Chapter 5
Chemical Potential or Partial Molal Gibbs Energy

Abstract The chapter concerns the definition of the chemical potential as being a partial molar Gibbs energy. It also mentions its physical meaning, some of its properties with, especially, its change accompanying a chemical transformation. The chemical potential is, by far for our purpose, the most important partial molal quantity. As we shall see it later, the value of the chemical potential of a species is, indeed, very often expressed in terms of the auxiliary functions that are the fugacity and the activity. The notion of chemical potential, notably, permits the study of the change in the Gibbs energy accompanying a chemical process and is the thermodynamic basis of the so-called mass action law.

Keywords Gibbs' relation • Mass action law • Partial molal Gibbs energy • Electromotive force

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The notion of chemical potential, notably, permits the study of the change in the Gibbs energy accompanying a chemical process and is the thermodynamic basis of the so-called mass action law. From the general standpoint, let us anticipate what is following by saying that the mass action law must be expressed in terms of activities.

5.1 Definitions of the Chemical Potential

– The chemical potential μ_k of a compound k in a given state (temperature T, pressure $\mathbf{p}$, numbers of moles of the different species making up the system n_i) is expressed by the following mathematical relation:

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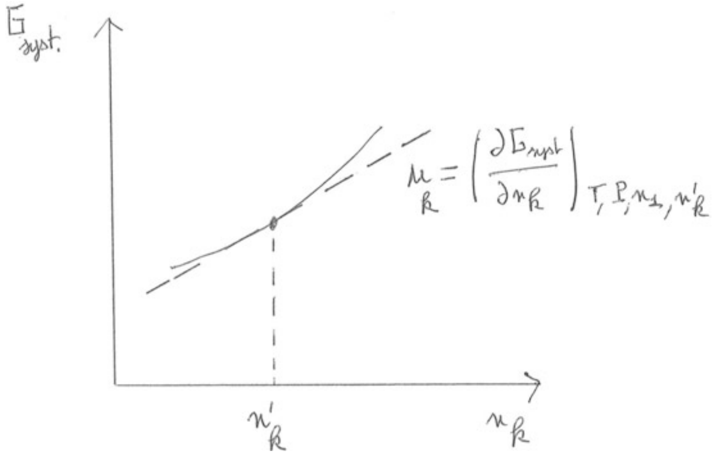

Fig. 5.1 Chemical potential μ_k or partial molal gibbs energy $\overline{G_k}$ in the case of a solute k in the solvent 1

$$\mu_k = (\partial G/\partial n_k)_{T,P,ni\neq nk} \tag{5.1}$$

Quite evidently, it is the partial molal Gibbs energy $\overline{G_k}$ defined by (viz. Chap. 4)

$$\overline{G_k} = (\partial G/\partial n_k)_{T,P,ni\neq nk} \tag{5.2}$$

In this case, G is the Gibbs energy of the whole solution considered as being the system (Fig. 5.1). According to what was mentioned before (viz. Chap. 4), one can write

$$G = n_1\overline{G_1} + n_k\overline{G_k}$$

Hence, both terms are synonymous and the unity of the chemical potential in use is J mol^{-1}.

- Let us also recall other definitions of the chemical potential based on the following relations:

$$\mu_k = (\partial U/\partial n_k)_{S,V,\, ni\neq nk} \quad \mu_k = (\partial H/\partial n_k)_{S,P,\, ni\neq nk} \quad \mu_k = (\partial A/\partial n_k)_{T,V,\, ni\neq nk}$$

Hence, the chemical potential turns to be, also, either a molal partial internal energy, a molal partial enthalpy, or a partial molal Helmholtz energy. But, it must be noticed that the variables maintained constant in the partial derivatives are not the same. However, it is demonstrated that all these definitions are equivalent such as they are written above.

5.2 Physical Meaning of the Chemical Potential: Equilibrium Condition

The chemical potential of a substance can be considered as being a quantity which represents its escaping tendency as does the molal Gibbs energy (viz. Chap. 3). It is by no means surprising since as we have seen it, it is also a molal Gibbs energy, but a partial one. With this point in mind, it appears that the chemical potential extends the notion of molal Gibbs energy to complex media.

Actually, the notion of molal Gibbs energy can be only applied to pure compounds. This is the reason why the chemical potential of a pure compound is also its molal Gibbs energy:

$$\mu_i = G_{\mathrm{m}}(i) \quad (\text{pure } i \text{ compound})$$

Hence, at this point of 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, chemical, or biochemical one.

