6.7: Equilibrium Constant for Gas Reactions

For clarity, we use an example reaction

$$|\nu_A|\,A + |\nu_B|\,B \leftrightharpoons |\nu_C|\,C + |\nu_D|\,D \tag{6.7.1}$$

with adaptation to other reactions being straightforward. At equilibrium we must have

$$\Delta G = 0 \,, \tag{6.7.2}$$

hence

$$\sum_i \nu_i \mu_i = \nu_A \mu_A + \nu_B \mu_B + \nu_C \mu_C + \nu_D \mu_D = 0 \,, \tag{6.7.3}$$

where the μ_i are *molar* chemical potentials. To solve this problem, we do not need to explicitly work with the grand canonical ensemble, as we can compute the μ_i from the results that we have already obtained for the canonical ensemble. According to one of Gibbs' fundamental equations, which we derived in the lecture course on phenomenological thermodynamics, we have

$$\mathrm{d}f = -s\mathrm{d}T - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i \,. \tag{6.7.4}$$

Comparison of coefficients with the total differential of $f(T, V, n_i)$ reveals that

$$\mu_i = \left(\frac{\partial f}{\partial n_i}\right)_{T,V,n_{j \neq i}} \,, \tag{6.7.5}$$

a result that we had also obtained in the lecture course on phenomenological thermodynamics. Using Equation ???), Equation ???), and Stirling's formula, we obtain for the contribution f_i of an individual chemical species to Helmholtz free energy

$$f_i = -k_B T \ln z_i \tag{6.7.6}$$

$$= -k_B T \ln \frac{1}{N_i!} Z_i^{N_i} \tag{6.7.7}$$

$$= -k_B T \left(N_i \ln Z_i - N_i \ln N_i + N_i\right) \tag{6.7.8}$$

$$= -n_i RT \ln \frac{Z_i}{n_i N_{Av}} - n_i RT \,, \tag{6.7.9}$$

where n_i is the amount of substance (mol). Equation 6.7.5) then gives

$$\mu_i = n_i RT \cdot \frac{1}{n_i} - RT \ln \frac{Z_i}{n_i N_{Av}} - RT \tag{6.7.10}$$

$$= -RT \ln \frac{Z_i}{n_i N_{Av}} \tag{6.7.11}$$

$$= -RT \ln \frac{Z_i}{N_i} \,. \tag{6.7.12}$$

Equation 6.7.12) expresses the dependence of the chemical potential, a *molar* property, on the *molecular* partition function. It may appear odd that this property depends on the *absolute* number of molecules N_i, but exactly this introduces the contribution of mixing entropy that counterbalances the differences in *standard* chemical potentials $\mu_i^{\ominus}$. Because of our habit of shifting energies by $\epsilon_{el,0}$ and by the zero-point vibration energies, we cannot directly apply Equation 6.7.12). We can avoid explicit dependence on the $\epsilon_{el,0,i}$ and the zero-point vibrational energies by relying on *Hess' law* and referencing energies of all molecules to the state where they are fully dissociated into atoms. The energies $\epsilon_{i,\mathrm{diss}}$ for the dissociated states can be defined at 0 K. We find

$$Z_{i,\mathrm{corr}} = \sum_j e^{-(\epsilon_{ij} - \epsilon_{i,\mathrm{diss}})/k_B T} \tag{6.7.13}$$

$$= e^{\epsilon_{i,\mathrm{diss}}/k_B T} \sum_j e^{-\epsilon_{ij}/k_B T} \tag{6.7.14}$$

$$= Z_i e^{\epsilon_{i,\mathrm{diss}}/k_B T} \,, \tag{6.7.15}$$

where index j runs over the states of molecule i.

With this correction we have

$$\Delta G = -RT \sum_i \nu_i \ln \frac{Z_i e^{\epsilon_{i,\mathrm{diss}}/k_\mathrm{B}T}}{N_i} \ . \tag{6.7.16}$$

For our example reaction, the equilibrium condition is

$$\nu_\mathrm{A}\mu_\mathrm{A} + \nu_\mathrm{B}\mu_\mathrm{B} = -\nu_\mathrm{C}\mu_\mathrm{C} - \nu_\mathrm{D}\mu_\mathrm{D} \ , \tag{6.7.17}$$

which gives

$$-RT\nu_\mathrm{A} \ln \frac{Z_\mathrm{A} e^{\epsilon_{\mathrm{A,diss}}/k_\mathrm{B}T}}{N_\mathrm{A}} - RT\nu_\mathrm{B} \ln \frac{Z_\mathrm{B} e^{\epsilon_{\mathrm{B,diss}}/k_\mathrm{B}T}}{N_\mathrm{B}}$$
$$= RT\nu_\mathrm{C} \ln \frac{Z_\mathrm{C} e^{\epsilon_{\mathrm{C,diss}}/k_\mathrm{B}T}}{N_\mathrm{C}} + RT\nu_\mathrm{D} \ln \frac{Z_\mathrm{D} e^{\epsilon_{\mathrm{D,diss}}/k_\mathrm{B}T}}{N_\mathrm{D}} \tag{6.7.18}$$

and can be rearranged to

$$\ln \frac{Z_\mathrm{A}^{-\nu_A} \cdot e^{-\nu_\mathrm{A}\epsilon_{\mathrm{A,diss}}/k_\mathrm{B}T} \cdot Z_\mathrm{B}^{-\nu_B} \cdot e^{-\nu_\mathrm{B}\epsilon_{\mathrm{B,diss}}/k_\mathrm{B}T}}{N_\mathrm{A}^{-\nu_\mathrm{A}} \cdot N_\mathrm{B}^{-\nu_\mathrm{B}}} = \ln \frac{Z_\mathrm{C}^{\nu_C} \cdot e^{\nu_\mathrm{C}\epsilon_{\mathrm{C,diss}}/k_\mathrm{B}T} \cdot Z_\mathrm{D}^{\nu_D} \cdot e^{\nu_\mathrm{D}\epsilon_{\mathrm{D,diss}}/k_\mathrm{B}T}}{N_\mathrm{C}^{\nu_\mathrm{C}} \cdot N_\mathrm{D}^{\nu_\mathrm{D}}} \tag{6.7.19}$$

