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LECTURE TEXT

Understanding Lewis activities

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Abstract

The notion of activity is of a purely thermodynamic nature. It is intimately linked to the *law of mass action* and more generally to that of equilibrium constant. It was conceived and introduced in the realm of chemistry at the beginning of twentieth century by Lewis (Proc Am Acad Arts Sci 37:49–69, 1901; Proc Am Acad Arts Sci 43:259–293, 1907; J Am Chem Soc 30:668–683, 1908) and Lewis and Randall (Thermodynamics and the free energy of chemical substances. McGraw-Hill Book Company, London, 1923). Its introduction permits us to overcome insuperable theoretical and practical difficulties encountered in chemistry, physics and biochemistry with great ease. Before discussing the notion of activity, it is necessary to introduce ideal and non-ideal chemical systems, the different scales of unities permitting one to express their composition and the concept of chemical potential. Here, we seek to locate the notion of activity within the framework of classical thermodynamics. We shall see that its introduction in chemistry enables us to generalize the use of the Gibbs energy function (formerly, and still in German, called the free enthalpy function) for introducing the concept of chemical equilibrium. This is carried out by the introduction of the pivotal function known as chemical potential. Then, we set out the interest that represents the handling of activities. It, purely and simply, permits one to formulate the mass action law when the studied chemical systems are not ideal. This is the vast majority of cases! This is followed by introducing the notions of fugacity and activity from a general viewpoint. We then confine ourselves to the study of the activity of gases, those of non-electrolytes in liquid solutions, the activities of electrolytes, the determination of activities of non-electrolytes and of electrolytes, calculation of activities of electrolytes essentially with the aid of Debye–Hückel relations and that of activity coefficients and activities, their relations with another thermodynamic function, that is to say the excess Gibbs energy, the determination of pH of an aqueous solution, the general principles of calculations involving activities in solutions, and finally, the determination of thermodynamic equilibrium constants of polyfunctional compounds.

Keywords Classical thermodynamics · Equilibrium constant · Fugacity · Activity · Ideal and non ideal systems · Chemical potential · Activity coefficient

General introduction

Thermodynamic systems

A system is a part of space and what this part contains. Its surroundings are all but the system. They are separated by a real or fictitious closed surface (Fig. 1).

The state of a system and state variables The state of a thermodynamic system is defined by the values of some parameters. Most often in chemistry (but not obligatorily), the state variables are (1) the composition, (2) the pressure p, (3) the volume V, and (4) the temperature T.

Transformations A transformation of a system is a process which expresses itself by one or several changes in at least one of the state variables.

Thermodynamic equilibrium One considers that a system is at thermodynamic equilibrium when the observed variables which characterize it do not change with time. In so-called simple systems, thermodynamic equilibrium entails that mechanical, thermal and chemical equilibria are satisfied simultaneously. In principle, all chemical reactions are equilibrated, but some are so complete toward the left or the right that they appear to be complete, and so they are called. However, all the chemical equilibria are not necessarily satisfied. Here, it should be mentioned that sometimes only conditional equilibria do exist.

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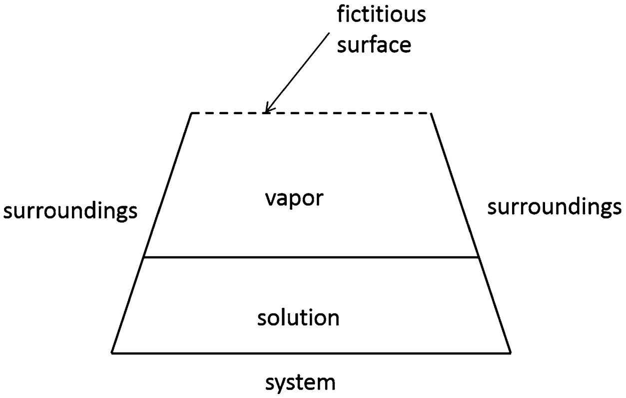

Fig. 1 Example of an isolated system constituted by the system under study itself and its surroundings

A simple example of chemical equilibrium

Let us consider the following chemical reaction:

$A + B \rightleftarrows M$

At the state of equilibrium, the composition of the system does not change further. If the molar concentrations are chosen to be one parameter defining the composition of this state, $[A]_{eq}$, $[B]_{eq}$ and $[M]_{eq}$ being the (constant) concentrations of reactants A, B and product M, one can write:

$$\frac{[M]_{eq}}{[A]_{eq}[B]_{eq}} = K \qquad (1)$$

where K is a constant called the *equilibrium constant*. It depends essentially on temperature and to a lesser degree on pressure. Equation (1) is a first expression of the so-called *law of mass action*. However, it is not general, for several reasons: (a) The first one is obvious. The chemical reaction under study is often more complicated than (1). There are more than three reactants and products. Moreover, they may be affected by different stoichiometric coefficients. A general chemical reaction may be written:

$$aA + bB + cC + \cdots \rightleftarrows mM + nN + nP + \cdots \qquad (2)$$

where A, B, C… and M, N, P… are the reactants and products, and a, b, c, m, n, p are stoichiometric coefficients. A general relation of kind (1) applies to equilibrium (2). This, then, is the law of mass action in its very general form, as we shall later see. (b) The second reason is that the composition of the system (2) is expressed in concentrations $[A]_{eq}$, $[B]_{eq}$, $[C]_{eq}$ etc.… In general terms, the law of mass action can be expressed in terms of concentrations only when the system under study is ideal. This condition is rather rare. This point must now be examined in some details.

Anticipating what will follow, it can already be said that when the system where the reaction $A + B \rightleftarrows M$ is evolving is not ideal, the law of mass action must be written as follows:

$$\frac{a_{M,\,eq}}{a_{A,\,eq}a_{B,\,eq}} = K$$

where $a_{M,\,eq}$, $a_{A,\,eq}$, $a_{B,\,eq}$ are the activities of species M, A, B at equilibrium. At this point of the introduction, it is true that the notion of activity seems to be particularly mysterious. Even more, when the system is ideal, the scales of concentrations in which the composition of the medium is expressed must be taken into account because activities exhibit different numerical values according to them. This point is rather omitted in some literature.

Expressions of the composition of the system

The different expressions of the composition of a solution Henceforth, we focus essentially on gaseous mixtures and liquid solutions. The composition of a liquid solution expresses the relative proportions of the solute(s) and of the solvent in the solution. We only mention the expressions which are the most common:

1. The amount of substance i (number of moles n_i of the species i): it is the total number of molecules of i N_i related to the Avogadro number N_A: $n_i = N_i / N_A$.
2. The molarity, also called amount concentration (IUPAC: International Union for Pure and Applied Chemistry). Its symbol is c_i. It is the number of moles related to the volume V of solution $c_i = n_i / V$. In SI units, it is expressed in mol m^{-3}.One rather uses the number of moles per dm^3 or equivalently per liter. A solution 1 mol L^{-1} is often called a molar solution and is often written as “1 M”. The symbol $[i]$ is very often encountered instead of c_i.
3. The molality is the number of moles of solute i per kilogram of pure solvent. Its symbol is m_i. According to SI, it is expressed in mol kg^{-1}.The molality is preferably used in physical chemistry. Its great advantage with respect to the molarity lies in the fact that it is independent of the density and hence of the temperature. For dilute aqueous solutions, the solute molality value differs very little from that of its molarity. The more diluted the solution, the more correct is this approximation.
4. The molar fraction is the ratio of the number of moles of the solute and the total number of moles in the solution. Its symbol is x. In a binary solution, the number of moles of the solute is n_i and that of the solvent is n_0; the molar fractions of the solute and of the solvent are respectively $x_i = n_i / \left(n_0 + n_i\right)$ (solute), and $x_0 = n_0 / \left(n_0 + n_i\right)$ (solvent). Molar fractions are dimensionless quantities. They are often used in thermody-

namics. The pathways from molar fractions to molalities and molarities are given by the following relations, in the case when there are several solutes i and when we focus on the solute A: $c_A = \left(1000\rho\Sigma n_i / \Sigma n_i M_i\right)x_A$ and $m_A = \left(1000\Sigma n_i / n_0 M_0\right)x_A$, where c_A and m_A are the molarity and the molality of A. The index 0 is the mark of the solvent. ρ is the density of the solution. n_i is the number of moles of species i and M_i (grams) its molar mass. Note that there is no proportionality between x_A and c_A, and this is also the case between m_A and x_A. However, for diluted aqueous solution (since for water at ambient temperature $\rho \approx 1$ applies), $m_A \approx c_A$. The above relations giving c_A and m_A are obtained as follows. By definition, the molar fraction of A is $x_A = n_A / \Sigma n_i$ with $\Sigma n_i = n_0 + n_A + n_B + \cdots$ The molar concentration of A is by definition $c_A = n_A / V$, where V is the total volume of the solution. Let us express c_A as a function of x_A. The mass of the solution $\Sigma n_i M_i$ (grams) is $\Sigma n_i M_i = n_0 M_0 + n_A M_A + n_B M_B + \cdots$, where M_0, M_A, M_B are the molar masses of the solvent and of the species A, B… The volume V of the solution is $V = \Sigma n_\mathrm{i} M_\mathrm{i} / 1000\rho$, where ρ is the density (g cm^{-3}) of the solution. The factor 1000 permits one to express the volume V in liters. Then, from the previous relations, one can immediately deduce the following ones: $c_A = 1000\rho n_A / \Sigma n_i M_i$, ≈and $c_A = \left(1000\rho\Sigma n_i / \Sigma n_i M_i\right)x_A$. Proportionality between x_A and c_A appears when the solution is sufficiently dilute. Under these conditions, it indeed holds that $\Sigma n_i \approx n_0$ and $\Sigma n_i M_i \approx n_0 M_0$, whence $c_A = \left(1000\rho / M_0\right)x_A$, where ρ is the density of the pure solvent since the solution is sufficiently diluted. In particular, for the solvent water at ambient temperature it holds that $\rho \approx 1$ and $c_A \approx \left(1000 / M_0\right)x_A$ (water at ambient temperature). The molality of A is by definition $m_A = 1000 n_A / n_0 M_0$. The factor 1000 is introduced since M_0 is expressed in grams and since m_A is expressed in moles per kilogram of solvent. By introducing the expression defining x_A in the latter, we obtain $m_A = \left(1000\Sigma n_i / n_0 M_0\right)x_A$. Again, there is no proportionality between m_A and x_A. However, it appears in dilute solutions, since then $\Sigma n_i \approx n_0$, whence $m_A \approx \left(1000 / M_0\right)x_A$. The latter relation clearly shows that in dilute aqueous solutions, $\rho \to 1$ and $\Sigma n_i M_i \to n_0 M_0$, i.e., $m_A \approx c_A$.

Ideal systems

We only consider the cases of ideal gases and ideal solutions, since they are most important for our purpose.

(a) There are several definitions of perfect gases. A gas is considered ideal when it obeys the law of perfect gases

$$pV = nRT,$$

where p is the gas pressure, V its volume, R the gas constant ($R = 8.31451$ JK^{-1} mol^{-1}), and T the absolute temperature of the system. A mixture of gases may also be ideal when the molecules constituting the system are independent of each other and when the mixture obeys the perfect gas law. There are no interactions between them. As to the amount of energy, each molecule of such a gas does possess only its own kinetic energy and no further energy, such as the potential energy of interaction with other molecules (of the gas). The internal energy of the system is only the sum of the kinetic energies of all molecules. (In this case, the kinetic energy of the molecule is described by E. Schrödinger as its "private" energy.) This property has enormous consequences in quantum chemistry, and notably at the level of the Schrödinger equation of the system. This property makes its otherwise mathematically impossible resolution, possible, but only in some few cases.

(b) The notions of "ideality" and "non-ideality" of solutions are central for our purpose. A solution is said to be ideal if the chemical potential (see later) of every component is a linear function of the logarithm of its mole fraction. The definition of ideal solutions is somewhat imprecise. Some authors, indeed, distinguish two types of ideal solutions: the perfect solutions and the sufficiently diluted ones. Here, we only consider the case of non-electrolytes from this standpoint. That of electrolytes will be studied later.

Perfect solutions They are ideal in the whole domain of concentrations of the solute(s). They obey Raoult's law, which stipulates that the partial vapor pressure p_i of each component i of the solution is proportional to its mole fraction (in solution) and to its vapor pressure $p_i^\ominus$ when it is pure at the total pressure of the system (Fig. 2):

$$p_i = x_i p_i^\ominus \tag{3}$$

According to this law, expression (3) must be verified at every temperature and at constant total pressure.

The case of perfect solutions is rather scarce:

The sufficiently diluted solutions They are solutions in which their solute(s) exhibit(s) an ideal behavior only in a limited domain of "concentrations". The solute(s) obey(s) Henry's law. Henry's law is such that the behavior of the solvent tends toward that described by Raoult's law, that is to say,

$$p_1 \to x_1 p_1^\ominus$$

(1: solvent) for $x_1 \to 1$ (solution increasingly dilute), whereas the behavior of the solute is not that of a solute in a

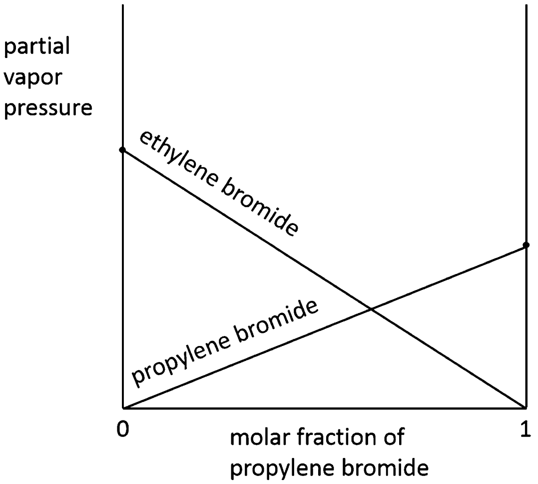

Fig. 2 Dependence of the partial vapor pressures of the components of a mixture of ethylene bromide and propylene bromide which form an ideal perfect solution on their mole fractions

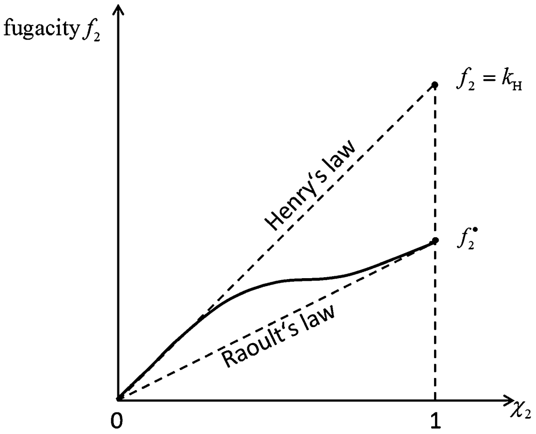

Fig. 3 Differences between Raoult's and Henry's laws

perfect gas. At constant temperature, the vapor pressure of a solute is proportional to its molar fraction, as it is in a perfect solution, but the proportionality constant k_H is not the same as before. Henry's law is

$$p_2 \to k_H x_2$$

(2: solute) (cf. Fig. 3). k_H is named Henry's constant. Henry's law applies to all diluted solutions.

Figure 3 shows the differences between Raoult's and Henry's laws. (Figure 3 represents the fugacity f_2 of the solute and does not represent its vapor pressure p_2. Raoult's and Henry's laws can also define perfect and sufficiently dilute solutions in terms of fugacity—see later.) The following comments must be given: (1) In the cases of ideal solutions, the solute molecules cannot be considered as being independent from each other when the mixture becomes very dilute, contrary to the case of molecules of ideal gases. In the case of solutions, there still exist physicochemical interactions between molecules of solute, molecules of solute and solvent, and molecules of solvent themselves. (2) There exists a common definition of ideal gases and solutions. It involves the notion of chemical potential (see above).

Gibbs energy change

It is a well-known fact that the knowledge of the changes in internal energy accompanying a process does not permit one to forecast their direction or their maximum possible extent. (However, with the exception of isoentropic systems, it is possible.) The introduction of a new function has become necessary to answer these questions. The entropy function S answers them. It is endowed with remarkable properties. Its SI unit is the joule per kelvin: JK^{-1}. It is a state function and is extensive. The second law of thermodynamics is based on the existence of this function. It states that the entropy of an isolated system cannot do anything other than increase during a spontaneous transformation. This assertion is quantified by the expression

$$\Delta S_{\text{isolated\_syst}} \geq 0.$$

A simple system is isolated when it cannot exchange heat, mechanical work and matter with its surroundings. The previous expression can be equivalently written as

$$\Delta S_{U,V} \geq 0.$$

The indices U and V mean "at constant internal energy and volume of the simple thermodynamic system under study". This symbolism recalls that the system is isolated. The sign "=" in the expression of the entropy change means that the system evolves reversibly:

$$\Delta S_{U,V} = 0$$

(reversible process). One of the difficulties in understanding the entropy concept comes from the mix-up between the entropy of the studied system and that of the isolated system *containing* the studied one. In thermodynamics, in order to study a process in the most general case, one may consider both the studied system and its surroundings with which it can exchange work, heat and matter. The studied system plus the surroundings constitute an isolated system. But the studied system, solely, may not be isolated.

As a consequence, the studied system (sensu stricto) may exhibit an increase or even a decrease in its entropy during a spontaneous process, provided the corresponding isolated system (in which the system under study is located) is effectively isolated.

The Gibbs energy function was introduced by Gibbs [5, 6]. Its symbol is G. The Gibbs energy is related to a process in which the temperature and the pressure of the studied system remain equal to the temperature and pressure of its surroundings (at least at the beginning and at the end of the process, provided in this case that during the process, the surroundings remain at the constant temperature T_{ext} and pressure p_{ext}): $p = p_{\text{ext}}$ and $T = T_{\text{ext}}$

The Gibbs energy is defined by the expression

$$G = U + pV - TS,$$

where U, p, V, T and S are respectively the internal energy, pressure, volume, temperature and entropy *of the studied system*. The unity of Gibbs energy is the joule J. Owing to its definition, it is a state function.

Writing it in differential form and, moreover, adopting some experimental conditions leads to a useful relation:

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T.$$

Let us suppose that the system only performs a work of expansion. In this case, the first law permits us to write

$$\mathrm{d}U = \mathrm{D}q - p\mathrm{d}V,$$

where $\mathrm{D}q$ is an inexact differential. Let us also suppose that the exchange of heat is reversible; then: $\mathrm{D}q = T\mathrm{d}S$. Taking into account these hypotheses, one obtains

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T.$$

The aim of introducing this function is the following: the Gibbs function constitutes a criterion of equilibrium and also of evolution which is particularly convenient for any process carried out at constant temperature and pressure. Let us, for example, study the process with the aid of which we want to recover *useful work* (every work other than that stemming from the change in the volume of the system). It is demonstrated that the work transferred to the surroundings is always smaller than the change in Gibbs energy of the system. In other words, the Gibbs energy of the system cannot do anything other than decrease when work is supplied to the surroundings, in any case when the process is *spontaneous*. Hence, for a spontaneous process:

$$\Delta G \le 0, \text{ or equivalently : } \mathrm{d}G \le 0.$$

At equilibrium,

$$\mathrm{d}G = 0.$$

For a system at equilibrium at given temperature and pressure, the Gibbs energy is at its minimum value.

Hence, with the introduction of the Gibbs energy function, the criterion of spontaneous evolution of a system, that is to say that of the change in the total entropy of the system plus its surroundings, is transformed into another criterion, which is that of the decrease of the Gibbs energy of the *studied system alone*.

The Gibbs energy function can be defined in a way other than the preceding one. Since

$$H = U + pV,$$

where H is the enthalpy of the system, the Gibbs energy can be defined by

$$G = H - TS.$$

The two definitions are equivalent. In German, the Gibbs function is called the free enthalpy function.

It is interesting to note that the changes in the Gibbs energy with pressure and temperature are given by the relations

$$(\partial G/\partial T)_{\text{p}} = -S, \ \ (\partial G/\partial P)_{\text{T}} = V.$$

In general, the Gibbs energy depends not only on the temperature and pressure, but also on the amount of substance. We shall see that the introduction of activities may be necessary at this point in considering the changes in the Gibbs energy of a system with temperature and pressure.

Remark The Gibbs function, owing to its property to give important indications on the possibilities of transformations of a system, is said to be a potential thermodynamic function. There is another well-known thermodynamic potential function. It is the Helmholtz function, which we shall not study further here.

Escaping tendency

The expression “escaping tendency” was introduced by 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 has be seen, commands the spontaneous process at constant temperature and pressure.

We know that every body with a temperature higher than that of another tends to leave its heat to the latter.

By analogy, one may conceive that a substance of a system may exhibit some tendency to modify its thermodynamic state by changing its number of moles. Lewis kept the same name “escaping-tendency” to characterize this tendency.

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

A second example is provided by the system made up of a solute in a solvent such as a solution of sodium chloride in water. The escaping tendency of sodium chloride may be either higher or lower than or equal to that of solid sodium chloride depending on whether or not the solution is saturated. In the first case, the sodium chloride spontaneously crystallizes. Only at the saturation point does equilibrium exist. 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.

The molar Gibbs energy of a substance as a measure of its escaping tendency

Let us again consider the system consisting of water and ice at 0 °C, under 1 atm, as an example. Because the system is maintained at constant temperature and pressure, it is judicious to reason by considering the Gibbs energies of both phases. Let us consider the transformation $H_2O_{(\text{solid},1\text{atm})} \rightarrow H_2O_{(\text{liquid},1\text{atm})}$ or its inverse. The Gibbs energy change ΔG accompanying the molar process is

$$\Delta G = G_{\text{m, liq}} - G_{\text{m, solid}}.$$

At equilibrium, at the melting point, under pressure of 1 atm, the following relation holds: $G_{\text{m, liq}} = G_{\text{m, solid}}$. At a temperature higher than the previous one, the transformation follows the direction already indicated, since $G_{\text{m, ice}} > G_{\text{m, liq}}$. At a lower temperature, it is the inverse, i.e., $G_{\text{m, liq}} > G_{\text{m, ice}}$. Hence, by this example, one can see that the molar Gibbs energy may be used to quantify the escaping tendency of a substance.

Change in molar Gibbs energy of a perfect gas with pressure

In this paragraph, we give a relation expressing the Gibbs energy of a perfect gas. This relation is particularly important for our purpose.

It can be considered as the model of the mathematical relation linking the chemical potential of a substance to its activity, as we shall later see.

For n moles of a perfect gas, it holds that $pV = nRT$. Let us consider the infinitesimal isothermal expansion of a pure perfect gas. Since, from the general theory, $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$, it follows that for an isothermal process, $\mathrm{d}T = 0$, and $\mathrm{d}G = V\mathrm{d}p$. Expressing V from the relation of perfect gases: $\mathrm{d}G = nRT\mathrm{d}p/p$. From the change in pressure from p_A to p_B it follows that

$$\Delta G = nRT \int_{p_A}^{p_B} \mathrm{d}p/p, \text{ i.e., } \Delta G = nRT \ln p_B/p_A, \text{ or}$$

$$G_B - G_A = nRT \ln p_B/p_A.$$

The Gibbs energy of a perfect gas depends on its pressure. Usually, the Gibbs energy G of a gas is related to its Gibbs energy $G^\ominus$ it possesses in a state called the *standard state*, which is arbitrarily chosen and in which the pressure is $p^\ominus$ and also in which its temperature is arbitrarily chosen to be T. As a consequence, for one mol of perfect gas, the molar Gibbs energy is given by the relation

$$G = G^\ominus + RT \ln p/p^\ominus.$$

When the pressure chosen for the standard state is $p^\ominus = 1$ atm, the molar Gibbs energy is then given by

$$G = G^\ominus + RT \ln p_{\text{atm}}/1 \text{ atm} \tag{4}$$

The index 1 atm is used here to recall that p and 1 are physical quantities which are dimensioned. The writing often encountered in the literature when $p^\ominus = 1$ atm is

$$G = G^\ominus + RT \ln p.$$

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

Gibbs energy change accompanying a reaction between perfect gas

Let us consider the following reaction going to completion: $\nu_M M + \nu_L L \rightleftarrows \nu_N N + \nu_P P$, where the ν_M, ν_L and so forth, are the stoichiometric coefficients, and M, L, N, P are perfect gases. Our goal is to calculate the maximal work which can be done by this system at constant temperature and pressure. The calculation may be carried out by taking into account the properties of Gibbs energy. The important point here 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 four gases. The change in the Gibbs energy $\Delta_r G_{\text{syst}}$ accompanying the above total transformation is

$$\Delta_r G_{\text{syst}} = \nu_N G_{\text{m, N}} + \nu_P G_{\text{m, P}} - \nu_M G_{\text{m, M}} - \nu_L G_{\text{m, L}} \tag{5}$$

where $G_{\text{m, M}}$ and $G_{\text{m, L}}$ are the molar Gibbs energies of L and M in the initial state and $G_{\text{m, N}}$ and $G_{\text{m, P}}$ those in the final state. (The index r recalls that the Gibbs energy is a reactional one.)

It is very important to note at this point of reasoning that relation (5), taking into account the molar Gibbs energies (and not the chemical potentials—see later), can be used here because the process concerns perfect gases which in mixtures exhibit the same behavior as they would have if they were alone. It is this property which authorizes the handling in the present case of the molar Gibbs energies and their expression by (4).

By replacing the molal Gibbs energies G_i in (5) by their expression in (4), one obtains

$$\Delta_r G_{\text{syst}} = \Delta G^{\ominus} - RT \ln \left(p_{\text{N}}^{\ominus \nu_{\text{N}}} p_{\text{P}}^{\ominus \nu_{\text{P}}} \Big/ p_{\text{L}}^{\ominus \nu_{\text{L}}} p_{\text{M}}^{\ominus \nu_{\text{M}}} \right) + RT \ln \left(p_{\text{N}}^{\nu_{\text{N}}} p_{\text{P}}^{\nu_{\text{P}}} \Big/ p_{\text{M}}^{\nu_{\text{M}}} p_{\text{L}}^{\nu_{\text{L}}} \right) \quad (6)$$

with $\Delta_r G^{\ominus} = \nu_{\text{N}} G_{\text{N}}^{\ominus} + \nu_{\text{P}} G_{\text{P}}^{\ominus} - \nu_{\text{M}} G_{\text{M}}^{\ominus} - \nu_{\text{L}} G_{\text{L}}^{\ominus}$. $\Delta_r G^{\ominus}$ is evidently a constant at a given temperature.

Hence, the change in Gibbs energy accompanying reaction (5), where the perfect gases L and M initially at pressures p_{L} and p_{M} are transformed at constant temperature and pressure into the perfect gases N and P at pressures p_{P} and p_{N}, is given by the expression (6).

The problem of calculating the Gibbs energy changes accompanying a chemical reaction is not so simple to solve as that involving perfect gases. Most often, it implies the use of activities.

Partial molar quantities

In determining the changes in thermodynamic quantities accompanying a chemical reaction, especially that of the Gibbs energy, the question of the physical interpretation of the measured change frequently arises. Actually, it is not the case when the studied reaction is one between perfect gases or when each of the reactants or products constitutes an independent phase. But it is set up as soon as there are intervening species in solution as reactants or products. The problem can be overcome by introducing partial molar quantities, among which is the *chemical potential*. It is convenient, firstly, to clarify the notions of closed and open systems:

- Closed systems are those whose composition is fixed, i.e., those in which the substance quantities are constant. There is no increase or decrease of matter in the system, nor can the system exchange it with the surroundings. In these conditions, all the relations previously recalled can be applied. For example, it is the case of the relation $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$, which entails a mechanical work as the only one which is developing.
- Open systems are systems which matter can enter or leave. That is to say, they are systems in which the quantity of matter may vary during the course of the transformation. Then the previous formula is no longer convenient. For example, the previous relation may be replaced by

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_{\text{i}} \left(\partial G / \partial n_{\text{i}} \right)_{T,P,n_{\text{j}}} \mathrm{d}n_{\text{i}} \quad (7)$$

The new last terms on the right-hand side take into account the exchanges of matter with the surroundings through the differentials $\mathrm{d}n_{\text{i}}$, which express the changes in the number of moles of the components i. The partial derivatives that appear are examples of partial molar quantities that are studied now. Let us note that when two phases are in contact, each one constitutes an open system, whereas when both are maintained in the same container which precludes any matter exchange with the surroundings, the whole system (constituted by both phases) is closed.

The need to introduce partial molar quantities notably appears when the species are in solution. In order to set up the problem, let us consider the reaction $\text{Ag}_{(\text{s})} + \frac{1}{2}\text{Cl}_{2(\text{g})} \rightarrow \text{AgCl}_{(\text{s})}$, where (s) and (g) indicate solid and gaseous states and focalize on the volume change accompanying the reaction. Let us define the system as being constituted by the chemical substances and the container, and consider the volume change $\partial V / \partial n$ of the system per mole of consumed silver, n being the number of moles of silver. We can write $\partial V / \partial n = \partial V_{\text{Ag}} \big/ \partial n + \partial V_{\text{Cl}_2} \big/ \partial n + \partial V_{\text{AgCl}} \big/ \partial n$. Among the partial derivatives of the right-hand member, none exhibits any difficulty of interpretation. Each represents the molar volume of the substance, that is to say its molar volume when it is pure. This is the case here, because each component constitutes a pure phase. For each phase, indeed, one can write$V = nv_{\text{m, i}}$, where $v_{\text{m, i}}$ is the *molar volume of the pure component*. It is evident that $\partial V / \partial n = v^{\cdot}$. As a result, for that system it follows that

$$\partial V / \partial n = v^{\cdot}_{\text{AgCl}} - v^{\cdot}_{\text{Ag}} - \tfrac{1}{2} v^{\cdot}_{\text{Cl}_2}, \text{ and } \partial V / \partial n = \Delta v.$$

There is no problem.

