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THE CALCULATION OF THERMODYNAMIC PROPERTIES OF GASES AT HIGH TEMPERATURES

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FOREWORD

The thermodynamic properties of gases at high temperatures have been of increasing general interest in recent years. With higher temperature, gases become more completely ionized and require theoretical treatment different from that which is adequate at more moderate temperatures. The present objective is to fulfill that requirement and thereby aid various practical calculations for which there is a great need.

Acknowledgement is made of the assistance furnished by Guy G. Ziegler of the Applied Mathematics Division for the coding and performance of the second virial coefficient calculation for the 12, 6, 4 potential for chapters 6 and 8.

Finally, it is desired to thank Mrs. Hattie N. Brown for typing the text in its final form.

ABSTRACT

The calculation of thermodynamic properties of gases at high temperature using ion solution theory is analyzed in regard to various details. Earlier work based on rigid sphere ions is enlarged on briefly. An extension to a more general case of realistic pair interactions is also obtained. With Debye screened ionic interactions, a study is made of effects of repulsions and both continuum and bound states for ionic attractions; simple approximate representations of the interaction effects for the two free particle interaction cases are given. For the bound states, the finite number of states available for occupancy as a result of Debye screening is explicitly indicated, and a numerical method to adjust from an arbitrary state sum to the "Debye screened" sum is explained. An extensive compensation between bound states just below the continuum and a partial state paucity within the continuum are also noted. Other details considered include the estimation of the dielectric constant up into the region of high density and high temperature, the semi-empirical estimation of nonbonding pair interactions involving neutral and ionized species, and corresponding virial-type exclusion effects. A table of second virials for constituents of air up to 20,000 ° K is included.

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for JOHN J. DISHUCK
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THE CALCULATION OF THERMODYNAMIC PROPERTIES OF GASES AT HIGH TEMPERATURES

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SUMMARY

High temperature gas properties are important in stellar problems and also for man-made processes of high intrinsic energy.

We cannot observe the deep interiors of stars, nor even their immediate sub-surface layers. Our knowledge here depends on indirect inference, based on accepted rules of behavior of matter, fields and radiation.

Even for man-made processes of rapid release of intense energy, direct observational evidence of the temperature field produced may be difficult to obtain. There is then a need for a broad phenomenological description which will include details of local conditions as parametric functions incidental to the prediction of quantities correlating with actual observables.

A genuinely high degree of success in the accurate description of high temperature properties should go even further. When predictions of behavior proceed directly with engineering-type reliability, there can be a favored option of choice of the economy of theoretical calculations as compared with the expense of cut-and-try experimentation. This well-established engineering concept must be expected to have application in new fields of endeavor, quite apart from any difficult questions of gauging what the actual costs of such experimentation may be.

The present collection of discussions of various topics is intended to contribute to the practical solution of some of the problems which occur in the calculation of thermodynamic properties of gases at high temperatures. It presents various considerations that have arisen in a re-examination and extension of an earlier study of these properties at such high temperatures that ionic solution theory should be used. Some of the earlier work along this line at the National Bureau of Standards has appeared in report form(1) and in a research paper(2) and in some other papers(3,4) of varying degrees of close connection with the present study.

In the earlier work related to this project, as reported in the first two publications here referred to(1,2), a procedure of calculation was put forward which was somewhat arbitrarily chosen with the objective of a particular type of simplicity. In order to employ the familiar technique of the theoretical chemists in the use of tables of thermodynamic functions for single constituents as components of the general mixture, it was desired to have so-called ideal gas functions that depend on the single variable, temperature. If the properties of the constituent are actually dependent on the state of the mixture as a whole, one must find a way to carry these adjustments separately from the chosen fundamental main tables of properties of the single constituents. As a result of the re-summing innovation of Mayer(5) and numerical work by Poirier(6), there was a table of ion solution properties available, primarily arranged for application to liquid solutions for which Debye-Hückel theory had had a very extensive application. Our ideal-gas functions which were arranged shortly thereafter for use with Mayer's ion solution theory were tailored to the Poirier tables for the expected convenience which that might give. This means, among other details, that the internal state sum was abridged to remove the classical phase space contribution outside of a chosen rigid sphere size (which was taken with the collision distance $a = 8a_0$) but that the state sum was also extended classically upward in energy throughout the continuum within the same rigid sphere.

Except for some very scant desk calculator computations by the writer and a few others, very little actual use of the Poirier tables in this connection has occurred in our calculations. Lack of urgent interest supporting such calculations and complexities of arranging items of the programming may be among the principal reasons for this neglect.

Indeed, it could be claimed that the results of such calculations as may have been made should have had at least a good measure of validity for over-all thermodynamic properties, since the various immediately relevant regions of phase space were included in one form or another. Nevertheless, it developed that there were some reasons for re-examining the calculation methods. An important consideration in this regard came from the realization that the tables had had extensive use as a basis for estimation of positive ion and electron concentrations. However, it is just here that it is most desired that occupancy of each and every state of a bound system for a given constituent should contribute to the count of members of that particular constituent, while the regions of phase space that do not at all involve states of the particular bound system may best have their thermodynamic effect brought in in some other way. Thus, it is primarily the general interest in concentrations of actual constituents, including free electrons, that suggests that a revision should be made in the calculation method.

It is naturally of interest and generally desirable that proper tables be available to help in making good estimates for the concentration of systems of particular stages of ionization. It is only then that good estimates would be expected as to the response to either a static electric field or to the impelling action due to relative motion across a magnetic field.

While it would be wished that the new formulation of methods of calculation would result in fulfilling the needs for the determination of species concentration in all relevant fields, any such hope must be recognized to be far too optimistic for actual realization. Many of the problems actually occurring in practice do not refer at all to local thermodynamic equilibrium. Some circumstances may be concerned with moderate departures from equilibrium such that equilibrium properties can be considered to be meaningful at least for comparison. Other situations involve ionized gases that are very far from such conditions. Our present efforts to improve the thermodynamic function treatment for ionized gases are naturally quite irrelevant for extreme non-equilibrium applications.

Reiterating that the intended principal application is to equilibrium thermodynamic properties, we would indicate that our approach should be particularly appropriate in extending calculations to higher densities and higher temperatures throughout the region in which a gas is appreciably yet not totally ionized. Actual limits on the validity of the proposed treatment may be hard to predict. Contributions that depend on empirical correlations have uncertainties which must reflect the quality of agreement with actuality. Comparison with calculations by astrophysical methods in extreme regions of high density and temperature could perhaps suggest that various known small correction terms could readily be combined with the present formulas to give a more extended range of application.

A short preview of our present approach may be helpful at this point. Our study begins with a consideration of a simple ionic assembly in that idealized condition of quasi-internal screening which is used in Debye-Hückel solution theory. From one point of view, this could be considered to recognize the propriety of diagram calculations of modern theory, since Mayer re-derived the Debye-Huckel limiting law by a re-summing over closed loop diagrams. However, we would also recall that of all possible power law interparticle potentials, the Coulomb 1/R potential is uniquely the one for which the divergence of the gradient is zero everywhere except at the $R = 0$ singular point. Out of this comes the capability of defining a single general electrical potential and of studying its local variations according to (1) the rules of statistical mechanics for occupancy of states and (2) the electrical requirements as specified by Poisson's equation. We do not proceed to a full solution of this special quantum mechanical problem of the full assembly here. Detailed consideration of some of its aspects have been considered by Plock(7) with Kirkwood and also by Brittin(8). Without the effort to include all possible small quantum effects, we still may hope to come to a very adequate treatment with the help of classical Debye-Hückel theory.

We note that in the range of low ion concentrations, the Mayer-Poirier treatment has been represented by Haga(9) in a series expansion approximation which is here quoted in some detail with minor corrections. This could be useful for calculations using the previously calculated thermodynamic functions of reference 1. Also in Chapter 1, pursuant to our present approach, we have tabulated the rearranged pair contributions for Coulomb repulsions with Debye screening. For this, the close approach contributions ($r < a$) are given analytically in reference 2, while for larger distances ($r > a$) the contributions are obtained mainly with the help of the Poirier tables as indicated in the same reference. Each of these combined repulsive pair contributions is proportional to a single function of a single variable involving temperature, the product of ionic charges for the pair, and the Debye screening parameter κ — or its inverse, the Debye length. Thus, the resulting functions no longer involve the $a = 8a_0$ radius which according to reference 2 entered into the computation of their arbitrarily divided parts. In application of the tabulated functions to an actual ionic mixture, one will wish to find a net contribution obtained by summing over all major repulsive pairs in the assembly. Each of these repulsive pair contributions is in principle capable of further adjustment - cf. Chapter 7 - to include the effects of short range repulsions that may apply at very close approach between positive ions. We note that the principal negative ions are the electrons, whose attractive interaction with the positive ions is the primal basis for the internal partition function for that pair as a single combined system.

As to the remaining topics here discussed, Chapter 2 treats the estimation of the dielectric constant for a medium at elevated densities, an item particularly relevant in applying ion solution theory to partially ionized dense fluids.

Chapter 3 examines some considerations affecting the choice of form of the potential energy function for short range repulsive potentials, a point resolved in favor of making provisional present estimates on the basis of the commonly used $1/R^{12}$ form.

In Chapter 4, actual estimates are arrived at for hypothetical non-bonding interactions between ground state atom and atomic ion fragments predicted to be appreciably present in air at somewhat elevated temperatures. These are based on a combined extension of Kihara diatomic core models to include heterogeneous pairs, with the pragmatic assumptions of additivity and permanence of intermolecular atom-atom interactions and the acceptance, with minor extensions, of the ordinary simple combination rules for interaction parameters.

In Chapter 5, we present formulas by which the second virial coefficient may be calculated for general polyreciprocal potentials, or generalizations beyond the Lennard-Jones form to include more than two potential terms.

In Chapter 6, the formulas of Chapter 5 are specialized to the case of a 12, 6, 4 potential to treat the ion-neutral interactions. A computed table covering the corresponding second virial coefficient and its first two derivatives ranging from the 12, 6 case to the 12, 4 case is included.

Chapter 7 presents tables for the small high-temperature second virial effect of a short range $1/R^{12}$ repulsion potential when added to a Coulomb $1/R$ type repulsion. Parameters for the effect are given for twelve positive ion pairs of moderately thermally ionized air when the $1/R$

potential is not diminished by a dielectric constant of more than unity. These are the pairs for which potential estimates are shown graphically in Chapter 4.

Second virial coefficient tables for specific pairs in high temperature air are given in Chapter 8.

General considerations pertaining to the application of these various segments of the treatment and plausible approximations for its extrapolation to higher densities are principal topics for a concluding discussion.

1. CONSIDERATIONS ON THE APPLICATION OF IONIC SOLUTION THEORY TO HIGH TEMPERATURE GASES

The thermodynamic properties of matter at high temperatures involve the effects of interactions among its mobile constituent systems, with this term referring to molecules and atoms and their ions, the free elementary particles, and, by extension, even the quanta of radiation. In its simplest form, it is a many-body problem that must be dealt with. Even if the interactions between separate molecule-like systems are well approximated as the sum of single pair potentials, there are very complicated effects of such a nature as would usually be associated with higher virial coefficients.

A currently popular theoretical approach to multi-neighbor effects in such a many-body problem involves attempts at the summation of diagrams as a solution method. We note that the important neighbors in an assembly may quite usually be nearest neighbors, but if the assembly is a gas at high temperature, there must be some extent of ionization. In that case, there are important ionic forces of a long range type, so that interparticle effects between more remote neighbors become important.

The present discussion is not for the purpose of suggesting that diagram techniques or their formal equivalents be avoided altogether. However, it does present some items related to a temporary expedient to furnish provisional estimates without theoretical study of elaborate diagrams. The principal justification for attempting such approximations may be the directness and basic simplicity of the approach.

We will make use of the well-known results of Mayer(5), who summed ring graphs for the long range Coulombic interaction effects and obtained the Debye-Hückel limiting law term. He also included the pair-wise short-range pair potentials using a quasi- second-virial type expression in which the Coulombic long range potential is in effect replaced by a Debye-screened Coulombic form.

For low or moderate concentrations of ionic constituents, Mayer's results for an assembly of rigid sphere ions in a solution can be represented in an analytic series approximation such as that given by Haga(9), carried to the 5th power of the Debye parameter κ. We shall give such a form presently for possible convenience of use. Poirier(6) has presented the results of Mayer in fuller detail by means of extensive tables.

An indication has been given elsewhere(10) as to a plausible approach toward the empirical estimation of higher virial effects by consideration of simple approximate theory and analogy with observational evidence for somewhat similar systems. It involves the inference of the magnitude of effective rigid sphere sizes or effective pair exclusion volumes taken as functions of temperature. Since this proposed exclusion volume is based on that part of a second virial coefficient that is contributed by a pair potential in its close approach or positive energy region, it is natural for the repulsion potentials to be of particular special interest. One of the topics to be given early consideration will be the pair-wise effects due to Debye screened Coulomb repulsion, which represents approximately the interactions between positive ions. Pair-wise effects arising from Debye screened Coulomb attractions will also be considered in some detail.

1. A Series Expansion

The series expansion representing Mayer's results up through the fifth power of ϕ or κa can be given in a previously used notation(2) but based on a single collision radius a as accepted by both Haga(9) and Poirier(6), in the form

$$
\begin{aligned}
-A/RT = (V/V_0)\Bigg\{\Bigg[& \sum_s C_s[(-A^\circ/RT)_s - \ln C_s - \ln T/T_0] - b(\sum C_s)^2 + b^{-1}\Bigg[\frac{\phi^3}{18} - \frac{\phi^4}{24} + \frac{\phi^5}{24} \\
& + \frac{1}{72}\phi^4 \alpha^{-1}(Z^{(1)})^2[1.675828 + \ln\phi - 3\phi] + \frac{1}{72}\phi^5 \alpha^{-2}(Z^{(2)})^2[0.963510 + \ln\phi] \\
& + \frac{1}{12}\phi^4 \sum_{\nu=4}^{\infty} \frac{(-1)^\nu \alpha^{2-\nu}}{\nu!(\nu-3)} (Z^{(\nu-2)})^2 + \frac{1}{12}\phi^5 \sum_{\nu=4}^{\infty} \frac{(-1)^\nu \alpha^{1-\nu}}{\nu!(\nu-3)} (Z^{(\nu-1)})^2 \Bigg]\Bigg\}. \qquad (1)
\end{aligned}
$$

The notation here includes $b = \frac{2\pi}{3}\frac{N_0 a^3}{V_0}$, which is a rigid sphere second virial in amagat units, and $Z^{(n)} = (\sum Z_s^{n+2} C_s)/(\sum Z_s^2 C_s)$. Other details of the notation include $\alpha = aDkT/\epsilon^2$, with D as dielectric constant, and $\kappa^2 = 4\pi\epsilon^2(N_0/V_0)(\sum Z_s^2 C_s)/DkT$. The numerical constants appearing in these expressions include $\gamma + \ln 3 = 0.577216.. + 1.098612.. = 1.675828..$ and $\gamma + \ln 4 - 1 = 0.577216 + 1.386294.. - 1 = 0.963510..$, where γ is Euler's constant.

Related functions obtainable by differentiation include

$$E/RT = (V/V_o)\left\{\sum_s C_s (E^o/RT) - b^{-1}\left[\frac{\phi^3}{12} - \frac{\phi^4}{12} + \frac{5\phi^5}{48} + \frac{1}{36}\phi^4 a^{-1}(Z^{(1)})^2 [1.925828.. + \ln\phi - \tfrac{15}{4}\phi] \right.\right.$$
$$+ \frac{5}{144}\phi^5 a^{-2}(Z^{(2)})^2 [1.163510 + \ln\phi] + \frac{1}{6}\phi^4 \sum_{\nu=4}^{\infty} \frac{(-1)^\nu a^{2-\nu}}{\nu!(\nu-3)} (Z^{(\nu-2)})^2$$
$$\left.\left. + \frac{5}{24}\phi^5 \sum_{\nu=4}^{\infty} \frac{(-1)^\nu a^{1-\nu}}{\nu!(\nu-3)} (Z^{(\nu-1)})^2 \right]\right\} \tag{2}$$

and

$$PV/RT = (V/V_o)\left\{\sum C_s + b(\sum C_s)^2 - b^{-1}\left[\frac{\phi^3}{36} - \frac{\phi^4}{24} + \frac{\phi^5}{16} + \frac{1}{72}\phi^4 a^{-1}(Z^{(1)})^2 [2.175828 + \ln\phi - \tfrac{9}{2}\phi] \right.\right.$$
$$+ \frac{1}{48}\phi^5 a^{-2}(Z^{(2)})^2 [1.296843 + \ln\phi] + \frac{1}{12}\phi^4 \sum_{\nu=4}^{\infty} \frac{(-1)^\nu a^{2-\nu}}{\nu!(\nu-3)} (Z^{(\nu-2)})^2$$
$$\left.\left. + \frac{1}{8}\phi^5 \sum_{\nu=4}^{\infty} \frac{(-1)^\nu a^{1-\nu}}{\nu!(\nu-3)} (Z^{(\nu-1)})^2 \right]\right\} \tag{3}$$

There is a further contribution to $PV/RT = V[\partial(-A/RT)/\partial V]_{T,\,N_i}$ arising from the dependence of the dielectric constant on the density. Since in the present approximation the dielectric constant D occurs in the ionic terms only and there D and T occur only in the product DkT, one finds that the additional contribution is

$$\frac{V}{D}\frac{dD}{dV} \cdot D\frac{\partial}{\partial D}(-\delta A/RT)_{\text{ionic}} = \frac{V}{D}\frac{dD}{dV} \cdot T\frac{\partial}{\partial T}(-\delta A/RT)_{\text{ionic}}$$

or

$$\delta\frac{PV}{RT} = \frac{V}{D}\frac{dD}{dV}\left(\frac{\delta E}{RT}\right)_{\text{ionic}} . \tag{4}$$

The Clausius-Mosotti relation

$$\frac{4\pi}{3}\frac{N}{V}\chi = \frac{D-1}{D+2}$$

then leads to

$$\delta\frac{PV}{RT} = -\frac{(D+2)(D-1)}{3D}\left(\frac{\delta E}{RT}\right)_{\text{ionic}}$$

from which the 3 was inadvertently omitted in RP 2916(2). However, a preferable formula, arising from the work of Onsager(11) and discussed in the next chapter,

$$\frac{4\pi}{3}\frac{N}{V}\chi = \frac{(D-1)(2D+1)}{9D}$$

produces a simpler expression,

$$\frac{PV}{RT} = -(D-1)\left(\frac{\delta_E}{RT}\right)_{\text{ionic}} , \tag{5}$$

which should be more acceptable.

As has already been indicated, these series expansions may be considered as patterned after Haga$^{(9)}$ though with a minor adjustment in his S_2 results affecting the first ϕ^5 term by a factor of 2. It may be noted also that within the order of terms covered, Haga obtained two additional ϕ^5 contributions which do not conform as contributions to an effective second virial form, but which are identically zero due to net charge neutrality if only singly charged ions are present. This points to the complexity which must be expected when more complicated diagrams are included.

It may be worthwhile to make a few additional comments about the present Haga-type expansions. The leading ionic term, which is $b^{-1}\phi^3/18$ in the case of the free energy function, may be recognized as the usual limiting law Debye-Hückel term. We may also note that the quantity b enters into the expressions in just two ways — directly as a factor due to rigid sphere exclusion volume for one term, and otherwise purely as a reciprocal factor multiplying all of the ionic contribution terms. This reversed role of the b apparently arises merely as a peculiarity of notation. It is of interest to note the behavior of these contributions as the collision radius a is varied. In particular, the effect of letting a approach zero may deserve clarification. The nature of the dependence may be more readily evident from the series expansion than in any other way. Since both ϕ and α contain a as a factor, the early terms of the ϕ expansion are well behaved in remaining constant or going to zero. Thus, terms that remain essentially constant include those in $b^{-1}\phi^3$, $b^{-1}\phi^4\alpha^{-1}$, and $b^{-1}\phi^5\alpha^{-2}$. The last two terms of the Haga expressions, involving here $b^{-1}\phi^4\alpha^{2-\nu}$ and $b^{-1}\phi^5\alpha^{1-\nu}$ for $\nu \geq 4$, become infinite as a goes to zero. There can thus be a genuine problem of selecting a most suitable a if the functions are to be used directly in a Mayer-type treatment.

2. Analysis of Phase Space Effects with Debye Screening

As a foundation for a treatment of some generality, a review of some fundamental details about pair effects in the ionic assembly should be appropriate. It may be noted first that the measure of local density of quantum states in general is given semi-classically apart from spin by

$$\prod_i (h^{-1}\, dp_i\, dq_i) \tag{6}$$

in terms of momenta p_i and coordinates q_i. In a simple binary encounter, in a case of dependence on distance of separation only and with spin weights included, there is a local number of states within the pair system

$$dN = \frac{(2s_i + 1)(2s_j + 1)}{h^3} \cdot 4\pi P^2\, dP \cdot 4\pi r^2 dr, \tag{7}$$

where $P^2 = p_x^2 + p_y^2 + p_z^2$, with $p_x = \mu\dot{x}$, etc., and where $\mu = \mu_{ij} = m_i m_j/(m_i + m_j)$ is the reduced mass for the pair. The momentum factor of the measure of phase space can be expressed in terms of the internal kinetic energy of the pair, $K = P^2/2\mu$, in the form

$$\begin{aligned} 4\pi P^2 dP &= \frac{4\pi}{3} \cdot \frac{3}{2} (P^2)^{1/2}\, d(P^2) \\ &= \frac{(2\pi\mu)^{3/2}}{\Gamma(3/2)} K^{1/2}\, dK. \end{aligned} \tag{8}$$

Three principal cases are to be examined: (a) repulsive pairs, (b) the continuum region for attractive pairs, and (c) the bound region for attractive pairs. For the first two of these, we will seek the contribution to the state sum, per pair, due to there being a potential energy U of pair interaction rather than no pair interaction. For the third case, we will be interested in the full number of bound states of the attracting pair.

For the repulsion case, (a), we have, including the temperature dependence of the Boltzmann factor,

$$\begin{aligned} Q_{rep} &= (2s_i + 1)(2s_j + 1)\left(\frac{2\pi\mu}{h^2}\right)^{3/2} \int_{r=0}^{\infty} \frac{1}{\Gamma(3/2)} \int_{K=0}^{\infty} \left(e^{-(U+K)/kT} - e^{-K/kT}\right) K^{1/2} dK \cdot 4\pi r^2 dr \\ &= (2s_i + 1)(2s_j + 1)\left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} \int_{r=0}^{\infty} \left(e^{-U/kT} - 1\right) \cdot 4\pi r^2 dr. \end{aligned} \tag{9}$$

For the continuum region of the attractive case, (b), for which $-U > 0$, we have

$$Q_{cont} = (2s_i+1)(2s_j+1)\left(\frac{2\pi\mu}{h^2}\right)^{3/2} \int_{r=0}^{\infty} \frac{1}{\Gamma(3/2)} \left[\int_{U+K=0}^{\infty} e^{-(U+K)/kT} K^{1/2} dK - \int_0^{\infty} e^{-K/kT} K^{1/2}\, dK\right] \cdot 4\pi r^2 dr$$

or

$$Q_{cont} = (2s_i+1)(2s_j+1)\left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} \int_{r=0}^{\infty} \frac{2}{\Gamma(3/2)} \left[e^{v^2}\int_v^{\infty} e^{-u^2} u^2 du - \int_0^{\infty} e^{-u^2} u^2 du\right] \cdot 4\pi r^2 dr,$$

by use of $u^2 = K/kT$ and $v^2 = -U/kT$. By integration by parts, or otherwise, this becomes

$$Q_{cont} = (2s_i+1)(2s_j+1)\left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} \int_{r=0}^{\infty} J(v) \quad 4\pi r^2 dr \tag{10}$$

with

$$J(v) = \frac{2v}{\sqrt{\pi}} + e^{v^2}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^v e^{-u^2} du\right) - 1$$

$$= \sum_{m=2}^{\infty} \frac{(-1)^m v^m}{\Gamma(1+\frac{m}{2})} . \tag{11}$$

For the bound region for attractive pairs, (c), we have the local measure of available states as

$$dN = (2s_i+1)(2s_j+1)\ \frac{2\pi\mu}{h^2}^{3/2}\ \frac{K^{1/2} dK}{(3/2)}\ .\ 4\pi r^2 dr. \tag{12}$$

Our immediate detailed consideration of these three cases will be in regard to Debye screened Coulomb interactions.

a) Ionic repulsion

For repulsion in case (a), and using reference 2, we note that eqs. 2.9 and 2.33 therein may be used respectively, with the present δQ_{rep} identified with

$$Q_i^e = \left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} b_{ij}$$

of the former equation and with a type of second virial coefficient indicated as $B_{ij} = -N_0 b_{ij}$ by the latter equation, giving

$$B_{ij} N_0^{-1} = \int_0^{\infty} (1 - e^{-U/kT})\, 4\pi r^2 dr$$

relevant to each ij pair. The spin factors have been divided out since they are present as factors also in the actual concentrations of the constituents i and j.

In his paper pointing out the second-virial-like form of Mayer's ionic solution formulation, Meeron(12) indicated that the formal second virial was able to account for a part of the limiting law Debye-Hückel term, and that a fractional part, namely 5/8 of the whole term, still needed to be carried explicitly apart from the second virial contribution. In the hope of clarifying further some details of our earlier presentation we quote the essence of Meeron's result. The Helmholtz free energy A, per mole at standard conditions, is approximated according to

$$-A/RT = (V/N_0)\left\{\sum C_i\left[(-A^\circ/RT)_i - \ln C_i - \ln T/T_0\right] - \sum_{i=1}\sum_{j=1} C_iC_jB_{ij}/N_0 + \frac{5}{144}b^{-1}\phi^3\right\} \qquad (13)$$

in the notation of eq. 1. B_{ij} here represents a formal second virial

$$B_{ij} = 2\pi N_0\int_0^\infty [1 - \exp U_{ij}/kT]\,r^2\,dr \qquad (14)$$

reduced by a factor of 2 for Mayer's form with the full double sum over all constituents. We note in the case of interionic repulsion that the integral for the pair effect converges even without the help of stronger short range repulsion - though evaluation is another question— and we wish now to let the distance of closest approach become zero for such a pair so that no artificial exclusion volume is required. We shall accordingly consider the integral

$$B_{ij}/N_0 = 2\pi\int_0^\infty [1 - \exp(-Z_iZ_j\frac{\epsilon^2}{DkTr}e^{-\kappa r})]\,r^2\,dr. \qquad (15)$$

If we take κr as a new variable ρ, the integral becomes

$$2\pi\kappa^{-3}\int_0^\infty [1 - \exp(-\frac{w}{\rho}e^{-\rho})]\rho^2\,d\rho \qquad (16)$$

with

$$w = Z_iZ_j\,\epsilon^2\kappa/DkT. \qquad (17)$$

The integral is clearly $2\pi\kappa^{-3}$ times a function of a single variable $w = x\phi$ where $x = x_{ij} = Z_iZ_j\epsilon^2/a\,DkT$ and $\phi = \kappa a$. We can break up the original integral into the sum of two integrals, for $r < a$ and for $r > a$, i.e., for $\rho < \phi$ and for $\rho > \phi$, and obtain

$$-2\pi K^{-3}\int_0^{\phi}\left\{\prod_{n=0} \exp\left[-\frac{(-1)^n w\rho^{n-1}}{n!}\right]\right\}\rho^2 d\rho + \frac{2\pi}{3} a^3$$

$$-2\pi K^{-3}\int_{\phi}^{\infty}\sum_{n=1}\frac{(-w)^n}{n!} e^{-n\rho}\rho^{2-n} d\rho \; . \tag{18}$$

For the first of these two integrals, all exponentials after the first may be expanded, after the first may be expanded, after which integration gives

$$-2\pi K^{-3}\left[\tfrac{1}{3}\sum q_n\phi^{n+3}\right]$$

in which the q_n's are functions of x defined in reference 2. For the second of the two integrals, a more detailed writing as

$$-2\pi K^{-3}\left[-w\left(\int_0^{\infty}e^{-\rho}\rho d\rho - \int_0^{\phi}e^{-\rho}\rho d\rho\right) + \frac{w^2}{2}\left(\int_0^{\infty}e^{-2\rho}d\rho - \int_0^{\phi}e^{-2\rho}d\rho\right)\right.$$

$$\left. + \sum_{n=3}\frac{(-w)^n}{n!}\int_{\phi}^{\infty}e^{-n\rho}\rho^{2-n}\,d\rho\right]$$

followed by comparison with the functions defined by Poirier shows that it is

$$2\pi K^{-3}\left(w - \frac{w^2}{4}\right) - 2\pi K^{-3}\sum_{n=0}(-1)^n x^n\phi(b_n + g_n) \, .$$

The combined pair virial B_{ij} from both regions $0 < \rho < \phi$ and $\phi < \rho < \infty$ is thus indicated by

$$B_{ij}/N_o = -2\pi K^{-3}\left[\tfrac{1}{3}\sum q_n\phi^{n+3}\right] + 2\pi K^{-3}\left(w - \frac{w^2}{4}\right) - 2\pi K^{-3}\sum_{n=0}(-1)^n x^n\phi(b_n + g_n). \tag{19}$$

It may appear debatable whether the terms $2\pi K^{-3}$ and $-2\pi K^{-3} \cdot w^2/4$ should be retained as specifically pairwise properties. The net contribution of such linear terms in w vanishes exactly for the assembly as a whole on the basis of its charge neutrality, a condition that is not modified in any manner by any chemical reaction -- including ionization reactions. The quadratic terms in w are part of the contribution to the limiting law Debye-Hückel term. We should note later that an additional contribution to the limiting law term arises from attractive ion pairs, so that ultimately the ordinary net limiting law term may be restored.

On this basis, one finds that the additional specific pair repulsion effect may be taken as

$$2\pi K^{-3} L = -2\pi K^{-3}\left[\frac{1}{3}\sum_{n=0} q_n\phi^{n+3} + \sum(-1)^n x^n\phi(b_n + g_n)\right]. \tag{20}$$

This was the implication intended in RP 2916(2), though the result may not have been clearly spelled out there in the present detail. We are indebted to A. R. Hochstim(13) for an indication that such a choice of extension into the close approach region has also been formally stated by Meeron by the simple device of modifying the second virial pair integral in a way which can be indicated as a change from

$$\int_0^\infty [\exp(-\frac{w}{\rho}e^{-\rho}) - 1]\rho^2\, d\rho$$

to

$$\int_0^\infty [\exp(-\frac{w}{\rho}e^{-\rho}) + \frac{w}{\rho}e^{-\rho} - \frac{1}{2}(\frac{w}{\rho}e^{-\rho})^2 - 1]\rho^2\, d\rho = -L \tag{21}$$

in our notation. Thus, there is agreement with our indicated procedure of reference 2, based on Mayer's formulation.

The special function L for pair repulsion contributions has been evaluated on the present basis, making use of values of b_n and g_n from the Poirier tables, with b_1 and g_1 values and q_n values from the formulas in reference 2. An example of one such evaluation is shown in Table 1.1. It will be seen that convenience of evaluation involves such a suitable choice of ϕ and x as may prove satisfactory for rapid convergence. A short list of values thus obtained is given in Table 1.2. Such evaluation by means of two infinite series involving tables can be somewhat tedious and we may prefer a simplifying practical approximation. It is now well known that the excluded volume for many simple power potentials can be approximated well by determining the collision distance at an energy corresponding in some way to the typical thermal excitation energy for the temperature in question. It is also known that this fails for power laws below the third, and the Coulomb law is far beyond this limit. However, the source of this difficulty may be the large radius at very low energies — a situation which is drastically modified by the Debye screening, even without the suppression of the w and w^2 terms here assigned to the general solution properties. We have accordingly examined the numerical values obtained for the integral L(w) on the basis that the exponent $\frac{w}{\rho}e^{-\rho}$ should be of the order of unity when $\frac{2\pi}{3}\rho^3$ (as $\frac{2\pi}{3}\rho^3_{eff} = \frac{2\pi}{3}L$) gives a measure of excluded volume corresponding through w to the thermal energy. Values of w^3/L are accordingly listed in the third column of Table 1.2. A plot of $(w^3/L)^{2/3}$ against $w^{1/2}$ appears fairly regular over an extensive range of w, as shown in Fig. 1.1. The roughly approximating curve is given by

$$L = w^3/(1 + 3w^{1/2} + \frac{1}{8}w + \frac{1}{16}w^{3/2})^{3/2} \quad . \tag{22}$$

This is a form based on the rough trend of numerical values only, so there would be no justification for expecting it to give accurate extrapolations. A better representation would naturally be desirable.

b) Ionic attraction and the continuum

For the continuum region of case (b), for ionic attraction, for which $-Z_iZ_j > 0$, we will have the potential

$$U = Z_iZ_j\epsilon^2 e^{-\kappa r}/Dr$$

or

$$U = -\left|Z_iZ_j\right|\epsilon^2 e^{-\kappa r}/Dr.$$

We would note first that we may take the first four terms of eq. 11 as an approximating polynomial for small values of v,

$$J(v) \sim v^2 - \frac{v^3}{\frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi}} + \frac{v^4}{2} - \frac{v^5}{\frac{5}{2}\cdot\frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi}}$$

$$\approx v^2 - 0.752253v^3 + 0.5v^4 - 0.300901v^5. \tag{23}$$

Parenthetically, we would also note that the full classical contribution including bound states as well as continuum would give $e^{v^2} - 1$ here, so that J(v) has the same leading term as does the expansion of $e^{v^2} - 1 = e^{-U/kT} - 1$. This leading term may be recognized as the relevant contribution coming from the Boltzmann factor for both the attractive and repulsive interactions comprising an essential part of the original derivation of Debye screening. It is especially worth noting that no part of the bound states for the attractive interaction would be required for this inference of Debye screening. It therefore follows that all pair states below ionization may be placed in their natural category of bound states in the somewhat separate problem of the internal sum of states for the combined pair. Such a separation off of the bound states will not contradict in any way the logical basis for the inference that Debye screening has some actual degree of validity. On the other hand, one should concede that Debye screening is an idealization which is but a reasonably good beginning at describing the actual ionic screening situation.

To prepare for the evaluation of eq. 10, one may introduce the variable $\rho = \kappa r$ and so obtain

$$v^2 \equiv -U/kT = \underline{w}_{ij} \rho^{-1} e^{-\rho}$$

where $\underline{w}_{ij} = \left|-Z_i Z_j\right| \epsilon^2 \kappa / DkT$. Then eq. 10 may be re-written as

$$\delta Q_{cont} = (2s_i + 1)(2s_j + 1) \cdot \left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} \cdot 4\pi\kappa^{-3} F(\underline{w}) \tag{24}$$

with

$$F(\underline{w}) = \int_0^{\infty} J(v) \rho^2 \, d\rho.$$

With eq. 23 as a polynomial approximation for J(v), integration gives

$$F(\underline{w}) \approx \sum_{m=2}^{5} C_m w^{m/2}$$

where

$$C_m = (-1)^m \left(\frac{m}{2}\right)^{\frac{m}{2} - 3} \Gamma(3 - \tfrac{m}{2}) / \Gamma(1 + \tfrac{m}{2}) \, .$$

This implies that

$$F(\underline{w}) \approx \underline{w} - \frac{2\sqrt{6}}{27} \underline{w}^{3/2} + \frac{1}{4} \underline{w}^2 - \frac{8\sqrt{10}}{75} \underline{w}^{5/2}$$

$$\approx \underline{w} - 0.181444 \, \underline{w}^{3/2} + 0.25 w^2 - 0.337310 w^{5/2} \, . \tag{25}$$

No additional terms can be carried to extend this polynomial in the same pattern, since only these terms have finite coefficients according to the relation obtained. The terms in $\underline{w}$ and $\underline{w}^2$ are closely related to the similar terms in w and w^2 which appear in eq. 19 in the cognate repulsion problem. As in the repulsion case, one obtains the corresponding second virial type contributions by reversing the sign and dividing out the internal momentum factor contribution, $(\frac{2\pi\mu kT}{h^2})^{3/2}$, the spin factors $(2s_i+1)(2s_j+1)$ and a factor of two to conform to the double sum over constituents in final application to the complete assembly. This gives the continuum contribution estimate here as

$$\begin{aligned}\delta B_{ij}/N_o &= -2\pi K^{-3}F(\underline{w})\\ &\approx -2\pi K^{-3}\left[\underline{w} - \frac{2\sqrt{6}}{27}\underline{w}^{3/2} + \frac{1}{4}\underline{w}^2 - \frac{8\sqrt{10}}{75}\underline{w}^{5/2}\right].\end{aligned} \tag{26}$$

It is now possible to explicitly combine the $\underline{w}$ and $\underline{w}^2$ terms with the w and w^2 terms of eq. 19 to obtain their combined incremental contribution to $\sum\sum C_iC_jB_{ij}/N_o$ as

$$\begin{aligned}\delta\sum_i\sum_j C_iC_jB_{ij}/N_o &\approx 2\pi K^{-3}\left[\sum_i\sum_j C_iC_j(w_{ij}-\frac{1}{4}w_{ij}^2)_{rep} - \sum_i\sum_j C_iC_j(\underline{w}_{ij}+\frac{1}{4}w_{ij}^2)_{att}\right]\\ &\approx 2\pi K^{-3}\left[(\sum C_iZ_i)^2\frac{\epsilon^2 K}{DkT} - \frac{1}{4}(\sum C_iZ_i^2)^2\frac{\epsilon^4K^2}{(DkT)^2}\right]\end{aligned} \tag{27}$$

so that the first term vanishes by $\sum C_iZ_i \equiv 0$, while the second term reduces to $-K^3(V_o/N_o)^2/32\pi$. Then after multiplying by $-VN_o/V_o^2$ to conform to eq. 13 for the Helmholtz free energy function, one obtains $(V/V_o)\left\{\left[\frac{1}{48}b^{-1}\phi^3\right]\right\}$ as the net pairwise contribution. By combining with the separate $(V/V_o)\left\{\left[\frac{5}{144}b^{-1}\phi^3\right]\right\}$ indicated by Meeron, one obtains the combined limiting law term $(V/V_o)\left\{\left[\frac{1}{18}b^{-1}\phi^3\right]\right\}$ as it occurs in eq. 1.

While it is pleasing that eqs. 25 and 26, based on eq. 23, are of such form as to provide conveniently interpretable and usable terms, we can suspect that the polynomial obtained still leaves something to be desired as a representation of the continuum contribution. With the $\underline{w}$ and $\underline{w}^2$ terms absorbed into the general ionic assembly properties, we have only the $\underline{w}^{3/2}$ and $\underline{w}^{5/2}$ terms left from the original approximation. The first of these, except for sign, appears to pertain to the number of accessible bound states, a quantity to be examined shortly in regard to the internal partition function for the pair comprising a positive ion plus an electron. One sees no reason to expect good approximation in regard to the remainder of the continuum contribution from the $\underline{w}^{5/2}$ term alone, especially since the series terminates as a polynomial just at this point. Accordingly, the function $G(\underline{w}) = F(\underline{w}) - \underline{w} - \frac{1}{4}\underline{w}^2$ has been examined directly numerically on the basis of a few values obtained by tabular integration. For this calculation, the tabulation was made in 20 equal steps for $e^{-\kappa r} = 1 - u$ from 1 to 0. The function actually chosen for integration was

$$M(v) = J(v) - v^2 + \frac{4}{3\sqrt{\pi}} v^3,$$

for which the integrand, $M(v)\rho^2 \frac{d\rho}{du}$, goes to zero at both ends of the tabulated region. J(v) is defined by eq. 11. Then we have

$$G(\underline{w}) = \int_0^\infty M(v)\rho^2 d\rho - \frac{2\sqrt{6}}{27}\underline{w}^{3/2} - \frac{1}{4} w^2 .$$

Tabulated values of $M(v)\rho^2 e^\rho$ for various values of $\underline{w}$ may be found in Table 1.3, while corresponding values of $\int_0^\infty M(v)\rho^2 d\rho = \int_0^1 M(v)\rho^2 e^\rho du$ and $-G(\underline{w})$ estimated by numerical integration are given in Table 1.4. Values are given also for estimates from

$$\frac{2\sqrt{6}}{27}\underline{w}^{3/2}, \; \frac{2\sqrt{6}}{27}\underline{w}^{3/2} + \frac{8\sqrt{10}}{75}\underline{w}^{5/2} = \frac{2\sqrt{6}}{27}\underline{w}^{3/2}\left[1 + \frac{12\sqrt{15}}{25}\underline{w}\right]$$

and a geometric mean truncation,

$$\frac{2\sqrt{6}}{27}\underline{w}^{3/2}\left[1 + \frac{12\sqrt{15}}{25}\underline{w}\right]^{1/2},$$

which does not differ grossly from the numerical integration results in this comparison region. Fig. 1.2 shows graphically how the continuum contribution varies over the tabulated range of the variable $\underline{w}$.

c) Ionic attraction and bound states

We now come to the ionic binding region, case (c), for which eq. 12 is relevant. Our immediate interest in this case centers on such systems as an ionic core or nucleus plus an interacting electron. We can claim that in the dense level regions of large quantum numbers, particularly, there will be a close correspondence between distributions of levels semi-classically and quantum mechanically. We note that there have been perplexities about the calculation of atomic partition functions due to an apparent divergence of the sum of states, arising when the intention is taken to sum over all bound states since the weights contain a factor of $2n^2$ from the outer electron, where n is the electron's principal quantum number. For a single system in otherwise completely empty infinite space, there would be no interference tending to limit the possible n values. With Debye screening, the number of states is finite. It is sometimes supposed that the semi-classical attractive ionic system is subject to just as serious a divergence difficulty due to the exponential from the Boltzmann factor applied to the phase space region of extremely negative energy near $r = 0$. We find that this is not actually a serious problem if we will consider the semi-classical approach as a procedure for estimating the distribution of discrete states, the lowest of which is the ground state for the single atom or atomic ion being described. The placement of the lower atomic levels is usually in little doubt since they are generally well observed spectroscopically.

In our present case with the Debye screened ionic attraction specialized to the case in which one particle of the pair is an electron, with spin factor $2s_1 + 1 = 2$ and $Z_1 = -1$, we find that the number of levels locally is measured by

$$dN = 2(2s_N + 1)\left(\frac{2\pi\mu}{h^2}\right)^{3/2} \frac{K^{1/2}\,dK}{\Gamma(3/2)} \cdot 4\pi r^2 dr \tag{28}$$

with K ranging from zero to $Z\epsilon^2 e^{-\kappa r}/Dr$. The total number of bound levels available for occupancy is readily estimated, since the integral over K is immediate, leading to

$$\begin{aligned} N &= 2(2s_N + 1)\left(\frac{2\pi\mu}{h^2}\right)^{3/2} \frac{1}{\frac{3}{2}\Gamma(3/2)} \int_{r=0}^{\infty} \left(\frac{Z\epsilon^2 e^{-\kappa r}}{Dr}\right)^{3/2} \cdot 4\pi r^2 dr \\ &= \frac{16}{27}\,\frac{\sqrt{3}}{\sqrt{\pi}}(2s_N + 1)\left(\frac{Z}{D\kappa a_o}\right)^{3/2}, \\ &= 0.579084(2s_N + 1)(Z/D\kappa a_o)^{3/2}, \end{aligned} \tag{29}$$

where $a_o = \hbar^2/\mu\epsilon^2$ is the radius of the first Bohr orbit for hydrogen and Z is the charge of the atomic core in protonic units. It is clear that this result, by simply omitting the nuclear spin factor $2s_N + 1$ — here also a practical equivalent for number of core states — gives a basis for a stopping point for the sum of the $2n^2$ pertaining to the weight factor for states due to the outer electron. For any electrons other than the outer one, the stopping point is essentially the same, since it is natural to claim that n for them cannot be greater than for the outermost one. Some small reduction in the total number of multi-electron states arises from the Pauli exclusion principle, due to the applicability of FD statistics.

The ionic environment also provides a change of ionization energy and a corresponding non-uniform change of placement of intermediate levels, particularly near ionization. To examine the distribution of available levels in the circumstance of Debye screening, eq. 28 is used with the kinetic energy expressed as $K = E - U$, so that the density of levels with respect to energy is

$$\frac{dN}{dE} = 8\pi \frac{(2s_N + 1)}{\Gamma(3/2)} \left(\frac{2\pi\mu}{h^2}\right)^{3/2} \int_0^{r_m} (E - U)^{1/2} r^2 dr, \tag{30}$$

where r_m is the r_{max} turning point corresponding to the given energy E. By taking κr as a new variable ρ, one obtains

$$\frac{dN}{dE} = \frac{8\pi(2s_N + 1)}{\Gamma(3/2)} \left(\frac{2\pi\mu}{h^2}\right)^{3/2} \frac{(Z\epsilon^2/D)^{1/2}}{\kappa^{5/2}} \int_0^{\rho_m} [\rho^{-1} e^{-\rho} - \rho_m^{-1} e^{-\rho_m}]^{1/2} \rho^2 d\rho . \tag{31}$$

By again introducing the Bohr orbit radius a_o and by using the new variables $y = 1 - \rho/\rho_m$ and $\chi = \rho_m$, one finds

$$\left(\frac{\kappa Z\epsilon^2}{D}\right) \frac{dN}{dE} = \frac{4\sqrt{2}}{\pi} \left(\frac{Z}{D\kappa a_o}\right)^{3/2} \chi^{5/2} e^{-\chi/2} \int_0^1 [y + (e^{\chi y} - 1)]^{1/2} (1 - y)^{3/2} dy .$$

The integrand may be expanded as a power series in χ and integrated in terms of the Beta function The result through the tenth power of the variable χ is found to be

$$\left(\frac{\kappa Z\epsilon^2}{D}\right) \frac{dN}{dE} = \frac{\sqrt{2}}{4} \left(\frac{Z}{D\kappa a_o}\right)^{3/2} \chi^{5/2} e^{-\chi/2} \left[1 + \frac{\chi}{2} - \frac{\chi^2}{32} + \frac{\chi^3}{32} - \frac{47\chi^4}{3072} + \frac{49\chi^5}{5120} - \frac{2077\chi^6}{327680} + \frac{91621\chi^7}{20643840} - \frac{4275289\chi^8}{1321205760} + \frac{3218221\chi^9}{1321205760} - \frac{511366339\chi^{10}}{271790899200} \cdots\right] . \tag{32}$$

In the ionization limit, the value attained for the level density is indicated by

$$\left(\frac{\kappa Z\epsilon^2}{D}\right) \left(\frac{dN}{dE}\right)_{\infty} = \frac{24}{\sqrt{\pi}} \left(\frac{Z}{D\kappa a_o}\right)^{3/2} = 13.54055 \left(\frac{Z}{D\kappa a_o}\right)^{3/2} , \tag{33}$$

obtained from eq. 31 with $\rho_m = \infty$. The calculated results for the classical distribution of available bound states are to be found in Table 1.5. The first column lists values of $e^{-\kappa r_m}$ at 20 equal intervals from 1 to 0. This function was arbitrarily selected to give the table spacing. The second column gives corresponding values of κr_m. The third column gives $(\kappa r_m)^{-1} e^{-\kappa r_m}$, which is a dimensionless measure of the local depth of the potential energy, scaled to the Debye energy depression, $\kappa Z\epsilon^2/D$. (This energy depression is the naive estimate for the decrease of the ionization potential, to be examined later in greater detail.) Column four shows the density of available states with respect to energy, calculated with numbers of states scaled to $(Z/D\kappa a_0)^{3/2}$ and energy scaled to $(\kappa Z\epsilon^2/D)$. The numbers in column four are based on eq. 32, but for the latter entries where the series becomes poorly convergent, or perhaps divergent, the evaluation has been made using special summation techniques including the Euler transformation(14, 15). The quantity in column five, obtained by multiplying column four by $[(\kappa r_m)^{-2} + (\kappa r_m)^{-1}]$, also represents density of states, but with respect to $e^{-\kappa r_m}$ for which the table is a uniform tabulation. Tabular integration of column five with respect to increments of $-e^{-\kappa r_m}$, using a 5-point Lagrangian integration formula, gives the function in column six, subject to two exceptions, viz., (1) that the first four entries are from a series representation for the integral

$$(D\kappa a_0/Z)^{3/2} N = \frac{\sqrt{2}}{6}\chi^{3/2}\left[1 - \frac{9}{32}\chi^2 - \frac{9}{64}\chi^3 - \frac{25}{1024}\chi^4 \ldots\right], \qquad (34)$$

and (2) that the final entry comes from eq. 29 since the final increment is not given accurately by the 5-point Lagrangian formula because of the exceptionally violent change of the integrand at the end of the range. The quantity N, we wish to explain, is the estimated number of states available for single outer electron occupancy up to an energy E designated as being below ionization by $\frac{Z\epsilon^2}{Dr_m} e^{-\kappa r_m}$.

We now wish to consider a use that could in principle be made using these tabulated quantities. As a preliminary step, we examine the effect on equation 32 occurring if we let the Debye screening parameter κ go to zero as a limiting value. The series within the bracket then reduces to unity, as also does $e^{-\chi/2}$. This leaves

$$\frac{(\kappa Z\epsilon^2/D)}{(Z/D\kappa a_0)^{3/2}} \frac{dN_{Coul}}{dE} = \frac{\sqrt{2}}{4}\chi^{5/2} = \frac{\sqrt{2}}{4}(\kappa r_m)^{5/2}, \qquad (35)$$

here written in a form in which $\kappa^{5/2}$ occurs as a factor, on both sides of the equation. By retaining this $\kappa^{5/2}$ factor, we can obtain a quantity corresponding via κr_m to that in column four, but which now applies to the case of the Coulomb field without Debye screening. Obviously, the energy for this Coulomb case is not identical with that for the case with screening at the same κr_m, as the Coulomb depression below ionization corresponds to $(\kappa r_m)^{-1}$ rather than to the screened $(\kappa r_m)^{-1} e^{-\kappa r_m}$ of column three. The conversion from dN_{Coul}/dE to $dN_{Coul}/d(-e^{\kappa r_m})$ involves multiplication by $(\kappa r_m)^{-2} e^{\kappa r_m}$ purely as an adaptation to the chosen variable of tabulation. The result, which appears in column eight, gives a density of levels versus the table variable applying to the unscreened Coulomb case and corresponding via κr_m to the values given in column five for the screened case.

The integral of the values in column eight with respect to the tabulation variable, $e^{-\kappa r_m}$, is a semi-classical measure of the number of available one-electron states up to the energy which in this unscreened Coulomb case corresponds to the κr_m value, or up to an energy $\kappa Z\epsilon^2/D\kappa r_m$ below ionization.

We now say simply that if the partition function for an atom or atomic ion has been obtained by summing over all the states that are included by letting the quantum number n of the outer electron take all values up to and including a terminal value n_1, then an adjustment in the partition function may be in order, for which the following recipe may be worthy of consideration. We define a fictitious number of available one-electron states for the outer electron as

$$N_f = \sum_{n=1}^{n_1} 2n^2 = \frac{n_1(n_1 + 1)(2n_1 + 1)}{3} .$$

This corresponds to the N_{Coul} of column nine in the table. By calculating $(D\kappa a_o/Z)^{3/2} N_f$, based on the κ for the actual high temperature gas mixture and interpolating in column nine, a determination can be made of the endpoint in the table corresponding to the chosen sum of states. One should now use the relevant $e^{-\epsilon_i/kT}$ factors in each case and put in the integral corresponding to the complete sum of $g_i e^{-\epsilon_i/kT}$ values based on column five as a replacement for the integral corresponding to the summation of $g_i e^{-\epsilon_i/kT}$ values based on column eight up to the indicated special endpoint. This over-all adjustment appears as if in a factor pertaining to the states of the outer electron only, in which case the sum of states for the core alone is a separate multiplier to be considered as a factor in an over-all weight of states, though here it is not a constant factor such as would arise from nuclear spin in the one electron case.

