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Thermodynamic Properties of Gases at High Temperature:

1. Chemical Equilibrium Among Molecules, Atoms, and Atomic Ions Considered as Clusters

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The equilibrium thermodynamic properties of gaseous mixtures at high temperatures are treated by an extension of the cluster theory of Ursell, omitting the assumption of additivity of pair energies. An effective partition function is introduced, which is a convenient function in expressing the increase of the partition function for the entire gas due to the joining together of the parts of the cluster. The law of mass action and the dependence of second and third virial coefficients upon the cluster integrals for pairs and triples of molecules in a mixture have been obtained therefrom. Extension to a partially ionized gas is made by incorporating Mayer's cluster-based extension of the Debye-Hückel theory.

1. Introduction

The calculation of the thermodynamic properties of gases at high temperatures involves a number of special problems which may well be disregarded at more moderate temperatures. The thermodynamic functions for a gaseous constituent in a mixture in chemical equilibrium are usually calculated from a partition function definable as a sum of Boltzmann factors for all states of the elementary unit of the constituent. The states of a single isolated molecule, atom, or atomic ion may be arranged in some kind of joint or compound progression of quantum numbers up through a range of moderate energies. For still greater energies, however, the number of states associated with the physical system comprising the constituent is enormously greater, with the states forming a continuum of values nominally of infinite extent, as the constituent dissociates, rather than occurring discretely. At some elevated temperature and beyond, the usual criterion for neglect of high-energy states based on the smallness of the Boltzmann factor is not fulfilled below the dissociation limit. The infinity of states immediately encountered at this energy does not permit the continuation of the same type of sum of states to indefinitely higher energies. A common procedure for avoiding the divergence which threatens to occur involves the termination of the sum of states at the dissociation energy or the inclusion of only that limited group of states above dissociation which still imply some of the typical structure of the undissociated constituent.

A different procedure for avoiding this divergence difficulty is to be discussed, involving the use of a method thought to have the merit of formal correctness, although it is admittedly not the only type of analysis with this appropriate feature. For this purpose, a special kind of partition function will be used, here to be termed an "effective partition function". These effective partition functions are related to the increase in the occupancy of states of a combined unit due to the joining together of parts of the unit, putting it together from any of all of the ways in which the unit may be considered as separated into component parts. The present procedure comprises an analysis using clusters of the Ursell type [1] [1] to specify the net thermodynamic effects of particle groupings in the combinations involved in forming molecules, atoms, and ions. As the populations of these clusters are measures of contribution to concentration due to interactions among several particles, it is admitted that they can give contributions of reversed sign if exclusion effects exceed the effects of combination.

The calculation procedure presented is a treatment of a multicomponent system including the principal quantum effects remaining at ordinary or elevated temperatures. As such it is in some degree a generalization of the treatments for pure substances given by Kahn and Uhlenbeck [2], Kahn [3], and Kilpatrick [4], and for the nonquantum multicomponent treatments of McMillan and Mayer [5], Fuchs [6], and Muto [7]. A restricting assumption of additivity of pair energies, made in some of these treatments, has not been retained in the

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[1] Figures in brackets indicate the literature references at the end of this paper.

present one. The assumption is considered to be a rather good approximation for mixtures of ordinary molecules but not universally for the many types of interaction occurring among the chemically unsaturated fragments of molecules existing at very high temperatures.

Though the cluster integral procedure provides a way of avoiding divergence difficulties associated with ordinary dissociation, there is a type of dissociation for which the separating parts of the molecule or cluster are oppositely charged. The distribution of rotational states for which such fragments occur as unexcited parts is similar to that existing when a single electron is nearly separated from a positive ion. In the latter case, just below the energy at which the continuum due to ionization begins, there is an infinity of discrete states, and each level of the outer electron specified by the principal quantum number n is actually a group of states whose number has $2n^2$ as a factor. In the method of Urey [8] and Fermi [9], discussed also by Fowler [10], the summation was halted at such electron orbits that at the given density an orbit based on one atomic ion would just "touch" an orbit of a neighboring atomic ion. Their method, which appears capable of extensive development and application, forms part of the basis for a treatment of high temperature thermodynamic properties of a gas given by Megreblian [11]. The method of Planck [12] involved the evaluation of a Gibbs phase integral with simplifying assumptions. The present treatment is somewhat related to that of Planck but takes some account of a known property of an ionic assembly in involving an exponential Debye shielding function multiplying the long range Coulombic ionic interaction, such as occurs in the Debye-Hückel theory of electrolytes. In their theory of a plasma, Bohm and Pines [13] made a canonical transformation to new coordinates of two kinds, one associated with pure translational motions, and one associated with a short-range interaction showing at least some resemblance to the Debye screened Coulomb potential. Of more immediate application, Mayer [14] derived thermodynamic quantities for ionic solutions including all ring-type graphs of interionic interaction, using an exponential shielding function multiplying the Coulombic ionic interaction as a tool in the mathematical analysis. In effect, as shown by Meeron [15], Mayer converted the calculated effect of interionic interactions as indicated by virial coefficients from a nonconvergent form for the unscreened Coulomb potential to a convergent form with the Debye screened potential and obtained also the well-known limiting law Debye-Hückel term. The avoiding of divergence in the integrals related to virial coefficients by using Debye screening corresponds in some degree with the avoiding of divergence by Ecker and Weizel [16] who noted that n, the principal quantum number for atomic states, must have an upper bound if the electron moves in a Debye screened potential field. The correspondence is not that of identity, however, since the virial-coefficient-type quantities receive part of their contribution from regions of phase space above the dissociation, or ionization energy.

As to the arrangement of the present paper, section 2, which follows, presents a number of items of cluster theory leading to the method of calculation used to treat chemical equilibrium and the virial coefficients related to further clustering of the aggregations considered as the chemical constituents. Many of the relations are so similar to those in earlier derivations of cluster theory as clearly to form obvious extensions from them. A somewhat extensive discussion pertaining to an analysis in rather elementary algebraic form has been included, however, which may serve to show the very simple physical meaning of the extended Ursell-type formulas and thereby permit an easy inference of the essential correctness of the treatment. The effect of quantization on the cluster integrals or effective partition functions for molecules is also treated.

In section 3, formulas are given for the Helmholtz free energy for the gaseous equilibrium mixture including molecules, atoms, and atomic ions, based in part on the ionic-solution theory of Mayer and in part on the equilibrium theory of clusters of section 2. Formulas for the equilibrium constants for chemical reactions which can occur among constituents are also given. Expressions for other themodynamic functions for the mixture in terms of functions for its constituents are given in the appendix.

Further discussion of the status of cluster theory, particularly in regard to its present application, will be found in section 4.

2. Application of Cluster Theory

Apart from effects associated with ionization, an accurate theory for the thermodynamic properties of equilibrium mixtures of chemically reacting substances at high temperatures may be directly formulated involving equilibrium constants identical with the quantum equivalent of the cluster integrals of gas theory. In the nonquantum treatment, the Gibbs phase integral

$$Q=\frac{1}{\prod\limits_{s_i} N_{s_i}!}\int \cdot \cdot \cdot \int \exp\frac{-\epsilon}{kT}\prod_{s=1}^{N} h^{-3}d^3p_s d^3r_s \tag{2.1}$$

is analyzed according to the method of Ursell [1]. The extension to the exact quantum mechanical treatment involves the replacement of the Boltzmann factor by a Slater sum so as to provide an exact equivalent to

$$Q=\sum_{n}\exp\frac{-\epsilon_n}{kT}. \tag{2.2}$$

The treatment should give results similar to those obtained by Kahn and Uhlenbeck [2], and Kahn [3], for a pure gaseous substance.

The theoretical analysis is made in terms of cluster integrals $b_{(l_i)}$ defined by

$$Vb_{(l_i)}\prod_{i} l_i!=\int \cdot \cdot \cdot \int U_l \prod_{i}^{t}\prod_{s}^{l_i} d^3r_s, \tag{2.3}$$

with U_l to be defined in terms of products of quantities W_j to be described. The number of particles of type i within a given cluster is l_i, with the different types of particles extending to $i=t$. This general cluster will be said to have composition (l_i). The cluster is to be thought of as subdivided arbitrarily into fragments, including every possible way of subdividing the cluster. The number of particles of type i within a particular type j of fragment of the cluster is to be indicated as $(l_i)_j$ and the number of fragments of type j by k_j. Conservation of matter then indicates that

$$\sum_{j} k_j(l_i)_j=l_i \tag{2.4}$$

for each type of particle in the cluster. The total number of fragments according to a particular way of subdividing the cluster is

$$k=\sum k_j. \tag{2.5}$$

The quantity U_l may now be defined as the sum

$$U_l=\sum(-1)^{k-1}(k-1)!\prod_{j}\frac{1}{k_j!}\left(\frac{W_j q_j}{\prod\limits_{i}(l_i)_j!}\right)^{k_j}\prod_{i=0}^{t} l_i!, \tag{2.6}$$

with the factor q_j arbitrarily separated to indicate an explicit counting of spin multiplicities for the fragments, if desired. The summation in eq (2.6) includes products formed according to every possible way of subdividing the cluster into fragments or groups of particles. Each product term involves different W_j's which together involve once and only once each particle of the cluster. W_j represents the probability of occurrence of an isolated fragment j of the cluster in a given geometric configuration as a relative probability compared with the occurrence of the fragment when there is no internal energy of interaction. Thus, W_j will represent a Boltzmann factor in a nonquantum treatment or a suitable Slater sum in a quantum treatment, such as is indicated by

$$W_j=\prod_{s}(h^2/2\pi m_s kT)^{3/2}\sum\psi_n\psi_n^*\exp[-\epsilon_n/kT]. \tag{2.7}$$

The integral of the Slater sum for each fragment or group of particles provides the sum over its quantized states, as far as quantized states exist, with the appropriate integral in the continuum for the remaining contribution. A number, q_j, of states of like spin may have essentially identical energy and then can naturally be counted together. The separation of this factor from eq (2.7) as written in eq (2.6) is clearly arbitrary. When completely separated, the spin factor $\prod_j q_j^{k_j}$ is the same as $\prod_{i=0}^{t} (2s_i+1)^i$, based on the individual spins of the constituent particles. The denominators $\prod_i (l_i)_j!$ under the W_j's in eq (2.6) occur as shown if the eigenfunctions in eq (2.7) are regarded as not restricted by the exclusion principle but instead as having the full number of states corresponding to the Boltzmann statistics as a limiting condition. If the Slater sum were obtained exactly according to the exclusion principle, then a compensatory multiplication by this factor would be required, as indicated in the theory for a pure gaseous substance as given by Kahn and Uhlenbeck and by Kahn.

