

## Chapter 6

# The Notion of Activity: An Overview

**Abstract** The chapter is a brief overview of the concept of activity. It can be considered as a general scientific introduction of the book. It mentions:

- Some properties of the quantity activity in relation to the chemical equilibria governed by the mass action law.
- Its relation with the corresponding concentration and the chemical potential of the substance, with its standard state and the arbitrary character of the choice of the latter.
- The link between a fugacity and an activity.
- The ideal character of a system and interactions between the particles constituting it and the intermolecular forces which may exist between them.

The possibility of their determination is also tackled. Finally, a recall of the genesis of the notion of activity is given.

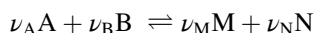
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It seems interesting for us, as a general scientific introduction of the book, to give a brief overview of the concept of activity before, of course, delving later into its more thorough study.

### 6.1 Some Properties of the Quantity Activity: Activities and Chemical Equilibria

A patent example of the interest in chemistry of the use of activities is the following.

Let us, for example, consider the following chemical reaction:



We shall see (viz. Chap. 17) that, *at equilibrium*, the activities  $a_A, a_B, \dots$  of the different species A, B, M, and N (participating in it through the relation above) are related to each other by the expression

$$K^\circ = a_M^{\nu_M} a_N^{\nu_N} / a_A^{\nu_A} a_B^{\nu_B} \quad (6.1)$$

This result is quite general.

Let us stress the fact that the activities taken into account in relation (6.1) are those and only those occurring once the equilibrium is reached.  $K^\circ$  is a constant at a given temperature. It is called *the standard equilibrium constant* (of the reaction) or *the thermodynamic equilibrium constant*. Relation (6.1) is well known under the name “mass action law.” Historically, it is interesting to recall in passing that it has been introduced into the scientific realm by starting from a reasoning which was not at all based on thermodynamic considerations!

The thermodynamic equilibrium constant  $K^\circ$  only depends on the temperature and pressure and not on the composition of the system. It is a true constant. This obvious sentence will take all its importance during the reading of the end of this chapter.

The thermodynamic constant must not be confused with the corresponding constant  $K$  which is related to the concentrations at the equilibrium of the reactive species, defined for the above reaction by the expression

$$K = [M]^{\nu_M} [N]^{\nu_N} / [A]^{\nu_A} [B]^{\nu_B} \quad (6.2)$$

The terms in brackets in the expression (6.2) are the concentrations at equilibrium. They can be expressed in molalities, molarities, molar fractions ... (viz. Chap. 1). The constant  $K$  may also be expressed in partial pressures. Each of these cases must be, in principle, distinguished from each other by an index located next to the symbol  $K$ . For example, the constant  $K$  is symbolized by  $K_c$  and  $K_m$  when the concentrations are expressed, respectively, in molarities and molalities.

Whereas thermodynamic equilibrium constants are absolutely dimensionless numbers since activities are themselves dimensionless, the equilibrium constants related to the concentrations may be dimensioned according to the stoichiometry of the reaction. The latter equilibrium constants are often called *formal or conditional constants*. They do not only depend on the temperature and total pressure. They also depend on the concentrations of the reactive species.

## 6.2 Activities and Concentrations

The activity  $a$  of a species in a given medium is related to its “concentration”  $C$  through the general expression

$$a = \gamma C \quad (6.3)$$

The factor  $\gamma$  is called *the activity coefficient*. The activity of a species and its concentration obey this relation, whatever the concentration scale is. Hence, this relation is general. Let us say that although the activities are dimensionless, the activity coefficients are also dimensionless whatever the scale of concentration  $C$  is.

The very big difficulty encountered in the handling of activities lies in the fact that relation (6.3) is not, actually, a true linear relation because the activity coefficient  $\gamma$  does vary with the “concentration”  $C$ . Here is the reason why the analogy between relations (6.1) and (6.2) must not mask the fact that the mathematical link between an activity and the corresponding concentration is complex and badly known. It is the matter of this book to somewhat make it clearer.

From another viewpoint, it must not be forgotten that there exist several kinds of activities which are of different numerical values for the same species in the same thermodynamic state according to the chosen standard state (*viz.* under) and the concentration scale to which they are related to and, eventually, according to the conditions defining the state of the system.

### 6.3 Chemical Potential and Activity of a Compound

We know (*viz.* Chap. 5) that one of the most central quantities of chemical thermodynamics is the chemical potential. Let us recall also that, essentially, its change governs the tendency of a system to change its thermodynamic state through a chemical or physical process.

