Chapter 3
Escaping Tendency

Abstract The "escaping tendency," notion due to the American scientist G.N. Lewis, is the tendency of a substance to leave its thermodynamic state by either a physical or a chemical process. Firstly, the content of the chapter shows the analogy of the equilibrium distribution of the matter with the thermal one which may exist between two bodies. Secondly, it also shows that the escaping tendency is closely related to the decrease of the Gibbs energy of the studied system which commands the spontaneous process at constant pressure and temperature.

Actually, in order to study the course of a chemical reaction from the thermodynamic standpoint, it is convenient to relate the criterion of the decrease of the Gibbs energy (and of its cancelling at equilibrium) to the chemical properties of the reactants and products of the studied reaction. In the case of ideal gases, it is shown that it is their molal Gibbs energy which is the essential property in the domain. The part played by the molal Gibbs energy in the case of ideal gases induces the introduction of the chemical potential in order to play this part in every kind of system. In addition, the chemical potential is nothing but a particular molal Gibbs energy. Actually, it will be further mentioned in the book that, in turn, the chemical potential induces the introduction of the notions of the auxiliary functions that are the fugacity and the activity for the study of nonideal systems.

The expression "escaping tendency" is due to G.N. Lewis. It is the tendency of a substance to leave its thermodynamic state by either a physical or a chemical process. Quite evidently, it must be closely related to the decrease of the Gibbs energy of the studied system which, as we have seen, commands the spontaneous process at constant pressure and temperature.

Actually, in order to study the course of a chemical reaction from the thermodynamic standpoint, it is convenient to relate the criterion of the decrease of the Gibbs energy (and of its cancelling at equilibrium) to the chemical properties of the reactants and products of the studied reaction. In the case of ideal gases, we shall see that their molal Gibbs energy is the essential property in the domain. The part played by the molal Gibbs energy in the case of ideal gases induces the introduction of the chemical potential in order to play this part in every kind of system. In

addition, it will be seen later that the chemical potential is nothing but a particular molal Gibbs energy. Later on, we shall see that, in turn, the chemical potential induces the introduction of the notions of the auxiliary functions that are the fugacity and the activity for the study of nonideal systems.

3.1 Analogy of the Equilibrium Distribution of the Matter with the Thermal One Between Two Bodies

We know that to make sure that a system is in thermal equilibrium, its temperature must be the same in every point. We also know that every body with a temperature higher than that of another tends to leave its heat. This is not the case of the second body. The tendency to leave heat of the first body is higher than that of the second one.

By analogy with this case, one may conceive that a substance of a system may exhibit some tendency to modify its thermodynamic state by changing its moles number. Lewis has introduced and also kept the name "escaping tendency" to this tendency.

The material equilibrium condition for this substance, that is to say the equilibrium of the distribution of its number of moles, is such that its escaping tendency might be the same at every point of the system.

Hence, as a first example, we must consider the system of water and ice. The escaping tendency at the fusion point of both phases is the same. At lower temperature, we may consider that the escaping tendency of water is larger than that of ice, since it tends to disappear. It, actually, spontaneously transforms into ice. The inverse is true for the temperatures which are higher than that of the fusion point.

A second example is provided by the system made up by a solute in a solvent, as for example a solution of sodium chloride in water. The escaping tendency of sodium chloride may be either higher or lower than that of solid sodium chloride (or equal) depending on whether the solution is saturated or not. In the first case, the sodium chloride spontaneously crystallizes. Just at the saturation point, there exists the equilibrium. In the last case, the solid sodium chloride is endowed with a larger escaping tendency than that it possesses in solution. Hence, it disappears by solubilization.

3.2 The Molal Gibbs Energy of a Substance as a Measure of Its Escaping Tendency

Let us again consider the example consisting of water and ice at 0 °C and under 1 atm. Owing to the fact that the system is maintained at constant pressure and temperature, it is judicious to reason by considering the Gibbs energies of both

phases. The status of thermodynamic potential conferred to this function permits to rationalize the evolution of the process.

Hence, let us consider the transformation

$$H_2O_{(solid, \ 1 \ atm.)} \ \rightarrow \ H_2O_{(liq, \ 1 \ atm.)}$$
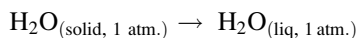
or its inverse. Let ΔG be the change in Gibbs energy accompanying it:

$$\Delta G = G_{liq} - G_{solid}$$

At equilibrium, at the melting point, under the pressure of 1 atm

$$G_{liq} = G_{solid}$$

At a temperature higher than the previous one, the transformation follows the direction already indicated since $G_{ice} > G_{liq}$. At a lower temperature, it is the inverse $\left(G_{liq} > G_{ice} \right)$.

Hence, the molal Gibbs energy may be used to quantify the escaping tendency of a substance. We must remark that the molal Gibbs energy function is an intensive quantity since it is related to one mole of substance. As a result, it is independent of the number of moles of substance. Of course, this example is particularly simple since the system only contains one substance. Only the temperature, pressure, and number of moles of the substance play a part as variables permitting to reach the equilibrium.

It remains to relate the molal Gibbs energy of a substance to the thermodynamic parameters of the system. This is done through the introduction of auxiliary functions such as the fugacity and the activity. Later, in turn, relating these last functions to some molecular parameters will be considered. The link will be obtained through application of statistical thermodynamics.

3.3   Change of Molal Gibbs Energy of a Perfect Gas with Pressure

In this paragraph, we give a relation expressing the Gibbs energy of a perfect gas as a function of the pressure. As we shall see later (viz. Chaps. 7 and 9) this relation is particularly important since it can be considered as a limit of the expression relating the chemical potential of a substance in a given thermodynamic state to its activity or to its fugacity.