With the preceding formulation, the cluster integrals are the equilibrium constants for cluster formation according to the equation

$$\frac{N_{(l_i)}}{V}=b_{(l_i)}\prod_i\left(\frac{N_{(i)}}{V}\right)^{l_i}, \tag{2.8}$$

where V is the volume accessible to the gas, where $N_{(l_i)}$ is the number of clusters of composition (l_i), and where $N_{(i)}$ is the number of separately occurring individual particles of type i, i. e., as "clusters" of one particle. This result can be inferred in accord with the analogy between the present case and the treatment for clusters for a single pure substance [2, 3]. Alternately, the result can similarly be easily inferred from the nonquantum formulation of Fuchs [6], on the grounds that the present formulation is equivalent except for its inclusion of quantum effects. Further indication of the correctness of these equations will be presented later in this section.

It is to be noted that the equilibrium constants of eq (2.8) are the theoretically exact ones for a treatment of the real gas as a mixture of ideal gas components. Hill [17] has pointed out that any modification of definition that would give clusters other than these (he terms the present ones "mathematical clusters"), would eliminate the ideal gas law dependence of each component cluster gas; this would not allow the simple mass action law of eq (2.8). Excluded volume effects are automatically included in our theoretical formulation at this stage and would not be added separately unless a compensating readjustment were introduced to remove an equivalent quantity from the cluster representation. It may be recognized that a cluster of a given composition can be called a molecule or free radical or ion, or a group of such entities, according to the normal custom for nomenclature. If a molecule happens to have various isomeric forms, the requirements of the particular application could determine whether the different forms would be treated together or separately according to a reasonable apportionment of accessible phase space.

The Helmholtz free energy for a mole of like clusters of type (l_i) in the absence of ionization may be represented as $A=kT\ln Q$ with

$$\begin{aligned}Q&=[Q_i^e]^N[Q_{tr}]^N/N!\\&=\left[b_{(l_j)}\left(\frac{h^2}{2\pi\Sigma m_s kT}\right)^{3/2}\prod_s\left(\frac{2\pi m_s kT}{h^2}\right)^{3/2}\right]^N\left[\left(\frac{2\pi\Sigma m_s kT}{h^2}\right)^{3/2}V\right]^N/N!.\end{aligned} \tag{2.9}$$

The first bracket indicates Q_i^e, the effective internal partition function, and the second indicates Q_{tr}, the translational partition function for a single cluster.

From eq (2.9) with eq (2.3) and (2.6), one may infer that the effective partition function for the cluster may be represented formally as

$$Q^e=\sum(-1)^{k-1}(k-1)!\prod\frac{1}{k_j!}Q_j^{k_j}, \tag{2.10}$$

with Q_j taken as

$$Q_j = \frac{1}{\prod_s (l_i)_j!} \int \cdot \cdot \cdot \int W_j \prod_s \left(\frac{2\pi m_s kT}{h^2} \right)^{3/2} d^3 r_s, \tag{2.11}$$

in accord with eq (2.1) and (2.7), since each W_j in eq (2.6) is a function of coordinates internal to the fragment j.

Even though the equations given follow plausibly from earlier investigations, it may be advantageous to examine some of the relations in greater detail. By such a procedure we may hope (1) to confirm definitely that the Ursell type formula is actually being extended correctly to mixtures with "non-additive" potentials, (2) to show that the structure of the correct Ursell-type formulas is simply that which provides the incremental contribution (per cluster) to the state sum, due to the particles being in the cluster rather than present in other, less combined forms, and further, (3) to obtain the result that the formation of a combined cluster from two component clusters is strictly analogous to the combination of two particles into a cluster of two, so that repeated application of a process analogous to calculating the second virial coefficient gives an analysis concerning clusters of any degree of complexity.

Thus it is informative to compare the effective partition functions for two cases differing in that in one case one additional particle is present within the cluster while in the other case it is counted as present in the assembly without interaction with other constituents of the cluster. The difference in magnitude between the state sum for the entire gas when the particle is combined and its value when the particle is uncombined includes the effect of inserting the particle into every subcluster or fragment of the cluster involved according to eq (2.6) or (2.10) for the effective partition function for the initial cluster. The numbers of subclusters after insertion of a single particle into one of them include k_{jr} of the type of the receptor subcluster (initially there were $k_{jr}+1$ of this type), k_{jp} of the type of the product subcluster (initially there were $k_{jp}-1$ of this type). The number of single particle subclusters for particles of type q after addition of the added particle of this type is to be indicated as k_{jq}. The increment in the total effective partition function for the system including the initial cluster and the added particle due to addition of the particle to the cluster will be indicated by

$$Q^e(l_1, l_2, \ldots l_q, \ldots) = \theta Q^e(l_1, l_2, \ldots l_q - 1, \ldots), \tag{2.12}$$

where θ is an operator operating on $Q^e(l_1, l_2 \ldots l_q - 1, \ldots)$, the effective partition function for the initial cluster. The total contribution to the effective partition function of the combined cluster formed by adding the new particle includes a contribution from each factor of each term of the partition function for the initial cluster. From this it can be seen that the numerical factors arising in use of the operator θ are identical with those occurring in a differentiation process. θ can be represented as $Q_1^* - Q_1$, in which Q_1^* is an operator which produces the ordinary partition function of a combined system when it operates on the ordinary partition function of the partial system, as $Q_1^* Q_b = \overline{Q_1 Q_b}$, while Q_1 is an ordinary partition function of the added particle.

Making use of eq (2.10) for the effective partition function of the initial cluster, the effective partition function of the combined cluster obtained with this operator θ is indicated in accord with eq (2.6) and (2.11) using the corresponding $U_l / \prod_i l_i!$ in terms of the W's, now to be written omitting the spin factor $\prod_i (2s_i + 1)$:

$$U_l / \prod l_i! = \sum (-1)^{k-1} (k-1)! \prod_j \frac{(W(l_1, l_2 \ldots))^{k_j}}{(k_j)! (\prod_i (l_i)_j!)^{k_j}} \left[\sum_j \frac{(k_{jr}+1)}{(k_{jr}+1)} (l_q)_j k_{jp} + \sum_j{}' \frac{k_j k_{jq}}{k-1} + \frac{(k_{jq}-1) k_{jq}}{k-1} \right] \frac{1.}{(l_q)} \tag{2.13}$$

On the right-hand side of the equation, the expression before the bracket is the regular expression for the combined cluster. The expression within the bracket includes contributions of various kinds arising from the addition of the particle to various possible fragments of the initial cluster. For the first term in the bracket, coming from the insertion of the added particle to a subcluster, the factor $k_{jr}+1$ in the numerator is due to there having been this number of subclusters to which the particle might be added to produce one particular type of product cluster. This modifies a particular product of the type preceding the bracket since there had been a factor $k_{jr}+1$ in the old factorial in the denominator and this factor now appears in the denominator of the term in the bracket. Similarly the new factor outside has a new factor k_{jp} in a factorial in its denominator (included in one of the $(k_j)!$ factors) which is balanced to the original by the k_{jp} in the numerator of the term in the bracket. Also, a new factor $(l_q)_j$ is in the denominator in front of the bracket (included as a net increase of one factor in the general $(l_i)_j!$) because of the k_j indicating k_{jp} instead of a former $k_{jp}-1$, and this is balanced in the term in the bracket by the $(l_q)_j$ in its numerator.

The other two terms in the bracket arise from the addition of the new particle as a separate subcluster arising in the $-Q_1$ term of the θ. For the initial cluster, the value of k was less by one than its value in such corresponding terms of the combined cluster, as are obtained using the Q_1 factor thus giving the opposite sign by $(-1)^k$, which, when combined with the minus sign on the $-Q_1$, gives positive contributions within the bracket for both terms. The occurrence of $k-1$ in their denominators is a compensation concerning the $(k-1)!$ factor and is also due to k for the terms for the initial cluster being one less than for the combined cluster. The first of these last two terms in the bracket has an origin somewhat analogous to that of its predecessor but with Q_1 involved rather than the combining Q_1^*. The prime on the summation sign is to indicate that the summation is to include only those j's for which the k's do not represent k_{jq}, so as to obtain the count of the number of terms which had been involved for the Q_1^*, except for those due to adding a single particle to a like particle. The effect of adding the separate single particle subcluster is to increase the exponent in front of the bracket for single particles q to k_{jq} from $k_{jq}-1$, its value in the initial cluster. To compensate for the matching extra factor in the factorial expression in the denominator preceding the bracket, the value k_{jq} occurs in the numerator of the present term in the bracket. The last term in the bracket is likewise analogous to the first term, with Q_1 involved rather than the combining Q_1^*. This term counts the number of separate occurrences in which the added particle enters into the formation of clusters of two like particles. This term appearing as a balancing quantity to which the effect of Q_1^* is compared, has the factor $k_{jq}-1$ for the number of initial subclusters in connection with which this final comparison process arises. In addition, the numerator contains the factor k_{jq}, as in the term preceding, to balance the augmented factorial in the denominator of the expression preceding the bracket.