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 $\mu_{i\alpha}$ whereas $\mu_{i\beta} = 0$, that is to say

$$\mu_{i\alpha} > \mu_{i\beta} \quad (\text{initial state})$$

By stirring both phases (this has the only effect to increase the speed of matter exchanges between the phases but does not change anything to the thermodynamic aspect of the process) a part of the solute spontaneously goes into the phase β. There exists a moment at which the transfer process ceases. Then, the concentrations in both 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

$$\mu_{i\alpha} = \mu_{i\beta} \quad (\text{equilibrium})$$

The partition spontaneously occurred because, initially, there existed an inequality of the chemical potentials. We also may notice that the matter exchange process follows the direction of a decreasing chemical potential. A difference of chemical potentials plays an analogous part as that played by an electrical potential difference. Electrons flow between two points of an electrical circuitry because there exists a difference of electrical potentials between them. It is also analogous to the differences in temperature and pressure which, respectively, command a heat transfer and a mechanical motion. Some authors assimilate the chemical potential to a kind of "chemical pressure."

Likewise, a spontaneous chemical reaction occurs when a well-defined linear combination of the chemical potentials of reactants and products of the reaction differs from 0 (viz. paragraph 4 below).

An equilibrium state related to a species is a state in which its escaping tendency is null. It is clear that the constancy of the chemical potential of a component is an equilibrium criterion. This result is general. Hence, the chemical potential values, as a rule, constitute a general criterion of evolution and equilibrium. It remains to quantify a chemical potential. It is at this point that the notions of fugacity and activity take all their importance (viz. Chaps. 7, 9, and 10).

5.3 Some Properties of the Chemical Potential

- The chemical potential is an intensive property, since it is a molal quantity,
- Since the chemical potential of a compound *i* is its partial molal Gibbs energy, it provides a way to quantify the infinitesimal change in the Gibbs energy of the whole system when the number of moles of species *i* varies under the influence of a physical or chemical process change of an infinitesimal quantity, other variables defining the state of the system (temperature, pressure, numbers of moles of other species) being maintained constant,
- The chemical potential is expressed in J mol^{-1},
- The chemical potential of a perfect gas tends toward $-\infty$ when its pressure tends toward zero. This property is endowed with important practical consequences.
- As all the other partial molal quantities, the chemical potentials very often vary with the composition of the system. In some scarce cases, it may be independent of it,
- The chemical potential of a pure compound is simply its molal Gibbs energy G_m:

$$\mu_i = G_m(i) \quad \text{(pure } i \text{ compound)}$$

- The absolute value of the chemical potential 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 an essential one. As we shall see it, it is one of the reasons of the introduction of the concept of activity (viz. Chap. 9),
- The influence of the temperature on the chemical potential is given by the expression

$$(\partial\mu_i/\partial T)_{P,nj} = -\,\overline{S_i}$$

$\overline{S_i}$ being the partial molal entropy of *i*. The demonstration of the obtaining of this result is as follows.

For an open system, the chemical potential of *i* is defined by relation (5.1). As a result

$$\begin{aligned}(\partial\mu_i/\partial T)_{P,nj} &= \left[\partial/\partial T(\partial G/\partial n_i)_{T,P,nj\neq ni}\right]_{P,ni}\\ &= \left[\partial/\partial n_i(\partial G/\partial T)_{P,ni}\right]_{T,P,nj\neq ni}\end{aligned}$$

equality which results from the crossing of the derivatives (viz. Appendix A: Schwartz's theorem). Since the occurrence of the relation (viz. Chap. 2)

$$(\partial G/dT)_P = -S$$

we find

$$\begin{aligned}&= -(\partial S/\partial n_i)_{T,P,nj\neq ni}\\ &= \ -\ \overline{S_i}\end{aligned}$$

Another interesting expression relating the temperature and the chemical potential is

$$[\partial(\mu_i/T)/\partial T]_{P,nj} = -\overline{H_i}/T^2$$

It results from the following expression, set up by a general reasoning starting from the Gibbs–Helmholtz relation (viz. Chap. 2):

$$\partial[(G/T)/\partial T]_{P,x} = -H/T^2$$

This last relation results itself from the Gibbs–Helmholtz equation (viz. Chap. 2).

- The influence of the pressure on the chemical potential is given by the expression

$$(\partial\mu_i/\partial\mathbf{p})_{T,nj} = \overline{V_{mi}}$$

The demonstration is analogous to the previous one. It results from the relation (viz. Chap. 2)

$$(\partial G/\partial\mathbf{p})_T = V_m$$

- A very important relation for the thermodynamic study of solutions and, hence, for our purpose is that of Gibbs–Duhem. It expresses the fact that the simultaneous changes in the temperature, pressure, and chemical potentials (all intensive quantities) are not independent from each other. They are “interrelated” by the Gibbs–Duhem's relation, which is

$$-SdT + Vd\mathbf{p} - \sum_i n_i d\mu_i = 0$$

S and V are the total entropy and the total volume of the phase. n_i is the number of moles of every component, and μ_i is its chemical potential. At constant temperature and pressure, it becomes

$$\sum_i n_i \, d\mu_i = 0$$

In these conditions, when the phase contains n components, only $(n-1)$ chemical potentials can vary independently. In the case of a binary solution, the Gibbs–Duhem's relation may be written in a different manner. It becomes