Now let us consider the following reaction: $\frac{1}{2}\text{H}_{2(\text{g})} + \text{AgCl}_{(\text{s})} \rightarrow \text{HCl}_{(\text{m})} + \text{Ag}_{(\text{s})}$, where (m) is the molality of the hydrochloric acid in solution. (Actually, this reaction is the global reaction of the well-known electrochemical cell conventionally represented by the scheme $\text{H}_2|\text{HCl}_{(\text{m})}|\text{AgCl}|\text{Ag}$. As a concrete example of such a study, it may be interesting to know the effect of the pressure on the electromotive force of this cell, that is to say, actually, on the change in Gibbs energy accompanying the reaction cell. In order to determine it, we use the general expression (already encountered) $(\partial G / \partial P)_T = V$) For the reaction cell it holds that $(\partial \Delta G / \partial P)_T = \Delta V$. In order to solve the problem, we must know the volume V of the system and its change. It is given by the relation $V = V_{\text{H}_2} + V_{\text{AgCl}} + V_{\text{HCl}_{\text{soln}}} + V_{\text{Ag}} + \text{constant}$. The volume change per mole of consumed silver $\partial V / \partial n$ is

$$\partial V / \partial n = \partial V_{\text{H}_2} \big/ \partial n + \partial V_{\text{AgCl}} \big/ \partial n + \partial V_{\text{HCl}_{\text{soln}}} \big/ \partial n + \partial V_{\text{Ag}} \big/ \partial n.$$

The true meaning of $\partial V_{\text{HCl}_{\text{soln}}} \big/ \partial n$ remains to be clarified. Here is the problem. Let us symbolize $\partial V_{\text{HCl}_{\text{soln}}} \big/ \partial n$ by $v_{\text{HCl}_{\text{barr}}}$. As we shall later see, $v_{\text{HCl}_{\text{barr}}}$ is called the partial molar volume of hydrochloric acid at the molality m. The change Δv of the system when one mole of silver has disappeared is given by the relation $\Delta v = v_{\mathrm{Ag}} + v_{\mathrm{HCl}_{\mathrm{barr}}} - \frac{1}{2}v_{\mathrm{H}_2} - v_{\mathrm{AgCl}}$. (The symbol v appears in place of V so that the reader is aware that the volumes which are in question are the molar ones, partial or not.)

From this last example, it is clear that one has to use some new variables to express the values of the "great functions of thermodynamics" in some conditions. Several authors have formally formulated the following relations:

$$\begin{aligned} U &= U(S, V, n_1, n_2, \ldots) \\ G &= G(T, p, n_1, n_2, \ldots) \\ H &= H(S, p, n_1, n_2, \ldots) \\ A &= A(T, V, n_1, n_2, \ldots) \end{aligned} \tag{8}$$

where $n_1, n_2, \ldots$ are the numbers of moles of the components 1, 2, etc. They are the supplementary variables evoked.

From a mathematical standpoint, the partial molar quantity X_{barr} is defined as its partial derivative with respect to the number of moles n_{i} of the compound i, that is to say: $X_{\mathrm{barr}} = \left(\partial X / \partial n_i\right)_{\mathrm{other\_variables}}$. The partial molar quantities are denoted by the same symbols as usual but they are highlighted. Their unity, of course, is that of the corresponding quantity. The introduction of the partial molar quantities permits one to write the thermodynamic quantities as usual variables even when the systems are open. Hence, the total differential of the Gibbs energy of an open system is written as

$$\begin{aligned} \mathrm{d}G = (\partial G/\partial T)_{p,n}\mathrm{d}T + (\partial G/\partial p)_{T,n}\mathrm{d}p + \left(\partial G/\partial n_1\right)_{T,p,n_j}\mathrm{d}n_1 \\ + \left(\partial G/\partial n_2\right)_{T,p,n_j}\mathrm{d}n_2 + \cdots \end{aligned} \tag{9}$$

An important point is that the variables (8) are not randomly associated with other variables. For example, the function G is associated with variables $T, p, n_1, n_2, \ldots$ and so forth. Likewise, the function internal energy U is associated with variables $S, V, n_1, n_2, \ldots$ and so forth. T, p, n_i and S, V, n_i are called the natural variables of V and U, respectively. Some authors consider the relations (8) as postulates.

The physical meaning of the partial molar quantities may be grasped by considering the example of the volume of a solution. Let us consider a binary solution and let components 1 and 2 be the solvent and the solute. (The fact that one component is the solvent and the other the solute does not confer any particular role for them to play in this context.) Their initial numbers of moles are respectively n_1 and n_2. The initial total volume of the solution is V_0. Let us successively add some quantities of solute to the solution. The total volumes change. Let us draw the diagram V as a function of n_2. The partial molar volume $v_{2_{\mathrm{barr}}}$ is defined by $v_{2_{\mathrm{barr}}} = \left(\partial V/\partial n_2\right)_{n_1 n_2'}$. The diagram is represented in Fig. 4.

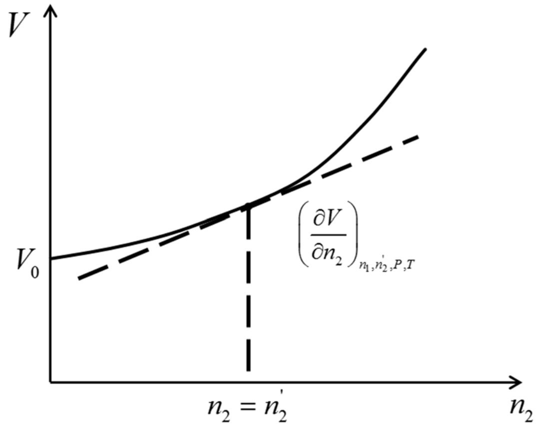

Fig. 4 Total volume of the solution V as a function of the number n_2 of moles of solute added

$v_{2_{\mathrm{barr}}}$ is nothing other than the slope of the curve V/n_2 for the values n_1 and n_2' considered. The immediate conclusion that can be drawn from this diagram is that the partial molar volume $v_{2_{\mathrm{barr}}}$ does vary with the instantaneous composition of the solution. It may happen, however, that a linear relation exists between the measured thermodynamic quantity and the number of moles of a component. It may be, for example (but not obligatorily), the case of the volume of a binary solution. Its volume varies linearly with the number n_2 of solute molecules. In this case, the partial molar volume $v_{2_{\mathrm{barr}}}$ is equal to the molar volume $v_{\mathrm{m},2}$. In this case, the definition of the partial molar volume shows that $v_{\mathrm{m},2}$ is the molar volume of the pure solute 2. Of course, all these considerations relative to the volumes are also valuable for other thermodynamic functions.

Partial molar quantities have been introduced in thermodynamics of mixtures because there exists a fundamental equation which links them. As a consequence of (9), one can write at constant temperature and pressure:

$$\mathrm{d}X = X_{1_{\mathrm{barr}}}\mathrm{d}n_1 + X_{2_{\mathrm{barr}}}\mathrm{d}n_2 + \cdots$$

The partial molar quantities $X_{1_{\mathrm{barr}}}, X_{2_{\mathrm{barr}}}$ are intensive quantities, since they are related to a well-defined quantity of matter (one mole). As such, they do not depend on the total quantity of each component but only on the relative composition of each one. As a result, if to a solution containing several components with a given relative composition is added an identical solution of the same composition, the partial molar quantities $X_{i_{\mathrm{barr}}}$ do not change, whereas the number of moles n_1, $n_2 \ldots$ varies. The consequence is that the total differential dX can be immediately integrated and we can write

$$X = n_1 X_{1_{\mathrm{barr}}} + n_2 X_{2_{\mathrm{barr}}} + \cdots$$

It is sufficient to consider the case in which an a linear relation exists between an extensive property of a solution and the number of moles of each of the components, to be convinced by its interest. In these conditions, we have seen above that the partial molar quantities are constant and, moreover, are equal to the molar properties of pure composition $X_{i_{(m)}}$, that is to say:

$$X = n_1 X_{1_{(m)}} + n_2 X_{2_{(m)}} + \cdots$$

Comparing the last two relations shows that partial molar quantities play the part of the molar quantities of pure compounds and that they can be handled in the same way. However, there exists a double difference between the two kinds of quantities:

(a) On the one hand, the partial molar quantities are not constant, whereas the molal ones are.
(b) On the other hand, the partial molar quantities may be positive or negative. This property is inconceivable with the molar quantities.

Moreover, it must be known that the relations between the thermodynamic partial molar quantities are the same as those which exist between molar quantities.

The partial molar quantities are experimentally accessible. In some cases, it is their absolute value which is accessible. In other cases it is their relative value. The reason lies simply in the fact that in some cases, the molar quantities of pure compounds themselves cannot be known in absolute values. This is the case, for example, of the enthalpy.

Chemical potential or partial molar Gibbs energy

The chemical potential μ_k of a compound k in a given state (temperature T, pressure p, numbers of moles of the different species n_i) is expressed by the following mathematical relation:

$$\mu_k = \left(\partial G / \partial n_k\right)_{T,p,n_i \neq n_k}.$$

It is also the partial molar Gibbs energy G_kbarr defined by the same relation:

$$G_{k_\mathrm{barr}} = \left(\partial G / \partial n_k\right)_{T,p,n_i \neq n_k}.$$

In this case, G is the Gibbs energy of the whole solution considered as the system (Fig. 5).

According to what was mentioned before, one can write for a binary solution:

$$G = n_1 G_{1_\mathrm{barr}} + n_2 G_{2_\mathrm{barr}}.$$

The unity of a chemical potential is J mol^{-1}.

There are other definitions of the chemical potential. They are defined as follows:

$$\mu_k = \left(\partial U / \partial n_k\right)_{S,V,n_i \neq n_k}$$

$$\mu_k = \left(\partial H / \partial n_k\right)_{S,p,n_i \neq n_k}$$

$$\mu_k = \left(\partial A / \partial n_k\right)_{T,V,n_i \neq n_k}$$

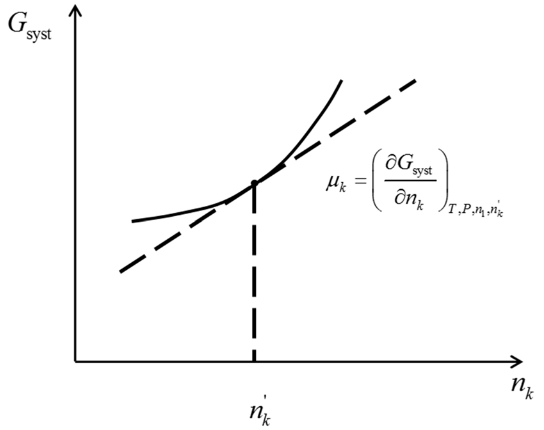

Fig. 5 Chemical potential μ_k of a solute k

Hence, the chemical potential turns out to be also a molar partial internal energy, a molar partial enthalpy or a partial molar Helmholtz energy A. (A is the symbol of Helmholtz energy. It is another potential energy.) It must be noted that the variables maintained constant in the partial derivatives are not the same. This fact has for property to confer the same physical meaning to these different definitions.

From the standpoint of the physical meaning, the chemical potential of a substance can be considered as a quantity which represents its escaping tendency, as does the molar Gibbs energy. It is by no means surprising, since as we have seen, it is also a molar Gibbs energy, albeit a partial one. From these assertions, it appears that the chemical potential extends the notion of molar Gibbs energy. Actually, the notion of molar Gibbs energy can only be applied to pure compounds. This is the reason why the chemical potential of a pure compound is also its molar Gibbs energy. For a pure compound i it is $\mu_i = G_\mathrm{m}(i)$. Hence, at this point in the reasoning, we can say that the chemical potential of a compound is a quantity which is liable to quantify its tendency to leave its current thermodynamic state by every sort of process, physical or chemical. In the realm of physical processes, a simple example is given by the partition of a solute i between two immiscible phases α and β. Let us suppose that at the beginning of the process the whole solute is only present in the phase α. Its chemical potential is then μ_{i_α}, whereas $\mu_{i_\beta} = 0$, that is to say $\mu_{i_\alpha} > \mu_{i_\beta}$ (initial state). By stirring both phases (this has only the effect of increasing the speed of matter exchanges between the phases but does not change anything in regard to the thermodynamic aspect of the process), a part of the solute spontaneously goes into phase β. There exists a moment at which the transfer process ceases. Then the concentrations in the two phases no longer vary. The partition equilibrium is reached. The equilibrium condition (concerning, of course, the exchange of *i*) is the equality of its chemical potential in both phases, that is to say: $\mu_{i_\alpha} = \mu_{i_\beta}$ (equilibrium). The partition occurred spontaneously because, initially, there existed an inequality in the chemical potentials. We may also note that the matter exchange process follows the direction of a decreasing chemical potential. Thus, a difference in chemical potentials plays an analogous part as that played by an electric potential difference. Electrons flow between two points of an electrical circuitry because there occurs a difference in electric potential between them. It is also analogous to the differences in temperature and pressure, which command a heat transfer and a mechanical motion, respectively. Some authors regard the chemical potential as a kind of "chemical pressure".

Among several properties of the chemical potential, let us mention the following:

- It is an intensive property since it is a molar property. Recall that an intensive property does not require any specification of the quantity of the sample to which it refers. The qualificative term here means "once for all".
- It is expressed in J mol^{-1};
- It tends toward $-\infty$ when it concerns a perfect gas and when its pressure tends toward zero.
- It varies with the composition of the system as all other partial molar quantities. In some scarce cases, it may be independent of it.
- For a pure compound, it is purely and simply its molar Gibbs energy G_m; its absolute value cannot be known since it is a Gibbs energy and since the absolute values of the Gibbs energies are not accessible. Only changes in chemical potentials can be measured. This property is essential. As we shall see, it is one of the reasons for the introduction of the concept of activity.
- Its value depends on the temperature of the system. The influence of the latter is given by the relation $\left(\partial\mu_k/\partial T\right)_{n_i,p} = -S_{k_\text{barr}}$; S_{k_barr} is the partial molar entropy of compound k. Another interesting expression relating the temperature and the chemical potential is $\left[\partial\left(\mu_k/T\right)/\partial T\right]_{p,n_\text{i}} = -H_{k_\text{barr}}/T^2$, where H_{k_barr} is the partial molar enthalpy of compound k.
- Its value also depends on the pressure of the system. The relation between them is $\left(\partial\mu_k/\partial p\right)_{T,n_j} = v_{k_\text{barr}}$, where v_{k_barr} is the partial molar volume of k.
- It obeys the very important Gibbs–Duhem relation.

The Gibbs–Duhem relation

This relation expresses the fact that the simultaneous changes in the temperature, pressure and chemical potentials are not independent of one another. They are "interrelated" by the Gibbs–Duhem relation, which is

$$-S\text{d}T + V\text{d}p - \sum_i n_i \text{d}\mu_i = 0.$$

When the system evolves at constant temperature and pressure, the relation becomes $\sum_i n_i \text{d}\mu_i = 0$.

Gibbs energy change accompanying a chemical transformation

A crucial relation for our purpose is the change in Gibbs energy accompanying a chemical transformation.

When a system is constituted by the components 1, 2…, the number of moles of which before the transformation (initial state) are indicated by n_1, n_2… and after the transformation (final state) by $n'_1, n'_2, \ldots$, the change in Gibbs energy in the system accompanying the chemical transformation is given by the expression

$$\Delta_r G_\text{syst} = \left(n'_1\mu'_1 + n'_2\mu'_2 + \cdots\right) - \left(n_1\mu_1 + n_2\mu_2 + \cdots\right),$$

where $\mu'_1, \mu'_2, \ldots, \mu_1, \mu_2, \ldots$ are the chemical potentials in the final and initial states. As an example, let us consider the following chemical reaction: $n_\text{A}\text{A} + n_\text{B}\text{B} \rightarrow n_\text{M}\text{M} + n_\text{N}\text{N}$ and suppose the reaction is complete. The change in the Gibbs energy accompanying the reaction is given by the expression

$$\Delta_r G_\text{syst} = \left(n_\text{M}\mu_\text{M} + n_\text{N}\mu_\text{N}\right) - \left(n_\text{A}\mu_\text{A} + n_\text{B}\mu_\text{B}\right).$$

This equation can be generalized to the case of a more complex reaction. When the linear combination of the kind just above is null, there is equilibrium.

Finally, let us recall that the electrical difference *E* that occurs at the terminals of an electrochemical cell is a function of the temperature and pressure of the system and also of the concentrations (activities: see later) of the species taking part in the electrochemical reaction which are developing at the electrodes. There exists a mathematical relationship between the decrease in Gibbs energy (of the chemical system) accompanying a reversible process occurring in the cell and the electric potential difference appearing in the cell up to obtaining the result. This is true at constant temperature and pressure and also at null current. This relation is

$$\Delta G = -nFE.$$

E is called the electromotive force of the cell, *n* is the number of exchanged electrons and *F* is the Faraday constant. This relation is of utmost importance. It is the basis of Nernst's relation. The use of electrochemical cells may permit one in some cases to determine the activities of non-electrolytes and those of electrolytes.

Interest of handling activities

Laws of thermodynamics are a consequence of the postulates of quantum theory. They are notably concerned with the quantum states of macroscopic systems. They may be rarely calculated or only approached by Schrödinger's equation, which most of the time cannot be solved. Even for extremely simple systems, Schrödinger's equation is mathematically difficult to solve (when it is!). Probably the greatest difficulty in handling its different forms lies in the fact that, in a chemical system, the tremendously large number of particles or species demands the resolution of the equation for each one! Furthermore, most of the time, the physical phenomena depending on Schrödinger's equation cannot be put in satisfactory analytical (mathematical) equations. This is the case when there exist intermolecular interactions. Unfortunately, they are quasi-systematically present.

These considerations being recalled, it is not necessary, for our purpose, to set out the insuperable difficulties encountered in the handling of chemical potentials, notably those of solutes. It is sufficient to say that *in principle*, chemical potentials could be calculated with the help of Schrödinger's equation…but the latter must be set up and after solved!!

Miraculously, the introduction of activities permits one to simply overcome these difficulties at least in part.

Fugacities and activities: activities of non-electrolytes

The quantity fugacity

The quantity fugacity was introduced by G.N. Lewis as early as 1901 in order to describe the behavior of imperfect gases. More precisely, fugacity permits us (as we shall later see) to express the molar Gibbs energy of an imperfect gas and also to express the chemical potential (the partial molar Gibbs energy) of a gas in a mixture of imperfect gases with a formalism analogous to that used in the case of perfect gases. For this reason, it can be said that the chemical potential, which is an abstract notion, can be, through the use of the fugacity notion, expressed in terms of a new function which is more easily identified with the physical reality than the chemical potential. We shall see that the chemical activity is also a quantity which, like the fugacity function, permits one to easily relate the chemical potential to the physical reality. Fugacity and activity are two intimately linked quantities. These are the reasons why a study, even brief, of the notion of fugacity provides an excellent introduction to that of activity.

Fugacity of a pure perfect gas For the definition of the fugacity f of a pure perfect gas, Lewis used the expressions

$$dG = RT d\ln f \tag{10}$$

or

$$G_m = RT\ln f + C(T). \tag{11}$$

$C(T)$ is the integration constant. It depends only on the nature of the substance and the temperature T as is asserted by considerations of statistical thermodynamics. G_m is the molar Gibbs energy of the gas. Expression (11) is, according to some authors, incorrect from a mathematical standpoint, since the logarithm of a quantity which is dimensioned does not possess any meaning, and as we shall immediately see, the fugacity is a quantity endowed with a dimension.[1] On the other hand, relation (10) is correct, since the ratio $df/f = d\ln f$ is dimensionless. It is interesting to observe the analogy between relation (10) and relation (12) under

$$dG = RT d\ln p \tag{12}$$

The latter links the molar Gibbs energy of a perfect gas to its pressure p. It comes from the expression $dG_T = v_m dp$, that is to say $(\partial G/\partial p)_T = v_m$, where v_m is the molar volume of the substance.

Definitions (10) and (11) are not sufficient for the definition of absolute values of the fugacity, since they do not specify the value of the constant $C(T)$ at a fixed temperature. Without any supplementary specification, they only specify the ratio between the fugacities f_f and f_i of the gas in the final and initial states defining an isothermal transformation. Given the molar Gibbs energies in the initial and final states G_{m_f} and G_{m_i}, the change in the Gibbs energy ΔG accompanying the process initial state → final state is

$$\Delta G = G_{m_f} - G_{m_i} \tag{13}$$

$$\Delta G = RT\ln\left(f_f/f_i\right).$$

A supplementary specification is hence necessary. That put forward by Lewis is universally adopted. It takes its origin in the following reasoning: Let us again consider the above transformation and recall that, by hypothesis, the gas is perfect. The notion of fugacity is, by definition, a general one. Hence, it also applies to perfect gases. In these conditions, the following two relations simultaneously pertain:

$$\Delta G = RT\ln\left(f_f/f_i\right) \text{ and } \Delta G = RT\ln\left(p_f/p_i\right),$$

p_f and p_i being the pressures in the final and the initial states of the process under study. It results from the comparison of the two relations that the fugacity must have a linear relation

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[1] Think of the famous aphorism: ln (3apples) = ln 3 + ln apples!.

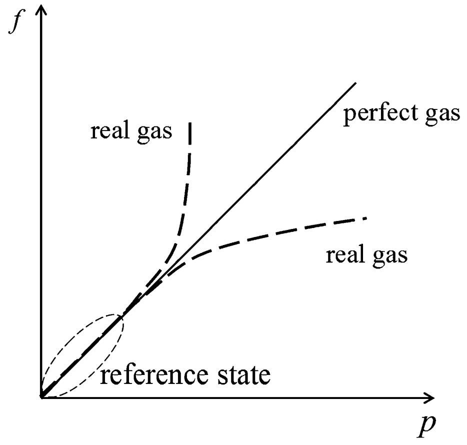

Fig. 6 Difference between the fugacity and the pressure of a pure gas

with the pressure. Since no gas is, from the standpoint of absolute scientific accuracy, perfect, but since the behavior of every gas also tends to be ideal when its pressure tends toward zero, a judicious choice (in order to fix the integration constant) is such that the value of the fugacity of pure gas goes over that of its pressure when the latter tends toward zero, that is to say, $f/p \to 1$, when $p \to 0$. Figure 6 exemplifies the choice. The state in which the fugacity is asserted to be equal to the pressure is called the *reference state*. Thus, the fugacity of a gas equates to its pressure in the reference state. This fact permits us to evaluate its fugacity at every other pressure. Hence, the proportionality constant between the fugacity and the pressure of a gas in the reference state was fixed to 1 by Lewis.

An outcome of the previous choice is that the fugacity of a *perfect gas* equates to its pressure regardless of whichever the latter is, unlike a real gas. We have seen, indeed, that in the case of a perfect gas, the fugacity is proportional to the pressure. By adopting the convention that the fugacity is equal to the pressure when the latter is very weak (in the reference state), it is clear that it is the same across the whole range of pressures in the case of a perfect gas, since, one for all, the linear relationship between the fugacity of a perfect gas and its pressure is established regardless of the value of the latter.

As a result of what is previously described, it appears that the fugacity must be endowed with the same unities as the pressure. (Most fugacity values are still expressed in atmospheres in the literature for historical reasons.)

Chemical potential of a perfect or real pure gas in terms of fugacity In the case of a *perfect gas*, we know that its molar Gibbs energy (or equivalently in this case its chemical potential) is partially defined by the expression

$$\mathrm{d}G = RT\mathrm{d}p/p.$$

After integration, one obtains

$$G_\mathrm{m} = Cte + RT\ln p \text{ or } \mu = Cte + RT\ln p,$$

where Cte is the integration constant. (These expressions are incorrect from a mathematical standpoint for the reason given above.) We know that the correct expression is $\mu = \mu^\ominus + RT\ln\left(p/p^\ominus\right)$, in which $\mu^\ominus$ is the chemical potential in an arbitrarily chosen state of the gas where it is at the pressure $p^\ominus$. We shall see that this state is called the *standard state*. It may be temporarily defined as the state of the gas in which it exhibits a perfect behavior at pressure $p^\ominus$. Usually $p^\ominus = 1$ pressure unit (historically 1 atm).

For a *real gas*, analogous considerations can be carried out. We have seen just above that

$$\mathrm{d}G = RT\mathrm{d}\ln f,$$

or, for its molar Gibbs energy:

$$\mu = \mu^\ominus + RT\ln\left(f/f^\ominus\right).$$

$\mu^\ominus$ is the integration constant. It is the chemical potential of the gas when its fugacity f is equal to $f^\ominus$. $f^\ominus$ is its fugacity in its standard state. Hence, $\mu^\ominus$ is the chemical potential of the gas in its standard state. It is arbitrarily chosen.

Let us anticipate at this point that *one definition* of the chemical activity a is given by the relation $a = f/f^\ominus$. It expresses the chemical activity of a gas when its fugacity is f in the considered state of chemical potential μ and $f^\ominus$ the fugacity in the arbitrary standard state of chemical potential $\mu^\ominus$.

Fugacity of liquids and solids The definition of the fugacity applies to liquid and solid states as well as to the gaseous state. Every substance in principle, indeed, exhibits a finite pressure vapor, even if in some cases it is exceedingly weak.

When the pure solid (or the liquid) is at equilibrium with its vapor (at a given temperature), the molar Gibbs energy (chemical potential of the species) is the same for both phases. As a result of the preceding considerations,

$$\mu_\mathrm{s}^\ominus + RT\ln\left(f_\mathrm{s}/f_\mathrm{s}^\ominus\right) = \mu_\mathrm{g}^\ominus + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}^\ominus\right) \text{ in case of the solid, and}$$

$$\mu_\mathrm{l}^\ominus + RT\ln\left(f_\mathrm{l}/f_\mathrm{l}^\ominus\right) = \mu_\mathrm{g}^\ominus + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}^\ominus\right) \text{ , in case of the liquid.}$$

$\mu_\mathrm{s}^\ominus$, $\mu_\mathrm{l}^\ominus$, $\mu_\mathrm{g}^\ominus$ are the standard chemical potentials of the chemical species in solid, liquid and vapor phases, and f_s, f_l and f_g are their fugacities in the same conditions (of course, not the standard ones, as the latter are $f_\mathrm{s}^\ominus$,$f_\mathrm{l}^\ominus$,$f_\mathrm{g}^\ominus$).

It is important to note the following point. The fact that the pure solid (or solid) is at equilibrium with its vapor does not, obligatorily, imply that their fugacities are identical in both cases. The reason is a question of choice of standard state. Let us recall that the choice of a standard state is arbitrary. Nothing precludes one from choosing the same standard state in order to quantify the fugacity of the species in solid or liquid phase as that which is the standard state in the vapor phase as well, for example. Then, of course, with such a choice, the fugacities in the standard states for the solid and liquid phases are no longer $f_s^\ominus$ and $f_l^\ominus$ but $f_g^\ominus$. Under these conditions, the equilibrium is expressed by the following two relations:

$$\mu_g^\ominus + RT\ln\left(f_s\Big/f_g^\ominus\right) = \mu_g^\ominus + RT\ln\left(f_g\Big/f_g^\ominus\right)$$
$$\mu_g^\ominus + RT\ln\left(f_l\Big/f_g^\ominus\right) = \mu_g^\ominus + RT\ln\left(f_g\Big/f_g^\ominus\right)$$

As a result, at equilibrium, $f_s = f_g$ and $f_l = f_g$.

The fugacity of the pure compound in the solid (or liquid) state is equal to its fugacity in the vapor state provided that the standard state adopted to quantify the fugacities is the same for both phases, i.e. that chosen for the vapor phase.

Fugacity coefficient of a real gas The fugacity may be larger or smaller than the pressure of the gas. One defines the fugacity coefficient ϕ of a gas by the ratio of its fugacity and of its pressure in the same thermodynamic state: $\phi = f/p$. It is a pure number.

Changes in fugacity with the temperature and the pressure One can demonstrate that the change in fugacity with temperature is given by the relation

$$(\partial\ln f/\partial T)_p = \left(H_m^* - H_m\right)\Big/RT^2,$$

where H_m^* is the molar enthalpy of the gas at null pressure. The difference $\left(H_m^* - H_m\right)$ is the change in the enthalpy accompanying the compression of the gas from the pressure p until the null one at constant temperature. The influence of pressure on the value of the fugacity of a gas at constant temperature is expressed by the relation

$$(\partial\ln f/\partial p)_T = v_m/RT.$$

v_m is the molar volume of the substance regardless of the phase under which it is and whatever its behavior is, perfect or not.

Physical significance of the fugacity According to what was previously mentioned, it is evident that the fugacity of a gas is a kind of fictitious pressure or is a corrected pressure. Considerations of statistical thermodynamics permit one to grasp a deeper knowledge of the relation between the fugacity and the pressure.

Expressions of the chemical potential of a component of a mixture of perfect gases We know that the change in the chemical potential μ_B of every component B of a gaseous mixture with pressure at constant temperature T and molar fraction y is given by the relation

$$\left(\partial\mu_B/\partial p\right)_{T,y} = v_{m_{barr}},$$

where $v_{m_{barr}}$ is the partial molar volume of the component B. This relation is found according to the same reasoning as that leading to $\left(\partial\mu_k\big/\partial p\right)_{T,n_j} = v_{k_{barr}}$ already encountered. In the case of a mixture of perfect gases, indeed, the law of perfect gases applies to the whole mixture. It is written as

$$V = \left(n_1 + n_2 + \cdots + n_n\right)RT/p,$$

where $n_1, n_2, \ldots, n_n$ are the numbers of moles of the different species, p is the total pressure and V the total volume of the system. The partial pressure p_B of each gas (here B) is given by definition by the relation $p_B V = n_B RT$. The partial volume of the component B being given by the expression $v_{m_B} = \left(\partial V/\partial n_B\right)_{T,P,n_j}$, we obtain by derivation of the perfect law applied to the whole mixture: $v_{m_B} = RT/P$ and according to the expression of $v_{m_{barr}}$:

$$\mathrm{d}\mu_B = RT(\mathrm{d}\ln P)_{T,n_j},$$

and according to the previous relations:

$$p_B = n_B(RT/V) \text{ and } P = \sum n_B(RT/V).$$

Since n_B and n are constant, the following equation is satisfied: $\mathrm{d}\ln p_B = \mathrm{d}\ln P$, whence:

$$\mathrm{d}\mu_B = RT\mathrm{d}\ln p_B.$$

After integration, one obtains $\mu_B = \mu_B^* + RT\ln p_B$. μ_B^* is the integration constant. Its value depends only on the nature of the gas and on the temperature as is justified by statistical thermodynamics. It is clear that μ_B^* is the chemical potential of the gas B at the given temperature when its partial pressure is equal to unity.

Hence, the chemical potential of every constituent of an ideal mixture of gases is determined by its partial pressure. (The last equation is not fully satisfactory because of its logarithmic term which seems to be dimensioned.)

