

$$[N_2] = p_{N2}$$

$$[H_2] = p_{H2}$$

$$[NH_3] = p_{NH3}$$
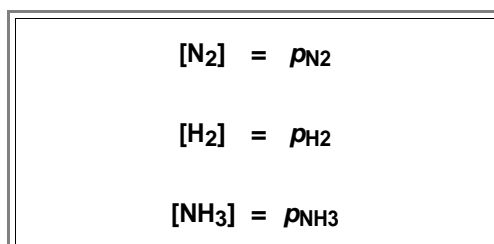
And the total pressure is $p = \Sigma\, p_i$

But what is the actual total pressure?

If we stick **1** mol N_2 and **3** mols H_2 in a vessel keeping the pressure at the beginning (before the reaction takes place) at its standard value, i.e. at atmospheric pressure, the pressure *must have changed* after the reaction, because we now might have only **2** mols of a gas in a volume that originally contained **4**!

If you think about it, that happens whenever the number of mols on both sides of a reaction equation is not identical. Since the stoichiometry coefficients ν count the number of mols involved, we only have identical mol numbers before and after the reaction if $\Sigma\nu_i = 0$.

This is a tricky point and it is useful to illustrate it. Lets construct some examples. We take one reaction where the mol count changes, and one example where it does not. For the first example we take our familiar

$$N_2 + 3H_2 \Leftrightarrow 2NH_3$$
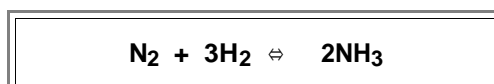
We put **1** mol N_2 and **3** mols H_2, i.e. $N_0 =$ mols into a vessel keeping the pressure at its standard value (i.e. atmospheric pressure p_0). This means we need **4** "standard" volumes which we call V_0.

Now let the reaction take place until equilibrium is reached. Lets assume that **90 %** of the starting gases react, this leaves us with **0,1** mol N_2, **0,3** mol of H_2, and **1,8** mols of NH_3 . We now have **N = 2,2** mols in our container

The pressure p must have gone down; as long as the gases are ideal, we have

$$p_0 \cdot V_0 = N_0 \cdot RT$$

$$p \cdot V_0 = N \cdot RT$$

$$\Rightarrow \quad p \cdot \frac{N}{N_0} = 0{,}55 \, p_0$$

● N or N_0 is the total number of mols contained in the reaction vessel at the pressure p or p_0, respectively.

● This equation is also valid for the partial pressure p_i of component i (with $\Sigma_i \, p_i = p$) and gives for the partial pressure and the number of mols N_i of component i, respectively

$$p_i = p_0 \cdot \frac{N_i}{N_0}$$

$$N_i = N_0 \cdot \frac{p_i}{p_0}$$

Now for the second example. Its actually not so easy to find a reaction between gases where the mol count does *not* change (think about it!), Lets take the formal reaction producing ozone, albeit a chemist might shudder:

$$2O_2 \Leftrightarrow O_3 + O$$
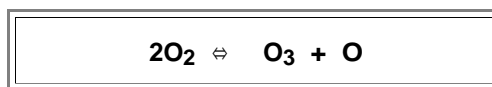
● Lets take comparable starting values: **2 mols O_2, 90 %** of which react, leaving **0,2** mol of O_2 and forming **0,8** mols of O_3 and **0,8** mols of O (think about it!) - *we always have two mols in the system*.

The mass action law followed from the chemical potentials and the decisive factor was **ln c_i** with c_i being a measure of the concentration of the component i. We had several ways of measuring concentrations, and it is quite illuminating to look closely at how they compare for our specific examples.

● In real life, for measuring concentrations, we could use for example:

- The *absolute number of mols $N_{i,mol}$* for component i. In general, the total number of mols in the reaction vessel, $\Sigma_i \, N_{i,mol}$, does *not* have to be constant as outlined above.
- The *absolute particle number $N_{i,p}$*, which is the same as the absolute number of mols $N_{i,mol}$ if you multiply $N_{i,mol}$ with Avogadros constant (or Lohschmidt's number) $A = 6{,}02214 \text{ mol}^{-1}$; i.e. $N_{i,p} = A \cdot N_{i,mol}$. Note that the absolute number of particles (= molecules) does *not* have to stay constant, while the *absolute number of atoms*, of course, never changes.
- The *partial pressure p_i* of component i, which is the pressure that we actually would find inside the reaction vessel if only the the component i would be present. The sum of all partial pressures p_i thus gives the *actual* pressure p inside the vessel; $\Sigma_i \, p_i = p$ and p does *not* have to be constant in a reaction. This looks like a violation of our basic principle that we look at the minimum of the free enthalpy at constant pressure and temperature to find the mass action law. However, the mass action law is valid for the equilibrium and the pressure at equilibrium - not for *how* you reach equilibrium!
- The *activity a_i* (or the fugacity f_i) which for ideal gases is identical to $a_i = p_i/p = p_i/\Sigma_i \, p_i$. This is more or less also what we called the *concentration c_i* of component i.
- The *mol fraction X_i*, which is the number of mols divided by the total number of mols present in the system: $X_i = N_{i,mol}/\Sigma_i \, N_{i,mol}$. This is the same thing as the concentration defined above because the partial pressure p_i of component i is proportional (for an ideal gas) to the number of mols in the vessel. We thus have $X_i = c_i$ ($= a_i = f_i$ as long as the gases are ideal).
- The *"standard" partial pressure $p_i{}^0$* defined relative to the standard pressure p^0. This is the pressure that we would find in our reaction vessel if we multiply all absolute partial pressure with a factor so that $p = p^0$. We thus have $p_i{}^0 = (p_i \cdot N_{i,mol}{}^0)/N_{i,mol}$ with $N_{i,mol}{}^0$ = number of mols of component i at the beginning of the reaction (and p = standard pressure) as outlined above.