[We can also point out that another tabulation should be possible for the Coulomb case, arranged to have the same energy as for the screened Coulomb case. However, the correspondence would end at the ionization energy of the screened Coulomb case and hence would apparently not be convenient in the adjustment from sums carried to high n values. When the adjustment is limited to the same energy region, the change would be in regard to density of states only, with values of $e^{-\mathcal{E}/kT}$ occurring singly, in common to the corresponding entries in the "screened" and the "unscreened" columns.]

It is hoped that the procedure indicated may prove to be entirely reasonable as an approximate adjustment to take account of the principal mutual screening effects in the ionic solution environment. It is but natural to regard the procedure as capable of analytic arrangement, at least in approximate form, for the performance of actual calculations of adjusting for the particular conditions of a given high temperature gas. The extension to the calculation of gas properties other than the directly given Helmholtz free energy would follow as usual by differentiation. We note that this may involve some contributions from the dependence of κ, the Debye screening constant, on other variables.

We should not close the present discussion without mentioning an item that appears worthy of note. We may recall the observation, already touched on in section b), that the count of available states for the Debye screened atomic ion is so closely matched by an almost compensating deficiency in the count of states in the continuum. This fact influences our interpretation of the effect on calculated thermodynamic functions.

We would first note that, at high temperatures, a conventional sum of states for an atomic ion has a very sensitive dependence on the cut-off value of the quantum number n at which the state sum is halted. In fact, the principal features of the specific heat can be indicated qualitatively by a modified Schottky curve based on two levels only -- a ground state of effective weight

g_o and an excited state of effective weight g_1 and at an energy $\mathcal{E}$ higher. It is then but a simple exercise to show that the maximum of the specific heat curve occurs at a given temperature T_m if the weights are related by

$$g_o/g_1 = \frac{e^{-\mathcal{E}/kT_m}(1 + 2kT_m/\mathcal{E})}{(1 - 2kT_m/\mathcal{E})} \tag{36}$$

and that at this maximum the relation

$$(C_v^o/R)_{max} = \frac{1}{2} + \frac{1}{4}\left(\frac{\mathcal{E}}{kT_m}\right)^2 \tag{37}$$

must apply. A simple examination of these formulas indicates that by taking $\mathcal{E}$ as the ionization energy and g_1 as the number of states counted near ionization, there is a possibility of obtaining a specific heat peak of any arbitrarily chosen height, occurring then at a temperature that is some corresponding small fraction of the temperature equivalent of the ionization potential.

We can admit that we had expected that the Debye-limited number of states would give a suitable control -- in effect by determining the g_1 -- now a variable, and indeed this expectation can be regarded as fulfilled. However, we have encountered the interesting complication that when we include the continuum for an electron with a positive ion, we have a negative contribution arising from the existence of the region of bound states in which occupancy is allowed in the other part of the treatment. The close relation of magnitude of plus and minus contributions is clearly not due to use of Debye screening, except insofar as the comparison is possible for finite quantities and unclear for infinite ones. An improved representation of the effect involved here would naturally be desirable.

Another item of some importance in regard to ionization equilibria is the effect of the ionic environment in reducing the ionization potential of the atoms and atomic ions. We note that the Schrodinger wave equation leads to radial eigenfunctions R (r) satisfying the differential equation

$$\frac{d^2(rR)}{dr^2} + \left[\frac{2\mu}{\hbar^2}(E - V) - \frac{\ell(\ell+1)}{r^2}\right](rR) = 0 \tag{38}$$

where V is the potential energy of the electron in the field of the atomic core or nucleus. If we assume the approximate validity of Debye screening, we may consider the potential energy to be given by an ordinary unperturbed part

$$V_o = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{Z\epsilon^2}{r} \tag{39}$$

plus a perturbation potential

$$V_1 = \frac{Z\epsilon^2}{r}(1 - e^{-\mathcal{K}r}) - \mathcal{K}Z\epsilon^2 \tag{40}$$

so arranged that the potential is held unchanged by the perturbation at the $r = 0$ limit.(16) Although degenerate perturbation theory is applicable, the perturbation potential does not involve φ and θ, the coordinates associated with the degeneracy, and the secular determinant involved is diagonal with respect to m and ℓ as a consequence, thus implying that nondegenerate perturbation theory may be used. Combining the energy eigenvalues of the unperturbed system with the contribution of the first order perturbation, the perturbed eigenvalues are approximated as

$$E = -\frac{Z^2\epsilon^2}{2a_o n^2} + \mathcal{K}Z\epsilon^2 \sum_{s=1}^{\infty} \frac{(-1)^s}{(s+1)!} \mathcal{K}^s \overline{r^s} \tag{41}$$

where $a_o = \hbar^2/\mu\epsilon^2$ is the Bohr orbit radius. One notes that this energy formula is compatible with a potential energy going to the value $\mathcal{K}Z\epsilon^2$ at $r = \infty$. The ionization energy above a state with an outer electron having quantum numbers n and ℓ in a nearly hydrogenic state is thus estimated as

$$I = I_o - \mathcal{K}Z\epsilon^2 - \mathcal{K}Z\epsilon^2 \sum_{s=1}^{\infty} \frac{(-1)^s}{(s+1)!} \mathcal{K}^s \overline{r^s} \tag{42}$$

with I_o as the corresponding ionization energy with $\mathcal{K} = 0$. The terms in $\overline{r}$ and $\overline{r^2}$ are unaffected if higher order perturbation theory is used. By quoting from a listing of $\overline{r^s}$ functions,(17) we obtain

$$\begin{aligned} I = I_o - \mathcal{K}Z\epsilon^2 + \mathcal{K}Z\epsilon^2 & \frac{\mathcal{K}a_o}{4Z}[3n^2 - \ell(\ell+1)] - \frac{1}{12}\left(\frac{\mathcal{K}a_o}{Z}\right)^2 [5n^2 + 1 - 3\ell(\ell+1)] \\ & + \frac{1}{192}\left(\frac{\mathcal{K}a_o}{Z}\right)^3 [35n^2(n^2-1) - 30n^2(\ell+2)(\ell-1) + 3(\ell+2)(\ell+1)\ell(\ell-1)] \ldots \end{aligned} \tag{43}$$

We must note that actual ionic screening would not be strictly of the Debye type, even on the average. There are several reasons for this, including the fact that the strongly screening free electrons of the ionized continuum are able to penetrate deeply into atomic ions and there to even exceed their normal concentrations in free space, while neighboring positive ions are strongly excluded from the close approach region and do not appreciably cancel any of the deep electron screening. We note also that polyelectron atoms typically involve quantum defect corrections with the quantum numbers.

In deriving the above ionization energy formula, the dielectric constant D has been left as if equal to unity. If a constant value different from unity were to be taken, the derivations leading to Table 1.5 show that it would occur in combinations with $\mathcal{K}Z\epsilon^2/D$ proportional to energy differences and with $D\mathcal{K}a_0/Z$ associated with quantum numbers and hence numbers of states. For distant separations of electrons from the atomic core, it is proper to recognize that the intervening medium would have effects as shown by the work of Fermi(18) and Amaldi and Segrè.(19) The simple introduction of a uniform dielectric constant in our formulas must be regarded as only schematic and subject to considerable refinement.

The problem of where to include the dielectric constant is not limited to the formulas immediately preceding. Duclos and Cambel(20) have recently pointed out its presumed suitability in eq. 3.1 of RP 2916,(2) so that within the square bracket there the term would appear as

$$\frac{1}{12\pi} \frac{h^2\epsilon^2}{m_e D\mathcal{K}^2T^2}$$

[An extra 1/2 which they accumulated is apparently due to a reduced mass factor].

We can suppose that the semi-theoretical estimates of other interaction effects of electrical origin will also be affected by the intervening matter. This may be successfully allowed for in the cases of interionic and ion-neutral interactions. These may provide additional corrections to the second virial type estimates under certain high density conditions and so affect the projected estimates of higher virial effects by resort to extensions of the rigid sphere equation of state.(10,21)

Our eq. 1 may be re-written on the basis of the newly estimated pair effects involving the function L of section a), the function G of section b) and the Debye screened internal partition functions of section c) as

$$-A/RT = (V/N_o) \left\{ \sum_s C_s[(-A^\circ/RT)_s - \ln C_s - \ln(T/T_o)] - \frac{1}{12\pi} \kappa^3 \frac{V_o}{N_o} - \sum_r \sum_s \frac{C_r C_s}{V_o} \left[B_{rs} \right.\right.$$

$$+ 2\pi N_o \left\{ \left[\frac{(Z_r^2 Z_s^2)^{1/2} + Z_r Z_s}{2} \cdot \frac{\epsilon^2}{D\kappa T} \right]^3 \cdot \frac{1}{[1 + 3w_{rs}^{1/2} + \frac{1}{8} w_{rs} + \frac{1}{16} w_{rs}^{3/2}]^{3/2}} \right.$$

$$\left.\left.\left. + \kappa^{-3/2} \left[\frac{(Z_r^2 Z_s^2)^{1/2} - Z_r Z_s}{2} \cdot \frac{\epsilon^2}{D\kappa T} \right]^{3/2} \cdot \frac{2\sqrt{6}}{27} [1 + \frac{12\sqrt{15}}{25} w_{rs}]^{1/2} \right\} \right] \right\} \qquad (44)$$

now with $w_{rs} = |Z_r Z_s| \epsilon^2 \kappa / DkT$. The quantity B_{rs} represents any pairwise, second virial type, effects of ordinary origin.

One proposed high density extrapolation(10) and mixture rule might suggest that the higher order virial type contributions to -A/RT be taken as

$$(V/N_o) \left\{ -\sum_{n=3} \frac{(3n^2 - 3n + 2)}{2^{2n-1} (n-1) V_o^{n-1}} \left[\sum C_s (b_e)_{ss}^{\frac{n-1}{n}} \right]^n \right\} . \qquad (45)$$

The excluded volume $(b_e)_{ss}$ between like pairs would be taken as roughly given by the bracketed coefficient of $C_r C_s$ with $r = s$ in eq. 44, for regions in which the B_{ss}'s are strongly positive.

It is apparent that careful consideration is appropriate in attempting extensions of the calculations to higher temperatures and higher pressures. At sufficiently high temperatures, the approximations commonly used in regard to stellar interiors would presumably provide an adequate continuation.

Table 1.1. Example of Calculation of Pair Effect of Debye Screened Ionic Repulsion for w = 0.2.

For $\varphi = 2.0$, $x = 0.1$

n	$(-x)^n\varphi(b_n+g_n)$	$(1/3)\,\varphi^{n+3}q_n$
0	-2.66666667	2.30188874
1	0.11879883	0.46037776
2	- .00981679	- .30438773
3	- .00000048	.12134357
4	+ .00000000	- .01978965
5		- .01123413
6		.01142954
Σ	-2.55768511	2.55_{962810}
	Total	$+0.00_{194299}$

For $\varphi = 1.0$, $x = 0.2$

n	$(-x)^n\varphi(b_n+g_n)$	$(1/3)\,\varphi^{n+3}q_n$
0	-0.33333333	0.24944723
1	.05284822	.04988944
2	- .00864664	- .01423209
3	- .00001740	.00169031
4	.00000021	.00035911
5		- .00023244
6		.00005736
Σ	-0.28914894	0.2869_{7892}
	Total	-0.0021_{7002}

For $\varphi = 0.4$, $x = 0.5$

n	$(-x)^n\varphi(b_n+g_n)$	$(1/3)\,\varphi^{n+3}q_n$
0	-0.02133333	0.01057554
1	.01231039	.00211511
2	- .00550670	- .00012379
3	- .00021121	- .00001602
4	.00001063	.00000378
5	- .00000050	- .00000024
6		- .00000003
Σ	-0.0147307_2	0.01255435
	Total	-0.0021763_7

For $\varphi = 0.2$, $x = 1.0$

n	$(-x)^n\varphi(b_n+g_n)$	$(1/3)\,\varphi^{n+3}q_n$
0	-0.00266667	0.00068850
1	.00350462	.00013770
2	- .00329678	.00000250
3	- .00060584	- .00000070
4	+ .00006695	.00000002
5	- .00000731	.00000000
6	.00000074	
7	- .00000007	
8	+ .00000001	
Σ	-0.00300435	0.00082802
	Total	-0.00217633

Table 1.2. Pair Effect of Debye Screened Ionic Repulsion.

w	L(w)	$w^3/L(w)$
0.01	0.0000007057	1.4171
0.04	0.00003140	2.038
.1	.00036029	2.7755
.2	.00217633	3.6759
.4	.0125249	5.1098
.8	.0682764	7.4989
1.0	.116436	8.5884
2.0	.588321	13.5980
4.0	2.8125	22.756

Table 1.3. Values of the Integrand M(v) ^{2}e for Various Values of w

$e^{-\kappa r}$	$M(v)\rho^{2}e^{\rho}$			
	w = 0.01	0.1	1	$10^{\frac{1}{2}}$
1	0.00000	0.00000	0.00000	0.00000
0.95	$0.37592\text{x}10^{-4}$	$0.25632\text{x}10^{-2}$	0.12580	0.79294
.90	.38197	.28588	.15689	1.03078
.85	.37313	.29374	.17327	1.17404
.80	.35877	.29226	.18206	1.26593
.75	.34157	.28550	.18596	1.32294
.70	.32263	.27528	.18629	1.35339
.65	.30251	.26262	.18382	1.36208
.60	.28155	.24809	.17904	1.35199
.55	.25993	.23209	.17228	1.32505
.50	.23780	.21487	.16377	1.28253
.45	.21524	.19662	.15366	1.22519
.40	.19233	.17748	.14209	1.15348
.35	.16911	.15755	.12912	1.06753
.30	.14562	.13690	.11482	0.96720
.25	.12188	.11560	.09920	.85206
.20	.09792	.09368	.08228	.72135
.15	.07375	.07118	.06403	.57387
.10	.04938	.04809	.04438	.40767
.05	.02481	.02440	.02319	.21937
.00	0.00000	0.00000	0.00000	0.00000

Table 1.4. Residual Continuum Contribution for Attractive Ionic Pairs.

$\underline{w}$	0.01	0.1	1	$10^{1/2}$
$\int_{\rho}^{\infty} M(v)\rho^2 d\rho$	...$0.2224\text{x}10^{-4}$	$0.1872\text{x}10^{-2}$	.1297	.9827
$-G$	...$1.842\text{x}10^{-4}$	$.6367\text{x}10^{-2}$	.3017	2.538
$\frac{2\sqrt{6}}{27}\underline{w}^{3/2}$	...$1.814\text{x}10^{-4}$	$.5738\text{x}10^{-2}$	.1814	1.0203
$\frac{2\sqrt{6}}{27}\underline{w}^{3/2}(1+\frac{12\sqrt{15}}{25}\underline{w})$	...$1.848\text{x}10^{-4}$	$.6738\text{x}10^{-2}$	.5188	7.0186
$\frac{2\sqrt{6}}{27}\underline{w}^{3/2}(1+\frac{12\sqrt{15}}{25}\underline{w})^{1/2}$	...$1.831\text{x}10^{-4}$	$.6216\text{x}10^{-2}$	.3068	2.676

Table 1.5. Available Single Electron State Densities and Numbers, N, for Ionic Attraction With and Without Debye Screening.

$e^{-\kappa r_m}$	κr_m	$(\kappa r_m)^{-1} e^{-\kappa r_m}$	$\frac{(\kappa Z\varepsilon^2/D)}{(Z/D\kappa a_o)^{3/2}} \frac{dN}{dE}$	$(\frac{D\kappa a_o}{Z})^{3/2} \frac{dN}{d(-e^{-\kappa r_m})}$	$(\frac{D\kappa a_o}{Z})^{3/2} N$	$\frac{(\kappa Z\varepsilon^2/D)}{(Z/D\kappa a_o)^{3/2}} \frac{dN}{dE}$ Coul	$(\frac{D\kappa a_o}{Z})^{3/2} \frac{dN_{Coul}}{d(-e^{-\kappa r_m})}$	$(\frac{D\kappa a_o}{Z})^{3/2} N_{Coul}$
1.00	0.000000	∞	0	0	0	0	0	0
.95	.051293	18.52094	0.00021059	0.08415	0.0027360	0.00021067	0.08429	0.00273813
.90	.105361	8.54210	.0012719	.12664	.0080340	.00127394	.12751	.00806084
.85	.162519	5.23016	.0037504	.16507	.015318	.00376456	.16768	.01544257
.80	.223144	3.585136	.0082580	.20285	.02456	.00831602	.20876	.02484507
.75	.287682	2.607045	.015520	.24148	.03566	.01569412	.25284	.03636913
.70	.356675	1.962571	.026420	.28175	.04874	.02686188	.30164	.05020797
.65	.430783	1.508881	.042067	.32434	.06388	.04306269	.35700	.06664253
.60	.510826	1.174569	.063877	.36984	.08122	.06593813	.42115	.08605433
.55	.597837	0.919983	.093690	.41885	.10092	.09770391	.49703	.10895268
.50	.693147	.721348	.13395	.47205	.12317	.14142254	.58871	.13601974
.45	.798508	.563551	.18793	.53022	.14821	.20144327	.70207	.16818312
.40	.916291	.436543	.26041	.59435	.17630	.28414382	.84608	.20673484
.35	1.049822	.333390	.35792	.66568	.20776	.39924941	1.03501	.25353465
.30	1.203973	.249175	.49056	.74588	.24301	.56233704	1.29313	.31137860
.25	1.386294	.180337	.67431	.83728	.28254	.80000673	1.66511	.38472192
.20	1.609438	.124267	.93644	.94336	.32698	1.16182459	2.24265	.48125481
.15	1.897120	.0790672	1.32882	1.06965	.37721	1.75263714	3.24647	.61589397
.10	2.302585	.0434294	1.96852	1.22620	.43446	2.84442330	5.36492	.82354490
.05	2.995732	.0166904	3.21956	1.43347	.50068	5.49177199	12.23874	1.22213236
0.00	∞	0	13.54055	0	.579084	∞	∞	∞

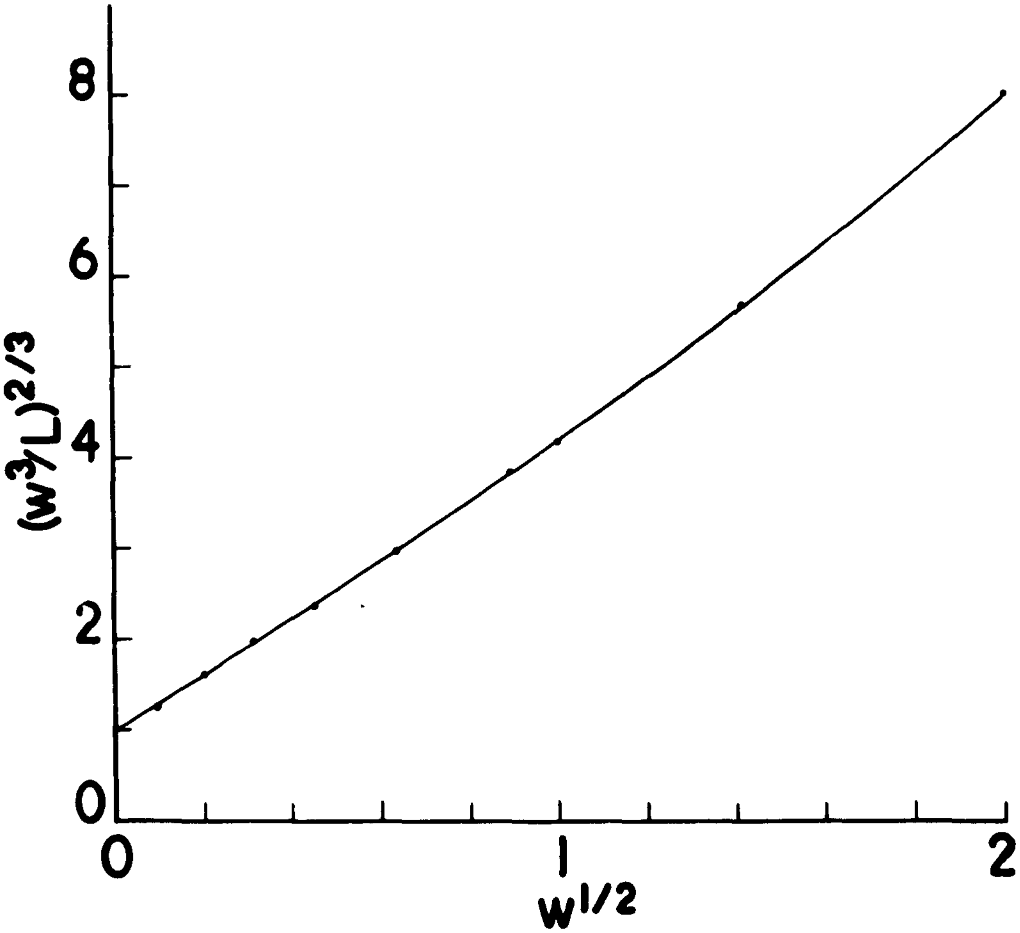

Fig. 1.1. An ionic pair repulsion effect of higher order than the limiting law

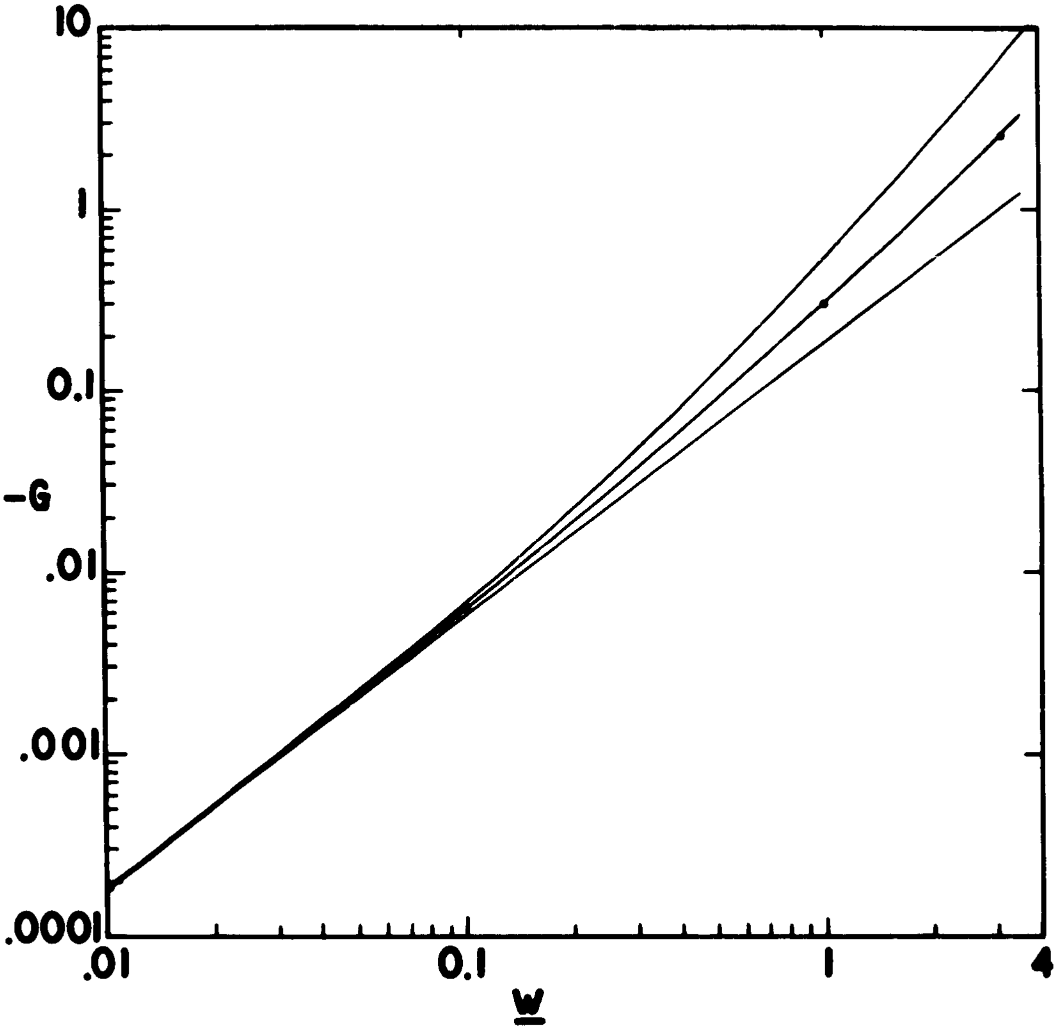

Fig. 1.2. A continuum ionic pair attraction effect of higher order than the limiting law. Circles show results of numerical integration. Low and high curves are for $\frac{2\sqrt{6}}{27}\underline{w}^{3/2}$ and $\frac{2\sqrt{6}}{27}\underline{w}^{3/2} + \frac{8\sqrt{10}}{75}\underline{w}^{5/2}$, respectively. A geometric mean curve is also shown.

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2. THE DIELECTRIC CONSTANT OF A DENSE GAS OF PLASMA

The present discussion is addressed to the purely practical problem of estimating the dielectric constant of a fluid mixture such as may occur in some applications involving Debye-Hückel theory. The thermodynamic properties of an ionic solution are in some degree dependent on its dielectric constant. If the system is a low density gas at such high temperatures that few ions are present, a good approximation for the thermodynamic purposes may be obtained using the assumption that the dielectric constant is unity. A more realistic estimate would be desired, however, if the fluid is of a high density approaching or typical of that of a liquid.

For the purposes of our brief considerations, some available approximations relating the dielectric constant of a fluid mixture and the properties of its constituent molecules will be mentioned. According to the well-known Clausius-Mosotti relation(22)

$$\frac{4\pi}{3}\frac{N}{V}\chi = \frac{D-1}{D+2}, \qquad (1)$$

the dielectric constant D may be obtained from the electric susceptibility χ as

$$D = \frac{1 + 2\left(\frac{4\pi}{3}\frac{N}{V}\chi\right)}{1 - \left(\frac{4\pi}{3}\frac{N}{V}\chi\right)} . \qquad (2)$$

For a mixture, the average susceptibility χ depends on mole fractions and susceptibilities of its individual constituents according to

$$\chi = \sum x_i \chi_i , \qquad (3)$$

with

$$\chi_i = \alpha_i + \frac{\mu_i^2}{3kT} \qquad (4)$$

where α_i is the mean polarizability and μ_i is the dipole moment for a molecule of the i^{th} constituent. For gases at high temperature involving atoms for which $\mu_i = 0$ and with $\mu_i^2/3kT$ negligible for any molecules present, equation 2 reduces to

$$D_1 = 1 + 4\pi\frac{N}{V}\sum x_i\alpha_i \qquad (5)$$

as a beginning approximation. When D_1 is estimated as equal to 4, then equation 2 gives infinity for D. A fairly extensive literature deals with the inaccuracy of the Clausius-Mosotti relation.

One of the objects of the present note is to point out that the Onsager relation(11)

$$\frac{4\pi}{3}\,\frac{N}{V}\,\chi = \frac{(D-1)(2D+1)}{9D} \tag{6}$$

is not too complicated for practical use in routine calculations, while it is completely well-behaved throughout the region of possible application. It can be put in the form

$$D = 1 + \frac{1}{4}[3(D_1-2) + (9D_1^2 - 12D_1 + 12)^{1/2}], \tag{7}$$

where D_1 is given by equation (5). An additional modification of Böttcher(23) relevant to molecular volume can lead to

$$\frac{4\pi}{3}\,\frac{N}{V}\,\chi = \frac{(D-1)(2D+1)}{9D}\left[1 - \frac{2(D-1)}{(2D+1)}\,\langle\alpha/a^3\rangle\right], \tag{8}$$

which gives

$$D = 1 + \frac{1}{4}\left[3\,\frac{D_1-2}{1-\langle\alpha a^{-3}\rangle} + \left\{9\left[\frac{D_1-2}{1-\langle\alpha a^{-3}\rangle}\right]^2 + 24(D_1-1)\right\}^{1/2}\right], \tag{9}$$

where $\langle\alpha a^{-3}\rangle$ is the effective value of the ratio between polarizability and the cube of the radius of the dielectric fluid cavity containing the polarized molecule. Table 2.1 gives extimated values of α/a^3 for the rare gases, based on measured polarizabilities, with the quantity "a" taken as half of the collision radius for the LJ 12, 6 potential. On the basis of the general trend in this table, one may note that α/a^3 appears to be of the general magnitude of 0.1 n, where n is the outer shell principal quantum number.

The over-all behavior of the calculated dielectric constant according to the Clausius-Mosotti and Onsager relations is shown in figure 2.1. As already noted, the former goes to infinity at $D_1 = 4$, and it also has a spurious branch of negative values coming in from $-\infty$ beyond $D_1 = 4$. The Onsager relation gives a single curve beginning quite identically with the other and becoming simply asymptotic with the dashed line $D = \frac{3}{2}D_1 - 1$ at higher density. If a Bottcher type relation with a $1 - \langle\alpha a^{-3}\rangle$ correction factor is used, the asymptote becomes

$$D = \frac{3(D_1+2)}{2(1-\langle\alpha a^{-3}\rangle)} - 2(1-\langle\alpha a^{-3}\rangle)\ . \tag{10}$$

An elaborate study of the dependence of experimental dielectric data over a wide range of gas density might be in order for some purposes. The intent in regard to the present discussion must be kept to the limited objective of providing estimation formulas that are not grossly in error. Nevertheless, it seems appropriate to examine a fragment of data having some special relevance to the question. As is well known, there is a connection between refractive index and dielectric constant. On page 6-111 of the Handbook of Physics,(24) there is a convenient comparison of some refractive index data (for the hydrogen F line) for water-ethanol liquid mixtures with data for the pure vapors (for the sodium D line) using the Lorenz-Lorentz equation, which has the form of the Clausius-Mosotti relation. On page 6-126 of the same reference work, one may find in connection with the discussion of the Ornstein-Zernicke theory of light scattering that it is helpful to use a formula of the Onsager type. Figure 2.2 shows these two alternate formulations and also, as a third, the Böttcher formula which includes the $1 - \langle \alpha a^{-3} \rangle$ correction, with $\langle \alpha a^{-3} \rangle$ taken as 0.15. The estimated refractive indices shown for the F line (4861Å) for the vapors are based on data of Wust and Reindel(25) in the case of H_2O and an extrapolation of data of Lorenz(26) (5893Å to 6708Å) for C_2H_5OH. The values shown by arrows are the less relevant vapor values for the sodium D line as indicated in the Handbook figure. The Böttcher formula can be made to give a closer fit by letting αa^{-3} vary from 0.13 for pure water to 0.175 for pure ethanol.

We should also mention that there is a literature of a priori treatment of the dielectric constant taking a more general point of view of statistical mechanics. In this connection, Brown(27) in a critical analysis of Bottcher's theory has indicated that its success may be due to compensation of errors.

It is possible that the discussion given may serve to support the view that simple estimates of dielectric constants should be feasible up into regions of high gaseous density. There still will be problems of finding acceptably estimated polarizabilities for the individual molecular and atomic species which may be present.

In connection with a presentation of shock tube results, Alpher and White(28) mention two forms for Kirkwood-type estimates of atomic polarizability. For N_I and O_I, they found that

$$\alpha = \frac{4}{9a_0} \sum (\langle r_i^2 \rangle^2), \qquad (11)$$

quoted from Hirschfelder, Curtiss and Bird,(22) gives estimates roughly 30 per cent greater than

Kirkwood's own equation,(29) with n as the number of electrons in an atom,

$$\alpha = \frac{4}{9a_0 n}\left[\sum \langle r_i^2 \rangle\right]^2 , \tag{12}$$

while experimental indications favor values intermediate between the two sets of estimates. The discrepancy becomes much larger for the heavier noble gases. The formula quoted from Hirschfelder et al, gives over 3 and 4 times the other in the cases of krypton and xenon, for which the experimental values are of the order of 2/3 of the smaller estimates.

Some difficulties arise in extending polarizability estimates to such high temperatures that there is extensive occupancy of higher atomic levels. It seems reasonable to assume that quite usually there is a single outermost electron for each atomic ion. Its principal quantum number should give a meaningful indication of the general magnitude of the polarizability of the ion. The strong dependence of the $\langle r_i^2 \rangle$ estimate on quantum number precludes a detailed analytical summing over the totality of thus sub-divided species. The difficulty in summing is especially inevitable when the sum diverges due to regarding the outer electron as being in a Coulomb field. We may improve the situation by accepting the modification due to Debye screening. A simple estimate can then be made if conditions involve such high temperatures that the occupancy of single states near the ionization limit and near the ground state are of the same general magnitude. The estimate may be based on the classical density of states, using

$$\langle r^m \rangle = \frac{h^{-3}\int_0^\infty \frac{4\pi}{3} p^3 \cdot r^m \cdot 4\pi r^2 dr}{h^{-3}\int_0^\infty \frac{4\pi}{3} p^3 \cdot 4\pi r^2 dr} \tag{13}$$

with $P^2/2\mu = (Z+1)(e^2/r)\exp{-\mathcal{K} r}$, where Z+1 is the charge of the ion without its outer electron. The result is

$$\langle r^m \rangle = (\tfrac{3}{2}\mathcal{K})^{-m}\,\Gamma(m+\tfrac{3}{2})/\Gamma(\tfrac{3}{2}) , \tag{14}$$

by which for a one electron system equation (11) gives

$$\frac{\alpha}{a_0^3} = \frac{100}{81(\mathcal{K} a_0)^4} . \tag{15}$$

An estimate for the dielectric constant using equation (7) with equation (5) could then be considered. However, with the Debye κ given by

$$\kappa^2 = \frac{4\pi e^2}{DkT} \frac{\sum Z_i^2 N_i}{V} = \frac{4\pi e^2}{DkT} \langle Z^2 \rangle \frac{N}{V} , \tag{16}$$

where

$$\langle Z^2 \rangle = \sum Z_i^2 N_i / \sum N_i = \sum Z_i^2 N_i / N,$$

there is an additional interrelation introduced in regard to D. This can be used in equation (6) and the result can be put in the form

$$D^3 (2D+1)^{-1} (D-1)^{-1} = \left[\frac{9}{10} \frac{e^2}{a_o kT} \langle Z^2 \rangle \right]^2 \frac{4\pi}{3} \frac{Na_o^3}{V} = x, \tag{17}$$

in which ground state contributions to the mean polarizability are ignored. The estimate for D is thus given by an implicit relation. A graphical representation of equation (17) is shown in Figure 2.3. It may be noticed that it seems to predict two distinct regimes, involving approach to the two asymptotes $D = 2x - \frac{1}{2}$ and $D = 1$. The intuitive line of argument leading to the result seems to have been of a nature favoring acceptance of the high dielectric constant prediction in preference to $D \approx 1$ for a highly dense but incompletely stripped plasma. There must naturally be a question whether there is any region of approximate applicability of (17) for actual physical systems. It is clear that exact validity is not to be attributed to the result, since all items in its schematic derivation are imprecise in one way or another. One may note, however, that the assumption may sometimes have been made that unity for the dielectric constant was appropriate for a dense plasma in the high ion density limit. On the basis of the present result, one may at least ask whether there may not be dense plasma-type physical systems for which the dielectric constant would be more like that for a liquid.

Table 2.1. Values of αa^{-3} for the Rare Gases

He	Ne	Ar	Kr	Xe
0.09	0.15	0.31	0.42	0.46

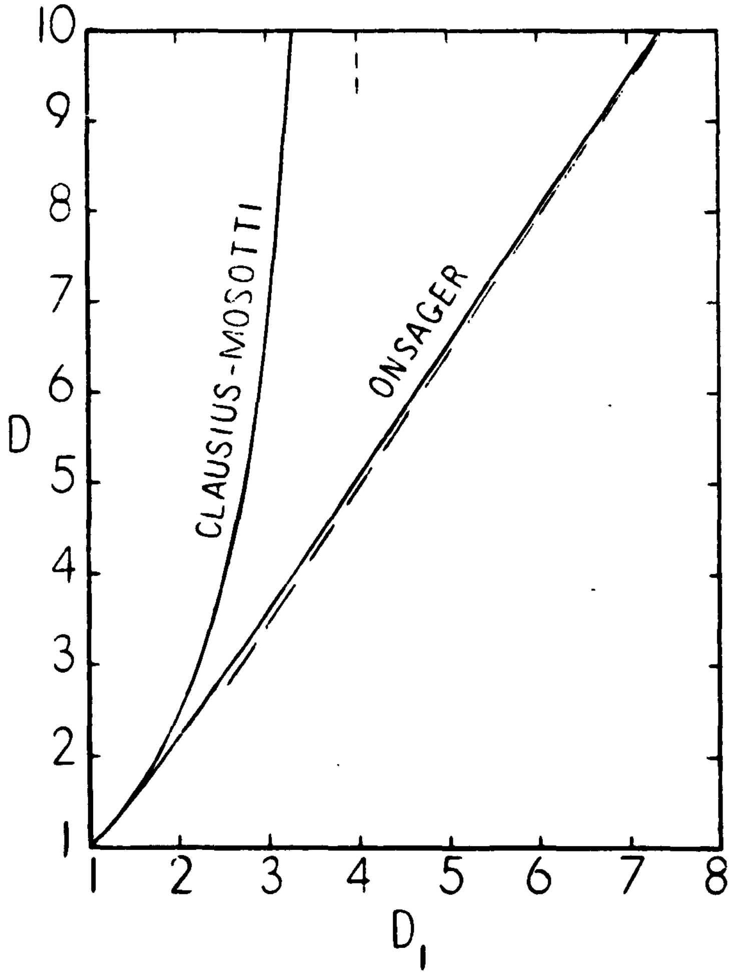

Fig. 2.1. Non-linearity of dielectric constant versus its first order linear estimate.

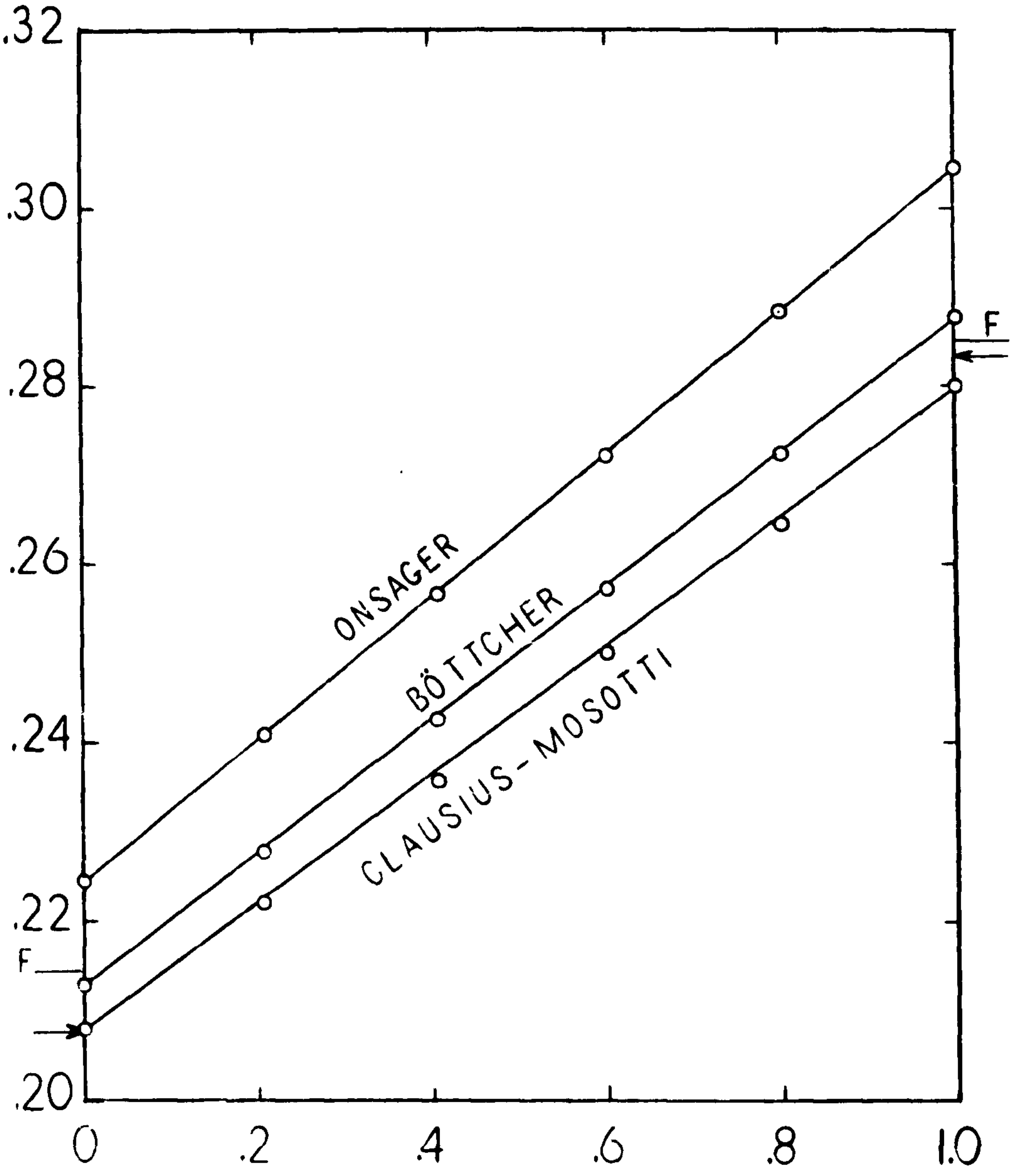

Fig. 2.2. Mean specific refractivity, $\frac{4\pi}{3} N\chi/\langle M\rangle$ versus weight fraction of ethanol in water-ethanol solutions, using $D = n^2$ in equations 1, 6 and 8. Values marked F are for the pure vapors.

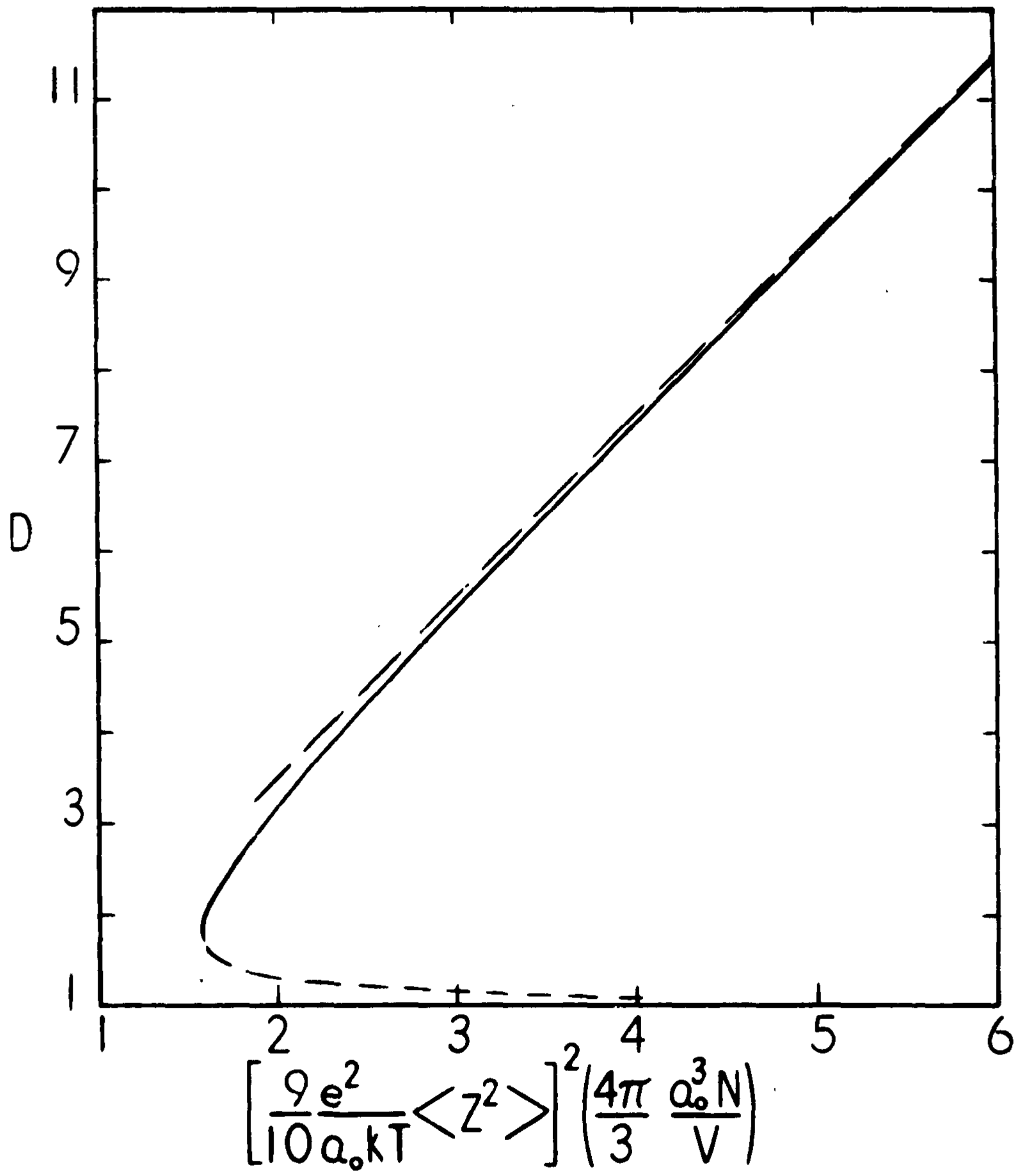

Fig. 2.3. Limiting estimate for dielectric constant of dense partially stripped plasmas.

3. CONSIDERATIONS ON INTERACTION POTENTIALS FOR THERMODYNAMIC ESTIMATES AT HIGH TEMPERATURES

In estimating thermodynamic effects attributable to excluded volumes for high temperature gases, one needs pair potential functions suited to the special needs of the problem. One extreme might be to assume that atoms and molecules could be considered as rigid spheres of suitable sizes. An opposite extreme would be to suppose that much could be known as to very exact details of the interaction potentials. We may recall that molecular orbital estimation of pair energies is in principle possible for any physical system, but the large number of kinds of pairs occurring simultaneously even in a relatively simple system would make such a program very difficult. In making estimates for large numbers of cases, it seems but natural to prefer to rely on empirical and semi-theoretical expressions in the absence of direct evidence opposing such a procedure.

In the relevant literature forming the immediate background as far as selection of potentials for high temperature calculation is concerned, we would mention in particular the interesting papers of Amdur and Mason,(30) of Amdur and Ross,(31) and, especially, of Amdur, Mason, and Jordan.(32). In the last, special emphasis as to the softness of the potential for the N_2-N_2 system is given, on the basis of Ar and He scattering in N_2 gas.

The one-exp-six potential resembles the exp-six potential in some ways, including the detail of having a somewhat softer repulsion at close approach than do the Lennard-Jones type potentials.(33) For a while, it was hoped that the new one-exp-six potential might prove useful in the representation of these indirect scattering results. After a somewhat lengthy study, it was inferred that this was quite difficult of accomplishment, however. This conclusion was arrived at somewhat indirectly, and in the following way.

The flexibility of the curve for equation 2 of reference 33 was studied in the case of the Ne-Ne interaction, with F_1 as given there for equation 3, but with F_2 and F_3^{-1} taken as polynomials in r/r_m with positive coefficients conforming approximately to the united atom treatment of Bingel.(34) The result, somewhat unhappily, seemed not completely successful for showing a capability for extensive adjustment of the potential curve. Actually, this should not be very disappointing for the case of neon, since the estimated parameters either based only on thermal data or modified to the proper Coulomb repulsion at close approach are in fairly close agreement with scattering data(33) and also with some preliminary MO calculations of Ransil(35) which give an intermediate indication between the curves for the two estimated γ parameter values.

The indirect scattering results of Amdur, Mason, and Jordan for the N_2-N_2 potential are shown by the solid line in figure 3.1. The dashed and dotted curves show the one-exp-six and the Lennard-Jones 12,6 curves, respectively, also reduced to virial data parameters.(36) Assuming that the scattering results are essentially correct, one must interpret these curves as indicating that little benefit can be gained from using the one-exp-six potential in preference to the LJ 12,6 potential for the N_2-N_2 interaction. As may be seen from the figure, the scattering data are in the general range of $U/\epsilon = 20$ to 100, while even at $U/\epsilon = 1000$ there is only a very moderate difference in the r/r_m prediction of the two other curves, particularly as compared with the indicated difference of the indirect scattering potential curve. Under this circumstance, it has appeared proper to follow the conservative course of using a 12th power repulsion potential with the usual 6th power attraction potential augmented by such other theoretical inverse power terms as the particular pair may require.

The field of application recommended for present use of such potentials is somewhat limited. The immediate objective is the estimation of excluded volume effects as they enter in thermodynamic property calculations for gases at somewhat elevated temperatures. It turns out that pairwise effects are comparatively easily estimated in this field when such Lennard-Jones type potentials and their extensions are available. It is naturally to be hoped that such estimates will be adequate for the type of use envisioned. Even if questions of reliability must arise at the highest temperatures of application, there still may be considerable usefulness for the simple magnitude estimates which are thus provided.

In the somewhat different field of transport properties of gases, it is often recognized that a more stringent requirement for accuracy of the potential function must apply. The entire transport effect is governed by the cross sections that are appropriate to the process, so that uncertainties about the potential function directly affect the whole result rather than some moderate or small correction quantity contributing to the result. Nevertheless, it can be hoped that estimates of the proper general magnitude can be arrived at in the transport field, also, since realistic estimates of sizes of atomic fragments are expected on the present basis.

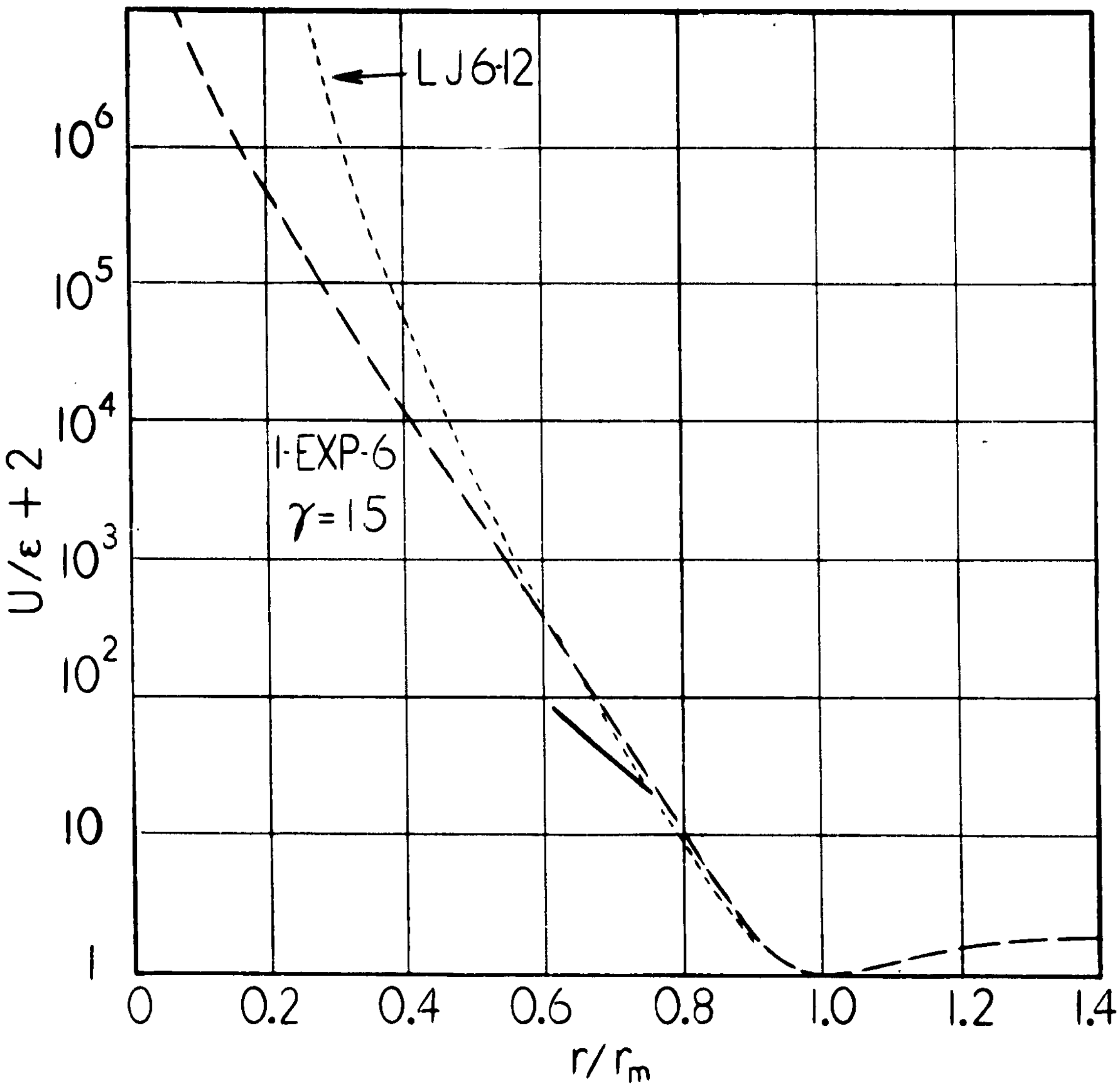

Fig. 3. 1. N_2-N_2 potential energy of interaction. The solid curve is based on indirect scattering evidence. The other curves show one-exp-six and Lennard-Jones 6-12 extrapolations based on virial and other data.

