Chemical reactions in the canonical ensemble

May 9, 2013

In the canonical ensemble, a box of volume V containing $N_{A,0}$ particles of type A and $N_{B,0}$ particles of type B has the following partition function:

$$Z(N_{A,0},N_{B,0},V,T) = \frac{1}{N_{A,0}!} \frac{1}{N_{B,0}!} \frac{1}{\lambda_A^{3N_{A,0}}} \cdot \frac{1}{\lambda_B^{3N_{B,0}}} \cdot \int \exp\left[-\beta H(\{r_A\},\{r_B\})\right] d^{3N_{A,0}} r_A d^{3N_{B,0}} r_B$$

In these notes, we will use this partition function as our starting point, and consider the possibility that A and B particles may undergo the following chemical reaction:

$$A + B \leftrightarrow C$$
 (1)

Treating this chemical reaction in the canonical ensemble, where the number of A and B molecules is fixed, may seem unorthodox, so let me explain. Even when an A particle is bound to a B particle to form a C particle, we still consider it to be an A particle. Thus we carefully distinguish between the number of free A particles, N_A , which is free to vary, and the *conserved* total number of A particles, $N_{A,0}$. The same goes for N_B and $N_{B,0}$. These quantities are related as follows:

$$N_{A,0} = N_A + N_C \tag{2}$$

$$N_{B,0} = N_B + N_C \tag{3}$$

The goal is to find the equilibrium values of N_A , N_B , and N_C . Because of the "conservation" equations above, only one of these quantities is independent. We consider N_C to be a parameter of the partition function:

$$Z(N_{A,0}, N_{B,0}, V, T; N_C)$$
 (4)

and we will then vary N_C so as to minimize the free energy.

Evaluation of partition function

Once we have taken into account the indistinguishability of the $N_{A,0}$ particles of type A and the $N_{B,0}$ particles of type B, the remaining integrals in the partition function are taken over the positions of *labelled* particles.

$$Z(N_{A,0},N_{B,0},V,T;N_C) = \frac{1}{N_{A,0}!} \frac{1}{N_{B,0}!} \frac{1}{\lambda_A^{3N_{A,0}}} \cdot \frac{1}{\lambda_B^{3N_{B,0}}} \cdot Z_{\text{labelled}}(N_{A,0},N_{B,0},V,T;N_C) \quad \textbf{(5)}$$

Now we must figure out the partition function for labelled particles. Given $N_{A,0}$ labelled A-particles and $N_{B,0}$ labelled B-particles, how many distinct ways are there to form exactly N_C bonds between A and B particles? We can construct such a pairing as follows: First, choose N_C of the A-particles to be those participating in bonds. Next, consider the first of the selected A-particles (remember, they are labelled so we can refer to them in order). There are $N_{B,0}$ choices for which B-particle to bond with this first A-particle. Then, there are $N_{B,0}-1$ choices for the B-particle to bond to the second selected A-particle. The number of distinct ways of making N_C bonds between the labelled A and B particles is then:

$$\binom{N_{A,0}}{N_C}N_{B,0}(N_{B,0}-1))\cdots(N_{B,0}-N_C+1) = \binom{N_{A,0}}{N_C}\frac{N_{B,0}!}{(N_{B,0}-N_C)!} = \binom{N_{A,0}}{N_C}\binom{N_{B,0}}{N_C}N_C!$$

Now, what about the rest of the partition function? There will be a factor associated with translational entropy, equal to

$$Z_{\text{trans}} = V^{N_A + N_B + N_C},\tag{6}$$

since $N_A + N_B + N_C$ is the number of centers of mass that can be independently moved throughout the volume V. Then there will be the part of the partition function associated with the internal degrees of freedom of a C molecule. Here, we will begin by choosing a cutoff distance, r_C , in such a way that if an A and a B particle are within a distance r_C of each other, then they are overwhelmingly likely to be bound into a C molecule. In a sense, this serves as our definition of what it means for particles to be bound. We then get a contribution from internal degrees of freedom:

$$Z_{\text{internal}} = \left(\int_{\|\vec{r}\| < r_C} \exp\left[-\beta V_{AB}(\vec{r}) \right] d^3 \vec{r} \right)^{N_C} \tag{7}$$

