# Chapter 1
# Thermodynamic Systems

**Abstract** Definitions and properties of some thermodynamic systems and of some quantities in relation with the notion of activity are recalled in this chapter. The properties of thermodynamic systems and of their states, and the notions of extensive and intensive properties, of transformations, equilibria, state functions, and reversible or irreversible processes are also mentioned. Especially, emphasis is given on the different expressions of the composition of a solution and on the pathways between them.

**Keywords** Composition (expressions) • Density number • Number of moles • Molality • Molar fraction • System (state) • State (functions) • Properties (extensive and intensive) • Process (reversible, quasi-static, irreversible) • System (thermodynamic) • Transformation • Equilibrium (thermodynamic)

Here, we recall the definitions and the properties of some thermodynamic systems and of some quantities in relation with our purpose.

## 1.1 Thermodynamic Systems

A system is a part of the space and its contents, delimited by a real or a fictitious closed surface. Figure 1.1 shows an example of system composed by a solution and its vapor and its container closed by a fictitious surface.

The surroundings of the system are all but the system. Said with some emphasis, surroundings are the remaining of the universe. According to the choice of the operator, the container may or may not be a part of the system. The essential point for the following operations is not going against the initial arbitrary definition of the system.

One distinguishes several kinds of systems:

– The closed system which can only exchange energy (heat and work) and not matter with the surroundings.
– The open system which exchanges energy (heat and work) and matter with the surroundings.

J.-L. Burgot, *The Notion of Activity in Chemistry*,
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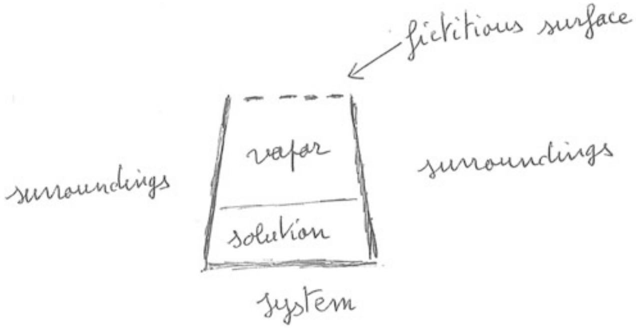

**Fig. 1.1** An example of a thermodynamic system with its surroundings

- The isolated system which exchanges nothing with the surroundings, neither energy nor matter. The definition of the isolated system inevitably rises the metaphysical question: Is the universe an isolated system?

As already said, **p** in order to specify that is a "p in minuscules" to indicate that it is a pressure in question and not a probability which must be written in majuscules.

## 1.2 State of a System

We are speaking here of thermodynamic state. The state of a thermodynamic system is defined by the values of some parameters. Most often in chemistry, but not obligatorily, the thermodynamic state of a system is defined by the values of four measurable properties, called "state variables" which are:

- The composition
- The pressure **p**
- The volume $V$
- The temperature $T$

of the system. When the system is homogeneous, that is to say when it is constituted by only one phase and when, moreover, the latter itself is composed by only one species, its composition is fixed quite evidently. Then, its state only depends on its volume, its pressure, and its temperature. Actually, the experience shows that only two of these three variables $V$, **p**, and $T$ are sufficient in order to fix the state of the system since they are related to each other by a mathematical equation called *equation of state*.

In unusual conditions of chemistry such as those resulting from the occurrence of intense electric, magnetic, and gravitational fields to which the system is submitted during a process, supplementary variables are necessary to define its state.

When the state variables are known, all the other physical properties of the system such as its mass, density, viscosity, refraction index, and dielectric constant are fixed.

## 1.3 Extensive and Intensive Properties

A property is said extensive when it is additive. This means that its value for the whole system is equal to the sum of the values of the different parts constituting it. In other words, the values of the extensive quantities are proportional to the quantity of matter under consideration. As examples, let us mention the volume and the mass.

An intensive property is not additive. It is not necessary to specify the quantity of sample under study to which the property is referring. As examples, let us mention the density, pressure, molar quantities, temperature, and "concentrations."

## 1.4 Transformation

We call transformation any process which expresses itself by one or several changes in, at least, one of the state variables of the system. This definition encompasses the cycles at the end of which the system is returned to its initial state.

