SOME PROBLEMS IN THE THERMODYNAMICS OF NONIDEAL CHEMICALLY RE-ACTING GAS MIXTURES

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A method has been developed for the exact and approximate calculation of the equilibrium composition and thermodynamic properties of mixtures of nonideal chemically reacting gases described by an equation of state in virial form. Certain characteristics of the thermodynamics of diatomic dissociating gases are analyzed.

Chemically reacting gas mixtures are now widely used as working media and heat-transfer agents in various new industrial processes. The pressures and temperatures are frequently such that in calculating the thermodynamic properties of the reacting gases we must allow for the fact that they are not ideal.

However, there have been virtually no studies in which a theory of the thermodynamic properties of nonideal chemically reacting gas mixtures is developed in any detail. Even in such an important modern handbook as [1], a nonideality correction for the dissociation-equilibrium constant is given only for the case of a mixture governed by the van der Waals equation. On the other hand, it is widely believed that taking into account the nonideality of chemically reacting gas mixtures does almost nothing to improve the accuracy with which their composition can be calculated [2]. Although, as we shall show below, this viewpoint is not always sufficiently justified, all the calculations of the thermodynamic properties of chemically reacting gases with which we are familiar have been made up to the highest pressures without consideration of non-ideality effects [3–5].

In what follows the effect of nonideality on the composition and thermodynamic properties of chemically reacting gas mixtures is examined by the standard methods of chemical thermodynamics [1, 6, 7] and the theory of nonideal gases [8].

Let a series of independent reactions take place in the system in question and let the equation of the k-th reaction have the form

$$\sum_i v_i^{(k)} A_i = 0. \tag{1}$$

The composition of the system can be described by introducing for each reaction the degree of completion $\beta^{(k)}$, which varies from 0 to 1 as reaction (1) proceeds from left to right. If before the reactions began (all $\beta^{(k)} = 0$), the molecules A_i were present in the number N_{0i}, in the mixture we have

$$N_i = N_{0i} + \sum_{(k)} N_0^{(k)} v_i^{(k)} \beta^{(k)}. \tag{2}$$

The quantities $N_0^{(k)}$ in (2) are so selected that at all $\beta^{(k)} = 1$

$$N_i \, (\beta^{(k)} = 1) = N_{0i} + \sum_{(k)} N_0^{(k)} v_i^{(k)} \geqslant 0. \tag{3}$$

(The equal sign in (3) holds for one or more starting substances given in the "minimum necessary" amount required for all reactions (1) to proceed completely from left to right; in this sense the other substances are present "in excess.") In the general case finding the numbers $N_0^{(k)}$ is scarcely a trivial problem, and we shall not dwell on it here.

At equilibrium the free energy of the system F(T, V) is minimum [6] for given temperature T and volume V, so that for each of the reactions the equation

$$\left(\frac{\partial F}{\partial \beta^{(k)}}\right)_{T,V} = \sum_i \left(\frac{\partial F}{\partial N_i}\right)_{T,V} \frac{\partial N_i}{\partial \beta^{(k)}} = 0 \tag{4}$$

is satisfied. Considering that

$$\left(\frac{\partial F}{\partial N_i}\right)_{T,V} = \bar{\mu}_i(T, V, N_{0i}, \beta^{(k)}), \tag{5}$$

which represents the partial chemical potential of the i-th component in the mixture as calculated for a single molecule [6, 7], and using (2), we obtain a system of equations for the composition of the system $\beta^{(k)}$ as a function of T and V:

$$\sum_i \bar{\mu}_i [T, V, N_{0i}, \beta^{(k)}(T, V)] v_i^{(k)} = 0. \tag{6}$$

We obtain the thermal equation of state of the system (pressure p as a function of T and V) by differentiating F(T, V) with respect to V:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T =$$

$$= -\left(\frac{\partial F}{\partial V}\right)_{T,\beta^{(k)}} - \sum_{(k)} \left(\frac{\partial F}{\partial \beta^{(k)}}\right)_{T,V} \left(\frac{\partial \beta^{(k)}}{\partial V}\right)_T. \tag{7}$$

