Law of Mass Action and Statistical Mechanics

Consider a reaction $A + B \leftrightarrows AB$. In equilibrium the Gibbs free energy is minimized, which says

$$dG = \mu_A dN_A + \mu_B dN_B + \mu_{AB} dN_{AB} = 0$$

where dN_A is the change in the number of A particles, etc. But for every increase in N_{AB}, there is an exactly equal decrease in N_A and N_B (and vice-versa), so

$$dN_{AB} = -dN_A = -dN_B$$

Plugging this in implies

$$\mu_A + \mu_B - \mu_{AB} = 0$$

is the equilibrium condition. Now we express μ in terms of the reference chemical potentials and concentrations:

$$\mu_A = \mu_A^0 + k_B T \ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) \qquad \mu_B = \mu_B^0 + k_B T \ln\left(\frac{[\mathrm{B}]}{[\mathrm{B}]_0}\right) \qquad \mu_{AB} = \mu_{AB}^0 + k_B T \ln\left(\frac{[\mathrm{AB}]}{[\mathrm{AB}]_0}\right)$$

which is valid for dilute concentrations. Plugging this into the equilibrium equation gives:

$$\mu_A^0 + k_B T \ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) + \mu_B^0 + k_B T \ln\left(\frac{[\mathrm{B}]}{[\mathrm{B}]_0}\right) - \mu_{AB}^0 - k_B T \ln\left(\frac{[\mathrm{AB}]}{[\mathrm{AB}]_0}\right) = 0$$

Using properties of the log we can rearrange this as

$$\ln\left(\frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{AB}]}\right) = \ln\left(\frac{[\mathrm{A}]_0[\mathrm{B}]_0}{[\mathrm{AB}]_0}\right) - \frac{\mu_A^0 + \mu_B^0 - \mu_{AB}^0}{k_B T}$$

Exponentiating both sides gives

$$\frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{AB}]} = \frac{[\mathrm{A}]_0[\mathrm{B}]_0}{[\mathrm{AB}]_0} \exp\left(-\frac{\mu_A^0 + \mu_B^0 - \mu_{AB}^0}{k_B T}\right)$$

The left hand side is what we define as the dissociation constant, K_d. The law of mass action basically says: if you vary the A or B concentration, the reaction will adjust to keep the combination [A][B]/[AB] constant. Originally it was a summary of experimental observation.

But the right hand side is a statistical mechanics derivation of the law of mass action. It shows that K_d depends only on the reference concentrations and reference chemical potentials. So it doesn't depend on what the actual [A] or [B] concentrations are.

Note that this only works for dilute concentrations, since our expression in terms of reference chemical potentials was applicable only for dilute concentrations.