4. ESTIMATES OF NON-BONDING INTERACTIONS IN HIGH TEMPERATURE GASES AND PARTIALLY IONIZED PLASMAS

The interactions between the molecules, or molecule-like fragments, in a gas are of interest in regard to various macroscopic properties. For many pure substances and for some mixtures, there are observational data capable of indicating the approximate behavior of these interactions. For the atoms and ions which may occur in a gas under conditions of high temperature or of other special excitation, there may not happen to be similar data pertaining to interactions. Under these circumstances, it may be useful, or at least of interest, to examine such predictions of non-bonding interactions as may be based on sound theoretical and semi-empirical rules. It is evident, of course, that effects of chemical bond formation would need to be taken into account separately if omitted from the interactions directly included.

There is thus a problem of estimating intermolecular interactions well enough to permit acceptable estimates of the associated macroscopic effects in question. This is a somewhat complex problem. At extremely high temperatures, the only constituents significantly present are electrons and atomic ions either singly or multiply charged, or even stripped to bare nuclei. At intermediate temperatures, and particularly at high density, molecular ions may be present in appreciable amounts. Further, in some range of moderate temperature, neutral atoms and molecules become sufficiently populous to require estimates for the interaction between charged and neutral particles. Finally, one may note that in the lower regions of elevated temperature, the constituents to be considered may well be limited to molecules and atoms only. We shall find it convenient to begin by considering the selection of interaction parameters for such a non-ionized mixture first, then moving on later to more complex cases.

1. Interaction effects in a non-ionized gas mixture

Even though we begin with a simplified problem of estimating interaction effects in the absence of ionization, we cannot hope to make estimates that are highly precise and reliable. It must be recognized that intermolecular interactions are of considerable complexity. In principle, estimates of different quality or involving various degrees of approximation are possible. In the present case of negligible ionization, we shall be satisfied to begin with known empirical parameters for conventionally accepted potentials. Extension of estimates to unobserved pair potentials will then follow from various "rules" which we hope are at least plausible.

A rule that is frequently used in estimating second virial coefficients for mixtures of gases for which the Lennard-Jones 12, 6 potential,

$$\varphi(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right], \tag{1-1}$$

is adequate approximates interaction force constants by using a geometric mean rule for the energy parameter

$$(\varepsilon/k)_{ij} = (\varepsilon/k)_i^{1/2}\,(\varepsilon/k)_j^{1/2}, \tag{1-2}$$

and an arithmetic mean rule for the collision distance, $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ or

$$(b_o)_{ij} = \left[\frac{1}{2}(b_o)_i^{1/3} + \frac{1}{2}(b_o)_j^{1/3}\right]^3 . \tag{1-3}$$

A geometric mean rule has sometimes been used for b_o also,

$$(b_o)_{ij} = (b_o)_i^{1/2}\,(b_o)_j^{1/2} . \tag{1-4}$$

One may note that a more elaborate potential function would require a correspondingly more complicated set of mixture relations. Under this circumstance, it is of interest to observe that some support for relatively simple combination rules can be found even when some effort is made to take account of molecular shape.

In initiating this special consideration of mixture rules, we shall examine pair excluded volumes using some relations for rigid convex molecules. Kihara(37) has shown that for spherocylindrical diatomic molecules the pair excluded volume is given by

$$b_o = \left[\frac{2\pi}{3} r_o^3 + \pi l r_o^2 + \frac{\pi}{4} l^2 r_o\right] N_o, \tag{1-5}$$

where l may be taken as the internuclear distance within the molecule and r_o is the value of σ, the exclusion radius between atoms of separate molecules. For diatomic compounds for which the two atoms do not have the same radius, as illustrated in Figure 4.1, we make use of general relations for rigid convex molecules. The second virial between two differing molecules according to a result quoted by Kihara is

$$B_{AB} = \left[\frac{1}{2}(V_A + V_B) + \frac{1}{8\pi}(M_B S_A + M_A S_B)\right] N_o . \tag{1-6}$$

We will take the exterior surface of the rigid convex model for either diatomic molecule as made up of two spherical surfaces for its two atoms, joined by a tangent conical surface, with R_1 and R_2 as the radii of the individual atoms and with ℓ as the distance between centers of the two spheres. Then the evaluation of the theoretical relations gives for the particular molecule

$$V = \frac{\pi}{3}\left\{\ell(R_1^2 + R_1R_2 + R_2^2)\left[1 - \left(\frac{R_1 - R_2}{\ell}\right)^2\right]^2 + R_1^3\left[2 + 3\left(\frac{R_1 - R_2}{\ell}\right) - \left(\frac{R_1 - R_2}{\ell}\right)^3\right]\right.$$

$$\left. + R_2^3\left[2 + 3\left(\frac{R_2 - R_1}{\ell}\right) - \left(\frac{R_2 - R_1}{\ell}\right)^3\right]\right\} \tag{1-7}$$

$$M = \pi\ell + 2\pi R_1\left[1 + \frac{R_1 - R_2}{\ell}\right] + 2\pi R_2\left[1 + \frac{R_2 - R_1}{\ell}\right] , \tag{1-8}$$

and

$$S = \pi\ell(R_1 + R_2)\left[1 - \left(\frac{R_1 - R_2}{\ell}\right)^2\right] + 2\pi R_1^2\left[1 + \frac{R_1 - R_2}{\ell}\right] + 2\pi R_2^2\left[1 + \frac{R_2 - R_1}{\ell}\right] . \tag{1-9}$$

One notes that in the case of like atoms the spherocylindrical case is regained and that with $r_o = R_1 + R_2 = 2R$, the prediction agrees with equation (1-5).

Values of ℓ have been obtained by taking values of r_e listed by Herzberg(38) and making an approximate adjustment to the ground vibrational state given by $\ell = r_e(1 + \frac{1}{4}\frac{\alpha_e}{B_e})$. These are listed in Table 4.1 for various diatomic molecules which can be formed from constituent atoms in high temperature air. In the cases of N_2 and O_2, we have determined the atomic radii on the basis of the empirical exclusion volumes b_o as obtained from the fitting of Lennard-Jones 12, 6 potentials to actual gases(39). The radius as thus found for the bound atom has also been taken as radius for the isolated atom and used in accord with the same fundamental formulas to estimate b_o for hypothetical atom-atom and atom-molecule second virials. The ordinary mixture rule for b_o was also tested on these numbers, in an estimate of the atom-molecule b_o from the atom-atom b_o and the molecule-molecule b_o using

$$(b_o)_{AM} = \left[\frac{1}{2}(b_o)_{AA}^{1/3} + \frac{1}{2}(b_o)_{MM}^{1/3}\right]^3 . \tag{1-10}$$

Actual numerical results from this and ensuing considerations are summarized in Table 4.2. The estimates in the present case are found to agree very well with $(b_o)_{AM}$ values obtained directly using formulas for the rigid-convex model.

A somewhat similar use of combination formulas was made in obtaining a radius for the C atom from the b_o for CO, taking the radius for the O atom the same as in O_2. Then with the known internuclear distance for C_2 and this C atom radius, the value of b_o for C_2 could be estimated as 87.5 cm^3/mole. A very consistent value of 86.1 cm^3/mole is obtained from the value of 69.22 cm^3/mole for b_o for CO and the value 54.7 cm^3/mole for b_o for O_2, using an extended rule

$$(b_o)_{CO} = \left[\frac{1}{2}(b_o)_{C_2}^{1/3} + \frac{1}{2}(b_o)_{O_2}^{1/3}\right]^3 . \tag{1-11}$$

One may note that the customary use of a rule of this form would be for the purpose of estimating b_o for the interaction virial between C_2 and O_2 molecules rather than between CO molecules!

We have been encouraged by this agreement to also apply the extended rule in making an estimate for b_o for the second virial due to purely hypothetical non-bonding interactions between CN's, taking the observed b_o for N_2 and the estimated b_o for C_2.

After b_o's between like "molecules" have been estimated in this way, one may use the similar regular combination rule to obtain b_o's for all mixture second virial coefficients.

Other provisional extensions of combination rules have also been employed in seeking estimates for the ϵ/k parameters. If it be assumed that the attraction potential varies as the 6th power of the distance as accepted for the dispersion energy term, and if the assumption be tried that the long-range attraction potential between diatomic molecules can be approximated as the sum of atom-atom attraction potentials,(32) then the relation

$$(\varepsilon/k)_{A_1A_2}(b_o)^2_{A_1A_2} + (\varepsilon/k)_{A_1A_{II}}(b_o)^2_{A_1A_{II}} + (\varepsilon/k)_{A_IA_2}(b_o)^2_{A_IA_2} + (\varepsilon/k)_{A_IA_{II}}(b_o)^2_{A_IA_{II}}$$

$$= (\varepsilon/k)_{M_1M_2}(b_o)^2_{M_1M_2}, \qquad (1\text{-}12)$$

is obtained. Here molecule M_1 is made up of atoms A_1 and A_I, while the molecule M_2 is made up of atoms A_2 and A_{II}. The proportionality between b_o and σ^3 has been used in obtaining this relation. We note that a discussion by Salem,(40) on short range repulsive forces, has indicated that the forces are locally additive over pairs of atoms, one in each of two interacting molecules, if their electron density is best described by localized orbitals and if the overlap of orbitals between molecules is in one localized interatomic region.

With values of b_o for the various pairs taken on the basis of mixture rules given earlier, this rule furnishes a method for interrelating ε/k values for atoms and molecules. Thus, from O_2, for which $\varepsilon/k = 116°$ empirically,(39) we now get $\varepsilon/k = 81.5°$ for O atoms and $\varepsilon/k = 95.1°$ for the O-O_2 interaction. We note that the geometric mean rule between 116° and 81.5° suggests that ε/k for the O-O_2 interaction might be near to 97.2°. Similarly, the empirical 95.42° for N_2 leads to $\varepsilon/k = 58.3°$ between non-bonding N atoms and to 73.3° for the N-N_2 non-bonding interaction. The geometric mean between 95.42° and 58.3° suggests that ε/k for the N-N_2 interaction might be near 74.6°, which appears satisfactorily near to the 73.3° estimate.

In the case of CO molecules, the relation has the form

$$(\varepsilon/k)_{C\cdot C}(b_o)^2_{C\cdot C} + 2(\varepsilon/k)_{C\cdot O}(b_o)^2_{C\cdot O} + (\varepsilon/k)_{O\cdot O}(b_o)^2_{O\cdot O} = (\varepsilon/k)_{CO\cdot CO}(b_o)^2_{CO\cdot CO}. \qquad (1\text{-}13)$$

Such a single relation alone could not determine both the $(\varepsilon/k)_{C\cdot C}$ and the $(\varepsilon/k)_{C\cdot O}$ values. In view of preceding apparent successes of simple regular relations, it seems reasonable to try the tentative assumption that the C·O interaction term might be taken to be approximated as the cross product term of a perfect square. Then with O·O constants inferred from O_2, one can arrive at $(\varepsilon/k)_{C\cdot C} = 54.7°$ and $(\varepsilon/k)_{C\cdot O} = 65.4°$. It is an item of some satisfaction that the geometric mean between this $(\varepsilon/k)_{C\cdot C} = 54.7°$ and the $(\varepsilon/k)_{O\cdot O} = 81.5°$ gives $(\varepsilon/k)_{C\cdot O}$ as 66.8°, in such good agreement with the other provisional estimate.

For molecular pairs in general, the ordinary geometric mean rule for $\mathcal{E}/k$ has been applied. The estimates accepted are listed in Table 4.3. These values ignore permanent dipole effects.

No claim is made that the special combination rules of the present bootstrap operation are exceptionally reliable. The situation is simply that resort to such rules has appeared appropriate in the absence of direct data.

For non-bonding systems, the fact that these various combination rules give estimates agreeing to within one or two percent is encouraging. We should not give too much credence to these estimates for bonding systems, however. Indeed, it is to be noted that in the case of NO, the geometric mean of $\mathcal{E}/k$'s for N_2 and O_2 is 105.2°, while an unpublished study of PVT data for NO has suggested a value of 119° with large additional association effects due to weak chemical bonding. Since CN also has an odd number of electrons, its mixture-type force constants would certainly be of poor reliability unless corresponding adjustments for association could also be made. For effect on the calculated over-all properties of air, this should be of small consequence since so little CN would be present. For mixtures in which chemically inactive constituents are the preponderant species, neglect of weak chemical association among trace species would appear quite inconsequential.

2. Interactions involving ions

We come now to the estimation of interactions in gases in which there is some ionization. We have already employed a model in which the interaction between two molecules is approximated as the sum of interactions between their respective atoms. Accepting empirical interactions between atoms as estimated on this basis, we wish to consider how the estimates of interatomic interaction need to be modified if one or both of the atoms would happen to be electrically charged.

In the preceding approximate treatment of interatomic interactions, we used the conventional L J 12, 6 potential. The empirical information concerning the repulsion potential is thus in a form pertaining to a simple R^{-12} function and appears likely to be most easily extended to other cases if this form is retained.

Thus, in making our admittedly tentative estimates of non-bonding pair effects due to atomic ions or atoms, it is expedient to postulate a hypothetical potential energy of the form

$$U = k_{12}R^{-12} - k_6R^{-6} - k_4R^{-4} + k_1R^{-1}. \qquad (2\text{-}1)$$

With U and R in atomic units (e^2/a_o for U and a_o for R) and with Z^* as net ionic charge, we have

$$k_1 = Z_A^* Z_B^* \qquad (2\text{-}2)$$

by the Coulomb relation, and

$$k_4 = \frac{1}{2}(Z_A^*\alpha_B + Z_B^*\alpha_A) \qquad (2\text{-}3)$$

as the approximate induction energy.(22) The quantity α is used here to represent polarizability in units of a_o^3. For k_6, the relation

$$k_6 = k_6^\bullet + \Delta k_6 \qquad (2\text{-}4)$$

is used, with $k_6^\bullet$ due to the London dispersion forces and Δk_6 due to induced quadrupole effects as derived by Margenau,(41) here with (hν)'s replaced by I's (but 2I has also been suggested),

$$\Delta k_6 = \frac{3}{8}\left[Z_A^{*2}\alpha_B^{\,2}I_H^{-1}f_B^{-1} + Z_B^{*2}\alpha_A^{\,2}I_AI_H^{-1}f_A^{-1}\right]. \qquad (2\text{-}5a)$$

We might also consider $f_i = \frac{1}{4}(I_i/I_H)^2\alpha_i$, based on a relation of Margenau(42) for a collection of harmonic oscillators, which would convert (2-5a) to

$$\Delta k_6 = \frac{3}{2}\left[Z_A^{*2}\alpha_B I_B^{-1} I_H + Z_B^{*2}\alpha_A I_A^{-1} I_H\right]. \qquad (2\text{-}5b)$$

The ionization energy of atom A or B is I_A or I_B, with I_H used here to convert to atomic units via $e^2/a_o = 2I_H$. The f values in Margenau's result have the meaning of oscillator strength as obtained empirically from the index of refraction. Some f values given by Margenau(42, 43) are listed in Table 4.4, with some conjectured estimates based on hopeful assumptions of additivity and regularity and presumed to be of the correct order of magnitude.

For $k_6^\bullet$ there are various approximate expressions. With I_A and I_B as above, one may consider

$$k_6^\bullet = \frac{3}{4}(I_A^{-1}I_H + I_B^{-1}I_H)^{-1}\alpha_A\alpha_B, \qquad (2\text{-}6)$$

which is closely related to an expression given by Hornig and Hirschfelder.(44) Another form is

$$k_6^\bullet = \frac{3}{2}\alpha_A\alpha_B \Big/ \left(\sqrt{\alpha_A/n_A^\bullet} + \sqrt{\alpha_B/n_B^\bullet}\right) \qquad (2\text{-}7)$$

where $n_A^\bullet$ and $n_B^\bullet$ are said to be the numbers of electrons in the outer shells of the two molecules according to reference 22. This is also written as

---

($a_o = 0.52917_2 \times 10^{-8}$ cm, $e^2/a_o = 27.21$ e.v. or 315,700°K equivalent).

$$k_6^\circ = \frac{4\left[\Sigma\overline{r_A^2}\right]^2\left[\Sigma\overline{r_B^2}\right]^2}{9\left[n_A^\circ\Sigma\overline{r_B^2} + n_B^\circ\Sigma\overline{r_A^2}\right]} \qquad (2\text{-}8)$$

with n_A° and n_B° now as the total numbers of electrons if based on the original Slater-Kirkwood result reported by Kirkwood(29). This becomes

$$k_6^\circ = \frac{2}{9n_A^\circ}\left[\Sigma\overline{r_A^2}\right]^3 \qquad (2\text{-}9)$$

for like pairs, still with the sums $\Sigma\overline{r^2}$ over the electrons expressed in atomic units when equation (2-1) is so expressed. Estimates for $\Sigma\overline{r^2}$ can be made using the well known-rules for Slater screening constants.

For mixture constants, convenience of estimation has led to use of the well-known combination rule

$$(k_6^\circ)_{AB} = (k_6^\circ)_A^{1/2}\,(k_6^\circ)_B^{1/2} \qquad (2\text{-}10)$$

which is regarded as rather successful for practical estimation purposes.

On the basis of equation (2-6), the Δk_6 due to Margenau can be written in the convenient form

$$\Delta k_6 = Z_A^{*2}(k_6^\circ)_B\big/f_B + Z_B^{*2}(k_6^\circ)_A\big/f_A. \qquad (2\text{-}11)$$

At this point, it appears appropriate to turn to observational results for empirical details for practical potential functions. One can take the L J 12, 6 potential

$$U = 4\varepsilon[(r_0/r)^{12} - (r_0/r)^6]$$

as used for the interaction energy between non-bonding neutral systems, and express the parameters in atomic units. One thus finds

$$k_{12} = \frac{2(\varepsilon/k)R_0^{12}}{(hc/k)R_\infty} \qquad (2\text{-}12)$$

and

$$k_6 = \frac{2(\varepsilon/k)R_0^{6}}{(hc/k)R_\infty}\,, \qquad (2\text{-}13)$$

where R_∞ is the Rydberg and $R_o = r_o/a_o$. If the force constants b_o and ϵ/k are in units of cm^3/mole and degrees K, respectively, these give

$$k_6 = b_o^2(\epsilon/k)\Big/(2759\ cm^6 deg\ mole^{-2})$$

and

$$k_{12} = 10^4 k_6 b_o^2\Big/(349.5\ cm^6 mole^{-2})$$

for practical calculations.

In Table 4.5, empirical parameters are listed for several atoms based on estimates from various sources, including Table 4.3. The values of k_{12} and k_6 in Table 5 follow from these parameters. Values of $(k_6)_{calc}$ based on equation (2-9) are also given.

The short range repulsion is the major contribution to the interaction potential for which no theoretical expression in an inverse power of the distance is at hand. It is often admitted that an exponential repulsion potential is superior to the inverse power representation. Some merit has been evident in a "one-exp-six" potential, also(33). For present purposes of convenient estimation, it has appeared appropriate to examine the behavior of k_{12} empirically in a fairly direct way. The repulsion interaction might be expected to show some relation to the wave functions for the electrons of the outermost shell of the atom. It may be noted that the exponential factor in the wave function, according to the Slater screening constant system, is $\exp(-Z_e R/n^*)$ where $Z_e = Z-S$ and S is the screening constant as given by well-known rules,(22) with n^* representing the effective principal quantum number. This can suggest the hypothesis that the interaction between outer shell electrons of different systems might be comparable at like average values of $Z_e R/n^*$. If the hypothesis were true, then it might be possible to write the repulsive potential $k_{12}R^{-12}$ as $t_n^2\left[\frac{n^*}{mZ_eR}\right]^{12}$, where t_n is the number of outer shell electrons for each of the two like systems, and m is an unknown parameter. The supposed relation can also be written as

$$n^*[k_{12}t_n^{-2}]^{-1/12} \approx mZ_e.$$

On evaluation, values as listed in Table 4.5 are obtained, with outer shell Z_e values as given by the Slater screening rules listed in the next column. These are plotted in Figure 4.2, in which a linear relation indeed appears to be very good but with a non-zero intercept for the line. The straight line shown is equivalent to the equation

$$k_{12} = t_n^2 \left[\frac{n^*}{0.28 + 0.128\,Z_e}\right]^{12} . \tag{2-14}$$

The filled circles show the points for Kr and Xe if n is used rather than the Slater n^* in calculating the ordinate. It might seem that improvements in screening rules for the effects of inner electrons should permit n^* to be replaced by n throughout the range covered. Following such a hypothesis, one finds that if 0.92 be taken as the screening due to each electron with n less by two than n for the valence electrons, the Kr and Xe can be plotted near the new straight line in Figure 4.3, for which

$$n[k_{12}t_n^{-2}]^{-1/12} = 0.30 + 0.12\,Z_e .$$

However, this modification appears unnecessary for the more immediate purpose of making estimates for atomic ions with n near 2 for the valence shell. Additional Z_e values from Slater screening constants for outer shell electrons for atomic ions ranging from negative to triply positive and up to argon are given in Table 4.6.

A direct correlation of Lennard-Jones 12, 6 force constants for molecules has been given by Brandt$^{(45)}$. He found that k_6 and σ (or r_0) could be related empirically to the molecular polarizability and that the relationships could be extended to interactions between segments of chain molecules. We do not use his correlation for the present estimates since we are interested in atomic ionic systems for which observed polarizabilities may not be available. Also, we would not be able to take σ to be unaffected by the presence of R^{-4} and R^{-1} potentials which occur for atomic ions.

In the present estimates of interactions between like atomic ions, equations (2-9) and (2-14) have been used for $k_6^{\bullet}$ and k_{12}. In case an isoelectronic atom with more directly known empirical $k_6^{\bullet}$ and k_{12} values exists, the ratio between observed and calculated values for it is used to obtain improved estimates for the atomic ion corresponding. Ratios of $k_6^{\bullet}/(k_6^{\bullet})_{calc}$ based on Table 4.5 are thought to compare favorably with the differing ratios of Table 13.3-1 of reference 22. For the interaction between unlike systems, it is found convenient to use the geometric mean rule not only for $k_6^{\bullet}$ according to equation (2-10), but also for k_{12}. This is equivalent to using equations (1-2) and (1-4) as combination rules in the absence of ionic effects. For the other k_n's, equation (2-2) has been used for k_1, (2-3) for k_4 and equations (2-4) and (2-11) in obtaining k_6 from $k_6^{\bullet}$. For values of polarizability to use in estimating k_4, theoretically conjectured magnitudes for atomic ions and experimental values for molecules were mainly used.

In the various parts of Table 4.7, estimates for the various k_n's are given for constituents of air present(4) to the extent of 10^{-4} or more in mole fraction up to atmospheric pressure and up to about 15,000°K.

The complete problem of estimation of pair interactions between molecule-like fragments in an ionized gas would be quite formidable if no simplifications were introduced. For isolated cases of interatomic and intermolecular interaction one might suppose it to be reasonable to study the interactions by making use of recent developments in solving the Schroedinger equation by means of high speed computing techniques. The calculation of even one pair potential by such methods appears still to be a special problem of considerable magnitude. The practical impossibility of introducing the complete <u>a priori</u> problem is made evident by counting the number of pair interactions when every possible constituent is considered.

For a gas mixture involving n_t elements of which n_b are capable of bond formation, we wish to count the number of molecule-like constituents including atomic ions, atoms and diatomic molecules and ions. For each constituent element of atomic number Z_i, the number of possible positive atomic ions is Z_i. For each element there can also be the neutral atom and quite usually a negative atomic ion, also. This makes $Z_i + 2$ mono-nuclear atomic ion type species for each element. For species with two nuclei, the diatomic molecules formed as all pairs between neutral bonding atoms are included, with an equal number of positive molecular ions and an equal number also of negative molecular ions formed by removal or addition of an electron. The total number of these species is evidently

$$N_n = \sum_{i=1}^{n_t} (Z + 2)_i + \frac{3}{2} n_b(n_b + 1).$$

The number of separate pair interactions among these N_n species is $\frac{1}{2}N_n(N_n+1)$. In this estimate, we omit multiply charged molecular ions from the total.

If air is the gas mixture under consideration, the elements present may be listed in their order of decreasing abundance as N, O, Ar, and C, with H added as at least a trace element if the occasional fiction of perfectly dry air is not adhered to. In some calculations, the rarer of the rare gases are sometimes considered as included in the argon. This counting of constituents would give $n_t = 5$ as the total number of elements, with $n_b = 4$ as the number that are bonding. The values of $Z_i + 2$ are 9, 10, 20, 8 and 3, respectively for the elements as listed, giving $\sum(Z+2)_i = 50$. With $\frac{1}{2}n_b(n_b+1) = 10$, one has $N_n = 50 + 30 = 80$ and the number of pairs among these is $\frac{1}{2}N_n(N_n+1) = \frac{1}{2} \cdot 80 \cdot 81 = 3240$. Of these, 120 are for neutral-neutral combinations, 975 are for ion-neutral combinations, and 2145 are for ion-ion combinations. Even this is an incomplete accounting since tri-atomic systems have been omitted.

For practical estimates, there is a useful simplification if interactions between trace species are seen to be too trivial for inclusion. Thus, the number of distinct species included in Table 4.7 is only 19. Not all of the interactions among these are important for estimation of their net thermodynamic effect. In Table 4.8, check marks are shown for the pair interactions for which the product of mole fractions(4) for the two species of the pair exceeds 10^{-4}. This includes 24 of the 45 neutral-neutral pairs listed, 15 of the 90 ion-neutral pairs, and 11 of the 55 ion-ion pairs. For the neutral-neutral pairs, the L J 12, 6 force constants have already been listed in Table 4.3, based on preferred combination rules. For the 15 ion-neutral pairs to be considered, with another added for comparison, the equivalent force constants b_m, ε/k and γ are listed in Table 4.9. The parameter γ here is the quantity in the interaction potential

$$U = \frac{1}{2}\varepsilon\left[(1+\gamma)(r_m/r)^{12} - 4\gamma(r_m/r)^6 - 3(1-\gamma)(r_m/r)^4\right]$$

as written by Mason and Schamp.(46) The quantity b_m is $\frac{2\pi}{3}N_o r_m^3$ and is not the same as the usual b_o. For $\gamma = 1$, the potential becomes the L J 12, 6 potential, for which $b_m = \sqrt{2}\ b_o$. Tabulated values of the second virial coefficient and its first and second derivatives, based on the 12, 6, 4 potential, given in Chapter 6. The analytic relations for obtaining r_m, ε/k and γ

from k_{12}, k_6, and k_4 are also included in that discussion. For the ion-ion repulsions, the estimated potentials are shown graphically in Figures 4.4 to 4.15. It may be of interest in regard to these to note how great the Coulomb repulsion energy is when the short range repulsion provides significant exclusion from closer approach. The approximate exclusion radius at still greater energies could presumably be based on these curves, also, with due consideration for uncertainties of extrapolation.

Discussion

It appears likely that an overly optimistic view is required to even offer for consideration such conjectural estimates of pair energies as are given here. In spite of the extreme uncertainty of some of the semi-theoretical quantities employed, it is hoped that the numbers may permit a meaningful extension of excluded volume effects into regions of high temperature.

It is desired to put very strong emphasis on a disclaimer as to completeness of solution ot the practical problem of estimating interaction effects. The force constant estimates given here are admittedly hypothetical. They are contingent on the assumption that chemical bonding may be excluded from consideration for certain applications. There is therefore also the cognate assumption that such direct effects of chemical bonding as must be included can actually be taken into account in some separate but compatible way.

An examination of the H-H hypothetical potential according to the LJ 12, 6 constants in table 4.5 has served to emphasize that it is inappropriate to assume that genuinely valid atom-atom potentials applying strictly for isolated atoms have been obtained. Theoretical $^3\Sigma$ potential estimates are well known for the case of hydrogen and are found to differ very considerably from the 12, 6 potential of table 4.5. In any cases in which theoretical or observational curves are available, their use is recommended in preference to the present hypothetical potentials.

It also appears well to point out that the force constants listed here are based on ground electronic states. At high temperatures, there is a large population of excited species, for each of which, in general, the effective force constants would be appreciably different. One possible approach would involve estimates of effective force constants including all excited states as functions of the temperature. A logically more correct treatment, theoretically capable of application at all temperatures, would subdivide the species' partition function so as to be based on groups of states giving like interaction force constants. Such a treatment in detail would be very elaborate. The modifications in equilibrium constants and compositions for the various sub-species would be kept distinct according to such a procedure. The detailed application would be relevant to the high energy cut-off in partition function calculations(47, 48, 49).

Table 4.1. Diatomic Bond Lengths

Molecule	r_e(Å)	(Å)
N_2	1.094	1.0965
O_2	1.2074	1.2107
NO	1.1508	1.1538
CO	1.1282	1.1307
C_2	1.3117	1.3151
CN	1.1718	1.1745
H_2	.7417	.7508
OH	.9706	.9798
NH	$[1.040_8]$	$[1.050_6]$
CH	1.1198	1.1301

Table 4.2. Summary of Combination Rule Estimates

Molecular Pair	Force Constants		Based on	Combination Rule (Equation numbers)
	b_o cm^3 mole^{-1}	ϵ/k deg K		
O - O	32.6		$O_2 - O_2$	(1-6) to (1-9)
		81.5	$O_2 - O_2$	(1-12)
N - N	40.3		$N_2 - N_2$	(1-6) to (1-9)
		58.3		(1-12)
C - C	54.2		O - O, CO - CO	(1-6) to (1-9)
		54.7	O - O, CO - CO	(1-13) ff.
H - H	21.54		$H_2 - H_2$	(1-6) to (1-9)
		20.0	$H_2 - H_2$	(1-12)
$C_2 - C_2$	87.5		C - C	(1-6) to (1-9)
	86.1		CO - CO, $O_2 - O_2$	(1-11)
		86.5	C - C	(1-12)
$O - O_2$	42.6		$O_2 - O_2$	(1-6) to (1-9)
	42.7		O - O, $O_2 - O_2$	(1-10)
	42.2		O - O, $O_2 - O_2$	(1-4)
		95.1	O - O	(1-12)
		97.3	O - O, $O_2 - O_2$	(1-2)
$N - N_2$	50.8		$N_2 - N_2$	(1-6) to (1-9)
	50.8		N - N, $N_2 - N_2$	(1-10)
	50.4		N - N, $N_2 - N_2$	(1-4)
		73.3	N - N	(1-12)
		74.6	N - N, $N_2 - N_2$	(1-2)
$C - C_2$	69.4		$C_2 - C_2$	(1-6) to (1-9)
	68.9		C - C, $C_2 - C_2$	(1-10)
	68.3		C - C, $C_2 - C_2$	(1-4)
		67.7	C - C	(1-2)
		68.8	C - C, $C_2 - C_2$	(1-2)
"CN" - "CN"	74.0		$N_2 - N_2$, $C_2 - C_2$	(1-11)
		91.9	C - C, N - N, C - N	(1-12)
		90.9	$C_2 - C_2$, $N_2 - N_2$	(1-2)
OH - OH	43.2		$O_2 - O_2$, $H_2 - H_2$	(1-6) to (1-9)
		84.6	$O_2 - O_2$, $H_2 - H_2$	(1-13) ff.
NH - NH	50.5		$N_2 - N_2$, $H_2 - H_2$	(1-6) to (1-9)
		64.0	$N_2 - N_2$, $H_2 - H_2$	(1-13) ff.
CH - CH	67.4		C - C, $H_2 - H_2$	(1-6) to (1-9)
		54.4	C - C, $H_2 - H_2$	(1-13) ff.

Table 43. Lennard-Jones 12, 6 Pair Potential Force Constants

Pair	b_o (cm^3/mole)	b_m (cm^3/mole)	ε/k (deg K)	Pair	b_o (cm^3/mole)	b_m (cm^3/mole)	ε/k (deg K)
N_2-N_2	63	89.1	95.42	NO-CO	65.1	92.1	109.1
O_2-O_2	54.7	77.4	116	NO-N	50.3	71.1	82.9
NO-NO	61.5	87.0	118	NO-O	45.6	64.5	98.0
CO-CO	69.22	97.9	100.8	NO-Ar	55.8	78.9	118.8
N-N	40.3	57.0	58.3	NO-C	57.8	81.7	80.4
O-O	32.6	46.1	81.5	NO-CN	67.6	95.6	104.0
Ar-Ar	50.5	71.4	119.5	$NO-C_2$	73.0	103.2	101.0
C-C	54.2	76.7	54.7				
CN-CN	74.0	104.7	91.9	CO-N	53.5	75.7	76.6
C_2-C_2	86.1	121.8	86.5	CO-O	48.6	68.7	90.6
				CO-Ar	59.4	84.0	109.8
N_2-O_2	58.8	83.2	105.2	CO-C	61.3	86.7	74.3
N_2-NO	62.3	88.1	106.1	CO-CN	71.7	101.4	96.3
N_2-CO	66	93.3	98.1	$CO-C_2$	77.5	109.6	93.4
N_2-N	50.8	71.8	73.3				
N_2-O	46.2	65.3	88.2	N-O	36.3	51.3	68.8
N_2-Ar	56.5	79.9	106.8	N-Ar	45.3	64.1	83.5
N_2-C	58.6	82.9	72.2	N-C	46.9	66.3	56.5
N_2-CN	68.4	96.7	93.6	N-CN	55.4	78.3	73.2
N_2-C_2	74.0	104.7	91.0	$N-C_2$	60.5	85.6	71.0
O_2-NO	58.0	82.0	117.0	O-Ar	41.0	58.0	98.7
O_2-CO	61.6	87.1	108.1	O-C	42.5	60.1	66.8
O_2-N	47.1	66.6	82.2	O-CN	50.7	71.7	86.5
O_2-O	42.7	60.4	95.1	$O-C_2$	55.1	77.9	84.0
O_2-Ar	52.6	74.4	117.7				
O_2-C	54.4	76.9	79.6	Ar-C	52.4	74.1	80.9
O_2-CN	64	90.5	103.2	Ar-CN	61.6	87.1	104.8
O_2-C_2	69.6	98.4	100.2	$Ar-C_2$	67.0	94.8	101.7
				C-CN	63.5	89.8	70.9
				$C-C_2$	69.0	97.6	68.8
				$CN-C_2$	79.6	112.6	89.2
				H_2-H_2	31.67	44.8	37.00
				$H-H_2$	26.3	37.2	27.2

Table 4.4. Estimated f Values

Substance	f	Substance	f
He	1.1	NH_3	2.72
Ne	2.37	Cl_2	6.55
Ar	4.58	HCl	4.25
Kr	4.90	HBr	4.71
Xe	5.61	HI	5.30
H_2	(1.5)	Na	1
N_2	4.61	K	(1)
O_2	3.11	O	(1.7)*
CO_2	5.70	N	(2.2)*
CH_4	4.60	C	(2.7)*

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*Conjectured.

Table 4.5. Interaction Parameters for Hypothetically Non-Bonding Atoms

Atom Pair	b_o cm^3/mole	ε/k deg K	Ref.	$10^{-4}k_{12}$	k_6	$(k_6)_{calc}$	$n^*\left(k_{12}t_n^{-2}\right)^{-1/12}$	$(Z_e)_{Slater}$
H - H	21.54	20.0	a	4.46	3.36	6	.41	1.0
He - He	21.07	10.22	b	2.09	1.644	0.99	.49	1.7
C - C	54.2	54.7	c	490.	58.2	54.3	.70	3.25
N - N	40.3	58.3	c	159.5	34.3	30.45	.79	3.90
O - O	32.6	81.5	c	95.4	31.4	18.3	.85	4.55
Ne - Ne	26.21	35.60	b	17.42	8.86	7.66	1.03	5.85
Ar - Ar	50.51	119.5	d	807	110.5	134	1.13	6.75
Kr - Kr	58.86	171	b	2128	215	430	1.28	7.25
Xe - Xe	86.94	221	b	13093	605	677	1.19	7.25

a - Rigid convex model, plus b_o and ε/k for H_2 in reference 5.

b - Parameters in reference 5.

c - Rigid convex model, parameters of NBS Circular C564. Also, see table 3.

d - Parameters in NBS Circular C564.

Table 4.6. Values of $Z_e = Z - S$, Based on Slater Screening Constants, for Ground State Outer Shell Electrons

		Z_e				
Z	Z-t:	-1	0	1	2	3
1	H	0.7	1			
2	He	0.3	1.7	2		
3	Li	0.95	1.3	2.7	3	
4	Be	1.60	1.95	2.3	3.7	4
5	B	2.25	2.60	2.95	3.3	4.7
6	C	2.90	3.25	3.60	3.95	4.3
7	N	3.55	3.90	4.25	4.60	4.95
8	O	4.20	4.55	4.90	5.25	5.60
9	F	4.85	5.20	5.55	5.90	6.25
10	Ne	1.20	5.85	6.20	6.55	6.90
11	Na	1.85	2.20	6.85	7.20	7.55
12	Mg	2.50	2.85	3.20	7.85	8.20
13	Al	3.15	3.50	3.85	4.20	8.85
14	Si	3.80	4.15	4.50	4.85	5.20
15	P	4.45	4.80	5.15	5.50	5.85
16	S	5.10	5.45	5.80	6.15	6.50
17	Cl	5.75	6.10	6.45	6.80	7.15
18	Ar	1.20	6.75	7.10	7.45	7.80

Table 4.7. Potential Term Coefficients in Atomic Units. Part A: R^{-12} Coefficients

(Values listed are $10^{-6}k_{12}$)

	N_2	O_2	Ar	CO_2	N	O	NO	CO	C	N^+	O^+	N^{++}	Ar^+	Ar^{++}	NO^+	O^-	N_2^+	O^{++}	C^+
N_2	15.6	13.0	11.2	41.6	5.00	3.86	16.5	19.4	8.74	3.25	2.27	1.77	7.14	4.90	12.4	5.92	12.7	1.37	4.59
O_2		10.8	9.32	34.6	4.15	3.20	13.7	16.1	7.26	2.68	1.88	1.47	5.94	4.07	10.3	4.92	10.6	1.14	3.81
Ar			8.07	30.0	3.60	2.78	11.9	13.9	6.29	2.32	1.63	1.27	5.14	3.53	8.94	4.26	9.16	0.985	3.30
CO_2				111.	13.4	10.3	44.1	51.6	23.4	8.63	6.06	4.72	19.1	13.1	33.2	15.8	34.0	3.65	12.3
N					1.60	1.24	5.30	6.20	2.80	1.03	0.726	0.566	2.29	1.57	3.98	1.90	4.08	0.439	1.47
O						0.955	4.09	4.79	2.16	0.799	0.561	0.436	1.77	1.21	3.08	1.47	3.15	0.338	1.14
NO							17.5	20.5	9.26	3.42	2.40	1.87	7.56	5.20	13.2	6.27	13.5	1.45	4.86
CO								24.0	10.8	4.00	2.82	2.19	8.86	6.08	15.4	7.35	15.8	1.70	5.69
C									4.90	1.81	1.27	0.99	4.00	2.75	6.96	3.32	7.14	0.766	2.57
N^+										0.66_9	0.47	0.366	1.48	1.02	2.58	1.23	2.64	0.28_3	0.95
O^+											0.33	0.25_7	1.04	0.71_3	1.81	0.861	1.85	0.199	0.668
N^{++}												0.20	0.80_9	0.555	1.41	0.671	1.44	0.15_5	0.52
Ar^+													3.27	2.24	5.69	2.71	5.83	0.62_6	2.10
Ar^{++}														1.54	3.90	1.86	4.00	0.430	1.44
NO^+															9.90	4.7_2	10.2	1.09	3.66
O^-																2.25	4.84	0.52	1.74
N_2^+																	10.4	1.12	3.75
O^{++}																		0.12	0.402
C^+																			1.35

Table 4.7. Part B: Dispersion Part of R^{-6} Coefficients, $k_6^{\bullet}$

	N_2	O_2	Ar	CO_2	N	O	NO	CO	C	N^+	O^+	N^{++}	Ar^+	Ar^{++}	NO^+	O^-	N_2^+	O^{++}	C^+
N_2	137	131	123	272	68.6	65.6	149	155	89.2	39.9	34.6	21.9	89.2	63.1	104	90.8	109	21.3	45.4
O_2		126	118	260	65.7	62.8	143	148	85.4	38.2	33.1	21.0	85.4	60.4	99.1	86.9	104	20.4	43.4
Ar			110	244	61.6	58.9	134	139	80.1	35.8	31.0	19.7	80.0	56.6	92.8	81.4	97.5	19.1	40.7
CO_2				537	136	130	295	307	176	78.9	68.4	43.4	176	125	205	179	215	42.1	89.7
N					34.2	32.8	74.5	77.5	44.6	20.0	17.3	11.0	44.6	31.5	51.6	45.4	54.2	10.6	22.7
O						31.4	71.3	74.1	42.7	19.1	16.5	10.5	42.6	30.2	54.5	43.4	52.0	10.2	21.7
NO							162	168	96.9	43.4	37.5	23.8	96.9	68.5	112	98.6	118	23.1	49.3
CO								175	101	45.1	39.0	24.7	101	71.2	117	102	123	24.0	51.2
C									58	25.9	22.5	14.2	58.0	41.0	67.3	59.0	70.6	13.8	29.5
N^+										11.6	10.0	6.36	25.9	18.3	30.1	26.4	31.6	6.2	13.2
O^+											8.7	5.5	22.5	15.9	26.1	22.9	27.4	5.4	11.4
N^{++}												3.5	14.2	10.1	16.5	14.5	17.3	3.4	7.2
Ar^+													58	41.0	67.3	59.0	70.6	13.8	29.5
Ar^{++}														29	47.6	41.7	49.9	9.8	20.9
NO^+															78	68.4	81.9	16.0	34.2
O^-																60	71.8	14.1	30.0
N_2^+																	86	16.8	35.9
O^{++}																		3.3	7.0
C^+																			15

Table 4.7. Part C: Induced Quadrupole Part of R^{-6} Coefficients, Δk_6

	N_2	O_2	Ar	CO_2	N	O	NO	CO	C	N^+	O^+	N^{++}	Ar^+	Ar^{++}	NO^+	O^-	N_2^+	O^{++}	C^+
N_2	0	0	0	0	0	0	0	0	0	29.8	29.8	119	29.8	119	29.8	29.8	29.8	119	29.8
O_2		0	0	0	0	0	0	0	0	40.5	40.5	162	40.5	162	40.5	40.5	40.5	162	40.5
Ar			0	0	0	0	0	0	0	24.1	24.1	96.5	24.1	96.5	24.1	24.1	24.1	96.5	24.1
CO_2				0	0	0	0	0	0	94.3	94.3	377	94.3	377	94.3	94.3	94.3	377	94.3
N					0	0	0	0	0	15.6	15.6	62.4	15.6	62.4	15.6	15.6	15.6	62.4	15.6
O						0	0	0	0	18.5	18.5	74	18.5	74	18.5	18.5	18.5	74	18.5
NO							0	0	0	41.5	41.5	166	41.5	166	41.5	41.5	41.5	166	41.5
CO								0	0	38	38	152	38	152	38	38	38	152	38
C									0	21.4	21.4	86	21.4	86	21.4	21.4	21.4	86	21.4
N^+										8.6	8.3	18.3	17.0	23.5	21.2	39.3	20.5	18.4	9.0
O^+											8.0	17.1	16.7	22.3	20.9	39.0	20.2	17.2	8.7
N^{++}												8.8	51.8	29.8	68.8	141	65.9	9.3	19.9
Ar^+													25.4	57	29.6	47.7	28.9	51.9	17.4
Ar^{++}														50.8	74.0	146	71.1	30.3	25.1
NO^+															33.8	51.9	33.1	68.9	21.6
O^-																70	51.2	141	39.7
N_2^+																	32.4	66.2	20.9
O^{++}																		9.8	20.0
C^+																			9.4

Table 4.7. Part D: R^{-6} Coefficients, k_6

	N_2	O_2	Ar	CO_2	N	O	NO	CO	C	N^+	O^+	N^{++}	Ar^+	Ar^{++}	NO^+	O^-	N_2^+	O^{++}	C^+
N_2	137	131	123	272	68.6	65.6	149	155	89.2	69.7	64.4	141	119	182	133	121	139	140	75
C_2		126	118	260	65.7	62.8	143	148	85.4	78.7	73.6	183	126	222	140	127	144	182	83.9
Ar			110	244	61.6	58.9	134	139	80.1	59.9	55.1	116	104	153	117	106	122	116	65
CO_2				537	136	130	295	307	176	173	163	420	270	502	299	273	309	419	184
N					34.3	32.8	74.5	77.5	44.6	35.6	32.9	73.4	60.2	93.9	67.2	61.0	69.8	73.0	38.3
O						31.4	71.3	74.1	42.7	37.6	35.0	84.5	61.1	104	73.0	61.9	70.5	84.2	40.2
NO							162	168	96.9	84.8	79.0	190	138	234	154	140	160	189	91
CO								175	101	83	77	177	139	223	155	140	161	176	89
C									58	47.3	43.9	100	79.4	127	88.7	80.4	92	100	50.9
N^+										20.2	18.3	24.7	42.9	41.8	51.3	65.7	52.1	24.6	22.2
O^+											16.7	22.6	39.2	38.2	47.0	61.9	47.6	22.6	20.1
N^{++}												12.3	66.0	39.9	85.3	156	83.2	12.7	27.1
Ar^+													83.4	98	96.9	107	99.5	65.7	46.9
Ar^{++}														79.8	122	188	121	40.1	46
NO^+															112	120	115	84.9	55.8
O^-																130	123	155	69.7
N_2^+																	118	83	56.8
O^{++}																		13.1	27
C^+																			24.4

Table 4.7. Part E: R^{-4} Coefficients, k_4

	N_2	O_2	Ar	CO_2	N	O	NO	CO	C	N^+	O^+	N^{++}	Ar^+	Ar^{++}	NO^+	O^-	N_2^+	O^{++}	C^+
N_2	0	0	0	0	0	0	0	0	0	5.7	5.7	23	5.7	23	5.7	5.7	5.7	23	5.7
O_2		0	0	0	0	0	0	0	0	5.0	5.0	20	5.0	20	5.0	5.0	5.0	20	5.0
Ar			0	0	0	0	0	0	0	13.6	13.6	54.4	13.6	54.4	13.6	13.6	13.6	54.4	13.6
CO_2				0	0	0	0	0	0	10	10	40	10	40	10	10	10	40	10
N					0	0	0	0	0	3.8	3.8	15.2	3.8	15.2	3.8	3.8	3.8	15.2	3.8
O						0	0	0	0	2.6	2.6	10.4	2.6	10.4	2.6	2.6	2.6	10.4	2.6
NO							0	0	0	5.8	5.8	23	5.8	23	5.8	5.8	5.8	23	5.8
CO								0	0	6.2	6.2	24.8	6.2	24.8	6.2	6.2	6.2	24.8	6.2
C									0	6.5	6.5	26	6.5	26	6.5	6.5	6.5	26	6.5
N^+										4.5	3.8	9.9	11	11.2	6	6.6	6.8	10	4.6
O^+											3.0	6.9	10.5	8.2	5.5	5.8	6.0	7.0	3.9
N^{++}												7.2	37	12.2	17	18.3	18.9	7.4	10.5
Ar^+													18	38	13	13.4	13.5	37	11.4
Ar^{++}														17.2	18.2	19.6	20.2	12.4	11.8
NO^+															8	8.4	8.5	17	6.4
O^-																8.7	8.8	18	6.8
N_2^+																	9	19	6.9
O^{++}																		7.6	10
C^+																			4.8

Table 4.7. Part F: R^{-1} Coefficients, k_1

	N_2	O_2	Ar	CO_2	N	O	NO	CO	C	N^+	O^+	N^{++}	Ar^+	Ar^{++}	NO^+	O^-	N_2^+	O^{++}	C^+
N_2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
O_2		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ar			0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_2				0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N					0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
O						0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO							0	0	0	0	0	0	0	0	0	0	0	0	0
CO								0	0	0	0	0	0	0	0	0	0	0	0
C									0	0	0	0	0	0	0	0	0	0	0
N^+										1	1	2	1	2	1	-1	1	2	1
O^+											1	2	1	2	1	-1	1	2	1
N^{++}												4	2	4	2	-2	2	4	2
Ar^+													1	2	1	-1	1	2	1
Ar^{++}														4	2	-2	2	4	2
NO^+															1	-1	1	2	1
O^-																1	-1	-2	-1
N_2^+																	1	2	1
O^{++}																		4	2
C^+																			1

Table 4.8. Pairs with $x_i x_j > 10^{-4}$, up to 15,000°K

	N_2	O_2	Ar	CO_2	N	O	NO	CO	C	N^+	O^+	N^{++}	Ar^+	Ar^{++}	NO^+	O^-	N_2^+	O^{++}	C^+
N_2	x	x	x	x	x	x	x	x		x	x				x				
O_2		x	x		x	x	x												
Ar					x	x	x			x	x								
CO_2																			
N					x	x	x		x	x	x		x		x	x	x		
O						x	x	x		x	x		x		x				
NO							x			x									
CO																			
C																			
N^+										x	x	x	x	x				x	
O^+											x	x	x	x					
N^{++}												x							
Ar^+																			
Ar^{++}																			
NO^+																			
O^-																			
N_2^+																			
O^{++}																			
C^+																			

Table 4.9. **Estimated Force Constants for Some 12, 6, 4 Potentials**

Pairs	b_m (cm³/mole)	ε/k (deg K)	γ
N_2 - NO^+	53.9	880	0.286
N_2 - N^+	34.3	1480	.222
N_2 - O^+	30.0	1770	.222
NO - N^+	33.8	1610	.256
N - N_2^+	41.9	810	.272
N - NO^+	41.8	800	.264
N - N^+	26.3	1380	.208
N - O^+	23.1	1640	.208
N - Ar^+	33.8	1070	.270
N - O^-	31.1	1220	.285
O - NO^+	40.1	680	.370
O - N^+	25.8	1085	.291
O - O^+	22.5	1300	.293
O - Ar^+	33.0	860	.358
Ar - N^+	23.4	5300	.114
Ar - O^+	20.6	6300	.114

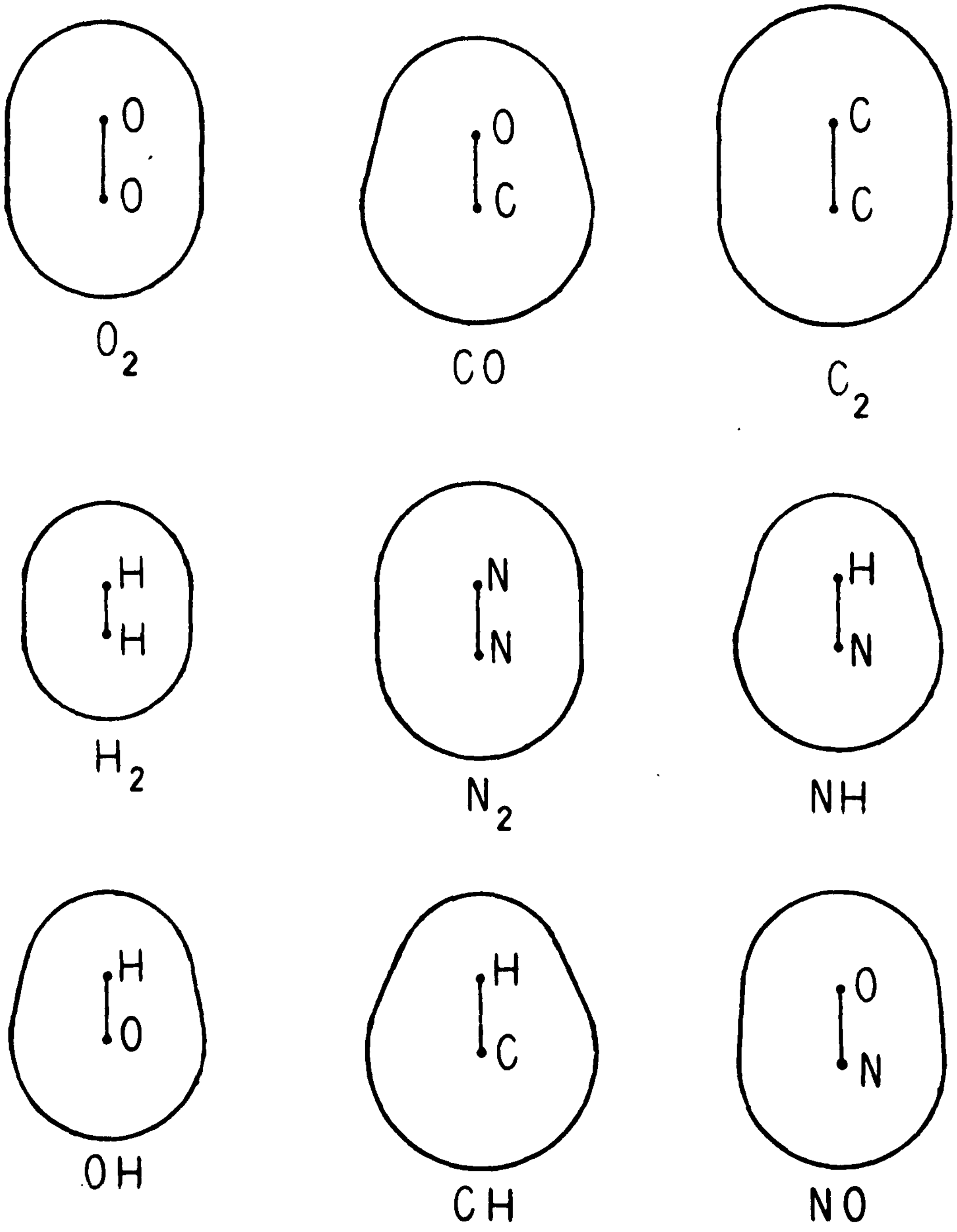

Fig. 4.1 Core models for diatomic molecules.