The quantities in the bracket may now be combined. For the first term, k_{jp} occurs only for the subclusters produced by adding the new particle to a previously existing subcluster. Thus, it does not include j's for single particle subclusters, so that

$$\sum (l_q)_j k_{jp} = \sum (l_q)_j k_j - k_{jq} = l_q - k_{jq}. \tag{2.14}$$

For the second term, $\sum_j{}' k_j k_{jq}$, the summation is over j's for which the k_j's do not represent k_{jq}. As the full sum $\sum_j k_j$ would have been equal to k, $\sum_j{}' k_j$ is $k-k_{jq}$. The three terms are now readily combined as

$$l_q - k_{jq} + \frac{(k-k_{jq})k_{jq}}{k-1} + \frac{(k_{jq}-1)k_{jq}}{k-1}, \tag{2.15}$$

which reduces to l_q. This is cancelled by the l_q in the denominator after the bracket, representing an additional factor in the general factorial of the denominator needed to convert from phase integral to partition function as indicated in eq (2.1). From this demonstration eq (2.6), or its equivalent, eq (2.10), may be seen to be an appropriate extension of the ordinary Ursell-type formula to mixtures. Thus, an effective partition function agreeing with the Ursell-type formula may be generated relevant to the combined cluster, starting with an Ursell-type formula for the cluster of one less particle by simply evaluating the increase in the net state sum due to counting an additional particle of the entire system as belonging to the cluster. On the one hand, one may see this as a logically correct process to build up the effective partition function, so that on the basis of the obvious correctness of the Ursell-type formula for small clusters of one or two particles, mathematical induction permits one to regard the present Ursell-type formula as clearly holding for clusters of arbitrary size and composition, but with due regard for details of particle statistics as required. Alternatively, for one who finds the present Ursell-type formula to be an obviously correct extension of the Ursell formulas previously known, the foregoing demonstration can show that the addition of a particle to a previous cluster can be treated formally in the simple form of a second virial coefficient as indicated, using the operator $\theta=Q_1^*-Q_1$ with eq (2.12). It may also be noted that the joining of one cluster with another to form a combined cluster may be treated similarly using an operator θ built from effective partition functions

$$\theta=Q_a^{e*}-Q_a^e, \tag{2.16}$$

since

$$Q_{ab}^e=\theta Q_b^e=\overline{Q_a^e Q_b^e}-Q_a^e Q_b^e \tag{2.17}$$

has a form identical with the pattern for obtaining the second virial coefficient for the effects of interaction between the two clusters. Thus, the calculation of the effective partition function for a diatomic molecule is directly related to and essentially identical with the calculation of the second virial coefficient for the interaction of its constituent atoms, no matter whether one regards the atoms as interacting particles or clusters of nuclei and electrons. Similarly, the treatment for a triatomic molecule is directly related to that for a cluster of three particles such as is involved in the cluster theory for the third virial coefficient. In all cases, states of higher electronic excitation should be allowed for if significantly present and should be understood as included in the present notation.

We now come to the particular advantage obtained by use of the effective partition functions as defined in the foregoing discussion. The partition function for the complete gas assembly can be written out readily when they are used in the analysis. Using total effective partition functions $\boldsymbol{Q}_j^e=Q_j^e(Q_{j\ \mathrm{trans}})$ for a cluster for which the number of particles of kind i is $(l_i)_j$, the partition function for an assembly involving N_i particles of each kind i is

$$Q_N=\sum_{(N)}\Big[\prod_j(\boldsymbol{Q}_j^e)^{m_j}/m_j!\Big], \tag{2.18}$$

with the sum including every kind of term consistent with the condition

$$\sum m_j(l_i)_j=N_i. \tag{2.19}$$

The most probable state may readily be found in the sense of determining the greatest term in the sum. This may be done on the basis that, in the immediate vicinity of the maximum, neighboring terms are almost exactly equal. If for a neighboring term, the number of clusters of type j is taken as m_j+n_j (where each n_j is a small integer) rather than the m_j of eq (2.18), then eq (2.19) takes the form $\sum(m_j+n_j)(l_i)_j=N_i$, and the difference between the two is the general conservation equation

$$\sum n_j(l_i)_j=0. \tag{2.20}$$

The requirement that neighboring terms near the maximum be approximately equal gives

$$\prod_j(\boldsymbol{Q}_j^e)^{m_j+n_j}/(m_j+n_j)!\approx\prod_j(\boldsymbol{Q}_j^e)^{m_j}/m_j!, \tag{2.21}$$

which reduces to

$$\prod_j(\boldsymbol{Q}_j^e)^{n_j}=\prod_j(m_j+n_j)!/m_j!, \tag{2.22}$$

or

$$\prod_j(\boldsymbol{Q}_j^e)^{n_j}\approx\prod_j m_j^{n_i}, \tag{2.23}$$

since $m_j \gg 1$ and n_j is a small integer. By substituting $Q_i^e Q_{j\ \mathrm{trans}}$ for $\boldsymbol{Q}_j^e$ and dividing by $\prod_{=1} V^{n_i}$, the relation

$$\prod_j \left(\frac{m_j}{V}\right)^{n_i} = \prod_j (Q_j^e)^{n_j} \left(\frac{Q_{j\ \mathrm{trans}}}{V}\right)^{n_j} \tag{2.24}$$

is obtained. Since $Q_{j\mathrm{trans}}$ contains V as a factor as shown in eq (2.9), or according to

$$Q_{j\,\mathrm{trans}} = V \Lambda_{(l_i)j}^{-3}, \tag{2.25}$$

with

$$\Lambda_{(l_j)j} = h/(2\pi [\sum_i (l_i)_j m_i] kT)^{1/2}, \tag{2.26}$$

the right-hand side of eq (2.24) is independent of V, and by further reduction using items relevant to eq (2.9), is equal to $\prod_i (b_{(l_i)})_j^{n_i}$ and forms an equilibrium constant to which the product of concentrations on the left-hand side of the equation is equated. The reaction equation to which this law of mass action is relevant is

$$\sum n_j' Y_j \rightarrow \sum n_j'' Y_j$$

or

$$\sum n_j Y_j = 0, \tag{2.27}$$

where n_j represents both n_j'' and $-n_j'$, with Y_j representing the chemical symbol for the type of cluster (or molecule) referred to. For the reaction of formation of a single cluster (or molecule) from elementary particles or clusters, the mass action equation can be reduced to eq (2.8), with $N_{(l_i)}$ corresponding to the m_j of the equations just concluded.

If the representation of gas properties is carried out directly in terms of particular kinds of clusters, then these clusters may be considered afresh as the constituents of a gas mixture whose interactions lead to the virial coefficients for this mixture gas. These virial coefficients for the gas are of course related to the cluster integrals—or the effective partition functions—for the clusters formed among its constituents. An adequate theory representing their effects formally can be given using the grand partition function. Exactly the same results may be obtained in the present case, however, by noting that the gas acts as a mixture of ideal gases subject to chemical equilibrium, as shown by eq (2.24). Then, the pressure of the gas is the sum of the partial pressures of all kinds of clusters of the constituents. Similarly, the net concentration of any kind of constituent particle is proportional to an analogous sum in which each term of the pressure sum is multiplied by the number of that kind of constituent particle in the corresponding cluster. While the various terms of these two expressions are expressible using cluster-integral-type or effective-partition-function-type equilibrium constants, multiplied by products of powers of density-type fugacities of the various constituents, the ideal-gas-type relations which apply to each constituent permit the density-type relations which apply to each constituent permit the density-type fugacity to be equated to the quotient of the partial pressure of the constituent, divided by kT, so that

$$\frac{p}{kT} = \sum_j [b_{(l_i)}]_j \prod_j \left(\frac{p_i}{kT}\right)^{(l_i)_j} \tag{2.28}$$

and

$$\frac{N_i}{V} = \sum_j (l_i)_j [b_{(l_i)}]_j \prod_i \left(\frac{p_i}{kT}\right)^{(l_i)_j}, \tag{2.29}$$

giving

$$\frac{pV}{NkT} = \frac{\sum_j [b_{(l_i)}]_j \prod_i \left(\frac{p_i}{kT}\right)^{(l_i)_j}}{\sum_j [\sum_i (l_i)_j] [b_{(l_i)}]_j \prod_i \left(\frac{p_i}{kT}\right)^{(l_i)_j}}. \tag{2.30}$$

The mole fraction of constituent i is $x_i = N_i/N$. The process of eliminating the fugacities (p_i/kT) from the expression for pV/NkT is more involved than that for a pure substance [18]. Using b_{ij} and b_{ijk} as the cluster integrals $b_{(l_i)}$ for two particles i and j and for three particles i, j, and k, respectively, the first two virial coefficients are obtained as

$$B = \sum\sum x_i x_j B_{ij} \tag{2.31}$$

and

$$C = \sum\sum\sum x_i x_j x_k C_{ijk}, \tag{2.32}$$

with

$$B_{ij} = -N b_{ij}, \tag{2.33}$$

and with

$$C_{ijk} = \frac{N^2}{3}\,[4b_{ij}b_{jk} + 4b_{ik}b_{kj} + 4b_{ki}b_{ij} - 6b_{ijk}]. \tag{2.34}$$

Higher virials may similarly be obtained, but much less readily due to the proliferation of algebriac expressions in the transformations. Even for the third virial, the problem of nonadditivity of pair potentials arises. For pure substances, Rosen [19] found nonadditive effects in the three helium atom interaction, Axilrod [20] has found such effects for the dispersion energies, and Jansen [21] has examined the entire problem at some length. Kihara [22] also has recognized the problem and has made use of Axilrod's results in estimating the effect on third virials for the pure noble gases. For gas mixtures, the problem is of added complexity as it involves the estimate of interaction between two unlike constituents as well as the nonadditivity among all the differing kinds of constituents considered three at a time, alike and unlike. In applications at elevated temperatures where the constituents may be other than ordinary stable substances, nonadditivity can be expected to have large effects. Where the prediction of properties of a gas mixture using rigorous theory is particularly impracticable, the use of empirical mixture rules becomes a natural expedient.