● For ease of writing (especially in **HTML**), the various measures of concentrations will always be given by the square bracket "**[i]**" for component i.

We now construct a little table writing down the *starting* concentrations and the *equilibrium* concentrations in the same system of measuring concentrations. We then compute the reaction constant **K** for the respective concentrations, always by having the reaction products in the denominator (i.e taking $K = [NH_3]^2/[H_2]^3 \cdot [N_2]$ or $K = \{[O_3] \cdot [O]\}/[O_2]^2$, respectively).

Measure for c	Starting values	Equilibrium values	Reaction constant
N_{Mol} absolute number of Mols equivalent via $N_{i,p} = A \cdot N_{i,mol}$ to $N_{i,p}$ the absolute number of particles	$[H_2] = 3$ $[N_2] = 1$ $[NH_3] = 0$ $p = p^0$ $\Sigma_i N = 4$	$[H_2] = 0,3$ $[N_2] = 0,1$ $[NH_3] = 1,8$ $p = 0,55p^0$ $\Sigma_i N_i = 2,2$	$K_N = 1200$
	$[O_2] = 2$ $[O_3] = 0$ $[O] = 0$ $p = p^0$ $\Sigma_i N = 2$	$[O_2] = 0,2$ $[O_3] = 0,8$ $[O] = 0,8$ $p = p^0$ $\Sigma_i N_i = 2$	$K_N = 16$
Partial pressure p_i in units of p^0	$[H_2] = 3/4$ $[N_2] = 1/4$ $[H_3] = 0$	$[H_2] = 0,3/4 = 0,075$ $[N_2] = 0,1/4 = 0,025$ $[NH_3] = 1,8/4 = 0,450$	$K = 19\,200\,(p^0)^{-2}$
	$[O_2] = 2/2 = 1$ $[O_3] = 0$ $[O] = 0$	$[O_2] = 0,2/2 = 0,1$ $[O_3] = 0,4$ $[O] = 0,4$	$K_p = 16$
Activity a_i identical to the concentration c_i identical to the Mol fraction X_i	$[H_2] = 3/4$ $[N_2] = 1/4$ $[H_3] = 0$	$[H_2] = 0,3/2,2 = 0,136$ $[N_2] = 0,1/2,2 = 0,0454$ $[N_3] = 1,8/2,2 = 0,818$	$K_{act} = 5\,808$
	$[O_2] = 2/2 = 1$ $[O_3] = 0$ $[O] = 0$	$[O_2] = 0,2/2 = 0,1$ $[O_3] = 0,8/2 = 0,4$ $[O] = 0,82 = 0,4$	$K = 16$
"Standard" partial pressure p_i^0	$[H_2] = 3/4$ $[N_2] = 1/4$ $[NH_3] = 0$	$[H_2] = 0,136$ $[N_2] = 0,045$ $[NH_3] = 0,818$ $p_i^0 = 1.1818p_i$	$K = 5\,914$
	$[O_2] = 2/2 = 1$ $[O_3] = 0$ $[O] = 0$	$[O_2] = 0,1$ $[O_3] = 0,4$ $[O] = 0,4$	$K = 16$

Well, you get the point. The reaction constant may be wildly different for different ways of measuring the concentration of the components involved *if the mol count changes in the reaction* (which it mostly does).

- Well, at least it appears that we do not have any trouble calculating **K** if the concentrations are given in whatever system. *But this is not how it works!* We do not want to compute **K** from measured concentrations, we want to use *known* reactions constants assembled from the standard reaction enthalpies or standard chemical potentials to calculate what we get.

- So we must have rules telling us how to change the reaction constant if we go from from one system of measuring concentrations to another one.

- Essentially, we need a translation from absolute quantities like particle numbers (or partial pressures) to relative quantities (= concentrations), which are always absolute quantities divided by some reference state like total number of particles or total pressure. The problem clearly comes from the changing reference state if the mol count changes in a reaction.

Lets look at the the conversion from activities to particle numbers; this essentially covers all important cases.

