

26.8: Equilibrium Constants in Terms of Partition Functions

Consider the general gas phase chemical reaction represented by



where A, B, C and D are the reactants and products of the reaction, and ν_A is the stoichiometric coefficient of chemical A, ν_B is the stoichiometric coefficient of chemical B, and so on. Each of the gases involved in the reaction will eventually reach an equilibrium concentration when the forward and reverse reaction rates become equal. The distribution of reactants to products at the equilibrium point is represented by the equilibrium constant (K_c):

$$K_c = \frac{[C]^{\nu_C} [D]^{\nu_D}}{[A]^{\nu_A} [B]^{\nu_B}}$$

If the system is not at equilibrium, a shift in the number of reactants and products will occur to lower the overall energy of the system. The difference in the energy of the system at this non-equilibrated point and the energy of the system at equilibrium for any particular species is termed chemical potential. When both temperature and volume are constant for both points aforementioned, the chemical potential μ of species i is expressed by the equation

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_{j \neq i}} \quad (26.8.2)$$

where A is the Helmholtz energy, and N_i is the number of molecules of species i . The Helmholtz energy can be determined as a function of the total partition function, Q :

$$A = -k_B T \ln Q$$

where k_B is the Boltzmann constant and T is the temperature of the system. The total partition function is given by

$$Q = \frac{q_i(V, T)^{N_i}}{N_i!}$$

where q_i is the molecular partition function of chemical species i . Substituting the molecular partition function into the equation for Helmholtz energy yields:

$$A = -k_B T \ln \left(\frac{q_i(V, T)^{N_i}}{N_i!} \right)$$

and then further substituting this equation into the definition of chemical potential (Equation 26.8.2) yields:

$$\mu_i = \left(\frac{\partial -k_B T \ln \left(\frac{q_i(V, T)^{N_i}}{N_i!} \right)}{\partial N_i} \right)_{T, V, N_{j \neq i}}$$

rearranging this equation the following derivative can be set-up:

$$\mu_i = -k_B T \left[\left(\frac{\partial N_i \ln(q_i(V, T))}{\partial N_i} \right) - \left(\frac{\partial \ln(N_i!)}{\partial N_i} \right) \right]_{T, V, N_{j \neq i}}$$

From this point [Sterling's approximation](#)

$$\ln N! = N \ln N - N$$

can be substituted into the derivative to yield:

$$\mu_i = -k_B T \left[\left(\frac{\partial N_i \ln(q_i(V, T))}{\partial N_i} \right) - \left(\frac{\partial (N_i \ln N_i - N_i)}{\partial N_i} \right) \right]_{T, V, N_{j \neq i}}$$

From here the derivative can be rearranged and solved:

$$\begin{aligned}
 \mu_i &= -k_B T \left[\ln(q_i(V, T)) \frac{\partial N_i}{\partial N_i} + N_i \frac{\partial \ln(q_i(V, T))}{\partial N_i} - \ln(N_i) \frac{\partial N_i}{\partial N_i} - N_i \frac{\partial \ln(N_i)}{\partial N_i} + \frac{\partial N_i}{\partial N_i} \right]_{T, V, N_{j \neq i}} \\
 &= -k_B T \left(\ln(q_i(V, T)) + 0 - \ln(N_i) - N_i \frac{1}{N_i} + 1 \right) \\
 &= -k_B T (\ln(q_i(V, T)) - \ln(N_i)) \\
 &= -k_B T \ln \left(\frac{q_i(V, T)}{N_i} \right)
 \end{aligned} \tag{26.8.3}$$

A variable, λ , is then defined such that $dN_j = \nu_j d\lambda$, where $j = A, B, C$ or D and ν_j is taken to be positive for products and negative for reactants. A change in λ therefore corresponds to a change in the concentrations of the reactants and products. Thus, at equilibrium,

$$\left(\frac{\partial A}{\partial \lambda} \right)_{T, V} = 0$$



Helmholtz Energy with respect to Equilibrium Shifts

From Classical thermodynamics, the total differential of A is:

$$dA = -SdT - pdV + \sum_j \mu_j dN_j$$

For a reaction at a fixed volume and temperature (such as in the canonical ensemble), dT and dV equal 0. Therefore,

$$\begin{aligned}
 dA &= \sum_j \mu_j dN_j \\
 &= \sum_j \mu_j \nu_j d\lambda \\
 &= d\lambda \sum_j \mu_j \nu_j
 \end{aligned}$$

with

$$\sum_j \mu_j \nu_j = 0$$

Substituting the expanded form of chemical potential (Equation 26.8.3):

$$\begin{aligned}
 -k_B T \sum_j \ln \left(\frac{q_i}{N_i} \right) \nu_j &= 0 \\
 \sum_j \ln \left(\frac{q_i}{N_i} \right) \nu_j &= 0 \\
 \sum_j \nu_j [\ln(q_j) - \ln(N_j)] &= 0
 \end{aligned}$$

