Chapter 7
The Fugacity Quantity

Abstract This chapter is devoted to the notion of fugacity. It is developed entirely under the standpoint of classical thermodynamics. The fugacity quantity has been introduced in order to describe the behavior of imperfect gases. It permits to express the molar Gibbs energy of a pure imperfect gas and, also, to express the chemical potential (the molar partial 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, expressed in terms of a new function which is more easily identified with the physical reality than the chemical potential is. The chapter mentions the definition of the fugacity of a pure gas, the chemical potential of a perfect or real pure gas in terms of it, the fugacity of liquids and solids, the notion of fugacity coefficient of a real gas, a coming back to the notion of reference state, and the changes in fugacity with the temperature and the pressure. It also mentions the expressions of the chemical potential of a component of a mixture of perfect gases, the fugacities of real gases in mixtures, and their changes with pressure and temperature together with their determination. From another viewpoint, the values of the fugacity of a species present in different phases may assert or not the state of partition equilibrium.

Fugacity and activity are two intimately linked quantities. This is the reason why an introductory study of the notion of fugacity is necessary to understand well that of activity.

Keywords Fugacity • Fugacity coefficient Lewis–Randall's rule • Molal Gibbs energy • Molar enthalpy • Molar volume • Partial molal quantities • Perfect gases • Reference state

The fugacity quantity has been introduced by G.N. Lewis as soon as 1901 in order to describe the behavior of imperfect gases. More precisely, fugacity permits (as we shall see it) to express the molar Gibbs energy of an imperfect pure gas and, also, to express the chemical potential (the molar partial 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

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potential is. We shall see that the chemical activity is also a quantity like the fugacity function permitting to relate the chemical potential to the physical reality.

From another viewpoint, the values of the fugacity of a species present in different phases may assert or not the state of partition equilibrium.

Fugacity and activity are two intimately linked quantities. This is the reason why an introductory study of the notion of fugacity is necessary to understand well that of activity.

7.1 Definition of the Fugacity of a Pure Gas

Although the fugacity notion has been overall used in the case of systems constituted by gas mixtures, it is firstly important to begin with by the definition of the fugacity f of a pure gas. Lewis did that by setting up the expressions

$$dG = RT\,d\ln f \tag{7.1}$$

or

$$G_{\mathrm{m}} = RT\ln f + C(T) \tag{7.2}$$

$C(T)$ is the integration constant. It is already important to notice that constant $C(T)$ depends only on the nature of the substance and temperature (vis Chap. 34). G_{m} is the molar Gibbs energy of the gas.

Expression (7.2) is, according to some authors, incorrect from the mathematical standpoint since the logarithm of a quantity which is dimensioned does not possess any sense, since the fugacity is a quantity endowed with a dimension![1]

On the other hand, relation (7.1) is correct since the ratio df/f is dimensionless.

It is interesting to notice the analogy between relations (7.1) and (7.3) under

$$dG = RT\,d\ln \mathbf{p} \tag{7.3}$$

which links the molar Gibbs energy of a perfect gas and its pressure **p**. It results from the application to the case of perfect gases of the general expression

$$dG_{\mathrm{m},T} = V_{\mathrm{m}}d\mathbf{p} \tag{7.4}$$

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[1] By virtue of the famous aphorism

$$\ln(3\text{apples}) = \ln 3 + \ln \text{apples} \quad !$$

3 and apples are mathematical objects from different nature.

applicable to every reversible, isothermal transformation, only involving an expansion work. V_m is the molar volume of the substance (vis Chap. 5).

Definitions (7.1) and (7.2) are not sufficient for the determination of absolute values of the fugacity since they do not specify how the value of the constant $C(T)$ is fixed at a given temperature. Without any supplementary specification, they only define 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 G_{mf} and G_{mi} in both states, the expression of the change in the Gibbs energy ΔG accompanying it is

$$\Delta G = G_{mf} - G_{mi}$$

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

A supplementary specification is necessary. That put forward by Lewis is universally adopted. It is based on the following reasoning.

