

Chapter 35

Activities of Gases in a Mixture of Imperfect Gases

Abstract The chapter is a simple generalization of a previous one. It is devoted to the study of a binary mixture. The case is studied with the aid of the grand ensemble and the activities of each gas are defined as for a sole imperfect one. In their definition intervene their absolute activities, the volume of the solute and the canonical partition functions when one molecule of each gas is present without any molecule of the other.

Relations linking the chemical potential of each gas to its partial pressure through statistical parameters are also mentioned.

Keywords Statistical gas activities in a mixture of perfect gases • Partial pressure • Grand ensemble • Configuration integrals • Chemical potentials of the gases

This chapter is a simple generalization of the previous one. We confine ourselves to the study of a binary mixture.

35.1 Activity of Both Gases

We have seen that, in the case of a fluid constituted by a binary mixture (viz. Chap. 24), the grand partition function is:

$$\Xi(\lambda_1, \lambda_2, V, T) = \sum_{N_1 \geq 0} \sum_{N_2 \geq 0} Q_{N_1 N_2}(V, T) \lambda_1^{N_1} \lambda_2^{N_2}$$

or, with a slightly simplified writing:

$$\Xi(\lambda_1, \lambda_2, V, T) = \sum_{N_1, N_2 \geq 0} Q_{N_1 N_2}(V, T) \lambda_1^{N_1} \lambda_2^{N_2}$$

$Q_{N_1 N_2}$ is the canonical partition function of the system for the number of particles N_1 and N_2 , and λ_1, λ_2 the absolute activities:

$$\lambda_1 = e^{\mu_1/kT} \quad \lambda_2 = e^{\mu_2/kT}$$

The function Ξ can be also written as:

$$\Xi(\lambda_1, \lambda_2, V, T) = 1 + \sum_{N_1, N_2 \geq 1} Q_{N_1 N_2}(V, T) \lambda_1^{N_1} \lambda_2^{N_2}$$

(This writing is strictly equivalent to the previous one). By expanding in series with respect to λ_1 and λ_2 , it becomes:

$$\Xi = 1 + Q_{10} \lambda_1^1 + Q_{01} \lambda_2^1 + Q_{20} \lambda_1^2 + Q_{10} Q_{01} \lambda_1^1 \lambda_2^1 + Q_{02} \lambda_2^2 + \dots \quad (35.1)$$

Symbols Q_{10} , Q_{01} , respectively, represent the canonical partition functions of the systems made up by only one molecule 1 and by zero molecule 2 on one hand and by zero molecule 1 and by one molecule of 2 on the other.

As previously, one defines the activities z_1 and z_2 of species 1 and 2 by the expressions:

$$z_1 = Q_{10} \lambda_1 / V \quad \text{and} \quad z_2 = Q_{01} \lambda_2 / V \quad (35.2)$$

As in the case of only one gas, z_1 and z_2 tend toward ρ_1 and ρ_2 when the latter ones tend toward zero. This assertion is justified by the series development in series of $\ln \Xi$ where Ξ is given by expression (35.1).

Let us replace λ_1 and λ_2 by their expressions in z_1 and z_2 (35.2), we obtain:

$$\begin{aligned} \Xi = 1 + Q_{10}(V/Q_{10}) z_1 + Q_{01}(V/Q_{01}) z_2 + Q_{20}(V/Q_{10})^2 z_1^2 \\ + Q_{10} Q_{01}(V/Q_{10})(V/Q_{01}) z_1 z_2 + Q_{02}(V/Q_{01})^2 z_2^2 + \dots \end{aligned}$$

Let us set up the general expression:

$$Q_{N_1 N_2} V^{N_1 + N_2} / Q_{10}^{N_1} Q_{01}^{N_2} = Z_{N_1 N_2} / N_1! N_2! \quad (35.3)$$

The $Z_{N_1 N_2}$ are the configuration integrals.

We obtain:

$$\Xi = 1 + V z_1 + V z_2 + \frac{1}{2} Z_{20} z_1^2 + Z_{11} z_1 z_2 + \frac{1}{2} Z_{02} z_2^2 + \dots \quad (35.4)$$

It appears the numeral 2 in the denominator of some terms. Its presence results from the definition of $Z_{N_1 N_2}$.

