

Extended Materials

How to calculate equilibrium constants in terms of partition function?

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Derivation of the expressions of chemical equilibrium constant in terms of partition functions

The equilibrium condition for a general chemical reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$ is

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D \quad (1)$$

where ν_k is the stoichiometric number of the component and μ_k is chemical potential. Let us assume the reaction takes place in the gas phase and all reactants and products behave as ideal gases. The chemical potential is given as

$$\mu_k = -k_B T \ln \frac{q_k(V, T)}{N_k} \quad k = A, B, C, D \quad (2)$$

Inserting in eq. 1 yields a simple equilibrium condition

$$\begin{aligned} \nu_A \mu_A + \nu_B \mu_B &= \nu_C \mu_C + \nu_D \mu_D \\ \ln \frac{q_A(V, T)}{N_A} + \nu_B \ln \frac{q_B(V, T)}{N_B} &= \nu_C \ln \frac{q_C(V, T)}{N_C} + \nu_D \ln \frac{q_D(V, T)}{N_D} \\ \ln \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} &= \ln \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \\ \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} &= \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \end{aligned} \quad (3)$$

Using absolute particle numbers is impractical. We therefore replace the particle numbers by concentrations

$$c_k = \frac{N_k}{v} \quad k = A, B, C, D. \quad (4)$$

with

$$v = \frac{V}{V^0} \quad (5)$$

where V^0 is the standard volume. We can then obtain

$$\frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{c_C^{\nu_C} c_D^{\nu_D}}{c_A^{\nu_A} c_B^{\nu_B}} \cdot \frac{v^{\nu_C + \nu_D}}{v^{\nu_A + \nu_B}} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} \quad (6)$$

We define the equilibrium constant K as

$$K = \frac{c_C^{\nu_C} c_D^{\nu_D}}{c_A^{\nu_A} c_B^{\nu_B}} = \frac{(q_C/v)^{\nu_C} (q_D/v)^{\nu_D}}{(q_A/v)^{\nu_A} (q_B/v)^{\nu_B}} \quad (7)$$

In an ideal gas, the single-particle function depends linearly on the volume

$$q_k = V \zeta_k(T) \quad k = A, B, C, D. \quad (8)$$

Therefore, the property corresponds to the single-particle partition function in a standard volume V^0 and only depends on the temperature:

$$\frac{q_k}{v} = \frac{q_k}{V} V^0 = \frac{V \zeta_k(T)}{V} V^0 = V^0 \zeta_k(T) \quad k = A, B, C, D. \quad (9)$$

Eq. 7 defines the equilibrium constant in a standard volume, which then only depends on the temperature.

In this class we have discussed the concept of the molecular partition function q^0 with respect to reference energy level ϵ_0 , where ϵ_0 was defined as the energy of the quantum mechanical ground state. To this we shifted the energy levels

$$\epsilon_i^0 = \epsilon_i - \epsilon_0 \quad (10)$$

where ϵ_i is the true quantum energy and ϵ_i^0 is the energy with respect to the reference energy level. The partition q is related to the shifted partition function q_k^0 by

$$\begin{aligned}
q_k &= \sum_{i=0} \exp\left(-\frac{1}{k_B T} \epsilon_i\right) \\
&= \sum_{i=0} \exp\left(-\frac{1}{k_B T} (\epsilon_i^0 + \epsilon_0)\right) = \sum_{i=0} \exp\left(-\frac{\epsilon_i^0}{k_B T}\right) \exp\left(-\frac{\epsilon_0}{k_B T}\right) \\
&= q_k^0 \exp\left(-\frac{\epsilon_0}{k_B T}\right)
\end{aligned} \tag{11}$$

The partition function q_k^0 can be calculated using the approximations discussed in this class. The factor $\exp\left(-\frac{\epsilon_0}{k_B T}\right)$ corrects the partition function, such q_k applies to the true ground state energy. So far, we have never explicitly calculated the correction factor. This however becomes necessary when dealing with chemical reactions. Inserting eq. 11 into eq. 7 yields

$$K = \frac{(q_C^0/v)^{\nu_C} (q_D^0/v)^{\nu_D}}{(q_A^0/v)^{\nu_A} (q_B^0/v)^{\nu_B}} \cdot \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \tag{12}$$

with

$$\Delta\epsilon_0 = \nu_C \epsilon_{0,C} + \nu_D \epsilon_{0,D} - \nu_A \epsilon_{0,A} - \nu_B \epsilon_{0,B}. \tag{13}$$

The chemical reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$ takes place in mixture of N_A particles of type A , N_B particles of type B , N_C particles of type C , and N_D particles of type D . Assuming ideal particles, the partition function of this mixture is

$$Q = \frac{q_A^{N_A}}{N_A!} \cdot \frac{q_B^{N_B}}{N_B!} \cdot \frac{q_C^{N_C}}{N_C!} \cdot \frac{q_D^{N_D}}{N_D!} \tag{14}$$

q_A , q_B , q_C , and q_D are the single-particle partition functions. The corresponding free energy is

$$\begin{aligned}
A &= -k_B T \ln Q \\
&= -k_B T [N_A \ln q_A + N_B \ln q_B + N_C \ln q_C + N_D \ln q_D - \ln N_A! - \ln N_B! - \ln N_C! - \ln N_D!]
\end{aligned} \tag{15}$$

The change of free energy with respect to a change of the particle numbers of one of the substances k defines the chemical potential of this substance in this reaction

$$\mu_k = \left(\frac{\partial A}{\partial N_k}\right)_{N_j, T, V} \quad k = A, B, C, D, \quad j \neq k. \tag{16}$$

If the numbers of particles are change in all four substances by small amounts dN_A , dN_B , dN_C , and dN_D , the corresponding change in free energy is given as

$$\begin{aligned}
\Delta A &= \left(\frac{\partial A}{\partial N_A}\right)_{N_B, N_C, N_D, T, V} dN_A + \left(\frac{\partial A}{\partial N_B}\right)_{N_A, N_C, N_D, T, V} dN_B + \left(\frac{\partial A}{\partial N_C}\right)_{N_A, N_B, N_D, T, V} dN_C + \left(\frac{\partial A}{\partial N_D}\right)_{N_A, N_B, N_C, T, V} dN_D \\
&= \mu_A dN_A + \mu_B dN_B + \mu_C dN_C + \mu_D dN_D
\end{aligned} \tag{17}$$

In a chemical reaction the relative the change in the number of particles (the ratio of dN_A to dN_B etc.) is not arbitrary but determined by the stoichiometric numbers ν_A , ν_B , ν_C , and ν_D . That is, if the number of particles of substance A changes by $-\nu_A \cdot N$, the number of particles in the other three substances have to change by $-\nu_B \cdot N$, $\nu_C \cdot N$, and $\nu_D \cdot N$ (forward reaction). Thus, eq. 17 becomes

$$\Delta A = -\nu_A \mu_A - \nu_B \mu_B + \nu_C \mu_C + \nu_D \mu_D \tag{18}$$

In equilibrium $\Delta A = 0$ and therefore

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D \tag{19}$$