If one attempts to obtain the effective molecular partition functions from second virial or cluster integral calculations, a classical type calculation may be simplest and thus might most naturally be used, with potential functions based on empirical spectroscopic constants and other known facts. Corrections for quantization effects in such cases would also be needed. A study of the effects of the change of spacing of levels when the quantum of action, h, is considered as approaching zero, as discussed in Appendix 1 (section 5.1) shows that the quantum effective partition function (referred to the lowest quantized level) may be obtained approximately at high temperature by multiplying the classical effective partition function (referred to the classical zero energy) by the correction factor,

$$\begin{aligned}\Bigg\{1 + \frac{1}{12}\frac{hc}{kT}\Big[\sum_i d_i(d_i+1)x_{ii} + \sum_{i<j}\sum d_i d_j x_i\,(3 - \omega_i\omega_j^{-1} - \omega_j\omega_i^{-1}) + f\Big] - \frac{1}{24}\left(\frac{hc}{kT}\right)^2 \sum_i d_i\omega_1^2 \\ + \frac{1}{5760}\left(\frac{hc}{kT}\right)^4\Big[\sum_i (5d_i+2)d_i\omega_1^4 + 10\sum_{i<j}\sum d_i d_j \omega_i^2\omega_j^2\Big]\Bigg\}\exp\frac{hc}{kT}\sum\frac{\omega_i d_i}{2},\end{aligned} \tag{2.35}$$

where for nonlinear polyatomic molecules

$$f = 2\sum_i q_{ii} + \tfrac{1}{2}\sum_i d_i\omega_i(A_e^{-1}\alpha_1^A + B_e^{-1}\alpha_1^B + C_e^{-1}\alpha_1^C) + (2A_e + 2B_e + 2C_e - A_eB_eC_e^{-1} - B_eC_eA_e^{-1}),$$

while for linear molecules

$$f = 2\sum_i g_{ii} + \sum_i d_i\omega_i B_e^{-1}\alpha_i + 4B_e.$$

The constants in these expressions follow the usual spectroscopic notation with vibrational energy given by

$$\sum_i \omega_i\left(v_i + \frac{d_i}{2}\right) + \sum_i x_{ii}\left(v_i + \frac{d_i}{2}\right)^2 + \sum_{i<j}\sum x_{ij}\left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_i}{2}\right) + \sum_i g_{ii} l_i^2,$$

with rotational constants

$$A_v = A_e - \sum_i \alpha_i^A \left(v_i + \frac{d_i}{2} \right),$$

$$B_v = B_e - \sum_i \alpha_i^B \left(v_i + \frac{d_i}{2} \right),$$

$$C_v = C_e - \sum_i \alpha_i^C \left(v_i + \frac{d_i}{2} \right),$$

for the nonlinear molecule, and

$$B_v = B_e - \sum_i \alpha_i \left(v_i + \frac{d_i}{2} \right)$$

for the linear molecule. The diatomic molecule may be regarded as a special case of the linear molecule. The terms purely in ω_i in the bracket in eq (2.35) amount to a simple extension of a result which Herzfeld and Teller [23] obtained by the method of Wigner and Kirkwood, and which others have used in other forms [24, 25]. Except for form, the terms linear in hc/kT agree exactly with the result of Mayer and Mayer [26] for diatomic molecules. It will be noticed that if the two kinds of partition functions, quantum and classical, are to be referred to the same zero of energy, say the classical zero or the zero of the potential energy function, then the additional required factor exp $[(-hc/kT)G_0]$, where G_0 is the zero point energy, removes the factor of exp $[(hc/kT)\Sigma(\omega^1 \mathrm{d}_1/2)]$ of eq (2.35) and replaces it with an exponential factor based on the much smaller anharmonicity constants. Thus, for such a quantization correction, the zero point energy might be considered as not being involved. The detailed procedure of taking a calculation with the zero of energy with the cluster particles dispersed and adjusting to a zero of energy at the lowest quantized level for the cluster to conform with custom in the tabulation of molecular thermal functions involves, in addition to eq (2.35), the use of the factor exp $[(-hc/kT)D_e]=$exp $[(hc/kT)(D_0+G_0)]$. This gives as the combined correction the expression in the bracket in eq (2.35), multiplied by exp $[(-hc/kT)D_0]$ exp $[(hc/kT)(\Sigma\{\omega_i d_i/2\}-G_0)]$. In the adoption of eq (2.35) as the approximate quantization correction, not only has the existence of other than Boltzmann statistics been ignored as of no importance in calculations at high temperature and up to moderate densities, but also the quantization correction contributions associated with fragments of the cluster have also been disregarded, since at moderate temperatures the net quantization effects due to the fragments would be very small because of reduction due to powerful Boltzmann factors.

The molar thermal functions for molecular-like clusters according to this formulation are to be consistent with

$$A = -kT \ln Q \tag{2.36}$$

as in eq (2.9), but with each effective internal partition function Q_i^e including its appropriate quantization effect given by eq (2.35) and also multiplied by exp $(-hc/kT)D_e$ so as to be based on the usual molecular zero of energy.

In eq (2.17) it is indicated that the effects of interactions between two different clusters or between a cluster and a particle may be indicated formally as a cluster integral for the joining of the two parts into a combined cluster. In making use of this principle as a guide in obtaining approximate thermodynamic functions for a gas mixture, it seems appropriate to emphasize its indication of the permissible arbitrariness of assignment of regions of phase space either completely to the formation of the combined cluster (in the style of the so-called mathematical cluster), or partly to the combined cluster (now possibly called a physical cluster), and partly to a second virial type interaction between the two parts of the cluster.

One application of this principle is in regard to the effective internal partition function for the interaction of two atoms forming a diatomic molecule. One alternative is to use the entire effect in this partition function and the corresponding thermodynamic functions. On the other hand, any part of this partition function may be used in obtaining the thermodynamic functions for the constituent, provided that the remainder of the effective partition function is retained as contributing in its appropriate way to the second virial type interaction between the corresponding atomic constituents.

Somewhat similarly, the combination of an added outer electron with a positive atomic ion to form an atom or a positive atomic ion with one unit less of charge may also be treated in good approximation using an arbitrary subdivision of phase space. In a gas in which considerable excitation of levels near ionization occurs, there is also considerable formation of free ions, for which the effective interaction potential in the assembly as a whole may be taken as the Debye screened Coulomb form. Meeron [15] has shown that the nonquantum-mechanical treatment of Mayer [14] for ionic solutions can be given this simple interpretation, using quantities corresponding to second virial coefficients, even though expansion of higher order terms would not be the equivalent of a higher virial evaluation using the Debye screened Coulomb potential. Application to a high-temperature gas involves details of quantized states of the combined atom with ionic screening to which the approximate treatment by Ecker and Weizel [16] is relevant. Further discussion of this subject may be presented in a later paper. It would appear that a conventional sum of states for the atom up to some moderate principal quantum number of the outer electron should be acceptable provided that the remainder of the effective partition function be used in obtaining corrections for equation of state quantities. A very different division of phase space has been used in the treatment which will be presented in the following section and in the next paper of the present series.

As the virial coefficients based on additive pair interactions as used by Mayer [14] in deriving quantities for his theory of ionic solutions are consistent with the cluster integrals for the Coulombic interaction, since this is additive, it is possible to treat the effect of ionization using Mayer's classical ion-solution theory, which he arranged primarily for an assembly of ions with each pair separated by a distance greater than its particular sphere radius. The interior of each ion sphere is a region actually accessible to the electrons of the system, as they can enter and become energetically attached so as to form ions of various numbers of electrons. As each such group is a cluster of particles, one would wish to evaluate contributions to the Ursell integrals for electrons within the sphere but with such quantization corrections as would be needed to approximate the effects due to the discrete states of the ions. Unfortunately for purposes of evaluation, the integrand of the general integral for the many-particle case is of such complexity and the integrals are so highly multiple that precise direct evaluation according to this procedure appears impossible. It is therefore appropriate to make use of convenient approximations. The effective partition function may be estimated approximately using the observed and estimated low lying quantized states with classically estimated contributions from higher energy regions of phase space within the assigned radii. These may depend on the representation of effective potential-energy functions, with simplifying approximations made possible by partial compensation for cognate fragment terms in the cluster integrals.

Because the thermodynamic functions obtained are specifically arranged for use with an ionic-gas treatment based on Mayer's development of ion-solution theory with specific values for the ion radii, it seems appropriate now to summarize the results of his approximate treatment when applied to such an ionic-gas mixture in chemical equilibrium.

3. Ionized Gas as an Ionic Solution

The nonquantum-mechanical theory of ionic solutions given by Mayer [14] retains terms applying to ions free to move to any accessible pair separation greater than their collision radius. By also including the contribution of Mayer's eq (46) due to the departure of the non-Coulombic pair potential from rigid-sphere form, an approximate expression consistent with the terms retained in his original derivation may be obtained. On this basis, the

Helmholtz free energy for the gaseous assembly of molecules, atoms, atomic ions, and electrons with the accompanying thermal radiation may be taken approximately as

$$-A/RT=(V/V_0)\Big\{\sum_s C_s[(-A^0/RT)_s-\ln C_s-\ln T/T_0]+\frac{2}{3}\pi^{1/2}(\sum Z_s^2C_s)^{3/2}\epsilon^3(DkT)^{-3/2}(N_0/V_0)^{1/2}$$

$$+\frac{1}{2(\sum Z_s^2C_s)}\sum_{s=1}\sum_{r=1}\sum_{\nu=\nu_{sr}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}[b_\nu(\varphi_{sr})+g_\nu(\varphi_{sr})]+\sum_s\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty h_{sr}2\pi R_{sr}^2dR_{sr}$$

$$+\left[\frac{1}{12\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{1}{32}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_e^2+\frac{8\pi^5}{45}\frac{k^3T^3}{h^3c^3}\frac{V_0}{N_0}\Big\}+\Delta(-A/RT),\quad(3.1)$$

where C_e is the C_s representing electron concentration and where terms are given for the first-order quantum corrections for an electron gas including Fermi-Dirac statistics [27, 28] for electrons.

The symbols used in the present ion-solution equations have the following meanings:

C_s=concentration relative to that of a pure ideal gas at standard conditions, i. e., $C_s=N_sV_0/N_0V$,
Z_s=ionic charge of each ion of type s, in protonic units,
ϵ=electronic charge,
D=effective dielectric constant, ~ unity for low density,
k=Boltzmann constant,
$\alpha_{sr}=a_{sr}DkT/\epsilon^2$,
a_{sr}=collision radius for ion s and ion r.

