17.1: Equilibrium Constant

There are many types of chemical reaction, but to focus our attention we shall consider a reaction involving two reactants A and B which, when mixed, form two resultants C and D. The reaction will proceed at a certain *rate* (fast or slow), and the rate at which the reaction proceeds is part of the subject of *chemical kinetics*, which is outside the scope of this chapter, and to some extent, though by no means entirely, outside the scope of this writer! We shall not, therefore, be concerned with how fast the reaction proceeds, but with what the final state is, and whether the reaction needs some heat to get it going, or whether it proceeds spontaneously and generates heat as it does so.

We shall suppose that the reaction is *reversible*. That is, that either

$$A+B\rightarrow C+D \tag{17.1.1}$$

or

$$\mathrm{C+D\rightarrow A+B} \tag{17.1.2}$$

is possible.

That is

$$A+B\leftrightarrow C+D. \tag{17.1.3}$$

The end result is a dynamic equilibrium in which the rates of forward and backward reaction are the same, and there is an equilibrium amount of A, of B, of C and of D. The question is: How much of A? Of B? Of C? Of D?

Let us suppose that in the equilibrium mixture there are NA moles of A, N_B of B, N_C of C and N_D of D. If we make the reasonable assumption that the rate of the forward reaction is proportional to $N_\mathrm{A}N_\mathrm{B}$ and the rate of the backward reaction is proportional to $N_\mathrm{C}N_\mathrm{D}$, then, when equilibrium has been achieved and these two rates are equal, we have

$$\frac{N_A N_B}{N_C N_D} = \text{"constant"}. \tag{17.1.4}$$

The “constant”, which is called the *equilibrium constant* for the reaction, is constant only for a particular temperature; in general it is a function of temperature.

A simpler type of reaction is the dissociation-recombination equilibrium of a diatomic molecule:

$$\mathrm{AB\leftrightarrow A+B.} \tag{17.1.5}$$

The *dissociation equilibrium constant* is then

$$\frac{N_A N_B}{N_{AB}}. \tag{17.1.6}$$

This “constant” is a function of the temperature and the dissociation energy of the molecule.

A similar consideration obtains for the ionization of an atom:

$$A\leftrightarrow A^+ + e^-. \tag{17.1.7}$$

In this situation,

$$\frac{N_+ N_-}{N_0}, \tag{17.1.8}$$

the *ionization equilibrium constant*, is a function of the temperature and the ionization energy. The equilibrium constants can be determined either experimentally or they can be computed from the partition functions of statistical mechanics. Some details of how to calculate the dissociation and ionization constants and how to use them to calculate the numbers of atoms, ions and molecules of various species in a hot gas are discussed in Stellar Atmospheres, Chapter 8, as well as in papers by the writer in *Publ. Dom. Astrophys. Obs.*, XIII (1) (1966) and by A. J. Sauval and the writer in *Astrophys. J. Supp.*, **56**, 193 (1984).