Let us recall that a perfect gas can be defined by the fact that it obeys an equation called state equation which is

$$\mathbf{p}V = nRT$$

where $\mathbf{p}$ and T are the pressure and the temperature of the gas, n its number of moles, and V the volume of the container into which it is. R is the (molar) gas constant. (Some complements concerning perfect gases are given in Chaps. 26 and 27.) By definition, the state equation of a system is the relation which occurs between the different state variables thermodynamically defining the system at equilibrium.

Let us study the infinitesimal isothermal expansion of a pure perfect gas. We know that (viz. Chap. 2)

$$dG = Vd\mathbf{p} - SdT$$

At constant temperature

$$dG = Vd\mathbf{p}$$

whence from the state equation

$$dG = nRT\,d\mathbf{p}/\mathbf{p}$$

From the change in pressure from $\mathbf{p}_A$ to $\mathbf{p}_B$, the change in the Gibbs energy ΔG accompanying the process is

$$\Delta G = G_B - G_A$$
$$\Delta G = nRT\int_{PA}^{PB} d\mathbf{p}/\mathbf{p}$$
$$\Delta G = nRT\ln(\mathbf{p}_B/\mathbf{p}_A)$$

We notice that the Gibbs energy of a perfect gas depends on the pressure. (In passing, let us recall that this is not the case of its internal energy nor of its enthalpy.)

Usually, the Gibbs energy of a gas is related to that $G°$ it possesses in a state called the "standard state" which is arbitrarily chosen and in which its pressure is $\mathbf{p}°$ and also in which its temperature is arbitrarily chosen to be T. (The imposition of a given temperature does not intervene in the definition of a standard state.) Its molal Gibbs energy G is then given by the relation

$$G = G° + RT\ln\mathbf{p}/\mathbf{p}° \tag{3.1}$$

When the pressure chosen for the standard state is $\mathbf{p}° = 1$ atm, its molal Gibbs energy is then given by

$$G = G° + RT\ln(\mathbf{p}_{atm}/1_{atm})$$

The index atm is used here to recall that $\mathbf{p}$ and 1 are physical quantities endowed with a dimension. The writing often encountered in the literature when $\mathbf{p}° = 1$ atm, i.e.,

$$G = G° + RT \ln \mathbf{p}$$

is fallacious. It appears, indeed at first sight, owing to the properties of the function logarithm, that the pressure is a dimensionless quantity!

3.4   Gibbs Energy Change Accompanying a Reaction Between Perfect Gases

Let us consider the following chemical reaction going to completion:

$$\nu_M M + \nu_L L \ \rightarrow \nu_N N + \nu_P P$$
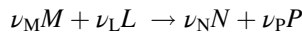
where ν_L, ν_M, ν_N, and ν_P are the stoichiometric coefficients. Our goal is to calculate the maximal work which can be done by this system at constant temperature and pressure. This calculation may be carried out by taking into account the properties of the Gibbs energy function (viz. Chap. 2). The important point, in the occurrence, is that the maximal work available is equal (in absolute values) to the change in the Gibbs energy. Let us define the system as being constituted by the four gases. The change in the Gibbs energy $\Delta_r G_{\text{syst}}$ accompanying the above total transformation is

$$\Delta_r G_{\text{syst}} = \nu_N G_N + \nu_P G_P - \nu_L G_L - \nu_M G_M \tag{3.2}$$

where G_L and G_M are the molal Gibbs energies of L and M in the initial state and G_N and G_P those of N and P in the final state. *It is very important to notice at this point of the reasoning that relation (3.2) taking into account the molal Gibbs energies can be used,* here, *because the process concerns perfect gases which in mixtures exhibit the same behavior as that they have when they are alone. It is this property which authorizes the handling, in the present case, of the molar Gibbs energies and expression of them by relation (3.1).*
  By replacing G_i by their expressions (3.1), one obtains

$$\Delta_r G_{\text{syst}} = \Delta G° - RT \ln \left(\mathbf{p}_N{}^{°\nu N} \mathbf{p}_P{}^{°\nu P} / \mathbf{p}_L{}^{°\nu L} \mathbf{p}_M{}^{°\nu M} \right) + RT \ln \left(\mathbf{p}_N{}^{\nu N} \mathbf{p}_P{}^{\nu P} / \mathbf{p}_M{}^{\nu M} \mathbf{p}_L{}^{\nu L} \right) \tag{3.3}$$

or

$$\Delta_r G° = \nu_N G_N{}° + \nu_P G_P{}° - \nu_L G_L{}° - \nu_M G_M{}°$$

$\Delta_r G°$ is evidently a constant at a given temperature.

Hence the change in Gibbs energy accompanying the reaction (3.2) where the perfect gases L and M, initially at pressures $\mathbf{p}_M$ and $\mathbf{p}_L$, are transformed at constant temperature and pressure into the perfect gases N and P at pressures $\mathbf{p}_N$ and $\mathbf{p}_P$, is given by the expression (3.3). We shall see (viz. Chap. 7) that the pressures $\mathbf{p}_M$, $\mathbf{p}_L$ and $\mathbf{p}_N$, $\mathbf{p}_P$ are, in the occurrence, called partial pressures. In these conditions, $\Delta_r G_{syst}$ is the maximal work available from the chemical energy supplied by the gases L and M. This process may be actually realized with a convenient galvanic cell working in the conditions of reversibility.

Unfortunately, in the case of reactions between non-perfect gases and also in the case of reactions between components in solutions, the problem of the calculation of the Gibbs energy changes accompanying the chemical reaction is not so simple to solve, as we shall see in the following chapters.