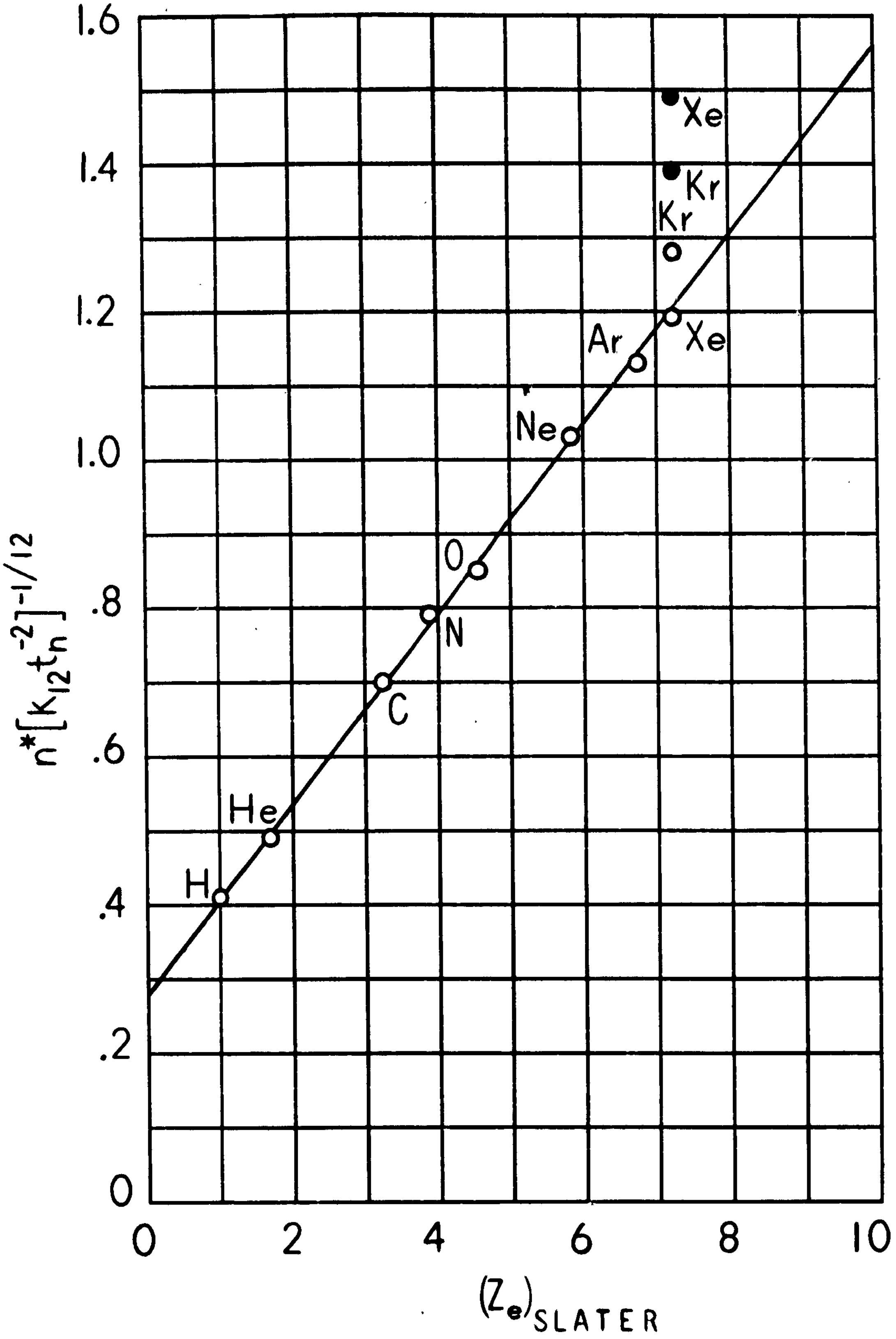

Fig. 4.2. Atom pair repulsion versus outer shell field for Slater screening. Filled circles have ordinates based on n rather than n*.

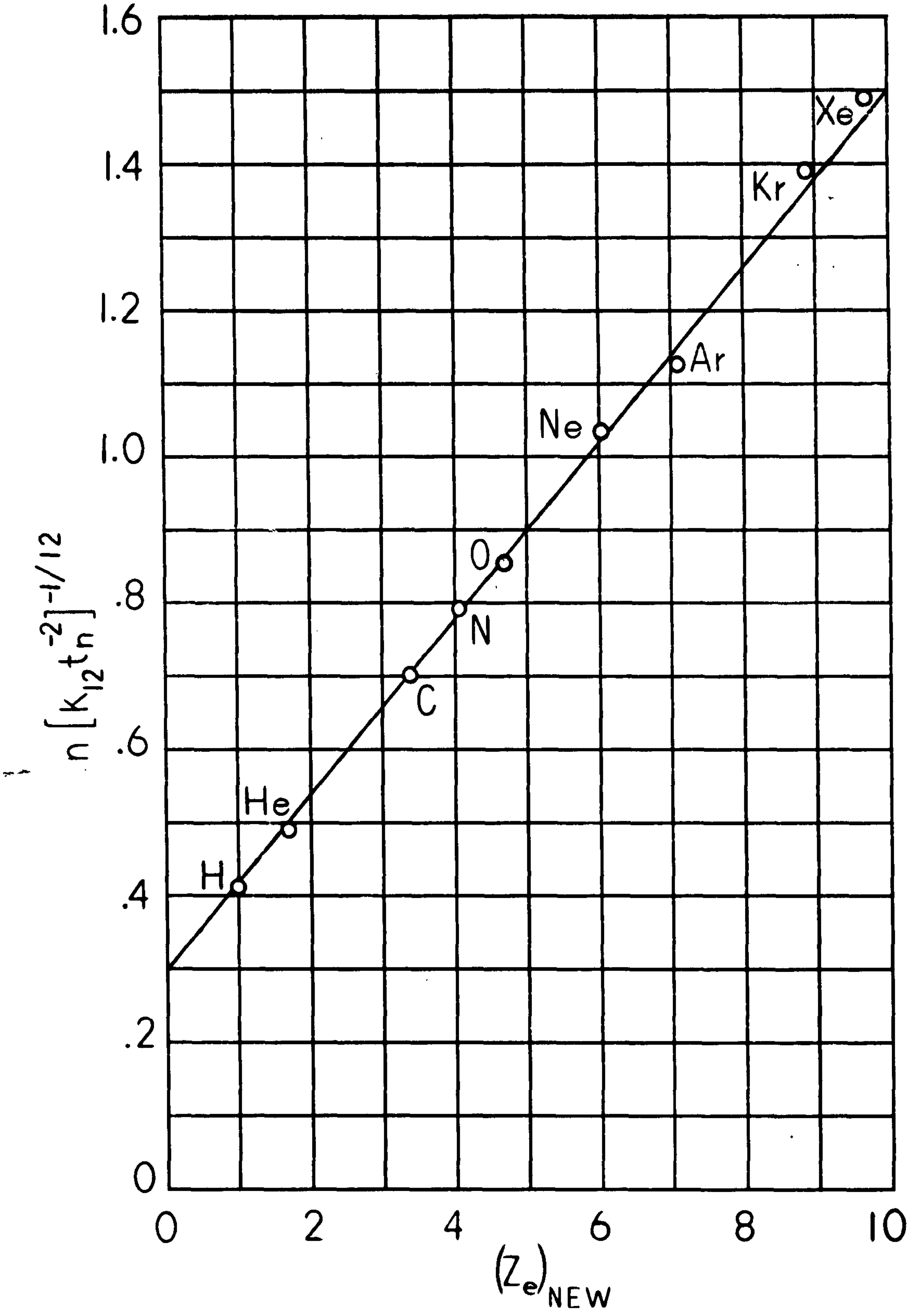

Fig. 4.3. Atom pair repulsion versus outer shell field for modified screening.

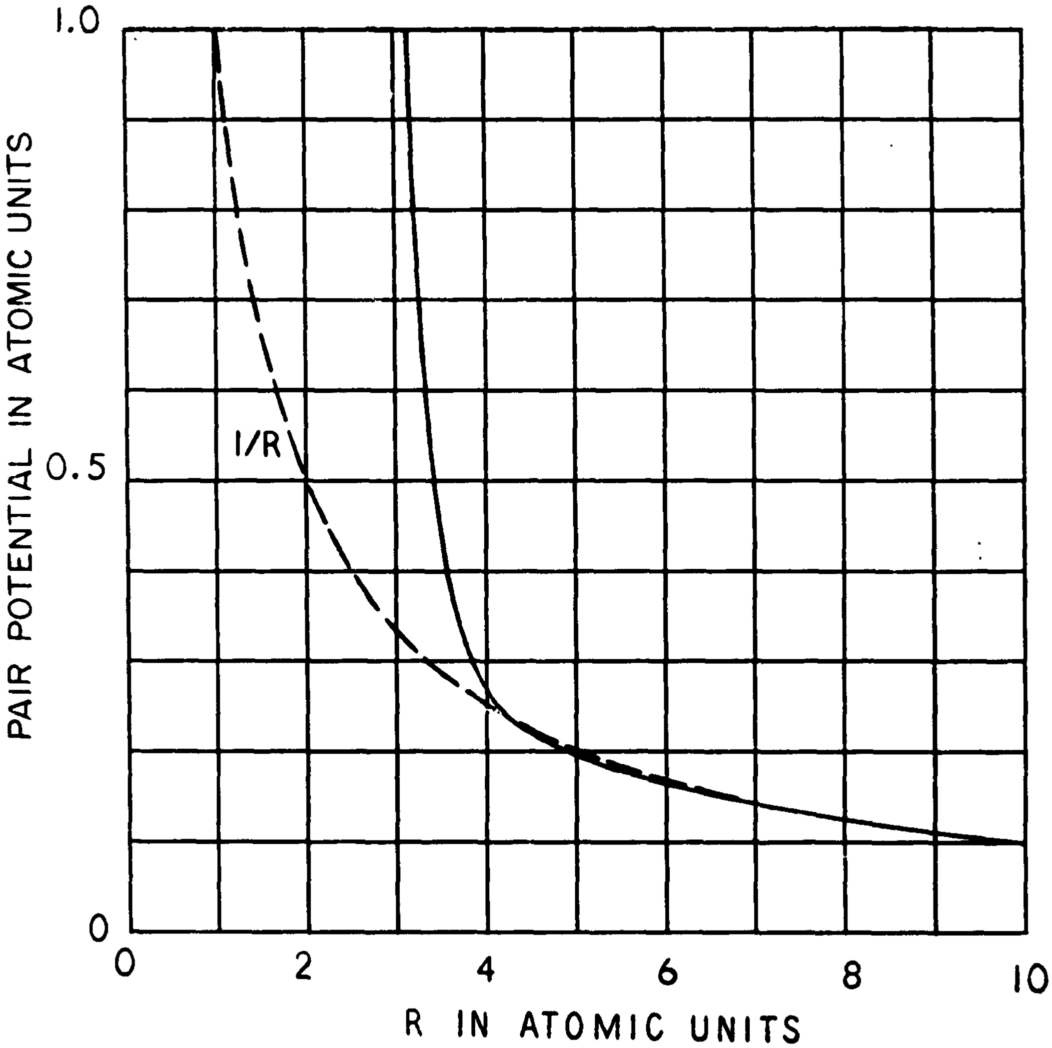

Fig. 4.4. Non-bonding pair potential for N^+-N^+.

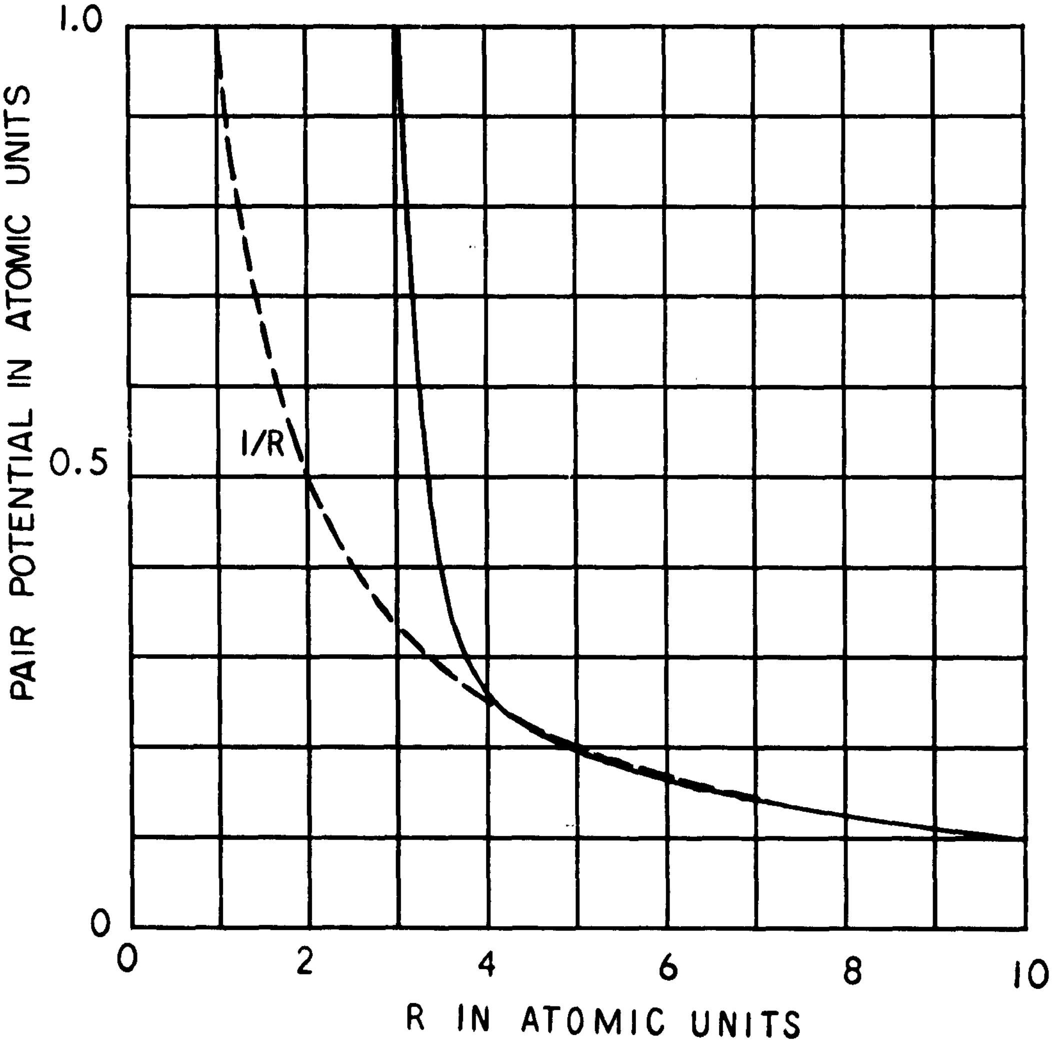

Fig. 4.5. Non-bonding pair potential for O$^+$-N$^+$.

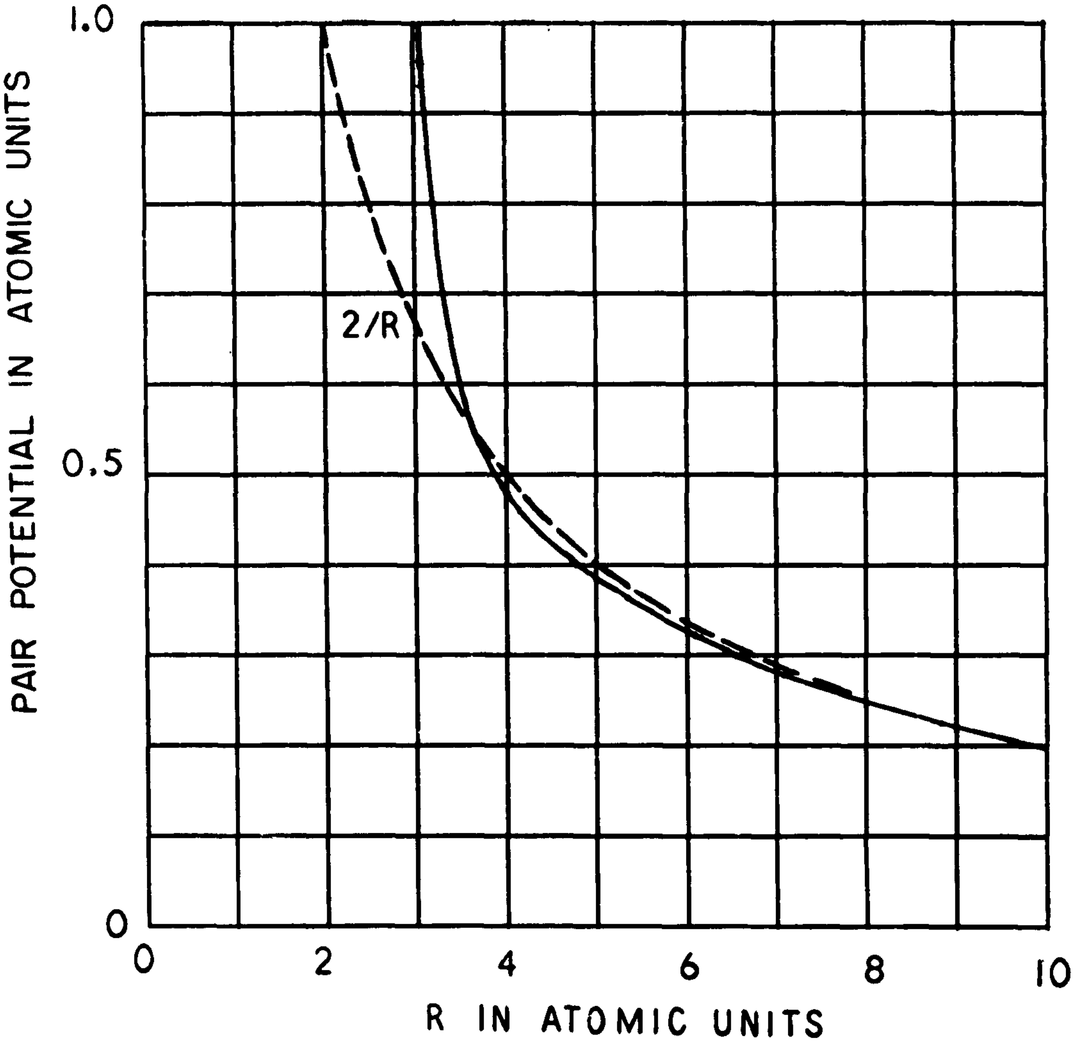

Fig. 4.6. Non-bonding pair potential for N^{++}-N^{+}.

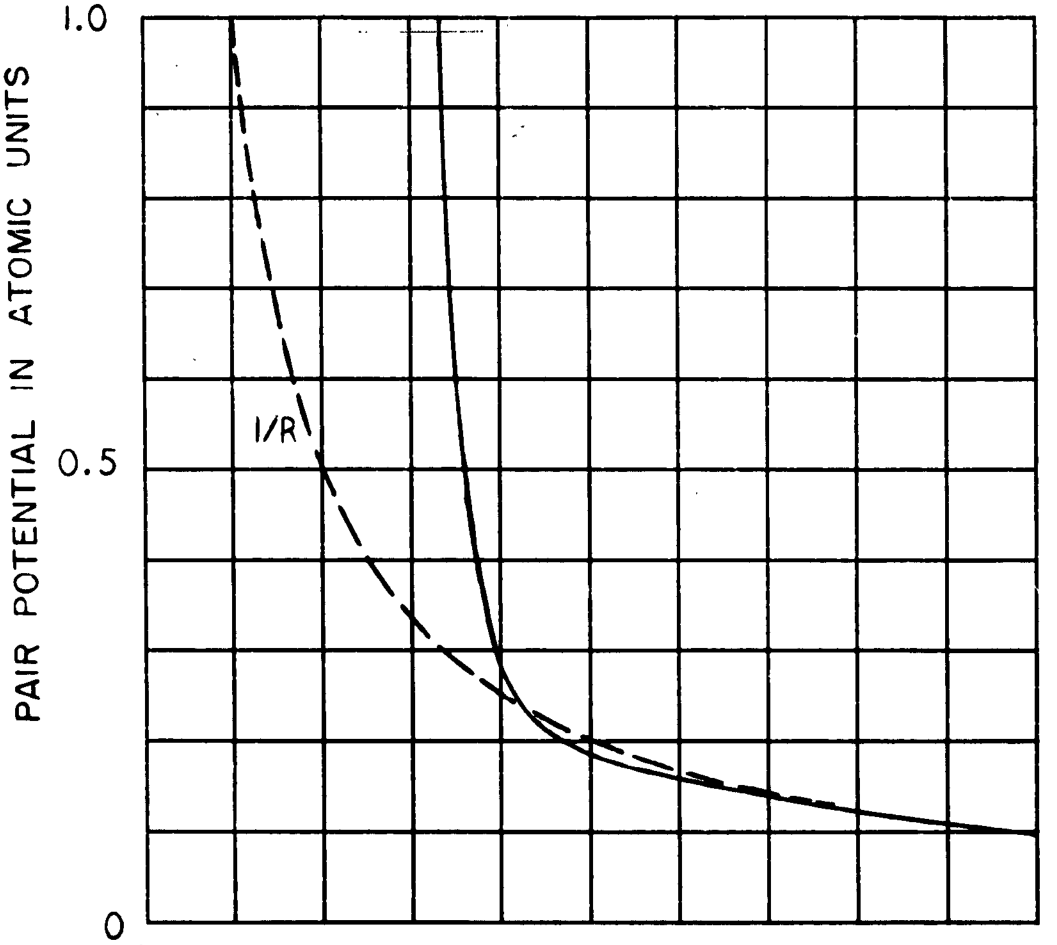

Fig. 4.7. Non-bonding pair potential for Ar^+-N^+.

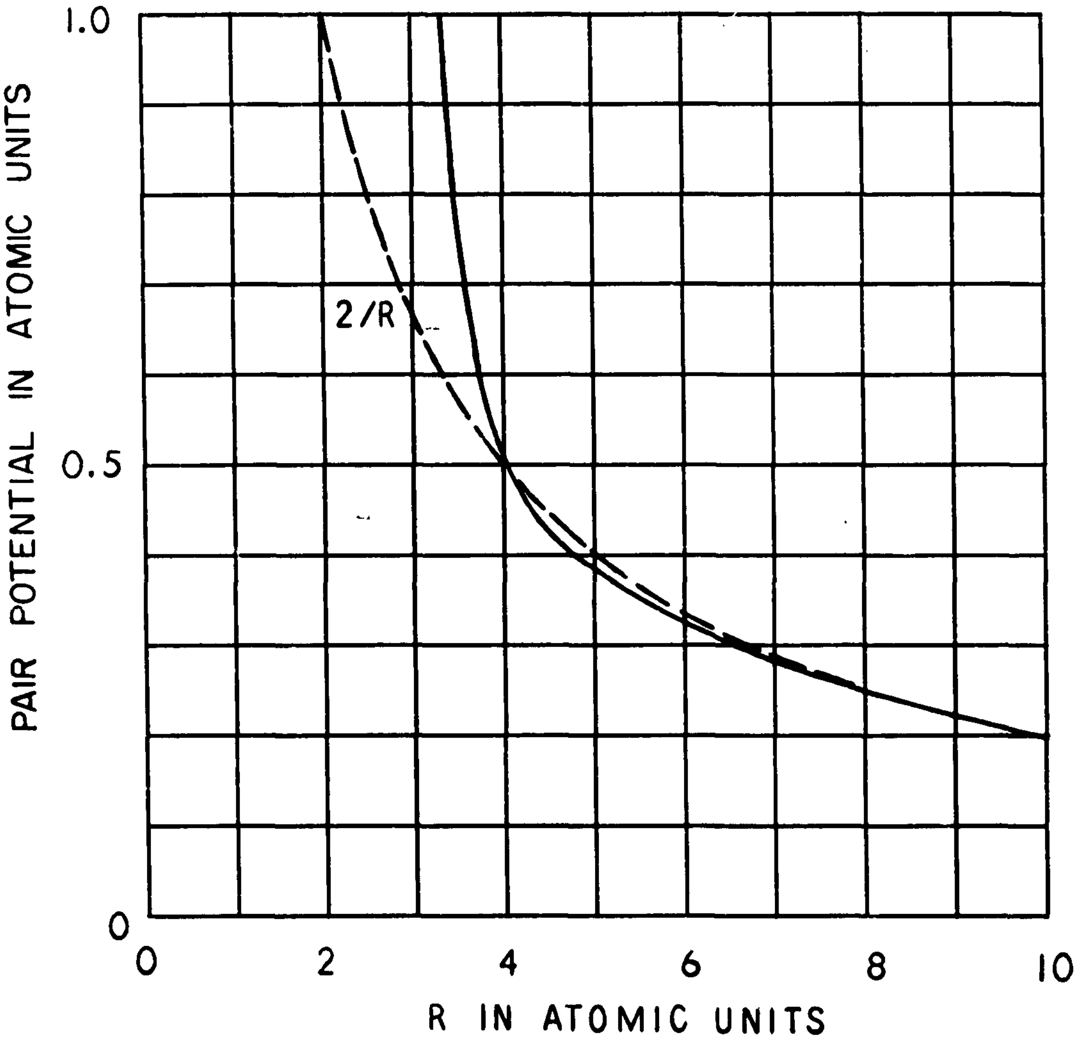

Fig. 4.8 Non-bonding pair potential for Ar^{++}-N^{+}.

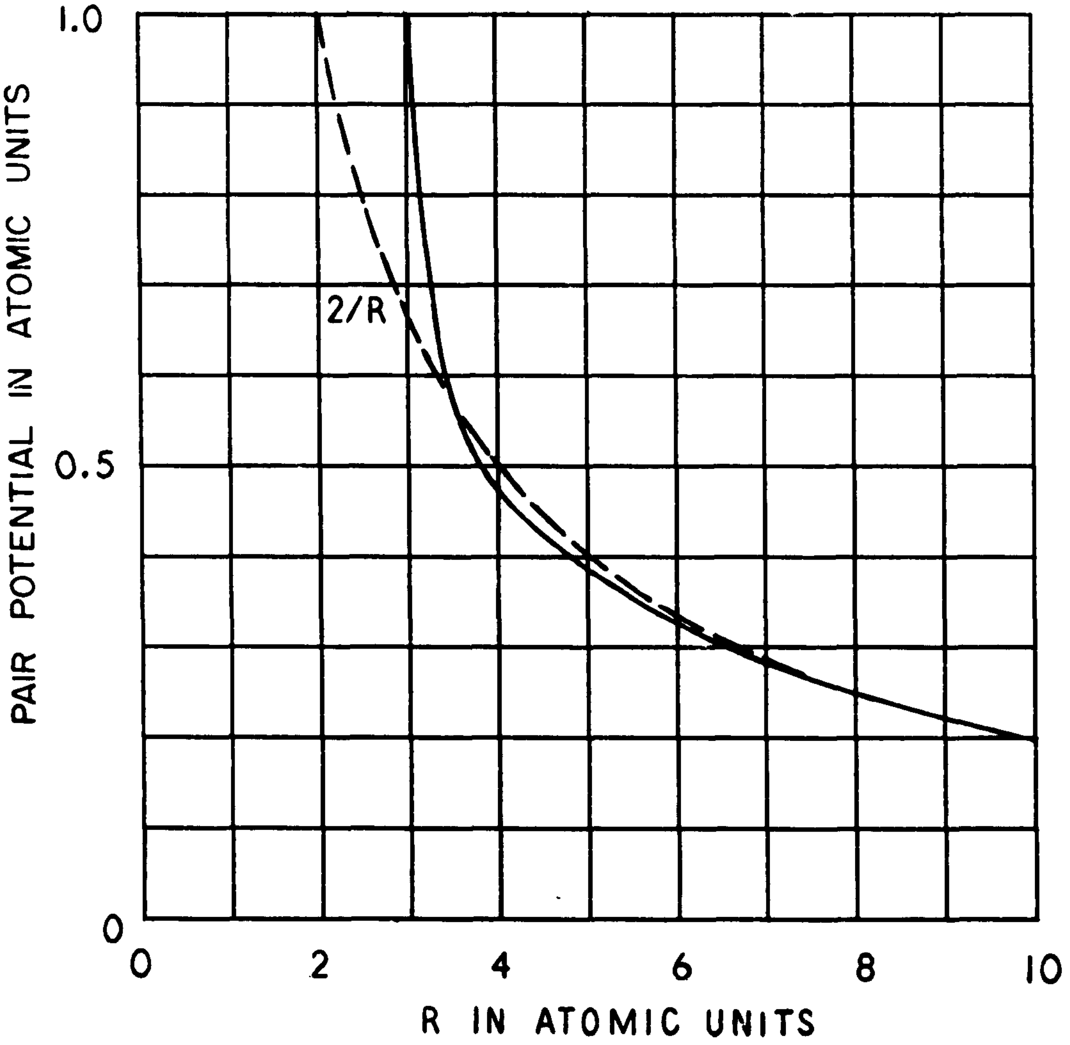

Fig. 4.9. Non-bonding pair potential for O^{++}-N^{+}.

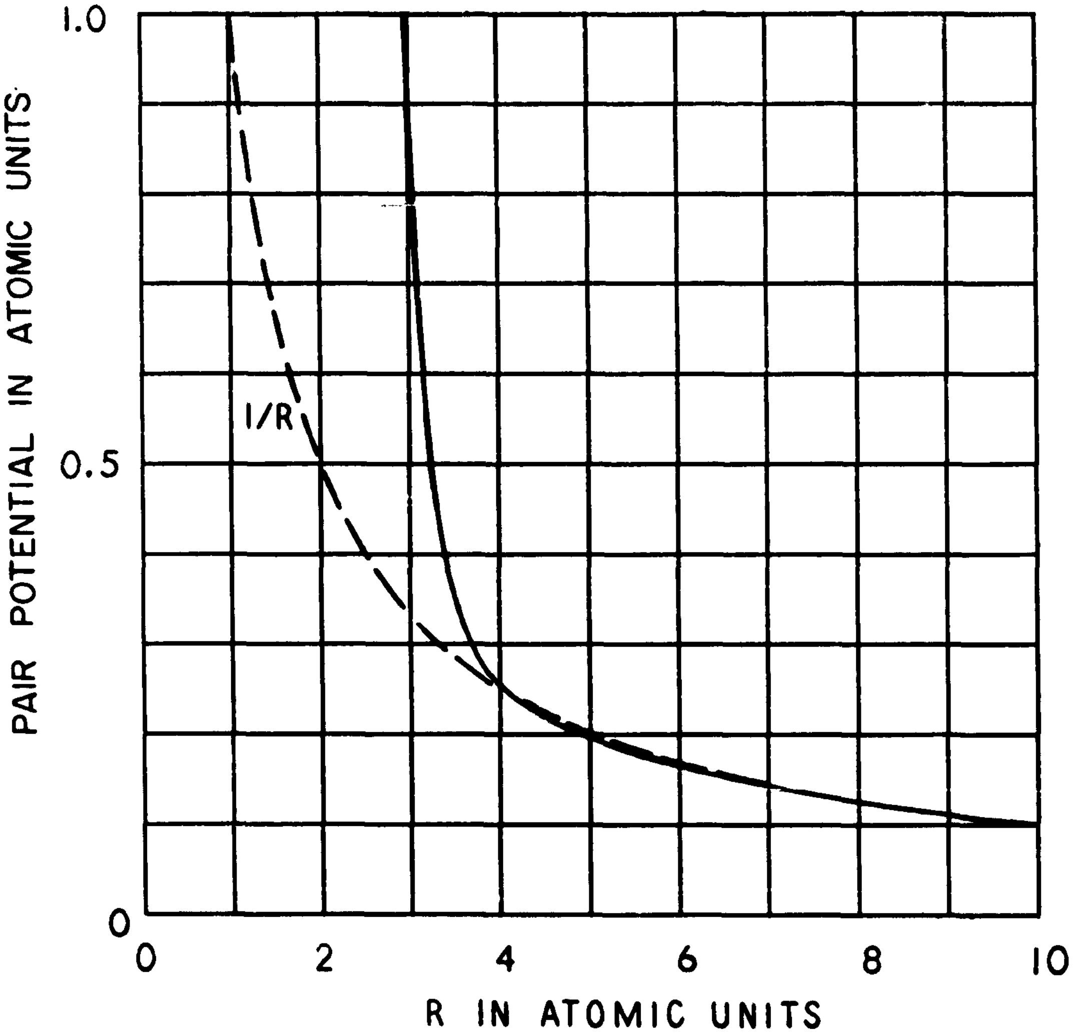

Fig. 4.10. Non-bonding pair potential for O^+-O^+.

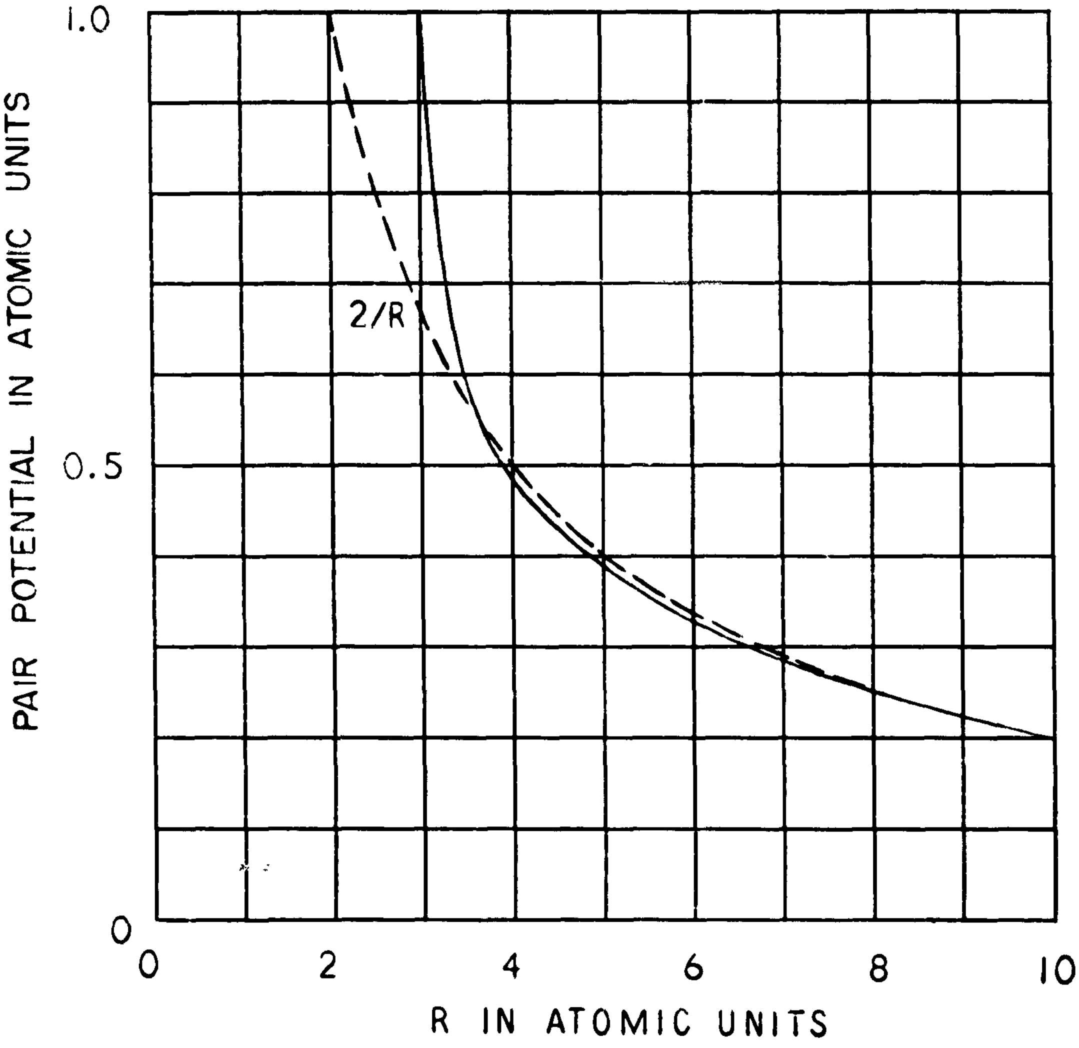

Fig. 4.11. Non-bonding pair potential for N^{++}-O^{+}.

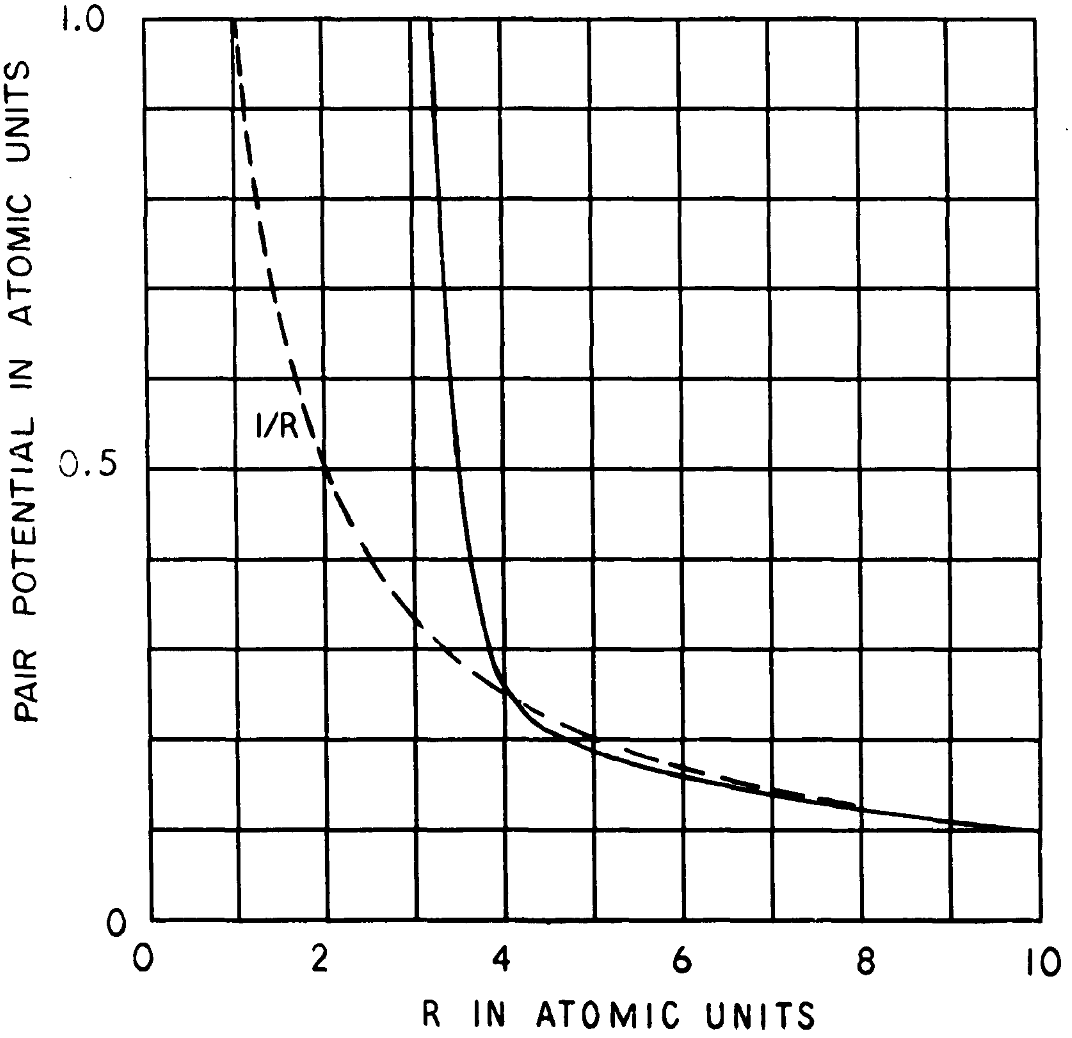

Fig. 4.12. Non-bonding pair potential for Ar^+-O^+.

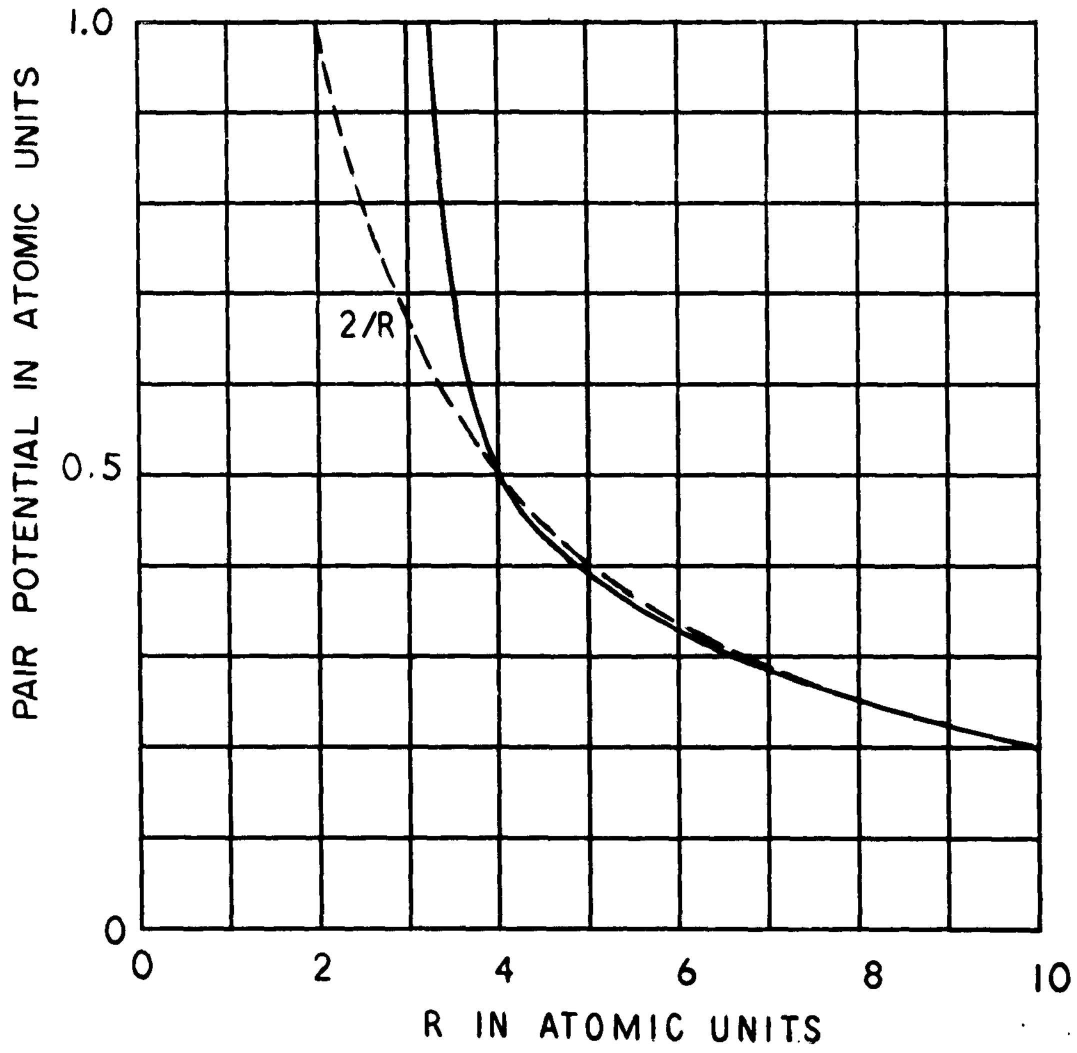

Fig. 4.13. Non-bonding pair potential for Ar^{++}-O^{+}.

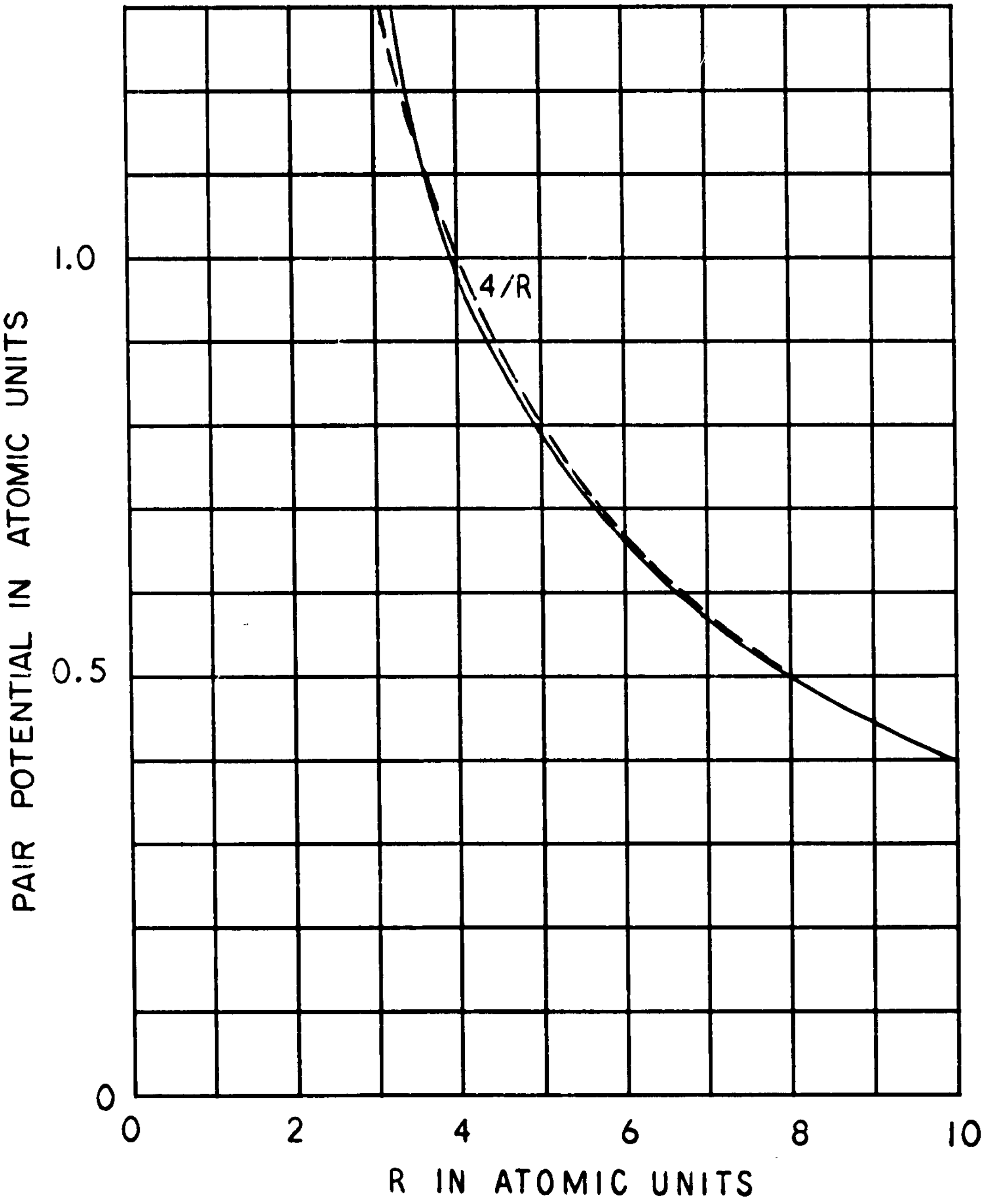

Fig. 4.14. Non-bonding pair potential for N^{++}-N^{++}.

