

## Chapter 36

# Chemical Equilibrium Between Gases and Statistical Thermodynamics

**Abstract** The chapter mentions an overview of the study of the chemical equilibrium from the standpoint of statistical thermodynamics. This subject is quite evidently of importance since equilibrium constants between gases (and also between species in solutions) are expressed in activity or fugacity terms once they do not exhibit an ideal behavior.

After a brief recall of the equilibrium condition in classical thermodynamics, several examples of chemical equilibria are examined from the viewpoint of statistical thermodynamics. Finally, the case of equilibria between imperfect gases is dealt with. It is in this context that activities and fugacities play an important part. From the developments of the chapter, it appears that the thermodynamic equilibrium constants are only function of the partition functions of the species involved in the equilibrium together with the stoichiometry of the reaction. The described theory is carried out within the framework of the canonical ensemble.

**Keywords** Chemical equilibria between gases and statistical thermodynamics • Partition function • Equilibrium constants and molecular partition functions • Absolute activities • Equilibrium constants and partition functions • Equilibrium constants expressed in activities and in concentrations

In this chapter, we give an overview of the study of the chemical equilibrium from the standpoint of statistical thermodynamics. This subject is quite evidently of importance since equilibrium constants between gases (and also between species in solutions) are expressed in activity or fugacity terms once they do not exhibit an ideal behavior.

After a brief recall of the equilibrium condition in classical thermodynamics, we study several examples of chemical equilibria from the viewpoint of statistical thermodynamics. Finally, we deal with the case of equilibria between imperfect gases. It is in this case that activities and fugacities play their part.

## 36.1 Some Recalls: Chemical Equilibria and Classical Thermodynamics

Let us recall (viz. Chap. 6) that, for example, for a reaction of the kind:



evolving in a closed system at constant pressure and temperature, the equilibrium condition from the standpoint of classical thermodynamics is given by the following expression, which must be satisfied:

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C \quad (36.2)$$

where the  $\nu_i$  are the stoichiometric coefficients and the  $\mu_i$  the chemical potentials, once the chemical equilibrium is reached. Let us also recall that this condition is general. Not only does it apply to ideal (or not) gases but also it applies to all types of chemical equilibria whether they occur between gases or not. It is a consequence of the second principle of thermodynamics.

## 36.2 Equilibrium Constants and Molecular Partition Functions of the Reactants and Products: Case of a Mixture of Ideal Gases

Let us consider the case of the reaction (36.1) in which the reactants and products A, B, and C are perfect gases. In order to treat the problem of this equilibrium from the statistical standpoint, we must relate the chemical potentials appearing in relation (36.2) to the partition function  $Q$  of the whole system and, through it, to the molecular partition functions  $q$  of every reactant and product participating to the equilibrium (viz. Chap. 26).

The first point we must take into account is that since the gases are perfect, their behaviors are independent from each other. They are as if they were alone in the container. This point is very important. Let us anticipate that is following by asserting that this property differentiates them from imperfect gases. More specifically, in the case of perfect gases, it is not fruitful to introduce the notions of activity and fugacity in order to express the equilibrium constants.

(At this point of the reasoning, the ability to express the equilibrium constants as a function of the activities and fugacities under an analogous form as in the case of equilibria between perfect gases probably constitutes the major practical interest of the introduction of the notions of activity and of fugacity.)

We know that when the gas (monoatomic, diatomic, or polyatomic) is *alone*, the partition function of the system  $Q$  can be written ( $q$  being the molecular partition function and  $N$  the number of molecules) (viz. Chap. 26):

$$Q(N, V, T) = q(V, T)^N / N!$$

Let us also recall that according to the fact the gas is monoatomic or polyatomic,  $q$  may be (or not) a composite function. For a mixture of two perfect gases 1 and 2 (and hence independent), the canonical partition function of the system is given by the general relation:

$$Q(N_1, N_2, V, T) = \left[ q_1(V, T)^{N_1} / N_1! \right] \left[ q_2(V, T)^{N_2} / N_2! \right] \quad (36.3)$$

$N_1$  and  $N_2$  are the numbers of moles of 1 and 2. The product of the molecular partition functions must be considered because each of all the levels of energy of molecule 2 can be associated with every level of molecule 1, since the gases are independent. Let us insist on the fact that the partition function  $Q(N_1, N_2, V, T)$  is that of the system composed by  $N_1$  molecules of 1 and by  $N_2$  molecules of 2.