## 1.5 Thermodynamic Equilibrium

One considers that a system is at the thermodynamic equilibrium when the observable values which characterize it do not change with time. The thermodynamic equilibrium entails that mechanical, thermal, and chemical equilibria are simultaneously reached. That means that the temperature, pressure, and concentrations must be identical in all the parts of the system.

## 1.6 State Functions

Let us consider a process taking place from an initial state up to a final state. It entails changes in one or several thermodynamic quantities. The changes may follow several pathways (Fig. 1.2).

When the change is independent of the pathway, the measured quantity is called *a thermodynamic state function.* Several thermodynamic functions are state functions. For example, let us mention the temperature, volume, etc. State functions

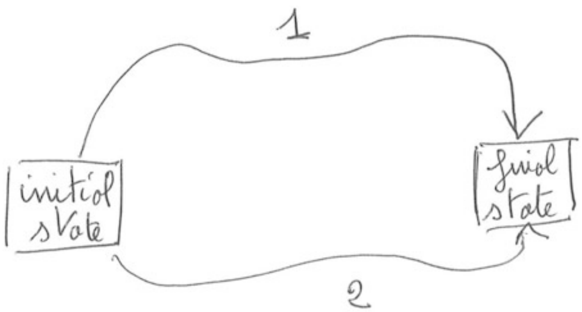

**Fig. 1.2** Different pathways of a change in a thermodynamic quantity

exhibit very interesting mathematical properties, the consequences of which are very important in thermodynamics (viz. total exact differential in Appendix A).

## 1.7 Reversible or Quasi-Static Processes and Irreversible Processes

A process is said reversible or quasi-static when, at every moment of its course, the system is at equilibrium. Said in other words, the process is reversible when it takes place through a succession of equilibrium states. If it is not the case, the process is said *irreversible*. A consequence of the reversibility is the fact that at every stage of the process, the state equation of the system applies.

One may conceive that one transformation carried out very slowly is reversible. Actually, the least infinitesimal departure from equilibrium, carried out reversibly, gives sufficient time to the system to recover the (further) equilibrium state, before the next departure occurs and so forth.

The concept of reversible process is extremely fruitful.

## 1.8 Different Expressions of the Composition of a Solution

The composition of a liquid solution expresses the relative proportions of the solute and of the solvent in the solution. Here, we only mention the expressions which are the most usual.

- The total number of particles of species $i$: $N_i$. It is a huge dimensionless number. This is the reason why one rather uses the notion of number of moles or that of quantity of molecules (viz. immediately under).
- The number of moles $n_i$. The unity is the mole, symbol mol. It is the total number of the species $N_i$ related to the Avogadro number ($N_{\mathrm{A}}$ or $L$). The latter is expressed in mol$^{-1}$:

$$n_i = N_i/N_A$$

- The density number $C_i$ or $\rho_i$ is the number of molecules per unit volume:

$$C_i = N_i/V$$

  It is expressed in $m^{-3}$. Actually, this expression of the composition is mainly used in statistical thermodynamics. $\rho_i$ is the symbol most often used.
- Molarity, also called amount concentration (IUPAC), is expressed by symbol $c_i$. It is the number of moles of molecules related to the volume $V$ of solution:

$$c_i = n_i/V$$

In SI units, it is expressed in mol $m^{-3}$. For practical reasons, 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 it is often written: solution 1 M. The symbol [i] is very often encountered instead of $c_i$. This unit is the most used in analytical chemistry.

- The molality is the number of moles of solute *i* per kilogram of pure solvent. Its symbol is $m_i$. In the SI system, it is expressed in mol $kg^{-1}$. Let $n_i$ be the number of moles of solute *i* dissolved in the mass $m_o$ of pure solvent. The molality $m_i$ is

$$m_i = n_i/m_o \quad \text{mass of pure solvent (in kg)}$$

It is easy to show that, in a binary solution (where the index 1 points out the solvent and index 2 the solute), the number of moles $n_2$ of solute in the solution is given by the expression

$$n_2 = (n_1 M_1/1000)m_2$$

where $M_1$ is the molar mass of the solvent and $n_1$ its number of moles, $m_2$ being the molality of the solute.