Let us again consider the previous transformation and suppose that the gas is perfect. The notion of fugacity is, by definition, a general one. Hence, it also applies to perfect gases. In these conditions, one can write

$$\Delta G = RT \ln (f_f / f_i) \qquad (7.5)$$

and since the gas is perfect by hypothesis, one can also write

$$\Delta G = RT \ln (\mathbf{p}_f / \mathbf{p}_i) \qquad (7.6)$$

$\mathbf{p}_f$ and $\mathbf{p}_i$ being the pressures in the final and initial states of the process under study. Since the Gibbs energy is a state function, it results from the comparison of expressions (7.5) and (7.6), in which in the case of a perfect gas the fugacity must be in linear relation with the pressure.

Since no gas is, from the standpoint of the absolute scientific accuracy, perfect but since, also, the behavior of every gas tends to be ideal when its pressure tends toward 0, 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 0, that is to say

$$f/\mathbf{p} \rightarrow 1 \quad \text{when} \quad \mathbf{p} \rightarrow 0$$

This is the choice that Lewis has done. Figure 7.1 exemplifies this specification.

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 its pressure in the reference state. The fact that the fugacity of every gas is set up to be equal to the value of its pressure in the reference state permits 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, evoked above, has been fixed to 1 by Lewis.

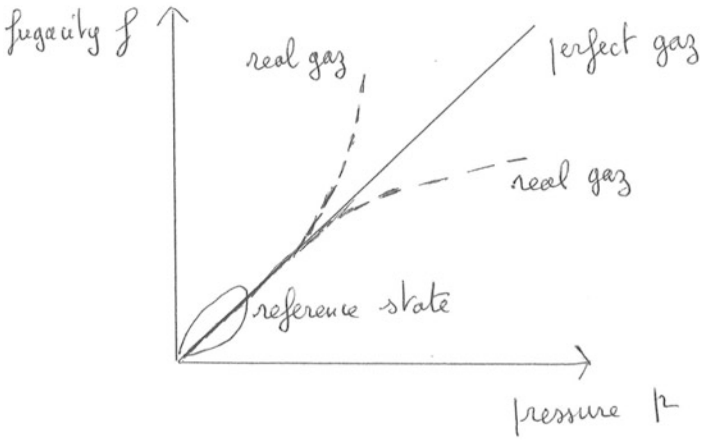

Fig. 7.1 Differences between the fugacity and the pressure of a pure gas

An outcome of the previous choice is that the fugacity of a perfect gas equates its pressure whichever the latter is, on the contrary of 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 remains as such in the whole range of pressures in the case of a perfect gas. In order to convince ourself, it is sufficient to consider the transformation described by relations (7.5) and (7.6) in which the initial pressure is very weak. As a result

$$\mathbf{p}_{\mathrm{i}} = f_{\mathrm{i}}$$

since

$$RT\ln(f_{\mathrm{f}}/f_{\mathrm{i}}) = RT\ln(\mathbf{p}_{\mathrm{f}}/\mathbf{p}_{\mathrm{i}})$$

Hence

$$\mathbf{p}_{\mathrm{f}} = f_{\mathrm{f}}$$

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

7.2 Chemical Potential of a Perfect or Real Pure Gas in Terms of Fugacities

1. In the case of a perfect gas, we know (vis Chaps. 3 and 5) that its molar Gibbs energy (or, equivalently in this case, its chemical potential) is partially defined by the expression

   $$dG = RT\, d\mathbf{p}/\mathbf{p}$$

   After integration, we obtain

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

   where Cte is the integration constant. (These expressions are incorrect from the mathematical standpoint for the reason given above.)

   We know that the correct expression is (vis Chaps. 3 and 5)

   $$\mu = \mu^{\circ} + RT \ln(\mathbf{p}/\mathbf{p}^{\circ})$$

   in which μ° is the chemical potential in an arbitrarily chosen state of the gas where it is at the pressure P°. We shall see (vis Chaps. 9 and 10) 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 $\mathbf{p}^{\circ}$. Usually, $\mathbf{p}^{\circ} = 1$ pressure unit (historically 1 atm).
2. For a real gas, analogous considerations can be carried out:

   We have seen just before that

   $$dG = RT\, d \ln f$$

   or for its molar Gibbs energy

   $$\mu = \mu^{\circ} + RT \ln(f/f^{\circ}) \tag{7.7}$$

   μ° is the integration constant. It is the chemical potential of the gas when its fugacity f is equal to its fugacity f°. f° is its fugacity in the standard state. Hence, μ° is the chemical potential of the gas in its standard state. It is arbitrarily chosen. Let us, at this point, anticipate one definition of the chemical activity a (vis Chap. 9) by already giving the following relation:

   $$a = f/f^{\circ}$$

   It expresses the chemical activity of a gas when its fugacity is f in the considered state of chemical potential μ and f° its fugacity in the arbitrary standard state of chemical potential μ°.