For the reaction in Equation 26.8.1:

$$[\nu_C \ln(q_C) - \nu_C \ln(N_C)] + [\nu_D \ln(q_D) - \nu_D \ln(N_D)] - [\nu_A \ln(q_A) - \nu_A \ln(N_A)] - [\nu_B \ln(q_B) - \nu_B \ln(N_B)] = 0$$

This equation simplifies to

$$\frac{(q_C)^{\nu_C} (q_D)^{\nu_D}}{(q_A)^{\nu_A} (q_B)^{\nu_B}} = \frac{(N_C)^{\nu_C} (N_D)^{\nu_D}}{(N_A)^{\nu_A} (N_B)^{\nu_B}}$$

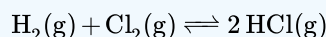
By dividing all terms by volume, and noting the relationship $\frac{N_A}{V} = \frac{\text{\#molecules}}{\text{volume}} = \rho_A = [A]$ where ρ is referred to a number density, the following equation is obtained:

$$K_c = \frac{\rho_C^{\nu_C} \rho_D^{\nu_D}}{\rho_A^{\nu_A} \rho_B^{\nu_B}} = \frac{(q_C/V)^{\nu_C} (q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}} \quad (26.8.4)$$

Hence, knowledge of the molecular partition function for all species in the reaction will ensure the calculation of the equilibrium constant.

✓ Example 26.8.1: Reacting Diatomic Molecules

Calculate the equilibrium constant (K_c) for the reaction of $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ at 650 K.



Solution

We will use Equation 26.8.4 that uses Molecular Partition Functions to evaluate K_c .

$$K_c(T) = \frac{\left(\frac{q_{\text{HCl}}}{V}\right)^2}{\left(\frac{q_{\text{H}_2}}{V}\right) \left(\frac{q_{\text{Cl}_2}}{V}\right)} \quad (26.8.5)$$

This equation is expanded into the rotational, vibrational, translational and electronic molecular partition functions of each species.

$$K_c(T) = \frac{\left(\frac{q_{\text{trans HCl}} q_{\text{rot HCl}} q_{\text{vib HCl}} q_{\text{elec HCl}}}{V}\right)^2}{\left(\frac{q_{\text{trans H}_2} q_{\text{rot H}_2} q_{\text{vib H}_2} q_{\text{elec H}_2}}{V}\right) \left(\frac{q_{\text{trans Cl}_2} q_{\text{rot Cl}_2} q_{\text{vib Cl}_2} q_{\text{elec Cl}_2}}{V}\right)}$$

A simple problem solving strategy for finding equilibrium constants via statistical mechanics is to separate the equation into the molecular partition functions of each of the reactant and product species, solve for each one, and recombine them to arrive at a final answer (e.g., for HCl).

$$\frac{q_{\text{HCl}}}{V} = \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}_{\text{translation}} \times \underbrace{\frac{2k_B T \mu r_e^2}{\sigma \hbar^2}}_{\text{rotation}} \times \underbrace{\frac{1}{1 - \exp\left(\frac{-h\nu}{k_B T}\right)}}_{\text{vibration}} \times \underbrace{g_1 \exp\left(\frac{D_0}{k_B T}\right)}_{\text{electronic}}$$

To simplify the calculations of molecular partition functions, the characteristic temperature of rotation (Θ_r) and vibration (Θ_ν) are used.

$$\frac{q_{\text{HCl}}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \times \frac{T}{\sigma \Theta_r} \times \frac{1}{1 - \exp\left(\frac{-\Theta_\nu}{T}\right)} \times g_1 \exp\left(\frac{D_0}{RT}\right) \quad (26.8.6)$$

These values are constants that incorporate the physical constants found in the rotational and vibrational partition functions of the molecules. Tabulated values of Θ_r and Θ_ν for select molecules can be found [here](#).