The relation between the chemical potentials of the species participating to the equilibrium and the system partition function is that very general already seen (viz. Chap. 26):

$$\mu_i = -kT \left( \partial \ln Q(N_i, N_j, T, V) / \partial N_i \right)_{T, V, N_j} \quad (j \neq i) \quad (36.4)$$

The calculation of  $\mu_1$  and  $\mu_2$  by starting from (36.3) by taking into account (36.4) easily leads to the following expressions (after the use of the Stirling's approximation):

$$\mu_1 = -kT \ln [q_1(V, T) / N_1] \quad \text{and} \quad \mu_2 = -kT \ln [q_2(V, T) / N_2] \quad (36.5)$$

Hence, we deduce that the chemical potential of each of the gas is the same as it would be alone, provided, of course, that the mixture behaves "ideally."

Let us apply to the reaction (36.1) the equilibrium condition (36.2) while taking into account expressions (36.5) permitting the calculation of the different chemical potentials, taking granted the fact that the canonical partition function of the system  $Q(N_A, N_B, N_C, T, V)$  is then given by the following expression:

$$Q(N_A, N_B, N_C, T, V) = \left[ q_A(T, V)^{N_A} / N_A! \right] \left[ q_B(T, V)^{N_B} / N_B! \right] x \left[ q_C(T, V)^{N_C} / N_C! \right]$$

We obtain:

$$N_C^{v_C} / N_A^{v_A} \cdot N_B^{v_B} = q_C^{v_C} / q_A^{v_A} q_B^{v_B} \quad (36.6)$$

$N_C$ ,  $N_A$ , and  $N_B$  are the numbers of molecules of C, A, and B at equilibrium.

The expression (36.6) can be differently written by introducing the density numbers  $\rho$  of the species. It is an easy task since the number of density is defined

as being the ratio of a number of molecules of a species and of the volume  $V$  of the system:

$$\rho_i = N_i/V$$

By dividing all the terms of expression (36.6) by  $V$  brought to the corresponding power, we obtain:

$$\rho_C^{v_C} / \rho_A^{v_A} \cdot \rho_B^{v_B} = (q_C/V)^{v_C} / (q_A/V)^{v_A} \cdot (q_B/V)^{v_B} \quad (36.7)$$

An important point to highlight is that the molecular partition functions  $q$  are equal to the volume  $V$  of the system multiplied by a function which only depends on the temperature, since they are of the type  $q = V \cdot f(T)$ . We have seen, indeed, (viz. Chap. 26) that:

$$q(V, T) = V(2\pi mkT/h^2)^{3/2} \quad (\text{perfect gas monoatomic gas})$$

$$q(V, T) = V[2\pi(m_1 + m_2)kT/h^2]^{3/2} \quad (\text{perfect diatomic gas})$$

$$q(V, T) = V \left[ 2\pi \left( \sum_i m_i \right) / kT/h^2 \right]^{3/2} \quad (\text{perfect polyatomic gas})$$

As a result, whatever the gas (monoatomic or polyatomic) is, the right member of the expression (36.7) only depends on the temperature. Hence, we can write:

$$\rho_C^{v_C} / \rho_A^{v_A} \cdot \rho_B^{v_B} = K(T) \quad (36.8)$$

Therefore, the mass action law is confirmed on the bases of statistical thermodynamics.

### 36.3 A Simple Example: A Dimerization Equilibrium

As an example, let us consider the following equilibrium of dimerization at constant volume and temperature:



Contrary to the preceding problem in which we wanted to relate the equilibrium constant value to those of the numbers moles existing at equilibrium, our present goal, here, is to obtain the numbers of moles of A and B once the equilibrium is reached, with the constraint that the initial matter must be conserved.

This constraint is explicit by the equality:

$$2N_A + N_B = N \quad (N : \text{constant})$$

Let  $N_A^0$  and  $N_B^0$  be the number of molecules A and B initially present in a container of volume  $V$  at the temperature  $T$ . From the experimental viewpoint, the obtaining of the equilibrium at constant volume and temperature can be obtained, for example, by addition of a catalysor, whereas, initially, the mixture was frozen to the number of moles  $N_A^0$  and  $N_B^0$  such as:

$$2N_A^0 + N_B^0 = N$$

The partition function of the system in the initial state  $Q(N_A^0, N_B^0, V, T)$  is given, as we have seen it previously, by the expression:

$$Q(N_A^0, N_B^0, V, T) = q_A^{N_A^0} / N_A^0! \quad q_B^{N_B^0} / N_B^0! \quad (36.9)$$