Fugacities and mixtures of real gases One partially defines the fugacity of the constituent B in the mixture, at a given constant temperature, by the relation $\mathrm{d}\mu_B = RT\mathrm{d}\ln f_B$, that is to say, after integration, by

$$\mu_B = \mu_B^* + RT\ln f_B. \tag{14}$$

μ_B^* depends on the nature of the gas and on the temperature of the system. The chemical potential of the gas B is also given by the expression

$$\mu_B = \mu_B^\ominus + RT\ln f_B/f_B^\ominus,$$

where $\mu_B^\ominus$ is the standard potential of B and f_B,$f_B^\ominus$ the fugacities of B in the state of the system and in the chosen standard state. The reference state to which is linked the standard state $\mu_B^\ominus$ (which has been just evoked) is the same as that which is retained for a gas alone or in the case of an ideal mixture, since, as has been demonstrated above, the behavior of each gas tends to be perfect when the total pressure tends to be null. Hence, $\mu_B^\ominus$ is the standard chemical potential of B alone, at the same temperature as that of the system. In these conditions, we shall see that the chemical potential in the standard and reference states are equal.

One of the advantages of introducing fugacity lies in the fact that the chemical potential of a component of a mixture of real gases may be expressed by the relation (14), which is formally analogous to that expressing the chemical potential of a mixture of perfect gases. Such expressions elucidate the significance of the chemical potential, since the significance of a corrected pressure is by far closer to a physical reality than is a chemical potential, which is essentially an abstract mathematical notion.

Change in the fugacity of one component of a gaseous mixture with the pressure One can demonstrate that the change in fugacity f_B with the total pressure is obtained by integration from $p = 0$ to $p = p'$, that is to say,

$$\ln\left(f_B/p_B\right) = \int_0^{p'} \left(v_{B_{barr}}/RT - 1/p\right)\mathrm{d}p,$$

with the reference state being such that $f_B^* = p_B^*$. The integration entails our knowing the partial molar volume as a function of the temperature. We can verify that for a mixture of ideal gases, the molar partial volume of a constituent is equal to its molar volume when it is pure, and $f_B = p_B$.

Change in the fugacity of a component of a mixture of real gases with the temperature It is given by the expression

$$\left(\partial \ln f_B/\partial T\right)_p = \left(H_B^* - H_{B_{barr}}\right)/RT^2.$$

$H_{B_{barr}}$ is the partial molar enthalpy of the component B in the mixture at the given pressure and temperature. H_B^* is the molar enthalpy of B when it is at very weak pressure.

- The determination of the fugacity of a gas in a gaseous mixture is possible.
- Under some conditions, the values of the fugacity may be a criterion of equilibrium between different phases. For example, let us consider the transfer of species i from the phase α (its solution) into the phase β (its vapor) at constant pressure and temperature. A first equilibrium criterion is the equality of the chemical potential of i in both phases: $\mu_{i_\alpha} = \mu_{i_\beta}$. By replacing the chemical potentials by their expression, one obtains $\mu_\alpha^\ominus + RT\ln f_{B_\alpha}\Big/f_{B_\alpha}^\ominus = \mu_\beta^\ominus + RT\ln f_{B_\beta}\Big/f_{B_\beta}^\ominus$.

Nothing precludes adopting the standard state of the vapor as the unique state for both phases. As a result, one obtains

$$\mu_{B_\beta}^\ominus + RT\ln f_{B_\alpha}\Big/f_{B_\beta}^\ominus = \mu_\beta^\ominus + RT\ln f_{B_\beta}\Big/f_{B_\beta}^\ominus,$$

that is to say, $f_{B_\alpha} = f_{B_\beta}$ and $f_{B_{solution}} = f_{B_{vapour}}$. One must pay attention, as it has already been said: this is only true if the standard state, at constant temperature, is the same for both phases.

Now, it is worth coming back to the reference state: In order to prepare the future discussion concerning the reference state and the standard state, it is important to note that *the reference state is a real state*. Moreover, it was already mentioned that the reference state is a (real) state in which its fugacity equals its pressure. Hence, we can deduce that the reference state may be defined as a real state in which its fugacity coefficient is equal to its unity. This is the commonly adopted definition for the reference state, in any case for gases. Later, we shall see that the notion of reference state is also linked to the notion of activity.

As has been seen, we have annotated every quantity considered at a very small pressure (that is to say in the reference state) by the symbol * located in exponents.

The notion of fugacity also exhibits a strong practical interest. We only mention the fact that taking into account the fugacities in order to study the equilibria between imperfect gases is often necessary. A striking example is provided by the synthesis of ammoniac.

The quantity activity

A way to express the chemical potential of a compound, distinct from that which directly involves the notion of fugacity, consists in using the quantity called *activity*. Generally speaking, in the case of solutions, this quantity is easier to handle than the notion of fugacity, whereas it is the converse in the case of gases. However, both notions can apply to the two types of phases. In addition, they are intimately linked.

Above all, one must distinguish the activity a_B or (B) of a species B from its absolute activity λ_B. This last notion is only used in statistical thermodynamics. In this paper, we confine our discussion to studying the notion of activity in classical thermodynamics. Hence, we may consider that there exist two definitions of "classical activity":

(a) From the notion of fugacity

The activity a_i of the species i in a given thermodynamic state is defined as being equal to the ratio of its fugacity f_i (in the state where it is studied) and of its fugacity $f_i^\ominus$ in another state called the standard state, generally chosen at the same temperature as the previous one, that is to say, $a_i = f_i/f_i^\ominus$. We see immediately that an activity is a dimensionless number.

(b) From the notion of the chemical potential

We have already seen that the chemical potentials μ and μ° of the studied product in its state and in its standard state obey the relations $\mu_i = \mu_i^* + RT\ln f_i$ and $\mu_i^\ominus = \mu_i^* + RT\ln f_i^\ominus$. Subtracting the latter expression from the former gives

$$\mu_i - \mu_i^\ominus = RT\ln\left(f_i/f_i^\ominus\right), \text{ and } \mu_i - \mu_i^\ominus = RT\ln a_i.$$

The two definitions are equivalent. (Let us note at this point that IUPAC defines the notion of activity without mentioning fugacity.)

This second definition suggests that the change in the chemical potential of a compound is related to its activity by the expression $\mathrm{d}\mu_i = RT\mathrm{d}\ln a_i$. Hence, the second definition of an activity consists, without any consideration of the notion of fugacity, in establishing that the activity is related to the chemical potential of the compound through the general relation

$$\mu_\mathrm{i} = Cte + RT\ln a_\mathrm{i}.$$

This last definition is evidently incomplete because of the occurrence of the integration constant which can take any value. Since in a given thermodynamic state there is only one value of the chemical potential of a species, and given that it is given by the expression $\mu_i = \mu_i^\ominus + RT\ln f_i/f_i^\ominus$, one finds that $Cte = \mu_i^\ominus$. $\mu_i^\ominus$ is called the *standard chemical potential* of *i*. It is a constant which depends only on the nature of *i* and on the temperature.

Consequence of the arbitrary character of the standard state The consequence of the arbitrary character of the choice of the integration constant (i.e. of the standard state) is that different choices must lead to different values of the activity of a compound in the same thermodynamic state. *This is the reality*. (This point is relatively unknown since, actually, some standard states are more judicious in their use than others, and because of that, they are quasi-universally chosen. In such conditions, the problem does not arise.)

Definition of the standard chemical potential of a species According to the previous equations, it appears that the standard chemical potential of a species is its chemical potential when its activity is equal to unity. This definition of the standard chemical potential is general, but it is purely formal. It must be completed.

The activity coefficient By definition, the activity of a species is related to its concentration by a general relation of the type

$$\gamma_i = a_i/c_i,$$

where γ_i is the activity coefficient of the species. An activity coefficient is defined as a dimensionless number regardless of what the "concentration" unit of the compound is, if ever it does possess one. When this is the case, in order to respect this definition, the activity coefficient must be defined by an expression of the type

$$\gamma_i = a_i/\left(C_i/C_i^\ominus\right),$$

where $c_i^\ominus$ is the "concentration" of the species in a particular state; c_i is expressed with the same unit as $c_i^\ominus$. (We shall see in the paragraph "Activities of non-electrolytes in liquid solutions" that there exist several types of activities. In principle, a particular symbolism takes this point into account, as we shall later see.)

A first look of the physical significance of the quantities activity and activity coefficient A physical significance of the activity a_i appears after consideration of the relations

$$\mu_i = \mu_i^\ominus + RT\ln f_i/f_i^\ominus$$
$$\mu_i = \mu_i^\ominus + RT\ln a_i^\ominus$$
$$\mu_i - \mu_i^\ominus = RT\ln a_i^\ominus.$$

We can note that the difference $\mu_i - \mu_i^\ominus$ is the Gibbs energy difference between the considered state and the standard one. It is a measurable quantity by measuring the work which must be developed in order to perform this change. Hence, we can deduce that an activity is a measurable quantity (see the case of ions, however, later). Hence, $\Delta G = RT\ln a_i$.

Since the chemical potential is a molar quantity, it appears that an activity is endowed with a meaning of a change in the molar Gibbs energy accompanying a process evolving from the standard state up to another.

In order to grasp the meaning of the activity coefficient, it is sufficient to write the expression $\mu_\mathrm{i} = Cte + RT\ln a_\mathrm{i}$ and to introduce the expression $\gamma_\mathrm{i} = a_\mathrm{i}/c_\mathrm{i}$ into it; one obtains

$$\mu_\mathrm{i} = Cte + RT\ln\gamma_\mathrm{i} + RT\ln c_\mathrm{i}.$$

We can realize that the term $RT\ln\gamma_\mathrm{i}$, that is to say finally the activity coefficient, represents the part of the chemical potential (belonging to the compound *i*) due to its electrostatic interactions. In some way, this term quantifies the deviation from ideality.

A first return to the standard state We have seen that the standard chemical potential of a species is its chemical potential when its activity is equal to unity. This definition is only a purely formal one, because it does not specify the thermodynamic state (that is to say the physicochemical parameters that describe the state—see chapter 1) in which the species is endowed with an activity unity, that is to say its standard state. It remains to be specify.

Let us begin by stressing the fact that there exists no particular temperature recommended to define a standard state. More precisely, standard states are defined for a given temperature arbitrarily chosen by the experimenter but, for practical reasons, chosen as being that of the studied process. The following two chapters devoted to the activities of gases and to the solutions of non-electrolytes will explain the notion of standard state.

Consequences of the arbitrary character of the standard state The arbitrary character of the choice of the standard state prompts the legitimate question as to the credibility of the numerical values of the thermodynamic quantities obtained through the handling of activities. Here, we already give an answer:

The arbitrary character of the choice of the standard state has no impact on the value of the Gibbs energy change accompanying a process and also has no impact on the changes in other thermodynamic state functions.

We will go deeper into the discussion by considering some equilibria taking into account activities.

In order to close (temporarily) this discussion, we must first bear in mind that the activity of a species is a direct measure of the difference of the partial molal Gibbs energies (chemical potentials) accompanying the crossing of the compound i from the chosen standard state to that studied, that is to say $\mu_i - \mu_i^{\ominus} = RT \ln a_i$. The very fact that the change in the Gibbs energy does not depend on the choice of standard states is demonstrated as follows.

Let us consider the crossing of one mole of gas from a gaseous mixture 1 to a gaseous mixture 2 at constant temperature and pressure (here, the final and initial states are also represented by the superscripts $'$ and $''$). Let us study this transfer in two cases. The first consists in choosing the state α as standard state (process 1), and the second in choosing the state β as the standard state (process 2). For process 1, the Gibbs energy change ΔG_{12} is, using the function fugacity,

$$\begin{aligned}\Delta G_{12}^{\alpha} = {} & \left[RT \ln f_2 + C(T)\right] - \left[RT \ln f_{\alpha}^{\ominus} + C(T)\right] \\ & - \left\{\left[RT \ln f_1 + C(T)\right] - \left[RT \ln f_{\alpha}^{\ominus} + C(T)\right]\right\}\end{aligned}$$

and for process 2,

$$\begin{aligned}\Delta G_{12}^{\beta} = {} & \left[RT \ln f_2 + C(T)\right] - \left[RT \ln f_{\beta}^{\ominus} + C(T)\right] \\ & - \left\{\left[RT \ln f_1 + C(T)\right] - \left[RT \ln f_{\beta}^{\ominus} + C(T)\right]\right\}.\end{aligned}$$

These relations are justified by the fact that fugacities of the solute f_1 and f_2 remain the same whatever the chosen standard state. (States 1 and 2 are indeed the same.) Once the standard state is chosen and maintained, indeed, the fugacities do possess a well-defined value. However, they are different in mixtures 1 and 2 since, owing to the process, the state of the system has changed. Both standard states, quite evidently, exhibit the different fugacities $f_{\alpha}^{\ominus}$ and $f_{\beta}^{\ominus}$. According to these relations,

$$\begin{aligned}\Delta G_{12}^{\alpha} &= RT \ln f_2 - RT \ln f_{\alpha}^{\ominus} - RT \ln f_1 - RT \ln f_{\alpha}^{\ominus}, \\ \Delta G_{12}^{\alpha} &= RT \ln f_2 / f_{\alpha}^{\ominus} - RT \ln f_1 / f_{\alpha}^{\ominus}, \\ \Delta G_{12}^{\alpha} &= RT \ln a_{\alpha}'' - RT \ln a_{\alpha}',\end{aligned}$$

where $a_{\alpha}', a_{\alpha}''$, a_{β}', a_{β}'' are the activities in mixtures 1 and 2 according to the standard states α and β. The difference in the molar Gibbs energy accompanying the crossing from states 1 and 2 (same final and initial states) is obligatorily the same, whatever the standard state: thus, we obtain $\Delta G_{12}^{\alpha} = \Delta G_{12}^{\beta}$ and $\Delta G_{12}^{\alpha} = RT \ln a_{\beta}'' - RT \ln a_{\beta}'$. It can be deduced from this thought experiment that the difference in the molar Gibbs energy is independent of the standard states, whence the proposal.

One consequence of this fact is that the ratio of the activities of a species in the same experimental conditions a and a' based on two different standard states is constant regardless of its concentration. Since the standard states are different, their fugacities are $f^{\ominus}$ and $f^{\ominus\prime}$, and as a result, the activities based on them are $a = f / f^{\ominus}$ and $a' = f / f^{\ominus\prime}$. The ratio of activities is $a / a' = f^{\ominus\prime} / f^{\ominus}$, since the fugacity is the same. The ratio of activities is evidently a constant at a given temperature.

However, we shall later see that if the arbitrary choice of standard states does not change the value of the Gibbs energy of an equilibrated process, it does change the value of the equilibrium constant.

Dependence of the activity on the pressure and on the temperature By starting from the dependence of the fugacity on pressure, one obtains

$$(\partial \ln a / \partial p)_{T,x} = v_{\mathrm{m}_{\mathrm{barr}}} / kT.$$

$v_{\mathrm{m}_{\mathrm{barr}}}$ is the partial molar volume of the compound. x, marked out in subscript, means “at composition constant of other compounds expressed in molar fractions”. By starting from the dependence of the fugacity on temperature, one obtains

$$(\partial \ln a / \partial p)_{p,x} = \left(H_{\mathrm{m}}^{\ominus} - H_{\mathrm{m}_{\mathrm{barr}}}\right) / RT^2.$$

The difference $\left(H_{\mathrm{m}}^{\ominus} - H_{\mathrm{m}_{\mathrm{barr}}}\right)$ is the change in enthalpy accompanying the transfer of one mole of species from the solution to the pure state under the pressure unity.

Activity of gases

Although equilibria in gaseous state are most often studied by handling fugacities, they can also be studied by handling activities. With the studies of solutions in mind, it is however interesting, in a first step, to introduce the notions of activities and of *standard states* in the cases of gases. This first approach is easier to grasp than that followed directly for the study of solutions and, hence, can be used for an introduction of the latter ones.

Usual standard state and activity of a pure gas The standard state of a pure gas is that in which it would exhibit an ideal behavior under a well-defined pressure, called the standard pressure, at the chosen temperature. The standard pressure most often retained is the pressure unity (historically: 1 atm). It is a hypothetical state since gases are no longer ideal at this pressure (with the exception of dihydrogen in some conditions).

Perfect gas Since the fugacity of a perfect gas is equal to its pressure (in all the domain of the latter—see above), its standard state is usually that of fugacity unit $\left(f^{\ominus} = 1\ \text{atm}\right)$ at the chosen temperature. But we must pay attention. This is true only if the gas is perfect. One gas, indeed, the behavior of which would not be ideal, would exhibit one fugacity equal to unity by numerical accident. However, it would not be in its standard state.

According to the general definition of an activity $a = f\big/f^{\ominus}$, if in this state $f^{\ominus} = 1$ (unity), we obtain $a = f/1$. In other words, $a = f$ (numerical values).

Hence, with the choice of the standard state such as $f^{\ominus} = 1$ (unity), the activity of a perfect gas is equal to its fugacity. Moreover, since its fugacity is equal to its pressure, its activity is also equal to its pressure, $a = p$.

It is interesting to note that, since the gas is perfect, its fugacity is always equal to its pressure, including its pressure in the standard state. Of course, when the pressure in the standard state is different from 1 (unity), it holds that $a = p\big/p^{\ominus}$ (perfect gas).

It is also interesting to note that it can be demonstrated that

$$\mu_i^{\ominus} = -kT\ln\left[\left(2\pi mkT\big/h^2\right)^{\frac{3}{2}}kT\right] \text{ (perfect monoatomic gas)}$$

where k and h are Boltzmann's and Planck's constants.

This relation, stemming from a reasoning of statistical thermodynamics, is interesting since it provides us with an expression (taking into account concrete molecular parameters) of the standard chemical potential. When it is introduced only in classical thermodynamics, as has been done up to now, the latter indeed appears to be a rather mysterious quantity.

Real gases The usual standard state is the same as that described previously. It is the hypothetical state in which the gas would exhibit an ideal behavior at the standard pressure $p^{\ominus} = 1$ at the chosen temperature. In the standard state, because of the hypothetical ideal behavior of the gas, $f^{\ominus} = p^{\ominus}$. With $p^{\ominus} = 1$ atm, we find $f^{\ominus} = 1$atm. The standard state remains that for which the numerical value of its activity a is equal to the value of its fugacity $f^{\ominus}$, at a given temperature, that is to say to the unity, $a = f^{\ominus}\big/1$ (standard state), $a = 1$ (standard state). However, in every state of the gas, its fugacity is different from its pressure (if it were on the contrary, it would no longer be real, contrary to the hypothesis). The fugacity coefficient is different from 1. But, owing to the general definition of the activity, $a = f\big/f^{\ominus}$. The latter remains equal to its fugacity (with $f^{\ominus} = 1$ atm): $a = f$ (real gas with $f^{\ominus} = 1$ atm) as a perfect gas. But, since $f \neq p$, it holds that $a \neq p$, or more generally, $a \neq p\big/p^{\ominus}$ (real gas).

There exists one exception to what was just mentioned, that is to say the exception to the fact that the fugacity of a real gas is different from its pressure: the exception is when the pressure is very weak, when interactions between atoms or molecules of gas no longer exist. (Besides, it is in this domain of interactions that the relation $f/p \to 1$ has been set up for $p \to 0$, in order to fix the values of the fugacities.) For these conditions it follows that $a = p\big/p^{\ominus}$ (real gas: very weak pressure).

Finally, the consequence of the choice of such a standard state ($f^{\ominus} = 1$ atm) is that the value of the activity of a gas is equal to the value of its fugacity.

Usual standard state and activity of a gas in a gaseous mixture: ideal mixture Let us consider the component i. We already know that its chemical potential is related to its partial pressure p_i through the expression $d\mu_i = RT\mathrm{d}\ln p_{\mathrm{i}}$. We shall see that the chemical potential μ_i may be expressed as

$$\mu_i = \mu_i^{\ominus} + RT\ln p_i\big/p_i^{\ominus} \text{ (ideal gas or ideal gas mixture),}$$

where $p_i^{\ominus}$ is the partial pressure of i in the standard state and $\mu_i^{\ominus}$ its chemical potential in the same state.$p_i^{\ominus}$ is an arbitrary pressure with respect to which μ_i is based. It is expressed in the same units as p_i. (We can immediately check that when $p_i = p_i^{\ominus}$,$\mu_i = \mu_i^{\ominus}$.) Usually, the standard state of the gas i is chosen in such a manner that its partial pressure is $p_i^{\ominus}$ is equal to 1 atm at the temperature of the system. Since the mixture also exhibits a perfect behavior by hypothesis, all the components also exhibit ideality. The notion of fugacity, applied to the perfect gases and to the real ones as well, results in the following equalities: $f_i = p_i$, and especially: $f_i^{\ominus} = p_i^{\ominus}$. As a result $a_i = f_i\big/f_i^{\ominus}$ as it must be, and $a_i = p_i$ (perfect mixture:$p_i^{\ominus} = 1$ unity) and more generally $a_i = p_i\big/p_i^{\ominus}$ (perfect mixture).

Non-ideal mixture of gases The activity of a gas i in the gaseous mixture is of course defined by the general relation $a_i = f_i\big/f_i^{\ominus}$, where f_i is the fugacity in the considered state and $f_i^{\ominus}$ its fugacity in the standard state. Usually, and as previously noted, the chosen standard state is that in which, at the given temperature, the gas would behave ideally at the partial pressure $p_i^{\ominus} = 1$ atm. It is a hypothetical state in which the mixture behaves ideally, i.e., $f_i^{\ominus} = p_i^{\ominus}$. The same considerations as the previous ones lead to the following facts: $f_i \neq p_i$, and $a_i \neq p_i\big/p_i^{\ominus}$. As previously determined, the result is that the numerical value of the activity is equal to its fugacity, $a_i = f_i\big/f_i^{\ominus}$. This comes from the choice of the adopted standard state, and one finds $a_i = f_i$ (numerical values $f_i^{\ominus} = 1$ unity) and that at very weak pressure p, the fugacity values tend toward those of the partial pressures: $a_i / p_i \rightarrow 1 (p \rightarrow 0)$ (numerical values).

Finally, with the chosen standard state ($p^{\ominus} = 1$ atm, ideal behavior), the value of the activity of the gas is equal to that of its fugacity, whether it is pure or real.

Reference state and standard state

Through the consideration of real gases, we saw that there exists a real state, hence experimentally accessible, in which all properties of the gas but one are the same as in the hypothetical standard state. The mutual properties are due to the ideal behavior exhibited by both the considered real state and the standard state. The real state is that in which the total pressure of the mixture (or that of the sole gas) is very weak. We know that the interactions between the gas molecules are then negligible. Its behavior becomes ideal. This state is the reference state. The reference state is a real state of a very weak "concentration" so that the interactions between the particles constituting the system are negligible. The property of a gas which is not the same in the reference state as in the standard one is, evidently, the value of its fugacity or its activity. Its values are, by far, much weaker in the reference state than in the standard state, since its fugacity and in the occurrence its activity (in numerical values) tend toward the value of its pressure or toward that of its partial pressure (both being then very weak), whereas concerning the activity in the standard state, it is equal to unity by definition.

It is interesting to note that in the mutual properties of the two states, there is the fugacity coefficient which is equal to the unity. By definition of fugacity, indeed, it is equal to unity in the reference state. In the standard state, owing to the ideal character it exhibits, its activity is equal to its pressure.

The reference and standard states must be not be confused. In brief, one can define the reference state of a gas as a real state in which its fugacity coefficient is equal to unity. (We shall see that in the case of solutions, the activity coefficient in the reference state is also equal to unity.) Its standard state is a virtual state in which both its fugacity coefficient and its activity are equal to the unity.

The fact that a reference state is real has the following real and fruitful consequence: the properties of the standard state are obtainable by extrapolation until the value unity of the pressure, of the properties truly exhibited in the reference state, which are experimentally accessible (see later).[2]

General expression of the chemical potential of a gas

The choice of the usual standard state permits one to express the chemical potential of a gas, perfect or real, pure or in mixture, under the following general relations: $\mu = \mu^{\ominus} + RT \ln a$ or $\mu_{\mathrm{i}} = \mu_{\mathrm{i}}^{\ominus} + RT \ln a_{\mathrm{i}}$.

Other standard states There are two ways to choose standard states. The first consists in varying the numerical values of the parameters defining the state. This is legitimate because the choice of a standard state is an arbitrary one. For example, the value $p^{\ominus} = 2$ atm and not the value 1 atm as previously chosen. The second way consists in choosing another physical quantity to which one assigns an arbitrary numerical value. For example, one chooses to relate an activity to the molar concentration of the species instead of its pressure. In this paragraph, we are only interested in the second way.

Let us note that the following considerations are valid for all types of systems (gaseous, liquid and solid). As an example, we choose to express the activity of a gas with respect to its molar concentration $c_i^{\ominus}$. In this case, the activity of a gas in an ideal mixture which at the concentration c_i is defined by the expression $a_{c_i} = c_i / c_i^{\ominus}$, where $c_i^{\ominus}$ is its concentration in the standard state. Its chemical potential is $\mu_i = \mu_{c_i}^{\ominus} + RT \ln a_{c_i}$ (the index c indicates that the chemical potentials and activities are related to the scale of molar concentrations). The chosen standard state in this case is the state in which the behavior of the gas is that of an ideal one at the molar concentration $c_i^{\ominus}$, for example 1 mol L^{-1}. Then its chemical potential is expressed by $\mu_i = \mu_{c_i}^{\ominus} + RT \ln \left(c_i / 1\right)$. The dimension of 1 is mol L^{-1}, and hence 1 represents 1 mol L^{-1}. $\mu_{c_i}^{\ominus}$ is the chemical potential that the gas would possess if its behavior were ideal at 1 molar concentration (or, possibly, at the concentration $c_i^{\ominus}$). When the concentration is such that $c_i = 1$ mol L^{-1}, or $c_i = c_i^{\ominus}$mol L^{-1}, we find again that $a_{c_i} = 1$. It is, as expected, the standard state (corresponding to the scale of molar concentration) since it obeys the general but formal definition according to which the activity of a species in its standard state is equal to unity.

It is interesting, at least from a theoretical standpoint, to relate the activity $a_{c_{\mathrm{i}}}$ to the fugacity of the gas f_i. The reasoning followed to determine the correspondence is based on the invariance of the chemical potential of a species in a given thermodynamic state. It can be demonstrated that the expressions being searched for are $a_{c_{\mathrm{i}}} = f_{\mathrm{i}} / RT$ and $a_{c_i} = a_i / RT$. They are only valid in numerical values. With this new standard state, the proportionality factor relating the fugacity to the activity is now $1 / RT$.

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[2] A possible confusion between the reference and the standard states comes from the fact that, in literature, states called "reference standard states" are sometimes mentioned for which a particular reference pressure is stipulated at a given temperature. We shall not use this term.

Activities of non-electrolytes in liquid solutions

The notion of activity in solution is more complicated than that in the gaseous state. However, its introduction in the case of liquid solutions obeys the same general principles as those in the case of gases. Notably, it also involves the choice of standard states. Among the causes of complexity, let us note the obligatory occurrence of the solvent in addition to that of the solutes, and we shall see that the standard states of solutes differ from those of the solvent for practical reasons. Moreover, the standard states chosen for a solute differ not only from those of the solvent but also according to the scale of "concentrations" adopted for it, even if the solute remains in the same thermodynamic state. In this chapter, we mention the most frequently encountered standard states adopted by the community of chemists.

General definition of an activity

Let us recall that the activity of a species in a given thermodynamic state is equal to the ratio of its fugacity f in the latter and of its fugacity in its standard state $f^{\ominus}$: $a = f/f^{\ominus}$. It is at this point that the fact that every substance, whatever its physical state (gaseous, liquid or solid), does possess a fugacity (and also a partial pressure, even if the latter is very weak) takes all its importance. It permits an identical definition of an activity in every circumstance.

Standard states of pure liquid or solid compounds

It turns out that during the study of chemical reactions in which pure solids and liquids are forming or disappearing, it is convenient to adopt these pure compounds under the pressure of 1 atm and at the temperature of the system, as standard states. According to this convention, the activity of a pure liquid or solid compound at the pressure unity, is taken to be *unity*. Therefore, their molar fraction of course is equal to 1 ($x = 1$): $a = 1$ (pure liquid or solid). Evidently, they form one phase only.

Standard states of liquids in mixtures

In this paragraph, we consider the case of fully miscible liquids, such as water and methanol. Usually, the chosen standard state is that of the component in its pure state, at the temperature of the system, under the unit pressure. The choice presents the interest in maintaining the symmetry of the theoretical treatment of both components. Let us designate them by the indices 1 and 2: $a_1 = 1$ standard state of compound 1 (when $x_1 = 1$), $a_2 = 1$ standard state of compound 2 (when $x_2 = 1$).

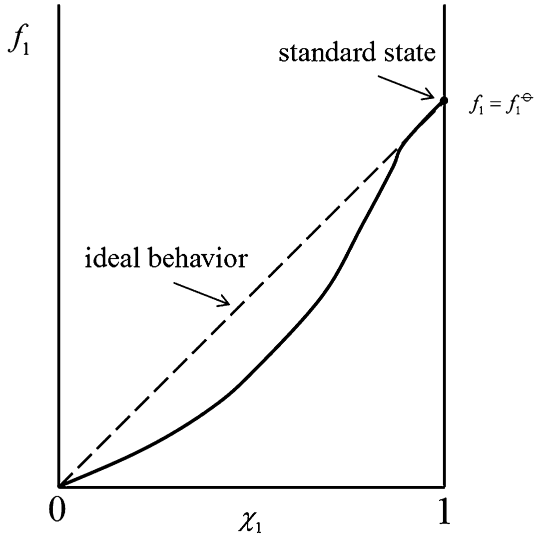

Fig. 7 Representation of the fugacity of the solvent and of its standard state as a function of its molar fraction

Standard states in solutions

We consider successively the cases of the standard states of the solvent and of the solute. Let us begin by recalling that the distinction between the solvent and the solute is not evident. We confine ourselves to naming the component of the solution which is in excess as being the solvent. In the following chapters, it will be marked by the index 1, whereas the solute will be marked by the index 2. We essentially consider binary solutions. From another side, the "concentrations" in solute are related to the anhydrous matter. Except when specifically mentioned, we consider only binary solutions.

Standard states, activities and activity coefficients of the solvent

The first point to mention is that the quasi-unanimously adopted scale of "concentration" for the solvent is that of molar fractions. It is particularly convenient from a practical standpoint, since in such a case the values x_1 are only located in the domain $0-1$.

The standard state quasi-systematically retained for the solvent is the pure solvent at the pressure of the solution and at the chosen temperature. Its fugacity $f_1°$ is given by the relation $f_1^{\ominus} = f_1^{:}$, where $f_1^{:}$ is the fugacity in the pure state ($x_1 = 1$) in the same conditions. The pressure is often, except by chance, very different from 1 atm. Figure 7, which represents the fugacity of the solvent as a function of its molar fraction, illustrates this choice.