Species	Θ_ν (K)	Θ_r (K)	D_0 (kJ mol ⁻¹)
$\text{Cl}_2(\text{g})$	6125	0.351	239.0
$\text{H}_2(\text{g})$	808	87.6	431.9

Species	Θ_v (K)	Θ_r (K)	D_0 (kJ mol ⁻¹)
HCl(g)	4303	15.2	427.7

We need to evaluate Equation 26.8.6 for each species then then evaluate Equation 26.8.5 directly.

For HCl:

$$\frac{q_{\text{HCl}}}{V} = \left(\frac{2\pi (2.1957 \times 10^{-24} \text{ kg}) (1.38065 \times 10^{-23} \text{ JK}^{-1}) (650 \text{ K})}{(6.62607 \times 10^{-34} \text{ Js})^2} \right)^{3/2} \times \frac{650 \text{ K}}{(1)(15.2 \text{ K})} \times \frac{1}{1 - \exp\left(\frac{-4303 \text{ K}}{650 \text{ K}}\right)}$$

$$\times (1) \exp\left(\frac{427,700 \text{ J mol}^{-1}}{(8.3145 \text{ J K mol}^{-1}) (650 \text{ K})}\right)$$

$$\frac{q_{\text{HCl}}}{V} = (1.4975 \times 10^{35} \text{ m}^{-3}) (42.76)(1.0013) (2.3419 \times 10^{34})$$

For H₂:

$$\frac{q_{\text{H}_2}}{V} = \left(\frac{2\pi (1.2140 \times 10^{-25} \text{ kg}) (1.38065 \times 10^{-23} \text{ JK}^{-1}) (650 \text{ K})}{(6.62607 \times 10^{-34} \text{ Js})^2} \right)^{3/2} \times \frac{650 \text{ K}}{(2)(87.6 \text{ K})} \times \frac{1}{1 - \exp\left(\frac{-808 \text{ K}}{650 \text{ K}}\right)}$$

$$\times (1) \exp\left(\frac{431,900 \text{ J mol}^{-1}}{(8.3145 \text{ J K mol}^{-1}) (650 \text{ K})}\right)$$

$$\frac{q_{\text{H}_2}}{V} = (1.9468 \times 10^{33} \text{ m}^{-3}) (3.71)(1.41) (5.0942 \times 10^{34})$$

For Cl₂:

$$\frac{q_{\text{Cl}_2}}{V} = \left(\frac{2\pi (4.2700 \times 10^{-24} \text{ kg}) (1.38065 \times 10^{-23} \text{ JK}^{-1}) (650 \text{ K})}{(6.62607 \times 10^{-34} \text{ Js})^2} \right)^{3/2} \times \frac{650 \text{ K}}{(2)(0.351 \text{ K})} \times \frac{1}{1 - \exp\left(\frac{-6125 \text{ K}}{650 \text{ K}}\right)}$$

$$\times (1) \exp\left(\frac{239,000 \text{ J mol}^{-1}}{(8.3145 \text{ J K mol}^{-1}) (650 \text{ K})}\right)$$

$$\frac{q_{\text{Cl}_2}}{V} = (5.4839 \times 10^{35} \text{ m}^{-3}) (925.9)(1.00) (1.606 \times 10^{19})$$

Combining the terms from each species, the following expression is obtained:

$$K_c = \frac{(1.9468 \times 10^{33} \text{ m}^{-3})^2}{(1.9468 \times 10^{33} \text{ m}^{-3}) (5.4839 \times 10^{35} \text{ m}^{-3})} \times \frac{(42.76)^2}{(3.71)(925.9)} \times \frac{(1.0013)^2}{(1.41)(1.00)} \times \frac{(2.3419 \times 10^{34})^2}{(1.606 \times 10^{19}) (5.0942 \times 10^{34})}$$

$$= (0.003550)(0.1333)(0.711) (6.7037 \times 10^{14})$$

$$= (2.26 \times 10^{11})$$

At 650 K, the reaction between H₂(g) and Cl₂(g) proceeds spontaneously towards the products. From a statistical mechanics point of view, the product HCl(g) molecule has more states accessible to it than the reactant species. The spontaneity of this reaction is largely due to the electronic partition function: two very strong H—Cl bonds are formed at the expense of a very strong H—H bond and a relatively weak Cl—Cl bond.