8.9: Molecular Equilibrium

The dissociation of diatomic molecules can be treated in a way that is very similar to Saha's equation for ionization. Consider, for example, the following reversible reaction

$$\mathrm{AB} \leftrightarrow \mathrm{A}+\mathrm{B} \tag{8.9.1}$$

The equilibrium is governed by an equation that is essentially identical to the Saha equation:

$$\frac{n_{\mathrm{A}} n_{\mathrm{B}}}{n_{\mathrm{AB}}}=K_{\mathrm{AB}}=\left(\frac{2 \pi m k T}{h^2}\right)^{\frac{3}{2}} \frac{u_{\mathrm{A}} u_{\mathrm{B}}}{u_{\mathrm{AB}}} e^{-D_0^0 /(k T)} . \tag{8.9.2}$$

Here K_{AB} is the equilibrium constant, m is $m_{\mathrm{A}} m_{\mathrm{B}} /(m_{\mathrm{A}} m_{\mathrm{B}})$, and D_0^0 is the dissociation energy. To a first approximation the partition function u_{AB} of the molecule is the product of the electronic, vibrational and rotational partition functions, although usually today more precise calculations are made. The equation is often written in terms of partial pressures:

$$\frac{p_{\mathrm{A}} p_{\mathrm{B}}}{p_{\mathrm{AB}}}=K_{\mathrm{AB}}^{\prime} \tag{8.9.3}$$

in which $K'_{AB}=kTK_{AB}$ where the gases may be considered to be ideal.

Let us consider again Problem 5 of section 8.6, in which we have methyl cyanate $\mathrm{CH_3CNO}$ held at some pressure P, but this time we'll work at some temperature where we shall suppose that the only species to be expected would be neutral atoms and neutral diatomic molecules. The species concerned are $\mathrm{C, H, O, N, C_2, CN, CO, CN, H_2, OH, NH, O_2, NO, N_2}$. We shall evidently need 14 equations. They are:

$$n_{\mathrm{C}}+n_{\mathrm{H}}+n_{\mathrm{O}}+n_{\mathrm{N}}+n_{\mathrm{C}_2}+n_{\mathrm{CH}}+n_{\mathrm{CO}}+n_{\mathrm{CN}}+n_{\mathrm{H}_2}+n_{\mathrm{OH}}+n_{\mathrm{NH}}+n_{\mathrm{O}_2}+n_{\mathrm{NO}}+n_{\mathrm{N}_2}=P /(k T), \tag{8.9.4}$$

$$n_{\mathrm{C}}+2 n_{\mathrm{C}_2}+n_{\mathrm{CH}}+n_{\mathrm{CO}}+n_{\mathrm{CN}}=2(n_{\mathrm{N}}+n_{\mathrm{CN}}+n_{\mathrm{NH}}+n_{\mathrm{NO}}+2 n_{\mathrm{N}_2}), \tag{8.9.5}$$

$$n_{\mathrm{H}}+n_{\mathrm{CH}}+2 n_{\mathrm{H}_2}+n_{\mathrm{OH}}+n_{\mathrm{NH}}=3(n_{\mathrm{N}}+n_{\mathrm{CN}}+n_{\mathrm{NH}}+n_{\mathrm{NO}}+2 n_{\mathrm{N}_2}), \tag{8.9.6}$$

$$n_{\mathrm{O}}+n_{\mathrm{CO}}+n_{\mathrm{OH}}+2 n_{\mathrm{O}_2}+n_{\mathrm{NO}}=n_{\mathrm{N}}+n_{\mathrm{CN}}+n_{\mathrm{NH}}+n_{\mathrm{NO}}+2 n_{\mathrm{N}_2}, \tag{8.9.7}$$

$$n_{\mathrm{C}}^2=K_{\mathrm{C}_2} n_{\mathrm{C}_2}, \quad n_{\mathrm{C}} n_{\mathrm{H}}=K_{\mathrm{CH}} n_{\mathrm{CH}}, \quad n_{\mathrm{C}} n_{\mathrm{O}}=K_{\mathrm{CO}} n_{\mathrm{CO}}, \quad n_{\mathrm{C}} n_{\mathrm{N}}=K_{\mathrm{CN}} n_{\mathrm{CN}}, \quad n_{\mathrm{H}}^2=K_{\mathrm{H}_2} n_{\mathrm{H}_2}, \tag{8.9.7-11}$$

$$n_{\mathrm{O}} n_{\mathrm{H}}=K_{\mathrm{OH}} n_{\mathrm{OH}}, \quad n_{\mathrm{N}} n_{\mathrm{H}}=K_{\mathrm{NH}} n_{\mathrm{NH}}, \quad n_{\mathrm{O}}^2=K_{\mathrm{O}_2} n_{\mathrm{O}_2}, \quad n_{\mathrm{N}} n_{\mathrm{O}}=K_{\mathrm{NO}} n_{\mathrm{NO}}, \quad n_{\mathrm{N}}^2=K_{\mathrm{N}_2} n_{\mathrm{N}_2} . \tag{8.9.12-16}$$

The first of these equations is the ideal gas equation. The next three express the stoichiometry of methyl cyanate. The remaining ten, which are nonlinear, are the equilibrium equations. Some skill and experience in the solution of multiple nonlinear simultaneous equations is necessary actually to solve these equations.