The molality is overall used in physical chemistry. The great advantage it exhibits with respect to the molarity lies in the fact that it is independent of the temperature. For dilute aqueous solutions, the solute molality value differs very little from that of its molarity, and the more diluted the solution is, the truer this assertion is (viz. under).

- The molar fraction

  The molar fraction is the ratio of the number of moles of the solute and of the total number of moles in the solution. Its symbol is $x$. If, in a binary solution, the number of moles of the solute is $n_i$ and that of solvent is $n_o$, the molar fractions of the solute and of the solvent are, respectively,

$$x_i = n_i/(n_o + n_i) \quad \text{and} \quad x_o = n_o\,/(n_o + n_i)$$

Molar fractions are dimensionless quantities. They are very often used in thermodynamics.

- Pathway from molar fractions to the molalities and molarities

  The pathway from a scale of "concentration" to another one is not obvious. It entails using the density of the solution.

Let us consider a solution composed of $n_o$ moles of solvent, $n_A$, $n_B, \ldots$ moles of solutes A, B,…. By definition the molar fraction of A is

$$x_A = n_A/\sum n_i \quad \text{with} \quad \sum n_i = n_o + n_A + n_B + \cdots$$

- The molar concentration of A is by definition

$$c_A = n_A/V$$

where $V$ is the total volume of the solution. Let us seek to express $c_A$ as a function of $x_A$. The mass of the solution $\sum n_i M_i$ (grams) is

$$\sum n_i M_i = n_o M_o + n_A M_A + n_B M_B + \cdots$$

where $M_o$, $M_A$, $M_B, \ldots$ are the molar masses (g mol$^{-1}$) of the solvent and of the solutes. The volume $V$ of the solution is

$$V = \sum n_i M_i/\rho 1000$$

where $\rho$ is the volumic mass (g cm$^{-3}$) of the solution. The factor 1000 permits to express the volume $V$ in liters. Then, from the previous relations, one can immediately deduce the following ones:

$$c_A = 1000\rho n_A/\sum n_i M_i$$

and

$$c_A = \left(1000\rho \sum n_\mathrm{i}/\sum n_i M_i\right) x_A$$

We notice that there is no proportionality between $c_A$ and $x_A$ since $\sum n$ and $\sum nM$ do change with $x_A$. However, proportionality appears when the solution is sufficiently dilute. Under this condition, indeed

$$\sum n_i \approx n_o$$
$$\sum n_i M_i \approx n_o M_o$$

whence

$$c_A = (1000\rho/M_o)x_A$$

where $\rho$[1] is the volumic mass of the pure solvent since the solution is diluted. In particular, for water at usual temperature,

$$\rho \approx 1$$

and

$$c_A = (1000/M_o)x_A \quad \text{(water—usual temperature)}$$

- The molality of A is by definition

  $$m_A = 1000 n_A / n_o M_o$$

  The factor 1000 is introduced since $M_o$ is expressed in grams and since $m_A$ is expressed in moles number per kilogram of solvent. By introducing the expression defining $x_A$ in the latter, we obtain

  $$m_A = \left(\sum n_i 1000/n_o M_o\right) x_A$$

  Again, there is no proportionality between $m_A$ and $x_A$. However, it appears in diluted solution, since then

  $$\sum n_i \approx n_o$$

  whence

  $$m_A = (1000/M_o)x_A$$

  The latest relation clearly shows that in diluted aqueous solutions

  $$\rho \to 1 \quad \text{and} \quad \sum n_i M_i \to n_o M_o$$
  $$m_A \approx c_A$$

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[1] Do not confuse $\rho$ (volumic mass here) with the density number.

In brief, it is only in sufficiently dilute aqueous solutions that the numerical values of the molality and of the molarity of a solute can be considered as being equal and that they are proportional to the molar fraction.

Generally, for the same kind of solution in different conditions as those of high dilution, just previously discussed above, the numerical values of the molar fractions differ considerably from those of their molality or molarity. However, numerical values of both latter ones remain close to each other.

In a gaseous mixture, the molar fraction is the most used unity. Its symbol is then $y$. In a gas mixture in which $n_i$ and $n_j$ are the mole numbers of gases $i$ and $j$, the respective molar fractions are

$$y_i = n_i \,/\left(n_i + n_j\right) \quad \text{and} \quad y_j = n_j/\left(n_i + n_j\right)$$