Given the general definition of an activity of a species in terms of its fugacities in its thermodynamic state and in the

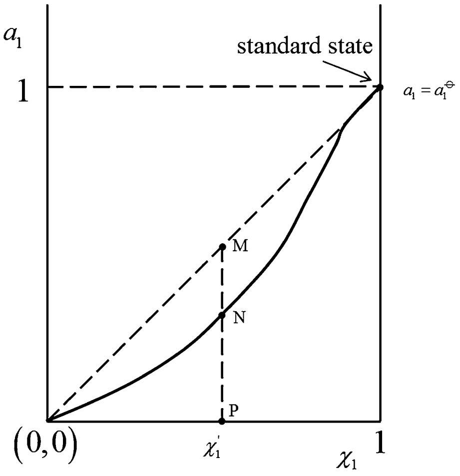

Fig. 8 Activity of the solvent as a function of its molar fraction

standard state, the activity of the pure solvent must be equal to unity since the fugacity in the pure state is equal to that in the standard state $a_1^{\ominus} = 1$. The activity of the solvent cannot be larger than unity, given the upper limit of its fugacity, which is that it possesses in the pure state. Figure 8 shows the activity of the solvent, the fugacity of which is given, as a function of its molar fraction, in Fig. 7. Quite evidently, both curves exhibit the same appearance, since values of activities stem from that of fugacities by division of each point of the latter by the constant $f_1^{\ominus}$. Note that the activity of the solvent as its molar fraction x_1' is given by the ratio NP/MP.

It is interesting to consider the behavior of the solvent in a perfect solution. According to Raoult's law and according to the definition of the standard state, the following relations are verified when the solution is perfect: $f_1 = x_1 f_1^{\cdot}$, $f_1 = x_1 f_1^{\ominus}$, and as a result, $a_1 = x_1 f_1^{\ominus}/f_1^{\ominus}$, and $a_1 = x_1$. In a perfect solution, the activity of the solvent is in linear relation to its molar fraction. Let us remark, before studying analogous but different cases, that there is no problem of dimension in the last equality, both quantities being dimensionless. The slope of the line is 1, since it goes through the points of coordinates (0,0) and (1,1). The dotted line of Fig. 8 is an illustration of this fact. That in dots of Fig. 7 shows the fugacity of the solvent in the ideal case. Its slope is no longer necessarily equal to1, since its fugacity in the pure state is not equal to unity except by numerical accident. From a practical viewpoint, the choice of this standard state is justified by the fact that the more diluted the solution is, the closer to unity the solvent activity (factor, of course, easily handled).

Two examples of the incidence of this choice of standard state on chemical equilibria are found in analytical and physical chemistry. They are encountered when the solvent simultaneously plays two roles in a process. The first is that of solvent and the second that of a reactant. In this case, its activity is taken equal to unity in the standard state, and this explains why, generally in the literature, the activity of the solvent most often does not appear in the expression of the mass law.

The first example is that of the definition of the constant K_a of acid dissociation of the acid HA in water. The equilibrium is

$$HA + H_2O \rightleftarrows H_3O^+ + A^-.$$

At equilibrium, the following thermodynamic constant $K^{\ominus}$ is obligatorily satisfied: $K^{\ominus} = a_{A^-} a_{H_3O^+} / a_{HA} a_{H_2O}$ or equivalently $K^{\ominus} a_{H_2O} = a_{A^-} a_{H_3O^+} / a_{HA}$, which in sufficiently dilute solutions can be written as follows: $K^{\ominus} 1 = a_{A^-} a_{H_3O^+} / a_{HA}$ (for sufficiently dilute solutions). In sufficiently diluted solutions, indeed, given the choice of this standard state, $x_1 \approx 1$, $a_{H_2O} \approx 1$, and by definition:

$$K_a = K^{\ominus} a_{H_2O}, \text{ and } K_a \approx K^{\ominus}.$$

The second example is provided by some so-called overall electrochemical reactions, such as

$$Zn_{(s)} + Cu^{2+} \rightleftarrows Zn^{2+} + Cu_{(s)}.$$

$Zn_{(s)}$ and $Cu_{(s)}$ mean that these metals are in the solid state. They are the electrodes. Each constitutes a pure solid phase. Their activity is, by convention, taken to be equal to unity, as has been mentioned. They usually do not appear in the expression of the mass action law, although they participate in the overall electrochemical reaction.

The values of the activity coefficient of the solvent stem from the previous considerations. The activity coefficient γ_r is,[3] by definition, given by the expression $\gamma_r = a_1/x_1$. Since the ordinate of each point of the line in dots of Fig. 8 is equal to its abscissa (slope = 1), it appears that the activity coefficient is equal to the ratio of both segments NP and MP. In the example shown in Fig. 8, the ratio is systematically less than 1. It is not inevitably the case. In any way, for a real solution, the ratio is different from unity. When the solvent is pure, it is equal to unity.

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[3] The index r recalls the word "rational" resulting from an ancient name. Actually, according to IUPAC in the present case, the activity coefficient should be symbolized by f when the standard state is obtained according to Raoult's law and when the different "concentrations" are expressed in molar fractions. We do not use this symbol, since confusion with fugacity is possible: $\gamma_r = NP/MP$, $\gamma_r = NP/x_1'$.

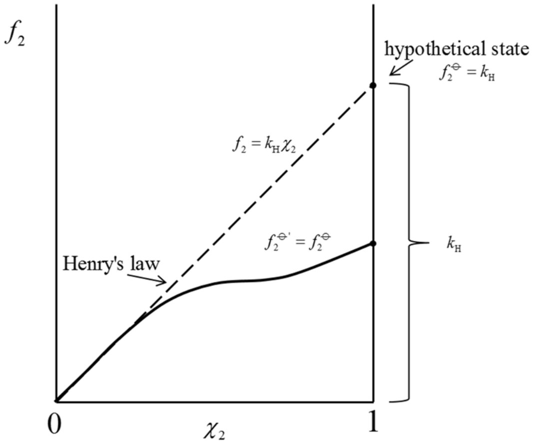

Fig. 9 Possible standard states of a solute (scale of molar fractions)

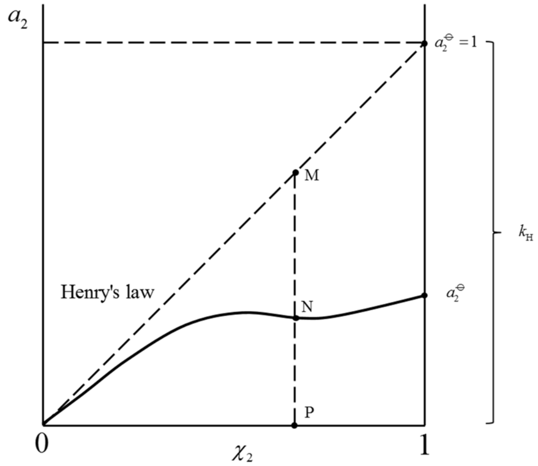

Fig. 10 Activity and activity coefficient of the solute when the standard state is based on Henry's law (scale of molar fractions)

Standard states, activities and activity coefficients of the solutes

In the case of solutes, two standard states are particularly interesting: the rational and the practical ones. There exists only one rational standard state. It is that in which the "concentration" of the solute is expressed in molar fractions. But there are two practical standard states regardless of whether the "concentration" of the solute is expressed in molality or in molarity.

Rational standard states

The concentration of the solute is expressed in molar fractions.

It is wise to choose the standard state in such a way that the value of the solute activity tends toward that of its molar fraction in very dilute solution, at the temperature of the solution, hence such that $a_2/x_2 \rightarrow 1$, when $x_2 \rightarrow 0$.

The interest of this choice lies in the fact that Henry's law is obeyed in this case. Let us take the example of a solute, the fugacity of which is known in the whole domain of the molar fractions (Fig. 9). We note that for the very weak molar fractions, Henry's law is obeyed. The curve of the fugacity is tangent to the line-equation for the low values of x_2:

$$f_2 = k_H x_2 \tag{15}$$

Since in the standard state the solution is by definition ideal, and since its activity coefficient and its activity then tend toward 1, we can write

$$\left(f_2/f_2^\ominus\right)/x_2 \rightarrow 1, \tag{16}$$

when $x_2 \rightarrow 0$.

The value of the fugacity $f_2^\ominus$ in the chosen standard state is obtained after comparison of relations (15) and (16). We immediately find that $k_H = f_2^\ominus$. The fugacity in the standard state is equal to the value of the constant of Henry's law k_H. It is marked on Henry's line for the abscissa $x_2 = 1$.This point (and then the standard fugacity) is experimentally accessible by extrapolation up to $x_2 = 1$ of the measures of fugacities for very weak values of molar fractions. Here is the interest in the choice of this standard state.

It is clear that the chosen standard state is a hypothetical one. We note, indeed, that the real fugacity $f_2^{\ominus\prime}$ of the solute in a pure state (at the same temperature) (viz. curve in solid line) is different from $f_2^\ominus$. Actually, as a rule, we can choose either the standard state of fugacity $f_2^\ominus$ or that of fugacity $f_2^{\ominus\prime} = f_2^{\cdot}$. From a practical viewpoint, the choice of the latter is awkward and even impossible, since it involves knowledge of the fugacity of the solute in the whole domain of the molar fractions such that it is often impossible for solubility reasons. Contrarily to, it is not the case for the first possibility, since Henry's law is all the more strictly obeyed as the mole fraction is weaker. Quite evidently, it is the domain of concentrations where there is less risk of solubility problems.

Figure 10 presents the activity of the solute as a function of its molar fraction, its fugacity being the same as in Fig. 9 and the standard state being obtained by extrapolation of Henry's law.

We note that the activity tends toward the molar fraction only for the weak values of the latter. It is clear that the values of the activities obtained with the pure compound of fugacity $f_2^{\ominus\prime}$ as standard state differ considerably from the previous ones ($a_2^{\cdot} < a_2^\ominus$). Hence, we can already see that the choice of the standard state governs the values of the equilibrium constants.

The activity coefficients γ_x are given by the ratios NP/MP They are dimensionless numbers, since the activities and the molar fractions are dimensionless numbers. It is very

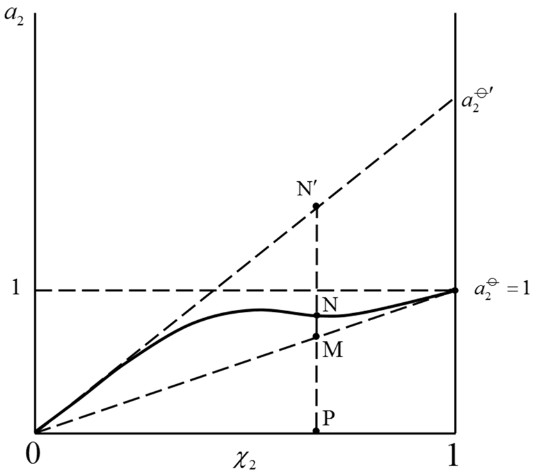

Fig. 11 Activity and activity coefficient of the solute when the standard state is the pure solute (scale of molar fractions)

interesting for our purpose to note that their values may change according to the chosen standard state, as is shown in Figs. 10 and 11. We see that in the first case (the hypothetical one based on Henry's law), the activity coefficient is less than unity, whereas it is the inverse in the second case, in which it is also given by the ratio NP/MP.

Practical standard states

This term means that the "concentration" of the solute is expressed either in molality or in molarity. The choice of these units must be preferred to that of molar fractions as soon as we consider the behavior of the solute. This is the present case. This assertion is explained by the fact that when we use the former unities, the numerical values x_2 are very weak, and hence difficult to handle, since the "concentrations" of the solutes are usually weak. Expressed in molality and molarity, the values obtained for the same quantities of matter in the solution are larger than with molar fractions. Furthermore, as already mentioned, the weak solubilities encountered in practice may remain, therefore, sufficient to determine the activities.

"Concentrations" of solutes expressed in molality Figure 12 shows the fugacity of the solute as a function of the "concentration" of the solute expressed in molality m_i, related to the molality $m_{\mathrm{i}}^{\ominus} = 1$ mol kg^{-1} in the standard state, m_{i} and $m_{\mathrm{i}}^{\ominus}$ being expressed in mol kg^{-1}. Most often, $m_{\mathrm{i}}^{\ominus} = 1$ mol kg^{-1}. In diluted solutions, Henry's law is satisfied. Although, in principle, it expresses a linear relation between the fugacity and the molar fraction of the solute, for very dilute solutions, the linear relation of the fugacity with the molality continues to be obeyed. This is not a surprise, since at very weak concentrations the molalities are proportional to the molar fractions (see chapter 1). It is the same thing with molar concentrations. The proportionality constants, of course, change from a scale of "concentration" to another (see further down). Hence, Henry's law can be written in the case of molalities as $f_2 = k_H' m_2$, when $m_2 \to 0$. Again, for the same reasons as previously stated, it is convenient to choose the standard state in such a way that in diluted solution, at the temperature of the system and at the atmospheric pressure:

$$a_{m_2}' \big/ m_2 \to 1, \quad \text{when } m_2 \to 0.$$

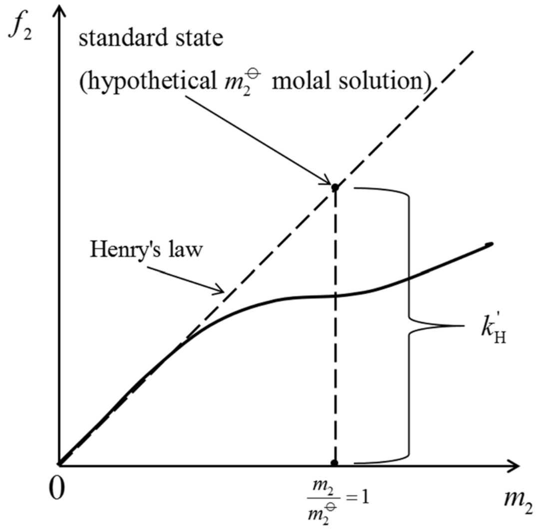

Fig. 12 Definition of the standard state of a solute (practical scale of concentrations expressed in molality)

Obeying simultaneously the last two relations leads directly to the fugacities $f_2^{\ominus}$ in the standard state: $f_2^{\ominus} = k_H'$ (for the standard state). This relation is only valid in numerical values, since fugacity is expressed in atmospheres, whereas the constant k_H' is expressed in atm kg^{-1} mol^{-1}. It is evident that the standard state is hypothetical. It is the state of a solution obeying Henry's law, the concentration of solute being most often 1 mol kg^{-1}. The activity of the solute a_2 is defined as previously described and, as it must be, by the expression $a_{m_2} = f_2 \big/ f_2^{\ominus}$. Figure 13 shows the activity as a function of the molality related to the standard molality. It is interesting to note that a real state, exhibiting an activity unity, may exist. In Fig. 13, it is the point marked on the activity curve for the molality m_2'. However, it is not the standard state, because it is not located on the limit line stemming from that of Henry. The activity coefficient γ_{m_2} is defined by the expression

$$a_{m_2} = \gamma_{m_2} \left(m_2 \big/ m_2^{\ominus} \right).$$

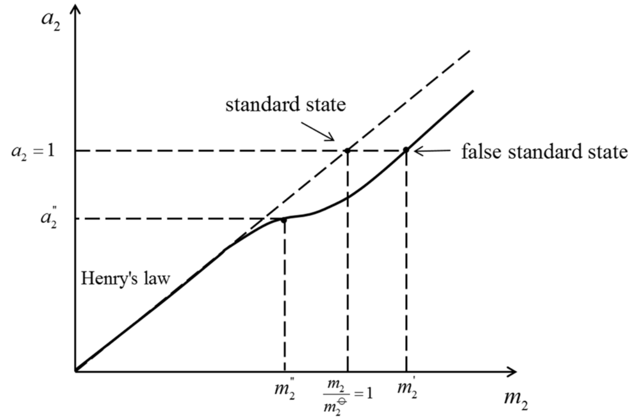

Fig. 13 Activity and activity coefficient of the solute (scale of molalities)

It is clear that it is a dimensionless number. It is easily accessible by considering the diagram in Fig. 13. Let us consider, indeed, the point of molality m_2'' and of activity a_{m_2}''. Let us draw the line which joins it to the origin. Its slope is a_{m_2}''/m_2''. It is by definition endowed by the slope γ_{m_2}.

Concentrations of the solute in molarities The considerations here are strictly analogous to those concerning molalities. They are based on Henry's law. The standard state is the hypothetical one in which the fugacity of the solute is equal to the constant of Henry's law for a concentration of 1 mol L^{-1} at the temperature of the system and at the atmospheric pressure. The concentration $c^{\ominus}$ in the standard state may differ from 1 mol L^{-1}. The activity coefficient of the solute γ_{c_2} is defined by the relation

$$a_{c_2} = \gamma_{c_2}\left(c_2/c_2^{\ominus}\right).$$

It is a dimensionless number. For the same solution, the activities of the solute obtained according to the scales of molalities and molarities exhibit very close numerical values, since the values of the "concentrations" themselves are also very close to each other. As an example, let us consider 1 L of an aqueous solution containing 192.6 g of potassium nitrate. Its molar fraction is 0.0348. Its molarity is 1.906 mol L^{-1} and its molality 2.004 mol kg^{-1}. However, we must note that this solution cannot actually be considered as being very diluted, at least according to the analytical chemists.

Relations between activity coefficients of the same solute, the "concentrations" of which are expressed according to the different scales of concentrations

It is the matter of this paragraph to set up the relations between the activity coefficients of a solute in the same thermodynamic state when its concentrations are related to the scales of molar fractions, molalities and molarities.

For one solution of molality m_2, the number of moles of solute is m_2, and the number of moles of solvent is $1000/M_1$, M_1 being the molar mass of the latter. The factor 1000 comes from the fact that M_1 is expressed in g mol^{-1}, whereas molality is expressed in mol kg^{-1}. As a result, a first expression of the molar fraction of the solute x_2 is

$$x_2 = m_2/\left(m_2 + 1000/M_1\right), \; x_2 = m_2M_1/\left(m_2M_1 + 1000\right). \tag{17}$$

For a solution of molarity c_2. the number of moles of solute is c_2. The number of moles of the solvent is $\left(1000\rho - c_2M_2\right)/M_1$. M_2 is the molar mass of the solute and ρ is the density of the solution. 1000ρ is the mass of 1 l of solution, whereas c_2M_2 is the mass of the solute it contains. The molar fraction, as a function of the molarity, is given by the expression $x_2 = c_2/\left[c_2 + \left(1000\rho - c_2M_2\right)/M_1\right]$ or equivalently by

$$x_2 = c_2M_1/\left[c_2\left(M_1 - M_2\right) + 1000\rho\right]. \tag{18}$$

From (17) and (18), we obtain

$$x_2 = m_2M_1/\left(m_2M_1 + 1000\right) = c_2M_1/\left[c_2\left(M_1 - M_2\right) + 1000\rho\right] \tag{19}$$

For a very dilute solution for which we symbolize the molality by m_2^*, the molality by c_2^* and the molar fraction by x_2^*, the density becomes that of the pure solvent, that is to say $\rho^{\ominus}$. Equation (19) changes and becomes

$$x_2^* = m_2^*M_1/1000 = c_2^*M_1/1000\rho^{\ominus} \tag{20}$$

The difference in the chemical potential of the solute in the solution where its concentrations are x_2, m_2 and c_2 and in that where they are x_2^*, m_2^* and c_2^* is given by the ratio of the activities in both states, that is to say by a_2/a_2^*. The activities in the less dilute state are respectively x_2y_x, m_2y_m and c_2y_c. In the dilute state, we know that with the chosen standard states, the activities are equal to the concentrations expressed according to their scale of concentrations. As a result, given the physical meaning of the ratio of two activities which corresponds to the change in the Gibbs energy accompanying the passage from one state to another which is the same whatever the scale of "concentration", we can write

$$x_2y_x/x_2^* = m_2y_m/m_2^* = c_2y_c/c_2^* \tag{21}$$

By using relations (19) and (20), relation (21) leads to

$$\gamma_x = \gamma_m\left(1 + 0.001m_2M_1\right) = \gamma_c\left[\rho + 0.001c_2\left(M_1 - M_2\right)\right]/\rho^{\ominus} \tag{22}$$

Relations (22) are those we search for. In sufficiently dilute solutions, when the values c_2 and m_2 are weaker than 0.1 mol L^{-1} and 0.1 mol kg^{-1}, the values of the three activity coefficients are quasi-identical. Handling in the same manner (as just previously) the relation (22) by taking into account relations (19) and (20), we obtain

$$\gamma_m = \gamma_c\left(\rho - 0,001c_2M_2\right)/\rho^{\ominus} \quad (23)$$

This relation is useful from a practical standpoint since it permits the passing from the activities based on the scale of molalities to those based on the scale of molarities and inversely. When all is said and done, we observe that if it is an indisputable fact that for the same thermodynamic state the activity of a species does vary with the adopted scale of "concentrations", it appears that it is essentially due to changes in the values of the "concentrations" themselves rather than changes in the activity coefficients, as is demonstrated just above. In relation to this point, let us recall that in physical-chemistry it is the scale of molalities which is generally used, whereas in analytical chemistry it is that of molarities.

Dependence of the activity coefficients on temperature and pressure

It is interesting to know the changes in the activity coefficients with temperature and pressure regardless of the scale of the "concentration" to which the activity is related.

Dependence on temperature Concerning the scale of molar fractions, using the relation $a_x = \gamma_x x$, and since x does not vary with temperature, one finds $\left(\partial \ln \gamma_x / \partial T\right)_{p,x} = \left(H^{\ominus}_{\mathrm{m}} - H_{\mathrm{m_{barr}}}\right)/RT^2$ for the scale of molalities, and one finds $\left(\partial \ln \gamma_m / \partial T\right)_{p,x} = \left(H^{\ominus}_{\mathrm{m}} - H_{\mathrm{m_{barr}}}\right)/RT^2$ for the scale of molarities; the fact that the density of the solution changes with the temperature must not be forgotten. As a result, the expression giving the change is $\left(\partial \ln \gamma_m / \partial T\right)_{p,x} = \left(H^{\ominus}_{\mathrm{m}} - H_{\mathrm{m_{barr}}}\right)/RT^2 + \left[\partial \ln\left(\rho^{\ominus}/\rho\right)/\partial T\right]_{p,x}$.

Dependence on pressure We already know that the change in an activity with pressure at constant temperature and molar fraction is $(\partial \ln a / \partial p)_{T,x} = v_{\mathrm{m_{barr}}}/RT$, where $v_{\mathrm{m_{barr}}}$ is the molar partial volume of the species. Since $a_m = m\gamma_m$, the result is $\left(\partial \ln \gamma_m / \partial p\right)_{T,x} = v_{\mathrm{m_{barr}}}/RT$.

Remark It is an experimental fact that the activity coefficients of non-electrolytes also vary with the charges of the ions in solution, and particularly with what is called the ionic strength of the solution. This point will be studied later.

Activities of electrolytes

The consideration of the solutions of electrolytes using the notion of activity is that which has been the matter of the largest number of studies, in any case in the realm of the study of activities. The handling of the activities is quasi-imperative as soon as we are faced with solutions of electrolytes, since, among all the solutions, the latter are those which exhibit the strongest non-ideality effects. This is due to the electrical charges brought by the ions. For example, even when their "concentrations" are weak, equilibria constants in which ions intervene are not constant, unlike the solutions of non-electrolytes. It is imperative, therefore, either to work with very weak "concentrations" so that these constants remain constants, or to use activities.

General considerations

Given the electrolyte of general formula $\mathrm{M}_{\nu_+}\mathrm{A}_{\nu_-}$, it ionizes in solution according to the equilibrium

$$\mathrm{M}_{\nu_+}\mathrm{A}_{\nu_-} \rightleftarrows \nu_+\mathrm{M}^{z+} + \nu_-\mathrm{A}^{z-}, \quad (24)$$

where $z+$ and $z-$ are the charges of the ions ($z+$ and $z-$ are not necessarily equal in absolute values), and ν_+ and ν_- are the stoichiometric coefficients. The ionization is total in the case of strong electrolytes.

We shall study the notion of activity in the case of (a) the electrolyte taken as a whole, such as the species $\mathrm{M}_{\nu_+}\mathrm{A}_{\nu_-}$ for example, and (b) the ions M^{z+} and A^{z-}.

As in the case of the non-electrolytes, the activity of every species (whatever it is, the electrolyte or one of its ions) is defined as being equal to the ratio of its fugacities f in the studied solutions and $f^{\ominus}$ in its standard state, that is to say $a = f/f^{\ominus}$.

In the literature, in a quasi-systematic manner, the activity a of the species of concern is chosen in such a way that its value tends toward the one of its concentration m expressed in molality or in molarity at infinite dilution. Let us recall that in the standard state, not only the fugacity of the species is $f^{\ominus}$ is equal to unity but its activity is also equal to unity by definition. Let us also recall that in the standard state, the properties of the species are the same as in infinite dilution. These definitions do not differ from those applying to non-electrolytes, and the previous considerations can be summarized by the following symbolism: $a/m \rightarrow 1$, when $m \rightarrow 0$. (Let us finally recall that such standard states are usually adopted for solubility reasons of the solute. It is only for strong dilutions that it is possible to have experimental data of its fugacity—vapor pressure—in hand.)

Given these considerations, it appears that the strategy which must be followed in order to define the activity of a strong electrolyte, and consequently in order to choose its standard state, consists in drawing Henry's line (that is to say in drawing the diagram fugacity—vapor pressure—of the species as a function, for example, of its molality, in prolonging it until the value unity of the molality, and hence in determining the fugacity in the standard state and ultimately its activity). Unfortunately, there exists a major difficulty in applying such a strategy as soon there is a dissociation (of the solute). As a result, the fugacity of the electrolyte tends toward 0 and *this process with a null slope*. Figure 14, which shows the case of hydrochloric acid, illustrates this point.

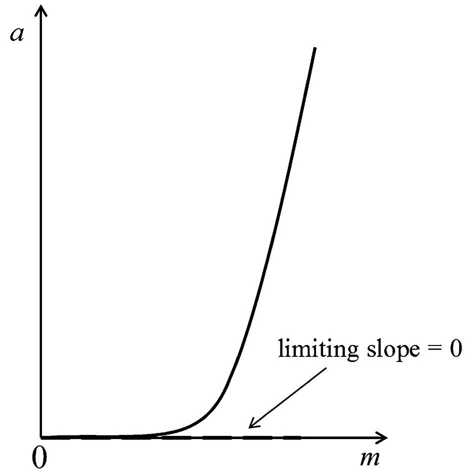

Fig. 14 Diagram of the relative fugacity (activity) of one electrolyte (hydrochloric acid) as a function of its molality

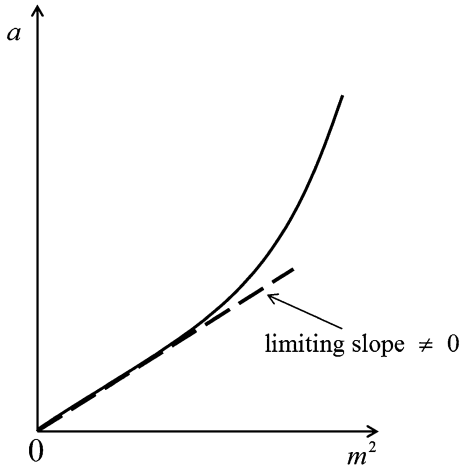

Fig. 15 Fugacity of a univalent strong electrolyte as a function of the square of its molality

Hence, with the electrolytes, it is impossible to proceed as with the non-electrolytes.

Activity of a strong electrolyte

In this case, reaction (24) goes to completion when it occurs from the left to the right.

Case of the univalent electrolyte

Choice of the standard state It is an experimental fact that in the case of a univalent strong electrolyte MA, the diagram of its fugacity as a function of the square of its molality shows a line of finite slope when its molality tends toward zero (Fig. 15). A good example is provided by a solution of hydrochloric gas in water. Hence, according to experimental data, we can set up the following relation:

$$f_2 = k_{\mathrm{H}} m^2, \tag{25}$$

when $m^2 \to 0$, where f_2 is the fugacity of the whole electrolyte and m its molality. k_{H} is the proportionality constant of Henry' s line. Since k_{H} possesses a finite value, it is convenient to choose the standard state in such a manner that the ratio of activity of the (whole) electrolyte a_2 and of the square of molality m_2 tends toward 1 when m tends toward 1, when m tends toward zero, that is to say

$$a_2 / m^2 \to 1 \tag{26}$$

when $m \to 0$. The remaining activity a_2 is defined by the general expression

$$a_2 = f_2 / f_2^{\ominus}, \tag{27}$$

where $f_2^{\ominus}$ is the fugacity of the whole electrolyte in the standard state. The expressions (25), (26) and (27) must be simultaneously verified. A very simple reasoning, starting from the last relations, shows that

$$f_2^{\ominus} = k_H \tag{28}$$

the fugacity in the chosen standard state is equal to the constant of Henry's law in numerical values. It is obtained experimentally by extrapolating Henry's line until the value $m^2 = 1$. Hence, the standard state of an electrolyte 1-1 is the hypothetical one which would exhibit the value of the Henry's law constant (at the pressure of 1 atm and at the temperature of the system) for the value of its fugacity. The chemical potential μ_2 of the whole electrolyte is given by the expression

$$\mu_2 = \mu_2^{\ominus} + RT \ln a_2 \tag{29}$$

Activity coefficient We can define the activity coefficient γ_2 of the whole electrolyte through the relation $a_2 = m_2 \gamma_2$. The comparison of this relation with the preceding equalities shows that in the standard state and also in very dilute solutions, $\gamma_2 \to 1$.

Case of the multivalent electrolytes

Choice of the standard states Regardless of the type of electrolyte, the most convenient standard state is such that the choice of which has the consequence that the ratio of the activity a_2 and the concentration of the electrolyte tends toward 1 (numerical value) when its molality tends toward zero.

Table 1 Equations of Henry's lines according to the kind of electrolyte

	NaCl	$MgSO_4$	Na_2SO_4	$AlCl_3$	$M_{\nu_+}A_{\nu_-}$
$f_2 =$	$k_H m^2$	$k_H m^2$	$k_H m^3$	$k_H m^4$	$k_H m^{(\nu_+ + \nu_-)}$

(a) In the case of a symmetrical electrolyte (in which the ions constituting it bring the same charge in absolute value), the fugacity of the electrolyte in the standard state is equal to the slope of Henry's line $f_2^{\ominus} = k_H$. Henry's law is drawn by writing the fugacity of the electrolyte as a function of the electrolyte, that is to say as a function of the square of its molality m^2; the reasoning behind this choice is strictly the same as that followed in the case of the univalent electrolyte.