Conversion of Reaction Constants

Well, lets go back to the [final stage](#) in the derivation of the mass action law and see what can be done. We had

$$\Pi \, (a_i)^i \; = \; \exp \, -\frac{G_0}{kT} \; = \; K \; = \; K_{act} \; = \quad \text{Reaction constant for activities}$$

- The a_i are the activities, which we defined when discussing the chemical potential analogous to the fugacities for gases. [Fugacities](#), in turn, were introduced to take care of non-ideal behavior of gases.
- However, as long as we look at gases and as long as they are ideal, the fugacity (or activity), the prime quantity in the chemical potential for gases was the *concentration* of gas **i** given by its [partial pressure](#) p_i divided by the actual pressure p, a relative quantity. For the purpose of this paragraph it is sufficient to consider

$$a_i \; = \; \frac{p_i}{p} \; = \; \frac{p_i}{\Sigma_i \, p_i}$$

Lets now switch to an absolute quantity. We take the number of mols of gas **i**. $N_{i, \, mol}$; now lets see how the mass action law changes.

- We [can express](#) p_i by

$$p_i \; = \; N_i \cdot \frac{p_0}{N^0}$$

- With $p^0 =$ standard pressure, and $N_0 =$ starting number of mols, and $p = \Sigma \, p_i = (\Sigma N_i) \cdot p_0 / N^0$.
- With this we can reformulate the mass action law by substituting

$$\frac{p_i}{p} \; = \; \frac{N_i \cdot \dfrac{p_0}{N^0}}{\Sigma N_i \cdot \dfrac{p_0}{N^0}} \; = \; \frac{N_i}{\Sigma N_i}$$

- This gives (afer some fiddling around with the products and sums)

$$\ln \Pi \, (a_i)^{\vee_i} \; = \; \ln \Pi \left(\frac{p_i}{p} \right)^{\vee_i} \; = \; \ln \Pi \left(\frac{N_i}{\Sigma N_i} \right)^{\nu_i} \; = \; \ln \left(\left((\Sigma \, N_i) \right)^{-\Sigma \nu_i} \cdot \left(\Pi \, N_i \right)^{\nu_i} \right) \; = \; \ln K_{act}$$

- If this looks a bit like magic, you are encouraged to go through the motions in fiddling around the products and the sums yourself. If you don't want to - after all we are supposed to be dealing with defects, not with elementary albeit tricky math - [look it up](#).
- We want the mass action law for the particle numbers N_i, i.e. we want an expression of the form

$$\Pi \, (N_i)^{\vee_i} \; = \; K_N$$

So if we write down the mass action law now for particle number N_i we have

$$\Pi(N_i)^{\nu_i} = \left(\Sigma N_i\right)^{\Sigma \nu_i} \cdot K_{act} = K_N$$

$$K_N = \left(\Sigma N_i\right)^{-\Sigma \nu_i} \cdot K_{act}$$

Lets try it. For our ammonia example we have

$$\Sigma N_i = 2{,}2$$

$$\Sigma \nu_i = 1 + 3 - 2 = 2$$

$$\left(\Sigma N_i\right)^{\Sigma \nu_i} = 2{,}2^2 = 4{,}84$$

- Well, the two constants from the table above are $K_N = 1200$ and $K_{act} = 5\,808$; $K_{act}/K_N = 4{,}84$ as it should be? Great - but shouldn't it be the other way around?
- Indeed, we should have $K_N/K_{act} = 4{,}84$ according to the formula above - just the other way around. However, the way we formulated the mass action law above, we should have written K^{-1} to compare with the values in the table!

OK; this is unfair - but look at the title of this subchapter!

One last word before we turn irreversibly into chemists:

- With the equations that couple pressure and mol-numbers, we can express ΣN_i by $\Sigma N_i = p \cdot (N^0/p_0)$ which, inserted into the expression between mass action constants from above, gives

$$K_N = \left(p \cdot \frac{N^0}{p_0}\right)^{\Sigma \nu_i} = p \cdot K'$$

- In words: The reaction constant is proprotional to the pressure. If you do not just accept whatever pressure you will get after a reaction, but keep the system at a certain pressure, you can influence how much (or little) of the reaction products you will get.

Lets deal with the $\ln \Pi (N_i/\Sigma N_i)^{\nu_i}$ term step by step:

- First it is important to realize that ΣN_i is a fixed number. Even so it has an index i, after the summation is done the index is gone and it does not get "afflicted" by the Π sign.
- We thus have .

$$\ln \Pi \left(\frac{N_i}{\Sigma N_i}\right)^{\nu_i} = \frac{\left(N_1\right)^{\nu_1} \cdot \left(N_2\right)^{\nu_2} \cdot \dots}{\left(\Sigma N_i\right)^{\nu_1} \cdot \left(\Sigma N_i\right)^{\nu_2} \cdot \dots} = \frac{\Pi \left(N_i\right)^{\nu_i}}{\Pi \left(\Sigma N_i\right)^{\Sigma \nu_i}}$$

- Keeping in mind that $\ln(a/b^x) = \ln(a \cdot b^{-x}) = \ln b^{-x} + \ln a$, we obtain .

$$\ln \Pi \left(\frac{N_i}{\Sigma N_i}\right)^{\nu_i} = \ln \left(\left(\Sigma N_i\right)^{-\Sigma \nu_i} \cdot \Pi \left(N_i\right)^{\nu_i}\right)$$