According to considerations of thermodynamics, we know that the equilibrium is reached when the Helmholtz energy  $A = -kT \ln Q$  of the whole system is minimized, i.e., when the function  $Q$  is maximal. Hence, the problem is to search for the number of moles  $N_A^*$  maximizing  $Q$ , the following constraint:

$$2N_A^* + N_B^* = N$$

being obligatorily satisfied. It is quite evident that it is not necessary to separately search for the value  $N_B^*$  since the mole numbers  $N_A^*$  and  $N_B^*$  are related to by the preceding expression. Hence, to solve the problem, it is sufficient to set up:

$$(\partial \ln Q / \partial N_A)_{N, V, T} = 0$$

It is a “mathematical fact” that the function  $Q$  is then maximal. We obtain:

$$N_B^{*2} / N_A^* = q_B^2 / q_A$$

This result is perfectly analogous to that previously obtained. The equilibrium constant is given by the expression:

$$K(T) = \rho_B^2 / \rho_A$$

Let us highlight the fact that the value of the canonical partition function regarded in this example  $Q(N_{A0}, N_{B0}, V, T)$  is imposed by the number of moles of species A and through it by that of B. Recall, indeed (viz. Chap. 21), that the different energetic states allowed by quantum mechanics are a function of the volume  $V$  and of the number of moles of the system. In the present case, the study is performed with the number of moles  $N_A^0, N_B^0$ , and  $N$  which are certainly arbitrary but fixed numbers.

### 36.4 Chemical Equilibrium Between Imperfect Gases

When one studies the equilibria between imperfect gases, the mass action law, as we shall see it now, is expressed in terms of activities and, no longer, in terms of density numbers. In order to study such a case, let us again consider the case of a dimerization equilibrium:



The equilibrium condition remains:

$$\mu_A = 2\mu_B$$

or, in terms of absolute activities:

$$\lambda_A = \lambda_B^2 \quad (36.10)$$

since the chemical potential of a species is related to its absolute activity through the relation  $\lambda = e^{\mu/kT}$ . We know that when the density numbers are sufficiently weak, the behavior of the species tends to be ideal and we have seen that (viz. the above paragraph) the equilibrium constant expresses as a function of them:

$$K(T) = \rho_B^2 / \rho_A$$

with:

$$K(T) = (Q_{01}/V)^2 / (Q_{10}/V)$$

the indices 01 and 10, respectively, being referred to compounds B and A. Symbols  $Q_{10}$  and  $Q_{01}$ , respectively, are related to the canonical partition functions of systems of only 1 molecule of 1 and of 0 molecule 2 on one hand and of 0 molecule of 1 and of 1 molecule of 2 on the other.

When the behavior is no longer perfect, the chemical potential must be expressed as a function of the activity of the species and not as a function of the density number as before in order to keep its significance of the tendency of the species to change its thermodynamic state. Finally, *the chemical potential when it is related to the activity of a species, quantifies its tendency to react according to physical or chemical transformations while taking into account its interactions with the other species of the medium.*

The equilibrium constant is expressed as a function of the activities with the help of the following reasoning. The equilibrium condition (36.10) expressed as a function of the absolute activities remains valid. From another standpoint, by definition of the activity  $z$  in statistical thermodynamics:

$$\lambda_A = Vz_A/Q_{10} \quad \text{and} \quad \lambda_B = Vz_B/Q_{01}$$

By applying relation (36.10), we immediately obtain:

$$z_B^2 V^2 / Q_{01}^2 = z_A V / Q_{10}$$

and since the ratios  $Q/V$  are only function of temperature:

$$K(T) = z_B^2 / z_A$$

It can also be written, by taking into account the activity coefficients  $\gamma_B$  and  $\gamma_A$  (viz. the following chapter):

$$K(T) = \rho_B^2 \gamma_B^2 / \rho_A \gamma_A$$

They are given by the expressions (viz. the preceding chapter):

$$z_A = \rho_A - 2b_{02}\rho_A^2 - b_{11}\rho_B\rho_A + \dots$$

As a result:

$$K(T) = \left( \rho_B^2 / \rho_A \right) [1 + (b_{11} - 4b_{20})\rho_B + \dots]$$

The term in square brackets expresses the deflection with respect to the “ideality.” Actually, we notice that:

$$K(T) = \left( \rho_B^2 / \rho_A \right)$$

when  $\rho_B$  and  $\rho_A$  tend toward zero.

The definition of the formal, or conditional constant  $K'(T)$  used, once the behaviors are no longer ideal, by the expression:

$$K'(T) = \left( \rho_B^2 / \rho_A \right)$$

differs from the thermodynamic constant  $K(T)$  by the term located between the square brackets. It varies with  $\rho_B$  and  $\rho_A$ .