(b) In the case of the dissymmetrical multivalent electrolytes, it turns out that, according to their stoichiometry, the experimental Henry's lines have their own equations (see Table 1). In the same line of view as previously, it seems at first sight that one must choose the standard states in which the fugacity $f_2^{\ominus}$ does possess the value of the Henry's law constant k_H, obtained by extrapolation of the line until the value $m^n = 1$, where n would be equal to $1, 2, 3, \ldots, n, \left(\nu_1 + \nu_2\right)$ according to the stoichiometry of the electrolyte.

Actually, there is a choice which proves to be more interesting than the preceding one. It takes into account the fact that the concentrations of the ions coming from the dissociation of these electrolytes are not obligatorily equal (see paragraph 3).

Activity coefficient As usual, the activity coefficient of the solute γ_2 is defined by the expression $\gamma_2 = a_2 / m^2$. It tends toward 1 when m^2 tends toward 0. It is equal to 1 in the standard state corresponding to the electrolyte.

Activity of ions resulting from the dissociation of strong electrolytes

We define strong electrolytes as those which are fully dissociated. Others are called weak electrolytes. Until now, we have not taken into account the dissociation of the electrolyte. However, we were able to set up thermodynamic relations concerning the behavior of the latter without having to take into account its dissociation. This lack of taking into account is not at all surprising, since the very structure of classical thermodynamics is independent of the notions of atoms or molecules. However, the dissociation is an experimental fact, the occurrence of which suffers no doubt. Hence, it appeared interesting to give a thermodynamic framework to the ionic theory, given its great importance.

Since classical thermodynamics do not take into account the phenomenon of dissociation, we can already forecast that a thermodynamic theory of it must stem from some arbitrary choices.

Monovalent electrolyte MA

By hypothesis, the electrolyte is fully dissociated. As a result, naming m_+ and m_- the molalities of the ions M^+ and A^-, the following equalities are satisfied: $m_+ = m$ and $m_- = m$. Since for the dilute solutions, the fugacity of the whole electrolyte MA is proportional to the square of its molality (Henry's line), that is to say, $f_2 = k_H m^2$, we can set up the equivalent relation

$$f_2 = k_H m_+ m_- \tag{30}$$

In other words, it is logical to relate the fact that the fugacity of the electrolyte is proportional to the square of its molality in dilute solution to its dissociation in two ions in the occurrence of the same "concentrations".

Chemical potentials and activities of the ions Since the occurrence of the ions is an unquestionable reality, it appeared interesting to assign a proper chemical potential and a proper activity to everyone. Let μ_+, a_+, μ_-, a_- be the symbols of these individual quantities. In the same spirit as the preceding, the activities of the ions are defined in such a manner that they approach their molality at infinite dilution, in absolute values, that is to say,

$$a_+ / m_+ \to 1 \text{ and } a_- / m_- \to 1 \tag{31}$$

when $m \to 0$. Concerning the definition of the chemical potentials of the ions, one sets up

$$\mu_+ = \mu_+^{\ominus} + RT \ln a_+ \text{ and } \mu_- = \mu_-^{\ominus} + RT \ln a_- \tag{32}$$

A first choice, which is arbitrary but intuitive, consists in laying down the chemical potential μ_2 of the whole electrolyte as being equal to the sum of the chemical potentials of both ions, that is to say,

$$\mu_2 = \mu_+ + \mu_- \tag{33}$$

Let us compare expression (29) and expression (34) just with (the latter resulting from (32) and (33)):

$$\begin{aligned} \mu_2 &= \mu_2^{\ominus} + RT \ln a_2 \\ \mu_2 &= \mu_+^{\ominus} + \mu_-^{\ominus} + RT \ln a_+ a_- \end{aligned} \tag{34}$$

It is evident that a second arbitrary choice, consistent with the first, is to set up

$$\mu_2^{\ominus} = \mu_+^{\ominus} + \mu_-^{\ominus} \tag{35}$$

The result is the equality

$$a_2 = a_+ a_- \tag{36}$$

One may remark that it is possible to recover the relation (36) according to other reasoning starting from the definitions (31). At infinite dilution, indeed, starting from them, we can write $a_+ = m_+$ and $a_- = m_-$, and according to $f_2 = k_H a_+ a_-$. Moreover, by definition, $a_2 = f_2 / f_2^\ominus$, and with the standard state chosen for the electrolyte, $a_2 = f_2 / k_H$. Thus, relation (36) is derived. This reasoning demonstrates that choosing the standard states so that the activity values are equal to the concentrations in dilute solutions permits us to automatically set up relation $\mu_2^\ominus = \mu_+^\ominus + \mu_-^\ominus$. Relation (36) is often used to calculate the activity of an electrolyte by starting from the activities of its ions. We shall see (viz. considerations below) that these relations can be generalized to all types of electrolytes, including the weak ones.

Activity coefficients of ions stemming from the dissociation of strong electrolytes The introduction of the activity of ions induces the notion of the activity coefficient of an ion. By analogy with other systems, and consistent with the definitions of the activities of ions typically adopted, the activity coefficients of ions are defined so that they obey the following relation, such as for a binary electrolyte, through

$$\gamma_{m_+} = a_+ / m_+ \text{ and } \gamma_{m_-} = a_- / m_- \tag{37}$$

Given the definitions adopted for the activities, it is evident that γ_+ and γ_- tend toward unity at infinite dilution: $\gamma_{m_+} \to 1$, when $m \to 0$, $\gamma_{m_-} \to 1$, when $m \to 0$. γ_{m_+} and γ_{m_-} are the activity coefficients on the scale of molalities. If the activities had been related to the molarities or to molar fractions, the symbols of the coefficients would have been $\gamma_{c_+}, \gamma_{c_-}, \gamma_{x_+}, \gamma_{x_-}$ and their values would have been different. (The coefficients γ_c, γ_m,γ_x are sometimes called molal, molar and rational coefficients.)[4] The activity coefficients of the ions, as others, are dimensionless numbers. From mathematical standpoint, relations (37) are incomplete. They should be written as follows: $\gamma_{m_+} = a_+ / \left(m_+ / m_+^\ominus \right)$ and $\gamma_{m_-} = a_- / \left(m_- / m_-^\ominus \right)$, where $m_+^\ominus$ and $m_-^\ominus$ are the molalities in the standard states (for example, 1 mol L^{-1}).

It is of utmost importance to note already here that the activities of the ions and their coefficients cannot be determined experimentally. This is because an ion cannot be alone in a solution. It must be obligatorily accompanied by a counterion in order that the electrical neutrality of the solution should be satisfied. The result is that all experimental information coming from the solution is actually only an emanation from the whole electrolyte and not from the only ion under study. However, their values can be approached, at least in some conditions, by calculations, for example through the use of Debye–Hückel's equations (see Chapter 7).

Mean activity coefficient This is the reason why the notion of mean activity coefficient $\gamma_\pm$ of an electrolyte has been introduced. It is experimentally accessible. This is not a surprise, since it takes into account the occurrence of both ions of opposed charges. It is defined as the geometrical mean of the coefficients of the ions. For example, in the case of a univalent electrolyte, it is given by the expression $\gamma_\pm = \left(\gamma_+ \gamma_- \right)^{\frac{1}{2}}$ or $\gamma_\pm = \left[\left(a_+ / m_+ \right) \left(a_- / m_- \right) \right]^{\frac{1}{2}}$ and according to (36): $\gamma_\pm = \left(a_2 \right)^{\frac{1}{2}} \Big/ m$. Defining the mean activity $a_\pm$ by $a_\pm = \left(a_+ a_- \right)^{\frac{1}{2}}$, we obtain the relation

$$\gamma_\pm = a_\pm / m \tag{38}$$

It is clear that $a_\pm = \left(a_2 \right)^{\frac{1}{2}}$. We note that, according to relation (38), by introducing the mean activity coefficients and the mean activities, one obtains a relation between them which is of the same type as that which is obtained with a non-dissociated derivative.

On the physical meaning of the chemical potential of an ion For some authors, the chemical potential of an ion is nothing more than a fiction. The argument is the following. Let us again consider the case of a strong univalent electrolyte MA. By the general definition of a chemical potential, the relations are $\mu_+ = \left(\partial G / \partial m_M \right)_{T,P,n_1,m_A}$, $\mu_- = \left(\partial G / \partial m_A \right)_{T,P,n_1,m_M}$. m_M and m_A are the molalities of the ions M^+ and A^-, and n_1 the number of moles of the solvent. G is the Gibbs energy of the whole system, and T and P are its temperature and pressure. The fictitious aspect comes from the fact that the chemical potential is a partial derivative. For example, the potential μ_+ is the change in the Gibbs energy of the system dG when the molality of M^+ is changed by the differential dm_M, all other variables defining the state of the system being constant. In particular, it is the case of the molality of the counterion. Now, from an operational standpoint, it is impossible to add an ion into the system without adding one counterion, since the electroneutrality must be verified. Moreover, even admitting that this addition is possible, the simple addition of an electric charge alone would confer supplementary electrical energy to the system, supplementary energy far larger than that which is of interest for our purpose concerning the activities. In brief, the notion of chemical potential of an ion is doubtful.

Some authors somewhat shade the previous reasoning, but their conclusion is the same. They consider that since the differential dm_M is an infinitely (fixed) weak quantity, as is every differential, it is not necessary to add the counterion to respect the electroneutrality. In this case, however, the change dG is immensely weak and hence is imperceptible, and the integration which permits one to obtain the change

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[4] In the following pages, we use the symbols γ_+ (and γ_-) for the scale of molalities.

in Gibbs energy is impractical. In other words, the differentiation process permitting the definition of the chemical potential of an ion, even if it is possible, cannot lead to measurable results, but from this standpoint it remains conceivable.

Multivalent ions

Definitions of the chemical potential and of the activities of multivalent ions The chemical potentials and the activities of the ions constituting the corresponding electrolytes are defined as previously.

Standard states in the case of symmetrical bivalent electrolytes There exist more convenient standard states for dissymmetrical electrolytes than those retained for the symmetrical ones. Concerning the symmetrical bivalent electrolytes, for example $MgSO_4$, the reasoning is identical to that followed in the case of monovalent electrolytes. Relations (11) and (12) apply without any difficulty. As was mentioned in Table 1, Henry's law line is of the type $f_2 = k_H m^2$ or $f_2 = k_H m_+ m_-$. The standard state quasi-unanimously retained is the hypothetical one, in which the fugacity of the electrolyte is equal to Henry's constant at the unit pressure and at the temperature of the system. One can verify that, as is called for by the formal definition of an activity, its activity in this state is equal to 1, since m_+ and m_- must be equal to unity in order that $f_2 = k_H$, while the ideal character is satisfied.

Standard state in the case of multivalent dissymmetrical electrolytes Let us consider the case of an electrolyte 2-1 such as sodium sulfate which dissociates in two cations and one anion. By a reasoning identical to that adopted in the case of symmetrical electrolytes, that is to say, by establishing that the chemical potential of the electrolyte is equal to the sum of the chemical potentials of both ions, we obtain the equality:

$$\begin{aligned} a_2 &= a_+ a_+ a_- \\ a_2 &= \left(a_+\right)^2 a_- \end{aligned} \tag{39}$$

The demonstration is very simple. The chemical potential $\mu_{Na_2SO_4}$ of the electrolyte taken as a whole, is given by the expression $\mu_{Na_2SO_4} = \mu^{\ominus}_{Na_2SO_4} + RT \ln a_{Na_2SO_4}$. The chemical potentials of the ions sodium and sulfate are given by the expressions $\mu_{Na^+} = \mu^{\ominus}_+ + RT \ln a_{Na^+}$, $\mu_{SO_4^{2-}} = \mu^{\ominus}_- + RT \ln a_{SO_4^{2-}}$. The first possible choice which can be made is to admit the following relation: $\mu_{Na_2SO_4} = 2\mu_{Na+} + \mu_{SO_4^{2-}}$. We obtain the relation (39) provided that we admit the following equality:

$$\mu^{\ominus}_{Na_2SO_4} = 2\mu^{\ominus}_{+,Na^+} + 1\mu^{\ominus}_{-,SO_4^{2-}} \tag{40}$$

It is important to note that if the standard potentials $\mu^{\ominus}_+$ and $\mu^{\ominus}_-$ are not endowed with a physical significance, their linear combination above (40) is, as is the case of the combination: $2\mu_{Na+} + \mu_{SO_4^{2-}}$.

Activities and mean activity coefficients The mean activity coefficient $a_\pm$ is defined, as previously described, as being the geometrical mean of the individual activities, that is to say

$$a_\pm = \left[\left(a_+\right)^2 a_-\right]^{\frac{1}{3}} \tag{41}$$

or, in principle, by relation (39):

$$a_\pm = \left(a_2\right)^{\frac{1}{3}} \tag{42}$$

These two relations lead to an inconsistency. When the solution is very diluted, it is once again interesting that the value of the activity of each ion could be equal to that of its concentration, that is to say,

$$a_+ = m_+ = 2m \tag{43}$$

$$a_- = m_- = m \tag{44}$$

where m is the molality of the whole electrolyte. Let us substitute a_+ and a_- by their expressions (43) and (44) into (41). We obtain

$$a_\pm = 4^{\frac{1}{3}} m \tag{45}$$

or in an equivalent way:

$$\begin{aligned} a_2 &= \left(a_\pm\right)^3 \\ a_2 &= 4m^3 \end{aligned} \tag{46}$$

We note that for the dilute solutions, the mean activity no longer tends toward m but rather toward the factor $4^{\frac{1}{3}} m$. In other words, $\gamma_\pm = a_\pm / m \rightarrow 4^{\frac{1}{3}}$, when $m \rightarrow 0$. There is no major drawback that it would be the case, but this is not consistent with the case of symmetrical electrolytes. Here is the new fact. In this context, it is interesting to note that the fugacity in the standard state, that is to say the variable defining the value of the activity, can still be obtained exactly as in the case of symmetrical electrolytes, but it leads to a result which is not consistent with relations (45) and (46).

The usual extrapolation process of Henry's line (in the present case, see Table 1) of Eq. 1 $f_2 = k_H m^3$ so that the value $m = 1$, leads by setting up $f_2^{\ominus} = k_H$ to

$$a_2 \rightarrow m^3, \quad m \rightarrow 0 \tag{47}$$

The only way to make relations (46) and (47) self-compatible is to adopt the quantity $f_2^{\ominus} = k_H / 4$ for the fugacity

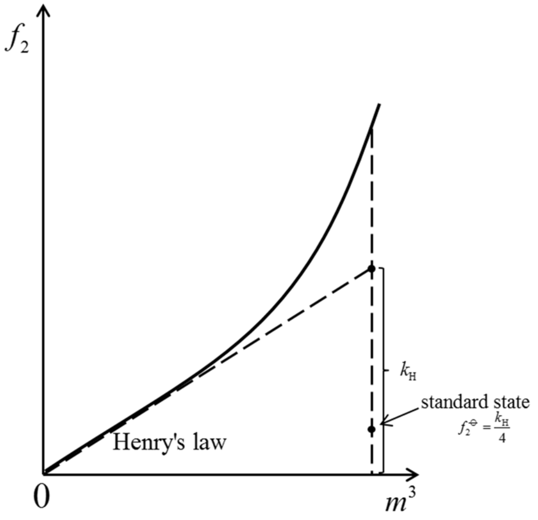

Fig. 16 Determination of the standard state for a ternary electrolyte (for example: Na_2SO_4)

in the standard state. Hence, the standard state is the hypothetical state in which the fugacity is equal to the Henry's constant divided by 4 (in the present case) at the unit pressure and at the temperature of the system. With this value, coherence is attained between the mean activity of the ions and the activity of the electrolyte. From a graphical standpoint, it is sufficient to prolong Henry's straight line until the molality unit and to divide the corresponding ordinate by 4 in order to obtain the standard fugacity (Fig. 16).

Generalization to every strong electrolyte

Let us consider the electrolyte $M_{\nu_+}A_{\nu_-}$ which ionizes by giving ν_+ ions M^{z+} and ν_- ions A^{z-} according to reaction (24). The fugacity f_2 in very dilute solution is given by the expression $f_2 = km^{(\nu_+ + \nu_-)}$ or $f_2 = km^{\nu}$, with $\nu = \nu_+ + \nu_-$. The individual activities of the ions are related to the activity a_2 of the electrolyte by the relation

$$(a\mathrm{M})^{\nu_+}(a\mathrm{A})^{\nu_-} = a_2 \tag{48}$$

It is obtained through the chemical potentials as in the case of the sodium sulfate solution (see above). The chemical potentials of the ions are defined by the expressions $\mu_{M^{z+}} = \mu^\ominus_{M^{z+}} + RT \ln a_{M^{z+}}$ and $\mu_{A^{z-}} = \mu^\ominus_{A^{z-}} + RT \ln a_{A^{z-}}$. One arbitrary sets up the following two expressions: $\mu^\ominus_{M_{\nu_+}A_{\nu_-}} = \nu_+ \mu^\ominus_{+,M^{z+}} + \nu_- \mu^\ominus_{-,A^{z-}}$ and $\mu_{M_{\nu_+}A_{\nu_-}} = \nu_+ \mu_{+,M^{z+}} + \nu_- \mu_{-,A^{z-}}$ from which the following relation is derived:

$$a_{2,M_{\nu_+}A_{\nu_-}} = (a_+)^{\nu_+}(a_-)^{\nu_-} \tag{49}$$

The mean ionic activity $a_\pm$ is given by the expression $a_\pm = (a_2)^{\frac{1}{(\nu_+ + \nu_-)}}$ or $a_\pm = \left[(a_M)^{\nu_+}(a_A)^{\nu_-}\right]^{\frac{1}{\nu}}$.

The mean activity coefficient $\gamma_\pm$ is given by the expression

$$\gamma_\pm = \left[(\gamma_+)^{\nu_+}(\gamma_-)^{\nu_-}\right]^{\frac{1}{\nu}} \tag{50}$$

Given relations (49) and (50), and since $m_+ = m\nu_+$ and $m_- = m\nu_-$, we obtain the following relation: $\ln a_\pm = \ln m_\pm + \ln \gamma_\pm$. $m_\pm$ is called the mean molality, defined by the expression $m_\pm = \left(m_+^{\nu_+} m_-^{\nu_-}\right)^{\frac{1}{\nu}}$. The fugacity in the standard state is given by the expression

$$f_2^\ominus = k_H / \left[(\nu_+ m)^{\nu_+}(\nu_- m)^{\nu_-}\right].$$

Activities of weak electrolytes

In this case, it is necessary to consider the existence of a supplementary species, the non-dissociated form. We shall see that, contrary to what may be perhaps intuitively forecast, the fact that the electrolyte is not fully dissociated does not change the preceding considerations.

Recall that, on one hand, the activity a_2 of the electrolyte $M_{\nu_+}A_{\nu_-}$ taken as whole, is equal to the product of the activities of the ions taken at the power equal to their stoichiometric coefficients. In other words, relation (47, 48) is still legitimate:

$$(a_M)^{\nu_+}(a_A)^{\nu_-} = a_2. \tag{51}$$

On the other hand, the activity a_{nd} (nd: non dissociated) of the non-dissociated fraction is equal to the activity a_2 of the whole electrolyte: $a_{nd} = a_2$. The demonstration of the result that weak electrolytes obey Eqs. (47, 48) is a consequence of the equality (51), which in turn must firstly be demonstrated.

One starts from the relation

$$(\partial G / \partial n)_{T,p,n,n_1} = 0.$$

Let us consider a solution containing the electrolyte $M_{\nu_+}A_{\nu_-}$ as a solute, which partially dissociates according to the equilibrium (24). Let n_1 be the number of moles of the solvent, n the total number of moles of solute, n_{nd} the number of moles of the non-dissociated solute, n_+ that of the ions M^{z+}, and n_- that of the ions A^{z-}. Starting from the stoichiometry of the dissociation reaction (24), we can write the following relations:

$$n_+ = \nu_+(n - n_{nd}) \tag{52}$$

$$n_- = \nu_-(n - n_{nd}) \tag{53}$$

An infinitesimal change dG in the Gibbs energy of the solution, at constant temperature and pressure, is given by (viz. Chapter 1)

$$\mathrm{d}G = \mu_{\mathrm{nd}}\mathrm{d}n_{\mathrm{nd}} + \mu_{+}\mathrm{d}n_{+} + \mu_{-}\mathrm{d}n_{-} + \mu_{1}\mathrm{d}n_{1} \tag{54}$$

According to (52) and (53), the following relations hold: $\mathrm{d}n_{+} = \nu_{+}\mathrm{d}n - \nu_{+}\mathrm{d}n_{\mathrm{nd}}$, and $\mathrm{d}n_{-} = \nu_{-}\mathrm{d}n - \nu_{-}\mathrm{d}n_{\mathrm{nd}}$. By replacing $\mathrm{d}n_{+}$ and $\mathrm{d}n_{-}$ with the last two relations in (54), we obtain

$$\mathrm{d}G = \left(\mu_{\mathrm{nd}} - \mu_{+}\nu_{+} - \mu_{-}\nu_{-}\right)\mathrm{d}n_{\mathrm{nd}} + \left(\nu_{+}\mu_{+} + \nu_{-}\mu_{-}\right)\mathrm{d}n + \mu_{1}\mathrm{d}n_{1} \tag{55}$$

The global equilibrium condition is such that $\mathrm{d}G = 0$. We immediately note that in order for this to be reached, we must simultaneously have the factors of (55) involving the differentials $\mathrm{d}n_{\mathrm{nd}}$, $\mathrm{d}n$ and $\mathrm{d}n_1$ equal to zero. The numbers of moles n and n_1 may be changed independently from each other; the numbers n_{nd} and n_{+} and n_{-} also, since each position of the dissociation equilibrium is possible. Hence, in order that equilibrium should be reached in these conditions, we must have $\left(\mathrm{d}G/\mathrm{d}n_{\mathrm{nd}}\right)_{T,p,n,n_1} = 0$. The result of this condition is

$$\mu_{\mathrm{nd}} = \nu_{+}\mu_{+} + \nu_{-}\mu_{-} \tag{56}$$

Equation (56) becomes

$$\mathrm{d}G = \left(\mu_{+}\nu_{+} + \mu_{-}\nu_{-}\right)\mathrm{d}n + \mu_{1}\mathrm{d}n_{1} \tag{57}$$

Otherwise, at equilibrium, it holds that $(\partial G/\partial n)_{T,P,n_1} = 0$. The partial derivative $(\partial G/\partial n)_{T,P,n_1}$ is, by definition, the chemical potential μ of the electrolyte, taken as a whole

$$(\partial G/\partial n)_{T,P,n_1} = \mu \tag{58}$$

After comparison of (58) and (57), since n and n_1 are independent from each other, we obtain

$$\mu = \nu_{+}\mu_{+} + \nu_{-}\mu_{-} \tag{59}$$

Moreover, the comparison of (56) and (59) shows that

$$\mu_{\mathrm{nd}} = \mu. \tag{60}$$

The chemical potential μ_{nd} of the undissociated electrolyte is equal to the chemical potential of the whole electrolyte.

Let us remark that relation (60) is no more or less than the classical expression of equilibrium of reaction (24).

The setting up of relation (50) is realized as follows. The chemical potentials of the ions are defined exactly as in the case of strong electrolytes. The chemical potential and the standard one of the undissociated electrolyte are those of the electrolytes taken as a whole, as we have just seen.

Determination of activities of electrolytes and non-electrolytes

The most frequently used methods for determining activities are mentioned in this chapter. Probably, these methods are those for binary mixtures by starting from the value of the activity of one of both components. It is founded on the Gibbs–Duhem relation we recall first. We also give the principles of determinations by some other methods.

Activity of one of the components of a binary solution from that of the other component

Once the activity of a component of a binary solution, solvent or solute is determined, it is possible to calculate the activity of the other component. The Gibbs–Duhem relation applied to a binary solution for a process evolving at constant pressure and temperature is

$$n_1\mathrm{d}\mu_1 + n_2\mathrm{d}\mu_2 = 0,\ \ \mathrm{d}p = \mathrm{d}T = 0 \tag{61}$$

By dividing by $n_1 + n_2$, we obtain $x_1\mathrm{d}\mu_1 + x_2\mathrm{d}\mu_2 = 0$, where x_1 and x_2 are the molar fractions. Since the chemical potentials are expressed by the relations $\mu_{\mathrm{i}} = \mu_{\mathrm{i}}^{\ominus} + RT\ln a_{\mathrm{i}}$ and $\mathrm{d}\mu_{\mathrm{i}} = RT\mathrm{d}\ln a_{\mathrm{i}}$, the Gibbs–Duhem relation becomes $x_1\mathrm{d}\ln a_1 + x_2\mathrm{d}\ln a_2 = 0$. This expression is applicable at constant pressure and temperature regardless of the standard state adopted, since the chemical potential of a species in a given state is constant for a given temperature. The previous expression can be rearranged according to

$$\mathrm{d}\ln a_1 = -\left(x_2/x_1\right)\mathrm{d}\ln a_2 \tag{62}$$

$$\mathrm{d}\ln a_2 = -\left(x_1/x_2\right)\mathrm{d}\ln a_1 \tag{63}$$

Activity of the solvent from that of the solute The integration of relation (62) gives $\ln\left(a_1/a_1'\right) = -\int_{x_2'}^{x_2}\left(x_2/x_1\right)\mathrm{d}\ln a_2$.$a_1$ and a_1' are the activities of the solvent in the two solutions where the molar fractions of the solute are x_2 and x_2'. The ratio a_1/a_1' is calculated by plotting the curve $\left(x_2/x_1\right)$ as a function of the values $\ln a_2$ in abscissas and by determining the area under the curve between the limits x_2' and x_2. Actually, the process is not convenient from the standpoint of the precision of the results, since when the solution is very dilute, $\ln a_2$ exhibits very large negative values, and as a result, the evaluation of the area under the curve is not precise. An interesting variant of this integration process has been proposed.

Activity of the solute as a function of that of the solvent The determination is based on the following relation: $\mathrm{d}\ln\left(a_2/x_2\right) = -\left(x_1/x_2\right)\mathrm{d}\ln\left(a_1/x_1\right)$. This relation comes from the following reasoning: $x_1 + x_2 = 1$, $\mathrm{d}x_1 + \mathrm{d}x_2 = 0$, $x_1\left(\mathrm{d}x_1/x_1\right) + x_2\left(\mathrm{d}x_2/x_2\right) = 0$, $x_1\mathrm{d}\ln x_1 + x_2\mathrm{d}\ln x_2 = 0$. Subtracting this expression from (61), we obtain

$$\mathrm{d}\ln\left(a_1/x_1\right) = -\left(x_2/x_1\right)\mathrm{d}\ln\left(a_2/x_2\right) \ \text{ and } \ \ln\left(a_2/x_2\right) = -\int_0^{x_2}\left(x_1/x_2\right)\mathrm{d}\ln\left(a_1/x_1\right).$$

The determination is made through the use of the curve $\left(x_1/x_2\right)/\log\left(a_1/x_1\right)$. Actually, the graphical integration is difficult, since for very dilute solutions the ratio x_1/x_2 tends toward infinity.

Determination by measurements of vapor pressure Given the fact that the activity of every component of a solution is equal to the ratio of its fugacity in the studied state and of its fugacity in the standard state, and given the fact that the fugacity and the vapor pressure of a species are interrelated, it is intuitive that measurements of partial pressure vapors may permit one to approach the values of the activities. The first condition for this strategy to be effective is that the partial pressure vapor must be sufficiently large to be measurable. However, it must not be too large to be assimilated to its fugacity. That is to say, the partial pressure must obey the perfect gas law. In these conditions the following relation holds: $a = f/f^{\ominus}$, i.e., $a \approx p/p^{\ominus}$. According to these considerations, we can determine the activity of either the solvent or the solute.

Activity of the solvent from determination of the freezing point This process is very general. Although it is in principle a method for determining the activity of the solvent, it also permits one to obtain that of the solute in the case of the binary solution. The activity of the solute is then determined using the Gibbs–Duhem relation, once the activity of the solvent is known.

The general principle is as follows: The temperature at which crystals of pure solvent are in equilibrium with a solution depends upon the activity of the solvent in the solution. Changes in the activity of the solvent can be determined, therefore, from measurements of the freezing-point depression due to the addition of solute. Since the activities of solvent and solute are related thermodynamically, it is possible to calculate the activity of the solute once that of the solvent is known.

We begin by setting up a general relation between the solvent activity and the depression of its freezing point. In a second step, we study the determination of the activity of the electrolytes by measuring the freezing-point depression of the solvent.

Concerning the first step, the phenomenon of the depression of the freezing point of the solvent of a binary dilute solution is a consequence of the solid–liquid equilibrium. When a solid is separating from a binary solution, three cases may exist according to the nature of the solid phase. The latter can be constituted by the following:

(a) The pure solute. In this case, the composition of the solution is purely and simply the solubility of the solute at the pressure and temperature of the system.

(b) The pure solvent. The temperature of the system is then named the freezing point of the solvent at the composition and pressure of the system.

(c) A solid solution of both constituents.

The interesting point for our purpose is the second one, and this is the reason why we limit our study to it. It can be demonstrated [7] that the activity of the solvent a_1 is related to the depression of the freezing point θ by the expression

$$-\ln a_1 = L_0\theta/RT_0^2 + \theta^2/RT_0^2\left(L_0/T_0 - \Delta C_p/2\right) \qquad (64)$$

with $T_0 - T = \theta$, where T_0 is the freezing temperature of the pure solvent and T is the freezing temperature in the conditions of the experience. L_0 is an integration constant. It is the molar latent heat of fusion at temperature T_0. ΔC_p is the difference of the molar calorific capacities at constant pressure of the solvent in the pure liquid state and in the pure solid state. The relation above gives the activity of the solvent at temperatures which vary with the solute concentration of the solution. It is desirable to transform the results obtained in this way into results at the same temperature. (Broadly speaking, the depression of the freezing point θ is of the order of 1/10 °C for solutions in which the concentrations in solutes are lower than 0.5 mol kg^{-1}. Let us note, in passing, that it is relatively easy to measure differences in temperature of the order of 10^{-4} °C.)