It is important to notice that this has units of volume N_C !! We now define the free energy change ΔF_{react} according to

$$Z_{\text{internal}} = \left(\int_{\|\vec{r}\| < r_C} \exp\left[-\beta V_{AB}(\vec{r}) \right] d^3 \vec{r} \right)^{N_C} \equiv r_C^{3N_C} \cdot \exp(-\beta N_C \Delta F_{\text{react}}) \tag{8}$$

Let's put it all together:

$$Z(N_{A,0}, N_{B,0}, V, T; N_{C})$$

$$= \frac{1}{N_{A,0}!} \frac{1}{N_{B,0}!} \frac{1}{\lambda_{A}^{3N_{A,0}}} \cdot \frac{1}{\lambda_{B}^{3N_{B,0}}} \cdot \binom{N_{A,0}}{N_{C}} \binom{N_{B,0}}{N_{C}} N_{C}! \cdot V^{N_{A}+N_{B}+N_{C}} r_{C}^{3N_{C}} \cdot \exp(-\beta N_{C} \Delta F_{\text{react}})$$

$$= \frac{1}{N_{A}! N_{B}! N_{C}!} \left(\frac{V}{\lambda_{A}^{3}}\right)^{N_{A,0}} \left(\frac{V}{\lambda_{B}^{3}}\right)^{N_{B,0}} \left(\frac{r_{C}^{3}}{V}\right)^{N_{C}} \cdot \exp(-\beta N_{C} \Delta F_{\text{react}}), \tag{9}$$

where a number of simplifications have occurred using the "conservation laws" for A and B.

Equilibrium constant

Now we will find the equilibrium constant by minimizing the free energy with respect to N_C .

$$\begin{split} \beta F(N_{A,0},N_{B,0},V,T;N_C) &= -\ln Z \\ &= \ln N_A! + \ln N_B! + \ln N_C! \\ &- N_{A,0} \ln \left(\frac{V}{\lambda_A^3} \right) - N_{B,0} \ln \left(\frac{V}{\lambda_B^3} \right) + N_C \ln \left(\frac{V}{r_C^3} \right) \\ &+ N_C \beta \Delta F_{\text{react}} \\ &\approx N_A \ln N_A - N_A + N_B \ln N_B - N_B + N_C \ln N_C - N_C \\ &- N_{A,0} \ln \left(\frac{V}{\lambda_A^3} \right) - N_{B,0} \ln \left(\frac{V}{\lambda_B^3} \right) + N_C \ln \left(\frac{V}{r_C^3} \right) \\ &+ N_C \beta \Delta F_{\text{react}} \\ &= (N_{A,0} - N_C) \ln (N_{A,0} - N_C) + (N_{B,0} - N_C) \ln (N_{B,0} - N_C) + N_C \ln N_C \\ &- N_{A,0} - N_{B,0} + N_C \\ &- N_{A,0} \ln \left(\frac{V}{\lambda_A^3} \right) - N_{B,0} \ln \left(\frac{V}{\lambda_B^3} \right) + N_C \ln \left(\frac{V}{r_C^3} \right) \\ &+ N_C \beta \Delta F_{\text{react}} \end{split}$$

Now we take the derivative of the free energy with respect to N_C

$$\begin{split} \frac{\partial \beta F}{\partial N_C} &= -\ln(N_{A,0} - N_C) - 1 + -\ln(N_{B,0} - N_C) - 1 + \ln N_C + 1 + 1 \\ &+ \ln\left(\frac{V}{r_C^3}\right) + \beta \Delta F_{\text{react}} \end{split}$$

In equilibrium, where this derivative vanishes, we get

$$e^{-\beta\Delta F_{\text{react}}} = \frac{N_C}{(N_{A,0} - N_C)(N_{B,0} - N_C)} \cdot \frac{V}{r_C^3} = \frac{N_C}{N_A N_B} \cdot \frac{V}{r_C^3},\tag{10}$$

or in terms of concentrations,

$$e^{-\beta\Delta F_{\text{react}}} = \frac{\rho_C}{\rho_A \rho_B r_C^3} \tag{II}$$