$b_\nu(\varphi)$, $g_\nu(\varphi)$, and $h_\nu(\varphi)$ are functions defined and tabulated by Poirier [29]. The argument of these functions is defined by

$$\varphi_{sr}=\frac{2\pi^{1/2}\alpha_{sr}(\sum Z_s^2C_s)^{1/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}=\kappa a_{sr},$$

where $\kappa^2=4\pi\epsilon^2\sum Z_s^2C_s/DkT$, as known from the Debye-Hückel theory.

The omission of b_1, g_1, and h_1 (h_ν appears in appendix 2) on the basis of net electrical neutrality for the complete assembly is acceptable in case there is but one value of a_{sr}, the case for which Poirier's tables were prepared. If there are several values of a_{sr}, then cancellation does not occur in general for ion separations between the least and greatest a_{sr}. Evaluation of the net contribution may then be based on the explicit expressions

$$b_1(\varphi)=\tfrac{1}{2}e^{-\varphi}[1+\varphi-\tfrac{1}{2}\varphi^2]-\tfrac{1}{2},$$

$$q_1(\varphi)=\tfrac{1}{2}e^{-\varphi}[1+\varphi+\tfrac{1}{2}\varphi^2]-\tfrac{1}{2},$$

and

$$h_1(\varphi)=\tfrac{1}{2}-\tfrac{1}{2}e^{-\varphi}[1+\varphi+\tfrac{1}{2}\varphi^2-\tfrac{1}{2}\varphi^3].$$

$\Delta(-A/RT)$ has been included to account for any further corrections omitted from the equation of state. As pointed out in the preceding section, nonionic equation-of-state effects at low and moderate density may be treated by cluster theory and could be accounted for by including all clusters as separate new constituents in the first term in the brackets in eq (3.1). Alternatively, the effects may be indicated in accord with the usual procedure employed to obtain thermodynamic corrections for nonideality. Thus, one might use

$$\Delta\left(-\frac{A}{RT}\right)=-\frac{V}{V_0}\left[\frac{(B-B_0)}{V_0}(\sum C_s)^2+\frac{(C-C_0)}{2V_0^2}(\sum C_s)^3+\frac{(D-D_0)}{3V_0^3}(\sum C_s)^4\cdots\right],\quad(3.2)$$

where $B-B_0$, $C-C_0$, and $D-D_0$ represent additional parts of the virial coefficients required over and above the zeroth order values implied by the remainder of the ion-solution-cluster treatment being used. Corrections to a nonvirial type representation could similarly be provided.

The quantity h_{sr} in eq (3.1) has the value

$$\exp\left\{\left[-U_{sr}+\frac{Z_sZ_r\epsilon^2}{DR_{sr}}\,(1-e^{-\kappa R_{sr}})\right]\Big/kT\right\},$$

for $0<R_{sr}<a_{sr}$ and the value

$$\exp\left\{\left[-U_{sr}+\frac{Z_sZ_r\epsilon^2}{DR_{sr}}\,(1-e^{-\kappa R_{sr}})\right]\Big/kT\right\}-\exp\left[-\frac{Z_sZ_r\epsilon^2}{DR_{sr}kT}\,e^{-\kappa R_{sr}}\right]$$

for $a_{sr}<R_{sr}<\infty$. In the present method of describing effects between ion cores and an outer electron, h_{sr} will be taken as zero in the range $0<R_{sr}<a_{sr}$, since this is a region which contributes to the internal sum of states determining the function $(-A°/RT)_s$ for the corresponding constituent of ion core with outer electron, and the effect is taken into account by that means. If a_{sr} is well chosen for the approach of two atomic ions, h_{sr} can be small in almost all of both regions, as pointed out by Mayer for his closely related k_{sr}. Thus for $R<a_{sr}$, h_{sr} is small because the pair potential U_{sr} is very large; while for $R>a_{sr}$, it is small because U_{sr} is almost identical with $Z_sZ_r\epsilon^2/DR_{sr}$.

If the contribution within the braces of eq (3.1) due to h_{sr} for the interaction of ions of like charge is to be based on the use of a Debye screened Coulomb repulsion for $R_{sr}<a_{sr}$ as well as for $R_{sr}>a_{sr}$, it may be given as

$$\frac{2\pi}{3}\,a_{sr}^3\,\frac{N_0}{V_0}\sum_s\sum_r C_sC_r\sum_{n=0}q_n(x_{sr})\varphi_{sr}^n,$$

with

$$x_{sr}=Z_sZ_r\epsilon^2/Da_{sr}kT=Z_sZ_r/\alpha_{sr}.$$

Formulas for $q_n(x)$ are given in Appendix 3 (section 5.3).

Equation (3.1) has been written in rather general form which allows it to be used in more than one way. An approximate treatment for an assembly including atomic ions under conditions of high-ion density may be obtained by choosing a single a_{sr} to apply throughout or a very small number of different a_{sr}'s, with suitably limited sums to represent the internal partition functions. For conditions of relatively low density, however, it may be desirable to use internal partition functions for the atomic ions based on an extensive set of levels extending to moderately large electron separations. The so-called "collision radius" between an electron and an atomic ion could in principle be taken correspondingly large in this case, but with the added detail that the ν_{sr}^0 or initial index in the summation in eq (3.1) and in similar expressions in Appendix 2 (section 5.3) would be greater than zero, signifying free entry into the ion sphere for this one case rather than having a zero value signifying the exclusion from the ion sphere such as is used in regard to the close approach of two atomic ions.

Calculations concerning the concentration of the various constituents of the gas mixture under conditions of equilibrium can be made based on this ion-solution treatment according to well known principles. Thus, we may consider a stoichiometric chemical reaction among substances Y_s with stoichiometric coefficients $n_{ks'}$ and $n_{ks''}$ in the reaction equation (c.f., eq (2.27))

$$\sum n_{ks'}Y_{s'}\rightarrow\sum n_{ks''}Y_{s''},$$

which may be written as

$$\sum n_{ks}Y_s=0, \tag{3.3}$$

with n_{ks} representing both $n_{ks''}$ and $-n_{ks'}$. The equation for chemical equilibrium for this kth reaction equation is

$$\sum n_{ks}\mu_s=0 \tag{3.4}$$

in terms of the chemical potentials μ_s, with

$$\mu_s=(\partial A/\partial N_s)_{T,V}. \tag{3.5}$$

This gives

$$K_k=\prod_s C_s^{n_{ks}}=\left(\frac{T_0}{T}\right)^{\Sigma n_{ks}}\exp\left[\sum n_{ks}\left(-\frac{F^\circ-H_0^\circ}{RT}\right)_s-\frac{\Delta H_0^\circ}{RT}\right]\prod_i \gamma_i=K_k{}^{(0)}\prod_s \gamma_i \tag{3.6}$$

where ΔH_0° is $\sum n_{ks}\ H_0^\circ$ for the reaction with

$$\gamma_1=\exp\left[\frac{\pi^{1/2}(\sum Z_s^2C_s)^{1/2}(\sum n_{ks}Z_s^2)\,\epsilon^3N_0^{1/2}}{V_0^{1/2}(DkT)^{3/2}}\right] \tag{3.7}$$

according to the Debye-Hückel theory, and with

$$\gamma_2=\exp\left\{\frac{1}{(\sum Z_s^2C_s)}\sum_s\sum_r\sum_\nu{}_{0}(-1)^\nu C_rZ_r^\nu Z_s^\nu\alpha_{sr}^{1-\nu}n_{ks}[b_\nu(\varphi_{sr})+g_\nu(\varphi_{sr})]\right.$$

$$\left.-\frac{(\sum Z_s^2n_{ks})}{(\sum Z_s^2C_s)^2}\sum_s\sum_r\sum_\nu{}_{\substack{0\\sr}}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}g_\nu(\varphi_{sr})\right\} \tag{3.8}$$

as the principal correction based on the tabulated functions representing Mayer's extension of the theory. A correction for the effect of the h_{sr} terms may be expressed by

$$\gamma_3=\exp\left\{2\sum_s\sum_r n_{ks}C_r\frac{N_0}{V_0}\int_0^\infty h_{sr}2\pi R_{sr}^2dR_{sr}+\frac{\left(\sum_s Z_s^2n_{ks}\right)}{2\left(\sum_s Z_s^2C_s\right)}\sum_s\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty \kappa\frac{\partial h_{sr}}{\partial\kappa}\cdot 2\pi R_{sr}^2dR_{sr}\right\}, \tag{3.9}$$

which for Debye screened Coulomb repulsion between ions takes the form

$$\gamma_3=\exp\left\{\frac{2\pi}{3}a_{sr}^3\frac{N_0}{V_0}\left[2\sum_s\sum_r C_r\sum_{n=0}q_n(x_{sr})\varphi_{sr}^n n_{ks}\right.\right.$$

$$\left.\left.+2\left[\frac{1}{12\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{1}{32}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_0n_{ko}+\left[\frac{\sum_s\sum_r C_sC_r}{2(\sum Z_s^2C_s)}\sum_n nq_n(x_{sr})\varphi_{sr}^n\right]Z_s^2n_{ks}\right]\right\}. \tag{3.9a}$$

An estimate for effect of dependence of dielectric constant D on composition may be made using

$$\gamma_4=\exp\left\{\left[-\frac{\pi^{1/2}(\sum Z_s^2C_s)^{3/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}-\frac{1}{2(\sum Z_s^2C_s)}\sum_{\nu\geq 0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}\right.\right.$$

$$\left.\left.[\nu b_\nu(\varphi_{sr})+(\nu-2)g_\nu(\varphi_{sr})]\right]\left[\sum n_{ks}\frac{d\ln D}{dC_s}\right]\right\}, \tag{3.10}$$

although a more detailed microscopic analysis of the kinds of screening affecting both γ_3 and γ_4 should be made. In fact, the rapid increase of atomic polarizability with principal quantum number poses another convergence problem unless each atomic state be taken as defining an independent constituent. Additional effects related to the equation of state may be estimated from

$$\gamma_5=\exp\{-\sum n_{ks}(\partial/\partial C_s)[(B-B_0)(\sum C_s)^2/V_0$$

$$+(C-C_0)(\sum C_s)^3/2V_0^2+(D-D_0)(\sum C_s)^4/3V_0^3+\ .\ .\ .]\} \tag{3.11}$$

It is also necessary to take into account the dependence of energies of states and the heats of formation and reaction on the ion density. Some indication of the dependence for atomic ions may be obtained from a study of atomic levels for a Debye screened atomic ion. Discussion of these effects will be deferred until a later publication.