Concerning now the second step, it is based on the previous expression (64), which can be written as

$$-\mathrm{d}\ln a_1 = 1/RT_0^2\left[L_0 + b\theta + c\theta^2 + \cdots\right]\mathrm{d}\theta,$$

where b and c are constants, and L_0 is the molar latent heat of fusion of the pure solvent at the freezing point of the solvent under 1 atm. It relates the freezing-point depression θ of the solution to the activity of the solvent a_1. The activity of the solute (which can be that of a non-electrolyte or that of a whole electrolyte, but never that of a single ion) is obtained from that of the solvent by using the Gibbs–Duhem relation

$$\mathrm{d}\ln a_2 = -\left(n_1/n_2\right)\mathrm{d}\ln a_1.$$

Determination of activities by the isopiestic method This is one of the simplest methods for determining activities of electrolytes, *through the determination of the mean activity coefficients*. It is based on the comparison of vapor pressures. If two solutions of different electrolytes in the same solvent are placed in an evacuated space, the solution of higher vapor pressure (i.e. higher activity or higher fugacity) of the solvent will distill over and into that of the lower vapor pressure until, when the equilibrium is attained, the solutions will all have the same vapor pressure (and fugacity). Such solutions are said to be *isopiestic* or *isotonic,* the solvent having the same activity in each recipient. Suppose one of these solutions contains a reference substance whose mean ionic activity coefficients at a number of molalities have been determined by a suitable method; it is then possible to calculate the activity coefficients in various solutions of other electrolytes.

At its end of application, indeed, the method is based on the relation $\mathrm{d}\ln a_1 = -\left(x_2/x_1\right)\mathrm{d}\ln a_2$. Let us recall that indexes 1 and 2 correspond respectively to the solvent and the solute in a binary mixture. The last reaction can be written as $\mathrm{d}\ln a_2 = -\left(n_1/n_2\right)\mathrm{d}\ln a_1$ since in the denominator $\left(n_1 + n_\mathrm{i}\right)$, n_i is negligible with respect to n_1 given the high dilution. Let us suppose that n_1 mol corresponds to 1 kg of solvent. In this case, $n_1 = 1000/M_1$, M_1 is the molar mass of the solvent. n_2 is then the number of moles of electrolyte in 1 kg of solvent. Hence, it is its molality *m*. Now, we can write $\mathrm{d}\ln a_2 = -\left(1000/mM_1\right)\mathrm{d}\ln a_1$. Then, according to the definition of the mean activity of the solute, $a_2 = a_\pm^\nu$, with $\nu = \nu_+ + \nu_-$ follows $\mathrm{d}\ln a_2 = \nu\mathrm{d}\ln a_\pm$ and $\left(\nu mM_1/1000\right)\mathrm{d}\ln a_\pm = -\mathrm{d}\ln a_1$. Now, for the reference electrolyte, whose molality and mean ionic activity are indicated by the subscript R, we can likewise write $\left(\nu_\mathrm{R} m_\mathrm{R} M_1/1000\right)\mathrm{d}\ln a_\mathrm{R} = -\mathrm{d}\ln a_1$, when the studied solution and that of reference are isopiestic, the activity of the solvent is the same in each case and it is legitimate to write $\nu m\mathrm{d}\ln a_\pm = \nu_\mathrm{R} m_\mathrm{R}\mathrm{d}\ln a_\mathrm{R}$. According to what is proceeding, $\mathrm{d}\ln a_\pm$ may be replaced by $\mathrm{d}\ln m\gamma_\pm$ and similarly for $\mathrm{d}\ln a_\mathrm{R}$. Hence, $\nu m\mathrm{d}\ln m\gamma_\pm = \nu_\mathrm{R} m_\mathrm{R}\mathrm{d}\ln m_\mathrm{R}\gamma_\mathrm{R}$, where γ_R is the mean activity coefficient of the ions in the reference solution. $\gamma_\pm$ is calculated by integration, since γ_R and a_R are supposed by hypothesis to be known at various molalities m_R. The integration is graphical.

Determination of mean activity coefficient from the practical osmotic coefficient of the solvent One defines the practical osmotic coefficient ϕ of the solvent according to the expression

$$\mu_1 = \mu_1^\ominus - \phi RT\left(M_1/1000\right)\Sigma m_\mathrm{i}.$$

Σm_i is the sum of molalities of all the ions present in the solution. For a single electrolyte, one molecule of which yields ν ions in solution,Σm_i is equal to νm, where *m* is the molality of the electrolyte. Hence, the preceding relation becomes

$$\mu_1 = \mu_1^\ominus - \phi RT\left(\nu mM_1/1000\right).$$

Comparison with the classical expression giving the chemical potential μ_1 leads to the equality

$$\ln a_1 = -\phi\nu mM_1/1000 \tag{65}$$

This expression relates the activity of the solvent to the practical osmotic coefficient. From another standpoint, by definition and also according to already established relations, one can write $x_2 = \nu m/\left(\nu m + 1000/M_1\right)$, and since for a binary solution $x_1 + x_2 = 1$ we deduce $x_1 = 1/\left[\left(\nu mM_1/1000\right) + 1\right]$, and since $x_2 \approx 0$, according to the series development of function $\ln x$: $\ln x_1 = -\nu mM_1/1000$. From the relation (already demonstrated), we have on one hand $\left(\nu mM_1/1000\right)\mathrm{d}\ln a_\pm = -\mathrm{d}\ln a_1$ and after differentiation of (65):

$$\mathrm{d}\ln a_1 = -\nu M_1/1000(\phi\mathrm{d}m + m\mathrm{d}\phi)$$

on the other. Combining these two expressions leads to the two expressions

$$m\mathrm{d}\ln a_\pm = \phi\mathrm{d}m + m\mathrm{d}\phi \text{ and } \mathrm{d}\ln\gamma_\pm = (\phi - 1)\mathrm{d}\ln m + \mathrm{d}\phi.$$

This relation gives the mean ionic activity coefficient $\gamma_\pm$ at the molality *m* in terms of the osmotic coefficient. The latter is determined from vapor pressure measurements. The activity a_1 of the solvent in a given solution is equal to $f_1/f_1^\ominus$, or approximately to $p_1/p_1^\ominus$, where p_1 is the vapor pressure of the solution and $p^\ominus$ is that of the pure solvent at the same temperature: $\ln a_1 \approx -\phi\nu mM_1/1000$, and $\phi \approx -\left(1000/\nu mM_1\right)\ln\left(p_1/p_1^\ominus\right)$. The practical osmotic coefficient can be derived simply from vapor pressure measurements. The determination also implies that one must proceed to one integration [7].

Other methods of determination of activities: by measure of electromotive forces The measurement of activities through that of electromotive forces can address electrolytes and also, somewhat surprisingly, may address some non-electrolytes. This is done with the aid of judiciously designed electrochemical cells. The emf *E* (electromotive force of a cell) may depend on the activities of the species participating in the reactions occurring onto the electrodes or on the activities of the species chemically reacting with the preceding ones.

Activity of non-electrolytes In some cells, the emf may depend on the composition of the electrolyte in the cell and in some other cases, it depends on the states of the electrodes. It is that of cells without a liquid junction. For example, let us mention cells equipped of electrodes constituted by metal solutions of changing concentrations such as metallic alloys or amalgams of different compositions. Thus, let us cite a cell, the electrodes of which are constituted by two thallium amalgams of different concentrations. The cell is represented by the scheme $\mathrm{Tl}\left(\text{amalgam } x_2'\right)|\text{thallous salt}|\mathrm{Tl}\left(\text{amalgam } x_2\right)$. Both electrochemical reactions are as follows:

(d) For the electrode on the left:

$$\mathrm{Tl} \rightleftarrows \mathrm{Tl}^+ + 1\mathrm{e}^-$$

(e) For that on the right:

$$\mathrm{Tl}^+ + 1\mathrm{e}^- \rightleftarrows \mathrm{Tl}$$

There is no global reaction of the cell. The sole net process occurring is the transformation:

$$\mathrm{Tl}\left(\text{amalgam } x_2'\right) \rightarrow \mathrm{Tl}\left(\text{amalgam } x_2\right)$$

The difference in Gibbs energy ΔG accompanying the transfer of one mole of thallium from the anode to the cathode is equal to the difference in the chemical potential μ_2 and μ_2' of thallium in both amalgams, that is to say: $\Delta G = \mu_2 - \mu_2'$, $\Delta G = RT\ln\left(a_2/a_2'\right)$. The increase in Gibbs energy of the system accompanying the transfer is given by the expression $\Delta G = -1FE$. F is the Faraday constant and E is the observed potential difference in the conditions of determination. 1 (unity) is the number of exchanged electrons. The measurement of E (at zero current, cf. [7]) permits one to obtain the ratio of activities. Actually, and moreover, the measurement of E also permits one to reach the activity of the metal in the amalgam and not only the ratio of the two activities, but this is possible only after the standard state of the metal has been fixed (see [7]).

The determination of activities in some cases can also be done with electrochemical cells without liquid junction. (In these cells, the anodic and cathodic compartments are not separated.) Let us consider the following cell without liquid junction:

$$\mathrm{Pt|H_2(1\,atm)|HCl_{(m)}|AgCl_{(s)}|Ag}.$$

The electromotive force (measured at zero current between the two electrodes) is a function of the Gibbs energy change accompanying the reaction:

$$\tfrac{1}{2}\mathrm{H_2} + \mathrm{AgCl_{(s)}} \rightleftarrows \mathrm{HCl_{(m)}} + \mathrm{Ag_{(s)}}.$$

This free-energy change depends on the activities of the four reactants and products. We can write

$$\Delta G = \Delta G^{\ominus} + RT\ln a_{\mathrm{HCl}}a_{\mathrm{Ag}} \Big/ a_{\mathrm{H_2}}^{\frac{1}{2}} a_{\mathrm{AgCl}}.$$

Since the emf is measured under equilibrium conditions (zero current), the cell emf E is given by the relation

$$-nFE = -nFE^{\ominus} + RT\ln a_{\mathrm{HCl}}a_{\mathrm{Ag}} \Big/ a_{\mathrm{H_2}}^{\frac{1}{2}} a_{\mathrm{AgCl}}.$$

$$E = E^{\ominus} - (RT/nF)\ln a_{\mathrm{HCl}}a_{\mathrm{Ag}} \Big/ a_{\mathrm{H_2}}^{\frac{1}{2}} a_{\mathrm{AgCl}}.$$

The cell emf depends only on the activities of hydrogen and chloride ions, since the silver halide, silver and dihydrogen are in their standard states (pure states) in the conditions of the experiment. (It is the same for the dihydrogen pressure **p** maintained at 1 atm.) As a result: $E = E^{\ominus} - (RT/nF)\ln a_{\mathrm{HCl}}$. This cell is convenient for determining the activity of dissolved hydrochloric acid. Note that hydrochloric acid is composed of two ions. It is only the whole electrolyte, the activity of which is determined, as has been previously discussed.

So far, however, we have no value of $E^{\ominus}$, the potential of the cell when the HCl is also at unit activity. The knowledge of $\gamma_{\pm}$ is impossible without an evaluation of $E^{\ominus}$. To this end, one can make use of one of the consequences of the specification of the standard state of the solute, namely that γ must approach unity as the molality of the solute approaches zero. As we shall see, an extrapolation process is necessary.

Utilizing the standard state which makes the activity of each ion equal to its molality at infinite dilution, one can write

$$E = E^{\ominus} - (RT/nF)\ln m_+m_- - (RT/nF)\ln\gamma_+\gamma_-.$$

In the present case (a HCl solution): $\gamma_+\gamma_- = \gamma^{\pm 2}$ and $m_+m_- = m^{\pm 2} = m^2$. The result is

$$E + (2RT/F)\ln m - E^{\ominus} = -(2RT/F)\ln\gamma_{\pm}.$$

This relation permits one to determine $\gamma_{\pm}$ in a hydrochloric solution of molality m from the measurement of E, but this necessitates knowing the value of $E^{\ominus}$. This is done by extrapolation. Taking the case that the determination is carried out at 298.16 K, the working equation becomes

$$E + 0.1183\log m - E^{\ominus} = -0.1183\log\gamma_{\pm}.$$

It will be seen in the discussion of the Debye–Hückel theory (see the next chapter) that the variation in the mean activity coefficient of a univalent electrolyte with molality is given by a relation of the kind

$$\log\gamma_{\pm} = -A\sqrt{m} + Cm,$$

where A is a known constant and C another, the value of which is immaterial. A combination of the last two relations gives the third:

$$E + 0.1183\log m - 0.0602\sqrt{m} = E^{\ominus} - 0.1183Cm.$$

The left-hand side of this equation is a linear function of the molality. Extrapolation of the straight-line plot to $m = 0$ gives the value $E^{\ominus}$. The value obtained in this way is 0.2224 V.

Determination of activities with cells with transference The determination of activities is also possible with cells with transference. The principle of their use to obtain activities, however, is more complicated to study than the previous one. Notably, it involves an integration which may be delicate.

Determination of the activities of the electrolytes from measurements of their solubilities The activity and the activity coefficient of a poorly soluble electrolyte may be obtained from measurements of its solubility when it is in a mixture with other electrolytes, once its solubility product is known. Let us consider the electrolyte $\mathrm{M}_{\nu_+}\mathrm{A}_{\nu_-}$ which dissociates according to the equilibrium (s: solid state) $\mathrm{M}_{\nu_+}\mathrm{A}_{\nu_-} \rightleftarrows \nu_+\mathrm{M}^{z+} + \nu_-\mathrm{A}^{z-}$. According to the usual conventions concerning the activities, that of a solid at atmospheric pressure and forming only one phase ($M_{\nu_+}A_{\nu_-}$) is chosen to be equal to unity. Hence, we can write $K_S = a_{M^{\nu+}} a_{A^{\nu-}}$. The equilibrium constant is called the solubility product and is symbolized by K_S. a_M and a_A are the activities of both ions at saturation of the solution, at atmospheric pressure at the chosen temperature. According to the preceding: $K_S = m_+\nu_+ m_-\nu_- \gamma_+\nu_+\gamma_-\nu_-$ or $K_S = \left(m_\pm \gamma_\pm\right)^\nu$. One deduces that

$$\gamma_\pm = K_S^{\frac{1}{\nu}} \Big/ m_\pm \tag{66}$$

Hence, the mean activity coefficient of a poorly soluble electrolyte can be determined provided that its solubility product is known, together with its mean ionic molality in the solution saturated with the electrolyte. In order to perform the determination, one begins by obtaining the solubility product K_S by measuring the mean ionic molalities at saturation of the electrolytes in the presence of variable quantities of other electrolytes. (Other electrolytes may or may not have one ion in common with the electrolyte under study. Even if only two ions are formed in solution by dissolution of a salt, their activities depend on the presence of other salts. Of course, one must take into account the concentrations of the ions in common with those of the electrolyte in the calculations.) The determination consists in drawing the mean ionic molalities obtained as a function of variable amounts of ions (actually and usually as a function of the *ionic strength of the solution*—see next chapter). The value $m_\pm$ obtained after extrapolation until a null value in added ions into the solution permits one to reach the solubility product. The simple consideration of the relation (66), indeed, shows that K_S is accessible since, then at infinite dilution, the mean activity coefficient is equal to 1, given the actual conventions on the standard states.

Non-ideal solutions of non-electrolytes and activities One knows that there exist empirical relations which permit one to calculate fairly well the fugacities and hence the activities of the components of non-ideal solutions of non electrolytes. The most well known are probably those of Margules and Van Laar: Margules' relation reads as follows:

$$f_1 = x_1 f_1^{\ominus} \exp\left[1/2\beta_1 x_2^2 + 1/2\gamma_1 x_2^3 + \cdots\right],$$
$$f_2 = x_2 f_2^{\ominus} \exp\left[1/2\beta_2 x_1^2 + 1/2\gamma_2 x_1^3 + \cdots\right].$$

It pertains to both solvent and solute. Given the general definition of an activity, one immediately obtains

$$a_1 = x_1 \exp\left[1/2\beta_1 x_2^2\right],\ a_2 = x_2 \exp\left[1/2\beta_2 x_1^2\right]$$

after having kept only the first term of each exponential, whence the expressions of the activity coefficients:

$$\gamma_1 = \exp\left[1/2\beta_1 x_2^2\right] \text{ and } \gamma_2 = \exp\left[1/2\beta_2 x_1^2\right].$$

Actually, it is to demonstrate that the constants β_1 and β_2 are equal. When the vapor pressures are not too high, those measured at different molar fractions in solution permit one to determine the corresponding activities.

Van Laar's relations are an interesting alternative to that of Margules. For two components, they are written as follows:

$$f_1 = x_1 f_1^{\ominus} \exp\left[\alpha_1 x_2^2 \Big/ \left(\beta_1 x_1 + x_2\right)^2\right],$$
$$f_2 = x_2 f_2^{\ominus} \exp\left[\alpha_2 x_1^2 \Big/ \left(x_1 + \beta_2 x_2\right)^2\right].$$

The constants β_1 and β_2 are not the same as those of Margules' equation. The different constants of Van Laar's equations are not independent of each other. Van Laar's relations lead to the following two relations expressing the activity coefficients of the components of a binary solution:

$$\log\gamma_1 = \mathrm{A}\Big/\left(1 + \mathrm{A}x_1/\mathrm{B}x_2\right)^2,\ \log\gamma_2 = \mathrm{B}\Big/\left(1 + \mathrm{B}x_2/\mathrm{A}x_1\right)^2.$$

Calculation of the activities of electrolytes: Debye–Hückel relations

The value of the activity of an ion cannot be determined experimentally, unlike that of an uncharged species. However, it is accessible through a calculation, at least in some conditions of concentrations. Hence, this possibility is of utmost importance from a theoretical standpoint and from a practical one as well. The calculation of the activity of ions is usually performed by applying equations of the kind of Debye–Hückel's relationships. Using Debye–Hückel's relations requires that we know the *ionic strength of the solution*. We begin with an explanation of the term "ionic strength".

Ionic strength

The notion of ionic strength was introduced in 1921 by Lewis and Randall on a purely empirical basis. Its introduction was theoretically justified some years later within the framework of Debye–Hückel's theory. The ionic strength is a function the value of which expresses the charge "in ions" of a solution. It is defined as the half sum of the terms obtained by multiplying the molality m_j of each ion present in solution by the square of its relative charge z_j, that is to say:

$$I_m = \frac{1}{2} \sum_j m_j z_j^2, \tag{67}$$

where I_m is the ionic strength of the solution on the scale of molalities. The index j indicates that the sum is over all the ions of the solution. It is expressed in mol kg^{-1}. It can also be defined in terms of molarities:

$$I_c = \frac{1}{2} \sum_j c_j z_j^2. \tag{68}$$

Then it is expressed in mol L^{-1}. Given that the notion of ionic strength is handled only in the cases of dilute and very dilute solutions, and since the numerical values of molalities are then very close to those of molarities, the numerical values of the ionic strengths expressed in both unities are very close to each other: $I_m \approx I_c$ (dilute solutions). (The symbol μ has also been used to symbolize ionic strength. It is no longer recommended.) It is very important to highlight the fact that the "concentration" m_j or c_j is the true "concentration" of the ions and not their total "concentration", also called "analytical concentration". As a result of this point, the calculation of the ionic strength entails taking into account the incomplete dissociation of some electrolytes. This is not without setting up some difficulties of calculation.

Let us confine ourselves, at the present time, to deduce the following conclusions relative to the fully dissociated electrolytes from relations (67) and (68).

(i) For those of the type 1-1, the ionic strength is equal to its molar concentration. For example, for a solution c molar of sodium chloride: $I = \frac{1}{2}\left\{\left[\mathrm{Na}^+\right]1^2 + [\mathrm{Cl}^-]1^2\right\}, I = c$ [mol L^{-1}].

(ii) For the multivalent ones, it is larger than the molar concentration. Its value increases all the more as charges of the ions themselves increase, since there are changes with the squares of these. For example, for 1 M solution of magnesium sulfate: $I = \frac{1}{2}\left\{\left[\mathrm{SO}_4^{2-}\right] \times 2^2 + \left[\mathrm{Mg}^{2+}\right] \times 2^2\right\}$, $I = 4c \times$ mol L^{-1}.

In direct relation to the use of all Debye–Hückel's relations (see below), the question that comes to mind is this: What are the ions which must be taken into account in order to calculate the ionic strength of the solution containing the ion under study? The answer is simple: all!

Ionic strength and activity of non-electrolytes

The ionic strength, overall, plays a very important role in the numerical value of the activities of the electrolytes, whereas it is rather marginal to study the influence of the ionic strength on the activity coefficients of non-electrolytes. Concerning this question, the most important point to know is that in dilute solutions, the activity coefficients of non-electrolytes are quasi-equal to 1, and hence their activities are quasi-equal to their concentrations in numerical values.

Nevertheless, in the cases of important ionic strengths, the following relation has been found on the basis of experimental data:

$$\ln\left(\gamma/\gamma_0\right) = kI_m,$$

where γ is the activity coefficient of the non-electrolyte when its solubility is m when it is in the presence of some quantity of electrolyte, and γ_0 its activity coefficient in pure water in which the solubility is m_0. I_m is the ionic strength of the solution based on the scale of molalities. It appears that ln γ is proportional to the ionic strength of the solution. This relation seems to be obeyed up to large ionic strengths such as 5 mol kg^{-1}. An interesting point to underline is that the solubility m of the non-electrolyte in the presence of an electrolyte is weaker as that m_0 it exhibits in the presence of pure water. The solubility of a non-electrolyte in water is weakened by the addition of an electrolyte in the solution. It is the basis of the phenomenon called "salting out", which is one of the processes used to resolve liquid phases into their constituents in proximate analysis.

General behavior of the mean ionic activity coefficients of electrolytes

In Table 2, we give experimental values for the mean ionic activity coefficients of several electrolytes in water at 25 °C as a function of their molalities (recall that these activity coefficients are measurable).

These values clearly show the following points:

1. When the molalities are weak, the numerical values of the activity coefficients begin by decreasing. They decrease all the more quickly as the electrolyte is constituted by the most charged ions. This result justifies the definition and the introduction of the ionic strength. For example, for a molality of 0.01 mol kg^{-1}, the activity coefficient of lanthanum chloride is 0.637, whereas for sodium chloride at the same molality, its value is 0.904. The lanthanum chloride activity a_{LaCl_3} is $0.637 \cdot 0.01 = 6.37 \cdot 10^{-3}$. Its value falls very quickly with respect to its concentration. From the standpoint of its thermodynamic behavior, it is as if the occurrence of interactions from several origins, in particular those due to the ion/ion interactions in the bulk solution, would decrease its *effective* presence.
2. The mentioned values show that when the molality of the electrolyte is weak, the activity coefficients of the same kind of electrolytes (from the viewpoint of the charges of the ions constituting them) are quasi-equal.

Table 2 Mean ionic activity coefficients in aqueous solutions at 25 °C (according to [8])

Molality	0.001	0.005	0.01	0.05	0.1	0.2	0.5	1.0	2.0
HCl	0.966	0.928	0.905	0.830	0.796	0.767	0.757	0.809	1.009
NaCl	0.966	0.929	0.904	0.823	0.778	0.732	0.679	0.656	0.670
NaBr	0.966	0.934	0.914	0.844	0.800	0.740	0.695	0.686	0.734
KCl	0.965	0.927	0.901	0.815	0.769	0.717	0.650	0.605	0.575
$CaCl_2$	0.888	0.789	0.732	0.584	0.531	0.482	0.457	0.509	0.807
Na_2SO_4	0.887	0.778	0.714	0.530	0.450	0.360	0.270	0.200	–
$ZnSO_4$	0.734	0.477	0.387	0.202	0.148	0.104	0.063	0.044	0.035
$LaCl_3$	0.853	0.716	0.637	0.417	0.356	0.298	0.303	0.387	0.954

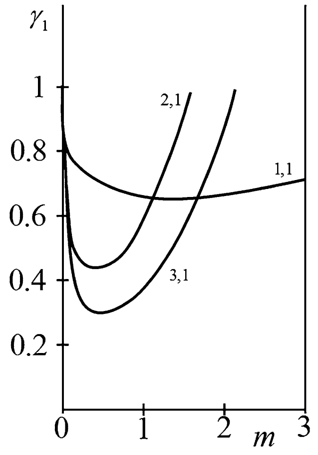

Fig. 17 General behavior of the mean ionic activity coefficients as a function of their molalities and according to the type of electrolyte (symbolism *i*, *j*: *i* metallic ion charge, *j* anion charge)

3. When the molality of the electrolyte increases, the values of the mean ionic activity coefficients begin by decreasing, then reach a minimum, and subsequently end up by increasing.

The general behavior of the mean ionic activity coefficient is shown in Fig. 17, where it is exemplified by three kinds of electrolytes. Sometimes, when the concentration of the electrolyte is very large, the mean ionic activity coefficient may take incredibly large numerical values. For example, for a molality $m = 20$ mol kg^{-1} of lithium bromide in water, the value of its activity coefficient $\gamma_\pm$ reaches 485!

It is interesting to note that there exists one concentration (more rigorously: ionic strength) at which the activity coefficient exhibits the value unity, as if the solution were ideal. This particular concentration varies with the nature of the electrolyte. In aqueous solutions at 25 °C, it is located in the domain about 3–4 mol kg^{-1}. This phenomenon has a practical application. Some authors take it into account in order to quickly approach the values of the equilibrium thermodynamic constants. Let us recall (chapter 1) that the latter are expressed in terms of activities. By fixing the ionic strength of the solution under study in the above range of molalities, the different activity coefficients are close to unity, and hence the values of equilibrium constants calculated by handling concentrations may not frankly differ from the thermodynamic ones. Calculations taking into account the activities, as they must do in all scientific rigor, may indeed be tedious (see chapters 11 and 12). With such a trick, they can be, at least in part, avoided. In any case, they are simplified.

Let us also note in passing that all these behaviors in water we have already mentioned are also recognized in non-aqueous media (ethanol, methanol) and in protic organic media such as the mixtures ethanol–water and dioxan–water. The condition for this is the case that the mixture exhibits a relatively large value of its relative permittivity constant $\varepsilon_{\mathrm{r.}}$ The Debye–Hückel theory and the equations resulting from it, at least in part, account for these results.

Debye–Hückel relations (1923)

One typically distinguishes the *limited Debye–Hückel* and the *extended Debye–Hückel* relations and certain others which are very close to the previous ones.

The limited equation law

Let us confine ourselves to mentioning only what is necessary in order to obtain the limit equation. Debye–Hückel adopted the hypothesis that ions are electrically charged points dispersed in a continuous medium, the permittivity of which is constant and equal to that of the pure solvent. In these conditions, the equation stemming from it, called the Debye–Hückel limiting law, is for a binary electrolyte, the charges of its ions being z_+ and z_-:

$$-\log \gamma_\pm = A\left|z_+ z_-\right|\sqrt{I} \tag{69}$$

where I is the ionic strength of the solution expressed in molalities or molarities. This distinction between the two scales does not matter, given the conditions in which the relation can legitimately be used (see below). A is a constant, the value of which depends only on the temperature and the solvent permittivity ε_r, according to the relations $A = 1.825 \cdot 10^6 (\varepsilon T)^{-\frac{3}{2}}$, $A = 0.509\ \mathrm{mol}^{-\frac{1}{2}} \mathrm{L}^{\frac{1}{2}}$ (water 25 °C). A comparison of the calculated values via expression (69) with those experimentally found for the mean ionic activity coefficients shows that the limiting law is verified only for ionic strengths lower than 10^{-3} mol L^{-1}.

The Debye–Hückel theory also provides us with the relation (70), which permits us to calculate the activity coefficient of one ion only of charge z in sufficiently dilute solution:

$$-\log \gamma = Az^2 \sqrt{I}. \tag{70}$$

As has already been stated, expression (70) cannot be directly compared with an experimental measurement, but it can be indirectly compared. Indirectly, this expression confirms what was experimentally found by studying the behavior of the whole electrolyte. The activity coefficient of an ion, cation or anion depends only on the ionic strength of the solution. This assertion is exact for sufficiently diluted solutions. It was proposed once in 1923 by Lewis and Randall.

Extended Debye–Hückel relation

The previous Debye–Hückel relation (69) leads to activity coefficient values that are much too small for the intermediary concentrations of electrolytes. A change in the limited equation enhancing the range of its applications is obtained by adopting the hypothesis that ions are spheres of finite radius, the other hypothesis prevailing in the setting up of the limiting law remaining the same as before. For a binary electrolyte, the new Debye–Hückel relation, called the extended Debye–Hückel law, is

$$-\log \gamma_{\pm} = A\left|z_+ z_-\right| \sqrt{I} \Big/ \left(1 + \mathrm{B}a\sqrt{I}\right) \tag{71}$$

and for only one ion:

$$-\log \gamma = Az^2 \sqrt{I} \Big/ \left(1 + \mathrm{B}a\sqrt{I}\right) \tag{72}$$

In both expressions, B is a function of the temperature and of the permittivity ε_r of the solvent. B can be calculated as follows: $\mathrm{B} = 50.3(\varepsilon T)^{-\frac{1}{2}}$, $\mathrm{B} = 0.328 \cdot 10^8 \mathrm{cm}^{-1} \mathrm{mol}^{-\frac{1}{2}} \mathrm{L}^{\frac{1}{2}}$ (for water at 25 °C). In (71) and (72), a is an adjustable parameter, corresponding approximately to the effective radius of the hydrated (solvated) ion measured in Å (10^{-10} m). The a parameter is called the "ion-size parameter" or "minimal approach distance" of the ion by another ion of the solution. The parameter A of both (limit and extended) relations is the same. In the case of a binary electrolyte constituted by monovalent ions, the extended Debye–Hückel relation is

$$-\log \gamma = Az^2 \sqrt{m} \Big/ \left(1 + \mathrm{B}a\sqrt{m}\right), \text{ given } m = I.$$

A brief discussion of the Debye–Hückel relations

At first sight, we can conceive that the parameter a is related to the radius r of the ions. By comparing the expressions (70) and (72), one can observe that it is the presence of the denominator in (72) which distinguishes them. This finding may be correlated to the fact that when the concentration of the ion (the ionic strength of the solution) increases, the ionic cloud gets closer to the considered ion, as is shown by the Debye–Hückel theory itself. As a result, the electrical interactions called "long-range" interactions are no longer the only ones that are efficient. "Short-range interactions" add to the previous ones.

One author (Kielland) has compiled the values of the parameter a for 136 inorganic and organic ions in water. They have not, of course, been directly measured. The values result from the comparison of mean activity coefficients already known, adjusted in an empirical manner such that the activity coefficient of an electrolyte can be forecasted in a mixture of other electrolytes. A calculation of the activity of a given ion can then be possible. It is interesting to observe, through the values of Kielland's table, that the activity coefficients do vary rather slightly with the parameter a.

The extended Debye–Hückel equation is satisfactory for ionic strengths varying up to 0.1 mol L^{-1}. The calculations of the mean ionic activity of binary monovalent electrolytes lead to accurate values at the level of 1%, whereas the use of the limited equation leads to errors of the order of 10% in the same conditions.