One of the possible definitions of the activity of a species consists in using the relation (6.4) linking it to its chemical potential:

$$\mu = \mu^\circ + RT \ln a \quad (6.4)$$

where  $R$  is the perfect gas constant and  $T$  the absolute temperature of the system.  $\mu^\circ$  is an *arbitrary* constant. We see that it is the chemical potential of the compound when its activity equates to unity.  $\mu^\circ$  is called the *standard chemical potential* of the species or more properly its *chemical potential in the standard state*.

### 6.4 Standard State and Activity

Relation (6.4) is only a formal definition. Hence, further, the standard state must be defined in terms of experimental variables defining this particular thermodynamic state.

Owing to the arbitrary character of a standard state, which is one of the characteristics of this quantity, it is clear that there exists an infinity of choices

for it. However, it turns out that some choices are easier to handle than others. Precisely, these choices can change according to the state of the matter of the compound (gaseous, liquid, solid), according to whether it is pure or in a solution and also according to the concentration scale of the species to which it is related to through relation (6.3).

The result of these considerations is that the notion of activity cannot be dissociated from that of standard state.

## 6.5 On the Arbitrary Character of the Choice of the Standard State

A puzzling point of the concept of the chemical activity lies in the arbitrary character of the choice of the concentration scale to which the chemical activity of the species is related to. One must realize that, for example, it is as correct to choose the molar fraction as to choose its molality or its molarity to express its concentration. Then, one can rise the legitimate question of the validity of the equilibrium constant value, which evidently varies with the choice of the retained scale of concentration, since the numerical values of the “concentrations” are then different. With this question in mind, it is quite admissible that the conclusions stemming from the study of a chemical equilibrium through the value of the equilibrium constant may be doubtful.

## 6.6 Activity and Fugacity

Although this book is mainly devoted to the concept of activity, it also mentions some aspects of the quantity called the fugacity.

Both notions are actually intimately linked. It is true that they can be separately introduced in the realm of classical thermodynamics without any mention of the other. This is not astonishing since the concept of fugacity was introduced to study the behavior of imperfect gases whereas that of activity was introduced mainly for the study of solutions. However, as we shall see it later, both can apply to every kind of phase.

There exist some simple mathematical relations linking them. Besides, they permit us to better grasp their significances. In particular, let us mention the occurrence of a very important one which, purely and simply, is one of the definitions of the chemical activity. According to it, the chemical activity is the ratio of the fugacity of the species of concern and of its fugacity in the standard state.

## 6.7 Ideal Character of a System and Interactions Between the Particles Constituting It

In the general introduction of this book, we have already recalled that the notion of chemical activity has been introduced by G.N. Lewis in order to treat the nonideal systems (in particular solutions) by using a formalism very close to that expressing the chemical potentials of species in ideal systems.

The ideal character of a system is related to the occurrence (or not) of interactions between particles constituting it. It has a somewhat different meaning according to the fact whether it is a gaseous phase or a solution which is considered. Even in the latter case, the conditions of “ideality” differ whether electrolyte or nonelectrolyte solutions are considered.

A pure gas is said ideal if no interaction does exist between its particles. It is the case when its pressure is very weak. Its behavior remains ideal as long as these interactions cannot be felt. It is the same thing for a gaseous mixture. Its behavior remains ideal as long as there do not exist interactions between the particles of the mixture whatever their component identity is.

It is different in the case of solutions. At least, there exist two components, the solute and the solvent, the particles of which are in interactions. Let us recall, indeed, that the gaseous state is a very “expanded” one in which the volume occupied by the particles is negligible with respect to that of the container. Hence, one can consider that it is only occasionally that two particles are sufficiently close to give rise to intermolecular forces. One can consider that the gas molecules move freely. This is not the case of liquids and solutions. Concerning the latter, the total volume of molecules quasi-fully occupies the whole volume of the system. The intermolecular forces are strong. However, they cannot preclude the easy movement of the particles in the medium. This is not the case for the other compact state of the matter which is the solid state. As a result, one can say that evoking the “ideality” notion to liquids, as it applies to the case of gases, is absurd, because of the occurrence of the remaining interactions between solvent and solute particles, even in highly dilute solutions.

A particularly interesting case of solutions is that of those containing ions. For the latter, the interactions between solute particles still exist at distances much higher than those separating two uncharged species when, precisely, the interactions in the latter case are vanishing. Hence, deviations from “ideality” appear for concentrations in charged molecules much weaker than with the uncharged ones. For example, in an aqueous solution of sodium chloride, deviations from thermodynamic laws expressing the ideal behavior by more than 5 % do appear once their concentration attains  $2 \times 10^{-3} \text{ mol L}^{-1}$ . In solutions only containing uncharged particles, the concentration of at least  $1 \text{ mol L}^{-1}$  must be reached to obtain such deviations.