7.3 Fugacity of Liquids and Solids

The definition of the fugacity applies to liquid and solid states as to the gaseous state as well. 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 the 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, we can set up by virtue of (7.7)

$$\mu^\circ{}_\mathrm{s} + RT\ln\left(f_\mathrm{s}/f_\mathrm{s}{}^\circ\right) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right) \quad \text{(case of a solid)}$$

or

$$\mu^\circ{}_\mathrm{l} + RT\ln\left(f_\mathrm{l}/f_\mathrm{l}{}^\circ\right) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right) \quad \text{(case of a liquid)}$$

$\mu^\circ{}_\mathrm{s}$, $\mu^\circ{}_\mathrm{l}$, and $\mu^\circ{}_\mathrm{g}$ are the standard chemical potentials of the chemical species in solid, liquid, and vapor phases. f_s, f_l, and f_g are their fugacity in the same conditions. Let us recall that the choice of a standard state is arbitrary. Nothing precludes to choose the same standard state in order to quantify the fugacity of the species in solid or in liquid phase as that being the standard state in phase vapor. Then, of course, the fugacities in the standard states for the solid and liquid phases are no longer $f_\mathrm{s}{}^\circ$ or $f_\mathrm{l}{}^\circ$ but $f_\mathrm{g}{}^\circ$. Under these conditions, the equilibrium is expressed by the two following relations:

$$\mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{s}/f_\mathrm{g}{}^\circ\right) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right)$$
$$\mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{l}/f_\mathrm{g}{}^\circ\right) = \mu^\circ{}_\mathrm{g} + RT\ln\left(f_\mathrm{g}/f_\mathrm{g}{}^\circ\right)$$

As a result, at equilibrium

$$f_\mathrm{s} = f_\mathrm{g}$$
$$f_\mathrm{l} = f_\mathrm{g}$$

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.

7.4 Fugacity Coefficient of a Real Gas

Figure 7.1 shows that the fugacity may be greater or weaker than the pressure of the gas.

One defines the fugacity coefficient ϕ_B of the gas B by the relation

$$\phi_B = f_B/p_B$$

It is sometimes called the activity coefficient of the gas. In the literature, there exist several values of ϕ permitting to calculate the fugacities of gases in given experimental conditions, notably of pressure. They are sometimes found with the help of approximations.

The fugacity coefficient is a pure number. It is dimensionless.

7.5 Coming Back to the Reference State

In order to prepare the future discussion concerning the reference and standard states (viz. the following chapters), it is important to recall the fact that the *reference state is a real state*.

Moreover, we have 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 usually 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 (viz. Chaps. 9, 10, and 11).

Henceforth, we shall annotate every quantity considered at a very weak pressure (that is to say in the reference state[2]) by the symbol * located in exponent.

7.6 Changes in Fugacity with the Temperature and the Pressure

- The fugacity changes with temperature. These changes are accessible. We give here only the principle of their determination at constant pressure. Let us consider two states of the gas, the molar Gibbs energy and the fugacities G_m, f and $G_m{}^*, f^*$. The state to which the quantities $G_m{}^*, f^*$ are related to is a state of very weak pressure in which the behavior of the gas is ideal (it is the state of reference). The change in the molar Gibbs energy accompanying the path from one state to the other is

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[2] In thermodynamics, for the definition of the reference state, one sometimes finds that it is the state attained from the standard state through a change in pressure. We shall not use this definition.

$$\Delta G_m = G_m - G_m{}^*$$

$$\Delta G_m = RT\ln f/f^*$$

or equivalently

$$R\ln\left(f/f^*\right) = G_m/T - G_m{}^*/T$$

whence after derivation with respect to the temperature at constant pressure

$$R\,(\partial\ln f/\partial T)_P - R\left(\partial\ln f^*/\partial T\right)_P = \partial[(G_m/T)/\partial T]_P - \partial\left[\left(G_m{}^*/T\right)/\partial T\right]_P$$