According to several authors, it seems that the meaning of hydrated radius of the ion under study given to the parameter a is without any thermodynamic base. In addition, inverse calculations of the parameter a as a function of $\sqrt{m}$ by introducing experimental values—log $\gamma_{\pm}$ show that a is not a constant.

The worst is that for some concentrations, a is endowed with fully aberrant values. For example, for molality of 1.8 mol kg^{-1} in HCl and 2.5 mol kg^{-1} in lithium chloride, the respective values of a are −41.12 nm and −14.19 nm! This is the reason why today, a is only considered as an adjustable parameter permitting one to obtain the best fit between the experimental values of the mean activity coefficients and the extended Debye–Hückel relation.

From another viewpoint, it must be noted that for some authors, it seems that the activity coefficients calculated with the Debye–Hückel relations are related to the scale of molar fraction, although the ionic strength values used for their calculations are expressed in molalities or molarities.

The question of the accuracy of the Debye–Hückel theory has arisen, since an ion's activity cannot be measured. Hence, calculations cannot be compared with experimental values. Fortunately, the Debye–Hückel equations can be checked indirectly. This is achieved by comparing the calculated values of mean activity coefficients with those determined experimentally. Mean activity coefficients can indeed be determined experimentally, unlike the activity coefficients of the sole ions. Moreover, they can be calculated from the values found for the individual ions of the electrolyte by using the Debye–Hückel laws. As a result, we can see that it is possible in this way to indirectly compare the experimental and calculated values of some activity coefficients.

Actually, the Debye–Hückel laws predict accurate values for mean activity coefficients. Herein lies their great triumph. It has been found in this way that activity coefficients of ions with the same charge number are identical for low ionic strengths, no matter what the ions are (limiting law). It has been similarly found that for higher ionic strengths, the activity coefficients predicted by the limiting law are too small and that they vary from one ion to another. Finally, in order to predict the correct mean activity coefficients, parameters must be added (viz. Davies and Guggenheim's equations).

The Debye–Hückel theory has achieved enormous success. It is considered among the greatest discoveries of the twentieth century in the realm of physical chemistry. However, it is not fully satisfactory. It leads to difficulties in some cases. For example, the parameter *a* can be endowed with a value that cannot be that of a hydrated ion radius. It can sometimes be negative! Debye himself said that the theory was awarded more success than it deserved. However, Debye–Hückel's laws are now irreplaceable. As just one example, they justify extrapolation procedures to obtain thermodynamic equilibrium constants to null ionic strength. Perhaps the best example of this kind is provided by the fact that Debye–Hückel's laws intervene by permitting reasonable pH values to be assigned to some reference solutions.

Other relations permitting the calculation of the mean activity coefficient of an electrolyte

Numerous relations which are more or less related to those of Debye–Hückel have been proposed. Either they stem from minor modifications of the extended Debye–Hückel equation or they differ from them by the presence of supplementary terms. In connection with this subject, it is interesting to note that from a mathematical standpoint, the Debye–Hückel relations (both limiting and extended) cannot, at all, explain the occurrence of minima in the curves $-\log \gamma_\pm / I$ or $-\log \gamma_\pm / c$ or *m*, as it can be definitively proved by an elementary calculation of derivatives.

Let us mention, as other equations, the *Güntelberg relation* By adopting the unique numerical value $a = 3.0$ Å for all the ions Güntelberg, starting from the extended Debye–Hückel relation, leads to the expression

$$-\log \gamma_\pm = A\left|z_+ \, z_-\right|\left[I \Big/ \left(1 + 1\sqrt{I}\right)\right].$$

The factor unity of $\sqrt{I}$ in the denominator is a real stroke of luck, since at 25 °C, $B = 0.328$ whence $Ba \approx 1$ with $a = 3.0$ Å. The Güntelberg relation seems to give values of $\gamma_\pm$ that are too weak, even in the range of ionic strength values less than 0.1 mol L^{-1}. Another relation very close to that of Güntelberg's plays a fundamental role in the anchoring of the pH scale of the National Bureau of Standards (pH scale of Bates and Guggenheim), that is Guggenheim's relation (1935):

$$-\log \gamma_\pm = A\left|z_+ \, z_-\right|\left[\sqrt{I} \Big/ \left(1 + \sqrt{I}\right)\right] - bI.$$

In this relation, there exists the empirical linear term $-bI$. For larger ionic strengths, supplementary linear terms may be added to the Guggenheim equation, whence the relations of the following kind are derived:

$$-\log \gamma_\pm = A\left|z_+ \, z_-\right|\left[\sqrt{I} \Big/ \left(1 + \sqrt{I}\right)\right] - bI + cI^2 + dI^3.$$

Quite evidently, the greater the number of terms added, the better the fit between the calculated and experimental values. But at the same time the latter added terms $cI^2, dI^3, \ldots$ etc., do possess a statistical weight which is progressively smaller.

A more elaborate form of the Guggenheim relation is

$$-\log \gamma_\pm = A\left|z_+ \, z_-\right|\left[\sqrt{I} \Big/ \left(1 + \sqrt{I}\right)\right] + \left[2\nu_+\nu_- / \left(\nu_+ + \nu_-\right)\right](2\beta m).$$

It applies to only one electrolyte, of which *m* is the molality and ν_+ and ν_- are the charges of the cation and of the anion. β is a parameter specific to each electrolyte. This relation is exact for an ionic strength up to 0.1 mol L^{-1} with univalent, bi-univalent and uni-bivalent electrolytes. The coefficient β of the linear term is adjustable according to the nature of the electrolyte. Guggenheim's equations are semi-empirical relations.

Davies' relations (1938) They are as follows:

$$-\log \gamma_\pm = A\left|z_+ \, z_-\right|\left[\sqrt{I} \Big/ \left(1 + \sqrt{I}\right)\right] - 0.2I, \text{ or}$$
$$-\log \gamma_\pm = Az^2\left[\sqrt{I} \Big/ \left(1 + \sqrt{I}\right)\right] - 0.2I.$$

They have been largely used to estimate the activity coefficients of ions “alone” at relatively large ionic strengths. It seems that for ionic strength of 0.5 mol L^{-1}, the error made by using it on the estimation of the activity coefficient is lower than 8%.

Concerning all these relations, including those comprising one or several linear terms, it is interesting to note that the presence of this term may, mathematically speaking, justify the existence of the minimum of the curves $\gamma_\pm/m$.

Broomley’s relation (1972) According to this theory, the mean activity coefficient of an electrolyte in a binary solution is given by the relation

$$-\log\gamma_\pm = A|z_+ z_-|\left[\sqrt{I}\Big/\left(1+\sqrt{I}\right)\right] + \mathrm{B}_{12}I \text{ with } \mathrm{B}_{12} = \left[(0.06+0.6\mathrm{B})\left(z_1z_2\right)\right]\Big/\left(\left(1+1.5/z_1z_2\right)I\right)^2 + \mathrm{B}.$$

B is the Broomley parameter, and z_1 and z_2 are the charges of both ions of the electrolyte. A is the Debye–Hückel constant A (=0.509). Broomley’s relation is also a semi-empirical relation, since it is based on one hand on those of Debye–Hückel, and on the other on arbitrary terms. Some extensions of Broomley’s relation exist. They permit one to study some mixtures of electrolytes.

Let us also mention the *theory of Meissner and Kusik* (1978), the mainspring of which is the reduced activity coefficient Γ_{AC} defined by

$$\Gamma_{\mathrm{AC}} = \gamma_\pm\left(1/z_+z_-\right),$$

The idea behind this relation is that the reduced activity coefficient is influenced mainly by the interactions between the anions and cations.

Examples of calculations of activity coefficients and of activities

The value of the activity coefficient of an ion, and hence its activity, can be reasonably approached by calculation with the aid of the Debye–Hückel relations and those of the same kinds, for at least some ranges of ionic strengths. Here, we give some examples of calculations of activity coefficients and activities.

The two main Debye–Hückel relations: Davies’ relation

(i) Let us recall the limited equation law $-\log\gamma = Az^2\sqrt{I}$. γ is the searched-for activity coefficient of the ion, z its charge, I the ionic strength of the solution, and A a constant, the value of which depends only on the temperature and the solvent permittivity ε_r. $A = 0.509\ \mathrm{mol}^{-1/2}\mathrm{l}^{1/2}$ (for water at 25 °C). This law is only verified for ionic strengths lower than 10^{-3} mol L^{-1}.

(ii) The extended Debye–Hückel law with the equation:

$$\log\gamma = -Az^2\sqrt{I_c}\Big/\left[1+\mathrm{B}a\sqrt{I_c}\right].$$

B is a constant depending only on the solvent (through its relative permittivity) and on the temperature. $B = 0.3291$ for water at 25 °C. The parameter a measured in angstroms (10^{-10} m) can be considered (at least in some conditions) as being the radius of the hydrated ion. Its occurrence permits its individualization. This was not possible, of course, with the limiting law. The extended law can be legitimately used for ionic strengths lower than 0.1 mol L^{-1}. For higher ionic strengths, the activity coefficients, and hence the activities, are too weak. It is interesting to recall that for ionic strengths lower than 0.1 mol L^{-1}, we can consider $I_c = I_m$ and $\gamma_m = \gamma_c = \gamma_x$, where the symbols m, c and x refer to the scales of “concentrations”: molalities, molarities and molar fractions.

(iii) Davies’ relation: For ionic strengths I_m up to 0.4 to 0.5 mol kg^{-1} (in H_2O), the Davies equation is

$$-\log\gamma = Az^2\left[\sqrt{I_m}\Big/\left(1+\sqrt{I_m}\right) - 0.2I_m\right]$$

and it seems to give a reasonable estimate of the activity coefficient. It has been strongly favored by some authors, in any case for 1-1 and 1-2 electrolytes [9].

Kielland’s tables

Of great interest for the calculation of activities are the Tables 3 and 4 established by Kielland in 1937. They result from a compilation of data present in the literature at the time. Tables 3 and 4 contain the values for 130 ions and the values of the activity coefficients as a function of the ionic strength. Table 3 contains values of the parameter a for ions classified as a function of their electrical charge. For example, the proton appears with the value $a = 9$. In table IV, activity coefficients are mentioned for the ionic strengths 10^{-3} and 10^{-1} mol L^{-1}; the proton exhibits the following respective values $\gamma = 0.967$ and 0.830. The anion citrate^{-3} would possess the value $a = 5$. Its activity coefficients for the ionic strengths 10^{-3} and 10^{-1} mol L^{-1} would present the respective values 0.728 and 0.115. In this occurrence, the striking fact is that the activities differ *considerably* from the concentrations. Here, we again find the influence of the charge of the ion.

Table 3 Values of the parameter *a* of several ions

Charge 1	
9	H^+
8	$(C_6H_5)_2CHCOO^-, (C_3H_7)_4N^+$
7	$OC_6H_2(NO_3)_3, (C_3H_7)_3NH^+, CH_3OC_6H_4COO^-$
6	$Li^+, C_6H_5COO^-, C_6H_4OHCOO^-, C_6H_4ClCOO^-, C_6H_5CH_2COO^-, CH_2^{2-}CHCH_2COO^-, (CH_3)_2CCHCOO^-, (C_2H_5)_4N^+, (C_3H_7)_2NH_2^+$
5	$CHCl_2COO^-, CCl_3COO^-, (C_2H_5)_3NH^+, (C_3H_7)NH_3^+$
4	$Na^+, CdCl^+, ClO_2^-, IO_3^-, HCO_3^-, H_2PO_4^-, HSO_3^-, H_2AsO_4^-, Co(NH_3)_4(NO_2)_2^+, CH_3COO^-, CH_2ClCOO^-, (CH_3)_4N^+, (C_2H_5)_2NH_2^+, NH_2CH_2COO^-, {}^+NH_3CH_2COOH, (CH_3)_3NH^+, C_2H_5NH_3^+$
3	$OH^-, F^-, CNS^-, CNO^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, Rb^+, CS^+, NH_4^+, Tl^+, Ag^+, HCOO^-, H_2(\text{citrate})^-, CH_3NH_3^+, (CH_3)_2NH_2^+$
Charge 2	
8	Mg^{2+}, Be^{2+}
7	$(CH_2)_5(COO)_2^{2-}, (CH_2)_6(COO)_2^{2-}, (\text{congo red})^{2-}$
6	$Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, C_6H_4(COO)_2^{2-}, H_2C(CH_2COO)_2^{2-}, (CH_2CH_2COO)_2^{2-}$
5	$Sr^{2+}, Ba^{2+}, Ra^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, S_2O_4^{2-}, WO_4^{2-}, Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, Co(NH_3)_5Cl^{2+}, Fe(CN)_5NO^{2-}, H_2C(COO)_2^{2-}, (CH_2COO)_2^{2-}, (CHOHCOO)_2^{2-}, (CCO)_2^{2-}, H(\text{citrate})^{2-}$
4	$Hg_2^{2+}, SO_4^{2-}, S_2O_3^{2-}, S_2O_8^{2-}, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}, S_2O_6^{2-}$
Charge 3	
9	$Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, In^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}$
6	$Co(\text{ethylenediamine})_3^{3+}$
5	Citrate^{3-}
4	$PO_4^{3-}, Fe(CN)_6^{3-}, Cr(NH_3)_6^{3+}, Co(NH_3)_6^{3+}, Co(NH_3)_5H_2O^{3+}$
Charge 4	
11	$Th^{4+}, Zn^{4+}, Ce^{4+}, Sn^{4+}$
6	$Co(S_2O_3)(CN)_5^{4-}$
5	$Fe(CN)_6^{4-}$
Charge 5	
9	$Co(S_2O_3)(CN)_4^{5-}$

From a practical viewpoint, the following questions can come to mind:

1. What value of *a* must be chosen for the relation $\log\gamma_\pm = -A|z_+ z_-|\sqrt{I}\Big/\left(1 + \mathrm{B}a\sqrt{I}\right)$, that of the cation or that of the anion? Answer: it is judicious to take the mean value.
2. What strategy must we adopt when the ion is not listed? Answer: generally, one takes the values of a listed one of the same charge and of about the same volume as that studied.

Exercises

(1) Ionic strength of the following solutions: KCl 0.1 mol L^{-1}; ZnCl$_2$ 0.1 mol L^{-1}; ZnSO$_4$ 0.1 mol L^{-1}; Al$_2$(SO$_4$)$_3$ 0.1 mol L^{-1}; NH$_3$ 0.1 mol L^{-1} knowing that $K_a(NH_4^+) = 5\ 10^{-10}$.

(2) Ionic strength and activities of the different species of a mixture of 10 cm^3 HCl solution 1/20 mol L^{-1} and 40 cm^3 of ZnCl$_2$ 1/80 mol L^{-1}.

(3) Calculation of γ_H for solutions HCl 10^{-1}, 10^{-2},10^{-3},10^{-4},10^{-5} mol L^{-1}.

(4) Ionic strength of (a) an aqueous solution of KCl 0.01 mol L^{-1}, and (b) of an aqueous solution of zinc chloride ZnCl$_2$ 0.02 mol L^{-1}?

(5) Calculation of activities (related to concentrations expressed in mol L^{-1}) of chloride ions in the following aqueous solutions: HCl 10^{-2} mol L^{-1}; KCl 10^{-3} mol L^{-1}; a mixture of KCl 10^{-3} mol L^{-1} and ZnCl$_2$ 10^{-3} mol L^{-1} (the concentrations apply once the mixture is carried out) (use the limited Debye–Hückel equation with $A = 0.509$).

Table 4 Values of the activity coefficients as a function of the ionic strength and of the parameter a (according to [10])

a	0.001	0.0025	0.005	0.01	0.025	0.05	0.1
Charge 1							
9	0.967	0.950	0.933	0.914	0.88	0.86	0.83
8	0.966	0.949	0.931	0.912	0.88	0.85	0.82
7	0.965	0.948	0.930	0.909	0.875	0.845	0.81
6	0.965	0.948	0.929	0.907	0.87	0.835	0.80
5	0.964	0.947	0.928	0.904	0.865	0.83	0.79
4	0.964	0.947	0.927	0.901	0.855	0.815	0.77
3	0.964	0.945	0.925	0.899	0.85	0.805	0.755
Charge 2							
8	0.872	0.813	0.755	0.69	0.595	0.52	0.45
7	0.872	0.812	0.753	0.685	0.58	0.50	0.425
6	0.870	0.809	0.749	0.675	0.57	0.485	0.405
5	0.868	0.805	0.744	0.67	0.555	0.465	0.38
4	0.867	0.803	0.740	0.660	0.545	0.445	0.355
Charge 3							
9	0.738	0.632	0.54	0.445	0.325	0.245	0.18
6	0.731	0.620	0.52	0.415	0.28	0.195	0.13
5	0.728	0.616	0.51	0.405	0.27	0.18	0.115
4	0.725	0.612	0.505	0.395	0.25	0.16	0.095
Charge 4							
11	0.588	0.455	0.35	0.255	0.155	0.10	0.005
6	0.575	0.43	0.315	0.21	0.105	0.055	0.027
5	0.57	0.425	0.31	0.20	0.10	0.048	0.021

(6) One mixes equal volumes of aqueous solutions of NaCl (0.02 mol L^{-1}) and of $ZnCl_2$ (8×10^{-3} mol L^{-1}). Ionic strength of the obtained solution? Activities (related to the molar concentrations) of ions Zn^{2+}, Na^+ and Cl^-?

(7) Ionic strength of the aqueous solution of potassium chromate K_2CrO_4 and ferric chloride $FeCl_3$ of respective concentrations 0.08 mol L^{-1} and 0.06 mol L^{-1}? (K_2CrO_4 and $FeCl_3$ can be considered as being strong electrolytes.)

(8) Calculation of the activity of the ceric ion Ce^{4+} in a solution of ionic strength 9×10^{-3} mol L^{-1}. Use the Debye–Hückel limiting law.

(9) Let us consider an aqueous solution of aluminum sulfate $Al_2(SO_4)_3$ 10^{-3} mol L^{-1}. (a) Calculate the concentrations (mol L^{-1}) of sulfate and aluminium ions. (b) Calculate the ionic strength of the solution. (c) Calculate the activity coefficients of the ions and (d) their activities. Use the following Debye–Hückel's relation:$\log \gamma_{\pm} = -Az^2\sqrt{I} \Big/ \left(1 + \mathrm{B}a\sqrt{I}\right)$ with $A = 0.509$, $B = 0.328$ and $a = 4$ for the sulfate ion and $a = 9$ for the aluminum ion.

Excess Gibbs energies and activities

Besides the fact that the introduction of the activities enables, among other processes, the quantification of chemical equilibria when the behavior of the fluids of the studied system is not ideal, it must be noted that, conversely, it also constitutes a means for studying non-ideal solutions. Another way to study them is to use excess functions which are experimentally accessible. For some authors, their handling would be the best and perhaps easiest means for studying real (that is to say non-ideal) solutions and even for studying equilibria between fluids. These few lines are sufficient to become cognizant of the existence of interesting mathematical expressions linking excess functions and activities. As this matter stands, it is evident that part of our purpose is to study the links between activities and excess Gibbs functions. They concern solutions of non-electrolytes and those of electrolytes as well. In this chapter, we study the determination of activities from excess Gibbs energies by using empirical relations. We are essentially interested in the binary solutions.

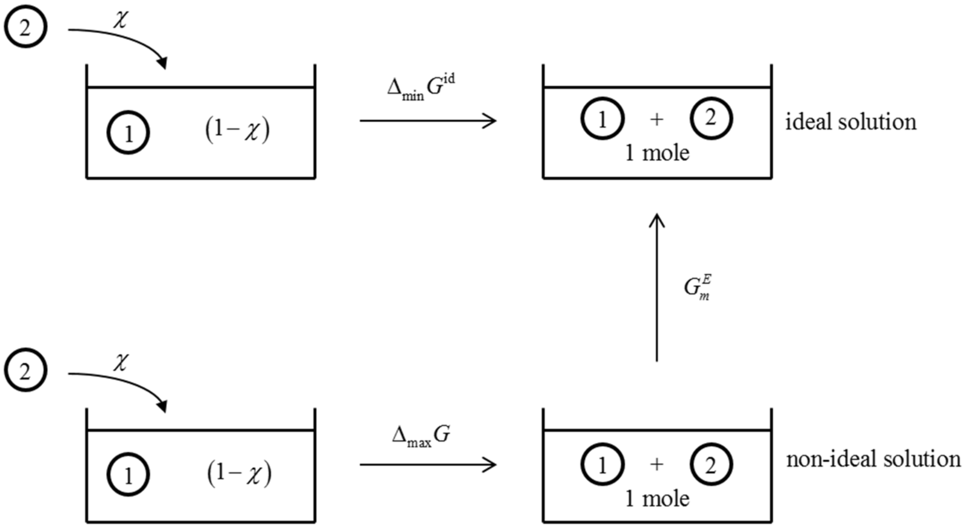

Fig. 18 Gibbs energies of mixing, ideal mixing and excess (x molar fraction of the solute and $1 - x$ that of the solvent)

Mixing and excess Gibbs energies

Mixing Gibbs energy

Let us consider the process which consists in mixing n_1 mol of species 1 (the solvent) and n_2 mol of species 2 (the solute i), with formation of a liquid solution. Species 2 may be a non-electrolyte or an electrolyte. The solvent and the solute are pure before the formation of the solution (initial state). In the latter, their chemical potentials (molar Gibbs energies, not yet partial ones because they are pure) are given by the expressions $\mu_i = \mu_i^\ominus + RT\ln x_i$, and since the solvent is pure, $x_1 = 1$, $\mu_1 = \mu_1^\ominus$, and in a similar manner since i is pure, $\mu_i = \mu_i^\ominus$. The Gibbs energy of the initial system G^{in} constituted by both components (which are still not in mixture) is given by the expression $G^{\mathrm{in}} = n_1\mu_1^\ominus + n_i\mu_i^\ominus$ (initial state). The formation of the mixture is accompanied by a Gibbs energy change, for two reasons. The first is due to the change in composition (entropic effect). The second is due to energetic interactions between the two types of particles, solute and solvent. It is an enthalpic effect. Let μ_1^f and μ_i^f be the chemical potentials of the two types of particles, once the mixture formed. Quite generally, they are given by the expressions $\mu_1^f = \mu_1^\ominus + RT\ln x_1\gamma_1$ and $\mu_i^f = \mu_i^\ominus + RT\ln x_i\gamma_i$, where x_1 and x_i are the molar fractions of the two components in the mixture, and γ_1 and γ_i their activity coefficients (on the scale of molar fractions). Hence, the Gibbs energy G^{f} of the system in the final system is $G^{\mathrm{f}} = n_1\mu_1^{\mathrm{f}} + n_{\mathrm{i}}\mu_{\mathrm{i}}^{\mathrm{f}}$ (final state) or

$$G^{\mathrm{f}} = n_1\mu_1^\ominus + n_1RT\ln x_1 + RT\ln\gamma_1 + n_{\mathrm{i}}\mu_{\mathrm{i}}^\ominus + n_{\mathrm{i}}RT\ln x_{\mathrm{i}} + RT\ln\gamma_{\mathrm{i}}.$$

The change in Gibbs energy $\Delta_{\mathrm{mix}}G$ accompanying the formation of the mixture, starting from the initial system, is called the Gibbs energy of mixing. It is given by the expression

$$\Delta_{\mathrm{mix}}G = G^f - G^{\mathrm{in}},\ \Delta_{\mathrm{mix}}G = n_1RT\ln x_1 + n_1RT\ln\gamma_1 + n_{\mathrm{i}}RT\ln x_{\mathrm{i}} + n_{\mathrm{i}}RT\ln\gamma_{\mathrm{i}}$$

Ideal mixing Gibbs energy

When the solution is ideal, the activity coefficients are equal to unity. The mixing Gibbs energy becomes the ideal mixing Gibbs energy $\Delta_{\mathrm{mix}}G^{\mathrm{id}}$. It is given by the expression

$$\Delta_{\mathrm{mix}}G^{\mathrm{id}} = n_1RT\ln x_1 + n_iRT\ln x_{\mathrm{i}}.$$

Excess Gibbs energy

The excess Gibbs energy is defined by the relation

$$\begin{aligned} G^E &= \Delta_{\mathrm{mix}}G - \Delta_{\mathrm{mix}}G^{\mathrm{id}}, \\ G^E &= n_1RT\ln\gamma_1 + n_{\mathrm{i}}RT\ln\gamma_{\mathrm{i}} \end{aligned}. \tag{73}$$

The links between the Gibbs energies of mixing, ideal mixing and excess are shown in Fig. 18. Clearly, the excess Gibbs energy has "something to do" with the activities and with the activity coefficients of the components. The excess Gibbs energy defined in Fig. 18 is for 1 mol of final solution. It is the *molar excess Gibbs energy* G_m^{E}. The excess Gibbs energy for a total number of moles $n_1 + n_i$ is symbolized by G^{E}. In this case, of course, the molar excess Gibbs energy G_m^{E} is given by the expression $G_m^{\mathrm{E}} = G^{\mathrm{E}}/(n_1 + n_i)$. G_m^{E} is also given by the expression

$$G_m^{\mathrm{E}} = [n_1/(n_1 + n_{\mathrm{i}})]RT\ln\gamma_1 + [n_{\mathrm{i}}/(n_1 + n_{\mathrm{i}})]RT\ln\gamma_{\mathrm{i}} \text{ or}$$
$$G_m^{\mathrm{E}} = x_1RT\ln\gamma_1 + x_{\mathrm{i}}RT\ln\gamma_{\mathrm{i}}.$$

Determination of the activity coefficients from the excess Gibbs energies

Let us calculate the differential dG^E from relation (73) at constant temperature and pressure, the variables being the numbers of moles n_1 and n_i and the activity coefficients γ_1 and γ_i. We obtain $dG^E = RTn_1 d\ln\gamma_1 + RTn_i d\ln\gamma_i + RT\ln\gamma_1 dn_1 + RT\ln\gamma_i dn_i$ Given the Gibbs–Duhem relation, it appears that the sum of the first two terms of the right number is zero at constant temperature and pressure: $dG^E = RT\ln\gamma_1 dn_1 + RT\ln\gamma_i dn_i$. The result is

$$\left(\partial G^E/\partial n_1\right)_{P,T,n_i} = RT\ln\gamma_1 \text{ and } \left(\partial G^E/\partial n_i\right)_{P,T,n_1} = RT\ln\gamma_i.$$

These relations constitute the theoretical basis on which is founded the determination of activity coefficients from the excess Gibbs energy. Let us mention, without insisting however, that this result can be generalized to the case for solutions constituted by more than two components. This is true because the Gibbs–Duhem relation is verified, in this case also, at constant temperature and pressure. That is to say,

$$\sum_j n_j d\ln\gamma_j = 0,\ \ dT = 0,\ \ dp = 0.$$

Without further insisting, let us mention that this theory can take into account the molal osmotic coefficient ϕ_m.

The quantity pH

The quantity pH involves the determination of the activity of the hydrogen ion. We confine ourselves to the study of the concept of pH in water.

Generalities: formal definition of pH

The quantity pH is considered today as a parameter that permits one to evaluate the acidity or basicity of a medium, rather than one parameter exactly quantifying the activity of the solvated proton (also called "hydrogen ion") in the studied medium. From a thermodynamic standpoint, a pH value is conceived in order to quantify the activity of the proton, since it is defined as the negative decadic logarithm of the activity of the solvated proton in the medium ($a_{H_{aq}}$ for water): $pH = -\log a_{H_{aq}}$ This is the *formal* definition of pH. From a historical viewpoint, the authors who have proposed this definition (as early in 1924) are Sørensen and Linderstrøm-Lang. It results from the conjunction of some experimental results and scientific facts which were then already known. Let us mention: (1) the use of hydrogen electrode by Sørensen in order to measure the acidity (in the occurrence, which was considered, at this time as being the proton concentration) of a medium, Le Blanc having before demonstrated that its behavior toward the hydrogen ion is reversible; (2) the fact, however, that Sørensen had found that the hydrogen electrode did not exactly respond to the concentrations of the H^+ ions; (3) the introduction of the quantity activity by Lewis as early as 1907; (4) Arrhenius' theory of the electrolytic dissociation and the hypothesis that it is the true concentration of ions H^+ rather than the total concentration of an acid, which quantifies the acidity in the best way.

Concerning now the fact that the quantity pH should be today considered as a parameter permitting us to evaluate the acidity of a medium rather than exactly reflecting its activity, as for it, is due to some difficulties inherent in the definition: (a) the first, but not the least, is the true nature of the species "hydrogen ion" in water (and also in other solvents). It is endowed with some doubts. We will not discuss this here; (b) the second is not of less interest than the previous one. It results from the impossibility of measuring the activity of an ion; (c) a third point, which is not truly pejorative but which is very important, is the generalized adoption of the potentiometric assembly in order to measure the pH, in the proper definition of pH (see below). It is undoubtedly for measurement facilities. The operative assembly is constituted by a glass electrode sensitive and selective to (notably) the aqueous proton, a reference electrode, and a part such as a liquid junction in order to permit the contact of the reference compartment with the solution under study. Finally, the assembly, of course, also possesses an electrometer for the measurement of potential difference and, hence, the pH. The question we are now facing is the following: what is the link between the measured electromotive force and the quantity pH?

The electromotive force and the quantity pH

Let us consider the Sørensen cell schematized by

$$\mathrm{Pt} \mid H_{2(g)} | \mathit{solution} || \mathit{KCl}_{(aq)} | \ AgCl_{(s)} | Ag.$$

It is a cell with a junction, the potential E_j of which is minimized (this fact is symbolized by the presence of two vertical straight lines in the scheme). We know that the cell reaction is

$$AgCl_{(s)} + \tfrac{1}{2}H_{2(g)} \rightarrow Ag_{(s)} + Cl^-_{(aq)} + H^+_{(aq)}.$$

Under usual conditions, this reaction spontaneously proceeds in the direction indicated. Here, the cell is a galvanic one. Its electromotive force is given by the expression (viz. electrochemistry)

$$E = E^{\ominus} - (RT/F)\ln\left[a_{Cl^-}a_{H^+}/\left(a_{H_2}\right)^{\frac{1}{2}}\right] + E_j.$$

$E^{\ominus}$ is the standard electromotive force, and a_{H^+} and a_{H_2} are the activities of the proton and of dihydrogen in the left compartment, whereas a_{Cl^-} is that of the chloride ion in the right one. E_j is the junction potential between the two compartments. This expression takes into account the fact that the activities a_{Ag} and a_{AgCl} are equal to unity, by convention on the activities because they are solid phases made up of only one component. At room temperature, for pressures of the order of 1 bar, the dihydrogen behavior is that of a perfect gas. Hence, it is legitimate, according to the unanimously adopted conventions for the activities, to write $a_{H_2} = p_{H_2}$ (in numerical values), where p_{H_2} is the pressure of dihydrogen. Thus, we obtain

$$E = E^{\ominus} - (RT/F)\ln\left[a_{Cl^-}a_{H^+}/\left(p_{H_2}\right)^{\frac{1}{2}}\right] + E_j \tag{74}$$

Unfortunately, as we know, the activities a_{Cl^-} and a_{H^+} (activities of ions alone) are not accessible, and E_j is also not experimentally accessible. Actually, the electromotive force depends on the activity of the solvated proton, but it also depends on the other two unknown quantities. This is the difficulty which must be overcome.