For the whole system,

$$\ln \Xi = pV/kT$$

By expanding in series $\ln \Xi$ stemming from (35.4), we obtain:

$$pV/kT = (Vz_1 + Vz_2 + \frac{1}{2}Z_{20}z_1^2 + Z_{11}z_1z_2 + \frac{1}{2}Z_{02}z_2^2 + \dots) \\ - (Vz_1 + Vz_2 + \frac{1}{2}Z_{20}z_1^2 + Z_{11}z_1z_2 + \frac{1}{2}Z_{02}z_2^2 + \dots)^2 / 2$$

and by truncating the development by limiting it to the terms up to the degree two:

$$pV/kT = Vz_1 + Vz_2 + 1/2Z_{20}z_1^2 - (V^2/2)z_1^2 + (Z_{11}/V)z_1z_2 - V^2z_1z_2 \\ + 1/2Z_{02}z_2^2 - (V^2/2)z_2^2$$

whence:

$$p/kT = z_1 + z_2 + (Z_{20}/2V - V/2)z_1^2 + (Z_{11}/V - V)z_1z_2 \\ + (Z_{02}/2V - V/2)z_2^2 \dots \quad (35.5)$$

which can be written after introduction of the intermediary coefficients b_{ij} :

$$p/kT = z_1 + z_2 + b_{20}(T)z_1^2 + b_{11}(T)z_1z_2 + b_{02}(T)z_2^2 + \dots \quad (35.6)$$

This expression is analogous to the relation (34.16) of the preceding chapter. The comparison of (35.5) and (35.6) permits to express the b_{ij} coefficients as a function of the configuration integrals Z_{ij} .

As previously, it is possible to relate the virial coefficients to the configuration integrals and to the different parameters after derivation.

In this case, the virial equation is:

$$p/kT = \rho_1 + \rho_2 + B_{20}(T)\rho_1^2 + B_{11}(T)\rho_1\rho_2 + B_{02}(T)\rho_2^2 + \dots$$

The reasoning which leads to this relation is the same as previously. It consists in, successively, expressing ρ_1 and ρ_2 as a function of z_1 and z_2 through the coefficients b_{ij} and b_{ji} , then, in expressing z_1 and z_2 as a function of ρ_1 and ρ_2 and, finally, in setting up an expression of p/kT as a function of the found relations and in comparing it to the virial equation.

The relation:

$$\overline{N}_1 = \lambda_1(\partial \ln \Xi / \partial \lambda_1)$$

remains valid. Given the definition of the activity z_1 , we obtain:

$$\overline{N}_1 = (V/Q_{10})z_1[\partial \ln \Xi / (V/Q_{10})\partial z_1]_{V,T,z_2}$$

$$\overline{N}_1 = z_1(\partial \ln \Xi / \partial z_1)_{V,T,z_2}$$

The reasoning leading to the expression (34.23) of the preceding chapter remains also valid. As a result (with $\bar{\rho}_1 = \bar{N}_1/V$ i.e. $= \bar{\rho}_1$):

$$\rho_1 = z_1 [\partial(p/kT)/\partial z_1]_{T,V,z_2}$$

According to (35.5):

$$[\partial(p/kT)/\partial z_1]_{T,V,z_2} = 1 + 2(Z_{20}/2V - V/2)z_1 + (Z_{11}/V - V)z_2 + \dots$$

$$[\partial(p/kT)/\partial z_1]_{T,V,z_2} = 1 + 2b_{20}z_1 + b_{11}z_2 + \dots$$

and

$$\rho_1 = z_1 + 2b_{20}z_1^2 + b_{11}z_1z_2 + \dots$$

$$\rho_2 = z_2 + 2b_{02}z_2^2 + b_{11}z_1z_2 + \dots$$

The expressions z_1 as a function of ρ_1 and z_2 as a function of ρ_2 are found by putting down:

$$z_1 = \rho_1 + a_{10}\rho_1^2 + \dots$$

$$z_2 = \rho_2 + a_{01}\rho_2^2 + \dots$$

By injecting the two latter expressions into the two preceding ones and by identifying the coefficients of the terms in ρ_1 and ρ_2 of the same degree, we find:

$$z_1 = \rho_1 - 2b_{20}\rho_1^2 - b_{11}\rho_1\rho_2 + \dots$$

$$z_2 = \rho_2 - 2b_{02}\rho_2^2 - b_{11}\rho_1\rho_2 + \dots$$

These two relations immediately provide us with the expressions of the corresponding activity coefficients $\gamma_1 = z_1/\rho_1$ and $\gamma_2 = z_2/\rho_2$.

