Alternative Derivations of the Mass Action Law

▌ 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 <u>as before</u>

$$\Sigma_i \, \nu_i \cdot A_i \;\; = \; 0$$

Advanced

● 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

$$G \;=\; \Sigma_i \, (N_i \cdot g_i) \;-\; T \, S_m$$

▌ S_m is calculated in the <u>usual way</u> by considering the number of possibilities for mixing the substances in question, as a result one obtains

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

● In this formulation the **ln** is negative because $(N_i / \Sigma_i N_i) \ll 1$, and we thus must assign a negative sign to the total entropy, cf. the <u>link</u>.

● The total free enthalpy now is

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

▌ 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 $\Delta G = \Sigma_i (\partial G / \partial N_i) \cdot \Delta N_i$. It is not much fun to go through the motions, but it is just a simple differentiation job without any problems. We obtain

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

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

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

● <u>We had that before</u>; we obtain

$$\Delta G \;=\; \Delta \xi \cdot \left(\Sigma_i \, g_i \cdot \nu_i \;+\; R T \cdot \Sigma_i \, \nu_i \cdot \ln N_i \;-\; R T \cdot \Sigma_i \, N_i \cdot \ln (\Sigma_i \nu_i) \right)$$

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

$$0 \;=\; \left(\Sigma_i \, g_i \cdot \nu_i \;+\; R T \cdot \Sigma_i \, \nu_i \cdot \ln N_i \;-\; R T \cdot \Sigma_i \, N_i \cdot \ln (\Sigma_i \, \nu_i) \right)$$

● Division with $R T$, 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

$$\prod_i N^V = \left(\sum_i N \right)^{\Sigma v} \cdot \exp -\frac{\Sigma_i\, g_i \cdot v_i}{RT}$$

- which is the mass action law in its [most general form](#).

▶ No chemical potentials **μ**, no standard chemical potential **μ₀**, 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.