In view of (4), at equilibrium the second term in (7) is equal to zero, and hence the thermal equation of state of an equilibrium system in which chemical reactions are taking place has the same form as for a nonreacting mixture of the same composition:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,\beta^{(k)}} = -\left(\frac{\partial F}{\partial V}\right)_{T,N_i} \tag{7a}$$

Similarly, in the form of the calorific equation of state, the chemical reactions in the system also go unreflected: the entropy of the system is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial F}{\partial T}\right)_{V, N_i}. \qquad (8)$$

We note that if the individual reactions proceed under nonequilibrium conditions, the right side of some of the equations in (4) may be nonzero. At the same time, the equilibrium of the system with respect to the translational and internal degrees of freedom of the molecules may be almost complete, which makes it possible to use the derivatives of F with respect to V to find p and with respect to T to compute S. In this case we obtain the following pressure and entropy corrections:

$$\Delta p^{\text{chem}} = -\sum_{(k)}\left(\frac{\partial F}{\partial \beta^{(k)}}\right)_{T,V}\left(\frac{\partial \beta^{(k)}}{\partial V}\right)_T =$$

$$= -\sum_{(k)}\left(\frac{\partial \beta^{(k)}}{\partial V}\right)_T N_0^{(k)}\sum_i \nu_i^{(k)}\bar\mu_i,$$

$$\Delta S^{\text{chem}} = -\sum_{(k)}\left(\frac{\partial F}{\partial \beta^{(k)}}\right)_{T,V}\left(\frac{\partial \beta^{(k)}}{\partial T}\right)_V =$$

$$= -\sum_{(k)}\left(\frac{\partial \beta^{(k)}}{\partial T}\right)_V N_0^{(k)}\sum_i \nu_i^{(k)}\bar\mu_i,$$

owing to the nonequilibrium character of the chemical reactions. However, finding the relation between $\beta^{(k)}$ and T and V under these conditions is a kinetic problem.

To determine the composition of the mixture it is necessary to find the relation between the chemical potentials $\bar\mu_i$ of the mixture components in (6) and the parameters indicated therein, and then solve that system of equations for $\beta^{(k)}$.

In the case of nonideal gases the free energy of the mixture can be written in the form of a virial series [8] in powers of 1/V:

$$F = \sum_i N_i f_i^{\text{id}} + \frac{kT}{1}\sum_i\sum_j N_i N_j \frac{b_{ij}}{V} +$$

$$+ \frac{kT}{2}\sum_i\sum_j\sum_k N_i N_j N_k \frac{c_{ijk}}{V^2} + \ldots, \qquad (9)$$

where

$$f_i^{\text{id}} = -kT \ln\left[\frac{eV}{N_i}\left(\frac{m_i kT}{2\pi h^2}\right)^{3/2} z_i\right].$$

Here, $b_{ij}(T)$ and $c_{ijk}(T)$ are virial coefficients, taking into account the interaction between particles of the species indicated by the subscripts (the virial coefficients, calculated per mole, $B_{ij}(T)$ and $C_{ijk}(T)$ are expressed in terms of b_{ij} and c_{ijk} and Avogadro's number N_A: $B_{ij} = N_A b_{ij}$, $C_{ijk} = N_A^2 c_{ijk}$, and so on); f_i^{id} is the free energy of a particle of the i-th species in a mixture of ideal gases of the given composition; z_i is its statistical sum over the internal degrees of freedom.

Differentiating (8) in accordance with (5), we obtain

$$\bar\mu_i = \bar\mu_i^{\text{id}} + \Delta\bar\mu_i^{\text{nonid}}, \qquad (10)$$

where

$$\bar\mu_i^{\text{id}} = -kT \ln\left[\frac{z_i}{n_i}\left(\frac{m_i kT}{2\pi h^2}\right)^{3/2}\right]; \qquad (11)$$

$$\Delta\bar\mu_i^{\text{nonid}} = kT\frac{2}{1}\sum_j n_j b_{ij} +$$

$$+ kT\frac{3}{2}\sum_j\sum_k n_j n_k c_{ijk} + \ldots. \qquad (12)$$

Here,

$$n_i = N_i/V \qquad (13)$$

is the number of particles of the i-th species per unit volume.