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

Dividing this relation by the total number of moles, it becomes

$$[n_1/(n_1 + n_2)]d\mu_1 + [n_2/(n_1 + n_2)]d\mu_2 = 0$$

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{5.3}$$

where x_1 and x_2 are the molar fractions of both components. The Gibbs–Duhem's relation may still be written in a different manner, at, as before, constant temperature and pressure (for a binary solution). In these conditions, the chemical potential of each component only depends on its molar fraction. Then, we can write

$$d\mu_i = (\partial\mu_i/\partial x_i)_{T,P}\, dx_i$$

Hence, (5.3) can be rewritten:

$$x_1(\partial\mu_1/\partial x_1)_{\mathrm{T,P}} dx_1 + x_2(\partial\mu_2/\partial x_2)_{\mathrm{T,P}} dx_2 = 0$$

or

$$(\partial\mu_1/\partial \ln x_1)_{\mathrm{T,P}}\, dx_1 + (\partial\mu_2/\partial \ln x_2)_{\mathrm{T,P}}\, dx_2 = 0$$

Since, in this reasoning, we only consider binary solutions

$$x_1 + x_2 = 1$$

$$dx_1 = -dx_2$$

and finally

$$(\partial\mu_1/\partial \ln x_1)_{\mathrm{T,P}} = (\partial\mu_2/\partial \ln x_2)_{\mathrm{T,P}} \tag{5.4}$$

It is clear that the great interest of the Gibbs–Duhem's relation lies in the fact that it provides information concerning the changes in the chemical potentials of the components of a solution.

- For a solution containing n components, the Gibbs energy of the whole chemical system (defined as being constituted by the solvent and all the solutes) G_{syst} is given by the relation

$$G_{\mathrm{syst}} = n_1\mu_1 + n_2\mu_2 + \cdots n_n\mu_n$$

where n_i are the numbers of moles of the components. This relation results from the fact that the function of Gibbs energy is extensive and that its mathematical counterpart is a homogeneous one (viz. Appendix A).

5.4 Change in the Gibbs Energy Accompanying a Chemical Transformation

When a system is constituted by the compounds 1, 2... before the transformation (initial state), the numbers of moles of which being n_1, n_2, ..., and after transformation (final state) by n'_1, n'_2... the change in Gibbs energy of the system accompanying the chemical transformation is given by the expression

$$\Delta_r G_{\mathrm{syst}} = \left(n'_1\mu'_1 + n'_2\mu'_2 + \cdots\right) - \left(n_1\mu_1 + n_2\mu_2 + \cdots\right) \tag{5.5}$$

where μ_1, μ_2, ...μ'_1, μ'_2 are the chemical potentials in the initial and final states.

This expression is absolutely general. As an example, let us consider the following chemical reaction:

$$n_{\mathrm{A}}\mathrm{A} + n_{\mathrm{B}}\mathrm{B} \rightarrow n_{\mathrm{M}}\mathrm{M} + n_{\mathrm{N}}\mathrm{N}$$

and suppose that the reaction is total. The change in the Gibbs energy accompanying the reaction is given by the expression

$$\Delta_{\mathrm{r}} G = (\nu_{\mathrm{M}}\mu_{\mathrm{M}} + \nu_{\mathrm{N}}\mu_{\mathrm{N}}) - (\nu_{\mathrm{A}}\mu_{\mathrm{A}} + \nu_{\mathrm{B}}\mu_{\mathrm{B}}) \tag{5.6}$$

This relation can be generalized to the case of a more complex reaction. When the linear combination of the kind of the type (5.6) just above is null, there is equilibrium (viz. Chap. 3).

5.5 Electromotive Force of a Reversible Electrochemical Cell and Change in the Gibbs Energy Accompanying the Reaction Cell

Let us recall that the electric potential difference E that occurs at the terminals of an electrochemical cell is a function of the temperature, pressure of the system, and, also, the activities of the species taking part in the electrochemical reactions which are developing onto the electrodes (viz. Chaps. 13 and 14). There exists a mathematical relationship between the decrease of the Gibbs energy (of the chemical system) accompanying a *reversible* process occurring in the cell and the electric potential difference until the obtaining of the equilibrium. This is true at constant pressure and temperature 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. This relation is of utmost important. It is the base of the Nernst's relation.

The use of electrochemical cells may permit, in some cases, to determine the activities of nonelectrolytes and those of electrolytes (viz. Chaps. 13 and 14).