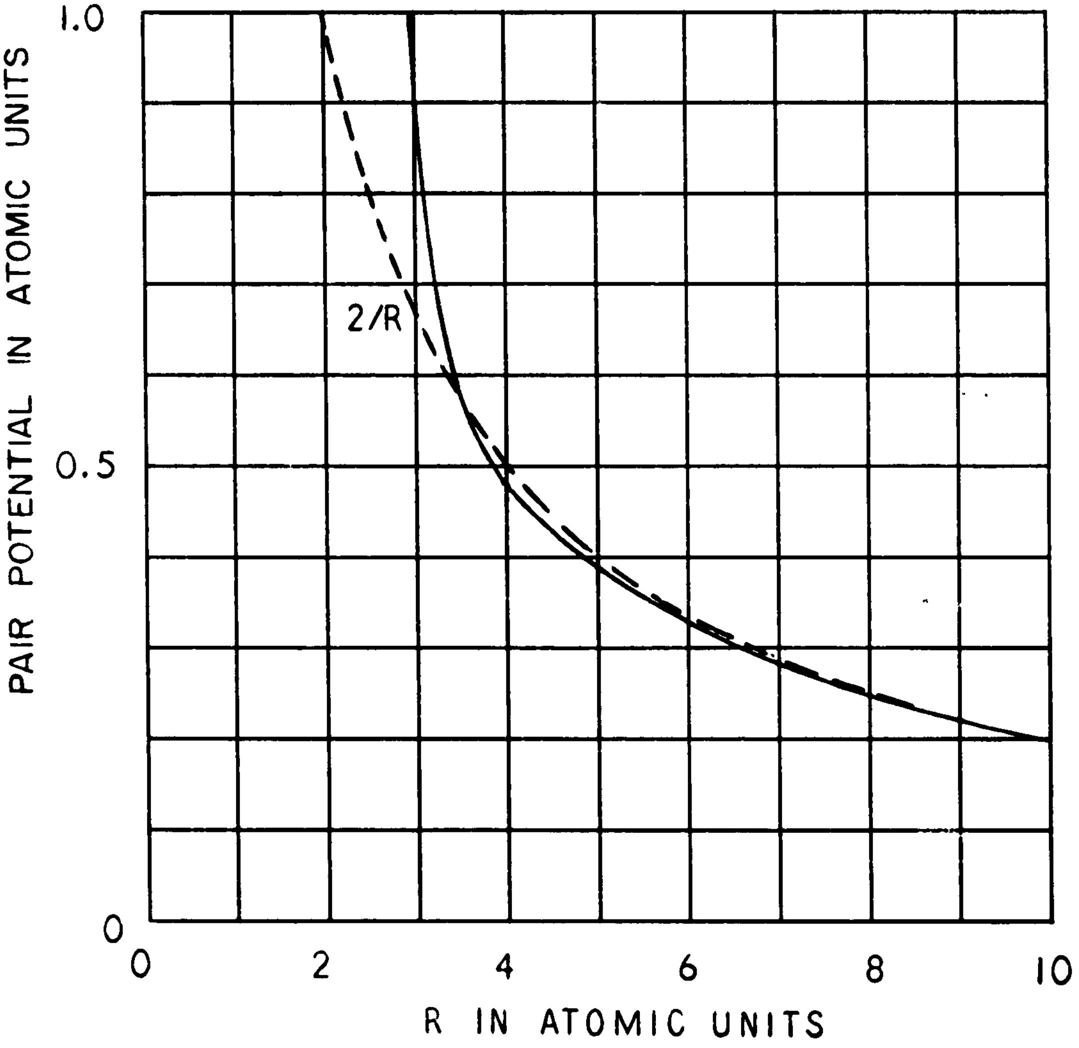

Fig. 4.15. Non-bonding pair potential for O^{++}-O^{+}.

5. SECOND VIRIAL COEFFICIENT CALCULATION FOR GENERAL POLYRECIPROCAL POTENTIALS

Pair interactions in non-polar gases are often approximated by means of a two-term reciprocal form usually referred to as the Lennard-Jones potential. Such an energy of interaction had been introduced by Gruneisen(50) in the theory of solids as a step beyond the reciprocal term for repulsion only which Mie used earlier.(51)* While the 12, 6 potential is quite commonly used in the study of second virial coefficients for simple-non-polar gases, we note that calculations have also been reported for a 9,6 form(52) and that even a 28, 7 potential has been found useful for large compact molecules.(53) It is conceded that theory and some empirical evidence, also, favor an exponential form for the repulsion term. However, there are well-known advantages for the simple power repulsion which have encouraged its continued use. For the attraction potential, the inverse 6th power is theoretically indicated as due to instantaneous dipole-dipole effects. Higher multipole effects are also theoretically present and estimates of 8th and 10th power attraction potentials of such origin have been reported.(44, 54) In the interaction of ions with neutral molecules or atoms, potential energy terms involving inverse powers of distance also appear. The leading term for the induction energy varies as the inverse 4th power, while a higher order term varies as the inverse 7th power.(55) In toto, a considerable variety of potential terms could be taken into account in estimating contributions to the second virial coefficient. With this in view, we shall consider the evaluation in the case of a general polyreciprocal potential.

The integral giving the second virial coefficient can be taken in a well-known form as

$$B_{ab} = N_o \int_0^{\infty} (1 - e^{-U_{ab}/kT}) \cdot 2\pi r^2 dr \qquad (1)$$

with a factor of two to be brought in automatically for unlike particles ($a \neq b$) by including the pair with reversed order in performing a double summation for the indices a and b. Integration by parts in the style of Lennard-Jones(56) is not the only possible evaluation procedure. We find that we have the option, instead, of directly separating out a factor due to the repulsive part of the

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*There has also been a rumor that, several years earlier than Lennard-Jones, R. H. Kent as a student at Harvard similarly applied this potential in the study of gas properties but that theoretical work was not acceptable there for a degree at that time.

potential, U_r,

$$B_{ab}=N_o\int_0^{\infty} e^{-U_r/kT}\left(e^{U/kT}-e^{-(U-U_r)/kT}\right)\cdot 2\pi r^2 dr. \tag{2}$$

We will use the general polyreciprocal potential function in the form

$$U = k_\delta r^{-\delta} - \sum_{i=1}^{l} k(\gamma_i)\, r^{-\gamma_i} \tag{3}$$

in which the leading repulsion term, varying as $r^{-\delta}$, is separated off while the other potential terms are shown as having the form of attraction terms. Thus, in this case, we have

$$B_{ab} = N_o\int_0^{\infty} e^{-(k_\delta/kT)r^{-\delta}}\left[\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{k_\delta}{kT}r^{-\delta}\right)^n - \prod_{i=1}^{l}\left[\sum_{s_i=0}^{\infty}\frac{1}{s_i!}\left(\frac{k_{\gamma_i} r^{-\gamma_i}}{kT}\right)^{s_i}\right]\right]\cdot 2\pi r^2 dr. \tag{4}$$

The single term arising for $s_i = 0$ for all i may be considered to be only formally present, since it is removed by the n = 0 term of the first summation. We now make a change of variable according to $r^{-\delta} = x\, kT/k_\delta$, obtaining

$$B_{ab} = \frac{2\pi}{3}N_o\left(\frac{k_\delta}{kT}\right)^{3/\delta}(3/\delta)\left[\sum_{n=0}^{\infty}\frac{1}{n!}\left(\int_0^{\infty} e^{-x}x^{n-3/\delta-1}dx\right) - \sum_{s_1=0}^{\infty}\cdots\sum_{s_l=0}^{\infty}\left(\int_0^{\infty} e^{-x}x^{\Sigma_i\gamma_i s_i-3/\delta-1}dx\right)\prod_{i=1}^{l}\left(\frac{1}{s_i!}\left[\frac{k_{\gamma_i}}{kT}\left(\frac{kT}{k_\delta}\right)^{\gamma_i/\delta}\right]^{s_i}\right)\right] \tag{5}$$

from which it follows that

$$B_{ab} = \frac{2\pi}{3}N_o\left(\frac{k_\delta}{kT}\right)^{3/\delta}(3/\delta)\left[\sum_{n=0}^{\infty}\frac{1}{n!}\Gamma(n-3/\delta) - \sum_{s_1=0}^{\infty}\cdots\sum_{s_l=0}^{\infty}\Gamma(\Sigma_i\gamma_i s_i/\delta-3/\delta)\prod_{i=1}^{l}\left(\frac{1}{s_i!}\left[\frac{k_{\gamma_i}}{kT}\left(\frac{kT}{k_\delta}\right)^{\gamma_i/\delta}\right]^{s_i}\right)\right] \tag{6}$$

To simplify the first summation, we make a formal binomial expansion of $(1-1)^{3/\delta}$, obtaining

$$\begin{aligned}(1-1)^{3/\delta} &= 1+\sum_{n=1}^{\infty}(3/\delta)(3/\delta-1)(3/\delta-2)\,\ldots\ldots\ldots(3/\delta+1-n)\,(-1)^n/n!\\ &= 1+\sum_{n=1}^{\infty}(n-1-3/\delta)\,(n-2-3/\delta)\ldots\ldots\ldots\ldots(-3/\delta)\,/n!\\ &= 1+\sum_{n=1}^{\infty}\frac{(n-1-3/\delta)\,(n-2-3/\delta)\ldots\ldots\ldots\ldots(-3/\delta)\;\Gamma(-3/\delta)}{n!\;\Gamma(-3/\delta)}\\ &= 1+\sum_{n=1}^{\infty}\Gamma(n-3/\delta)/n!\,\Gamma(-3/\delta)\ ,\end{aligned}$$

which by its origin is identically zero. Thus, it follows that $\sum_{n=1}^{\infty}\Gamma(n-3/\delta)/n! = -\Gamma(-3/\delta)$, with the final result that

$$B_{ab} = \frac{2\pi}{3}N_o\left(\frac{k_\delta}{kT}\right)^{3/\delta}(-3/\delta)\sum_{s_1=0}^{\infty}\cdots\sum_{s_l=0}^{\infty}\Gamma(\Sigma_i\gamma_i s_i/\delta-3/\delta)\prod_{i=1}^{l}\left(\frac{1}{s_i!}\left[\frac{k_{\gamma_i}}{kT}\left(\frac{kT}{k_\delta}\right)^{\gamma_i/\delta}\right]^{s_i}\right) \tag{7}$$

The first and second derivatives follow directly in the forms

$$\begin{aligned}T\;dB_{ab}/dT &= \frac{2\pi}{3}N_o\left(\frac{k_\delta}{kT}\right)^{3/\delta}(-3/\delta)\sum_{s_1=0}^{\infty}\cdots\sum_{s_l=0}^{\infty}\left[\Sigma_i(\gamma_i/\delta-1)s_i-3/\delta\right]\Gamma(\Sigma\gamma_i s_i/\delta-3/\delta)\\ &\quad\cdot\prod_{i=1}^{l}\left(\frac{1}{s_i!}\left[\frac{k_{\gamma_i}}{kT}\left(\frac{kT}{k_\delta}\right)^{\gamma_i/\delta}\right]^{s_i}\right)\end{aligned} \tag{8}$$

and

$$\begin{aligned}T^2d^2B_{ab}/dT^2 &= \frac{2\pi}{3}N_o\left(\frac{k_\delta}{kT}\right)^{3/\delta}(-3/\delta)\sum_{s_1=0}^{\infty}\cdots\sum_{s_l=0}^{\infty}\left[\Sigma_i(\gamma_i/\delta-1)s_i-3/\delta-1\right]\left[\Sigma_i(\gamma_i/\delta-1)s_i-3/\delta\right]\\ &\quad\cdot\Gamma(\Sigma_i\gamma_i s_i/\delta-3/\delta)\prod_{i=1}^{l}\left(\frac{1}{s_i!}\left[\frac{k_{\gamma_i}}{kT}\left(\frac{kT}{k_\delta}\right)^{\gamma_i/\delta}\right]^{s_i}\right).\end{aligned} \tag{9}$$

We note that these results are readily applicable to the case in which a $1/r^4$ induction energy term is added to the 12, 6 potential. Results of calculations for the combined potential are presented in Chapter 6, covering the second virial coefficient and its first two derivatives.

6. TABLES FOR THE ESTIMATION OF SECOND VIRIAL COEFFICIENTS FOR ION-NEUTRAL INTERACTIONS

The interaction of ions with neutral molecules and atoms includes an attractive potential varying as r^{-4}. For non-polar gases, the Lennard-Jones 12, 6 potential is commonly used in the correlation and prediction of various thermodynamic and transport properties. By adding the r^{-4} induction term to a Lennard-Jones 12, 6 form of potential, a useful approximation for the ion-neutral interaction,

$$U = k_{12}r^{-12} - k_6 r^{-6} - k_4 r^{-4}, \tag{1}$$

is obtained.

Mason and Schamp(46) have used such a potential in discussing ionic mobility, pointing out that Margenau(41) derived an induced quadrupole contribution to the r^{-6} term. They wrote the potential in the form

$$U = \frac{1}{2}\varepsilon\left[(1+\gamma)(r_m/r)^{12} - 4\gamma(r_m/r)^6 - 3(1-\gamma)(r_m/r)^4\right], \tag{2}$$

which reduces to the 12, 6 potential for $\gamma = 1$ and to the 12, 4 potential for $\gamma = 0$. The use of r_m, the separation at the energy minimum, rather than σ, the collision diameter, for the scale of distance is appropriate for involved types of potential functions. ε is the maximum binding energy, corresponding to the distance r_m.

We have calculated the second virial coefficients, B, and its first two temperature derivatives, based on this potential. Values of γ at intervals of 0.1 from 0 to 1 were used, with the temperature variable taken as $T^* = kT/\varepsilon$. The quantity tabulated in Table 6.1 is B^*, where $B = b_m B^*$, with $b_m = \frac{2\pi}{3} N_0 r_m^3$, and with N_0 as Avogadro's number, $6.023_{22} \times 10^{23}$ molecules/mole. The frequent custom of using $b_0 = \frac{2\pi}{3} N_0 \sigma^3$ has not been followed in the present table. We note that for the 12, 6 potential, $b_m/b_0 = 2^{1/2} = 1.41421\ldots$, while for the 12, 4 potential,

$b_m/b_0 = 3^{3/8} = 1.50980$. These are special cases of the general LJ-δ,γ potential, for which $b_m/b_0 = (\delta/\gamma)^{3/(\delta-\gamma)}$. The derivative functions tabulated in Tables 6.2 and 6.3 are, respectively,

$$B^*(1) = T^* dB^*/dT^* \tag{3}$$

and

$$B^*(2) = T^{*2} d^2B^*/dT^{*2}. \tag{4}$$

The formulas used in this evaluation may be obtained by specializing to the 12, 6, 4 potential from the general polyreciprocal potential function for which a derivation of the second virial coefficient is given in Chapter 5. The formulas are

$$B^* = -\frac{1}{4}(u/kT)^{1/4} \sum_{s=0}^{\infty} \sum_{t=0}^{\infty} \Gamma\left(\frac{s}{2}+\frac{t}{3}-\frac{1}{4}\right) (s!\,t!)^{-1} \left[(w/kT)^{2/3}\right]^t \left[(v/kT)^{1/2}\right]^s, \tag{5}$$

$$B^*(1) = -\frac{1}{4}(u/kT)^{1/4} \sum_{s=0}^{\infty} \sum_{t=0}^{\infty} \left(\frac{s}{2}+\frac{2t}{3}+\frac{1}{4}\right) \Gamma\left(\frac{s}{2}+\frac{t}{3}-\frac{1}{4}\right) (s!\,t!)^{-1} \left[(w/kT)^{2/3}\right]^t \left[(v/kT)^{1/2}\right]^s, \tag{6}$$

$$B^*(2) = -\frac{1}{4}(u/kT)^{1/4} \sum_{s=0}^{\infty} \sum_{t=0}^{\infty} \left(\frac{s}{2}+\frac{2t}{3}+\frac{5}{4}\right)\left(\frac{s}{2}+\frac{2t}{3}+\frac{1}{4}\right) \Gamma\left(\frac{s}{2}+\frac{t}{3}-\frac{1}{4}\right) (s!\,t!)^{-1} \left[(w/kT)^{2/3}\right]^t \left[(v/kT)^{1/2}\right]^s. \tag{7}$$

$$\left.\begin{aligned} \text{Here, } u &= \tfrac{1}{2}(1+\gamma)\varepsilon \\ v &= 8\gamma^2(1+\gamma)^{-1}\varepsilon \\ \text{and } w &= 3^{3/2}\cdot 2^{-1}(1-\gamma)^{3/2}(1+\gamma)^{-1/2}\varepsilon . \end{aligned}\right\} \tag{8}$$

It is readily possible to convert from the doubly infinite summations to an arrangement with one infinite and one finite summation, but with a more complex indexing. The form shown here was more convenient for simple coding, making use of a rapid gamma function sub-routine and halting the summations where further contributions were completely negligible.

In order to use the present tables, one needs values of the parameters ε/k, b_m and γ. These may be obtained from k_{12}, k_6 and k_4, which may be the more readily available from theoretical and empirical relations.

If we set rdU/dr equal to zero to determine r_m, starting with eq. (1), we have

$$12k_{12}r_m^{-12} - 6k_6r_m^{-6} - 4k_4r_m^{-4} = 0. \tag{9}$$

Taking k_4 and k_{12} as most important in determining r_m, we find

$$r_m^{-8} = \frac{k_4}{k_{12}}\left(1 + \frac{3k_6}{2k_4}r_m^{-2}\right)$$

which, using the variables

$$x = (3k_{12}/k_4)^{1/4}r_m^{-2}$$

and

$$q = \frac{3k_6}{2k_4}\left(\frac{k_4}{3k_{12}}\right)^{1/4},$$

becomes

$$x = (1 + qx)^{1/4} . \tag{10}$$

This can be solved iteratively using multinomial expansion, or by binomial expansion of the right-hand side followed by series inversion, giving

$$x = 1 + \frac{1}{4}q - \frac{1}{32}q^2 + \frac{7}{2048}q^4 - \frac{1}{1024}q^5 \ldots . \tag{11}$$

For the binding energy $\mathcal{E}$, eq. (1) gives

$$-\mathcal{E} = k_{12}r_m^{-12} - k_6r_m^{-6} - k_4r_m^{-4} .$$

We eliminate $k_{12}r_m^{-12}$ from the expression with the help of eq. (9), obtaining

$$\mathcal{E} = \frac{2}{3}k_4r_m^{-4}\left(1 + \frac{3k_6}{4k_4}r_m^{-2}\right)$$

$$= \frac{2k_4}{3}\left(\frac{k_4}{3k_{12}}\right)^{1/2} x^2(1 + \frac{1}{2}qx).$$

On substituting the series for x, one has

$$= \frac{2k_4^{3/2}}{3^{3/2}k_{12}^{1/2}}\left[1 + q + \frac{3}{8}q^2 + \frac{1}{32}q^3 - \frac{1}{128}q^4 + \frac{9}{2048}q^5 \ldots\right]. \tag{12}$$

If one adopts this value of ϵ, consistent values of γ and r_m follow from the exact relationships

$$\gamma = \sqrt{(1+\delta)^2 - 1} + \delta, \tag{13}$$

where $\delta = k_6^2/16k_{12}\epsilon$, and

$$r_m = [3(1-\gamma)k_{12}/(1+\gamma)k_4]^{1/8}. \tag{14}$$

Somewhat similarly, the equations may be solved to obtain σ. Setting U of eq. (1) equal to zero,

$$\sigma^{-8} = \frac{k_4}{k_{12}}(1 + \frac{k_6}{k_4}\sigma^{-2})$$

or

$$y = (1 + py)^{1/4}$$

where $y = (k_{12}/k_4)^{1/4}\sigma^{-2}$ and $p = k_6(k_{12}k_4^3)^{-1/4}$. The solution for y in terms of p is identically as for x in terms of q in eq. (11). Then one may obtain σ immediately as

$$\begin{aligned} \sigma &= (k_{12}/k_4)^{1/8} y^{-1/2} \\ &= (k_{12}/k_4)^{1/8}\left[1 - \frac{1}{8}p + \frac{5}{128}p^2 - \frac{11}{1024}p^3 + \frac{51}{32768}p^4 + \frac{33}{262144}p^5 \dots\right] \end{aligned} \tag{15}$$

by use of the multinomial theorem.

The code prepared for the calculation of Tables 6.1, 6.2, and 6.3 involves a different formulation. It was prepared at a time when the use of another parameter λ instead of γ appeared preferable. The two are related by $\lambda = 2\gamma/(1+\gamma)$ or $\gamma = \lambda/(2-\lambda)$. With λ, the relations

$$\lambda = 2\left[\sqrt{(1+\delta)^2 - 1} - \delta\right], \tag{16}$$

$$r_m = [3(1-\lambda)k_{12}/k_4]^{1/8}, \tag{17}$$

$$\left.\begin{aligned} u &= (2-\lambda)^{-1}\varepsilon, \\ v &= 4\lambda^2(2-\lambda)^{-1}\varepsilon\,, \\ w &= [3(1-\lambda)]^{3/2}(2-\lambda)^{-1}\varepsilon \end{aligned}\right\} \tag{18}$$

and

obtain. The corresponding potential function using λ is

$$U = \varepsilon(2-\lambda)^{-1}[(r_m/r)^{12} - 2\lambda(r_m/r)^6 - 3(1-\lambda)(r_m/r)^4]. \tag{19}$$

Table 6.1. The Second Virial Coefficient for the 12, 6, 4 Potential

B^*

T^*	$\gamma = 0$	$\gamma = 0.1$	$\gamma = 0.2$	$\gamma = 0.3$	$\gamma = 0.4$	$\gamma = 0.5$
0.30	-33.95845	-32.38962	-30.85725	-29.35939	-27.89438	-26.46058
0.35	-24.28699	-23.09386	-21.92338	-20.77447	-19.64610	-18.53734
0.40	-18.79595	-17.82959	-16.87878	-15.94277	-15.02092	-14.11262
0.45	-15.28798	-14.47368	-13.67079	-12.87878	-12.09717	-11.32554
0.50	-12.86076	-12.15580	-11.45965	-10.77188	-10.09212	-9.42007
0.55	-11.08315	-10.46081	-9.84551	-9.23692	-8.63473	-8.03870
0.60	-9.72528	-9.16769	-8.61588	-8.06960	-7.52857	-6.99260
0.65	-8.65399	-8.14856	-7.64801	-7.15210	-6.66061	-6.17338
0.70	-7.78695	-7.32449	-6.86624	-6.41195	-5.96146	-5.51461
0.75	-7.07065	-6.64424	-6.22149	-5.80221	-5.38623	-4.97341
0.80	-6.46876	-6.07305	-5.68056	-5.29113	-4.90462	-4.52089
0.85	-5.95582	-5.58654	-5.22017	-4.85653	-4.49548	-4.13692
0.90	-5.51338	-5.16714	-4.82353	-4.48239	-4.14358	-3.80700
0.95	-5.12779	-4.80182	-4.47823	-4.15690	-3.83769	-3.52049
1.00	-4.78872	-4.48071	-4.17489	-3.87113	-3.56932	-3.26935
1.10	-4.22005	-3.94246	-3.66676	-3.39282	-3.12055	-2.84986
1.20	-3.76181	-3.50902	-3.25790	-3.00833	-2.76021	-2.51347
1.30	-3.38465	-3.15249	-2.92182	-2.69253	-2.46453	-2.23775
1.40	-3.06882	-2.85407	-2.64068	-2.42854	-2.21757	-2.00769
1.50	-2.80048	-2.60064	-2.40205	-2.20461	-2.00823	-1.81285
1.60	-2.56971	-2.38277	-2.19700	-2.01229	-1.82857	-1.64576
1.70	-2.36913	-2.19348	-2.01892	-1.84536	-1.67271	-1.50091
1.80	-2.19322	-2.02752	-1.86285	-1.69912	-1.53624	-1.37417
1.90	-2.03771	-1.88085	-1.72497	-1.56997	-1.41579	-1.26237
2.00	-1.89926	-1.75030	-1.60229	-1.45512	-1.30872	-1.16303
2.10	-1.77522	-1.63338	-1.49244	-1.35231	-1.21292	-1.07420
2.20	-1.66347	-1.52807	-1.39354	-1.25977	-1.12672	-0.99432
2.30	-1.56229	-1.43274	-1.30402	-1.17606	-1.04877	-0.92211
2.40	-1.47026	-1.34605	-1.22264	-1.09997	-0.97795	-0.85653
2.50	-1.38619	-1.26687	-1.14834	-1.03052	-0.91333	-0.79672
2.60	-1.30911	-1.19430	-1.08025	-0.96689	-0.85415	-0.74197
2.70	-1.23820	-1.12754	-1.01763	-0.90839	-0.79975	-0.69166
2.80	-1.17274	-1.06593	-0.95985	-0.85443	-0.74959	-0.64529
2.90	-1.11214	-1.00890	-0.90638	-0.80450	-0.70320	-0.60241
3.00	-1.05588	-0.95597	-0.85677	-0.75819	-0.66017	-0.56266
3.10	-1.00353	-0.90672	-0.81061	-0.71511	-0.62016	-0.52572
3.20	-0.95468	-0.86078	-0.76756	-0.67495	-0.58288	-0.49129
3.30	-0.90902	-0.81784	-0.72733	-0.63742	-0.54804	-0.45915
3.40	-0.86623	-0.77761	-0.68965	-0.60228	-0.51544	-0.42906
3.50	-0.82606	-0.73985	-0.65430	-0.56931	-0.48485	-0.40085
3.60	-0.78829	-0.70435	-0.62105	-0.53833	-0.45611	-0.37436
3.70	-0.75270	-0.67091	-0.58975	-0.50915	-0.42906	-0.34942
3.80	-0.71912	-0.63935	-0.56022	-0.48164	-0.40355	-0.32592
3.90	-0.68738	-0.60954	-0.53232	-0.45565	-0.37947	-0.30373
4.00	-0.65735	-0.58133	-0.50592	-0.43106	-0.35669	-0.28275
4.10	-0.62888	-0.55459	-0.48091	-0.40778	-0.33512	-0.26290
4.20	-0.60186	-0.52922	-0.45719	-0.38569	-0.31467	-0.24407
4.30	-0.57619	-0.50512	-0.43465	-0.36471	-0.29525	-0.22620
4.40	-0.55177	-0.48220	-0.41322	-0.34477	-0.27679	-0.20922
4.50	-0.52851	-0.46037	-0.39287	-0.32579	-0.25922	-0.19307
4.60	-0.50634	-0.43956	-0.37337	-0.30770	-0.24248	-0.17768
4.70	-0.48518	-0.41970	-0.35481	-0.29044	-0.22652	-0.16301
4.80	-0.46496	-0.40074	-0.33709	-0.27396	-0.21129	-0.14902
4.90	-0.44563	-0.38260	-0.32016	-0.25822	-0.19673	-0.13564
5.00	-0.42713	-0.36525	-0.30395	-0.24316	-0.18281	-0.12286
6.00	-0.27827	-0.22576	-0.17379	-0.12231	-0.07125	-0.02057
7.00	-0.17478	-0.12892	-0.08359	-0.03873	0.00572	0.04981
8.00	-0.09908	-0.05820	-0.01784	0.02207	0.06159	0.10074
9.00	-0.04160	-0.00458	0.03193	0.06800	0.10367	0.13900
10.00	0.00333	0.03727	0.07070	0.10369	0.13629	0.16856
20.00	0.18674	0.20675	0.22630	0.24544	0.26424	0.28272
30.00	0.23430	0.24960	0.26445	0.27892	0.29305	0.30688
40.00	0.25202	0.26491	0.27737	0.28945	0.30121	0.31268
50.00	0.25924	0.27065	0.28164	0.29226	0.30256	0.31259
60.00	0.26189	0.27228	0.28226	0.29189	0.30121	0.31025
70.00	0.26228	0.27193	0.28118	0.29008	0.29867	0.30700
80.00	0.26148	0.27056	0.27925	0.28759	0.29563	0.30342
90.00	0.26004	0.26867	0.27690	0.28480	0.29241	0.29976
100.00	0.25824	0.26650	0.27437	0.28191	0.28915	0.29615
200.00	0.23830	0.24470	0.25076	0.25651	0.26200	0.26727
300.00	0.22300	0.22865	0.23396	0.23900	0.24380	0.24838
400.00	0.21154	0.21673	0.22162	0.22624	0.23063	0.23487

Table 6.1. The Second Virial Coefficient for the 12, 6, 4 Potential - Cont.

B^*

T^*	$\gamma = 0.5$	$\gamma = 0.6$	$\gamma = 0.7$	$\gamma = 0.8$	$\gamma = 0.9$	$\gamma = 1.0$
0.30	-26.46058	-25.05668	-23.68126	-22.33319	-21.01127	-19.71453
0.35	-18.53734	-17.44743	-16.37559	-15.32110	-14.28333	-13.26169
0.40	-14.11262	-13.21733	-12.33459	-11.46394	-10.60495	-9.75724
0.45	-11.32554	-10.56350	-9.81073	-9.06689	-8.33172	-7.60490
0.50	-9.42007	-8.75542	-8.09793	-7.44736	-6.80349	-6.16611
0.55	-8.03870	-7.44858	-6.86419	-6.28533	-5.71184	-5.14355
0.60	-6.99260	-6.46150	-5.93509	-5.41324	-4.89579	-4.38262
0.65	-6.17338	-5.69023	-5.21103	-4.73564	-4.26397	-3.79588
0.70	-5.51461	-5.07125	-4.63126	-4.19454	-3.76098	-3.33050
0.75	-4.97341	-4.56362	-4.15676	-3.75273	-3.35145	-2.95283
0.80	-4.52089	-4.13983	-3.76134	-3.38534	-3.01175	-2.64049
0.85	-4.13692	-3.78073	-3.42682	-3.07512	-2.72557	-2.37808
0.90	-3.80700	-3.47257	-3.14018	-2.80976	-2.48127	-2.15463
0.95	-3.52049	-3.20524	-2.89184	-2.58023	-2.27035	-1.96216
1.00	-3.26935	-2.97115	-2.67464	-2.37977	-2.08647	-1.79469
1.10	-2.84986	-2.58067	-2.31291	-2.04653	-1.78148	-1.51771
1.20	-2.51347	-2.26803	-2.02383	-1.78082	-1.53896	-1.29821
1.30	-2.23775	-2.01212	-1.78759	-1.56411	-1.34164	-1.12013
1.40	-2.00769	-1.79885	-1.59099	-1.38406	-1.17804	-0.97287
1.50	-1.81285	-1.61841	-1.42487	-1.23216	-1.04027	-0.84915
1.60	-1.64576	-1.46382	-1.28269	-1.10234	-0.92272	-0.74381
1.70	-1.50091	-1.32992	-1.15967	-0.99014	-0.82130	-0.65310
1.80	-1.37417	-1.21284	-1.05222	-0.89226	-0.73292	-0.57419
1.90	-1.26237	-1.10964	-0.95758	-0.80613	-0.65527	-0.50498
2.00	-1.16303	-1.01801	-0.87361	-0.72979	-0.58653	-0.44380
2.10	-1.07420	-0.93612	-0.79863	-0.66169	-0.52528	-0.38936
2.20	-0.99432	-0.86252	-0.73128	-0.60057	-0.47036	-0.34062
2.30	-0.92211	-0.79603	-0.67048	-0.54544	-0.42088	-0.29676
2.40	-0.85653	-0.73567	-0.61533	-0.49547	-0.37606	-0.25709
2.50	-0.79672	-0.68065	-0.56508	-0.44998	-0.33531	-0.22105
2.60	-0.74197	-0.63031	-0.51913	-0.40840	-0.29810	-0.18818
2.70	-0.69166	-0.58407	-0.47696	-0.37027	-0.26400	-0.15810
2.80	-0.64529	-0.54148	-0.43812	-0.33518	-0.23264	-0.13047
2.90	-0.60241	-0.50211	-0.40225	-0.30279	-0.20372	-0.10501
3.00	-0.56266	-0.46563	-0.36902	-0.27281	-0.17697	-0.08148
3.10	-0.52572	-0.43173	-0.33816	-0.24498	-0.15217	-0.05969
3.20	-0.49129	-0.40016	-0.30944	-0.21909	-0.12910	-0.03945
3.30	-0.45915	-0.37069	-0.28263	-0.19495	-0.10762	-0.02061
3.40	-0.42906	-0.34312	-0.25757	-0.17239	-0.08755	-0.00303
3.50	-0.40085	-0.31728	-0.23410	-0.15127	-0.06878	0.01340
3.60	-0.37436	-0.29302	-0.21206	-0.13146	-0.05118	0.02879
3.70	-0.34942	-0.27019	-0.19134	-0.11284	-0.03465	0.04323
3.80	-0.32592	-0.24869	-0.17183	-0.09531	-0.01911	0.05680
3.90	-0.30373	-0.22839	-0.15342	-0.07879	-0.00446	0.06957
4.00	-0.28275	-0.20921	-0.13603	-0.06319	0.00935	0.08161
4.10	-0.26290	-0.19106	-0.11959	-0.04844	0.02241	0.09298
4.20	-0.24407	-0.17386	-0.10400	-0.03447	0.03476	0.10372
4.30	-0.22620	-0.15754	-0.08923	-0.02123	0.04646	0.11389
4.40	-0.20922	-0.14204	-0.07520	-0.00867	0.05756	0.12352
4.50	-0.19307	-0.12729	-0.06186	0.00326	0.06810	0.13267
4.60	-0.17768	-0.11325	-0.04916	0.01462	0.07811	0.14135
4.70	-0.16301	-0.09987	-0.03707	0.02543	0.08765	0.14960
4.80	-0.14902	-0.08711	-0.02554	0.03573	0.09672	0.15745
4.90	-0.13564	-0.07492	-0.01453	0.04556	0.10538	0.16494
5.00	-0.12286	-0.06327	-0.00401	0.05495	0.11364	0.17207
6.00	-0.02057	0.02978	0.07981	0.12957	0.17906	0.22833
7.00	0.04981	0.09357	0.13704	0.18024	0.22320	0.26593
8.00	0.10074	0.13958	0.17814	0.21644	0.25450	0.29234
9.00	0.13900	0.17402	0.20876	0.24324	0.27750	0.31155
10.00	0.16856	0.20052	0.23221	0.26366	0.29488	0.32589
20.00	0.28272	0.30092	0.31888	0.33662	0.35415	0.37150
30.00	0.30688	0.32045	0.33379	0.34691	0.35984	0.37259
40.00	0.31268	0.32390	0.33488	0.34567	0.35626	0.36669
50.00	0.31259	0.32237	0.33192	0.34128	0.35046	0.35947
60.00	0.31025	0.31905	0.32764	0.33603	0.34424	0.35229
70.00	0.30700	0.31509	0.32297	0.33066	0.33817	0.34553
80.00	0.30342	0.31096	0.31830	0.32545	0.33244	0.33926
90.00	0.29976	0.30687	0.31379	0.32051	0.32707	0.33348
100.00	0.29615	0.30291	0.30948	0.31586	0.32208	0.32815
200.00	0.26727	0.27233	0.27721	0.28192	0.28649	0.29093
300.00	0.24838	0.25277	0.25699	0.26106	0.26499	0.26879
400.00	0.23482	0.23883	0.24267	0.24637	0.24994	0.25339

Table 6.2. First Derivative of the Second Virial Coefficient for the 12, 6, 4 Potential

$B^*(1) = T^*D(B^*(0))/D(T^*)$

T^*	$\gamma = 0$	$\gamma = 0.1$	$\gamma = 0.2$	$\gamma = 0.3$	$\gamma = 0.4$	$\gamma = 0.5$
0.30	79.52332	76.52927	73.65334	70.88857	68.22840	65.66716
0.35	49.17297	47.19358	45.28075	43.43074	41.64033	39.90648
0.40	34.28169	32.82614	31.41278	30.03942	28.70420	27.40527
0.45	25.83105	24.68666	23.57130	22.48355	21.42213	20.38596
0.50	20.52379	19.58291	18.66318	17.76363	16.88337	16.02162
0.55	16.93565	16.13736	15.35516	14.58833	13.83624	13.09832
0.60	14.37144	13.67828	12.99778	12.32938	11.67262	11.02704
0.65	12.45861	11.84605	11.24371	10.65117	10.06803	9.49397
0.70	10.98241	10.43357	9.89317	9.36084	8.83631	8.31927
0.75	9.81149	9.31428	8.82416	8.34082	7.86403	7.39355
0.80	8.86160	8.40706	7.95856	7.51585	7.07873	6.64699
0.85	8.07641	7.65774	7.24428	6.83582	6.43218	6.03320
0.90	7.41700	7.02890	6.64536	6.26617	5.89119	5.52029
0.95	6.85570	6.49398	6.13626	5.78239	5.43222	5.08564
1.00	6.37230	6.03357	5.69839	5.36662	5.03815	4.71287
1.10	5.58262	5.28203	4.98430	4.68931	4.39697	4.10721
1.20	4.96513	4.69490	4.42702	4.16141	3.89799	3.63668
1.30	4.46920	4.22372	3.98022	3.73862	3.49886	3.26088
1.40	4.06221	3.83730	3.61409	3.39249	3.17247	2.95395
1.50	3.72222	3.51469	3.30862	3.10395	2.90064	2.69863
1.60	3.43396	3.24130	3.04991	2.85975	2.67077	2.48294
1.70	3.18644	3.00665	2.82798	2.65040	2.47386	2.29833
1.80	2.97159	2.80306	2.63552	2.46895	2.30331	2.13856
1.90	2.78334	2.62473	2.46701	2.31016	2.15414	1.99892
2.00	2.61704	2.46723	2.31625	2.17004	2.02258	1.87585
2.10	2.46904	2.32712	2.18594	2.04547	1.90568	1.76655
2.20	2.33649	2.20166	2.06751	1.93400	1.80112	1.66884
2.30	2.21707	2.08866	1.96087	1.83367	1.70704	1.58096
2.40	2.10893	1.98635	1.86434	1.74288	1.62194	1.50150
2.50	2.01054	1.89328	1.77655	1.66033	1.54458	1.42931
2.60	1.92064	1.80825	1.69636	1.58494	1.47397	1.36343
2.70	1.83816	1.73026	1.62283	1.51583	1.40925	1.30307
2.80	1.76223	1.65848	1.55515	1.45223	1.34971	1.24756
2.90	1.69209	1.59217	1.49266	1.39352	1.29475	1.19634
3.00	1.62711	1.53075	1.43477	1.33915	1.24387	1.14892
3.10	1.56673	1.47369	1.38100	1.28865	1.19662	1.10491
3.20	1.51049	1.42054	1.33092	1.24163	1.15264	1.06394
3.30	1.45797	1.37091	1.29417	1.19773	1.11158	1.02571
3.40	1.40881	1.32446	1.24042	1.15666	1.07318	0.98996
3.50	1.36270	1.28090	1.19939	1.11815	1.03717	0.95645
3.60	1.31936	1.23996	1.16083	1.08197	1.00335	0.92497
3.70	1.27855	1.20142	1.12454	1.04791	0.97151	0.89535
3.80	1.24007	1.16506	1.09031	1.01579	0.94150	0.86742
3.90	1.20370	1.13072	1.05797	0.98545	0.91315	0.84105
4.00	1.16928	1.09821	1.02737	0.95675	0.88633	0.81611
4.10	1.13667	1.06741	0.99838	0.92955	0.86092	0.79248
4.20	1.10572	1.03818	0.97086	0.90374	0.83681	0.77007
4.30	1.07630	1.01041	0.94472	0.87923	0.81391	0.74877
4.40	1.04831	0.98398	0.91985	0.85590	0.79213	0.72852
4.50	1.02164	0.95880	0.89615	0.83368	0.77138	0.70924
4.60	0.99621	0.93479	0.87356	0.81249	0.75159	0.69085
4.70	0.97193	0.91187	0.85198	0.79227	0.73271	0.67330
4.80	0.94872	0.88996	0.83137	0.77293	0.71466	0.65653
4.90	0.92651	0.86899	0.81164	0.75444	0.69739	0.64049
5.00	0.90524	0.84892	0.79275	0.73674	0.68086	0.62513
6.00	0.73341	0.68674	0.64020	0.59377	0.54744	0.50122
7.00	0.61269	0.57283	0.53307	0.49341	0.45383	0.41434
8.00	0.52324	0.48844	0.45373	0.41910	0.38454	0.35005
9.00	0.45432	0.42343	0.39262	0.36187	0.33120	0.30058
10.00	0.39961	0.37183	0.34412	0.31647	0.28887	0.26134
20.00	0.15880	0.14478	0.13080	0.11687	0.10297	0.08912
30.00	0.08139	0.07185	0.06236	0.05291	0.04350	0.03412
40.00	0.04379	0.03647	0.02919	0.02196	0.01476	0.00760
50.00	0.02185	0.01584	0.00989	0.00398	-0.00190	-0.00774
60.00	0.00762	0.00249	-0.00259	-0.00762	-0.01262	-0.01758
70.00	-0.00225	-0.00676	-0.01122	-0.01563	-0.02001	-0.02434
80.00	-0.00945	-0.01350	-0.01749	-0.02144	-0.02534	-0.02921
90.00	-0.01489	-0.01857	-0.02220	-0.02579	-0.02933	-0.03284
100.00	-0.01911	-0.02251	-0.02585	-0.02914	-0.03240	-0.03562
200.00	-0.03565	-0.03775	-0.03980	-0.04180	-0.04375	-0.04567
300.00	-0.03929	-0.04096	-0.04257	-0.04413	-0.04565	-0.04713
400.00	-0.04026	-0.04170	-0.04309	-0.04443	-0.04572	-0.04699

Table 6.2. First Derivative of the Second Virial Coefficient for the 12, 6, 4 Potential – Cont.

$B^*(1) = T^*D(B^*(0))/D(T^*)$

T^*	$\gamma = 0.5$	$\gamma = 0.6$	$\gamma = 0.7$	$\gamma = 0.8$	$\gamma = 0.9$	$\gamma = 1.0$
0.30	65.66716	63.19936	60.82011	58.52484	56.30927	54.16945
0.35	39.90648	38.22634	36.59740	35.01736	33.48388	31.99490
0.40	27.40527	26.14099	24.90991	23.71057	22.54169	21.40203
0.45	20.38596	19.37393	18.38508	17.41853	16.47339	15.54889
0.50	16.02162	15.17763	14.35078	13.54042	12.74596	11.96684
0.55	13.09832	12.37404	11.66290	10.96445	10.27830	9.60402
0.60	11.02704	10.39226	9.76790	9.15364	8.54915	7.95413
0.65	9.49397	8.92867	8.37185	7.82324	7.28259	6.74969
0.70	8.31927	7.80950	7.30675	6.81082	6.32152	5.83866
0.75	7.39355	6.92919	6.47075	6.01807	5.57099	5.12935
0.80	6.64699	6.22049	5.79904	5.38253	4.97081	4.56376
0.85	6.03320	5.63875	5.24868	4.86287	4.48122	4.10362
0.90	5.52029	5.15332	4.79020	4.43081	4.07506	3.72286
0.95	5.08564	4.74254	4.40283	4.06641	3.73320	3.40313
1.00	4.71287	4.39068	4.07150	3.75524	3.44185	3.13125
1.10	4.10721	3.81994	3.53509	3.25261	2.97244	2.69453
1.20	3.63668	3.37743	3.12018	2.86488	2.61149	2.35996
1.30	3.26088	3.02462	2.79004	2.55711	2.32577	2.09601
1.40	2.95395	2.73691	2.52131	2.30710	2.09426	1.88276
1.50	2.69863	2.49789	2.29840	2.10011	1.90300	1.70705
1.60	2.48294	2.29622	2.11058	1.92599	1.74244	1.55989
1.70	2.29833	2.12379	1.95019	1.77752	1.60577	1.43490
1.80	2.13856	1.97469	1.81166	1.64946	1.48807	1.32747
1.90	1.99892	1.84449	1.69081	1.53788	1.38567	1.23416
2.00	1.87585	1.72982	1.58447	1.43980	1.29577	1.15239
2.10	1.76655	1.62805	1.49018	1.35291	1.21623	1.08014
2.20	1.66884	1.53713	1.40600	1.27541	1.14537	1.01585
2.30	1.58096	1.45541	1.33038	1.20586	1.08183	0.95828
2.40	1.50150	1.38156	1.26209	1.14309	1.02454	0.90644
2.50	1.42931	1.31449	1.20011	1.08616	0.97263	0.85951
2.60	1.36343	1.25332	1.14361	1.03430	0.92537	0.81683
2.70	1.30307	1.19728	1.09188	0.98684	0.88217	0.77784
2.80	1.24756	1.14578	1.04435	0.94326	0.84251	0.74209
2.90	1.19634	1.09826	1.00052	0.90310	0.80600	0.70920
3.00	1.14892	1.05430	0.95998	0.86597	0.77225	0.67882
3.10	1.10491	1.01350	0.92238	0.83154	0.74098	0.65070
3.20	1.06394	0.97553	0.88740	0.79953	0.71192	0.62457
3.30	1.02571	0.94011	0.35477	0.76969	0.68485	0.60024
3.40	0.98996	0.90700	0.82428	0.74180	0.65956	0.57754
3.50	0.95645	0.87596	0.79571	0.71568	0.63588	0.55629
3.60	0.92497	0.84682	0.76889	0.69117	0.61367	0.53637
3.70	0.89535	0.81940	0.74366	0.66813	0.59279	0.51766
3.80	0.86742	0.79355	0.71989	0.64642	0.57314	0.50004
3.90	0.84105	0.76915	0.69745	0.62593	0.55459	0.48343
4.00	0.81611	0.74608	0.67623	0.60656	0.53707	0.46774
4.10	0.79248	0.72422	0.65614	0.58823	0.52048	0.45290
4.20	0.77007	0.70349	0.63709	0.57085	0.50476	0.43883
4.30	0.74877	0.68380	0.61899	0.55434	0.48984	0.42549
4.40	0.72852	0.66508	0.60179	0.53865	0.47566	0.41281
4.50	0.70924	0.64725	0.58541	0.52372	0.46217	0.40076
4.60	0.69085	0.63025	0.56980	0.50949	0.44932	0.38927
4.70	0.67330	0.61403	0.55491	0.49591	0.43705	0.37832
4.80	0.65653	0.59853	0.54068	0.48295	0.42535	0.36786
4.90	0.64049	0.58371	0.52707	0.47055	0.41415	0.35787
5.00	0.62513	0.56952	0.51404	0.45869	0.40344	0.34832
6.00	0.50122	0.45510	0.40907	0.36313	0.31728	0.27151
7.00	0.41434	0.37492	0.33558	0.29631	0.25711	0.21797
8.00	0.35005	0.31563	0.28127	0.24697	0.21272	0.17853
9.00	0.30058	0.27001	0.23951	0.20905	0.17864	0.14828
10.00	0.26134	0.23385	0.20641	0.17902	0.15167	0.12436
20.00	0.08912	0.07529	0.06150	0.04773	0.03399	0.02027
30.00	0.03412	0.02477	0.01545	0.00615	-0.00312	-0.01237
40.00	0.00760	0.00047	-0.00663	-0.01371	-0.02076	-0.02780
50.00	-0.00774	-0.01354	-0.01932	-0.02508	-0.03081	-0.03652
60.00	-0.01758	-0.02251	-0.02741	-0.03229	-0.03714	-0.04198
70.00	-0.02434	-0.02865	-0.03293	-0.03718	-0.04140	-0.04561
80.00	-0.02921	-0.03305	-0.03686	-0.04064	-0.04440	-0.04814
90.00	-0.03284	-0.03632	-0.03976	-0.04318	-0.04658	-0.04995
100.00	-0.03562	-0.03880	-0.04196	-0.04509	-0.04820	-0.05128
200.00	-0.04567	-0.04756	-0.04941	-0.05124	-0.05305	-0.05483
300.00	-0.04713	-0.04858	-0.05000	-0.05140	-0.05276	-0.05411
400.00	-0.04699	-0.04821	-0.04941	-0.05058	-0.05173	-0.05286

Table 6.3. Second Derivative of the Second Virial Coefficient for the 12, 6, 4 Potential

B*(2) = T*2D2(B*(0))/D(T*)2

T*	$\gamma = 0$	$\gamma = 0.1$	$\gamma = 0.2$	$\gamma = 0.3$	$\gamma = 0.4$	$\gamma = 0.5$
0.30	-347.75459	-335.99607	-324.81946	-314.18604	-304.06019	-294.41000
0.35	-190.83807	-183.98301	-177.43068	-171.16187	-165.16024	-159.40988
0.40	-121.13211	-116.54191	-112.13230	-107.89276	-103.81421	-99.88789
0.45	-84.73507	-81.37215	-78.12771	-74.99534	-71.96916	-69.04407
0.50	-63.43581	-60.81660	-58.28069	-55.82352	-53.44140	-51.13073
0.55	-49.88134	-47.75121	-45.68235	-43.67181	-41.71688	-39.81510
0.60	-40.68759	-38.89925	-37.15789	-35.46127	-33.80746	-32.19463
0.65	-34.13358	-32.59569	-31.09489	-29.62952	-28.19806	-26.79915
0.70	-29.27234	-27.92495	-26.60758	-25.31892	-24.05780	-22.82314
0.75	-25.54862	-24.35053	-23.17725	-22.02773	-20.90098	-19.79616
0.80	-22.61954	-21.54139	-20.48407	-19.44671	-18.42853	-17.42883
0.85	-20.26379	-19.28397	-18.32189	-17.37683	-16.44813	-15.53523
0.90	-18.33328	-17.43545	-16.55295	-15.68510	-14.83140	-13.99134
0.95	-16.72569	-15.89725	-15.08215	-14.27984	-13.48989	-12.71183
1.00	-15.36836	-14.59937	-13.84211	-13.09613	-12.36099	-11.63636
1.10	-13.20678	-12.53432	-11.87116	-11.21691	-10.57127	-9.93396
1.20	-11.56630	-10.96881	-10.37886	-9.79617	-9.22048	-8.65156
1.30	-10.28134	-9.74376	-9.21242	-8.68710	-8.16758	-7.65371
1.40	-9.24901	-8.76036	-8.27700	-7.79871	-7.32532	-6.85668
1.50	-8.40219	-7.95430	-7.51092	-7.07190	-6.63706	-6.20630
1.60	-7.69543	-7.28200	-6.87248	-6.46672	-6.06461	-5.66601
1.70	-7.09689	-6.71297	-6.33248	-5.95529	-5.58128	-5.21036
1.80	-6.58362	-6.22527	-5.86995	-5.51754	-5.16795	-4.82108
1.90	-6.13869	-5.80271	-5.46943	-5.13874	-4.81055	-4.48480
2.00	-5.74937	-5.43312	-5.11929	-4.80779	-4.49853	-4.19145
2.10	-5.40588	-5.10717	-4.81064	-4.51621	-4.22380	-3.93336
2.20	-5.10060	-4.81758	-4.53653	-4.25740	-3.98010	-3.70458
2.30	-4.82750	-4.55859	-4.29150	-4.02614	-3.76246	-3.50040
2.40	-4.58176	-4.32563	-4.07116	-3.81827	-3.56693	-3.31707
2.50	-4.35947	-4.11495	-3.87196	-3.63043	-3.39032	-3.15158
2.60	-4.15743	-3.92351	-3.69101	-3.45986	-3.23001	-3.00143
2.70	-3.97299	-3.74679	-3.52591	-3.30428	-3.08386	-2.86461
2.80	-3.80395	-3.58870	-3.37467	-3.16180	-2.95006	-2.73940
2.90	-3.64846	-3.44147	-3.23561	-3.03084	-2.82712	-2.62441
3.00	-3.50495	-3.30561	-3.10732	-2.91006	-2.71377	-2.51843
3.10	-3.37209	-3.17985	-2.98860	-2.79830	-2.60892	-2.42043
3.20	-3.24874	-3.06311	-2.87841	-2.69461	-2.51167	-2.32956
3.30	-3.13391	-2.95444	-2.77587	-2.59813	-2.42121	-2.24506
3.40	-3.02674	-2.85305	-2.68020	-2.50814	-2.33685	-2.16629
3.50	-2.92650	-2.75823	-2.59074	-2.42400	-2.25799	-2.09268
3.60	-2.83253	-2.66934	-2.50690	-2.34517	-2.18412	-2.02374
3.70	-2.74426	-2.58586	-2.42817	-2.27115	-2.11478	-1.95904
3.80	-2.66119	-2.50730	-2.35409	-2.20152	-2.04956	-1.89821
3.90	-2.58287	-2.43325	-2.28426	-2.13589	-1.98811	-1.84090
4.00	-2.50890	-2.36331	-2.21833	-2.07394	-1.93010	-1.78681
4.10	-2.43893	-2.29717	-2.15598	-2.01536	-1.87526	-1.73569
4.20	-2.37265	-2.23451	-2.09693	-1.95988	-1.82334	-1.68729
4.30	-2.30977	-2.17507	-2.04091	-1.90726	-1.77410	-1.64140
4.40	-2.25003	-2.11861	-1.98771	-1.85729	-1.72734	-1.59784
4.50	-2.19321	-2.06491	-1.93710	-1.80977	-1.68288	-1.55642
4.60	-2.13909	-2.01377	-1.88892	-1.76452	-1.64056	-1.51700
4.70	-2.08749	-1.96501	-1.84299	-1.72139	-1.60021	-1.47943
4.80	-2.03823	-1.91847	-1.79914	-1.68023	-1.56172	-1.44359
4.90	-1.99117	-1.87400	-1.75726	-1.64091	-1.52495	-1.40936
5.00	-1.94615	-1.83147	-1.71720	-1.60331	-1.48979	-1.37663
6.00	-1.58432	-1.48972	-1.39541	-1.30138	-1.20762	-1.11411
7.00	-1.33205	-1.25154	-1.17125	-1.09118	-1.01131	-0.93163
8.00	-1.14609	-1.07601	-1.00611	-0.93638	-0.86681	-0.79740
9.00	-1.00332	-0.94127	-0.87937	-0.81762	-0.75599	-0.69450
10.00	-0.89026	-0.83459	-0.77904	-0.72362	-0.66830	-0.61310
20.00	-0.39406	-0.36649	-0.33898	-0.31152	-0.28411	-0.25674
30.00	-0.23369	-0.21525	-0.19685	-0.17850	-0.16018	-0.14190
40.00	-0.15490	-0.14096	-0.12706	-0.11321	-0.09939	-0.08560
50.00	-0.10832	-0.09706	-0.08584	-0.07466	-0.06351	-0.05240
60.00	-0.07770	-0.06871	-0.05876	-0.04936	-0.03998	-0.03065
70.00	-0.05613	-0.04790	-0.03971	-0.03156	-0.02345	-0.01538
80.00	-0.04017	-0.03288	-0.02563	-0.01843	-0.01126	-0.00413
90.00	-0.02794	-0.02137	-0.01485	-0.00838	-0.00194	0.00446
100.00	-0.01828	-0.01230	-0.00636	-0.00047	0.00539	0.01121
200.00	0.02246	0.02586	0.02921	0.03251	0.03577	0.03899
300.00	0.03394	0.03649	0.03898	0.04143	0.04383	0.04619
400.00	0.03869	0.04082	0.04288	0.04490	0.04687	0.04880

Table 6.3. Second Derivative of the Second Virial Coefficient for the 12, 6, 4 Potential - Cont.