Using (2) and (13), in (10)–(12) we can express all the n_i in terms of $\beta^{(k)}$ and as a result of the numerical solution of system (6) for given V and T find $\beta^{(k)}(V, T)$ and consequently $n_i(V, T)$ with any desired degree of accuracy.

In practice it is usually more convenient to describe the system by means of the variables T and p, also introducing the mole fractions x_i of the components:

$$x_i = N_i/\sum_i N_i. \qquad (14)$$

In these variables the components of (10) can be written as follows:

$$\bar\mu_i^{\text{id}} = -\kappa T \ln\left[\frac{z_i kT}{x_i p}\left(\frac{m_i kT}{2\pi h^2}\right)^{3/2}\right]; \qquad (11a)$$

$$\Delta\bar\mu_i^{\text{nonid}} = p\left[2\sum_j x_j b_{ij} - \sum_j\sum_k x_j x_k b_{jk}\right] +$$

$$+ p^2\left[\frac{3}{2}\left(\sum_j\sum_k x_j x_k b_{jk}\right)^2 - \sum_i\sum_j\sum_k x_i x_j x_k c_{ijk} -\right.$$

$$- 2\left(\sum_j\sum_k x_j x_k x_{jk}\right)\left(\sum_j x_j b_{ij}\right) +$$

$$\left. + \frac{3}{2}\sum_j\sum_k x_j x_k c_{ijk}\right]\Big/kT + \ldots. \qquad (12a)$$

Now the quantities $\beta^{(k)}$ can be found from the system of equations (6) as a function of T and p.

In most cases of practical importance, however, taking into account the nonideality of the gas mixture has a relatively weak (though not negligible) effect on the result of the composition calculations. If, in general, we neglect the effect of nonideality, the "ideal" mixture composition $\beta_{\text{id}}^{(k)}$ can be obtained from the system of equations

$$\sum_i \bar\mu_i^{\text{id}}\left[T, V, N_{0i}, \beta_{\text{id}}^{(k)}(T, V)\right]\nu_i^{(k)} = 0, \qquad (15)$$

where $\bar\mu_i^{\text{id}}$ are found from Eqs. (11) and (11a). For example, with Eq. (11), system (15) can be written in the standard form

$$\prod_i (n_i^{\text{id}})^{\nu_i^{(k)}} =$$

$$\equiv \prod_i \left(n_{0i} + \frac{1}{V} \sum_{(k)} N_0^{(k)} v_i^{(k)} \beta^{(k)} \right)^{v_i^{(k)}} = K_n^{(k)\,id}(T), \quad (16)$$

where $K_n^{(k)\,id}(T)$ is the ideal-gas equilibrium constant of the reaction,

$$K_n^{(k)\,id}(T) = \prod_i \left[z_i \left(\frac{m_i kT}{2\pi \hbar^2} \right)^{3/2} \right]^{v_i^{(k)}}. \quad (17)$$

The latter is related to the well-known pressure constant $K_p^{(k)}(T)$ [6] by the obvious equation

$$K_p^{(k)}(T) = K_n^{(k)\,id}(T)\,(kT)^{\sum_i v_i^{(k)}} \quad (18)$$

If we take $\beta_{id}^{(k)}$ as the zero-order approximation to the exact solution, in the first (and usually sufficient) approximation $\beta^{(k)}$ can be obtained by assuming that the contribution of terms with $\Delta\bar{\mu}_i^{nonid}$ in (6) is small and computing these quantities for $\beta_{id}^{(k)}$

$$\sum_i \left[\bar{\mu}_i^{id}(T, V, \beta^{(k)}) + \Delta\bar{\mu}^{nonid}(T, V, \beta_{id}^{(k)}) \right] v_i^{(k)} \approx 0.$$