From another standpoint, by putting back these expressions of z_1 and z_2 into (35.6) and by comparing the obtained expression with that of the virial, we obtain the “statistical” expressions of the coefficients of the latter. Hence, we obtain:

$$B_{20} = -b_{20} \quad B_{11} = -b_{11} \quad B_{02} = -b_{02}$$

It is significant to notice that the coefficients B_{20} and B_{02} are purely and simply the second order coefficients of the virial expansion of each of the pure gas. However, the coefficient B_{11} is new. It depends on the properties of the two different particles in the same volume V . It is given by the expression:

$$B_{11} = -1/V(Z_{11} - V^2)$$

$$B_{11} = - \int_0^\infty \exp[-U_{11}(r)/kT - 1] 4\pi r^2 dr$$

U_{11} is the intermolecular potential between a molecule of each type.

In the particular case in which there is a mixture of two gases constituted by spherical particles (gases without any internal structure), the term $Z_{N_1N_2}$ present in the expression below:

$$Q_{N_1N_2} = Z_{N_1N_2} / (N_1! N_2! \Lambda_1^{3N_1} \Lambda_2^{3N_2})$$

is one of the configuration integrals of the system, defined by the expression:

$$Z_{N_1N_2} = \int_V \exp[-U_{N_1N_2}/kT] d\{N_1\} d\{N_2\}$$

where $d\{N_1\}$ means $d\mathbf{r}_1 \dots d\mathbf{r}_{N_1}$ and so forth ... so that we can write in an equivalent manner:

$$Z_{N_1N_2} = \int_V \exp[-U_{N_1N_2}/kT] d\{\mathbf{R}_1\} d\{\mathbf{R}_2\}$$

35.2 Chemical Potentials of Both Components as a Function of Their Partial Pressure

It is interesting to express the chemical potential of each of the two components of the mixture. Besides, these expressions will be handled in the case of diluted solutions (viz. Chap. 38). Let us only reason on the compound 1 (the reasoning is quite identical for the compound 2). According to relations (35.2), we can write:

$$\rho_1 = Q_{10} \lambda_1 / V$$

since for a very weak density number ρ_1 tends toward z_1 . Hence, we can write:

$$N_1 / V = Q_{10} \lambda_1 / V$$

Owing to the perfect gas law (applied at the molecular level), obligatorily satisfied, once we have admitted the equivalence activity–concentration, we can write:

$$\begin{aligned} pV &= N_1 kT \\ p/kT &= Q_{10} \lambda_1 / V \end{aligned}$$

where k is the Boltzmann's constant. From another standpoint, according to the properties of the grand ensemble (viz. Chap. 24),

$$\lambda_1 = e^{\mu_1/kT}$$

As a result, after the handling of the last two relations:

$$(V/Q_{10}) (p/kT) = e^{\mu_1/kT}$$

$$\mu_1 = kT \ln[V/(kTQ_{10})] + kT \ln p_1 \quad (35.7)$$

In the same manner, we would find:

$$\mu_2 = kT \ln[V/(kTQ_{01})] + kT \ln p_2 \quad (35.8)$$

The factors $kT \ln[V/(kTQ_{10})]$ or $kT \ln[V/(kTQ_{01})]$ represent the corresponding standard potentials according to the meaning of classical thermodynamics. These expressions of standard potentials are only accurate in the eventuality of the species concentrations being indirectly expressed in terms of pressures. It is significant to recall that when the latter ones are expressed in terms of density numbers, these quantities do not exhibit the same value.

Besides, the following reasoning permits to calculate the standard potential of a species according to the adopted type of “concentration” and that by starting from another kind of “concentration.”

Let us, for example, reason with compound 2. According to relation (35.8), the chemical potential μ_2 may be written:

$$\mu_2 = -kT \ln kT + kT \ln V/Q_{01} + kT \ln p_2$$

From another standpoint, we can explicit the chemical potential as a function of the activity. Now, let us take the example of compound 1. We know (viz. paragraph 2) that $\rho_1 = Q_{10} \lambda_1 / V$. In very dilute solution, we can assimilate ρ_1 and z_1 , and by expressing λ_1 , we obtain:

$$\mu_1 = kT \ln V/Q_{01} + kT \ln z_1$$

and likewise:

$$\mu_2 = kT \ln V/Q_{02} + kT \ln z_2$$

In this case, the standard potential becomes:

$$\mu_2^0(z) = kT \ln(V/Q_{01})$$

The chemical potential μ_2 being obligatory the same, we can deduce from the preceding result that:

$$\mu_2^0(p) = \mu_2^0(z) - kT \ln kT \quad (35.9)$$

Besides, this result may be directly found by using the perfect gas law, i.e.:

$$\begin{aligned}pV &= NkT \\p &= \rho kT \\ \ln p &= \ln kT + \ln \rho\end{aligned}$$

In sufficiently dilute solution $z \rightarrow \rho$, whence:

$$\ln p = \ln kT + \ln z$$