We know that (viz. Chap. 2—Gibbs–Helmholtz relation)

$$\partial((G_m/T)/\partial T)_P = -H_m/T^2$$

where, in this equation, H_m is the molar enthalpy of the system at the pressure P and G_m its molar Gibbs energy. In the relation before the latter, the second term of the left member is null since, in the reference state, the fugacity f^* is equal to the pressure P^* and since the derivation is carried out at constant pressure. Both latter relations immediately lead, after derivation, to

$$(\partial\ln f/\partial T)_P = \left(H_m{}^* - H_m\right)/RT^2 \tag{7.8}$$

where $H_m{}^*$ is the molar enthalpy of the gas at null pressure. The difference ($H_m{}^* - H_m$) is the change in the enthalpy accompanying the "compression" of the gas from the pressure P until the null one at constant temperature. For the easiness of the calculations, it is a fact that the curves $(H_m{}^* - H_m)/RT^2$ as functions of the temperature are experimentally accessible either by the study of the diagrams **p**–V–T of the gases or by using the appropriate state equations. After this step, the obtention of f is carried out by integration.

- The influence of the pressure on the value of the fugacity of a gas at constant temperature is expressed by the relation

$$(\partial\ln f/\partial\mathbf{p})_T = V_m/RT$$

since, by definition of the fugacity, $dG = RTd\ln f$ and since, in a general manner (viz. Chap. 2),

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

Let us recall that V_m is the molar volume of the substance whatever the phase under which it is and whatever its behavior is, perfect or not.

7.7 Physical Significance of the Fugacity

According to what is previously mentioned, it is evident that the fugacity of a gas is a kind of a fictitious pressure or of a corrected pressure. Statistical thermodynamics (Chap. 34) permits to grasp a deeper knowledge of the relation existing between the fugacity and the pressure.

7.8 Expressions of the Chemical Potential of a Component of a Mixture of Perfect Gases

Before considering the fugacity notion applied to the case of a mixture of real gases, case where it exhibits all its importance, it is convenient, at the beginning, to mention different relations expressing the chemical potential of a component of a mixture of ideal gases.

Generally speaking, 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 (vis Chap. 5)

$$(\partial\mu_B/\partial\mathbf{p})_{T,y}=\overline{V_{\mathrm{mB}}} \tag{7.9}$$

where $\overline{V_{\mathrm{mB}}}$ is the partial molar volume of the component B.

In the case of a mixture of perfect gases, the law of perfect gases applies to the whole mixture. It is written as

$$V=(n_1+n_2+\cdots+n_{\mathrm{B}}+\cdots)RT/P \tag{7.10}$$

where $n_1, n_2, \ldots$ are the numbers of moles of species 1,2,... in the gaseous mixture, P the total pressure, and V the total volume of the system. Since, by hypothesis, each gas of the mixture exhibits a behavior different from that of any other (of the mixture), the partial pressure of each one p_{B} is given, by definition, by the relation

$$p_{\mathrm{B}}V = n_{\mathrm{B}}RT \tag{7.11}$$

The partial molar volume of the component B being given by the expression

$$\overline{V_{\mathrm{mB}}} = (\partial V/\partial n_{\mathrm{B}})_{T,P,nj}$$

we obtain through derivation of (7.10)

$$\overline{V_{\mathrm{mB}}} = RT/P$$

and hence, after using (7.9),

$$d\mu_B = RT\,(dP/P)_{T,nj} \quad \text{or} \quad d\mu_B = RT\,(d\ln P)_{T,nj}$$

Then, according to (7.10) and (7.11),

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

Since n_B and n (n total number of moles in the mixture: $n = \sum n_B$) are constant, the following equality is satisfied:

$$d\ln p_B = d\ln P$$

That is,

$$d\mu_B = RT\,d\ln p_B$$

After integration, we obtain

$$\mu_B = \mu_B{}^* + RT\ln p_B \tag{7.12}$$

$\mu_B{}^*$ is the integration constant. Its value depends only on the nature of the gas and on the temperature as it is justified by statistical thermodynamics (viz. Chap. 34). It is clear that $\mu_B{}^*$ is the chemical potential of the gas B, at the given temperature, when its partial pressure is equal to unity. Let us also recall that in order to obtain this result, the underlying hypothesis was that the mixture should behave ideally.

Hence, the chemical potential of every constituent of an ideal mixture of gases is determined by its partial pressure.