By analogy with (16) we can now write

$$\prod_i (n_i)^{v_i^{(k)}} \equiv \prod_i \left(n_{0i} + \right.$$

$$\left. + \frac{1}{V} \sum_{(k)} N_0^{(k)} v_i^{(k)} \beta^{(k)} \right)^{v_i^{(k)}} \approx K_n^{(k)}(T, V), \quad (19)$$

where

$$K_n^{(k)}(T, V) = K_n^{(k)\,id}(T) \times$$

$$\times \exp \left[-\frac{\sum_i v_i^{(k)} \Delta\bar{\mu}_i^{nonid}(T, V, \beta_{id}^{(k)})}{kT} \right]. \quad (20)$$

Undoubtedly, the system of equations (19), (20) is much easier to solve for $\beta^{(k)}$ than the starting system (6) with (10)–(12).

As an example we will consider the determination of the composition of a diatomic gas dissociating under equilibrium conditions:

$$A_2 \rightleftarrows 2A_1$$

and we confine ourselves to the region of parameters described by an equation of state with the second virial coefficient only. In this case in accordance with (12)

$$\Delta\bar{\mu}_1^{nonid} = 2kT\,(n_1 b_{11} + n_2 b_{21}),$$

$$\Delta\bar{\mu}_2^{nonid} = 2kT\,(n_1 b_{12} + n_2 b_{22})$$

(it is understood that $b_{12} = b_{21}$), and in accordance with (20)

$$K_2(T, V) = n_1^2/n_2 =$$

$$= K_2^{id}(T) \exp \{ -2 [n_1^{id} (2b_{11} - b_{12}) +$$

$$+ n_2^{id} (2b_{21} - b_{22})] \}, \quad (21)$$

where

$$K_2^{id}(T) = (n_1^{id})^2/n_2^{id}. \quad (22)$$

In the same approximation

$$+ \frac{x_1^2}{x_2} = \frac{K_p(T)}{p} \exp \frac{p}{kT} \{ [(x_1^{id})^2 b_{11} +$$

$$+ 2 x_1^{id} x_2^{id} b_{12} + (x_2^{id})^2 b_{22}] -$$

$$- 2 [x_1^{id} (2b_{11} - b_{12}) + x_2^{id} (2b_{12} - b_{22})] \}.$$

Using (21), we can, in the simplest case, easily estimate the effect of nonideality on the composition of the chemically reacting gas mixture. Using (14), we can write the ideality correction for the equilibrium constants in the form

$$\exp \left\{ -\frac{2p}{\mu RT} \left[x_1^{id} (2B_{11} - B_{12}) + x_2^{id} (2B_{21} - B_{22}) \right] \right\},$$

where $\mu R = N_A k$. Consequently, the deviation of the equilibrium constant is determined by the difference of this exponential from 1. Assuming, for simplicity, that $x_2^{id} \sim 1$ and that the nonideality is small, for the relative error due to neglecting nonideality in calculating the equilibrium constant, and hence the composition of the mixture, we obtain

$$\delta K_2 = \left| \frac{2p}{\mu RT} (2B_{21} - B_{22}) \right|. \quad (23)$$

We will estimate the value of (23) for dissociating hydrogen. At temperatures of the order of several thousands of degrees the quantity B_{22} can be estimated using the Buckingham 6-exp potential [9], and B_{12} using the Lennard-Jones 6–12 potential [10]. We find that $B_{22} \gtrsim 10$ cm^3/mole, $B_{12} \sim 15$ cm^3/mole.

Thus, in accordance with (23), $\delta K_2 \sim 0.5\,p/T$, where p is in atm, and T in °K. At the rather high temperature T = 5000° K and the very moderate pressure p = = 100 atm $\delta K_2 \sim 0.01$, i.e., the error reaches 1%. Of course, it becomes much greater at lower temperatures and higher pressures.