The equations for "mass" and charge balance are well known and obvious but may be represented here for completeness. Thus if the number of atoms of element $X^{(i)}$ in a molecule of constituent Y_s is l_{is}, then

$$\sum_s C_sl_{is}=C^{(i)} \tag{3.12}$$

is the local average concentration of this element, usable either directly or in ratio to other similar quantities in the expression of conservation of each chemical element. Similarly, if the electric charge on each molecule of constituent Y_s is Z_s in protonic units, then

$$\sum_s C_s Z_s = 0 \tag{3.13}$$

states that, on the average the gas is electrically neutral.

The concentrations of constituents as given by these equations may be termed nominal concentrations of clusters considered as molecules. To obtain the actual molecular concentrations $C_s^{(m)}$ from the corresponding nominal cluster concentrations C_s, one may make use of the ratio

$$C_s^{(m)}/C_s = Q_s^{(m)}/Q_s^{\mathrm{eff}} = \sum_i g_i \exp\,(-\epsilon_i/kT)/Q_s^{\mathrm{eff}}, \tag{3.14}$$

with the partition function

$$Q_s^{(m)} = \sum_i g_i \exp\,(-\epsilon_i/kT), \tag{3.15}$$

formed by a sum over whatever group of states is deemed to comprise the specification of the molecular form (or similarly for atoms and atomic ions). The concentration of molecules in their ground states is given by

$$C_s g_0 \exp\,(-\epsilon_0/kT)/Q_s^{eff}, \tag{3.16}$$

where g_0 is the *a priori* weight of the ground-state level and ϵ_0 is its energy relative to the energy zero used in obtaining $Q_s{}^{\mathrm{eff}}$.

It is to be emphasized that nominal concentrations of clusters are in general not identical with concentrations of molecules or ions bearing the equivalent name. If accurate estimates for concentrations of these species are required, then (3.14) and (3.15) must be used.

4. Discussion

The calculation of thermodynamic properties of gas mixtures in chemical equilibrium at high temperature and moderate density, with each molecule, atom, or ion considered as a cluster of its constituent particles, has been discussed. The method of calculation may be used for very high temperatures at which the number density of ions is high, using ion-solution theory in Mayer's formulation.

The detailed discussion of the method of calculation of thermodynamic functions for the atoms and atomic ions that form the principal constituents of the gas mixture at high temperature is reserved for paper II of this series. Under conditions of considerably elevated density, the proportion of small molecules may be enough to make accurately descriptive functions desirable, even at rather high temperatures. Methods of calculating such functions for diatomic molecules may be discussed further in paper III of this series, including both conventional partition functions and the effective partition functions provided by cluster integrals. Molecular cluster integrals automatically include distortion and stretching effects due to centrifugal forces and so are especially suited to calculation at high temperature. The effect of quantization on the molecular cluster integrals has been included in considerable detail, yielding estimated "effective partition functions." Ratios between these functions give proper equilibrium constants for the treatment of a gas mixture as a mixture of ideal gases in the absence of ionization for the purpose of representing the over-all thermodynamic properties of the mixture.

Special emphasis can be given to the concept of the "effective partition function" considered as a convenient function for expressing the increase of the partition function of the entire gas due to the joining together of the parts of the cluster. It is thought that this concept is useful in clarifying the physical meaning of the kind of cluster which has sometimes been called a "mathematical cluster."

The analysis of the gas-mixture properties by means of equilibrium constants for cluster formation, or the cluster integrals for clusters of all compositions for small numbers of particles is formally no less complete than the representation of the gas properties according to a virial series expansion carried through virials of an equivalent order, or involving interactions of an identical number of particles as in the highest virial coefficient included. Indeed, in the low density region the cluster integral representation as a treatment of chemical equilibria is considerably the more complete when applied to effects of chemical bond formation under conditions that favor the formation of small clusters (molecules) only. This detail of good representation may be touched on again in connection with paper III of this series, dealing with diatomic molecules. If triatomic molecules were the largest molecules formed, then a cluster treatment including all clusters of three atoms would include all chemical bonding effects varying directly exactly as the third power of the free atom concentration and would include higher order virial type effects due to chemical bonds in pairs and triples of atoms. In the high-density region, however, the higher virial coefficients have large excluded volume effects which are not included in a treatment covering only pairs and triples of atom particles as clusters. For these, the cluster treatment would need to be carried through for clusters of the same number of particles as the numerical order of the virial coefficient in order to give a complete representation for the given coefficient. Application in the high-density region is complicated further by the detail that for an ordinary chemically inert gas, the virial expansion itself, to which the cluster treatment is formally equivalent, is found to be progressively poorer as a representation when extended to higher and higher density. This might suggest that the virial expansion itself may be correct only asymptotically in the limit of low density. Nevertheless, the virial expansion is to be regarded as a useful approximation capable in principle of giving good estimates up into regions of considerable density. As the equivalent cluster treatment gives a still less suitable extension to high density, the problem of practical estimation of properties of chemically reacting gas mixtures at high density and temperature calls for further estimates of volume effects beyond accessible cluster evaluation, so as to be either in accord with empirical and relevant theoretical knowledge of higher virial coefficients or in accord with gas theory of still broader application.

5. Appendices

5.1. Appendix 1

For high temperature calculations of thermodynamic functions for molecules according to the present cluster approach, one might first obtain the ordinary nonquantum cluster integrals based on potential functions agreeing with empirical spectroscopic constants and other known facts, following which, one would wish to combine quantum corrections based on known molecular spectroscopic constants. By taking the ratio between the ordinary partition function for the molecule and a limiting partition function consistent with it, obtained by reducing the spacing between levels uniformly to zero with a proportionate reduction in weight per level, one may readily obtain a principal correcting factor for the effect of quantization. Since the fragment submolecules implied in the cluster integral occur at much higher energy than the combined molecule, only a small error is introduced by ignoring the quantization corrections for these fragments.

In a well-known system of notation, the logarithm of the ordinary partition function, with energy referred to the ground-state level of a molecule, may be written as

$$\ln Q=\ln Q_R+\frac{\theta_1}{T}-\sum_i d_i \ln(1-e^{-u_i})-\left(\frac{hc}{kT}\right)\Big\{\sum_i x_{ii}d_i(d_i+1)e^{-2u_i}(1-e^{-u_i})^{-2}$$
$$+\sum\sum_{i<j} x_{ij}d_id_je^{-u_i}e^{-u_j}(1-e^{-u_i})^{-1}(1-e^{-u_j})^{-1}+2\sum g_{ii}e^{-u_i}(1-e^{-u_i})^{-2}\Big\}+\sum_i a_id_ie^{-u_i}(1-e^{-u_i})^{-1}. \tag{A1.1}$$

Here Q_R is the rotational partition function for the ground vibrational state in classical approximation, θ_1 represents the Stripp-Kirkwood [30] correction for nonlinear molecules or the Mulholland correction for linear molecules due to the finite spacing of the rotational levels. The variable u_i may be expressed in terms of the usual vibrational constants of

$$G=\sum_i \omega_i(v_i+d_i/2)+\sum_i x_{ii}(v_i+d_i/2)^2+\sum_{i<j}\sum x_{ij}(v_i+d_i/2)(v_j+d_j/2)+\sum g_{ii}l_i^2 \qquad \text{(A1.2)}$$

according to

$$u_i=\frac{hc}{kT}\left[\omega_i+(d_i+1)x_{ii}+\tfrac{1}{2}\sum_{j\neq i}d_j x_{ij}\right]. \qquad \text{(A1.3)}$$

In view of the principal vibrational dependence of the rotational partition function, representable by a factor $\exp\sum a_i v_i$, $\ln Q_R$ may be replaced by $\ln Q_{Re}+\frac{1}{2}\sum_i d_i a_i$, where Q_{Re} refers to the equilibrium configuration. The derivation of the main part of the vibrational effect proceeds as already stated with a factor λ for the level spacing appearing wherever a quantum number factor $(v_i+d_i/2)$ appears in the fundamental expressions:

$$\begin{aligned}\ln Q(\lambda)=&\sum_i d_i\ln\lambda-\sum d_i\ln[1-e^{-u_i(\lambda)}]-\left(\frac{hc}{kT}\right)\lambda^2\Big\{\sum_i x_{ii}d_i(d_i+1)e^{-2u_i(\lambda)}(1-e^{-u_i(\lambda)})^{-2}\\&+\sum_{i<j}\sum x_{ij}d_id_je^{-u_j(\lambda)}e^{-u_j(\lambda)}(1-e^{-u_i(\lambda)})^{-1}(1-e^{-u_j(\lambda)})^{-1}+2\sum_i g_{ii}e^{-u_i(\lambda)}(1-e^{-u_i(\lambda)})^{-2}\Big\}\\&+\lambda\sum_i g_id_i[e^{-u_i(\lambda)}(1-e^{-u_i(\lambda)})^{-1}+\tfrac{1}{2}]\end{aligned} \qquad \text{(A1.4)}$$

with

$$u_i(\lambda)=\frac{hc}{kT}[\lambda\omega_i+\lambda^2(d_i+1)x_{ii}+\tfrac{1}{2}\lambda^2\sum_{j\neq i}d_jx_{ij}]. \qquad \text{(A1.5)}$$

The quantity $\ln Q(\lambda=1)-\ln Q(\lambda=0)$ gives the vibrational quantization correction, to be put in suitable form by expansion of the various functions, either directly or giving the form

$$\begin{aligned}Q(\lambda=1)/Q(\lambda=0)=&\Big\{1+\frac{1}{12}\frac{hc}{kT}[\sum d_i(d_i+1)x_{ii}+\sum_{i<j}\sum d_id_jx_{ij}(3-\omega_i\omega_j{}^{-1}-\omega_j\omega_i{}^{-1})\\&+\sum_i d_ia_i+2\sum_i g_{ii}]-\frac{1}{24}\left(\frac{hc}{kT}\right)^2\sum_i d_i\omega_i{}^2+\frac{1}{5760}\left(\frac{hc}{kT}\right)^4[\sum_i(5d_i+2)d_i\omega_i{}^4\\&+10\sum_{i<j}\sum d_id_j\omega_i^2\omega_j^2]\Big\}\exp\frac{hc}{kT}\sum_i\frac{\omega_id_i}{2}.\end{aligned} \qquad \text{(A1.6)}$$

The rotational quantization correction is already known, being given by the factor $1+\theta_1/T$ as indicated earlier above.