There exist other expressions of the chemical potential μ_B equivalent to the previous one.

Let us notice that relation (7.12) may be considered as being not satisfactory since the logarithm of a dimensioned quantity is under consideration. However, it can be written according to the following one which is perfectly correct:

$$\mu_B = \mu_B RT \;+\; \ln(p_B/1)$$

where 1 is a quantity which is endowed with the same dimension as that adopted for p_B. Therefore, 1 is the unity of pressure.

Let us also notice the chemical potential μ_B of a constituent of an ideal mixture of gases, as every other compound in every system may be expressed under different manners according to the used concentration scales and also according to the retained standard states. (We shall again consider this subject, but then at greater length, when we shall discuss the expressions of the chemical potentials with respect to the adopted standard states in order to define the different kinds of activities in solutions—viz. Chap. 11.)

Let us confine ourselves to mention that by introducing the molar fraction $y_B = (n_B/n)$ of B in the gaseous mixture, the expression of its chemical potential is

$$\mu_{\mathrm{B}} = \mu_{y\mathrm{B}}{}^{*} + RT\ln y_{\mathrm{B}} \tag{7.13}$$

where

$$\mu_{y\mathrm{B}}{}^{*} = \mu_{\mathrm{B}}{}^{*} + RT\ln P$$

We notice that, this time, the integration constant $\mu_{yB}{}^{*}$ depends not only on the nature of B and on the temperature, but also on the total pressure P. The reasoning leading to this expression is based on the fact that the chemical potential of a component in a given thermodynamic state is an invariant quantity, whatever the expression of its quantity of matter is.

7.9 Fugacities and Mixtures of Real Gases

7.9.1 *Expressions of the Chemical Potential of the Components*

The above considerations taking into account the partial pressures are no longer correct once we are facing mixtures of real gases. Again, in this case, introducing the fugacity notion simplifies the problem. In an analogous manner as that followed in the case of a pure real gas, one partially defines the fugacity of the constituent B in the mixture, at a given constant temperature, by the relation

$$d\mu_{\mathrm{B}} = RT\,d\ln f_{\mathrm{B}} \tag{7.14}$$

that is to say, after integration, by

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}{}^{*} + RT\ln f_{\mathrm{B}} \tag{7.15}$$

$\mu_{\mathrm{B}}{}^{*}$ 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

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}{}^{\circ} + RT\ln f_{\mathrm{B}}/f_{\mathrm{B}}{}^{\circ} \tag{7.16}$$

where $\mu_{\mathrm{B}}{}^{\circ}$ is the standard potential of B and $f_{\mathrm{B}}, f_{\mathrm{B}}{}^{\circ}$ 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 $\mu_{\mathrm{B}}{}^{\circ}$ (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 it has been demonstrated above, the behavior of each gas tends to be perfect when the total pressure tends to be null. Hence, $\mu_{\mathrm{B}}{}^{\circ}$ is the standard chemical potential of B, alone, at the same temperature as that of the system. In these conditions, we shall see (viz. Chap. 10) that the chemical potentials in the standard and reference states are equal.

One of the advantages that presents the introduction of the fugacity lies in the fact that the chemical potential of a component of a mixture of real gases may be expressed by the relation (7.15) which is formally analogous to that expressing the chemical potential of a component of a mixture of perfect gases. Such expressions enlighten 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.

7.9.2 Change of the Fugacity of One Component of a Gaseous Mixture with the Pressure

The change of the fugacity of the constituent of a gaseous mixture with the pressure is obtained from the following relation:

$$(\partial \ln f_{\mathrm{B}} / \partial P)_{T,y} = \overline{V_{\mathrm{B}}} / RT \tag{7.17}$$

where $\overline{V_{\mathrm{B}}}$ is the partial molal volume of the constituent (viz. Chap. 4). This relation immediately follows from (7.9) and (7.15) after derivation with respect to P at constant temperature and pressure and by taking into account the fact that in these conditions $\mu_{\mathrm{B}}{}^{*}$ is a constant. Before proceeding to the integration, let us subtract the term $RT\, d\ln \mathbf{p}_{\mathrm{B}}$ from both members of the expression (7.17). We obtain

$$RT\, d\ln(f_{\mathrm{B}}/\mathbf{p}_{\mathrm{B}}) = \overline{V_{\mathrm{B}}}\, dP - RT d\ln \mathbf{p}_{\mathrm{B}}$$