$B^*(2) = T^*2D2(B^*(0))/D(T^*)2$

T^*	$\gamma = 0.5$	$\gamma = 0.6$	$\gamma = 0.7$	$\gamma = 0.8$	$\gamma = 0.9$	$\gamma = 1.0$
0.30	-294.41000	-285.20679	-276.42295	-268.03388	-260.01639	-252.34955
0.35	-159.40988	-153.89711	-148.60854	-143.53220	-138.65689	-133.97205
0.40	-99.88789	-96.10585	-92.46099	-88.94636	-85.55570	-82.28307
0.45	-69.04407	-66.21512	-63.47779	-60.82785	-58.26152	-55.77507
0.50	-51.13073	-48.88841	-46.71139	-44.59684	-42.54224	-40.54513
0.55	-39.81510	-37.96420	-36.16206	-34.40679	-32.69651	-31.02955
0.60	-32.19463	-30.62109	-29.08540	-27.58607	-26.12174	-24.69122
0.65	-26.79915	-25.43155	-24.09406	-22.78559	-21.50521	-20.25187
0.70	-22.82314	-21.61396	-20.42937	-19.26850	-18.13058	-17.01485
0.75	-19.79616	-18.71250	-17.64927	-16.60580	-15.58143	-14.57566
0.80	-17.42883	-16.44698	-15.48238	-14.53450	-13.60280	-12.68682
0.85	-15.53523	-14.63758	-13.75470	-12.88613	-12.03145	-11.19028
0.90	-13.99134	-13.16440	-12.35040	-11.54873	-10.75910	-9.98120
0.95	-12.71183	-11.94531	-11.18997	-10.44548	-9.71155	-8.98789
1.00	-11.63636	-10.92188	-10.21726	-9.52223	-8.83652	-8.15990
1.10	-9.93396	-9.30472	-8.68333	-8.06958	-7.46326	-6.86419
1.20	-8.65156	-8.08923	-7.53328	-6.98357	-6.43993	-5.90221
1.30	-7.65371	-7.14529	-6.64218	-6.14427	-5.65141	-5.16349
1.40	-6.85668	-6.39267	-5.93315	-5.47801	-5.02715	-4.58047
1.50	-6.20630	-5.77950	-5.35654	-4.93734	-4.52182	-4.10988
1.60	-5.66601	-5.27085	-4.87903	-4.49046	-4.10508	-3.72281
1.70	-5.21036	-4.84243	-4.47744	-4.11530	-3.75594	-3.39933
1.80	-4.82108	-4.47687	-4.13523	-3.79613	-3.45949	-3.12527
1.90	-4.48480	-4.16140	-3.84031	-3.52146	-3.20481	-2.89032
2.00	-4.19145	-3.88649	-3.58359	-3.28270	-2.98379	-2.68680
2.10	-3.93336	-3.64484	-3.35817	-3.07332	-2.79024	-2.50891
2.20	-3.70458	-3.43080	-3.15870	-2.88826	-2.61942	-2.35217
2.30	-3.50040	-3.23992	-2.98099	-2.72355	-2.46758	-2.21306
2.40	-3.31707	-3.06867	-2.82166	-2.57604	-2.33176	-2.08880
2.50	-3.15158	-2.91416	-2.67804	-2.44319	-2.20957	-1.97717
2.60	-3.00143	-2.77408	-2.54792	-2.32293	-2.09908	-1.87635
2.70	-2.86461	-2.64649	-2.42948	-2.21355	-1.99868	-1.78485
2.80	-2.73940	-2.52980	-2.32123	-2.11367	-1.90708	-1.70146
2.90	-2.62441	-2.42268	-2.22192	-2.02209	-1.82317	-1.62515
3.00	-2.51843	-2.32400	-2.13048	-1.93782	-1.74603	-1.55507
3.10	-2.42043	-2.23280	-2.04601	-1.86004	-1.67486	-1.49047
3.20	-2.32956	-2.14826	-1.96775	-1.78801	-1.60902	-1.43076
3.30	-2.24506	-2.06968	-1.89504	-1.72113	-1.54792	-1.3754.
3.40	-2.16629	-1.99645	-1.82731	-1.65886	-1.49107	-1.32392
3.50	-2.09268	-1.92805	-1.76407	-1.60074	-1.43804	-1.27595
3.60	-2.02374	-1.86400	-1.70488	-1.54638	-1.38846	-1.23113
3.70	-1.95904	-1.80392	-1.64937	-1.49541	-1.34201	-1.19217
3.80	-1.89821	-1.74743	-1.59721	-1.44754	-1.29840	-1.14979
3.90	-1.84090	-1.69423	-1.54810	-1.40249	-1.25738	-1.11278
4.00	-1.78681	-1.64404	-1.50178	-1.36001	-1.21873	-1.07792
4.10	-1.73569	-1.59661	-1.45802	-1.31990	-1.18224	-1.04503
4.20	-1.68729	-1.55172	-1.41661	-1.28195	-1.14773	-1.01395
4.30	-1.64140	-1.50916	-1.37737	-1.24601	-1.11506	-0.98453
4.40	-1.59784	-1.46877	-1.34013	-1.21191	-1.08408	-0.95665
4.50	-1.55642	-1.43038	-1.30475	-1.17951	-1.05466	-0.93018
4.60	-1.51700	-1.39385	-1.27109	-1.14870	-1.02669	-0.90503
4.70	-1.47943	-1.35904	-1.23902	-1.11936	-1.00005	-0.88110
4.80	-1.44359	-1.32583	-1.20843	-1.09138	-0.97467	-0.85829
4.90	-1.40936	-1.29412	-1.17923	-1.06467	-0.95045	-0.83654
5.00	-1.37663	-1.26381	-1.15132	-1.03916	-0.92731	-0.81577
6.00	-1.11411	-1.02085	-0.92783	-0.83503	-0.74246	-0.65011
7.00	-0.93163	-0.85214	-0.77284	-0.69370	-0.61474	-0.53594
8.00	-0.79740	-0.72813	-0.65901	-0.59003	-0.52118	-0.45246
9.00	-0.69450	-0.63312	-0.57187	-0.51072	-0.44969	-0.38876
10.00	-0.61310	-0.55800	-0.50300	-0.44809	-0.39327	-0.33855
20.00	-0.25674	-0.22941	-0.20213	-0.17488	-0.14767	-0.12049
30.00	-0.14190	-0.12365	-0.10542	-0.08723	-0.06906	-0.05092
40.00	-0.08560	-0.07184	-0.05810	-0.04440	-0.03071	-0.01705
50.00	-0.05240	-0.04132	-0.03026	-0.01923	-0.00821	0.00278
60.00	-0.03065	-0.02134	-0.01205	-0.00279	0.00644	0.01566
70.00	-0.01538	-0.00733	0.00069	0.00869	0.01666	0.02462
80.00	-0.00413	0.00298	0.01006	0.01711	0.02414	0.03115
90.00	0.00446	0.01084	0.01718	0.02351	0.02981	0.03608
100.00	0.01121	0.01700	0.02276	0.02850	0.03421	0.03991
200.00	0.03899	0.04217	0.04533	0.04846	0.05157	0.05466
300.00	0.04619	0.04852	0.05082	0.05309	0.05533	0.05756
400.00	0.04880	0.05070	0.05257	0.05441	0.05623	0.05802

7. THERMODYNAMIC EFFECTS OF SHORT RANGE REPULSIONS BETWEEN POSITIVE IONS

Short range repulsions between positive ions must have very small thermodynamic effects up to moderately high temperatures since close approaches are very infrequent because of the strong Coulomb repulsions. Nevertheless, it may be useful to have estimates of such effects, even if only for purposes of a survey of general orders of magnitude.

The thermodynamic effects of repulsion between positive atomic ions may be estimated on the basis of their pair-wise contribution to the Helmholtz free energy

$$\Delta(-A/RT) = \frac{V}{V_O}\frac{N_O}{V_O}\sum_i\sum_j C_i C_j \int_0^\infty (e^{-U_{ij}/kT} - 1)\, 2\pi r_{ij}^2\, dr_{ij}, \tag{1}$$

where C_i, or C_j, indicates the concentration of the species i, or j, relative to that of a pure ideal gas at standard conditions

$$C_i = N_i V_O / N_O V. \tag{2}$$

N_i is the number of atomic ions of species i in the volume V, and N_O is the number of molecules of an ideal gas in the standard molar volume V_O at standard conditions. U_{ij} is the pair potential between two individual atomic ions. For the present purpose of estimating the effect of short range repulsions only, it will be convenient to omit the r^{-4} and r^{-6} attraction potentials, so that the interaction potential between two isolated ions would be taken as

$$U = a r_{ij}^{-12} + Z_i Z_j e^2 r_{ij}^{-1}. \tag{3}$$

We now note that we can re-write the integral in equation (1) according to

$$\int_0^\infty (e^{-U/kT} - 1)\, 2\pi r^2 dr = \int_0^\infty \left[\exp\left\{(-ar^{-12} - Z_i Z_j e^2 r^{-1})/kT\right\} - \exp\left\{-Z_i Z_j e^2 r^{-1}/kT\right\}\right] 2\pi r^2 dr + \int_0^\infty \left[\exp\left\{-Z_i Z_j e^2 r^{-1}/kT\right\} - 1\right] 2\pi r^2 dr. \tag{4}$$

The second of the two integrals on the right hand side of equation (4) represents the negative of the pairwise virial based on the Coulomb potential, which diverges, as is well known. Mayer showed,$^{(5)}$ however, that a re-summing technique involving the whole ionic assembly removes the divergence difficulty in a way which demonstrates the validity and equivalence of Debye type screening.(12)

The first of the two integrals on the right hand side of equation (4) represents the pairwise effect of the presence of the short range repulsion potential. The corresponding contribution to the Helmholtz free energy can be indicated as

$$\Delta(-\frac{A}{RT}) = -\frac{V}{V_o^2}\sum C_i C_j \Delta B_{ij} \tag{5}$$

and to PV/RT as

$$\Delta(\frac{PV}{RT}) = \frac{V}{V_o^2}\sum C_i C_j\ \Delta B_{ij}, \tag{6}$$

where ΔB_{ij} is a second virial type contribution

$$\Delta B = 2\pi N_o a_o^3\int_0^{\infty} e^{-k_1/RkT}\left[1 - e^{-k_{12}/R^{12}kT}\right]R^2 dR, \tag{7}$$

in which atomic units have been introduced, with $k_1 = Z_i Z_j$ and $R = r_{ij}/a_o$. [The Boltzmann constant k is 3.168×10^{-6} atomic units of energy per degree K, since one atomic unit of energy (27.21 e.v.) is equivalent to 315700 degrees K].

Integration by parts permits the second virial contribution to be written in an equivalent form,

$$\Delta B = \frac{2\pi N_o a_o^3}{3kT}\int_0^{\infty}(R^3 - R_c^3)\,e^{-U/kT}\,dU, \tag{8}$$

where R and R_c are separation distances as a function of U for the actual and the Coulomb potentials, respectively.

For purposes of evaluation by approximate numerical integration, there is some convenience in calculating the integral using values of U and of T spaced evenly on a logarithmic scale. We re-write the potential energy expression in the form

$$U/U_o = (R_o/R)^{12} + (R_o/R) \tag{9}$$

where $R_o = (k_{12}k_1^{-1})^{1/11}$ indicates the separation at which the two terms of the potential are equal and $U_o = k_{12}^{-1/11}k_1^{12/11}$ is the contribution of each of the two terms at this separation.

ΔB and its derivatives follow from

$$(-T)^{-s}\, d^s(\Delta BkT/U_0)/d(T^{-1})^s = b_0 \int_0^{\infty} \left[(R/R_0)^3 - (U_0/U)^3\right] (U/kT)^s e^{-U/kT}\, d(U/U_0), \tag{10}$$

where $b_0 = \frac{2\pi}{3} N_0 a_0^{\ 3}\ \ R_0^{\ 3}$. Values of

$$(R/R_0)^3 = [(R/R_0)^3 - (U_0/U)^3],$$

the increment in $(R/R_0)^3$ due to the $(R_0/R)^{12}$ term in the repulsion potential, are listed in Table 7.1 for values of U/U_0 that are positive and negative integer powers of $10^{0.1} = 1.25892541$, ranging from 10^{-1} to 10^4. [To about eight digits, these are 1.25892541, 1.58489320, 1.99526230, 2.5118864, 3.1622776, 3.9810717, 5.0118723, 6.3095734, 7.9432823, 10.00000000, times various powers of 10]. For small values of U/U_0,

$$(R/R_0)^3 = 3(U/U_0)^8\left[1 - 10(U/U_0)^{11} + \frac{496}{3}(U/U_0)^{22} - 3311(U/U_0)^{33} + 73458(U/U_0)^{44} \ldots\right], \tag{11}$$

is readily evaluated, particularly since all powers of U/U_0 required are given numerically by the U/U_0 listing, with the appropriate negative power of 10 evident by inspection. For quite large values of U/U_0, it is possible to use

$$(R/R_0)^3 = (U_0/U)^{1/4}\left[1 + \frac{1}{4}(U_0/U)^{11/12} + \frac{13}{96}(U_0/U)^{22/12} + \frac{1}{12}(U_0/U)^{33/12} \ldots\right]. \tag{12}$$

This equation, like equation (11), can be obtained using a specialization from

$$(R/R_0)^3 = \frac{\Gamma\left(\frac{\delta-3}{\delta}\right)}{\Gamma\left(-\frac{3}{\delta}\right)} \sum_{k=0} \frac{(-1)^{kt}}{k!} \frac{\Gamma\left(\frac{k\gamma-3}{\delta}\right)}{\Gamma\left(\frac{k[\gamma-\delta] + \delta - 3}{\delta}\right)} (U/U_0)^{(k[\gamma-\delta]-3)/\delta} \tag{13}$$

which represents the potential

$$U/U_0 = (R_0/R)^{\delta} - (-1)^t (R_0/R)^{\gamma}, \tag{14}$$

using $t = 1$ and alternative identifications of γ and δ with 12 and 1. For $t = 0$ and with both γ and δ greater than 3, direct integration gives the ordinary Lennard-Jones second virial coefficient in its familiar form except for the detail of the ϵ to U_0 ratio.

For intermediate values of U/U_0, equation (9) was solved by iterating with an arrangement of Newton's method

$$\left(\frac{R_o}{R}\right)_{i+1} = \left(\frac{R_o}{R}\right)_i \left\{\frac{11(R_o/R)_i^{12} + U/U_o}{12(R_o/R)_i^{12} + (R_o/R)_i}\right\},$$

for which each later iteration roughly doubles the number of correct digits.

The integrals required for equation (10) can also be indicated by

$$\beta_s = \frac{(-1)^s T^{*-s-1} d^s(T^*\Delta B/b_o)}{d(T^{*-1})^s}$$

$$= (0.1\ \ell n\,10)\int_0^\infty \Delta(R/R_o)^3 (U/kT)^{s+1} e^{-U/kT} dn \qquad (15)$$

with $U/U_o = e^{(0.1\,\ell n\,10)n}$, and for which T^* represents kT/U_o.

The remaining factor in the integrand of equation (15), $(U/kT)^{s+1} e^{-U/kT}$ is listed in Table 7.2, for $s = 0$, 1 and 2, for the same type of $U/kT = x$ values as used for U/U_o in Table 7.1.

Approximate values of the integrals indicated by equation (15) were obtained as $0.1\,\ell n 10 = 0.23026$ times the sum of integrand values at integer n's, for which a cumulative product can be used. These are given as β_0, β_1, and β_2 in columns 2, 3, and 4 of Table 7.3. We note that $\Delta B/b_o = \beta_0$. In columns 5 and 6 are values of

$$T^* d(\Delta B/b_o)/dT^* = \beta_1 - \beta_0$$

and

$$T^{*2} d^2(\Delta B/b_o)/dT^{*2} = \beta_2 - 4\beta_1 + 2\beta_0,$$

which could be of possible convenience for thermodynamic estimates.

While the interval of tabulation used in the numerical integration is somewhat larger than might be desired for accuracy, the resulting final table is clearly adequate numerically for a survey of approximate magnitudes. More serious objection may be made to the use of the R^{-12} potential over wide ranges of energy. The course of the values obtained for β_0, β_1 and β_2 as functions of T^* may be seen from the log-log plot in Fig. 7.1.

Estimated values of k_{12}, in atomic units, have been given in Chapter 4 for various pairs of atomic ions in their ground states. Some of these are listed in Table 7.4, with corresponding values of R_0, b_0 and U_0, with the last quantity expressed in alternative units, namely, in atomic units, equivalent degrees Kelvin, and electron volts.

It may be of interest to note from the U_0 values of Table 7.4 that the present β_s tabulation to $\log_{10} T^* = 2$ is nominally up to 9 million degrees K for the $Ar^+ - O^+$ pair and up to over 40 million degrees K for the $N^{++} - N^{++}$ pair.

Table 7.1. Increase in $(R/R_o)^3$ Versus U/U_o, Due to Adding $(R_o/R)^{12}$ to the R_o/R Coulombic Potential.

$m+\log_{10} U/U_o$	$(R/R_o)^3 - (U_o/U)^3$				
	m = 1	m = 0	m = -1	m = -2	m = -3
0	$3.0000 \cdot 10^{-8}$	.61376	0.57952	0.31740	0.17791
0.1	$1.8929 \cdot 10^{-7}$	.80455	.54414	.29943	.16794
0.2	$1.1943 \cdot 10^{-6}$	.87417	.51134	.28252	.15854
0.3	$7.5357 \cdot 10^{-6}$	.87520	.48091	.26659	.14966
0.4	$4.7547 \cdot 10^{-5}$	.84374	.45261	.25159	.14128
0.5	$2.9999 \cdot 10^{-4}$	.79922	.42621	.23744	.13337
0.6	$1.8921 \cdot 10^{-3}$	.75121	.40155	.22410	.12591
0.7	0.011884	.70402	.37847	.21153	.11886
0.8	.071043	.65942	.35682	.19966	.11221
0.9	.29882	.61794	.33650	.18847	.10593

Table 7.2. The Integrand Factors, $x^{s+1} e^{-x}$.

$\log_{10} x$	$x\ e^{-x}$	$x^2\ e^{-x}$	$x^3\ e^{-x}$
- 2.6	0.00251	$6.3 \cdot 10^{-6}$	$1.6 \cdot 10^{-8}$
- 2.5	.00315	$1.00 \cdot 10^{-5}$	$3.2 \cdot 10^{-8}$
- 2.4	.00397	$1.58 \cdot 10^{-5}$	$6.3 \cdot 10^{-8}$
- 2.3	.00499	$2.50 \cdot 10^{-5}$	$1.25 \cdot 10^{-7}$
- 2.2	.00627	$3.94 \cdot 10^{-5}$	$2.50 \cdot 10^{-7}$
- 2.1	.00788	$6.25 \cdot 10^{-5}$	$4.96 \cdot 10^{-7}$
- 2.0	.00990	$9.90 \cdot 10^{-4}$	$9.90 \cdot 10^{-6}$
- 1.9	.01243	$1.565 \cdot 10^{-4}$	$1.970 \cdot 10^{-6}$
- 1.8	.01560	$2.472 \cdot 10^{-4}$	$3.9185 \cdot 10^{-6}$
- 1.7	.01956	$3.902 \cdot 10^{-4}$	$7.786 \cdot 10^{-6}$
- 1.6	.02450	$6.153 \cdot 10^{-4}$	$1.5456 \cdot 10^{-5}$
- 1.5	.03064	$9.689 \cdot 10^{-4}$	$3.0638 \cdot 10^{-5}$
- 1.4	.03826	0.001523	$6.063 \cdot 10^{-5}$
- 1.3	.04767	.002389	$1.1974 \cdot 10^{-4}$
- 1.2	.05924	.003738	$2.3583 \cdot 10^{-4}$
- 1.1	.07337	.005828	$4.629 \cdot 10^{-4}$
- 1.0	.09048	.009048	$9.048 \cdot 10^{-4}$
- 0.9	.11100	.01397	0.001759
- .8	.13526	.02144	.003398
- .7	.16344	.03261	.006506
- .6	.19539	.04908	.01233
- 0.5	0.23050	0.07289	0.02305
- .4	.26736	.10644	.04237
- .3	.30362	.15217	.07627
- .2	.33572	.21183	.13365
- .1	.35894	.28512	.22648
0.0	.36788	.36788	.36788
0.1	.35748	.45004	.56657
.2	.32486	.51486	.81600
.3	.27131	.54134	1.08011
.4	.20375	.51180	1.28559
.5	.13386	.42329	1.33857
.6	.074309	.29583	1.17772
.7	.033371	.16725	0.83825
.8	.011476	.072408	.45686
.9	.002820	.022401	.17794
1.0	$4.540 \cdot 10^{-4}$	.004540	.04540
1.1	$4.291 \cdot 10^{-5}$	$5.402 \cdot 10^{-4}$	.006801
1.2	$2.074 \cdot 10^{-6}$	$3.288 \cdot 10^{-5}$	$5.211 \cdot 10^{-4}$
1.3	$4.312 \cdot 10^{-8}$	$8.604 \cdot 10^{-7}$	$1.717 \cdot 10^{-5}$
1.4	$3.098 \cdot 10^{-10}$	$7.78 \cdot 10^{-9}$	$1.95 \cdot 10^{-7}$
1.5	$5.84 \cdot 10^{-13}$	$1.85 \cdot 10^{-11}$	$5.8 \cdot 10^{-10}$

Table 7.3. Second Virial Contribution Due to Short Range Repulsion Between Positive Ions.

$\log_{10} T^*$	$\beta_o = \Delta B/b_o$	β_1	β_2	$T^* \, d(\Delta B/b_o)/dT^*$	$T^{*2} \, d^2(\Delta B/b_o)/dT^{*2}$
-1.4	$7.6 \cdot 10^{-7}$	$6.8 \cdot 10^{-6}$	$6.7 \cdot 10^{-5}$	$6.0 \cdot 10^{-6}$	$4.1 \cdot 10^{-5}$
-1.2	$2.68 \cdot 10^{-5}$	$2.25 \cdot 10^{-4}$	$2.05 \cdot 10^{-3}$	$1.98 \cdot 10^{-4}$	$1.20 \cdot 10^{-3}$
-1.0	$5.90 \cdot 10^{-4}$	$4.10 \cdot 10^{-3}$	.0304	$3.51 \cdot 10^{-3}$	0.0152
-0.8	$6.24 \cdot 10^{-3}$	0.03318	.1894	0.02694	.0692
-0.6	0.03312	.1321	.5762	.0990	.1140
-0.4	.1033	.3102	1.0556	.2069	+ .0214
-0.2	.2190	.5044	1.3885	.2854	- .1911
0	.3541	.6421	1.4942	.2880	- .3660
0.2	.4740	.6985	1.4393	.2245	- .4067
0.4	.5568	.6903	1.3132	.1335	- .3344
0.6	.5978	.6455	1.1718	.0477	- .2146
0.8	.6038	.5862	1.0384	- .0176	- .0988
1.0	.5851	.5249	0.9195	- .0602	- .0099
1.2	.5513	.4673	.8153	- .0840	+ .0487
1.4	.5098	.4153	.7239	- .0945	.0823
1.6	.4655	.3690	.6435	- .0965	.0985
1.8	.4216	.3281	.5726	- .0935	.1034
2.0	.3798	.2918	.5097	- .0880	.1021

Table 7.4. Estimated Short Range Repulsion Parameters for Atomic Ions in Their Ground States.

Pairs	$10^{-6}k_{12}$	k_1	R_0	b_0	U_0		
	(a.u.)	(a.u.)	(a.u.)	(cc/mole)	(a.u.)	(°K)	(e.v.)
$N^+ - N^+$	0.669	1	3.39	7.3	0.295	93000	8.03
$O^+ - N^+$	0.47	1	3.28	6.6	.305	96000	8.31
$N^{++} - N^+$	0.366	2	3.01	5.1	.665	210000	18.1
$Ar^+ - N^+$	1.48	1	3.64	9.0	.275	87000	7.49
$Ar^{++} - N^+$	1.02	2	3.30	6.7	.606	192000	16.5
$O^{++} - N^+$	0.283	2	2.94	4.8	.680	215000	18.5
$O^+ - O^+$	0.33	1	3.18	6.0	.314	99000	8.55
$N^{++} - O^+$	0.257	2	2.92	4.6	.685	216000	18.6
$Ar^+ - O^+$	1.04	1	3.53	8.2	.284	90000	7.73
$Ar^{++} - O^+$	0.713	2	3.20	6.1	.625	198000	17.0
$N^{++} - N^{++}$	0.20	4	2.67	3.6	1.50	474000	40.8
$O^{++} - O^+$	0.199	2	2.85	4.3	.702	222000	19.1

$\frac{2\pi}{3} N_o a_o^3 = 0.1870$ cc/mole

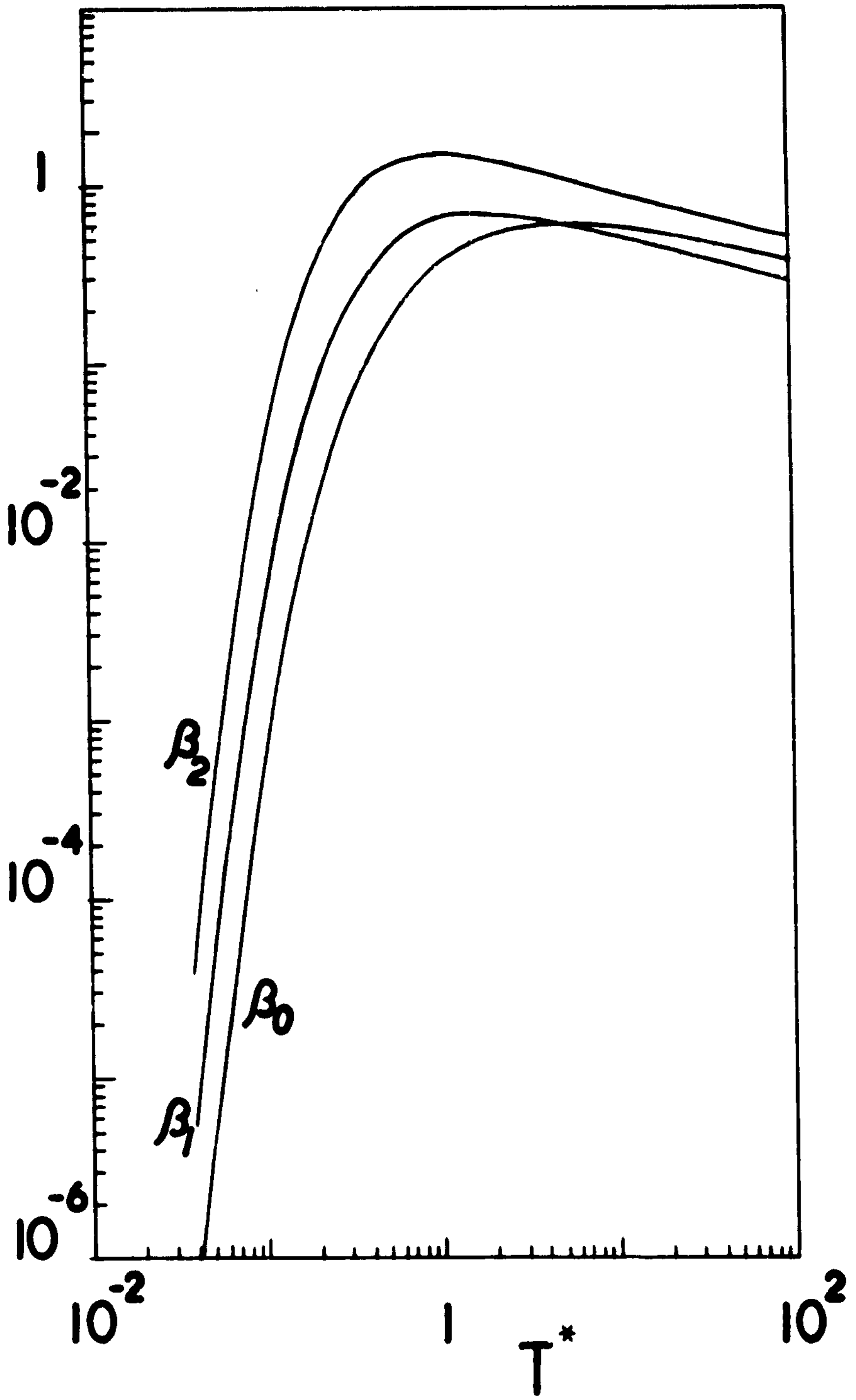

Fig. 7.1. Thermodynamic contributions due to R^{-12} potential between positive ions.

8. SECOND VIRIAL COEFFICIENTS AND THEIR DERIVATIVES FOR CONSTITUENT PAIRS INVOLVING NEUTRAL SPECIES IN HIGH TEMPERATURE AIR

The procedures of calculation of second virial coefficients which have been given should be capable of use either with the values of potential parameters suggested or with values improved by better empirical rules or by improved theory. It is natural to suppose that, in the main, improved theory will be relevant to other forms of potential function than those used in the present second virial study. Under this circumstance, the interesting end product of the present work, theoretically as well as practically, may be the actual magnitudes and trends of the numerical estimates obtained for the second virials and their derivatives. A table of computed values of B, TdB/dT and T^2d^2B/dT^2 is accordingly given for neutral-neutral and ion-neutral pairs present appreciably in air up to 15,000°K. The parameters used in their computation are given in Chapter 4 and the calculation procedure is that given in Chapter 6.

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air.

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	$T^2\, d^2B/dT^2$ cm^3 $mole^{-1}$
1000.	A	A	21.427	11.889	-30.496
2000.	A	A	26.146	2.856	-11.566
3000.	A	A	26.684	0.011	-5.556
4000.	A	A	26.480	-1.348	-2.625
5000.	A	A	26.089	-2.125	-0.903
6000.	A	A	25.655	-2.618	0.222
7000.	A	A	25.225	-2.951	1.008
8000.	A	A	24.814	-3.187	1.584
9000.	A	A	24.429	-3.360	2.023
10000.	A	A	24.067	-3.490	2.365
11000.	A	A	23.730	-3.589	2.638
12000.	A	A	23.414	-3.665	2.860
13000.	A	A	23.119	-3.724	3.042
14000.	A	A	22.841	-3.771	3.194
15000.	A	A	22.579	-3.808	3.322
1000.	CO	A	26.317	12.217	-32.155
2000.	CO	A	31.008	2.532	-11.868
3000.	CO	A	31.371	-0.514	-5.409
4000.	CO	A	31.003	-1.962	-2.261
5000.	CO	A	30.469	-2.786	-0.415
6000.	CO	A	29.912	-3.305	0.789
7000.	CO	A	29.374	-3.654	1.628
8000.	CO	A	28.870	-3.900	2.242
9000.	CO	A	28.399	-4.078	2.707
10000.	CO	A	27.963	-4.210	3.070
11000.	CO	A	27.556	-4.309	3.358
12000.	CO	A	27.178	-4.385	3.591
13000.	CO	A	26.825	-4.444	3.782
14000.	CO	A	26.494	-4.488	3.940
15000.	CO	A	26.183	-4.523	4.073
1000.	N	A	22.118	5.724	-16.997
2000.	N	A	23.949	0.250	-5.500
3000.	N	A	23.679	-1.452	-1.825
4000.	N	A	23.140	-2.246	-0.042
5000.	N	A	22.587	-2.687	0.996
6000.	N	A	22.071	-2.958	1.666
7000.	N	A	21.601	-3.135	2.128
8000.	N	A	21.174	-3.255	2.463
9000.	N	A	20.786	-3.338	2.713
10000.	N	A	20.431	-3.397	2.905
11000.	N	A	20.105	-3.438	3.056
12000.	N	A	19.805	-3.467	3.176
13000.	N	A	19.526	-3.487	3.273
14000.	N	A	19.267	-3.501	3.353
15000.	N	A	19.025	-3.509	3.418

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	$T^2 d^2B/dT^2$ cm^3 $mole^{-1}$
1000.	N2	A	25.347	11.104	-29.499
2000.	N2	A	29.558	2.166	-10.779
3000.	N2	A	29.824	-0.643	-4.815
4000.	N2	A	29.437	-1.975	-1.909
5000.	N2	A	28.907	-2.733	-0.205
6000.	N2	A	28.364	-3.209	0.904
7000.	N2	A	27.844	-3.528	1.677
8000.	N2	A	27.357	-3.752	2.242
9000.	N2	A	26.905	-3.914	2.670
10000.	N2	A	26.486	-4.034	3.003
11000.	N2	A	26.098	-4.124	3.267
12000.	N2	A	25.736	-4.192	3.481
13000.	N2	A	25.398	-4.244	3.656
14000.	N2	A	25.082	-4.283	3.800
15000.	N2	A	24.785	-4.313	3.922
1000.	NO	A	23.755	13.017	-33.445
2000.	NO	A	28.910	3.100	-12.663
3000.	NO	A	29.486	-0.024	-6.063
4000.	NO	A	29.253	-1.515	-2.844
5000.	NO	A	28.816	-2.368	-0.954
6000.	NO	A	28.333	-2.908	0.281
7000.	NO	A	27.855	-3.274	1.144
8000.	NO	A	27.400	-3.533	1.777
9000.	NO	A	26.973	-3.722	2.258
10000.	NO	A	26.573	-3.864	2.633
11000.	NO	A	26.199	-3.972	2.933
12000.	NO	A	25.850	-4.055	3.176
13000.	NO	A	25.523	-4.120	3.376
14000.	NO	A	25.216	-4.171	3.542
15000.	NO	A	24.926	-4.211	3.682
1000.	O	A	18.995	7.051	-19.297
2000.	O	A	21.562	1.100	-6.829
3000.	O	A	21.601	-0.765	-2.850
4000.	O	A	21.247	-1.646	-0.913
5000.	O	A	20.821	-2.144	0.220
6000.	O	A	20.401	-2.454	0.956
7000.	O	A	20.006	-2.661	1.468
8000.	O	A	19.641	-2.805	1.841
9000.	O	A	19.304	-2.908	2.122
10000.	O	A	18.994	-2.983	2.340
11000.	O	A	18.706	-3.038	2.513
12000.	O	A	18.440	-3.080	2.652
13000.	O	A	18.192	-3.111	2.765
14000.	O	A	17.961	-3.134	2.859
15000.	O	A	17.744	-3.151	2.937

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T	Pair		B	T dB/dT	$T^2 d^2B/dT^2$
°K			cm^3 $mole^{-1}$	cm^3 $mole^{-1}$	cm^3 $mole^{-1}$
1000.	O2	A	22.513	12.096	-31.162
2000.	O2	A	27.288	2.840	-11.766
3000.	O2	A	27.804	-0.076	-5.604
4000.	O2	A	27.571	-1.467	-2.599
5000.	O2	A	27.151	-2.262	-0.834
6000.	O2	A	26.691	-2.765	0.318
7000.	O2	A	26.238	-3.106	1.123
8000.	O2	A	25.807	-3.346	1.714
9000.	O2	A	25.402	-3.522	2.162
10000.	O2	A	25.023	-3.654	2.512
11000.	O2	A	24.670	-3.754	2.791
12000.	O2	A	24.340	-3.831	3.017
13000.	O2	A	24.031	-3.892	3.204
14000.	O2	A	23.741	-3.938	3.359
15000.	O2	A	23.468	-3.975	3.489
1000.	N	A+	-147.050	203.868	-504.704
2000.	N	A+	-55.951	81.282	-180.859
3000.	N	A+	-29.880	50.049	-108.848
4000.	N	A+	-17.654	35.764	-77.418
5000.	N	A+	-10.627	27.569	-59.810
6000.	N	A+	-6.101	22.254	-48.546
7000.	N	A+	-2.966	18.526	-40.718
8000.	N	A+	-0.681	15.769	-34.961
9000.	N	A+	1.049	13.646	-30.548
10000.	N	A+	2.396	11.962	-27.058
11000.	N	A+	3.470	10.594	-24.229
12000.	N	A+	4.341	9.461	-21.889
13000.	N	A+	5.060	8.508	-19.921
14000.	N	A+	5.660	7.694	-18.243
15000.	N	A+	6.166	6.992	-16.796
1000.	O	A+	-98.778	138.096	-327.799
2000.	O	A+	-35.733	57.319	-126.048
3000.	O	A+	-17.287	35.486	-77.114
4000.	O	A+	-8.622	25.314	-55.146
5000.	O	A+	-3.658	19.427	-42.664
6000.	O	A+	-0.477	15.588	-34.611
7000.	O	A+	1.711	12.888	-28.984
8000.	O	A+	3.295	10.885	-24.829
9000.	O	A+	4.485	9.342	-21.636
10000.	O	A+	5.403	8.117	-19.104
11000.	O	A+	6.129	7.122	-17.048
12000.	O	A+	6.712	6.297	-15.346
13000.	O	A+	7.188	5.602	-13.913
14000.	O	A+	7.581	5.010	-12.690
15000.	O	A+	7.909	4.499	-11.635

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B $cm^3\ mole^{-1}$	T dB/dT $cm^3\ mole^{-1}$	$T^2\ d^2B/dT^2$ $cm^3\ mole^{-1}$
1000.	CO2	AR	22.976	23.336	-56.429
2000.	CO2	AR	32.911	7.350	-22.734
3000.	CO2	AR	34.794	2.312	-12.176
4000.	CO2	AR	35.091	-0.116	-7.030
5000.	CO2	AR	34.902	-1.522	-3.998
6000.	CO2	AR	34.539	-2.427	-2.010
7000.	CO2	AR	34.115	-3.049	-0.611
8000.	CO2	AR	33.677	-3.498	0.421
9000.	CO2	AR	33.245	-3.833	1.211
10000.	CO2	AR	32.827	-4.090	1.832
11000.	CO2	AR	32.428	-4.291	2.332
12000.	CO2	AR	32.047	-4.450	2.741
13000.	CO2	AR	31.686	-4.579	3.081
14000.	CO2	AR	31.342	-4.683	3.366
15000.	CO2	AR	31.016	-4.768	3.609
1000.	N2O	AR	30.959	27.660	-67.521
2000.	N2O	AR	42.607	8.380	-26.950
3000.	N2O	AR	44.681	2.300	-14.195
4000.	N2O	AR	44.899	-0.626	-7.977
5000.	N2O	AR	44.562	-2.317	-4.314
6000.	N2O	AR	44.037	-3.402	-1.913
7000.	N2O	AR	43.454	-4.147	-0.226
8000.	N2O	AR	42.863	-4.683	1.018
9000.	N2O	AR	42.287	-5.081	1.969
10000.	N2O	AR	41.736	-5.385	2.716
11000.	N2O	AR	41.211	-5.622	3.316
12000.	N2O	AR	40.713	-5.810	3.806
13000.	N2O	AR	40.242	-5.960	4.212
14000.	N2O	AR	39.796	-6.081	4.554
15000.	N2O	AR	39.373	-6.180	4.843
1000.	A	C	25.771	6.212	-18.802
2000.	A	C	27.692	0.100	-5.957
3000.	A	C	27.318	-1.796	-1.850
4000.	A	C	26.667	-2.678	0.140
5000.	A	C	26.012	-3.167	1.298
6000.	A	C	25.406	-3.466	2.044
7000.	A	C	24.856	-3.660	2.558
8000.	A	C	24.358	-3.791	2.929
9000.	A	C	23.906	-3.881	3.206
10000.	A	C	23.494	-3.944	3.419
11000.	A	C	23.116	-3.988	3.586
12000.	A	C	22.767	-4.018	3.718
13000.	A	C	22.445	-4.039	3.825
14000.	A	C	22.145	-4.052	3.911
15000.	A	C	21.865	-4.059	3.982

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	C	C	28.322	2.281	-10.771
2000.	C	C	28.302	-1.805	-2.034
3000.	C	C	27.301	-3.025	0.740
4000.	C	C	26.348	-3.566	2.061
5000.	C	C	25.519	-3.848	2.813
6000.	C	C	24.802	-4.007	3.287
7000.	C	C	24.176	-4.100	3.605
8000.	C	C	23.625	-4.155	3.828
9000.	C	C	23.134	-4.185	3.989
10000.	C	C	22.692	-4.201	4.108
11000.	C	C	22.291	-4.205	4.197
12000.	C	C	21.925	-4.203	4.264
13000.	C	C	21.589	-4.196	4.316
14000.	C	C	21.278	-4.185	4.355
15000.	C	C	20.990	-4.172	4.385
1000.	CO	C	30.720	6.071	-19.495
2000.	CO	C	32.386	-0.439	-5.780
3000.	CO	C	31.769	-2.446	-1.397
4000.	CO	C	30.924	-3.372	0.722
5000.	CO	C	30.112	-3.881	1.949
6000.	CO	C	29.375	-4.188	2.737
7000.	CO	C	28.714	-4.384	3.278
8000.	CO	C	28.119	-4.514	3.667
9000.	CO	C	27.582	-4.602	3.956
10000.	CO	C	27.094	-4.661	4.176
11000.	CO	C	26.648	-4.701	4.347
12000.	CO	C	26.237	-4.727	4.482
13000.	CO	C	25.858	-4.743	4.590
14000.	CO	C	25.507	-4.751	4.677
15000.	CO	C	25.179	-4.754	4.748
1000.	CO2	C	30.853	13.278	-35.381
2000.	CO2	C	35.869	2.539	-12.887
3000.	CO2	C	36.163	-0.835	-5.719
4000.	CO2	C	35.679	-2.435	-2.227
5000.	CO2	C	35.030	-3.344	-0.180
6000.	CO2	C	34.366	-3.915	1.153
7000.	CO2	C	33.732	-4.298	2.081
8000.	CO2	C	33.139	-4.566	2.759
9000.	CO2	C	32.590	-4.760	3.273
10000.	CO2	C	32.080	-4.902	3.672
11000.	CO2	C	31.608	-5.010	3.989
12000.	CO2	C	31.168	-5.091	4.245
13000.	CO2	C	30.758	-5.152	4.454
14000.	CO2	C	30.375	-5.199	4.628
15000.	CO2	C	30.015	-5.235	4.773

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T	Pair		B	T dB/dT	$T^2 d^2B/dT^2$
°K			cm^3 $mole^{-1}$	cm^3 $mole^{-1}$	cm^3 $mole^{-1}$
1000.	N	C	24.414	2.213	-9.819
2000.	N	C	24.513	-1.451	-1.999
3000.	N	C	23.683	-2.551	0.486
4000.	N	C	22.874	-3.040	1.672
5000.	N	C	22.166	-3.296	2.349
6000.	N	C	21.550	-3.443	2.776
7000.	N	C	21.013	-3.530	3.063
8000.	N	C	20.538	-3.582	3.265
9000.	N	C	20.114	-3.612	3.412
10000.	N	C	19.732	-3.628	3.521
11000.	N	C	19.386	-3.635	3.603
12000.	N	C	19.070	-3.635	3.666
13000.	N	C	18.779	-3.630	3.714
14000.	N	C	18.510	-3.622	3.751
15000.	N	C	18.261	-3.612	3.779
1000.	N2	C	29.535	5.443	-17.883
2000.	N2	C	30.952	-0.587	-5.167
3000.	N2	C	30.308	-2.443	-1.104
4000.	N2	C	29.475	-3.296	0.858
5000.	N2	C	28.685	-3.762	1.993
6000.	N2	C	27.972	-4.043	2.721
7000.	N2	C	27.334	-4.221	3.220
8000.	N2	C	26.763	-4.339	3.578
9000.	N2	C	26.247	-4.417	3.843
10000.	N2	C	25.778	-4.469	4.045
11000.	N2	C	25.351	-4.504	4.201
12000.	N2	C	24.958	-4.526	4.324
13000.	N2	C	24.595	-4.539	4.423
14000.	N2	C	24.258	-4.544	4.501
15000.	N2	C	23.945	-4.545	4.565
1000.	N2O	C	40.266	15.462	-42.045
2000.	N2O	C	45.946	2.544	-14.983
3000.	N2O	C	46.094	-1.507	-6.350
4000.	N2O	C	45.370	-3.422	-2.146
5000.	N2O	C	44.479	-4.505	0.314
6000.	N2O	C	43.594	-5.183	1.914
7000.	N2O	C	42.759	-5.634	3.026
8000.	N2O	C	41.985	-5.949	3.837
9000.	N2O	C	41.270	-6.174	4.449
10000.	N2O	C	40.611	-6.339	4.924
11000.	N2O	C	40.001	-6.462	5.301
12000.	N2O	C	39.434	-6.554	5.604
13000.	N2O	C	38.907	-6.623	5.851
14000.	N2O	C	38.414	-6.674	6.056
15000.	N2O	C	37.952	-6.712	6.226

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	NO	C	28.456	6.764	-20.551
2000.	NO	C	30.532	0.071	-6.482
3000.	NO	C	30.107	-2.005	-1.985
4000.	NO	C	29.383	-2.970	0.195
5000.	NO	C	28.658	-3.504	1.462
6000.	NO	C	27.988	-3.831	2.278
7000.	NO	C	27.380	-4.043	2.841
8000.	NO	C	26.830	-4.185	3.247
9000.	NO	C	26.332	-4.283	3.550
10000.	NO	C	25.876	-4.352	3.783
11000.	NO	C	25.459	-4.400	3.965
12000.	NO	C	25.075	-4.432	4.109
13000.	NO	C	24.719	-4.455	4.225
14000.	NO	C	24.389	-4.468	4.320
15000.	NO	C	24.080	-4.476	4.397
1000.	O	C	21.692	3.274	-11.558
2000.	O	C	22.394	-0.736	-3.077
3000.	O	C	21.827	-1.961	-0.370
4000.	O	C	21.178	-2.520	0.934
5000.	O	C	20.580	-2.822	1.685
6000.	O	C	20.048	-3.001	2.164
7000.	O	C	19.577	-3.113	2.491
8000.	O	C	19.156	-3.185	2.724
9000.	O	C	18.778	-3.231	2.896
10000.	O	C	18.436	-3.261	3.026
11000.	O	C	18.124	-3.280	3.126
12000.	O	C	17.838	-3.290	3.204
13000.	O	C	17.575	-3.295	3.266
14000.	O	C	17.330	-3.295	3.315
15000.	O	C	17.103	-3.292	3.354
1000.	O2	C	26.848	6.237	-19.073
2000.	O2	C	28.739	0.006	-5.974
3000.	O2	C	28.319	-1.925	-1.785
4000.	O2	C	27.629	-2.821	0.244
5000.	O2	C	26.941	-3.318	1.422
6000.	O2	C	26.307	-3.620	2.182
7000.	O2	C	25.733	-3.816	2.705
8000.	O2	C	25.215	-3.948	3.082
9000.	O2	C	24.744	-4.038	3.364
10000.	O2	C	24.315	-4.101	3.580
11000.	O2	C	23.922	-4.145	3.748
12000.	O2	C	23.560	-4.175	3.882
13000.	O2	C	23.225	-4.195	3.990
14000.	O2	C	22.914	-4.207	4.077
15000.	O2	C	22.623	-4.214	4.149

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B $cm^3\ mole^{-1}$	T dB/dT $cm^3\ mole^{-1}$	$T^2\ d^2B/dT^2$ $cm^3\ mole^{-1}$
1000.	A	C2	30.693	12.134	-32.819
2000.	A	C2	35.184	2.083	-11.764
3000.	A	C2	35.341	-1.070	-5.048
4000.	A	C2	34.806	-2.563	-1.778
5000.	A	C2	34.135	-3.408	0.137
6000.	A	C2	33.464	-3.937	1.382
7000.	A	C2	32.829	-4.290	2.248
8000.	A	C2	32.239	-4.536	2.880
9000.	A	C2	31.694	-4.713	3.358
10000.	A	C2	31.190	-4.843	3.729
11000.	A	C2	30.724	-4.940	4.022
12000.	A	C2	30.291	-5.012	4.259
13000.	A	C2	29.887	-5.067	4.453
14000.	A	C2	29.510	-5.108	4.613
15000.	A	C2	29.157	-5.139	4.746
1000.	C	C2	35.064	5.720	-19.614
2000.	C	C2	36.400	-1.009	-5.398
3000.	C	C2	35.539	-3.071	-0.858
4000.	C	C2	34.511	-4.014	1.330
5000.	C	C2	33.555	-4.526	2.592
6000.	C	C2	32.701	-4.832	3.400
7000.	C	C2	31.940	-5.024	3.952
8000.	C	C2	31.261	-5.149	4.346
9000.	C	C2	30.649	-5.231	4.638
10000.	C	C2	30.095	-5.284	4.859
11000.	C	C2	29.590	-5.318	5.029
12000.	C	C2	29.126	-5.338	5.163
13000.	C	C2	28.698	-5.349	5.269
14000.	C	C2	28.302	-5.351	5.353
15000.	C	C2	27.933	-5.349	5.421
1000.	C2	C2	41.629	11.648	-33.910
2000.	C2	C2	45.484	0.834	-11.216
3000.	C2	C2	45.087	-2.534	-3.962
4000.	C2	C2	44.117	-4.110	-0.440
5000.	C2	C2	43.097	-4.990	1.613
6000.	C2	C2	42.136	-5.532	2.939
7000.	C2	C2	41.255	-5.887	3.857
8000.	C2	C2	40.452	-6.129	4.522
9000.	C2	C2	39.719	-6.299	5.020
10000.	C2	C2	39.049	-6.420	5.404
11000.	C2	C2	38.433	-6.506	5.706
12000.	C2	C2	37.864	-6.568	5.947
13000.	C2	C2	37.337	-6.611	6.142
14000.	C2	C2	36.846	-6.641	6.301
15000.	C2	C2	36.387	-6.661	6.433