It may be noted that the expression is in such form as to change from a classical treatment with energy measured from the classical $v_i=0$ or potential minimum value to a quantum treatment with energy measured from the quantum $v_i=0$ or ground-state energy.

5.2. Appendix 2.

Additional thermodynamic functions and relations for the equilibrium gas mixture as derived from eq (3.1) are:

$$\begin{aligned}\frac{PV}{RT}=\frac{V}{V_0}\Big\{&\sum C_s-\frac{1}{3}\frac{\pi^{1/2}(\sum Z_s^2C_s)^{3/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}-\frac{1}{2(\sum Z_s^2C_s)}\sum_s\sum_r\sum_{\nu=\nu_{si}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}[b_\nu(\varphi_{sr})-g_\nu(\varphi_{sr})]\\&-\sum_s\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty\left(h_{sr}+\frac{\kappa}{2}\frac{\partial h_{sr}}{\partial\kappa}\right)\cdot 2\pi R_{sr}^2dR_{sr}-\left[\frac{1}{12\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{1}{32}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_0^2\\&+\frac{8}{45}\pi^5\frac{k^3T^3}{h^3c^3}\frac{V_0}{N_0}\Big\}+\Delta\frac{PV}{RT},\end{aligned} \qquad \text{(A2.1)}$$

with

$$\frac{\Delta PV}{RT}=\frac{V}{V_0}\left[\frac{(B-B_0)}{V_0}(\sum C_s)^2+\frac{(C-C_0)}{V_0^2}(\sum C_s)^3+\frac{(D-D_0)}{V_0^3}(\sum C_s)^4+\dots\right].$$

The dependence of the dielectric constant D on the gas density using the Clausius-Mosotti relation provides as a further contribution[2] to PV/RT, the quantity

$$-\frac{(D+2)(D-1)}{D}\left(\frac{\delta E}{RT}\right)_{\text{ionic}},$$

where $(\delta E/RT)_{\text{ionic}}$ includes the ordinary ionic terms in eq (A2.2), i. e., the limiting law Debye-Hückel term and the Mayer-Poirier terms for which the dependence on D is of the same form as for T.

$$\begin{aligned}\frac{E}{RT}=\frac{V}{V_0}\Bigg\{&\sum C_s\left(\frac{E^0}{RT}\right)_s-\frac{\pi^{1/2}(\sum Z_s^2C_s)^{3/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}\\&-\frac{1}{2(\sum Z_s^2C_s)}\sum_s\sum_r\sum_{\nu=\nu_{sr}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}[\nu b_\nu(\varphi_{sr})+(\nu-2)g_\nu(\varphi_{sr})]\\&+\sum_s\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty\frac{Tdh_{sr}}{dT}\cdot 2\pi R_{sr}^2dR_{sr}-\left[\frac{1}{6\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{3}{64}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_0^2\\&+\frac{8}{15}\pi^5\frac{k^3T^3}{h^3c^3}\frac{V_0}{N_0}\Bigg\}+\frac{\Delta E}{RT},\end{aligned}\qquad\text{(A2.2)}$$

with

$$\begin{aligned}\frac{\Delta E}{RT}=-\frac{V}{V_0}\Bigg[&\frac{T(dB/dT-dB_0/dT)}{V_0}(\sum C_s)^2+\frac{T(dC/dT-dC_0/dT)}{2V_0^2}(\sum C_s)^3\\&+\frac{T(dD/dT-dD_0/dT)}{3V_0^3}(\sum C_s)^4+\dots\Bigg].\end{aligned}$$

$$\begin{aligned}\frac{H}{RT}=\frac{V}{V_0}\Bigg\{&\sum C_s\left(\frac{H^0}{RT}\right)_s-\frac{4}{3}\frac{\pi^{1/2}(\sum Z_s^2C_s)^{3/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}\\&-\frac{1}{2(\sum Z_s^2C_s)}\sum_s\sum_r\sum_{\nu=\nu_{sr}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}[(1+\nu)b_\nu(\varphi_{sr})-(3-\nu)g_\nu(\varphi_{sr})]\\&+\sum_s\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty\left(T\frac{dh_{sr}}{dT}-\frac{\kappa}{2}\frac{\partial h_{sr}}{\partial\kappa}-h_{sr}\right)\cdot 2\pi R_{sr}^2dR_{sr}-\left[\frac{1}{4\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{5}{64}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_0^2\\&+\frac{32}{45}\pi^5\frac{k^3T^3}{h^3c^3}\frac{V_0}{N_0}\Bigg\}+\frac{\Delta H}{RT},\end{aligned}\qquad\text{(A2.3)}$$

with

$$\begin{aligned}\frac{\Delta H}{RT}=\frac{V}{V_0}\Bigg\{&\frac{B-B_0-T(dB/dT-dB_0/dT)}{V_0}(\sum C_s)^2\\&+\frac{2(C-C_0)-T(dC/dT-dC_0/dT)}{2V_0^2}(\sum C_s)^3+\frac{3(D-D_0)-T(dD/dT-dD_0/dT)}{3V_0^3}(\sum C_s)^4\dots\Bigg\}\end{aligned}$$

$$\begin{aligned}\frac{S}{R}=\frac{V}{V_0}\Bigg\{&\sum C_s\left[\left(\frac{S_0}{R}\right)_s-\ln C_s-\ln\frac{T}{T_0}\right]-\frac{1}{3}\frac{\pi^{1/2}(\sum Z_s^2C_s)^{3/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}\\&+\frac{1}{2(\sum Z_s^2C_s)}\sum_s\sum_r\sum_{\nu=\nu_{sr}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}[(1-\nu)b_\nu(\varphi_{sr})+(3-\nu)g_\nu(\varphi_{sr})\\&+\sum\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty\left(T\frac{dh_{sr}}{dT}+h_{sr}\right)2\pi R_{sr}^2dR_{sr}-\left[\frac{1}{12\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{1}{64}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_0^2\\&+\frac{32}{45}\pi^5\frac{k^3T^3}{h^3c^3}\frac{V_0}{N_0}\Bigg\}+\frac{\Delta S}{R},\end{aligned}\qquad\text{(A2.4)}$$

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[2] The approximate contribution to PV/RT due to the effect of the dielectric constant should apply also to the closely related H/RT and F/RT of (A2.3) and (A2.5). E/RT and H/RT are also subject to a small contribution not given here due to the dependence of specific polarizabilities on the temperature. This will also affect C_v/R of eq (A2.6).

with

$$\frac{\Delta S}{R}=-\frac{V}{V_0}\left\{\frac{(d/dT)[T(B-B_0)]}{V_0}\left(\sum C_s\right)^2+\frac{(d/dT)[T(C-C_0)]}{2V_0^2}\left(\sum C_s\right)^3+\frac{(d/dT)[T(D-D_0)]}{3V_0^3}\left(\sum C_s\right)^4\right.$$

$$\left.+\cdots\right\},\ -\frac{F}{RT}=\frac{V}{V_0}\left\{\sum C_s\left[\left(-\frac{F^0}{RT}\right)_s-\ln C_s-\ln T/T_0\right]+\frac{\pi^{1/2}\left(\sum Z_s^2C_s\right)^{3/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}\right.$$

$$+\frac{1}{\left(\sum Z_s^2C_s\right)}\sum_s\sum_r\sum_{\nu=\nu_{sr}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}b_\nu(\varphi_{sr})+\sum_s\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty\left(2h_{sr}+\frac{\kappa}{2}\frac{\partial h_{sr}}{\partial\kappa}\right)$$

$$\left.\cdot 2\pi R_{sr}^2dR_{sr}+\left[\frac{1}{6\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{1}{16}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_0^2\right\}+\Delta\left(-\frac{F}{RT}\right), \tag{A2.5}$$

where

$$\Delta\left(-\frac{F}{RT}\right)=-\frac{V}{V_0}\left\{2\frac{(B-B_0)}{V_0}\left(\sum C_s\right)^2+\frac{3}{2}\frac{(C-C_0)}{V_0^2}\left(\sum C_s\right)^3+\frac{4}{3}\frac{(D-D_0)}{V_0^3}\left(\sum C_s\right)^4+\ldots\right\}.$$

$$\frac{C_v}{R}=\frac{V}{V_0}\left\{\sum C_s\left(\frac{C_v^0}{R}\right)_s+\sum C_s\frac{d\ln C_s}{d\ln T}\left(\frac{E^0}{RT}\right)_s+\frac{1}{2}\frac{\pi^{1/2}\left(\sum Z_s^2C_s\right)^{3/2}\epsilon^3}{(DkT)^{3/2}}\left(\frac{N_0}{V_0}\right)^{1/2}\right.$$

$$-\frac{3}{2}\frac{\pi^{1/2}\left(\sum Z_s^2C_s\right)^{1/2}\epsilon^3}{(DkT)^{3/2}}\left(\sum Z_s^2C_s\frac{d\ln C_s}{d\ln T}\right)\left(\frac{N_0}{V_0}\right)^{1/2}+\frac{1}{2\left(\sum Z_s^2C_s\right)}\sum_s\sum_r\sum_{\nu=\nu_{sr}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}[\nu^2b_\nu(\varphi_{sr})$$

$$+(\nu-1)(\nu-3)g_\nu(\varphi_{sr})+h_\nu(\varphi_{sr})]+\frac{1}{2\left(\sum Z_s^2C_s\right)^2}\sum_s\sum_r\sum_{\nu=\nu_{sr}^0}(-1)^\nu C_sC_rZ_s^\nu Z_r^\nu\alpha_{sr}^{1-\nu}\left[\sum Z_{s'}^2C_{s'}\frac{d\ln C_{s'}}{d\ln T}\right.$$