But

$$\mathbf{p}_{\mathrm{B}} = y_{\mathrm{B}} P$$

The molar fraction y_{B} being a constant, since we are searching for the fugacity change with the pressure at constant temperature and composition, the preceding relation becomes

$$RT\, d\ln(f_{\mathrm{B}}/\mathbf{p}_{\mathrm{B}}) = \left(\overline{V_{\mathrm{B}}} - RT/P\right) dP$$

The change of the fugacity f_{B} with the total pressure is obtained by integration from $P = 0$ to $P = P'$, that is to say

$$\ln(f_{\mathrm{B}}/\mathbf{p}_{\mathrm{B}}) = \int_0^{P'} \left(\overline{V_{\mathrm{B}}}/RT - 1/P\right) dP$$

Let us recall that in the reference state, $f_{\mathrm{B}}{}^{*} = \mathbf{p}_{\mathrm{B}}{}^{*}$. Of course, the integration entails that we know the partial molal volume as a function of the pressure. As a special case, we shall see (viz. the following chapter) that for a mixture of ideal gases, the molal partial volume of a constituent is equal to its molar volume when it is pure.

7.9.3 Change in the Fugacity of a Component of a Mixture of Real Gases with the Temperature

The change in the fugacity of the component with the temperature is given by the relation

$$(\partial \ln f_{\mathrm{B}}/\partial T)_P = \left(H_{\mathrm{B}}{}^{*} - \overline{H_{\mathrm{B}}}\right)/RT^2 \tag{7.18}$$

where $\overline{H_{\mathrm{B}}}$ is the partial molal enthalpy of the component in the mixture at the given pressure and temperature and $H_{\mathrm{B}}{}^{*}$is the molar enthalpy of the gas at the same temperature in the reference state. The relation is obtained as follows. According to (7.15)

$$R\ln f_{\mathrm{B}} = \mu_{\mathrm{B}}/T - \mu_{\mathrm{B}}{}^{*}/T$$

and according to the general properties of the chemical potential (viz. Chap. 5)

$$[\partial(\mu_{\mathrm{B}}T)/\partial T]_P = -\overline{H_{\mathrm{B}}}/T^2$$

$$R(\partial \ln f_{\mathrm{B}}/\partial T)_P = -\overline{H_{\mathrm{B}}}/T^2 + \overline{H_{\mathrm{B}}{}^{*}}/T^2$$

$\overline{H_{\mathrm{B}}}$ is the partial molar enthalpy of the gas at the pressure P. $\overline{H_{\mathrm{B}}{}^{*}}$ is that in the state of reference, that is to say at a null total pressure. In these conditions the behavior of the gas is the same as that of a gas which should be alone, at a very weak pressure. Then its molar partial enthalpy in the reference state equates its molar enthalpy when it is in pure state, at a very weak pressure $H_{\mathrm{B}}{}^{*}$:

$$\overline{H_{\mathrm{B}}{}^{*}} = H_{\mathrm{B}}{}^{*}$$

7.10 Determination of the Fugacity of a Gas in a Gaseous Mixture

The determination of the fugacity of a gas in a gaseous mixture is possible. It is carried out after obtention of the diagrams: total pressure/volume of the mixture and subsequent determinations of partial molar volumes. The knowledge of the couples of experimental data *P*–*V* for the mixture permits to determine the molar partial volumes of the components of the mixture. Then, one carries out the integration by graphical means. It can also be carried out by approached calculations.

7.11 Fugacity and Heterogeneous Equilibria

Under some conditions, the values of the fugacities may be a criterion of equilibrium between different phases. We give two examples of this possibility here.

From a general standpoint, this criterion applies when one considers a closed system constituted by two phases (or more). The whole system is closed but the constituting phases are open systems. In principle, the general equilibrium concerns three processes: the heat transfer, the changes in the limits of the phases (due to a mechanical work), and the transfer of matter from one phase into the other. We are only concerned here by the transfer of matter.