Thus, for calculations of improved accuracy, especially in calculating the transport coefficients in chemically reacting gas mixtures, which are very sensitive to errors in mixture composition, it is necessary to take nonideality into account.

Apart from their practical usefulness, the formulas obtained have a certain methodological interest in relation to research in the thermodynamics of dissociating gases. For example, the equation of state of a nonideal diatomic dissociating gas can be written both in the standard form for a mixture of monomers A_1 and dimers A_2, following from Eqs. (8) and (6):

$$p/kT = (n_1 + n_2) + \sum_i \sum_j n_i n_j b_{ij}(T) +$$

$$+ \sum_i \sum_j \sum_k n_i n_j n_k c_{ijk}(T) + \cdots, \quad (24)$$

and in the form of a virial series for N starting atoms ($N = N_1 + 2N_2$):

$$p/kT = n + b(T)n^2 + c(T)n^3 + d(T)n^4 + \ldots . \quad (25)$$

The equivalence of forms (24) and (25) is known [11, 12].

Using (21) and (22), we can obtain the expansion of n_1 and n_2 in powers of n:

$$n_1 = n - \frac{2}{K_2^{id}}n^2 +$$

$$+ \frac{4}{K_2^{id}}\left(\frac{2}{K_2^{id}} - 2b_{11} + b_{12}\right)n^3 + \ldots ,$$

$$n_2 = \frac{1}{K_2^{id}}n^2 - \frac{2}{K_2^{id}}\left(\frac{2}{K_2^{id}} - 2b_{11} + b_{12}\right)n^3 + \ldots ,$$

and then the relation between the virial coefficients of series (24) and (25):

$$b = b_{11} - 1/K_2^{id}. \quad (26)$$

$$c = c_{111} + \frac{4}{K_2^{id}}\left(\frac{1}{K_2^{id}} - 2b_{11} + b_{12}\right). \quad (27)$$

In (26) b_{11} is the contribution to $b(T)$ due to the interaction of two unbound atoms A_1, while

$$- 1/K_2^{id} = b_{bound}(T) \quad (28)$$

is nothing other than the contribution to $b(T)$ due to the formation of bound states A_2 of the starting atoms. Similarly, in (27) c_{111} is the contribution to $c(T)$ due to the interaction of three unbound atoms A_1, while

$$\frac{4}{K_2^{id}}\left(\frac{1}{K_2^{id}} - 2b_{11} + b_{12}\right) = c_{bound}(T) \quad (29)$$

is the bound part of the third virial coefficient $c(T)$ (provided that the bound states of the three atoms are not formed simultaneously).

Whereas expressions of the type (26) and (28) for the second virial coefficient are well known [13, 14], formulas (27) and (29), which make it possible to separate and compute the bound and unbound components in the third virial coefficient, are an undoubted achievement of the present method. (The formulas needed to calculate the quantities in (27) and (29) are known: for $c(T)$ they are given in [8], for $b_{11}(T)$ in [14], for $b_{12}(T)$ in [8]; a method of calculating $K_2^{id}(T)$ has been beautifully worked out [15]. The method of calculating b_{11} and b_{12} has been improved by the author.)

Series (25) does not converge satisfactorily if an appreciable number of molecules appears in the gas, since the values of the virial coefficients b, c, and d are anomalously large. In practice this series can be used only in the region of total dissociation. In the region of partial dissociation, however, it is necessary to base the calculations on formula (24), explicitly taking into account the existence of a mixture of unbound atoms and molecules, which causes a certain amount of inconvenience connected with the necessity

of making a preliminary calculation of the mixture composition.