$$\left.-\frac{2d\ln C_r}{d\ln T}\left(\sum Z_{s'}^2C_{s'}\right)\right]\cdot[\nu b_\nu(\varphi_{sr})+(\nu-2)g_\nu(\varphi_{sr})]+\sum_s\sum_r C_sC_r\frac{N_0}{V_0}\int_0^\infty\left[2T\frac{dh_{sr}}{dT}\left(1+\frac{d\ln C_s}{d\ln T}\right)\right.$$

$$\left.\left.+\frac{T^2d^2h_{sr}}{dT^2}\right]2\pi R_{sr}^2dR_{sr}+\left[\frac{1}{6\pi}\frac{h^2\epsilon^2}{mk^2T^2}\frac{N_0}{V_0}-\frac{3}{128}\left(\frac{h^2}{\pi mkT}\right)^{3/2}\frac{N_0}{V_0}\right]C_0^2+\frac{32}{15}\pi^5\frac{k^3T^3}{h^3c^3}\frac{V_0}{N_0}\right\}+\Delta\frac{C_v}{R}, \tag{A2.6}$$

with

$$\Delta\frac{C_v}{R}=-\frac{V}{V_0}\frac{d}{dT}\left\{\frac{T^2}{V_0}\frac{d(B-B_0)}{dT}\left(\sum C_s\right)^2+\frac{T^2}{2V_0^2}\frac{d(C-C_0)}{dT}\left(\sum C_s\right)^3+\frac{T^2}{3V_0^3}\frac{d(D-D_0)}{dT}\left(\sum C_s\right)^4+\cdots\right\}.$$

For such ion interactions as are taken to have identical radii α_{sr}, the factors $\sum_s\sum_r C_sC_rZ_s^\nu Z_r^\nu$ in (3.1) and (A2.1) to (A2.6) can be grouped together as $\left(\sum_s C_sZ_s^\nu\right)\left(\sum_r C_rZ_r^\nu\right)$, reducing further to the form used by Poirier if all are identical.

5.3. Appendix 3

Functions relevant to the Coulombic interaction in the close approach region for ions of like sign include a contribution to $-A/RT$ due to h_{sr} given by

$$\frac{V}{V_0}\frac{2\pi}{3}\frac{N_0}{V_0}\sum_s\sum_r C_sC_r a_{sr}^3\sum_{n=0}q_n(x_{sr})\varphi_{sr}^n, \tag{A3.1}$$

with

$$x_{sr}=Z_sZ_r/\alpha_{sr},$$

where

$$q_0(x)=\left(1-\frac{1}{2}x+\frac{1}{2}x^2\right)e^{-x}+\frac{1}{2}x^3\,\mathrm{Ei}\,(-x),$$

$$q_1(x)=xq_0(x),$$

$$q_2(x)=-\frac{3}{8}xe^{-x}+\frac{5}{8}x^2q_0(x),$$

$$q_3(x)=\frac{1}{10}(x-4x^2)e^{-x}+\frac{3}{10}x^3q_0(x),$$

$$q_4(x)=-\frac{1}{48}\left(x-\frac{43}{5}x^2+\frac{223}{20}x^3\right)e^{-x}+\frac{343}{2880}x^4q_0(x),$$

$$q_5(x)=\frac{1}{280}\left(x-\frac{53}{3}x^2+\frac{578}{15}x^3-\frac{407}{15}x^4\right)e^{-x}+\frac{64}{1575}x^5q_0(x),$$

$$q_6(x)=-\frac{1}{1920}\left(x-\frac{249}{7}x^2+\frac{1763}{14}x^3-\frac{9043}{70}x^4+\frac{17443}{280}x^5\right)e^{-x}+\frac{2187}{179200}x^6q_0(x).$$

The related contribution to PV/RT is

$$-\left(\frac{V}{V_0}\right)\cdot\frac{2\pi}{3}\frac{N_0}{V_0}\sum_s\sum_r C_sC_ra_{sr}^3\sum_{n=0}\left(1+\frac{n}{2}\right)q_n(x_{sr})\varphi_{sr}^n. \tag{A3.2}$$

A similar contribution to E/RT is given by

$$\left(\frac{V}{V_0}\right)\frac{2\pi}{3}\frac{N_0}{V_0}\sum_s\sum_r C_sC_ra_{sr}^3\sum_{n=0}e_n(x_{sr})\varphi_{sr}^n, \tag{A3.3}$$

with

$$e_n(x_{sr})=-\frac{n}{2}q_n(x_{sr})-x_{sr}\frac{d}{dx_{sr}}q_n(x_{sr}),$$

giving

$$e_0=-3q_0+3e^{-x},$$

$$e_1=-\frac{9}{2}xq_0+3xe^{-x},$$

$$e_2=-\frac{15}{4}x^2q_0+\left(\frac{3}{4}x+\frac{3}{2}x^2\right)e^{-x},$$

$$e_3=-\frac{9}{4}x^3q_0-\left(\frac{1}{4}x-\frac{3}{2}x^2-\frac{1}{2}x^3\right)e^{-x},$$

$$e_4=-\frac{343}{320}x^4q_0+\left(\frac{1}{16}x-\frac{59}{80}x^2+\frac{429}{320}x^3+\frac{1}{8}x^4\right)e^{-x},$$

$$e_5=-\frac{224}{525}x^5q_0-\left(\frac{1}{80}x-\frac{23}{80}x^2+\frac{41}{50}x^3-\frac{307}{400}x^4-\frac{1}{40}x^5\right)e^{-x},$$

$$e_6=-\frac{6561}{44800}x^6q_0+\left(\frac{1}{480}x-\frac{313}{3360}x^2+\frac{923}{2240}x^3-\frac{18029}{33600}x^4+\frac{14643}{44800}x^5+\frac{1}{240}x^6\right)e^{-x}.$$

The contribution to H/RT is given by

$$\left(\frac{V}{V_0}\right)\frac{2\pi}{3}\frac{N_0}{V_0}\sum_s\sum_r C_sC_ra_{sr}^3\sum_{n=0}h_n(x_{sr})\varphi_{sr}^n, \tag{A3.4}$$

with

$$h_n(x_{sr})=e_n(x_{sr})-\left(1+\frac{n}{2}\right)q_n(x_{sr}),$$

or

$$h_0=-4q_0+e^{-x},$$

$$h_1=-6xq_0+3xe^{-x},$$

$$h_2=-5x^2q_0+\left(\frac{3}{2}x+\frac{3}{2}x^2\right)e^{-x},$$

$$h_3=-3x^3q_0-\left(\frac{1}{2}x-\frac{5}{2}x^2-\frac{1}{2}x^3\right)e^{-x},$$

$$h_4=-\frac{343}{240}x^4q_0+\left(\frac{1}{8}x-\frac{51}{40}x^2+\frac{163}{80}x^3+\frac{1}{8}x^4\right)e^{-x}.$$

The contribution to S/R is

$$\left(\frac{V}{V_0}\right)\frac{2\pi}{3}\frac{N_0}{V_0}\sum_s\sum_r C_sC_ra_{sr}^3\sum s_n(x_{sr})\varphi_{sr}^n, \tag{A3.5}$$

with

$$s_n=q_n+e_n,$$

or

$$s_0=-2q_0+3e^{-x},$$

$$s_1=-\frac{7}{2}xq_0+3xe^{-x},$$

$$s_2=-\frac{25}{8}x^2q_0+\left(\frac{3}{8}x+\frac{3}{2}x^2\right)e^{-x},$$

$$s_3=-\frac{39}{20}x^3q_0-\left(\frac{3}{20}x-\frac{11}{10}x^2-\frac{1}{2}x^3\right)e^{-x},$$

$$s_4=-\frac{343}{360}x^4q_0+\left(\frac{1}{24}x-\frac{67}{120}x^2+\frac{133}{120}x^3+\frac{1}{8}x^4\right)e^{-x}.$$

The contribution to $-F/RT$ is

$$\left(\frac{V}{V_0}\right)\frac{2\pi}{3}\frac{N_0}{V_0}\sum_s\sum_r C_sC_ra_{sr}^3\sum_{n=0}\left(\frac{n+4}{2}\right)q_n(x_{sr})\varphi_{sr}^n. \tag{A3.6}$$

The contribution of this kind to C_v/R is

$$\left(\frac{V}{V_0}\right)\frac{2\pi}{3}\frac{N_0}{V_0}\sum_s\sum_r C_sC_ra_{sr}^3\left\{\sum_n\left[\left(1-\frac{n}{2}\right)-\frac{n}{2}\left(\frac{d\ln D}{d\ln T}\right)_V+2\left(\frac{d\ln C_s}{d\ln T}\right)_V\right.\right.$$
$$\left.\left.+\frac{n}{2}\sum Z_{s'}^2C_{s'}\left(\frac{d\ln C_{s'}}{d\ln T}\right)_V\right]e_n(x_{sr})\varphi_{sr}^n-\sum_n\left[1+\left(\frac{d\ln D}{d\ln T}\right)_V\right]\left(x_{sr}\frac{de_n}{dx_{sr}}(x_{sr})\right)\varphi_{sr}^n\right\} \tag{A3.7}$$

with the e_n as given above, and with xde_n/dx obtainable by differentiation, giving relations such as

$$xde_0/dx = -9q_0 + (9-3x)e^{-x},$$

$$xde_1/dx = -18xq_0 + \left(\frac{33}{2}x - 3x^2\right)e^{-x},$$

$$xde_2/dx = -\frac{75}{4}x^2q_0 + \left(\frac{3}{4}x + \frac{27}{2}x^2 - \frac{3}{2}x^3\right)e^{-x},$$

$$xde_3/dx = -\frac{27}{2}x^3q_0 - \left(\frac{1}{4}x - \frac{13}{4}x^2 - \frac{27}{4}x^3 + \frac{1}{2}x^4\right)e^{-x},$$

$$xde_4/dx = -\frac{343}{20}x^4q_0 + \left(\frac{1}{16}x - \frac{123}{80}x^2 + \frac{1523}{320}x^3 + \frac{19}{8}x^4 - \frac{1}{8}x^5\right)e^{-x}.$$

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