As a first example, let us consider the transfer of the species i from the phase α (its solution) into the phase β (its vapor) at constant temperature and pressure. A first criterion of equilibrium is the equality of the chemical potential of i in both phases (viz. Chap. 5):

$$\mu_i{}^{\alpha} = \mu_i{}^{\beta} \quad \text{(equilibrium)}$$

By replacing the chemical potentials by their expressions (7.16), we obtain

$$\mu_{\mathrm{B}}{}^{\circ\alpha} + RT \ln f_{\mathrm{B}}{}^{\alpha}/f_{\mathrm{B}}{}^{\circ\alpha} = \mu_{\mathrm{B}}{}^{\circ\beta} + RT \ln f_{\mathrm{B}}{}^{\beta}/f_{\mathrm{B}}{}^{\circ\beta} \tag{7.19}$$

The reasoning is the same as that followed in paragraph 3. Nothing precludes to adopt the standard state of the vapor as the unique one for both phases. As a result, we obtain

$$\mu_{\mathrm{B}}{}^{\circ\beta} + RT \ln f_{\mathrm{B}}{}^{\alpha}/f_{\mathrm{B}}{}^{\circ\beta} = \mu_{\mathrm{B}}{}^{\circ\beta} + RT \ln f_{\mathrm{B}}{}^{\beta}/f_{\mathrm{B}}{}^{\circ\beta}$$

that is to say

$$f_{\mathrm{B}}{}^{\alpha} = f_{\mathrm{B}}{}^{\beta}$$

The equality

$$f_{\mathrm{B}} \ (s\text{olution}) = f_{\mathrm{B}} \ (\text{vapour})$$

is the condition of this equilibrium (at constant temperature) provided that the reference states of the species are the same in both phases.

Let us consider, now, the equilibrium, at constant temperature, of a species B present in two immiscible solvents, as a second example. At the equilibrium, the expression (7.19) is still verified. Let us suppose, now, that the standard potentials in both phases $\mu_{\mathrm{B}}{}^{\circ\alpha}$ and $\mu_{\mathrm{B}}{}^{\circ\beta}$ are equal. The condition of equilibrium is still

$$f_{\mathrm{B}}{}^{\alpha} = f_{\mathrm{B}}{}^{\beta}$$

The common standard potential may be that of the vapor phase which would simultaneously be in equilibrium with both solutions.

The criterion of equality of fugacities (in some conditions) is easier to handle than that of the chemical potentials.

7.12 Other Use of the Fugacities

Outside what has been mentioned just previously about the theoretical interests exhibited by the notion of fugacity, it also exhibits a strong practical one. We confine ourselves to mention the fact that taking into account the fugacities in order to study the equilibria between imperfect gases is essential.

A striking example is provided by us with the values of the equilibrium constant of the reaction of synthesis of ammoniac by starting from dihydrogen and dinitrogen. The equilibrium constant, determined at 450 °C from measurements of partial pressures, does not cease to enhance with the total pressure. Its values are, respectively, 6.59×10^{-3} atm under 10 atm and 23.28×10^{-3} under 1000 atm. At 600 atm, it is 12.94×10^{-3}. Taking into account the fugacities instead of partial pressures, the equilibrium constant remains more and less constant ($6.51–7.42 \times 10^{-3}$ atm). At 1000 atm, it has the value 10.32×10^{-3} atm. But, it must be noticed that this latter is somewhat abnormal. This is probably not due to the failure of the concept of fugacity but may be rather attributed to the simplifying rule of Lewis and Randall used to calculate the fugacities. Hence, the last result does not question the interest of the introduction of the fugacity in this field.

(The Lewis–Randall's rule consists in setting up that the fugacity f_i of the species in the mixture is equal to the product of its molar fraction y_i in the vapor phase by its fugacity in the pure state at the temperature and total pressure of the system f_i. It is not reliable because it is based on a simplification which may or may not by far be justified.)

7.13 Fugacity and the Gibbs–Duhem Relation

The Gibbs–Duhem equation can also be expressed in terms of fugacities. It can be written (viz. Chap. 5) as

$$(\partial\mu_1/\partial\ln x_1)_{T,P} = (\partial\mu_2/\partial\ln x_2)_{T,P} \tag{7.20}$$

Let us recall the fact that as such it is written above, it applies to a binary solution at constant temperature and pressure. In order to express it in fugacity terms, it is sufficient to use the relation (7.14) above. The relation being searched for is

$$(\partial f_1/\partial \ln x_1)_{T,P} = (\partial f_2/\partial \ln x_2)_{T,P} \tag{7.21}$$