

Alternative Derivations of the Mass Action Law

Advanced

If despite all the efforts made in this Hyperscript you still don't like chemical potentials - here is the physicists way to deduce the mass action law *without* invoking chemical potentials and all that.

We start from the reaction equation with stoichiometric indices [as before](#)

$$\sum_i \nu_i \cdot A_i = 0$$

- If we denote with N_i the quantity of substance A_i in *mols*, the free enthalpy G of the mixture contains the sum of the free enthalpies g_i of the constituents and the mixing entropy S_m , we have

$$G = \sum_i (N_i \cdot g_i) - T S_m$$

S_m is calculated in the [usual way](#) by considering the number of possibilities for mixing the substances in question, as a result one obtains

$$S_m = - R \cdot \left(\sum_i N_i \cdot \ln \frac{N_i}{\sum_i N_i} \right)$$

- In this formulation the \ln is negative because $(N_i/\sum_i N_i) < 1$, and we thus must assign a negative sign to the total entropy, cf. the [link](#).
- The total free enthalpy now is

$$G = \sum_i (N_i \cdot g_i) + T \cdot R \left(\sum_i N_i \cdot \ln \frac{N_i}{\sum_i N_i} \right)$$

We are looking for the minimum of the free enthalpy. For that we consider what happens if we change the N_i by some ΔN_i .

- This changes G by some ΔG expressible as a total differential $\Delta G = \sum_i (\partial G / \partial N_i) \cdot \Delta N_i$. It is not much fun to go through the motions, but it is just a simple differentiation job without any problems. We obtain

$$\Delta G = \sum_i (\Delta N_i \cdot g_i) + T \cdot R \left(\sum_i \ln (N_i \cdot \Delta N_i) + \sum_i (\Delta N_i) - \sum_i \left(\Delta N_i \cdot \ln (\sum_i N_i) \right) - \sum_i \left(N_i \cdot \frac{\sum_i \Delta N_i}{\sum_i N_i} \right) \right)$$

- Horrible, but it can be simplified (the third and fifth term actually cancel each other) and expressed via the reaction coordinate ξ using

$$\Delta N_i = \nu_i \cdot \Delta \xi_i$$

- [We had that before](#); we obtain

$$\Delta G = \Delta \xi \cdot \left(\sum_i g_i \cdot \nu_i + RT \cdot \sum_i \nu_i \cdot \ln N_i - RT \cdot \sum_i N_i \cdot \ln (\sum_i \nu_i) \right)$$

For equilibrium we demand $\Delta G = 0$ and this means that the expression in large brackets must be zero by itself:

$$0 = \left(\sum_i g_i \cdot \nu_i + RT \cdot \sum_i \nu_i \cdot \ln N_i - RT \cdot \sum_i N_i \cdot \ln (\sum_i \nu_i) \right)$$

- Division with RT , putting both sides in the exponent, noticing that a sum in an exponent can be written as a product, and dropping the index i at ν , g , and N because it is clear enough by now (and cannot be written properly in **HTML** anymore), yields

$$\prod_i N^{\nu_i} = \left(\sum_i N \right)^{\sum \nu_i} \cdot \exp - \frac{\sum_i g_i \cdot \nu_i}{RT}$$

- which is the mass action law in its [most general form](#).
- No chemical potentials μ , no standard chemical potential μ_0 , no fugacities or activities. *Everything is clear.*
- The catch, of course, is the entropy formula. It is *only* valid for classical non-interacting particles. However, if this is not the case, it is clear what need to be modified - it may not be so clear, however, how.
- The other issue that takes perhaps a little thought, is the sum of the free enthalpies g_i of the constituents. Since we look at the equilibrium situation, it is the free enthalpy of one mol of the substances present with respect to the prevailing condition.