Operational definition of pH

The *operational* definition of pH is based on the use of the Sørensen cell. It involves two operations:

(i) The first consists in conventionally assigning values of pH to some buffer solutions called standard buffers. It is imperative that they are compatible with the formal definition of pH. It is at this level that it is necessary to advance one hypothesis on the activity of an ion alone. *Such a hypothesis is founded on the Debye–Hückel relations.*

(ii) In the second operation, one uses a device which reasonably allows the measurement of the pH difference between two solutions.

Concerning the first operation, let us consider the Sørensen cell working for two different acid solutions *X* (unknown solution) and *S* (standard reference solution). It is quite possible, from an experimental standpoint, to choose experimental conditions such as that the dihydrogen pressure p_{H_2} and the activity a_{Cl^-} of the chloride ions are constant during the entirety of the measurements performed and that they are, each one, in both solutions. a_{Cl^-} depends only on the concentration of potassium chloride in the right compartment, and one can admit that it is not perturbed by the ions of the liquid junction. The electromotive forces measured in identical conditions with both solutions are respectively *E*(*X*) and *E*(*S*). Admitting the hypothesis that during the two experiments, the potential of liquid junction E_j remains the same, one immediately finds the following two relations, starting from relation (74) applied to the solutions *X* and *S*:

$$E(\mathrm{X}) - E(\mathrm{S}) = -(RT/F)\ln\left[a_{H^+}(\mathrm{X})/a_{H^+}(\mathrm{S})\right]$$

and by introducing the formal definition of pH:

$$\mathrm{pH(X)} - \mathrm{pH(S)} = F[E(\mathrm{X}) - E(\mathrm{S})]/(2.303RT).$$

Concerning, now, the second operation, let us begin by noting that, according to the last relation, once one has assigned a pH value to the solution *S*, that of solution *X* is settled once the potential difference is measured. The second operation consists in assigning a pH value which must be compatible with the formal definition to the solution standard *S*. Several methodologies have been proposed. Here, we only briefly mention the method proposed by the National Bureau of Standards (NBS) in Washington DC, developed by Bates and Guggenheim. The assignation of the pH values to the chosen standard solutions is performed once for all after studying the electromotive forces of galvanic cells of the so-called Harned cell type: Pt | $H_{2(g)}$|buffer solution,Cl^-| $AgCl_{(s)}$|$Ag_{(s)}$. The standard solutions are those containing the buffer mixture. These cells are without junction. This characteristic, of course, eliminates the problem of the junction potential. These cells also do possess known molalities m_{Cl^-} of chloride ions, and the assignation of the pH values is carried out by a linear extrapolation process of the quantity $-\log\left(a_{H^+}\gamma_{Cl^-}\right)$ (which is experimentally accessible with these cells) down to $m_{Cl^-} = 0$. In this extrapolation process, the relation $\log\gamma_{Cl^-} = A\sqrt{I}/\left(1 + 1.5\sqrt{I}\right)$ has been used for the calculation of γ_{Cl^-}. It is evidently a remnant of the Debye–Hückel relations. The NBS proposed a number of standards, called primary standards, and secondary standards were later proposed.

The range of validity of the operational scale of pH is limited by two constraints. The first is that the ionic strength of the solution under study does not exceed 0.1 mol L^{-1}. The second is that the pH range of the solution is between 2 and 12. With these constraints obeyed, one can admit that the pH value keeps its significance of a measure of the acidity of the solution. Of course, the measurement of pH can be performed by other physicochemical means, not obligatorily by electrochemical methods.

General principles of calculations involving activities in solutions

This chapter describes a methodology in order to obtain thermodynamic equilibrium constants. First, however, it is necessary to recall the different ways to write the mass law.

Doing that will avoid possible confusion which is sometimes encountered in the literature.

Different ways to write the mass law

Let us consider the following chemical reaction:

$$\nu_A\text{A} + \nu_B\text{B} \rightleftarrows \nu_M\text{M} + \nu_N\text{N}.$$

We know that at equilibrium, the activities of the different species A,B,M,N are related to each other by the expression

$$K^{\ominus} = a_M^{\nu_M} a_N^{\nu_N} \Big/ a_A^{\nu_A} a_B^{\nu_B}.$$

Recall that the activities a_M, a_N…etc., taken into account in this relation are those, and only those, occurring once the equilibrium is reached. $K^{\ominus}$ is a constant at a given temperature. It is called the *standard equilibrium constant* or the *thermodynamic equilibrium constant.* $K^{\ominus}$ depends only on the temperature and pressure and not on the composition of the system. It is a true constant. The thermodynamic constant must not be confused with the corresponding constant K which is related to the concentrations at equilibrium of the reactive species defined for the above reaction by the expression

$$K = [\text{M}]^{\nu_M}[\text{N}]^{\nu_N}/[\text{A}]^{\nu_A}[\text{B}]^{\nu_B}.$$

The terms in brackets in this expression are the concentrations at equilibrium. They can be expressed in molalities, molarities, molar fractions, … The constant K may also be expressed in partial pressures. Each of these cases, in principle, must be 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. One knows that the expression of the general mass law can be written as

$$K^{\ominus} = \left(C_M^m C_N^n \big/ C_A^a C_B^b\right)\left(\gamma_{C_M^m}\gamma_{C_N^n} \Big/ \gamma_{C_A^a}\gamma_{C_B^b}\right).$$

The symbolism in this relation is as follows: C is the generic symbol of the composition at equilibrium of the system in the species (M, N, etc.) regardless of the scale of concentration (molar fraction, molarity, molality, including the partial pressures), and the γ_c the corresponding activity coefficients on the chosen scale of concentration. Therefore, in addition to the thermodynamic equilibrium constant $K^{\ominus}$, one distinguishes the constant K_c related only to molarities (at equilibrium) among others:

$$K_c = C_M^m C_N^n \big/ C_A^a C_B^b.$$

K_c is called the *apparent or formal concentration equilibrium constant*. It is not necessarily dimensionless, since concentrations are affected by unities, except for molar fractions. The important point is the fact that K_c does change with ionic strength, while $K^{\ominus}$ does not. Of course, the K_c values depend on the chosen scale of concentrations. This dependence remains relatively ignored in the literature.

Dilute solutions tend to ideality. Activities are then equal to their concentrations in numerical values, and the activity coefficients tend to be unity. The result is $K_c \to K^{\ominus}$ (for dilute solutions). Sometimes in the literature the symbol K_c is related only to equilibrium constants for which the concentrations of the species at equilibrium are expressed in molarities. In the same manner, one encounters the symbols K_m and K_p when the composition at equilibrium is expressed in molalities or in partial pressures.

General principles of calculations of equilibrium constants involving activities

These principles are given through some examples from calculations of concentrations and activities of species in aqueous solutions. In particular, we show that thermodynamic equilibrium constants involving some ions can be approached by calculations using the Debye–Hückel relations.

Fundamental difficulty

These calculations suffer from a fundamental difficulty whose origin lies in the chain of the following facts: (1) the ionic strength of the solution must be known in order to calculate the activity coefficients of the ions through the Debye–Hückel relations; (2) the knowledge of the ionic strength entails that the extent of dissociation of the electrolytes (which are not obligatorily strong) must be known. The knowledge of this extent, in turn, entails the prior determination of the thermodynamic equilibrium constants! A set of facts which has the appearance of a vicious circle! However, this difficulty may be overcome.

The domains of non-ideality corrections

(a) For rough calculations, non-ideality corrections can be neglected. Under these conditions, the values found for the concentrations and those of the equilibrium constants obtained are only approached. Moreover, they vary with the ionic strength of the solution.

(b) For ionic strengths of the solution less than 10^{-2} mol L^{-1}, the calculations are relatively simple. They are based on Debye–Hückel's limited equation. There is no reason to take into account the identity of the ions, i.e. to use the extended relation.

(c) For ionic strengths ranging in the interval 10^{-2}–10^{-1} mol L^{-1}, it must be used. However, then the nature of the ions must be taken into account by introducing the "ion-size parameter" *a*. This complicates the calculations.

(d) For ionic strength forces greater than 10^{-1} mol L^{-1}, Davies' relation, which gives reasonable results up to ionic strengths of the order of 5×10^{-1}mol L^{-1}, may be used. Roughly speaking, it can be said that the theoretical prediction of the activity coefficients is satisfactory up to ionic strengths of 0.1 mol L^{-1}. When only 1-1 electrolytes are involved, the activity coefficients may then be obtained with accuracy of 3% by basing the calculations on the limited equation. When an adjustable parameter, just as the so-called ion-size parameter *a*, is used, the accuracy may amount to up to ±1%. For polycharged ions, accuracy nearly as good as the preceding may be obtained, provided of course that all the existing equilibria are taken into account.

Reasoning allowing the calculation of the concentrations of the different species at equilibrium

Before beginning the calculations based on Debye–Hückel's equations of the activities and those of the equilibrium constants, it is judicious to give the strategy of the calculation of the different species concentrations at equilibrium. The strategy is based on the fact that the species concentrations at equilibrium must *obligatorily* obey some mathematical relations. They are, of course, the reflection of intangible physical laws. It happens that, from an absolute standpoint, they are systematically of sufficient number that the resultant mathematical system (of equations) is obligatorily determined. These relations are the following:

1. the mass balance of the solution,
2. the charge balance,
3. the equilibrium state.

Let us take the intentionally simple example of the dissolution of C_0 mol of acetic acid in 1 L of water. The matter is to calculate the concentrations of the different species stemming from the ionization of acetic acid, once the thermodynamic equilibria are reached. The two chemical equilibria are the following:

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+ \text{ and } H_2O \rightleftarrows H^+ + OH^- + .$$

The corresponding mathematical equations which must be satisfied are the expressions of the equilibria, which we write *temporarily* as

$$|CH_3COO^-||H^+| / |CH_3COOH| = K_a \tag{75}$$

$$|H^+||OH^-| = K_w, \tag{76}$$

where the quantities located between vertical lines are, at this point of the reasoning, concentrations. The conservation of matter gives

$$|CH_3COO^-| + |CH_3COOH| = C_0. \tag{77}$$

There is no reason to take into account the water balance, because this theory is only valid in dilute aqueous solutions. Since the "concentration" of water is expressed in molar fractions (see Chapter 4), it can be considered constant and equal to unity. Here, the equilibria are written according to Arrhenius' theory, equivalent in the occurrence to that of Brønsted.

The charge balance is

$$|H^+| = |OH^-| + |CH_3COO^-|, \tag{78}$$

as the solution is electrically neutral.

Hence, for this example, there exist four equations for four unknowns $|H^+|$,$|OH^-|$, $|CH_3COOH|$ and $|CH_3COO^-|$. The system is mathematically determined. It is easily reduced into one equation with only one unknown, which can be solved. It is

$$|H^+|^3 + K_a|H^+|^2 - \left(K_w + K_aC_0\right)|H^+| - K_aK_w = 0 \tag{79}$$

This relation depends on the parameters K_aK_w and C_0 which govern the system. Once the root $|H^+|$ is found, all the other concentrations are immediately accessible through the handling of the initial relations which are obligatorily satisfied at equilibrium and already mentioned.

Taking into account the activities

The taking into account of the activities is performed by using Debye–Hückel's equations, since some ions intervene in the equilibrium. Concerning the uncharged species, one assigns the value unity to their activity coefficients since the solutions are sufficiently dilute that this is legitimate. Let us recall that the problem we are faced with is that we must know the ionic strength of the solution in order to use Debye–Hückel's equations, and consequently we must know the true species concentrations which are actually searched for. Before entering into the problem of the unknown ionic strength, the fact that some relations are expressed in terms of activities and others expressed in terms of concentrations must be handled simultaneously. For example, in the above case of acetic acid, (75) and (76) are expressed in principle in activities, that is to say according to

$$\left(CH_3COO^-\right)\left(H^+\right) / \left(CH_3COOH\right) = K_a^{\ominus} \text{ and } \left(H^+\right)\left(OH^-\right) = K_w^{\ominus},$$

where the terms located in round brackets are activities. However, expressions (77) and (78) are expressed in concentrations. Let us also recall that the conditional constants K_a' and K_w' are given by the expressions

$$\left[H^+\right]\left[CH_3COO^-\right]/\left[CH_3COOH\right] = K'_a \text{ and } \left[H^+\right][OH^-] = K'_w$$

and that thermodynamic and conditional constants are linked by the relations

$$K_a^{\ominus} = K'_a\left(\gamma_{CH_3COOH}/\gamma_{H^+}\gamma_{CH_3COO^-}\right) \text{ and } K_w^{\ominus} = K'_w/\gamma_{H^+}\gamma_{OH^-}.$$

According to the retained scale of "concentrations" (molarities or molalities), the constants should of course be symbolized by K'_{a_c} or K'_{a_m}.

Calculations

The calculation of concentrations and of activities of the species are performed in an iterative way. Let us suppose that, for calculations, we have at our disposal the thermodynamic equilibrium constants (in the example of acetic acid:$K_a^{\ominus}$ and $K_w^{\ominus}$). The four Eqs. (75)–(78) are not homogeneous when we compare them. The first two are expressed in activities and the latter two in concentrations. Solving the system as has been done above, that is to say by not taking into account this inhomogeneity, induces the problem of the physical significance of the calculated quantities. Are they activities or concentrations? The answer is given and the whole problem overcome by adopting the following iterative process:

- In the first step of operations, one operates by mixing activities and concentrations, i.e. one mixes activities and concentrations. The system of the initial equations is reduced to a single one, the unknown of which is $|H^+|$ (viz Eq. (79) in the case of acetic acid-. It is solved. One obtains a first value $|H^+|_1$ which has neither the meaning of an activity nor that of a concentration, since it is obtained from initial equations involving both kinds of quantities. Nevertheless, from the first value, one calculates a kind of other pseudo-concentrations or pseudo-activities $|CH_3COO^-|_1$, $|CH_3COOH|_1$ and $|OH^-|_1$. Thus, with these pseudo-quantities, one can calculate a first ionic strength I_1. (In passing, note the use of symbols with vertical lines—and not round or square brackets—which means that the quantities are a kind of mixture of activity and of concentration.) Once obtained, the value I_1 is introduced into the judicious Debye–Hückel equation (that applies for the value I_1). It permits us to calculate a first set of pseudo-activity coefficients $\gamma_{H_1^+}$, $\gamma_{CH_3COO_1^-}$, $\gamma_{OH_1^-}$. The latter ones, in turn, permit us to obtain a first set of the values of the conditional constants k'_{a_1} and k'_{w_1} by using the following relations: $K'_{a,1} = K_a^{\ominus}/\gamma_{H^+}\gamma_{CH_3COO^-}$ and $K'_{w,1} = K_w^{\ominus}/\gamma_{H^+}\gamma_{OH^-}$ and by setting up $\gamma_{CH_3COOH} = 1$ as has already been mentioned. The first iteration is finished. It is important to note that the constants $K'_{a,1}$ and $K'_{w,1}$ do not yet have the meaning of pure formal constants. However, they approach them, and hence their meaning begins to deviate from that of thermodynamic constants, given the manner which has permitted us to obtain them.
- The second iteration is then initiated. It is strictly performed just like the first one, but in the calculations intervene the pseudo-constants $K'_{a,1}$ and $K'_{w,1}$ stemming from the preceding iteration. At the end of the second iteration, we obtain a new set of pseudo-concentrations $|H^+|_2$ ….a new pseudo-ionic strength I_2, new pseudo-activity coefficients $\gamma_{H_2^+}$ etc., and new formal equilibrium pseudo-constants. After this second iteration, constants $k'_{a,2}$ and $k'_{w,2}$ do possess the meaning of formal constants more than did $K'_{a,1}$ and $K'_{w,1}$ obtained at the end of the previous iteration. It is the same thing concerning the activity coefficients of ionic species which tend more and more to the coefficients such as they are defined, that is to say, in such a manner that they transform pure concentrations into pure activities.
- The further iterations evolve strictly in an analogous manner. The process is stopped when the pseudo-ionic strength I_n is equal to the preceding one I_{n-1}. The pseudo-ionic strengths do not change further. They are now *true ionic strengths*. Then, the constants $K'_{a,n}$ and $K'_{w,n}$ are the true *conditional or formal constants*. The equation is then homogeneous. They are all expressed in terms of *concentrations*. At the end of this n^{nd} (and definitive) loop of iteration, the concentrations of all the species are found. They are no longer a cross of concentrations and activities. The problem is solved.

At this point of operations, one can immediately calculate the activities of the different species, since their concentrations are known and also because of the knowledge of the true "ionic strength". It suffices to calculate the activity coefficients through the Debye–Hückel equations and to multiply them by their concentrations. Besides, the activity coefficients are known through the calculations performed during the last iteration. Generally, the convergence of the whole process is fast. The number of iterations is weak, of the order of 3 or 4.[5]

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[5] These calculations can be easily performed on some pocket calculators. This process is general. The difficulty often lies at the level of obtaining the suitable root of the single equation stemming from the reduction of the system of initial equations which must be satisfied. Equations of the fourth order are not rare in this realm. Abel's theorem stipulates that there are no general analytic solutions to equations with one unknown of order greater than four. However, several calculation routines permitting us to obtain the root, with the required precision, exist in the literature.

Determination of thermodynamic equilibrium constants of polyfunctional compounds

We finish this text by showing, with the help of an example, that the use of computers may greatly facilitate the handling of activities and obtaining equilibrium constants. The chosen example is that of the determination of the successive acidity constants K_{a_1} and K_{a_2} of the dibasic acid H_2A:

$$H_2A \rightleftarrows HA^- + H^+ \text{with } K_{a_1}, \text{ and } HA^- \rightleftarrows A^{2-} + H^+ \text{ with } K_{a_2}.$$

The analytical instrumental method used is the UV–visible spectrophotometry, when the dibasic acid H_2A and the base A^{2-} forms exhibit spectra clearly distinct from each other. In this case, of course, the use of spectrophotometry is convenient.

Determination for a monoacid

Here, we recall the principle of the determination of the pK_a of the monobasic HA by UV–visible spectrophotometry. It is based on the relation

$$pK_a = pH + \log [HA]/[A^-], \qquad (80)$$

where [HA] and [A$^-$] are the concentrations of these conjugate forms at a given pH value. The principle of the method consists in fixing the pH of the solution with the help of a buffer and measuring both concentrations by spectrophotometry. Then, relation (80) permits us to calculate pK_a. Let us already remark, however, that relation (80) is not homogeneous, since pH is defined as being rather a measurement of the activity of the proton (solvated), whereas [HA] and [A$^-$] are concentrations, since the UV–visible spectrophotometry responds to the concentrations, through the Beer-Lambert law [11, 12]. In order to obtain [HA] and [A$^-$], one uses this law, which at a given fixed wavelength relates the absorbance A of the solution to the concentration(s) of the species. For example, at a very acidic pH value, provided that the pK_a value is not too low, it holds that $A = \varepsilon_{HA} l[HA]$ (acid pH), where ε_{HA} is the molar absorption coefficient of the form HA. [HA] is its concentration (for example in mol L^{-1}), and l the optical path length in the cuvette cell. ε_{HA} is a constant for a given temperature, wavelength and solvent. (Pay attention: A is the absorbance of the solution. It is the quantity experimentally measured. It absolutely must not be confused with the species A^-.) In a similar manner, in a very basic medium, provided that the pK_a value is not too large, the equation $A = \varepsilon_{A^-} l[A^-]$ is valid (basic pH). At intermediary pH, that is to say in the pH interval where both forms are present, the total absorbance A of the solution is the sum of the absorbances of both forms, since the two are present and also because of the properties of the Beer-Lambert law: $A = \varepsilon_{HA} l[HA] + \varepsilon_{A^-} l[A^-]$ (intermediary pH).

From another standpoint of reasoning, since in the solution the sum of concentrations of the acid forms is constant, i.e.,

$$[HA] + [A^-] = C \text{ and } K_a = |A^-||H^+| / |HA|,$$

by assimilating activities (quantities in which the pK_a is expressed) and concentrations, we obtain the two relations

$$|HA| = |H^+| / \left[|H^+| + K_a\right] \text{ and } |A^-| = |A^-| / \left[|H^+| + K_a\right],$$

and by handling the preceding relations, we obtain

$$pK_a = pH + \log \left(A - \varepsilon_{A^-} l\right) / \left(\varepsilon_{HA} l - A\right).$$

$\varepsilon_{A^-} l$ and $\varepsilon_{HA} l$ are the absorbances of the sole basic and acid forms at the total concentration C of the whole species. These values are easily determined. It is sufficient to "work" at the judicious pH. The measurement of the absorbance A at an intermediary pH immediately gives the pK_a value. The problem of the activities is discussed further down. In principle, one measurement is sufficient for the determination, but several are indicated in order to take into account a maximum amount of experimental information and thus to obtain optimal precision. In order to perform the determination, the working wavelength (the "analytical wavelength") must be chosen such that the spectra of the pure acid and basic forms differ as much as possible from each other. When neither HA nor A^- absorbs in the UV–visible domain, of course, the determination is not possible. However, let us note that when only one form does absorb, the determination remains possible.

Case of the dibasic acid H_2A

The preceding considerations can be generalized, but a supplementary difficulty may often occur. Both acidities K_{a1} and K_{a2} may indeed overlap. Then it is impossible to experimentally determine the molar absorption ε_{HA} since the intermediary form HA$^-$ cannot exist alone, unlike the forms H_2A and A^{2-}. HA$^-$ is always accompanied by one of the other two forms H_2A or A^{2-}, and even sometimes by both. This is due to the overlapping of the two constants K_{a1} and K_{a2}. Its spectrum in a pure state (in the solvent) is therefore not directly accessible experimentally. However, at the extreme pH values, H_2A and A^{2-} exist alone, whence the possible registering of their spectra in the "pure" state remains possible. The absorbance at a given pH is the sum of the absorbances of the three present forms:

$$A = \varepsilon_{H_2A}\left[H_2A\right]_i l + \varepsilon_{HA}[HA^-]_i l + \varepsilon_{A^{2-}}\left[A^{2-}\right]_i l \qquad (81)$$

The handling of the equations which are obligatorily satisfied: $K_{a1} = |H^+|_i |HA^-|_i / |H_2A|_i$ and $K_{a2} =$

$K_{a2} = |\mathrm{H}^+|_i|\mathrm{A}^{2-}|_i / |\mathrm{HA}^-|_i$,and$C = \left[\mathrm{H_2A}\right]_i + [\mathrm{HA}^-]_i + \left[\mathrm{A}^{2-}\right]_i$ lead to the following expressions:

$$\left[\mathrm{H_2A}\right]_i = \left[\mathrm{H}^+\right]_i^2 C/D,\ [\mathrm{HA}^-]_i = K_{a_1}\left[\mathrm{H}^+\right]_i C/D,\ \left[\mathrm{A}^{2-}\right]_i = K_{a1}K_{a2}/D \text{ with } D = |\mathrm{H}^+|_i^2 + K_{a1}|\mathrm{H}^+|_i + K_{a1}K_{a2} \quad (82)$$

The index i marks the pH value at which the measurement is carried out. The examination of the last two relations shows that the absorbance at the value pH_i depends on the three molar extinction coefficients, on the constants K_{a1} and K_{a2}, on C, and of course on the pH.

Determination of constants K_{a1} and K_{a2} without taking into account the activities

The two unknowns to determine are both constants K_{a1} and K_{a2}. Their determination entails that the molar extinction coefficient ε_{HA} of the intermediary form, which is not directly accessible by experimental means, must be known. Therefore, it is considered as the third unknown. On the other hand, the pH is known and also the coefficients ε_{H_2A} and $\varepsilon_{A^{2-}}$ which are respectively determined in very acid and basic media. The methodology used to determine the three unknowns is a process of mathematical simulation. In a first step, it consists in choosing the analytical wavelength and in performing absorbance measurements at several pH$_i$ values. In order to attain the highest precision, one must choose a number of pH values far larger than the number of unknowns. In a second step, one arbitrarily choose values of the three unknowns K_{a1}, K_{a2} and ε_{HA}, and thanks to these values, one calculates the total absorbance A_{calc} for each retained pH$_i$. The calculation is performed through relations (81) and (82). Then, for this set of the three parameters, one calculates the function U defined by the relation

$$U = \sum_{\mathrm{i}} \left(A_{\mathrm{i,\,calc}} - A_{\mathrm{i,\,exp}}\right)^2,$$

where $A_{i,\,\exp}$ is the measured absorbance at the same pH$_i$ as that for which $A_{i,\,\mathrm{calc}}$ is calculated. The function U is the cost function. In the following steps, one modifies the values of the three parameters according to some order of logical decisions and one calculates the function U at each time up to obtaining the set of the values of the three parameters leading to the value U as small as possible. In other words, the process is repeated until the following three conditions are satisfied simultaneously:

$$\left(\partial U/\partial K_{a1}\right)_{K_{a2},\varepsilon_{HA}} = 0,\ \left(\partial U/\partial K_{a2}\right)_{K_{a1},\varepsilon_{HA}} = 0,$$
$$\left(\partial U/\partial \varepsilon_{HA}\right)_{K_{a1},K_{a2}} = 0.$$

One also has to check that, when it is the case, this is not a singular point or a maximum of the function U. The values of the parameters which minimize the cost function are those being searched for. The described methodology is a least squares process, in the occurrence of a nonlinear one, since the constants K_{a1} and K_{a2} (contrarily to ε_{HA}) do not intervene linearly in the calculation of $A_{\mathrm{i,\,calc}}$. This is a general methodology. The difficulty that this methodology may encounter is that the research of the parameters minimizing the function U may be difficult and lengthy. There exist several described algorithms permitting one to point toward the *minimum minimorum* of the cost function, but none is infallible. There exists no mathematical process permitting us to automatically reach this point.

Taking into account the activities

As a rule, one can imagine that one can assimilate activities and concentrations when the equilibrium constants are determined by UV–visible spectrophotometry. The case is not rare, indeed, to work with concentrations of the order of 10^{-4} to 5×10^{-4} mol L^{-1} of the compound with UV–visible spectrophotometry, and it seems unnecessary in these conditions to take into account activities. (Quite evidently, it must not be forgotten that the working concentration interval depends on the values of molar extinction coefficients.) But, whichever the case, assimilating activities and concentrations is a simplification, since there is a fact which must be into account: the presence of the buffer which fixes the pH values to which the determinations are performed. Even so, we know that to be effective, the buffer solutions must be rather concentrated. Let us admit that for the determination of the pK_a value, the concentration 10^{-4} mol L^{-1} of the species under study is satisfactory. That of the buffer must be taken of the order of 10^{-2} mol L^{-1} in order to be effective. The ionic strength exhibits about this value, the ions coming from the compound itself contributing for a negligible amount. As a result, the activity coefficients cannot be neglected.

In the chosen example, one converts the retained pH values into concentrations by the following relations:

$$a_{\mathrm{H}^+} = 10^{-\mathrm{pH}}\text{and } \left[\mathrm{H}^+\right] = a_{\mathrm{H}^+}/\gamma_{\mathrm{H}^+} \cdot \gamma_{\mathrm{H}^+}$$

are obtained via the Debye–Hückel relations since the ionic strength is known. Under these conditions, the calculations are performed with homogeneous equations. Therefore, the K_{a1} and K_{a2} constants are the conditional ones. It is very easy to go back to the thermodynamic constants, since the ionic strength is known.

Conclusion: what is an activity?

Perhaps this text thus far does not fully provide an answer to the following pivotal question: what is an activity? In its conclusion, we try, very briefly, to answer this question solely by considering the physicochemical viewpoint. This means that we give some results relating the quantity activity to some other physicochemical quantities, essentially to some coming from thermodynamics.

Concerning the significance of an activity Let us take the example of a solute in a very dilute solution. We know that its chemical potential μ is given by a relation of the kind

$$\mu = Cte + RT \ln C \text{ (very dilute solution)},$$

where C is an expression of its concentration and Cte is a constant. When the solution is not sufficiently dilute, this relation no longer correctly describes the behavior of the solute. In order to keep this relation, the chemical potential has to be expressed by the expression

$$\mu = Cte + RT \ln a \text{ (any solution)},$$

where a is the activity of the solute. It is a quantity arbitrarily introduced by Lewis. It permits one to correctly describe the behavior of the solute with a value that confers to its chemical potential μ. We observe that, owing to the fact that the (second) relation applies to every solution, and in particular to very dilute ones, the constant Cte is the same in both expressions for identical pressure and temperature of the systems, since for dilute solutions, indeed, the activity is defined as being equal to its concentration: $a = C$ (for very dilute solutions). In brief, an activity may be considered as being a kind of fictitious concentration of a component in a given thermodynamic system, in such a manner that it does exhibit an ideal behavior under these conditions, while it keeps the value of the chemical potential that it actually possesses in the non-ideal system. This definition was put forward by Lewis, but it was mentioned rather in terms of statistical thermodynamics.

Concerning now the relation between the activity of a non-electrolyte and its molecular quantities It must be known that classical thermodynamics does not provide an answer to this question. Two theories coming from the realm of statistical thermodynamics, and more precisely stemming from the handling of "grand ensembles", permit one to begin to approach this question: The first is the McMillan–Mayer theory. It relates the activity of a gas to its density number (concentration) by a power series. This relation is a true scientific advance. It permits one, at least formally, to calculate the activity starting from the corresponding value of the concentration. A very interesting point of this theory is that we know the significance of every coefficient of the power series. It is not always the case for every coefficient of a power series in physics, which very often is empirical by essence. The second is that of Kirkwood and Buff. It is based on the properties of spatial pair-correlation functions (Kirkwood–Buff's integrals), the values of which depend on that of another function called the "radial distribution function". The value of the latter is experimentally accessible. The theory reduces the interactions between particles to the electrostatic ones within pairs. It leads to several expressions of chemical potentials and, hence through them, of activities. Among other results, it permits us to distinguish three kinds of ideal fluids: the ideal gases, the symmetrical solutions and the dilute ones.

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