## 1.6 THE MOLE

The concept of *amount of substance* is central to chemical measurement. The amount of substance of a system is proportional to the number of elementary entities of that substance present in the system. The elementary entities must be described; they may be atoms, molecules, ions, or specified groups of such particles. The entity itself is a natural unit for measuring the amount of substance; for example, we can describe the amount of substance in a sample of iron by saying that there are $2.0 \times 10^{24}$ Fe atoms in the sample. The amount of substance in a crystal of NaCl can be described by saying that there are $8.0 \times 10^{20}$ ion pairs, $Na^+Cl^-$, in the crystal.

Since any tangible sample of matter contains such an enormous number of atoms or molecules, a unit larger than the entity itself is needed to measure the amount of substance. The SI unit for amount of substance is the *mole*. The mole is defined as the amount of substance in exactly 0.012 kg of carbon-12. One mole of any substance contains the same number of elementary entities as there are carbon atoms in exactly 0.012 kg of carbon-12. This number is the Avogadro constant, $N_A = 6.022045 \times 10^{23}\ \mathrm{mol^{-1}}$.

## 1.7 CHEMICAL EQUATIONS

A chemical equation is a shorthand method for describing a chemical transformation. The substances on the left-hand side of the equation are called *reactants*; those on the right-hand side are called *products*. The equation

$$\mathrm{MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2}$$

expresses the fact that manganese dioxide will react with hydrogen chloride to form manganous chloride, water, and chlorine. As it is written, the equation does little besides record the fact of the reaction and the proper formulas for each substance.

If the equation is balanced,

$$\mathrm{MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2},$$

it expresses the fact that the number of atoms of a given kind must be the same on both sides of the equation. Most important, *the balanced chemical equation is an expression of the law of conservation of mass.* Chemical equations provide the relationship between the masses of the various reactants and products, which is ordinarily of utmost importance in chemical problems.

### 1.7.1 Stoichiometry

Consider a system having an initial composition described by a set of mole numbers: $n_1^0, n_2^0, \ldots, n_i^0$. If a reaction occurs, these mole numbers change as the reaction progresses. The mole numbers of the various species do not change independently; the changes are related by the stoichiometric coefficients in the chemical equation. For example, if the reaction of manganese dioxide and hydrogen chloride given above occurs once as written, we say that *one mole of reaction* has occurred. This means that 1 mole of $MnO_2$ and 4 moles of HCl are consumed and that 1 mole of $MnCl_2$, 2 moles of $H_2O$ and 1 mole of $Cl_2$ are produced. After $\xi$ moles of reaction occur, the mole numbers of the substances are given by

$$\begin{aligned} &n_{\mathrm{MnO_2}} = n^0_{\mathrm{MnO_2}} - \xi; \qquad n_{\mathrm{HCl}} = n^0_{\mathrm{HCl}} - 4\xi; \\ &n_{\mathrm{MnCl_2}} = n^0_{\mathrm{MnCl_2}} + \xi; \qquad n_{\mathrm{H_2O}} = n^0_{\mathrm{H_2O}} + 2\xi; \qquad n_{\mathrm{Cl_2}} = n^0_{\mathrm{Cl_2}} + \xi. \end{aligned} \tag{1.1}$$

Since reactants are consumed and products are produced, the algebraic signs appear as shown in Eqs. (1.1).

The variable $\xi$ was first introduced by DeDonder who called it the "degree of advancement" of the reaction. Here we shall call it simply the *advancement* of the reaction. Equations (1.1) show that the composition at any stage of the reaction is described by the initial mole numbers, the stoichiometric coefficients, and the advancement.

We can see how to generalize this description if we rewrite the chemical reaction by moving the reactants to the right side of the equation. It becomes

$$0 = \mathrm{MnCl_2} + 2\mathrm{H_2O} + \mathrm{Cl_2} + (-1)\mathrm{MnO_2} + (-4)\mathrm{HCl}$$

This form suggests that any chemical reaction can be written in the form

$$0 = \sum_i \nu_i \mathrm{A}_i \tag{1.2}$$

where the $A_i$ represent the chemical formulas of the various species in the reaction, and we agree that the stoichiometric coefficients, $\nu_i$, will be given a negative sign for reactants and a positive sign for products. Then we see that each of the mole numbers in Eqs. (1.1) has the form

$$n_i = n_i^0 + \nu_i \xi \tag{1.3}$$

Equation (1.3) is the general relation between the mole numbers and the advancement of any reaction.

Differentiating, we obtain

$$dn_i = \nu_i \, d\xi$$

or

$$\frac{dn_i}{\nu_i} = d\xi \tag{1.4}$$

This equation relates changes of all the mole numbers to the change in the one variable, $d\xi$.