It is possible to construct a "hybrid" of Eqs. (24) and (25), explicitly summing the most weakly converging part of the latter. Accordingly, we will first consider how Eq. (25) will appear when our system is a mixture of ideal gases—atoms and molecules:

$$p/kT = n_1^{id} + n_2^{id}.$$

Finding n_1^{id} and n_2^{id} from (22), we obtain

$$p/kT = \frac{n}{2} - \frac{K_2^{id}}{8}\left[1 - \sqrt{1 + 8n/K_2^{id}}\right] \equiv$$

$$\equiv n\left[\frac{1}{2} + \frac{1}{1 + \sqrt{1 + 8n/K_2^{id}}}\right]. \quad (30)$$

Then expanding the right side of (30) in powers of n/K_2^{id}, we find

$$p/kT = n - \frac{1}{K_2^{id}}n^2 + \frac{4}{(K_2^{id})^2}n^3 - \frac{20}{(K_2^{id})^3}n^4 + \ldots . \quad (31)$$

The relation between expressions (25) and (31), taking account of (26)–(29), is obvious.

It can be shown that at temperatures $T \lesssim (0.2-0.3)D_e/k$, where D_e is the dissociation energy of the molecule, b_{bound} in Eqs. (26) and (28) is almost equal to b, i.e., the quantity

$$b'(T) \equiv b_{11}(T) = b(T) - b_{bound}(T) \quad (32)$$

is much smaller in absolute magnitude than b(T). Similarly,

$$c'(T) = c(T) - 4[b_{bound}(T)]^2 \quad (33)$$

is also a small quantity as compared with c(T), and so is

$$d'(T) = d(T) - 20[b_{bound}(T)]^3 \quad (34)$$

as compared with d(T), while at the temperatures in question

$$\left|\frac{b'(T)}{b(T)}\right| \sim \left|\frac{c'(T)}{c(T)}\right| \sim \left|\frac{d'(T)}{d(T)}\right| \sim \ldots \sim e^{-D_e/kT} \ll 1. \quad (35)$$

Taking (32)–(34) into account and comparing Eq. (31) with the starting equation (25), we can write a new equation identical with (25):

$$p/kT = n\left[\frac{1}{2} + \frac{1}{1 + \sqrt{1 + 8n/K_2^{id}}}\right] + b'(T)n^2 +$$

$$+ c'(T)n^3 + d'(T)n^4 + \ldots . \quad (36)$$

However, other things being equal, the series on the right side of (36) already will converge incomparably more rapidly than the starting series (25), which is immediately clear from (35).

If we formally substitute $-b(T)$ for K_2^{id} in (30) and perform all the subsequent calculations as before, instead of (36) we obtain

$$p/kT = n\left[\frac{1}{2} + \frac{1}{1 + \sqrt{1 - 8b(T)n}}\right] +$$

$$+ c_{(ijk)}(T)\, n^3 + d_{(ijkl)}\, n^4 + \ldots, \qquad (37)$$

where

$$c_{(ijk)}(T) = c(T) - 4\,[b(T)]^2, \qquad (38)$$

$$d_{(ijkl)}(T) = d(T) - 20\,[b(T)]^3. \qquad (39)$$

Series (37) is identical with expression (36), but, as may be seen from (38) and (39), the coefficients $c_{(ijk)}$ and $d_{(ijk\,l)}$ are of the same order as c' and d' in (33) and (34). However, the term proportional to the square of the density, which in (36) takes into account the interaction of two unbound atoms, is absent from the right side of series (37), since it has been incorporated in the radicand. Moreover, the structure of the coefficients in (38) and (39) is simpler than that of the quantities in (33) and (34), and to determine them it is not at all necessary to introduce the concept of a mixture. A method of calculating $c_{(ijk)}$ has been developed by the author. Thus, series (37) is as simple as the starting series (25). However, it converges much more rapidly and is therefore suitable for practical calculations.

Inverting series (37) with respect to pressure, we obtain the following equation for the volume per atom:

$$\bar{v} = \frac{1}{n} = \frac{kT}{p}\left\{\frac{1}{2}\left(1 + \frac{1}{\sqrt{1 - 4\dfrac{b(T)\,p}{kT}}}\right) + \right.$$

$$\left. + c_{(ijk)}(T)\left(\frac{p}{kT}\right)^2 + \ldots\right\}. \qquad (40)$$

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