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

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

  - 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

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

- 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

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

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

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

  - We had that before; we obtain

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

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

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

  - 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

$$\prod_i N^{\nu} = \left(\Sigma_i N\right)^{\Sigma\nu} \cdot \exp - \frac{\Sigma_i g_i \cdot \nu_i}{RT}$$

  - 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.