### 1.7.2 The Advancement Capacity

The value of $\xi$ increases as the reaction advances, reaching a limiting value when one or more of the reactants is exhausted. This limiting value of $\xi$ is the *advancement capacity*, $\xi^0$, of the reaction mixture. If we divide Eq. (1.3) by $-\nu_i$, we obtain

$$n_i = (-\nu_i)\left(\frac{n_i^0}{-\nu_i} - \xi\right) \tag{1.4}$$

If we define $\xi_i^0 = n_i^0/(-\nu_i)$, then we have

$$n_i = (-\nu_i)(\xi_i^0 - \xi) \tag{1.5}$$

The quantity, $n_i^0/(-\nu_i) = \xi_i^0$, is called the *advancement capacity* of the $i$th substance. Clearly, if substance $i$ is a reactant, then $-\nu_i$ is positive; thus the advancement capacities of the reactants are all positive. If the values of $\xi_i^0$ are all equal, then this common value of $\xi_i^0 = \xi^0$, the *advancement capacity of the mixture.* If the $\xi_i^0$ are not all equal, then there is at least one smallest value, $\xi_j^0$. This value identifies the substance $j$ as the limiting reagent, and $\xi_j^0 = \xi^0$, the advancement capacity of the mixture. The value of $\xi$ may not exceed $\xi^0$, since that would mean that reactant $j$ (and possibly others) would have a negative mole number. Thus, $\xi^0$ is the greatest value of $\xi$.

Similarly, if the substance $i$ is a product, then $-\nu_i$ is negative and $n_i^0/(-\nu_i) = \xi_i^0$ is negative. Then it is possible, if *none* of the product $n_i$ is zero, for the reaction to move in the reverse direction ($\xi$ is negative). In this case the $\xi_i^0$ are the advancement capacities of the products. If $\xi_k^0$ is the least negative of this set, the substance $k$ is the limiting reagent for the reverse reaction and $\xi_k^0$ is the advancement capacity of the mixture for the reverse reaction. The value of $\xi$ may not be less than $\xi_k^0$, since this would mean that the product $k$ (and possibly others) would have a negative mole number. Thus $\xi_k^0 = \xi_l$, the least value of $\xi$. (Note: quite commonly, no products are present at the beginning of the reaction. Then $n_i^0 = 0$ for all the products; the advancement capacity of the reverse reaction is zero and $\xi$ may only have positive values.)

If the reaction goes to completion, then $\xi = \xi^0$, and the final number of moles of the various species is given by

$$n_i(\text{final}) = n_i^0 + \nu_i \xi^0 = (-\nu_i)(\xi_i^0 - \xi^0) \tag{1.6}$$

If there were no products present initially, then for the product species, $n_i(\text{final}) = \nu_i \xi^0$; the number of moles of any product is the advancement capacity of the mixture multiplied by its stoichiometric coefficient.

The utility of this formulation for simple stoichiometric calculations is illustrated by Example 1.2, in which the quantities appropriate to each species are arranged underneath the formula of that species in the chemical equation. Its utility in other applications will be demonstrated in later parts of the book.

■ **EXAMPLE 1.2** Assume that 0.80 mole of ferric oxide reacts with 1.20 mol of carbon. What amount of each substance is present when the reaction is complete?

| *Equation:* | $Fe_2O_3$ + | $3C$ $\longrightarrow$ | $2Fe$ + | $3CO$ |
|---|---|---|---|---|
| $\nu_i$ | $-1$ | $-3$ | $+2$ | $+3$ |
| $n_i^0$ | 0.80 | 1.20 | 0 | 0 |
| $\xi_i^0 = n_i^0/(-\nu_i)$ | 0.80 | 0.40 | 0 | 0 |
| Therefore, $\xi^0 = 0.40$ | | | | |
| $n_i = (-\nu_i)(\xi_i^0 - \xi)$ | $0.80 - \xi$ | $3(0.40 - \xi)$ | $2\xi$ | $3\xi$ |
| When $\xi = \xi^0 = 0.40$ | | | | |
| $n_i(\text{final}) = (-\nu_i)(\xi_i^0 - \xi^0)$ | 0.40 | 0 | 0.80 | 1.20 |

## 1.8 THE INTERNATIONAL SYSTEM OF UNITS, SI

In the past, several systems of metric units were commonly used by scientists, each system having its advantages and disadvantages. Recently international agreement was reached on the use of a single set of units for the various physical quantities, as well as on a recommended set of symbols for the units and for the physical quantities themselves. The SI will be used in this book with only a few additions. Because of its importance in defining the standard state of pressure, the atmosphere will be retained as a unit of pressure in addition to the pascal, the SI unit. The litre will be used with the understanding that $1\ \mathrm{L} = 1\ \mathrm{dm}^3$(exactly).

Any system of units depends on the selection of "base units" for the set of physical properties that are chosen as a dimensionally independent set. In Appendix III we give the definitions of the base units, some of the most commonly used derived units, and a list of the prefixes that are used to modify the units. You should become thoroughly familiar with the units, their symbols, and the prefixes because they will be used in the text without explanation.