and further rearranged to

$$\frac{N_\mathrm{C}^{|\nu_\mathrm{C}|} \cdot N_\mathrm{D}^{|\nu_\mathrm{D}|}}{N_\mathrm{A}^{|\nu_\mathrm{A}|} \cdot N_\mathrm{B}^{|\nu_\mathrm{B}|}} = \frac{Z_\mathrm{C}^{|\nu_\mathrm{C}|} \cdot Z_\mathrm{D}^{|\nu_\mathrm{D}|}}{Z_\mathrm{A}^{|\nu_\mathrm{A}|} \cdot Z_\mathrm{B}^{|\nu_\mathrm{B}|}} \cdot e^{(\nu_\mathrm{A}\epsilon_{\mathrm{A,diss}} + \nu_\mathrm{B}\epsilon_{\mathrm{B,diss}} + \nu_\mathrm{C}\epsilon_{\mathrm{C,diss}} + \nu_\mathrm{D}\epsilon_{\mathrm{D,diss}})/k_\mathrm{B}T} \ . \tag{6.7.20}$$

In Equation 6.7.20) we can make the identifications

$$K_N(V, T) = \frac{N_\mathrm{C}^{|\nu_\mathrm{C}|} \cdot N_\mathrm{D}^{|\nu_\mathrm{D}|}}{N_\mathrm{A}^{|\nu_\mathrm{A}|} \cdot N_\mathrm{B}^{|\nu_\mathrm{B}|}} \ , \tag{6.7.21}$$

where $K_N(V, T)$ is a volume-dependent equilibrium constant expressed with particle numbers, and, since dissociation energies are negative energies of formation,

$$\Delta U_0 = -N_\mathrm{Av} \left(\nu_\mathrm{A}\epsilon_{\mathrm{A,diss}} + \nu_\mathrm{B}\epsilon_{\mathrm{B,diss}} + \nu_\mathrm{C}\epsilon_{\mathrm{C,diss}} + \nu_\mathrm{D}\epsilon_{\mathrm{D,diss}} \right) \ , \tag{6.7.22}$$

where ΔU_0 is the molar reaction energy at 0 K. Hence, we have

$$K_N(V, T) = \frac{Z_\mathrm{C}^{|\nu_\mathrm{C}|} \cdot Z_\mathrm{D}^{|\nu_\mathrm{D}|}}{Z_\mathrm{A}^{|\nu_\mathrm{A}|} \cdot Z_\mathrm{B}^{|\nu_\mathrm{B}|}} e^{-\Delta U_0/RT} \ . \tag{6.7.23}$$

The dependence on volume arises from the dependence of the canonical partition functions on volume.

By dividing all particle numbers by $N_\mathrm{Av}^{\nu_i}$ and volume V^{ν_i}, we obtain the equilibrium constant $K_c(T)$ in molar concentrations

$$K_c(T) = \frac{Z_\mathrm{C}^{|\nu_\mathrm{C}|} \cdot Z_\mathrm{D}^{|\nu_\mathrm{D}|}}{Z_\mathrm{A}^{|\nu_\mathrm{A}|} \cdot Z_\mathrm{B}^{|\nu_\mathrm{B}|}} \cdot (N_\mathrm{Av}V)^{-\sum_i \nu_i} \cdot e^{-\Delta U_0/RT} \ . \tag{6.7.24}$$

By dividing them by the total particle number $N = \sum_i N_i$ to the power of ν_i we obtain

$$K_x(V, T) = \frac{Z_\mathrm{C}^{|\nu_\mathrm{C}|} \cdot Z_\mathrm{D}^{|\nu_\mathrm{D}|}}{Z_\mathrm{A}^{|\nu_\mathrm{A}|} \cdot Z_\mathrm{B}^{|\nu_\mathrm{B}|}} \cdot N^{-\sum_i \nu_i} \cdot e^{-\Delta U_0/RT} \ , \tag{6.7.25}$$

which coincides with the thermodynamical equilibrium constant $K^\dagger$ at the standard pressure $p^\ominus$. The most useful equilibrium constant for gas-phase reactions is obtained by inserting $p_i = c_i RT$ into Equation 6.7.24)[21]:

$$K_p(T) = \frac{Z_\mathrm{C}^{|\nu_\mathrm{C}|} \cdot Z_\mathrm{D}^{|\nu_\mathrm{D}|}}{Z_\mathrm{A}^{|\nu_\mathrm{A}|} \cdot Z_\mathrm{B}^{|\nu_\mathrm{B}|}} \cdot \left(\frac{RT}{N_\mathrm{Av}V} \right)^{\sum_i \nu_i} \cdot e^{-\Delta U_0/RT} \ . \tag{6.7.26}$$

For each molecular species, the molecular partition function is a product of the contributions from individual modes, Equation ???), that we have discussed above. In the expression for equilibrium constants, the nuclear-spin contribution cancels out since the number of nuclei and their spins are the same on both sides of the reaction equation. Symmetry requirements on the nuclear wavefunction are considered in the symmetry numbers σ_i for the rotational partition function. The electronic contribution often reduces to the degeneracy of the electronic ground state and in the vibrational contribution, normal modes with $\Theta_{\mathrm{vib},i} > 5T$ can be neglected.