At once, let us notice that the more dilute the solutions are, the weaker the interactions between the solute molecules or between the ions are and the more the activity values do approach those of the corresponding concentrations. It is the

same for gases. The weaker their partial pressures, the closer their fugacity values approach those of the latter. These properties are very interesting since they provide us with a strategy for the determination of equilibrium thermodynamic constants. It consists in determining them in very dilute solutions or at very weak partial pressures. It is at this level of quantities of matter that the reliability of the values of the obtained thermodynamic equilibrium constants may be expected to be good.

## 6.8 Intermolecular Forces

Intermolecular forces that operate between the molecules of a pure substance or between the molecules of a mixture command the thermodynamic properties of the system constituted by them. Since it is these intermolecular forces that are responsible for the deviations from “ideality” exhibited by a system and since the chemical activities have been introduced to overcome the problem, it is interesting to briefly evoke these operating intermolecular forces. The intermolecular forces give rise to potential energy functions. This term is often used to explicit the force.

Several intermolecular forces are operating and, hence, they can be classified in several different manners. The different retained classifications are purely arbitrary. For our own part, we distinguish:

- The electrostatic forces they exert between charged particles (ions) and between permanent dipoles and quadrupoles.
- The induction forces they exert between a permanent dipole (or quadrupole) and an induced dipole. The latter is induced in a molecule with polarizable electrons.
- The forces of attraction called dispersion forces and the forces of repulsion between nonpolar molecules.
- The chemical forces (or specific forces) responsible for association and solvation phenomena: Among them, we can mention the formation of hydrogen bonds and association complexes called charge-transfer complexes.

Further considerations of these intermolecular forces are given in Chap. 46.

## 6.9 Determination of Activities

The determination of activities of all types of compounds is experimentally possible *except* in the case of ions. This is a fact: the activity of an individual ion is not measurable. However, fortunately, its value can be approached, at least in some well-defined conditions, by using theoretical expressions which permit the calculation of activity coefficients.

## 6.10 Genesis of the Chemical Activity Concept

G.N. Lewis has successively introduced the concepts of fugacity (1901) and activity (1907). According to his own comments, two strategies were in this period followed in order to study chemical equilibria.

The first one, followed in particular by Gibbs, Duhem, Planck, and other authors, consisted in forecasting the evolution of systems by using the properties of their entropy and also those of their thermodynamic potentials (viz. Chap. 2).

The second strategy, followed by Van't Hoff, Ostwald, Nernst, Arrhenius, and others, consisted in using equilibrium constants, *calculated through the concentration values at the equilibrium* because the notion of intangibility of the values of the equilibrium constants was already sensed since some years.

Today, we know that handling the thermodynamic potentials is perfectly legitimate, but it is complicated in the realm of chemistry, by far more complicated than in mechanics. This is the reason why the second method is more used than the previous.

But using the second strategy, at that time, led to the following conclusion:

Equilibrium constants calculated by using concentrations at equilibrium are not truly constant.

This conclusion was followed by a series of numerous discussions and works essentially devoted to the case of electrolytes. The question was the following one: Do the equilibrium constants vary because of an incomplete dissociation of the electrolyte or because of another phenomenon? The hypothesis of an incomplete dissociation of actually strength electrolytes has been ruled out, notably with the help of conductometric experiences and thanks to the Debye–Hückel relations. Today, we know that the changes in the equilibrium constant values, when they are obtained only from concentrations at equilibrium, are the result of interactions between the species and not to an incomplete dissociation. Because of their occurrence, it is said that the system no longer exhibits an *ideal* behavior.

It is in order to mathematically take into account this phenomenon that Lewis has empirically introduced the notion of chemical activity. Likewise, he had introduced the fugacity concept some years before. It was, of course, in order to take into account the interactions between molecules of gas.

It is important to notice that taking into account the interactions between the particles by the introduction of both notions of fugacity and activity stems from a purely phenomenological reasoning. A rigorous theoretical study which would take perfectly into account these phenomena of “nonideality” would require that the term of the potential energy of the Schrödinger’s equation of the whole system would contain all the terms describing the interactions between all the particles. This is quite impossible to do, because on the one hand one cannot know how we can perfectly modelize the interactions between these moving particles and because, on the other hand, if we did know how to do, it would be an insuperable work to carry out it, owing to the great number of particles.

Hence, it appears that the introduction of the notion of chemical activity is a genial trick permitting to overcome this colossal problem.