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 mole^{-1}	$T\,dB/dT$ cm^3 mole^{-1}	$T^2\,d^2B/dT^2$ cm^3 mole^{-1}
1000.	CN	C2	38.144	11.412	-32.694
2000.	CN	C2	42.021	1.071	-11.006
3000.	CN	C2	41.750	-2.155	-4.075
4000.	CN	C2	40.900	-3.668	-0.707
5000.	CN	C2	39.982	-4.515	1.257
6000.	CN	C2	39.109	-5.039	2.529
7000.	CN	C2	38.305	-5.383	3.409
8000.	CN	C2	37.570	-5.619	4.048
9000.	CN	C2	36.898	-5.786	4.528
10000.	CN	C2	36.282	-5.905	4.898
11000.	CN	C2	35.715	-5.991	5.189
12000.	CN	C2	35.190	-6.053	5.422
13000.	CN	C2	34.704	-6.098	5.611
14000.	CN	C2	34.251	-6.129	5.766
15000.	CN	C2	33.827	-6.150	5.894
1000.	CO	C2	36.595	12.085	-33.869
2000.	CO	C2	40.843	1.499	-11.680
3000.	CO	C2	40.728	-1.811	-4.592
4000.	CO	C2	39.970	-3.368	-1.146
5000.	CO	C2	39.116	-4.244	0.868
6000.	CO	C2	38.290	-4.788	2.173
7000.	CO	C2	37.523	-5.148	3.079
8000.	CO	C2	36.819	-5.396	3.737
9000.	CO	C2	36.172	-5.573	4.233
10000.	CO	C2	35.578	-5.700	4.616
11000.	CO	C2	35.030	-5.793	4.919
12000.	CO	C2	34.523	-5.862	5.161
13000.	CO	C2	34.052	-5.912	5.359
14000.	CO	C2	33.613	-5.948	5.521
15000.	CO	C2	33.201	-5.974	5.656
1000.	CO2	C2	33.904	23.765	-59.310
2000.	CO2	C2	43.656	6.536	-23.147
3000.	CO2	C2	45.123	1.102	-11.716
4000.	CO2	C2	45.045	-1.503	-6.140
5000.	CO2	C2	44.535	-3.002	-2.859
6000.	CO2	C2	43.897	-3.959	-0.712
7000.	CO2	C2	43.235	-4.612	0.794
8000.	CO2	C2	42.587	-5.078	1.901
9000.	CO2	C2	41.968	-5.422	2.745
10000.	CO2	C2	41.382	-5.683	3.406
11000.	CO2	C2	40.831	-5.884	3.936
12000.	CO2	C2	40.312	-6.041	4.367
13000.	CO2	C2	39.823	-6.166	4.724
14000.	CO2	C2	39.363	-6.265	5.022
15000.	CO2	C2	38.928	-6.345	5.274

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	N	C2	30.589	5.407	-18.019
2000.	N	C2	31.950	-0.705	-5.123
3000.	N	C2	31.252	-2.583	-1.003
4000.	N	C2	30.378	-3.445	0.985
5000.	N	C2	29.554	-3.915	2.135
6000.	N	C2	28.813	-4.197	2.871
7000.	N	C2	28.152	-4.376	3.375
8000.	N	C2	27.559	-4.493	3.736
9000.	N	C2	27.025	-4.571	4.003
10000.	N	C2	26.541	-4.622	4.207
11000.	N	C2	26.098	-4.656	4.364
12000.	N	C2	25.692	-4.677	4.488
13000.	N	C2	25.317	-4.688	4.586
14000.	N	C2	24.970	-4.693	4.665
15000.	N	C2	24.646	-4.693	4.728
1000.	N2	C2	35.252	11.011	-31.237
2000.	N2	C2	39.051	1.183	-10.629
3000.	N2	C2	38.860	-1.887	-4.045
4000.	N2	C2	38.098	-3.328	-0.845
5000.	N2	C2	37.260	-4.137	1.023
6000.	N2	C2	36.459	-4.638	2.234
7000.	N2	C2	35.717	-4.968	3.072
8000.	N2	C2	35.038	-5.195	3.681
9000.	N2	C2	34.416	-5.356	4.139
10000.	N2	C2	33.846	-5.471	4.493
11000.	N2	C2	33.320	-5.555	4.771
12000.	N2	C2	32.834	-5.616	4.994
13000.	N2	C2	32.382	-5.661	5.176
14000.	N2	C2	31.962	-5.692	5.325
15000.	N2	C2	31.568	-5.714	5.448
1000.	N2O	C2	44.175	27.537	-69.618
2000.	N2O	C2	55.300	7.123	-26.808
3000.	N2O	C2	56.786	0.687	-13.244
4000.	N2O	C2	56.516	-2.392	-6.628
5000.	N2O	C2	55.777	-4.160	-2.738
6000.	N2O	C2	54.912	-5.284	-0.194
7000.	N2O	C2	54.036	-6.048	1.586
8000.	N2O	C2	53.191	-6.592	2.895
9000.	N2O	C2	52.391	-6.991	3.890
10000.	N2O	C2	51.638	-7.293	4.669
11000.	N2O	C2	50.931	-7.524	5.292
12000.	N2O	C2	50.269	-7.703	5.798
13000.	N2O	C2	49.646	-7.845	6.216
14000.	N2O	C2	49.061	-7.957	6.565
15000.	N2O	C2	48.509	-8.045	6.859

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T	Pair		B	T dB/dT	$T^2\, d^2B/dT^2$
°K			$cm^3\ mole^{-1}$	$cm^3\ mole^{-1}$	$cm^3\ mole^{-1}$
1000.	NO	C2	33.503	13.055	-35.402
2000.	NO	C2	38.317	2.195	-12.653
3000.	NO	C2	38.464	-1.211	-5.396
4000.	NO	C2	37.871	-2.822	-1.863
5000.	NO	C2	37.134	-3.734	0.206
6000.	NO	C2	36.399	-4.305	1.551
7000.	NO	C2	35.705	-4.685	2.486
8000.	NO	C2	35.061	-4.951	3.168
9000.	NO	C2	34.467	-5.141	3.684
10000.	NO	C2	33.917	-5.281	4.084
11000.	NO	C2	33.409	-5.384	4.401
12000.	NO	C2	32.937	-5.462	4.656
13000.	NO	C2	32.497	-5.521	4.864
14000.	NO	C2	32.087	-5.564	5.037
15000.	NO	C2	31.701	-5.597	5.181
1000.	O	C2	26.837	7.039	-20.828
2000.	O	C2	29.103	0.342	-6.766
3000.	O	C2	28.787	-1.741	-2.270
4000.	O	C2	28.138	-2.713	-0.089
5000.	O	C2	27.469	-3.253	1.180
6000.	O	C2	26.845	-3.586	2.000
7000.	O	C2	26.274	-3.802	2.566
8000.	O	C2	25.756	-3.950	2.976
9000.	O	C2	25.285	-4.052	3.283
10000.	O	C2	24.854	-4.124	3.519
11000.	O	C2	24.458	-4.175	3.703
12000.	O	C2	24.094	-4.212	3.851
13000.	O	C2	23.755	-4.237	3.970
14000.	O	C2	23.441	-4.253	4.067
15000.	O	C2	23.147	-4.264	4.147
1000.	O2	C2	32.043	12.279	-33.401
2000.	O2	C2	36.551	2.014	-11.898
3000.	O2	C2	36.666	-1.205	-5.037
4000.	O2	C2	36.088	-2.726	-1.697
5000.	O2	C2	35.379	-3.587	0.258
6000.	O2	C2	34.674	-4.125	1.528
7000.	O2	C2	34.009	-4.484	2.412
8000.	O2	C2	33.393	-4.734	3.056
9000.	O2	C2	32.824	-4.913	3.543
10000.	O2	C2	32.300	-5.044	3.920
11000.	O2	C2	31.814	-5.141	4.219
12000.	O2	C2	31.364	-5.214	4.460
13000.	O2	C2	30.944	-5.269	4.657
14000.	O2	C2	30.552	-5.309	4.819
15000.	O2	C2	30.185	-5.340	4.955

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	A	CN	27.856	11.729	-31.370
2000.	A	CN	32.265	2.185	-11.380
3000.	A	CN	32.497	-0.812	-5.009
4000.	A	CN	32.048	-2.233	-1.905
5000.	A	CN	31.455	-3.039	-0.086
6000.	A	CN	30.853	-3.545	1.097
7000.	A	CN	30.280	-3.884	1.922
8000.	A	CN	29.745	-4.121	2.524
9000.	A	CN	29.249	-4.292	2.980
10000.	A	CN	28.790	-4.418	3.333
11000.	A	CN	28.364	-4.512	3.614
12000.	A	CN	27.968	-4.584	3.841
13000.	A	CN	27.599	-4.638	4.027
14000.	A	CN	27.254	-4.679	4.181
15000.	A	CN	26.930	-4.710	4.309
1000.	C	CN	32.098	5.654	-18.864
2000.	C	CN	33.516	-0.748	-5.356
3000.	C	CN	32.782	-2.715	-1.040
4000.	C	CN	31.863	-3.617	1.042
5000.	C	CN	30.998	-4.110	2.246
6000.	C	CN	30.220	-4.405	3.017
7000.	C	CN	29.526	-4.592	3.545
8000.	C	CN	28.905	-4.714	3.923
9000.	C	CN	28.344	-4.796	4.203
10000.	C	CN	27.836	-4.850	4.416
11000.	C	CN	27.372	-4.885	4.580
12000.	C	CN	26.946	-4.906	4.710
13000.	C	CN	26.553	-4.918	4.813
14000.	C	CN	26.188	-4.923	4.895
15000.	C	CN	25.848	-4.923	4.962
1000.	CN	CN	35.143	11.211	-31.656
2000.	CN	CN	39.039	1.276	-10.827
3000.	CN	CN	38.878	-1.828	-4.173
4000.	CN	CN	38.130	-3.287	-0.938
5000.	CN	CN	37.301	-4.106	0.951
6000.	CN	CN	36.504	-4.614	2.175
7000.	CN	CN	35.766	-4.950	3.023
8000.	CN	CN	35.089	-5.180	3.640
9000.	CN	CN	34.469	-5.344	4.103
10000.	CN	CN	33.899	-5.462	4.462
11000.	CN	CN	33.375	-5.547	4.744
12000.	CN	CN	32.889	-5.610	4.971
13000.	CN	CN	32.438	-5.656	5.155
14000.	CN	CN	32.018	-5.688	5.306
15000.	CN	CN	31.624	-5.711	5.431

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 mole^{-1}	T dB/dT cm^3 mole^{-1}	$T^2 d^2B/dT^2$ cm^3 mole^{-1}
1000.	CO	CN	33.505	11.808	-32.648
2000.	CO	CN	37.740	1.680	-11.426
3000.	CO	CN	37.729	-1.491	-4.650
4000.	CO	CN	37.073	-2.986	-1.353
5000.	CO	CN	36.308	-3.829	0.574
6000.	CO	CN	35.560	-4.354	1.826
7000.	CO	CN	34.861	-4.703	2.694
8000.	CO	CN	34.216	-4.944	3.327
9000.	CO	CN	33.623	-5.117	3.804
10000.	CO	CN	33.077	-5.242	4.173
11000.	CO	CN	32.573	-5.334	4.465
12000.	CO	CN	32.106	-5.402	4.700
13000.	CO	CN	31.671	-5.453	4.891
14000.	CO	CN	31.266	-5.490	5.048
15000.	CO	CN	30.886	-5.517	5.179
1000.	CO2	CN	30.808	23.092	-57.247
2000.	CO2	CN	40.360	6.547	-22.496
3000.	CO2	CN	41.878	1.328	-11.527
4000.	CO2	CN	41.880	-1.177	-6.177
5000.	CO2	CN	41.449	-2.621	-3.027
6000.	CO2	CN	40.884	-3.544	-0.965
7000.	CO2	CN	40.287	-4.174	0.481
8000.	CO2	CN	39.699	-4.625	1.546
9000.	CO2	CN	39.134	-4.959	2.358
10000.	CO2	CN	38.598	-5.213	2.995
11000.	CO2	CN	38.091	-5.409	3.506
12000.	CO2	CN	37.614	-5.563	3.922
13000.	CO2	CN	37.164	-5.685	4.266
14000.	CO2	CN	36.738	-5.783	4.555
15000.	CO2	CN	36.337	-5.862	4.799
1000.	N	CN	27.824	5.304	-17.231
2000.	N	CN	29.242	-0.479	-5.042
3000.	N	CN	28.658	-2.261	-1.147
4000.	N	CN	27.882	-3.081	0.735
5000.	N	CN	27.142	-3.530	1.825
6000.	N	CN	26.472	-3.801	2.524
7000.	N	CN	25.872	-3.974	3.003
8000.	N	CN	25.334	-4.088	3.347
9000.	N	CN	24.848	-4.164	3.602
10000.	N	CN	24.406	-4.216	3.797
11000.	N	CN	24.003	-4.250	3.948
12000.	N	CN	23.632	-4.272	4.067
13000.	N	CN	23.289	-4.285	4.162
14000.	N	CN	22.971	-4.292	4.239
15000.	N	CN	22.675	-4.293	4.300

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	N2	CN	32.265	10.704	-29.969
2000.	N2	CN	36.033	1.342	-10.346
3000.	N2	CN	35.938	-1.586	-4.078
4000.	N2	CN	35.272	-2.963	-1.030
5000.	N2	CN	34.520	-3.738	0.751
6000.	N2	CN	33.793	-4.220	1.905
7000.	N2	CN	33.117	-4.538	2.706
8000.	N2	CN	32.495	-4.758	3.289
9000.	N2	CN	31.925	-4.914	3.727
10000.	N2	CN	31.402	-5.027	4.067
11000.	N2	CN	30.918	-5.110	4.334
12000.	N2	CN	30.471	-5.170	4.549
13000.	N2	CN	30.055	-5.215	4.724
14000.	N2	CN	29.668	-5.247	4.867
15000.	N2	CN	29.305	-5.270	4.987
1000.	N20	CN	40.431	26.873	-67.448
2000.	N20	CN	51.384	7.198	-26.169
3000.	N20	CN	52.951	0.994	-13.107
4000.	N20	CN	52.786	-1.978	-6.735
5000.	N20	CN	52.146	-3.686	-2.987
6000.	N20	CN	51.371	-4.775	-0.535
7000.	N20	CN	50.576	-5.516	1.182
8000.	N20	CN	49.803	-6.045	2.445
9000.	N20	CN	49.067	-6.434	3.407
10000.	N20	CN	48.373	-6.729	4.161
11000.	N20	CN	47.721	-6.955	4.763
12000.	N20	CN	47.108	-7.132	5.254
13000.	N20	CN	46.531	-7.272	5.659
14000.	N20	CN	45.988	-7.383	5.998
15000.	N20	CN	45.476	-7.471	6.284
1000.	NO	CN	30.673	12.709	-34.086
2000.	NO	CN	35.432	2.322	-12.329
3000.	NO	CN	35.662	-0.940	-5.393
4000.	NO	CN	35.156	-2.485	-2.014
5000.	NO	CN	34.499	-3.362	-0.034
6000.	NO	CN	33.834	-3.911	1.253
7000.	NO	CN	33.202	-4.279	2.150
8000.	NO	CN	32.613	-4.537	2.805
9000.	NO	CN	32.067	-4.722	3.300
10000.	NO	CN	31.562	-4.858	3.685
11000.	NO	CN	31.094	-4.960	3.990
12000.	NO	CN	30.659	-5.037	4.237
13000.	NO	CN	30.254	-5.095	4.438
14000.	NO	CN	29.874	-5.140	4.605
15000.	NO	CN	29.518	-5.173	4.744

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	$T^2 d^2B/dT^2$ cm^3 $mole^{-1}$
1000.	O	CN	24.506	6.857	-19.962
2000.	O	CN	26.775	0.491	-6.602
3000.	O	CN	26.541	-1.492	-2.332
4000.	O	CN	25.971	-2.420	-0.259
5000.	O	CN	25.370	-2.937	0.949
6000.	O	CN	24.804	-3.256	1.730
7000.	O	CN	24.285	-3.466	2.270
8000.	O	CN	23.813	-3.608	2.662
9000.	O	CN	23.382	-3.708	2.955
10000.	O	CN	22.987	-3.779	3.181
11000.	O	CN	22.624	-3.830	3.359
12000.	O	CN	22.289	-3.866	3.501
13000.	O	CN	21.979	-3.892	3.615
14000.	O	CN	21.690	-3.909	3.709
15000.	O	CN	21.420	-3.921	3.787
1000.	O2	CN	29.129	11.876	-31.941
2000.	O2	CN	33.558	2.125	-11.518
3000.	O2	CN	33.752	-0.936	-5.006
4000.	O2	CN	33.262	-2.385	-1.834
5000.	O2	CN	32.634	-3.207	0.024
6000.	O2	CN	32.001	-3.722	1.233
7000.	O2	CN	31.399	-4.067	2.074
8000.	O2	CN	30.840	-4.307	2.688
9000.	O2	CN	30.322	-4.480	3.153
10000.	O2	CN	29.843	-4.608	3.513
11000.	O2	CN	29.399	-4.703	3.799
12000.	O2	CN	28.987	-4.774	4.030
13000.	O2	CN	28.602	-4.828	4.219
14000.	O2	CN	28.243	-4.869	4.375
15000.	O2	CN	27.906	-4.900	4.505
1000.	CO	CO	31.807	12.342	-33.496
2000.	CO	CO	36.353	2.063	-11.962
3000.	CO	CO	36.486	-1.161	-5.092
4000.	CO	CO	35.920	-2.686	-1.748
5000.	CO	CO	35.220	-3.549	0.211
6000.	CO	CO	34.522	-4.089	1.483
7000.	CO	CO	33.863	-4.449	2.369
8000.	CO	CO	33.251	-4.700	3.014
9000.	CO	CO	32.687	-4.880	3.502
10000.	CO	CO	32.166	-5.012	3.881
11000.	CO	CO	31.683	-5.110	4.180
12000.	CO	CO	31.235	-5.183	4.422
13000.	CO	CO	30.818	-5.238	4.619
14000.	CO	CO	30.428	-5.280	4.782
15000.	CO	CO	30.063	-5.310	4.918

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 mole^{-1}	T dB/dT cm^3 mole^{-1}	T^2 d^{2}B/dT^2 cm^3 mole^{-1}
1000.	CO2	CO	28.741	23.875	-58.636
2000.	CO2	CO	38.725	7.052	-23.262
3000.	CO2	CO	40.429	1.745	-12.122
4000.	CO2	CO	40.544	-0.806	-6.690
5000.	CO2	CO	40.193	-2.279	-3.491
6000.	CO2	CO	39.688	-3.222	-1.395
7000.	CO2	CO	39.140	-3.869	0.077
8000.	CO2	CO	38.592	-4.333	1.161
9000.	CO2	CO	38.060	-4.677	1.989
10000.	CO2	CO	37.553	-4.940	2.640
11000.	CO2	CO	37.073	-5.144	3.161
12000.	CO2	CO	36.618	-5.305	3.587
13000.	CO2	CO	36.188	-5.433	3.940
14000.	CO2	CO	35.782	-5.536	4.237
15000.	CO2	CO	35.397	-5.620	4.488
1000.	N2	CO	30.624	11.223	-30.791
2000.	N2	CO	34.695	1.714	-10.867
3000.	N2	CO	34.740	-1.266	-4.508
4000.	N2	CO	34.161	-2.673	-1.413
5000.	N2	CO	33.472	-3.467	0.398
6000.	N2	CO	32.793	-3.963	1.574
7000.	N2	CO	32.156	-4.293	2.391
8000.	N2	CO	31.567	-4.521	2.986
9000.	N2	CO	31.024	-4.685	3.435
10000.	N2	CO	30.524	-4.805	3.783
11000.	N2	CO	30.062	-4.893	4.059
12000.	N2	CO	29.633	-4.959	4.280
13000.	N2	CO	29.234	-5.008	4.461
14000.	N2	CO	28.862	-5.044	4.610
15000.	N2	CO	28.513	-5.070	4.734
1000.	N2O	CO	37.975	27.960	-69.434
2000.	N2O	CO	49.516	7.865	-27.236
3000.	N2O	CO	51.325	1.527	-13.912
4000.	N2O	CO	51.303	-1.514	-7.412
5000.	N2O	CO	50.761	-3.267	-3.587
6000.	N2O	CO	50.059	-4.386	-1.083
7000.	N2O	CO	49.322	-5.151	0.674
8000.	N2O	CO	48.597	-5.698	1.967
9000.	N2O	CO	47.901	-6.102	2.953
10000.	N2O	CO	47.242	-6.409	3.726
11000.	N2O	CO	46.620	-6.646	4.345
12000.	N2O	CO	46.033	-6.832	4.850
13000.	N2O	CO	45.480	-6.980	5.268
14000.	N2O	CO	44.958	-7.098	5.617
15000.	N2O	CO	44.465	-7.194	5.913

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 mole^{-1}	T dB/dT cm^3 mole^{-1}	$T^2 d^2B/dT^2$ cm^3 mole^{-1}
1000.	NO	CO	28.940	13.256	-34.963
2000.	NO	CO	34.016	2.711	-12.875
3000.	NO	CO	34.392	-0.605	-5.842
4000.	NO	CO	33.979	-2.180	-2.414
5000.	NO	CO	33.388	-3.077	-0.404
6000.	NO	CO	32.773	-3.641	0.906
7000.	NO	CO	32.181	-4.021	1.820
8000.	NO	CO	31.626	-4.287	2.488
9000.	NO	CO	31.109	-4.481	2.994
10000.	NO	CO	30.629	-4.624	3.388
11000.	NO	CO	30.183	-4.732	3.701
12000.	NO	CO	29.768	-4.814	3.954
13000.	NO	CO	29.380	-4.877	4.162
14000.	NO	CO	29.017	-4.925	4.335
15000.	NO	CO	28.676	-4.962	4.479
1000.	O2	CO	27.483	12.348	-32.670
2000.	O2	CO	32.193	2.475	-11.991
3000.	O2	CO	32.519	-0.628	-5.405
4000.	O2	CO	32.115	-2.102	-2.195
5000.	O2	CO	31.548	-2.940	-0.313
6000.	O2	CO	30.962	-3.467	0.913
7000.	O2	CO	30.399	-3.822	1.768
8000.	O2	CO	29.872	-4.070	2.393
9000.	O2	CO	29.381	-4.250	2.866
10000.	O2	CO	28.926	-4.383	3.234
11000.	O2	CO	28.504	-4.484	3.527
12000.	O2	CO	28.110	-4.560	3.764
13000.	O2	CO	27.743	-4.618	3.957
14000.	O2	CO	27.399	-4.663	4.118
15000.	O2	CO	27.076	-4.697	4.253
1000.	CO2	CO2	19.648	43.311	-101.200
2000.	CO2	CO2	38.827	15.605	-42.080
3000.	CO2	CO2	43.267	6.934	-23.933
4000.	CO2	CO2	44.627	2.740	-15.132
5000.	CO2	CO2	44.954	0.292	-9.946
6000.	CO2	CO2	44.857	-1.297	-6.538
7000.	CO2	CO2	44.570	-2.402	-4.134
8000.	CO2	CO2	44.193	-3.209	-2.353
9000.	CO2	CO2	43.779	-3.818	-0.984
10000.	CO2	CO2	43.351	-4.292	0.098
11000.	CO2	CO2	42.924	-4.667	0.973
12000.	CO2	CO2	42.504	-4.970	1.692
13000.	CO2	CO2	42.096	-5.218	2.294
14000.	CO2	CO2	41.702	-5.423	2.802
15000.	CO2	CO2	41.322	-5.595	3.237

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	N2O	CO2	27.537	50.621	-118.909
2000.	N2O	CO2	49.814	17.865	-49.223
3000.	N2O	CO2	54.822	7.593	-27.730
4000.	N2O	CO2	56.254	2.626	-17.292
5000.	N2O	CO2	56.503	-0.270	-11.141
6000.	N2O	CO2	56.277	-2.147	-7.099
7000.	N2O	CO2	55.842	-3.450	-4.249
8000.	N2O	CO2	55.317	-4.399	-2.139
9000.	N2O	CO2	54.755	-5.115	-0.518
10000.	N2O	CO2	54.187	-5.669	0.762
11000.	N2O	CO2	53.625	-6.108	1.796
12000.	N2O	CO2	53.078	-6.461	2.646
13000.	N2O	CO2	52.549	-6.750	3.355
14000.	N2O	CO2	52.040	-6.988	3.954
15000.	N2O	CO2	51.550	-7.186	4.466
1000.	CO	N	26.655	5.665	-17.782
2000.	CO	N	28.287	-0.215	-5.408
3000.	CO	N	27.802	-2.032	-1.453
4000.	CO	N	27.089	-2.872	0.461
5000.	CO	N	26.394	-3.336	1.571
6000.	CO	N	25.759	-3.617	2.285
7000.	CO	N	25.187	-3.797	2.776
8000.	CO	N	24.671	-3.918	3.129
9000.	CO	N	24.205	-4.000	3.392
10000.	CO	N	23.780	-4.056	3.593
11000.	CO	N	23.392	-4.095	3.750
12000.	CO	N	23.034	-4.120	3.874
13000.	CO	N	22.704	-4.136	3.973
14000.	CO	N	22.397	-4.146	4.054
15000.	CO	N	22.111	-4.150	4.119
1000.	CO2	N	26.592	12.228	-32.231
2000.	CO2	N	31.278	2.510	-11.877
3000.	CO2	N	31.630	-0.546	-5.396
4000.	CO2	N	31.252	-1.998	-2.237
5000.	CO2	N	30.710	-2.824	-0.385
6000.	CO2	N	30.146	-3.344	0.823
7000.	CO2	N	29.602	-3.694	1.664
8000.	CO2	N	29.092	-3.940	2.280
9000.	CO2	N	28.617	-4.118	2.747
10000.	CO2	N	28.176	-4.250	3.110
11000.	CO2	N	27.766	-4.350	3.399
12000.	CO2	N	27.384	-4.426	3.632
13000.	CO2	N	27.028	-4.484	3.824
14000.	CO2	N	26.694	-4.528	3.983
15000.	CO2	N	26.380	-4.562	4.116

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T	Pair		B	T dB/dT	$T^2 d^2B/dT^2$
°K			cm^3 $mole^{-1}$	cm^3 $mole^{-1}$	cm^3 $mole^{-1}$
1000.	N	N	20.926	2.112	-8.880
2000.	N	N	21.112	-1.153	-1.927
3000.	N	N	20.429	-2.136	0.284
4000.	N	N	19.747	-2.575	1.342
5000.	N	N	19.145	-2.808	1.947
6000.	N	N	18.620	-2.941	2.329
7000.	N	N	18.160	-3.021	2.587
8000.	N	N	17.753	-3.070	2.770
9000.	N	N	17.390	-3.100	2.902
10000.	N	N	17.062	-3.116	3.001
11000.	N	N	16.765	-3.124	3.076
12000.	N	N	16.493	-3.125	3.133
13000.	N	N	16.243	-3.123	3.178
14000.	N	N	16.012	-3.117	3.212
15000.	N	N	15.797	-3.109	3.238
1000.	N2	N	25.508	4.879	-15.832
2000.	N2	N	26.815	-0.432	-4.638
3000.	N2	N	26.282	-2.069	-1.061
4000.	N2	N	25.571	-2.822	0.667
5000.	N2	N	24.893	-3.235	1.668
6000.	N2	N	24.280	-3.484	2.310
7000.	N2	N	23.730	-3.643	2.750
8000.	N2	N	23.236	-3.748	3.066
9000.	N2	N	22.790	-3.818	3.301
10000.	N2	N	22.385	-3.865	3.480
11000.	N2	N	22.015	-3.897	3.618
12000.	N2	N	21.675	-3.917	3.728
13000.	N2	N	21.361	-3.929	3.815
14000.	N2	N	21.070	-3.935	3.885
15000.	N2	N	20.798	-3.937	3.942
1000.	N20	N	35.188	14.463	-38.845
2000.	N20	N	40.593	2.615	-14.029
3000.	N20	N	40.842	-1.104	-6.117
4000.	N20	N	40.257	-2.866	-2.263
5000.	N20	N	39.501	-3.865	-0.005
6000.	N20	N	38.736	-4.492	1.464
7000.	N20	N	38.011	-4.911	2.486
8000.	N20	N	37.335	-5.204	3.233
9000.	N20	N	36.709	-5.415	3.797
10000.	N20	N	36.130	-5.570	4.236
11000.	N20	N	35.593	-5.686	4.584
12000.	N20	N	35.095	-5.773	4.864
13000.	N20	N	34.630	-5.839	5.094
14000.	N20	N	34.195	-5.889	5.284
15000.	N20	N	33.788	-5.927	5.443

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T	Pair		B	$T\,dB/dT$	$T^2\,d^2B/dT^2$
°K			cm^3 mole^{-1}	cm^3 mole^{-1}	cm^3 mole^{-1}
1000.	NO	N	24.578	6.260	-18.666
2000.	NO	N	26.567	0.235	-6.012
3000.	NO	N	26.253	-1.637	-1.967
4000.	NO	N	25.649	-2.509	-0.005
5000.	NO	N	25.032	-2.994	1.137
6000.	NO	N	24.458	-3.292	1.874
7000.	NO	N	23.935	-3.485	2.382
8000.	NO	N	23.461	-3.616	2.750
9000.	NO	N	23.029	-3.707	3.025
10000.	NO	N	22.635	-3.771	3.236
11000.	NO	N	22.273	-3.817	3.402
12000.	NO	N	21.940	-3.848	3.534
13000.	NO	N	21.631	-3.870	3.640
14000.	NO	N	21.343	-3.884	3.727
15000.	NO	N	21.075	-3.893	3.798
1000.	O2	N	23.072	5.765	-17.279
2000.	O2	N	24.887	0.175	-5.534
3000.	O2	N	24.578	-1.562	-1.779
4000.	O2	N	24.006	-2.370	0.041
5000.	O2	N	23.424	-2.819	1.100
6000.	O2	N	22.884	-3.094	1.784
7000.	O2	N	22.392	-3.273	2.255
8000.	O2	N	21.947	-3.394	2.596
9000.	O2	N	21.542	-3.478	2.850
10000.	O2	N	21.172	-3.537	3.046
11000.	O2	N	20.833	-3.578	3.199
12000.	O2	N	20.521	-3.607	3.321
13000.	O2	N	20.231	-3.627	3.419
14000.	O2	N	19.962	-3.640	3.499
15000.	O2	N	19.710	-3.647	3.565
1000.	A	N+	-3241.661	13555.480	-88529.130
2000.	A	N+	-462.108	889.548	-3288.198
3000.	A	N+	-232.275	354.680	-1036.092
4000.	A	N+	-152.736	214.162	-559.092
5000.	A	N+	-112.356	152.316	-373.681
6000.	A	N+	-87.892	117.893	-278.395
7000.	A	N+	-71.474	96.029	-221.108
8000.	A	N+	-59.693	80.923	-183.078
9000.	A	N+	-50.832	69.864	-156.063
10000.	A	N+	-43.927	61.418	-135.908
11000.	A	N+	-38.397	54.755	-120.306
12000.	A	N+	-33.872	49.365	-107.875
13000.	A	N+	-30.102	44.914	-97.740
14000.	A	N+	-26.914	41.176	-89.318
15000.	A	N+	-24.184	37.992	-82.211

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B $cm^3\ mole^{-1}$	T dB/dT $cm^3\ mole^{-1}$	$T^2\ d^2B/dT^2$ $cm^3\ mole^{-1}$
1000.	N	N+	-170.916	244.485	-649.879
2000.	N	N+	-65.802	90.469	-206.310
3000.	N	N+	-37.018	54.871	-120.515
4000.	N	N+	-23.642	39.071	-84.715
5000.	N	N+	-15.965	30.138	-65.101
6000.	N	N+	-11.012	24.393	-52.719
7000.	N	N+	-7.570	20.386	-44.191
8000.	N	N+	-5.050	17.432	-37.957
9000.	N	N+	-3.133	15.165	-33.201
10000.	N	N+	-1.631	13.369	-29.453
11000.	N	N+	-0.428	11.913	-26.423
12000.	N	N+	0.555	10.707	-23.922
13000.	N	N+	1.371	9.694	-21.823
14000.	N	N+	2.057	8.830	-20.036
15000.	N	N+	2.640	8.084	-18.497
1000.	N2	N+	-244.295	356.200	-971.673
2000.	N2	N+	-93.396	128.029	-294.884
3000.	N2	N+	-52.802	77.134	-170.280
4000.	N2	N+	-34.024	54.790	-119.118
5000.	N2	N+	-23.263	42.225	-91.312
6000.	N2	N+	-16.324	34.169	-73.843
7000.	N2	N+	-11.502	28.561	-61.847
8000.	N2	N+	-7.971	24.433	-53.100
9000.	N2	N+	-5.283	21.268	-46.438
10000.	N2	N+	-3.177	18.763	-41.194
11000.	N2	N+	-1.487	16.732	-36.958
12000.	N2	N+	-0.106	15.052	-33.466
13000.	N2	N+	1.042	13.640	-30.536
14000.	N2	N+	2.008	12.436	-28.044
15000.	N2	N+	2.829	11.398	-25.897
1000.	NO	N+	-266.560	400.220	-1131.071
2000.	NO	N+	-100.500	138.034	-322.458
3000.	NO	N+	-56.952	82.351	-183.196
4000.	NO	N+	-36.943	58.274	-127.265
5000.	NO	N+	-25.508	44.834	-97.200
6000.	NO	N+	-18.144	36.253	-78.437
7000.	NO	N+	-13.028	30.298	-65.609
8000.	NO	N+	-9.282	25.923	-56.284
9000.	NO	N+	-6.430	22.572	-49.198
10000.	NO	N+	-4.194	19.924	-43.630
11000.	NO	N+	-2.399	17.778	-39.139
12000.	NO	N+	-0.931	16.004	-35.440
13000.	NO	N+	0.290	14.514	-32.341
14000.	NO	N+	1.318	13.244	-29.706
15000.	NO	N+	2.193	12.150	-27.438

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	$T^2 d^2B/dT^2$ cm^3 $mole^{-1}$
1000.	O	N+	-112.638	156.868	-390.106
2000.	O	N+	-42.715	62.235	-138.744
3000.	O	N+	-22.766	38.269	-83.326
4000.	O	N+	-13.421	27.329	-59.209
5000.	O	N+	-8.053	21.059	-45.718
6000.	O	N+	-4.596	16.995	-37.095
7000.	O	N+	-2.202	14.146	-31.106
8000.	O	N+	-0.457	12.038	-26.703
9000.	O	N+	0.863	10.416	-23.330
10000.	O	N+	1.891	9.130	-20.662
11000.	O	N+	2.711	8.085	-18.500
12000.	O	N+	3.376	7.219	-16.712
13000.	O	N+	3.924	6.491	-15.208
14000.	O	N+	4.382	5.870	-13.927
15000.	O	N+	4.768	5.334	-12.821
1000.	CO2	N2	28.097	21.964	-54.235
2000.	CO2	N2	37.225	6.337	-21.398
3000.	CO2	N2	38.721	1.407	-11.043
4000.	CO2	N2	38.766	-0.960	-5.993
5000.	CO2	N2	38.393	-2.326	-3.020
6000.	CO2	N2	37.887	-3.199	-1.072
7000.	CO2	N2	37.346	-3.797	0.294
8000.	CO2	N2	36.809	-4.225	1.301
9000.	CO2	N2	36.292	-4.543	2.069
10000.	CO2	N2	35.801	-4.784	2.672
11000.	CO2	N2	35.336	-4.971	3.155
12000.	CO2	N2	34.897	-5.118	3.549
13000.	CO2	N2	34.482	-5.235	3.876
14000.	CO2	N2	34.091	-5.329	4.149
15000.	CO2	N2	33.720	-5.405	4.381
1000.	N2	N2	29.535	10.208	-28.337
2000.	N2	N2	33.175	1.398	-9.874
3000.	N2	N2	33.140	-1.359	-3.979
4000.	N2	N2	32.551	-2.659	-1.111
5000.	N2	N2	31.873	-3.391	0.566
6000.	N2	N2	31.211	-3.846	1.654
7000.	N2	N2	30.594	-4.149	2.409
8000.	N2	N2	30.026	-4.358	2.958
9000.	N2	N2	29.503	-4.507	3.373
10000.	N2	N2	29.023	-4.615	3.693
11000.	N2	N2	28.579	-4.694	3.946
12000.	N2	N2	28.168	-4.753	4.150
13000.	N2	N2	27.786	-4.796	4.315
14000.	N2	N2	27.429	-4.828	4.452
15000.	N2	N2	27.095	-4.850	4.565

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B $cm^3\ mole^{-1}$	$T\,dB/dT$ $cm^3\ mole^{-1}$	$T^2\,d^2B/dT^2$ $cm^3\ mole^{-1}$
1000.	N2O	N2	37.181	25.762	-64.373
2000.	N2O	N2	47.738	7.046	-25.091
3000.	N2O	N2	49.309	1.143	-12.672
4000.	N2O	N2	49.209	-1.686	-6.613
5000.	N2O	N2	48.643	-3.314	-3.049
6000.	N2O	N2	47.941	-4.353	-0.716
7000.	N2O	N2	47.213	-5.061	0.919
8000.	N2O	N2	46.503	-5.567	2.121
9000.	N2O	N2	45.824	-5.940	3.038
10000.	N2O	N2	45.183	-6.222	3.756
11000.	N2O	N2	44.580	-6.440	4.331
12000.	N2O	N2	44.012	-6.610	4.799
13000.	N2O	N2	43.477	-6.745	5.186
14000.	N2O	N2	42.973	-6.853	5.510
15000.	N2O	N2	42.497	-6.939	5.783
1000.	N	N2+	-124.026	170.816	-399.708
2000.	N	N2+	-45.446	71.981	-157.329
3000.	N	N2+	-22.232	44.753	-96.887
4000.	N	N2+	-11.294	31.988	-69.495
5000.	N	N2+	-5.017	24.578	-53.857
6000.	N	N2+	-0.991	19.739	-43.739
7000.	N	N2+	1.781	16.330	-36.656
8000.	N	N2+	3.789	13.802	-31.419
9000.	N	N2+	5.297	11.852	-27.390
10000.	N	N2+	6.463	10.303	-24.194
11000.	N	N2+	7.384	9.044	-21.597
12000.	N	N2+	8.125	8.000	-19.446
13000.	N	N2+	8.729	7.122	-17.634
14000.	N	N2+	9.229	6.373	-16.088
15000.	N	N2+	9.646	5.727	-14.753
1000.	N2O	N2O	37.314	58.190	-137.516
2000.	N2O	N2O	62.745	20.063	-56.623
3000.	N2O	N2O	68.273	8.086	-31.562
4000.	N2O	N2O	69.723	2.298	-19.378
5000.	N2O	N2O	69.843	-1.072	-12.197
6000.	N2O	N2O	69.442	-3.253	-7.479
7000.	N2O	N2O	68.821	-4.764	-4.154
8000.	N2O	N2O	68.109	-5.862	-1.694
9000.	N2O	N2O	67.369	-6.689	0.194
10000.	N2O	N2O	66.630	-7.327	1.683
11000.	N2O	N2O	65.907	-7.831	2.885
12000.	N2O	N2O	65.207	-8.236	3.872
13000.	N2O	N2O	64.535	-8.565	4.695
14000.	N2O	N2O	63.890	-8.836	5.390
15000.	N2O	N2O	63.272	-9.061	5.982

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T	Pair		B	T dB/dT	$T^2 d^2B/dT^2$
°K			$cm^3 mole^{-1}$	$cm^3 mole^{-1}$	$cm^3 mole^{-1}$
1000.	CO2	NO	26.092	22.767	-55.683
2000.	CO2	NO	35.659	6.843	-22.182
3000.	CO2	NO	37.340	1.821	-11.645
4000.	CO2	NO	37.497	-0.595	-6.507
5000.	CO2	NO	37.202	-1.991	-3.481
6000.	CO2	NO	36.754	-2.887	-1.497
7000.	CO2	NO	36.260	-3.501	-0.104
8000.	CO2	NO	35.763	-3.942	0.923
9000.	CO2	NO	35.278	-4.270	1.708
10000.	CO2	NO	34.815	-4.521	2.325
11000.	CO2	NO	34.375	-4.716	2.819
12000.	CO2	NO	33.957	-4.870	3.224
13000.	CO2	NO	33.563	-4.993	3.559
14000.	CO2	NO	33.189	-5.092	3.841
15000.	CO2	NO	32.835	-5.173	4.079
1000.	N2	NO	28.028	12.110	-32.248
2000.	N2	NO	32.607	2.326	-11.754
3000.	N2	NO	32.880	-0.748	-5.224
4000.	N2	NO	32.443	-2.206	-2.042
5000.	N2	NO	31.854	-3.034	-0.177
6000.	N2	NO	31.251	-3.555	1.037
7000.	N2	NO	30.676	-3.904	1.883
8000.	N2	NO	30.137	-4.148	2.501
9000.	N2	NO	29.638	-4.325	2.969
10000.	N2	NO	29.175	-4.455	3.332
11000.	N2	NO	28.746	-4.553	3.621
12000.	N2	NO	28.347	-4.627	3.854
13000.	N2	NO	27.974	-4.683	4.046
14000.	N2	NO	27.625	-4.726	4.204
15000.	N2	NO	27.298	-4.759	4.336
1000.	N2O	NO	33.865	29.784	-72.798
2000.	N2O	NO	46.390	8.976	-29.019
3000.	N2O	NO	48.600	2.414	-15.251
4000.	N2O	NO	48.816	-0.743	-8.538
5000.	N2O	NO	48.438	-2.568	-4.584
6000.	N2O	NO	47.859	-3.738	-1.992
7000.	N2O	NO	47.219	-4.541	-0.172
8000.	N2O	NO	46.573	-5.119	1.170
9000.	N2O	NO	45.944	-5.548	2.196
10000.	N2O	NO	45.342	-5.875	3.002
11000.	N2O	NO	44.769	-6.130	3.649
12000.	N2O	NO	44.227	-6.332	4.177
13000.	N2O	NO	43.714	-6.493	4.616
14000.	N2O	NO	43.228	-6.623	4.984
15000.	N2O	NO	42.767	-6.729	5.296

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 mole^{-1}	T dB/dT cm^3 mole^{-1}	$T^2\ d^2B/dT^2$ cm^3 mole^{-1}
1000.	NO	NO	26.290	14.202	-36.560
2000.	NO	NO	31.901	3.347	-13.814
3000.	NO	NO	32.513	-0.072	-6.589
4000.	NO	NO	32.245	-1.703	-3.066
5000.	NO	NO	31.756	-2.635	-0.996
6000.	NO	NO	31.220	-3.226	0.355
7000.	NO	NO	30.691	-3.626	1.299
8000.	NO	NO	30.187	-3.908	1.992
9000.	NO	NO	29.714	-4.115	2.518
10000.	NO	NO	29.272	-4.269	2.928
11000.	NO	NO	28.859	-4.387	3.255
12000.	NO	NO	28.474	-4.478	3.521
13000.	NO	NO	28.112	-4.549	3.740
14000.	NO	NO	27.773	-4.604	3.922
15000.	NO	NO	27.454	-4.647	4.075
1000.	O2	NO	24.892	13.207	-34.083
2000.	O2	NO	30.094	3.071	-12.845
3000.	O2	NO	30.644	-0.121	-6.097
4000.	O2	NO	30.378	-1.643	-2.806
5000.	O2	NO	29.910	-2.513	-0.873
6000.	O2	NO	29.400	-3.064	0.388
7000.	O2	NO	28.898	-3.436	1.269
8000.	O2	NO	28.421	-3.699	1.915
9000.	O2	NO	27.973	-3.891	2.406
10000.	O2	NO	27.556	-4.035	2.789
11000.	O2	NO	27.166	-4.144	3.094
12000.	O2	NO	26.801	-4.228	3.342
13000.	O2	NO	26.460	-4.294	3.545
14000.	O2	NO	26.140	-4.345	3.715
15000.	O2	NO	25.839	-4.384	3.857
1000.	N	NO+	-122.429	168.445	-393.233
2000.	N	NO+	-44.845	71.148	-155.380
3000.	N	NO+	-21.894	44.257	-95.783
4000.	N	NO+	-11.077	31.638	-68.730
5000.	N	NO+	-4.868	24.308	-53.274
6000.	N	NO+	-0.887	19.520	-43.269
7000.	N	NO+	1.855	16.147	-36.262
8000.	N	NO+	3.840	13.644	-31.081
9000.	N	NO+	5.331	11.714	-27.094
10000.	N	NO+	6.483	10.181	-23.931
11000.	N	NO+	7.393	8.935	-21.361
12000.	N	NO+	8.124	7.902	-19.231
13000.	N	NO+	8.722	7.033	-17.438
14000.	N	NO+	9.215	6.291	-15.908
15000.	N	NO+	9.627	5.652	-14.586

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	N2	NO+	-176.826	243.756	-579.088
2000.	N2	NO+	-65.552	101.226	-222.299
3000.	N2	NO+	-32.953	62.779	-136.056
4000.	N2	NO+	-17.610	44.876	-97.373
5000.	N2	NO+	-8.801	34.516	-75.402
6000.	N2	NO+	-3.144	27.762	-61.232
7000.	N2	NO+	0.759	23.011	-51.331
8000.	N2	NO+	3.591	19.489	-44.021
9000.	N2	NO+	5.724	16.774	-38.404
10000.	N2	NO+	7.375	14.619	-33.951
11000.	N2	NO+	8.684	12.866	-30.335
12000.	N2	NO+	9.739	11.414	-27.341
13000.	N2	NO+	10.603	10.192	-24.820
14000.	N2	NO+	11.319	9.150	-22.670
15000.	N2	NO+	11.919	8.251	-20.814
1000.	O	NO+	-85.270	121.823	-279.065
2000.	O	NO+	-28.672	52.230	-113.861
3000.	O	NO+	-11.828	32.429	-70.609
4000.	O	NO+	-3.921	23.051	-50.692
5000.	O	NO+	0.588	17.580	-39.230
6000.	O	NO+	3.456	13.998	-31.779
7000.	O	NO+	5.414	11.472	-26.546
8000.	O	NO+	6.817	9.596	-22.669
9000.	O	NO+	7.860	8.149	-19.681
10000.	O	NO+	8.657	6.999	-17.309
11000.	O	NO+	9.279	6.065	-15.379
12000.	O	NO+	9.773	5.291	-13.780
13000.	O	NO+	10.170	4.640	-12.433
14000.	O	NO+	10.493	4.084	-11.283
15000.	O	NO+	10.758	3.606	-10.290
1000.	CO	O	23.163	7.166	-20.374
2000.	CO	O	25.627	0.749	-6.917
3000.	CO	O	25.493	-1.255	-2.617
4000.	CO	O	24.989	-2.196	-0.527
5000.	CO	O	24.437	-2.723	0.693
6000.	CO	O	23.909	-3.050	1.483
7000.	CO	O	23.422	-3.265	2.030
8000.	CO	O	22.975	-3.413	2.428
9000.	CO	O	22.567	-3.518	2.726
10000.	CO	O	22.192	-3.593	2.957
11000.	CO	O	21.847	-3.647	3.139
12000.	CO	O	21.528	-3.687	3.284
13000.	CO	O	21.232	-3.716	3.402
14000.	CO	O	20.956	-3.736	3.499
15000.	CO	O	20.697	-3.750	3.579

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B $cm^3\ mole^{-1}$	T dB/dT $cm^3\ mole^{-1}$	$T^2\ d^2B/dT^2$ $cm^3\ mole^{-1}$
1000.	CO2	O	22.148	14.549	-36.564
2000.	CO2	O	28.068	3.873	-14.167
3000.	CO2	O	28.906	0.507	-7.079
4000.	CO2	O	28.807	-1.105	-3.621
5000.	CO2	O	28.452	-2.032	-1.587
6000.	CO2	O	28.026	-2.622	-0.257
7000.	CO2	O	27.590	-3.024	0.675
8000.	CO2	O	27.166	-3.310	1.360
9000.	CO2	O	26.764	-3.521	1.882
10000.	CO2	O	26.384	-3.680	2.291
11000.	CO2	O	26.027	-3.803	2.618
12000.	CO2	O	25.692	-3.899	2.883
13000.	CO2	O	25.377	-3.974	3.103
14000.	CO2	O	25.080	-4.034	3.287
15000.	CO2	O	24.800	-4.082	3.442
1000.	N	O	18.430	3.007	-10.310
2000.	N	O	19.132	-0.530	-2.837
3000.	N	O	18.680	-1.614	-0.451
4000.	N	O	18.140	-2.110	0.699
5000.	N	O	17.637	-2.379	1.363
6000.	N	O	17.188	-2.540	1.787
7000.	N	O	16.788	-2.641	2.077
8000.	N	O	16.431	-2.706	2.284
9000.	N	O	16.110	-2.749	2.438
10000.	N	O	15.818	-2.778	2.554
11000.	N	O	15.553	-2.795	2.643
12000.	N	O	15.309	-2.806	2.714
13000.	N	O	15.084	-2.811	2.769
14000.	N	O	14.876	-2.813	2.814
15000.	N	O	14.682	-2.811	2.849
1000.	N2	O	22.195	6.480	-18.671
2000.	N2	O	24.376	0.557	-6.246
3000.	N2	O	24.198	-1.290	-2.274
4000.	N2	O	23.695	-2.155	-0.346
5000.	N2	O	23.157	-2.639	0.779
6000.	N2	O	22.648	-2.938	1.507
7000.	N2	O	22.179	-3.135	2.011
8000.	N2	O	21.751	-3.269	2.376
9000.	N2	O	21.360	-3.363	2.650
10000.	N2	O	21.002	-3.431	2.862
11000.	N2	O	20.673	-3.479	3.028
12000.	N2	O	20.368	-3.514	3.161
13000.	N2	O	20.086	-3.539	3.269
14000.	N2	O	19.823	-3.557	3.357
15000.	N2	O	19.577	-3.568	3.430

