E4211: Chemical potential: the law of mass action

Submitted by: Shay Izbitski

The problem:

(1) Consider ideal gases of atoms A, atoms B and atoms C undergoing the reaction $\nu C \leftrightarrow A + B$ (ν is an integer). n_A, n_B and n_C denote the respective densities. determine the values of the exponents a, b and c in the low of mass action

$$n_A^a n_B^b n_C^c = K(T)$$

The quantity $K\,(T)$ is known as the *equilibrium constant* of the reaction.
(2) Write explicit expression for $K(T)$ for the reaction $H_2 + D_2 \leftrightarrow 2HD$ when the masses m_H, m_D and ω_0 the vibrational frequency of HD are given. assume the temperature is high enough to allow classical approximation of the rotational motion.
(3) What is $K(\infty)$?

The solution:

(1) We first realize that the chemical potentials must obey the reaction by

$$\mu_A + \mu_B = \nu\mu_C$$

We now take the chemical potential of an ideal gas $\mu = \tau lan(\frac{1}{\lambda_T^3 n})$ and substituting it into the former equation resulting with

$$\tau lan(\frac{1}{\lambda_{TA}^3 n_A}) + \tau lan(\frac{1}{\lambda_{TB}^3 n_B}) = \nu\tau lan(\frac{1}{\lambda_{TC}^{3\nu} n_C^\nu})$$

From here we derive the law of mass action and we now can determine the values of a, b and c

$$n_A^{-1} n_B^{-1} n_C^\nu = V^{2-\nu}\frac{z_{1C}^\nu}{z_{1A}z_{1B}} = \frac{\lambda_{TC}^{-3\nu}}{\lambda_{TA}^{-3}\lambda_{TB}^{-3}}$$

(2) We'll look at the hamiltonian of a diatomic molecule with vibrational and rotational degrees of freedom

$$H = \frac{p^2}{2m} + \hbar\omega_0(n + \frac{1}{2}) + \frac{l(l+1)\hbar^2}{2I}$$

Now we'll calculate a single diatomic hetronuclear molecule partition function

$$z_1 = \frac{V}{\lambda_T^3}\sum_n e^{-\beta\hbar\omega_0(n+\frac{1}{2})}\sum_l (2l+1)e^{-\beta\frac{l(l+1)\hbar^2}{2I}}$$

The first sum can be summarized easily while the second one can be summarized under the approximation of the classical limit

$$\sum_l (2l+1)e^{-\beta\frac{l(l+1)\hbar^2}{2I}} \cong \int_0^\infty e^{-\beta\frac{l(l+1)\hbar^2}{2I}} d[l(l+1)] = \frac{2I}{\beta\hbar^2}$$

We end up with

$$z_1 = \frac{V}{\lambda_T^3} \cdot \frac{e^{-\frac{1}{2}\beta\hbar\omega_0}}{1-e^{-\beta\hbar\omega_0}} \cdot \frac{2I}{\beta\hbar^2}$$

This calculation allows us to find $z_{1HD}.z_{1HH}$ and z_{1DD} are single diatomic homonuclear molecule partition functions, they differ from the z_{1HD} case in the amount of degenerated states of the rotation. the amount of degenerated states are $l+1$ instead of $2l+1$ resulting in a factor $\frac{1}{2}$, substituting everything together in the law of mass action gives rise to the *equilibrium constant* of the reaction.

(3) Under the approximation of a very high temperature we can expand the vibrational term into $\frac{1}{\beta\hbar\omega_0}$, in addition we recall that $\frac{1}{\lambda_T^3} = (\frac{m}{2\pi\beta\hbar^2})^{\frac{3}{2}}$. that leads us into the next expression for the single diatomic hetronuclear molecule partition function

$$z_1 = const \cdot m^{\frac{3}{2}} \frac{I}{\omega_0}$$

The kinetic term is related with the translational mass $m_t = m_A + m_B$ and the vibrational and rotational term is related with the reduced mass $m_r = \frac{m_A m_B}{m_A + m_B}$. we recall on the relation between I and ω_0 and the mass, $I = m_r r^2$ and $\omega_0 = \sqrt{\frac{k}{m_r}}$ and get

$$z_1 = const \cdot m_t^{\frac{3}{2}} m_r^{\frac{3}{2}} = const \cdot (m_A m_B)^{\frac{3}{2}}$$

All we have left to do is substituting z_{1HH}, z_{1DD} and z_{1HD} into the law of mass action and get

$$K(\infty) = \frac{z_{1HD}^2}{z_{1HH} z_{1DD}} = \frac{const^2 \cdot (m_H m_D)^3}{const \cdot (m_H m_H)^{\frac{3}{2}} \cdot \frac{1}{2} const \cdot (m_D m_D)^{\frac{3}{2}} \cdot \frac{1}{2}} = 4$$