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	N2O	O	29.796	17.427	-44.400
2000.	N2O	O	36.771	4.337	-16.960
3000.	N2O	O	37.631	0.212	-8.256
4000.	N2O	O	37.392	-1.760	-4.010
5000.	N2O	O	36.868	-2.889	-1.515
6000.	N2O	O	36.273	-3.607	0.115
7000.	N2O	O	35.679	-4.093	1.256
8000.	N2O	O	35.108	-4.438	2.093
9000.	N2O	O	34.570	-4.692	2.730
10000.	N2O	O	34.065	-4.882	3.227
11000.	N2O	O	33.593	-5.027	3.625
12000.	N2O	O	33.151	-5.140	3.948
13000.	N2O	O	32.736	-5.228	4.214
14000.	N2O	O	32.345	-5.298	4.436
15000.	N2O	O	31.978	-5.353	4.623
1000.	NO	O	21.179	7.745	-21.258
2000.	NO	O	23.987	1.178	-7.499
3000.	NO	O	24.015	-0.879	-3.108
4000.	NO	O	23.615	-1.851	-0.970
5000.	NO	O	23.138	-2.399	0.280
6000.	NO	O	22.668	-2.741	1.092
7000.	NO	O	22.227	-2.969	1.656
8000.	NO	O	21.819	-3.127	2.067
9000.	NO	O	21.444	-3.240	2.377
10000.	NO	O	21.098	-3.322	2.618
11000.	NO	O	20.779	-3.383	2.808
12000.	NO	O	20.482	-3.428	2.961
13000.	NO	O	20.207	-3.462	3.086
14000.	NO	O	19.949	-3.487	3.188
15000.	NO	O	19.708	-3.505	3.274
1000.	O	O	16.004	3.923	-11.819
2000.	O	O	17.227	0.089	-3.763
3000.	O	O	17.003	-1.101	-1.188
4000.	O	O	16.602	-1.654	0.060
5000.	O	O	16.197	-1.962	0.786
6000.	O	O	15.822	-2.150	1.254
7000.	O	O	15.480	-2.272	1.577
8000.	O	O	15.171	-2.354	1.810
9000.	O	O	14.891	-2.411	1.985
10000.	O	O	14.634	-2.451	2.119
11000.	O	O	14.399	-2.479	2.223
12000.	O	O	14.183	-2.499	2.307
13000.	O	O	13.982	-2.512	2.374
14000.	O	O	13.796	-2.520	2.428
15000.	O	O	13.622	-2.525	2.473

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	$T^2 d^2B/dT^2$ cm^3 $mole^{-1}$
1000.	O2	O	20.045	6.879	-19.123
2000.	O2	O	22.492	0.928	-6.653
3000.	O2	O	22.462	-0.934	-2.671
4000.	O2	O	22.060	-1.811	-0.734
5000.	O2	O	21.598	-2.305	0.399
6000.	O2	O	21.149	-2.612	1.133
7000.	O2	O	20.730	-2.816	1.643
8000.	O2	O	20.344	-2.957	2.014
9000.	O2	O	19.990	-3.058	2.294
10000.	O2	O	19.664	-3.130	2.510
11000.	O2	O	19.363	-3.184	2.681
12000.	O2	O	19.084	-3.223	2.818
13000.	O2	O	18.825	-3.252	2.930
14000.	O2	O	18.583	-3.273	3.022
15000.	O2	O	18.356	-3.289	3.098
1000.	A	O+	-6440.021	33972.100	-258244.799
2000.	A	O+	-581.908	1301.352	-5466.581
3000.	A	O+	-268.998	445.038	-1420.652
4000.	A	O+	-172.217	252.535	-701.860
5000.	A	O+	-125.347	174.044	-447.282
6000.	A	O+	-97.650	132.259	-323.749
7000.	A	O+	-79.340	106.469	-252.293
8000.	A	O+	-66.331	89.003	-206.144
9000.	A	O+	-56.613	76.400	-174.027
10000.	A	O+	-49.078	66.879	-150.441
11000.	A	O+	-43.067	59.434	-132.410
12000.	A	O+	-38.161	53.451	-118.189
13000.	A	O+	-34.082	48.539	-106.690
14000.	A	O+	-30.640	44.433	-97.202
15000.	A	O+	-27.696	40.949	-89.242
1000.	N	O+	-193.261	290.212	-824.283
2000.	N	O+	-73.171	99.592	-232.926
3000.	N	O+	-41.761	59.386	-132.112
4000.	N	O+	-27.331	42.031	-91.734
5000.	N	O+	-19.082	32.352	-70.056
6000.	N	O+	-13.767	26.175	-56.537
7000.	N	O+	-10.072	21.889	-47.299
8000.	N	O+	-7.365	18.741	-40.585
9000.	N	O+	-5.302	16.330	-35.485
10000.	N	O+	-3.684	14.425	-31.478
11000.	N	O+	-2.384	12.882	-28.246
12000.	N	O+	-1.320	11.606	-25.585
13000.	N	O+	-0.434	10.534	-23.356
14000.	N	O+	0.312	9.621	-21.460
15000.	N	O+	0.949	8.834	-19.829

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	$T^2 d^2B/dT^2$ cm^3 $mole^{-1}$
1000.	N2	O+	-279.414	432.196	-1271.157
2000.	N2	O+	-104.299	142.214	-337.290
3000.	N2	O+	-59.671	83.976	-188.231
4000.	N2	O+	-39.305	59.213	-129.807
5000.	N2	O+	-27.694	45.501	-98.776
6000.	N2	O+	-20.222	36.787	-79.548
7000.	N2	O+	-15.029	30.758	-66.464
8000.	N2	O+	-11.225	26.337	-56.984
9000.	N2	O+	-8.326	22.957	-49.798
10000.	N2	O+	-6.051	20.289	-44.163
11000.	N2	O+	-4.222	18.129	-39.625
12000.	N2	O+	-2.723	16.345	-35.891
13000.	N2	O+	-1.476	14.846	-32.766
14000.	N2	O+	-0.424	13.570	-30.111
15000.	N2	O+	0.474	12.470	-27.827
1000.	O	O+	-126.534	180.812	-473.405
2000.	O	O+	-48.166	67.933	-154.263
3000.	O	O+	-26.524	41.292	-90.626
4000.	O	O+	-16.459	29.396	-63.827
5000.	O	O+	-10.685	22.651	-49.079
6000.	O	O+	-6.965	18.305	-39.744
7000.	O	O+	-4.384	15.272	-33.304
8000.	O	O+	-2.498	13.033	-28.590
9000.	O	O+	-1.066	11.314	-24.991
10000.	O	O+	0.053	9.953	-22.153
11000.	O	O+	0.948	8.848	-19.856
12000.	O	O+	1.678	7.933	-17.960
13000.	O	O+	2.281	7.164	-16.369
14000.	O	O+	2.788	6.508	-15.013
15000.	O	O+	3.217	5.942	-13.845
1000.	N	O-	-160.745	226.941	-582.457
2000.	N	O-	-61.293	87.122	-196.379
3000.	N	O-	-33.468	53.211	-116.376
4000.	N	O-	-20.487	37.938	-82.257
5000.	N	O-	-13.034	29.243	-63.362
6000.	N	O-	-8.232	23.628	-51.358
7000.	N	O-	-4.901	19.701	-43.054
8000.	N	O-	-2.468	16.801	-36.966
9000.	N	O-	-0.624	14.572	-32.311
10000.	N	O-	0.817	12.806	-28.637
11000.	N	O-	1.968	11.372	-25.662
12000.	N	O-	2.905	10.184	-23.204
13000.	N	O-	3.680	9.185	-21.139
14000.	N	O-	4.328	8.334	-19.380
15000.	N	O-	4.878	7.599	-17.864

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	$T^2 d^2B/dT^2$ cm^3 $mole^{-1}$
1000.	CO2	O2	24.116	23.743	-57.538
2000.	CO2	O2	34.199	7.413	-23.132
3000.	CO2	O2	36.084	2.265	-12.342
4000.	CO2	O2	36.360	-0.214	-7.083
5000.	CO2	O2	36.145	-1.650	-3.984
6000.	CO2	O2	35.757	-2.573	-1.952
7000.	CO2	O2	35.310	-3.208	-0.523
8000.	CO2	O2	34.850	-3.666	0.531
9000.	CO2	O2	34.397	-4.007	1.338
10000.	CO2	O2	33.961	-4.268	1.972
11000.	CO2	O2	33.544	-4.472	2.482
12000.	CO2	O2	33.148	-4.634	2.899
13000.	CO2	O2	32.772	-4.764	3.246
14000.	CO2	O2	32.415	-4.870	3.537
15000.	CO2	O2	32.076	-4.956	3.784
1000.	N2	O2	26.566	11.275	-30.116
2000.	N2	O2	30.812	2.121	-10.941
3000.	N2	O2	31.045	-0.754	-4.830
4000.	N2	O2	30.621	-2.118	-1.853
5000.	N2	O2	30.058	-2.891	-0.109
6000.	N2	O2	29.485	-3.377	1.027
7000.	N2	O2	28.938	-3.703	1.818
8000.	N2	O2	28.428	-3.931	2.396
9000.	N2	O2	27.955	-4.095	2.833
10000.	N2	O2	27.517	-4.216	3.173
11000.	N2	O2	27.111	-4.307	3.443
12000.	N2	O2	26.733	-4.376	3.660
13000.	N2	O2	26.380	-4.428	3.839
14000.	N2	O2	26.051	-4.468	3.986
15000.	N2	O2	25.741	-4.497	4.110
1000.	N2O	O2	32.255	27.834	-68.140
2000.	N2O	O2	43.939	8.334	-27.120
3000.	N2O	O2	45.979	2.184	-14.214
4000.	N2O	O2	46.158	-0.774	-7.921
5000.	N2O	O2	45.787	-2.483	-4.214
6000.	N2O	O2	45.230	-3.579	-1.785
7000.	N2O	O2	44.619	-4.331	-0.079
8000.	N2O	O2	44.003	-4.871	1.178
9000.	N2O	O2	43.405	-5.272	2.139
10000.	N2O	O2	42.833	-5.578	2.894
11000.	N2O	O2	42.290	-5.816	3.500
12000.	N2O	O2	41.775	-6.004	3.995
13000.	N2O	O2	41.289	-6.155	4.405
14000.	N2O	O2	40.828	-6.276	4.749
15000.	N2O	O2	40.391	-6.375	5.041

Table 8.1. Second Virial Coefficient and Derivatives for Pairs in High Temperature Air. (Cont.)

T °K	Pair		B cm^3 $mole^{-1}$	T dB/dT cm^3 $mole^{-1}$	T^2 d^2B/dT^2 cm^3 $mole^{-1}$
1000.	02	02	23.602	12.298	-31.816
2000.	02	02	28.431	2.820	-11.959
3000.	02	02	28.924	-0.164	-5.648
4000.	02	02	28.660	-1.587	-2.570
5000.	02	02	28.211	-2.399	-0.763
6000.	02	02	27.725	-2.913	0.416
7000.	02	02	27.249	-3.261	1.240
8000.	02	02	26.796	-3.506	1.844
9000.	02	02	26.372	-3.685	2.302
10000.	02	02	25.977	-3.818	2.660
11000.	02	02	25.608	-3.920	2.945
12000.	02	02	25.264	-3.998	3.176
13000.	02	02	24.941	-4.059	3.366
14000.	02	02	24.638	-4.106	3.524
15000.	02	02	24.354	-4.143	3.657

DISCUSSION

In the preceding several chapters, a method has been given for estimating thermodynamic properties of gases in the high temperature region of partial ionization, not only at quite low pressure but also for higher pressures where isolated short range pair interactions are important, and on even to where multi-neighbor exclusion effects become significant. Further comment on a number of the topics covered may be in order.

In the interest of clarity we mention again that the type of partition function taken here for atomic ions and atoms has been strongly influenced by considerations of dynamic response of the ion in electric or magnetic fields. For the sake of obtaining realistic information in regard to concentrations of ions and free electrons in a gas mixture, it has appeared reasonable to count as single systems those which have actual stability when in a small electric field. Thus, for a particular ion, we do not include in its population any of the systems composed of the next higher stage of ionization with the previous outermost electron still considered in it even though promoted to the continuum. The thermodynamic effects of such continuum electrons in local ionic fields are nevertheless included in the over-all estimates for the complete assembly. To obtain correct compositions, we must adjust for the number of available atomic states as influenced by Debye screening.

Naturally, there are various numerical uncertainties and deficiencies in theory which affect our proposed density dependent corrections. This affects the range of validity or the accuracy of the resulting thermodynamic property predictions.

The difficulty of estimating the dielectric constant satisfactorily has been mentioned in Chapter 2. The dielectric constant affects various quantities that depend on electric field, even though no formula may be at hand for estimating these effects. These dependent quantities include the $1/R^6$ dispersion potential commonly present and the $1/R^4$ induction potential for neutrals near an ion. For both dispersion and induction energies, the complexities of the situation imply that pairwise additivity of energy may not be perfectly valid. In the case of the $1/R^4$ induction potential term, at least nominal care is appropriate to avoid including the same induction energy in duplicate in the stored electrical energy in the gas considered as a dielectric medium. The $1/R^{12}$ short range repulsion effects between atomic ions, discussed in Chapter 7, are also affected by the dielectric constant, since its introduction as D into the k_1/R repulsion energy leads to factors of $D^{3/11}$ and $D^{-12/11}$, respectively, in the b_o and U_o estimates of Table 7.4. Thus, the short range ionic repulsion effects outlined there may not be negligible if the dielectric constant is large.

Our high density extrapolation, as suggested at the end of Chapter 1, would employ a rigid sphere virial approximation of Reiss, Frisch and Lebowitz (see reference 5 of the Appendix) for the system of numerical coefficients predicting the higher virials. We suppose that the slightly high pressures as compared with computer results for a collection of rigid spheres in a box as shown graphically in Fig. 1 of the Appendix may be an advantage in the present use, in view of the fact that near-neighbor repulsions produce a static pressure contribution in the high density region for non-rigid-sphere molecules. Another feature of the mixture rule proposed for the higher virials is its automatic generation of the theoretically correct dependence on composition, as may be seen in the Appendix. We may add that in the high pressure limit, the mixture rule indicates additivity of species volumes, which is close to Amagat's law of volumes for mixtures of permanent gases. There is still the latent empirical problem of achieving a suitable join with data at high temperature and high pressure for such single substances as are involved and with the best available theoretical estimates accepted for the extreme high energy region.(57)

No apology may be needed for the present simplification of including chemical bonding effects only within the individual molecular species. Since non-bonding states also occur, they should be allowed for with their suitable complementary weights, and not with the full weight of all possible states. In general, we would suggest that non-bonding effects be treated on the basis of explicit repulsion estimates where available, since they are preferable to our over-all $1/R^{12}$ correlation. The complete detail of distribution of quasi-bondings in the dense gas at high temperature would be quite complex. Under such conditions, it is hoped that a model of Coulombic interactions may give an acceptable high temperature mean of bonding and antibonding effects, since electric fields are basic to all significant interactions in the system, in the present non-nuclear sense.

We would also allow freedom to correct the present omission of various explicit effects from our incomplete outline. Thus, recent results by diagram summing or an equivalent technique should give a more suitable representation of electron-electron effects in the electron gas part of the mixture than does our representation of pair repulsion effects for positive ions. Similarly, the radiation and relativity effects can be incorporated into the treatment as needed in accord with well-known high temperature astrophysical procedures.

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APPENDIX

Effects of Intermolecular Interactions on Thermodynamic Properties of Gases at High Temperatures and Pressures

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Abstract

It is proposed that non-ideality effects for gases at high temperature may be analyzed and estimated using an effective rigid sphere volume depending on pair potential energy and temperature. Empirical type estimates for higher virials for the rigid sphere gas are proposed. Some theoretical values of second, third, and fourth virials and some experimental fourth and fifth virials for non-polar gases are examined on this basis. A simple mixture rule for higher virials at high temperatures is shown to be supported by theoretical calculations of mixture third virials while exactly conforming to theory in regard to composition dependence for all orders of higher virials.

EFFECTS OF INTERMOLECULAR INTERACTIONS ON THERMODYNAMIC PROPERTIES OF GASES AT HIGH TEMPERATURES AND PRESSURES

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INTRODUCTION

When we try to estimate thermodynamic properties for gases at very high temperature and pressure, we encounter a two-fold difficulty. As a result of partial dissociation and other reactions arising at the very high temperature, the gaseous fluid involves many constituents for which direct experimental interaction data are lacking. But further, as a result of the high gas densities of interest, these interactions are important not only for effects of separate pairs of molecules, but also for virial coefficients of higher order, pertaining to larger groups. Even if the pair interactions were accurately known, we would not have exact numerical values for the higher virials, because the mathematical expressions for all but the first few of the virials involve multidimensional integrations which have never been performed.

We note that in the ordinary thermal collisions involving two particular molecule-like systems, the mutual approach of colliding molecules can be closer when the collisions are more energetic. We can thus think of a pair exclusion-volume which decreases as the temperature is raised. It seems natural to consider applying the idea of a pair-exclusion volume to the study of higher virials. For this purpose, we shall make the arbitrary assumption that these virials may be approximately compounded empirically in terms of effective rigid-sphere volumes plus an additional part which brings in effects arising from van der Waals binding energies. Accordingly, we shall first examine estimates concerning higher virials for a rigid sphere gas. We shall then come to the question of estimating exclusion-volumes for realistic potentials and we shall next examine the behavior of the virials for pure gases on the basis of such exclusion-volumes. Finally, we shall consider the problem of virial coefficients for mixtures, since gases at very high temperatures are typically mixtures of products of dissociative reactions.

THE RIGID SPHERE GAS

For a rigid-sphere gas, the virial coefficients are known exactly through the fourth, while a Monte Carlo estimate [1] is available for the fifth, giving

$$PV/RT = 1 + b/V + 0.625b^2/V^2 + 0.28695b^3/V^3 + 0.115b^4/V^4. \qquad (1)$$

We shall take as an axiom that the true function for PV/RT would be an infinite series rather than terminating as a polynomial. It may then be plausible to speculate about the probable law of variation of the numerical coefficients. The function

$$PV/RT = \exp[b/V + 0.125b^2/V^2]$$

expands into

$$PV/RT = 1 + b/V + 0.625b^2/V^2 + 0.2917b^3/V^3 + 0.112b^4/V^4$$
$$+ 0.0370b^5/V^5 + 0.0108b^6/V^6 + \ldots \quad . \qquad (2)$$

A similar equation,

$$PV/RT = \exp[B/V + (C - 0.5B^2)/V^2]$$

has previously [2] been used for hydrogen at ordinary temperatures and above.

Another set of coefficients of proper general magnitude may be obtained by the following scheme. If n is the power of b/V in the general term of the series and if 1 + 0.6n is taken as the ratio of the corresponding coefficient to the next one, the resulting series is

$$PV/RT = 1 + b/V + 0.625b^2/V^2 + 0.2841b^3/V^3 + 0.1015b^4/V^4$$
$$+ 0.0298b^5/V^5 + 0.0075b^6/V^6 + 0.00162b^7/V^7$$
$$+ 0.000312b^8/V^8 + 0.0000538b^9/V^9 + \ldots \quad . \qquad (3)$$

We also note that no account has been taken of the limiting density at which no space would be available for rigid-sphere molecular motion. A reasonable limiting density can be made by introducing a suitable choice of the ratio of coefficients in the limit of large n. This choice effectively defines the region of series convergence. This has been done while arranging other details by replacing the previous ratio 1 + 0.6n by

$$\frac{1 + (0.6 + 1.6a)n + dc\, n(n-1)}{1 + an + dn(n-1)}$$

with the constants a, c and d to be suitably chosen. This fixes the limiting density at b/V equal to c. Then a and d can be adjusted to give a close approximation for the fourth virial and to give satisfactory overall agreement with recent Monte Carlo [3] and equation of motion calculations [4] for a collection of spheres. With c taken as 3 to approximate the strict close packing value of 2.964... and with $a = 0.15$ and $d = 0.092$, the series becomes

$$\begin{aligned} PV/RT = {} & 1 + b/V + 0.625b^2/V^2 + 0.28697b^3/V^3 + 0.11100b^4/V^4 \\ & + 0.03912b^5/V^5 + 0.01310b^6/V^6 + 0.004263b^7/V^7 \\ & + 0.001365b^8/V^8 + 0.000433b^9/V^9 + 0.000137b^{10}/V^{10} \\ & + 0.000043b^{11}/V^{11} + 0.000014b^{12}/V^{12} + \ldots \quad . \end{aligned} \tag{4}$$

A very good equation of state for rigid spheres has been obtained recently by Reiss, Frisch and Lebowitz [5] on the basis of physical principles. They used an approximating polynomial for the distribution function. The limiting value of b/V in their equation is 4. We note that a general numerical coefficient can be written from their results as $2^{-(2n+1)}(3n^2 + 3n + 2)$, giving the series

$$\begin{aligned} PV/RT = {} & 1 + b/V + 0.625b^2/V^2 + 0.296875b^3/V^3 + 0.121093b^4/V^4 \\ & + 0.044921b^5/V^5 + 0.015625b^6/V^6 + 0.005188b^7/V^7 \\ & + 0.011663b^8/V^8 + \ldots \quad . \end{aligned} \tag{5}$$

Their fourth virial is slightly too large and we may see in Fig. 1 that their function, shown as curve 5, is slightly high as compared with electronic computer results for collections of rigid sphere molecules.*

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*[Note added after presentation of paper]. This departure has also been commented on recently by Rice [see J. Chem. Phys. 32: 1277 (1960)].

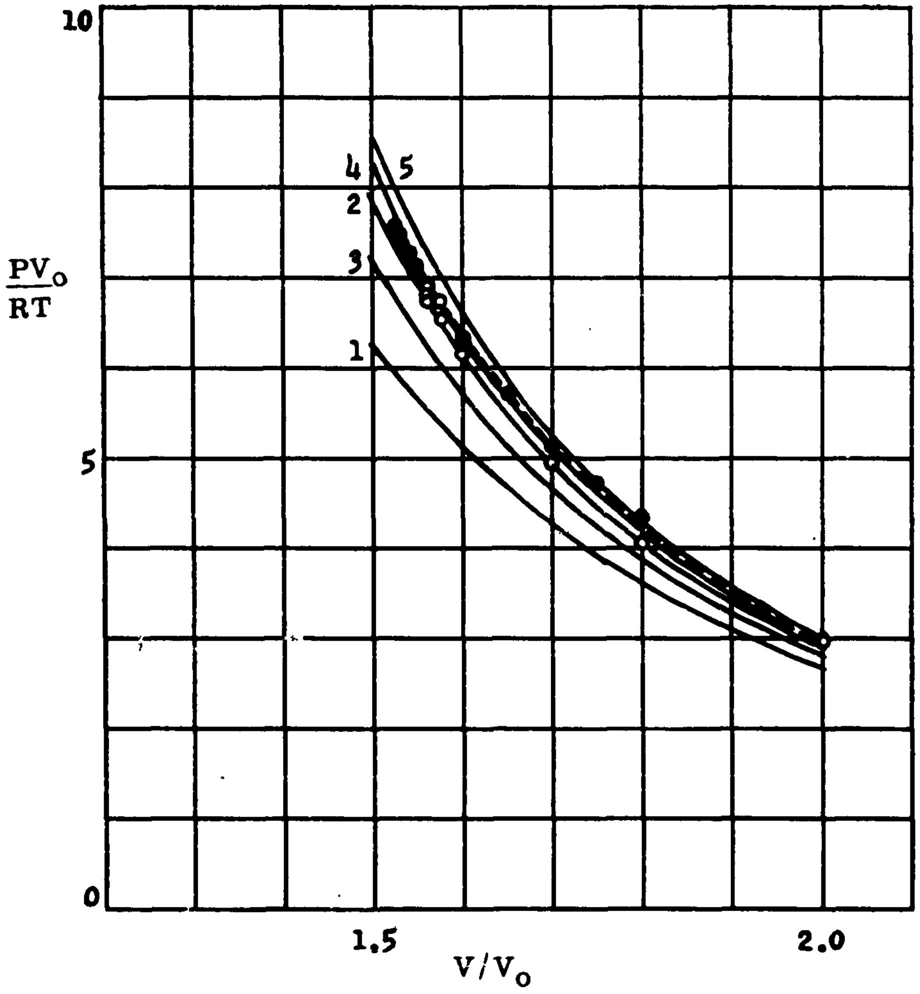

Fig. 1–Equation of state for hard spheres. Solid curves 1 to 5 refer to Equations 1 to 5. Dashed curve and filled circles show results of Alder and Wainwright for 108 and 32 molecules. Open circles show Monte Carlo results of Wood and Jacobson.

From curve 1, we may see that the use of virial coefficients only through the fifth is insufficient in the region of density used in the present comparison. The exponential form indicated by curve 2 shows some merit, as it agrees fairly well with the Monte Carlo result. The simplest numerical ratio rule tried for numerical coefficients gives the results shown by curve 3. They fall considerably below the computer results. The set of coefficients given by the more complex ratio-rule quoted permits closer agreement with the computer estimates for rigid spheres. This is shown by curve 4.

PAIR EXCLUDED VOLUME

If we apply the rigid sphere coefficients just obtained to an actual gas, we need a method of estimating effective sphere sizes for the molecules as a function of the temperature. Examining the expression for the classical second virial coefficient in case the pair potential can be considered as a function only of intermolecular distance,

$$B = 2\pi N \int_0^\infty [1 - \exp(-U/kT)] r^2 dr,$$

we note that we can separate a portion of the integral from $r = 0$ to $r = \sigma$, the collision radius at zero energy. Calling this part of the integral b_e, we have

$$B = b_e + 2\pi N \int_\sigma^\infty [1 - \exp(-U/kT)] r^2 dr \qquad (6)$$

with

$$b_e = \frac{2\pi N}{3kT} \int_{U=0}^{\infty} r^3 e^{-U/kT} dU \qquad (7)$$

For repulsion potentials varying as an inverse power of r, this gives the result obtained by Hirschfelder and Eliason [6] that the rigid sphere radius may be obtained from the potential function by taking the energy at a fixed fraction θ of the value of kT for the particular temperature occurring. For a repulsion potential varying as the inverse δ power of the distance, they indicate that the fraction θ has the value

$\theta_\delta = [\Gamma(\frac{\delta-3}{\delta})]^{-\delta/3}$ giving $\theta_{12} = 0.4434$, $\theta_9 = 0.4027$ and $\theta_6 = 0.3183$.

For more realistic potentials involving attraction at larger separation and repulsion at close approach, we may rewrite the b_e as

$$b_e = \frac{1}{kT}\int_0^\infty e^{-U/kT} b(U)dU$$

where $b(U) = \frac{2\pi}{3} Nr^3$. We can consider b(U) to be expanded as a Taylor series in U at $r = \sigma$, and integrate term by term to obtain b_e as a power series in kT. Then considering this b_e to be representable by the original Taylor series using an effective value of U, we may equate the two representations of b_e and solve for the appropriate effective value of the potential, U_e, by series inversion. The result can be written as

$$\theta = \frac{U}{kT} = 1 + \frac{1}{2}(2 - u_2 u_1^{-1})(kT/u_1)$$
$$+ \frac{1}{6}(12u_2^2 u_1^{-2} - 5u_3 u_1^{-1} - 18u_2 u_1^{-1} - 2)(kT/u_1)^2 + \ldots$$

where $u_n = r^n d^n U/dr^n$ at $r = \sigma$. For a Lennard-Jones δ-γ potential,

$$U = \varepsilon\delta^{\delta/(\delta-\gamma)}\gamma^{\gamma/(\gamma-\delta)}(\delta-\gamma)^{-1}[(\sigma/r)^\delta - (\sigma/r)^\gamma], \tag{8}$$

which gives

$$\theta = 1 + \frac{1}{2}(3+\delta+\gamma)(kT/u_1) + \frac{1}{6}(7\delta^2 + 7\gamma^2 + 19\gamma\delta + 27\gamma + 27\delta + 18)(kT/u_1)^2 + \ldots .$$

In the case of a 12, 6 potential $\theta = 1 - 0.4375\,kT/\varepsilon + 0.90625(kT/\varepsilon)^2 + \ldots$ Unfortunately, this form does not give a satisfactorily convergent representation in that the known terms oscillate and become large for large kT. However, the closed approximation

$$\theta = [1 - 4(2 - u_2 u_1^{-1})(kT/u_1)]^{-\frac{1}{8}}$$

when expanded gives the linear term in kT correctly and approximates the quadratic term fairly well. Still, no tendency to approach θ_δ at high temperature has as yet been provided. This may be remedied for the Lennard-Jones potentials in an ad hoc manner by using the approximation

$$\theta = \left[\frac{1 + 4\theta_\delta^{8}(1 - \theta_\delta^{8})^{-1}(3 + \delta + \gamma)\delta^{\delta/(\gamma-\delta)}\gamma^{\gamma/(\delta-\gamma)}(kT/\varepsilon)}{1 + 4(1 - \theta_\delta^{8})^{-1}(3 + \delta + \gamma)\delta^{\delta/(\gamma-\delta)}\gamma^{\gamma/(\delta-\gamma)}(kT/\varepsilon)}\right]^{1/8} . \qquad (9)$$

When applied to the 12, 6 potential, with $\theta_{12} = 0.4434$, equation 9 gives

$$\theta = \left[\frac{1 + 0.005237\, kT/\varepsilon}{1 + 3.505237\, kT/\varepsilon}\right]^{1/8}$$

which expands for small kT/ε into $\theta = 1 - 0.4375(kT/\varepsilon) + 0.863906(kT/\varepsilon)^2 + \ldots$. Then using U_e/ε as $\theta \cdot kT/\varepsilon$, the solution with the 12, 6 potential gives

$$b_e/b_o = [2/(1 + \sqrt{1 + U_e/\varepsilon})]^{1/2} . \qquad (10)$$

For the 9, 6 potential, with $\theta_9 = 0.4027$, we have

$$\theta = \left[\frac{1 + 0.002461\, kT/\varepsilon}{1 + 3.558016\, kT/\varepsilon}\right]^{1/8}$$

and

$$b_e/b_o = 3/\left[1 + \left(1 + 2U_e/\varepsilon + 2\sqrt{U_e^2/\varepsilon^2 + U_e/\varepsilon}\right)^{1/3} + \left(1 + 2U_e/\varepsilon - 2\sqrt{U_e^2/\varepsilon^2 + U_e/\varepsilon}\right)^{1/3}\right] . \qquad (11)$$

For the 12, 4 potential, which is somewhat representative of the interaction effect between an ion and a neutral molecule, the approximate θ

is

$$\left[\frac{1 + 0.005471\,kT/\varepsilon}{1 + 3.662023\,kT/\varepsilon}\right]^{1/8}$$

with the effective rigid-sphere volume indicated by

$$b_e/b_o = 3^{3/8}\left[2U_e/\varepsilon + 3(U_e/\varepsilon + \sqrt{U_e^2/\varepsilon^2 - 1})^{1/3} + 3(U_e/\varepsilon - \sqrt{U_e^2/\varepsilon^2 - 1})^{1/3}\right]^{-1/4}. \tag{12}$$

Another procedure for calculation of b_e/b_o for Lennard-Jones potentials will be shown in connection with the second virials.

Fig. 2 shows values of b_e/b_o for the three potentials obtained in the range of T^* or kT/ε from 1 to 200. The fourth curve shown and marked "exp," represents the corresponding result for both the exp-six potential for $\alpha = 13.5$ and for a one-exp-six potential at a corresponding γ of 12.3. This latter potential as recently proposed [7] has the form

$$\frac{U}{\varepsilon} = \frac{1+\gamma}{\gamma - 5 + 8\gamma(e^{\gamma}-1)^{-1}}\left[\frac{6 - 8\gamma(e^{\gamma}-1)^{-1}}{1+\gamma}\,\frac{r_m}{r}\,\exp[\gamma(1 - r/r_m)] - \left(\frac{r_m}{r}\right)^6\left(\frac{1 - \exp(-\gamma r/r_m)}{1 - e^{-\gamma}}\right)^8\right] \tag{13}$$

and is close to the exp-six in behavior near its potential valley if γ is taken about 1.2 less than the corresponding value of α for the exp-six potential. For the exp-six potential, a graphical solution to obtain b_e/b_o based on an estimated θ was used. For the one-exp-six, direct tabular integration was used to evaluate the equation defining b_e. The resulting points when plotted appeared as a single curve for the scale of the graph used here.

VIRIAL COEFFICIENTS

For the present discussion, we shall assume that the equation of state can be written in a virial development as

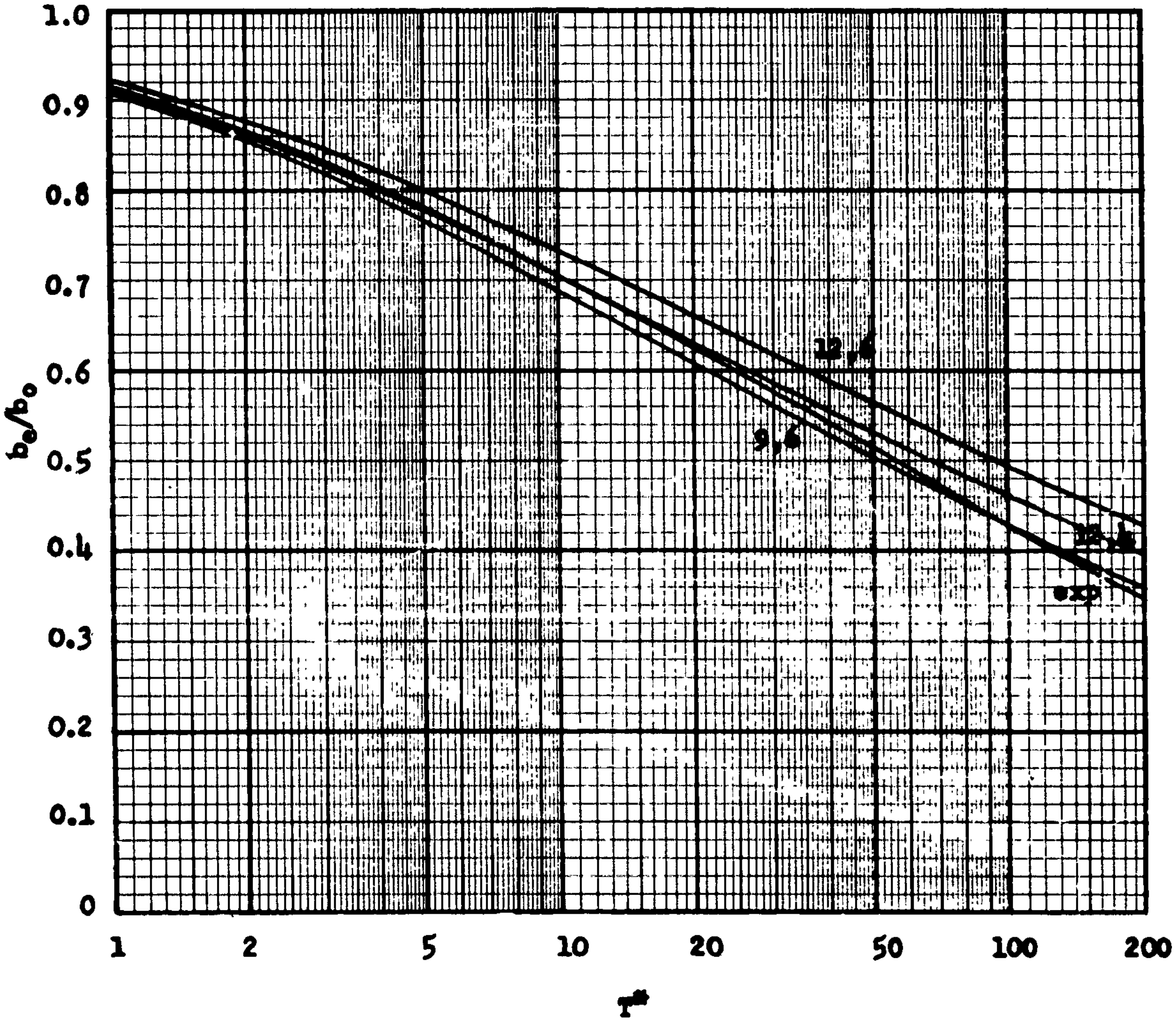

Fig. 2 – Effective pair excluded volume for various potentials. The exp-six for $\alpha = 13.5$ and a one-exp-six for $\gamma = 12.3$ appear as one curve marked "exp."

$$PV/RT = 1 + \sum_{n=2} B_n V^{1-n},$$

representing one mole of gaseous substance, with B_n as the n^{th} virial coefficient. We shall assume further that a practical approximation for the virials for a pure non-polar substance may be based on the form

$$B_n = d_n b_e^{n-1} - b_o^{n-1} \sum_{m=1} e_{nm}(\varepsilon/kT)^m \tag{14}$$

with the coefficients d_n essentially as taken earlier for the gas of rigid spheres. In Fig. 3, this relation is shown for n=2. The quantity $(b_e - B)/b_o$ is plotted as a function of ε/kT for the 12, 6, the 9, 6, and an exp-six potential for $\alpha = 13.5$. The simplicity of behavior of these graphs could be expected on the basis of the defining equations.

For potential functions for which the second virial is available, the pair excluded volume may be obtained from

$$b_e/b_o = B/b_o + (b_e - B)/b_o$$

since

$$(b_e - B)/b_o = 2\pi N \int_{\sigma}^{\infty} [\exp(-U/kT) - 1] r^2 dr$$

can be evaluated directly for some potentials. For the Lennard-Jones δ, γ potential

$$(b_e - B)/b_o = \sum_{n=1} e_{2n}(\varepsilon/kT)^n, \tag{15}$$

with the coefficients

$$e_{2n} = 3\left[\delta^{\delta/(\delta-\gamma)}\gamma^{\gamma/(\gamma-\delta)}\right]^n \Big/ \prod_{s=0}^{n} [n\delta - 3 - s(\delta-\gamma)].$$

For the 12, 6 potential, equation 15 reduces to

$$(b_e - B)/b_o = \frac{8}{1\cdot 3}\left(\frac{\varepsilon}{kT}\right) + \frac{8\cdot 8}{3\cdot 5\cdot 7}\left(\frac{\varepsilon}{kT}\right)^2 + \frac{8\cdot 8\cdot 8}{5\cdot 7\cdot 9\cdot 11}\left(\frac{\varepsilon}{kT}\right)^3 + \frac{8\cdot 8\cdot 8\cdot 8}{7\cdot 9\cdot 11\cdot 13\cdot 15}\left(\frac{\varepsilon}{kT}\right)^4 + \ldots \tag{17}$$

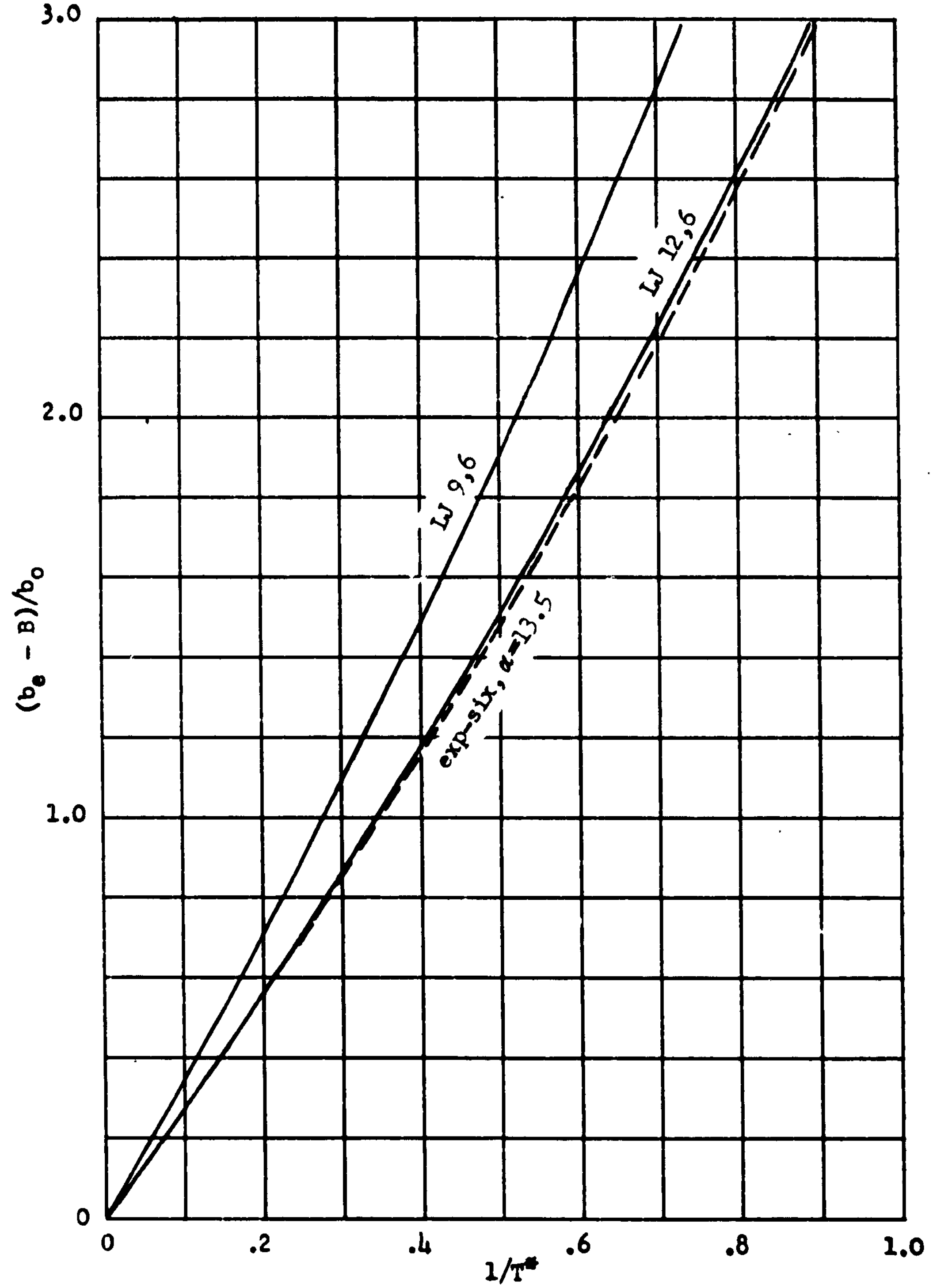

Fig. 3 - Second virial difference from effective rigid sphere gas.

and for the 9, 6 potential it is

$$(b_e - B)/b_o = \frac{1}{1\cdot 2}\left(\frac{27}{4}\frac{\varepsilon}{kT}\right) + \frac{1}{3\cdot 4\cdot 5}\left(\frac{27}{4}\frac{\varepsilon}{kT}\right)^2 + \frac{1}{5\cdot 6\cdot 7\cdot 8}\left(\frac{27}{4}\frac{\varepsilon}{kT}\right)^3 + \frac{1}{7\cdot 8\cdot 9\cdot 10\cdot 11}\left(\frac{27}{4}\frac{\varepsilon}{kT}\right)^4 + \ldots\ldots, \quad (18)$$

In the case of the 12, 4 potential the result is

$$(b_e - B)/b_o = \frac{3}{1\cdot 9}(12\sqrt{3}\frac{\varepsilon}{kT}) + \frac{3}{5\cdot 13\cdot 21}(12\sqrt{3}\frac{\varepsilon}{kT})^2 + \frac{3}{9\cdot 17\cdot 25\cdot 33}(12\sqrt{3}\frac{\varepsilon}{kT})^3 + \frac{3}{13\cdot 21\cdot 29\cdot 37\cdot 45}(12\sqrt{3}\frac{\varepsilon}{kT})^4 + \ldots \quad . \quad (19)$$

For the third virial, the potential functions for which calculated virials are available include the Lennard-Jones 12, 6 [8], the 9, 6 [9], and the single exp-six potential function for $\alpha = 13.5$ [10]. These third virials are plotted directly in Fig. 4. In Fig. 5, the same third virials are shown by means of the difference $(0.625\, b_e^2 - C)/b_o^2$. It is thought that the curves of Fig. 5 show a systematic behavior more clearly than do the direct graphs of C/b_o^2 in Fig. 4. The coefficient 0.625 was taken for use in this difference on a basis of expected practical utility. Kihara [11] has reported, however, from theoretical third virial calculations based on inverse power repulsion potentials that a better coefficient would be somewhat lower than this.

For the fourth virial coefficient, no theoretical values based on Lennard-Jones potentials have been available until very recently. Early this year, theoretical results for the case of a 12, 6 potential at eight temperatures were published by Boys and Shavitt [12]. Their treatment included the use of the sum of from 3 to 6 Gaussian functions in representing the pair distribution function. The mean of the four values based on the different representations has here been accepted for the D/b_o^3 in calculating $(0.287\, b_e^3 - D)/b_o^3$. This quantity is shown in Fig. 6 as a function of $1/T^*$, and includes the range of the four values

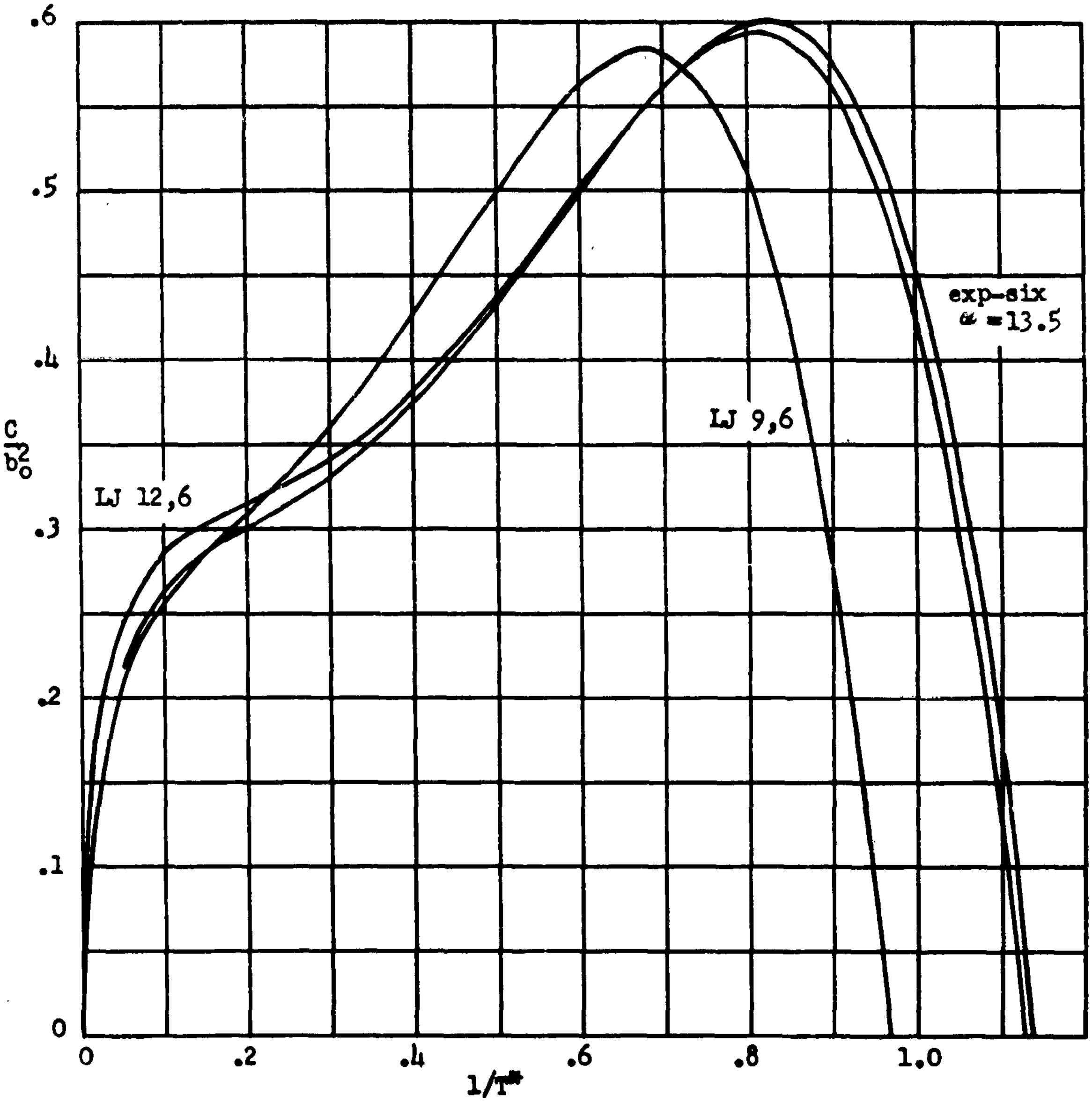

Fig. 4 – Third virial comparison.

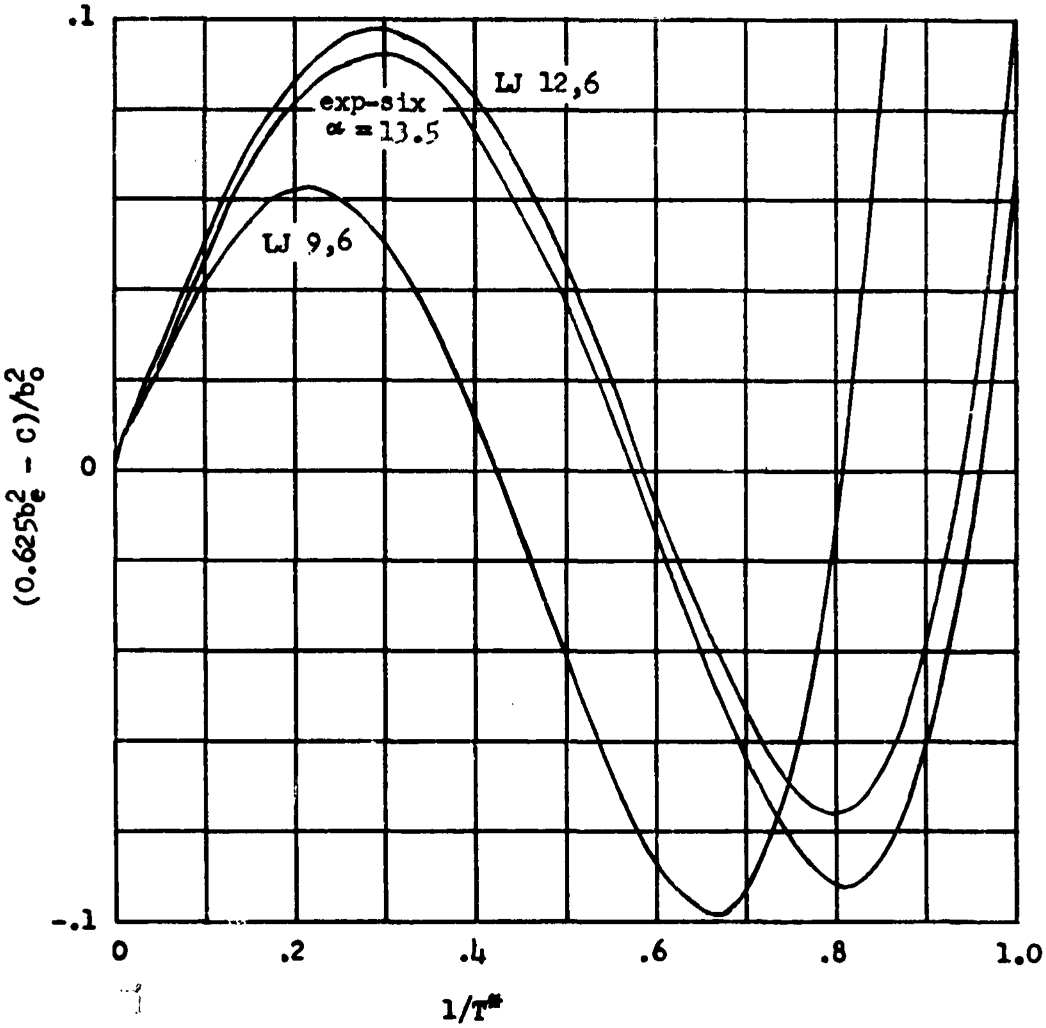

Fig. 5 – Third virial difference from effective rigid sphere gas.

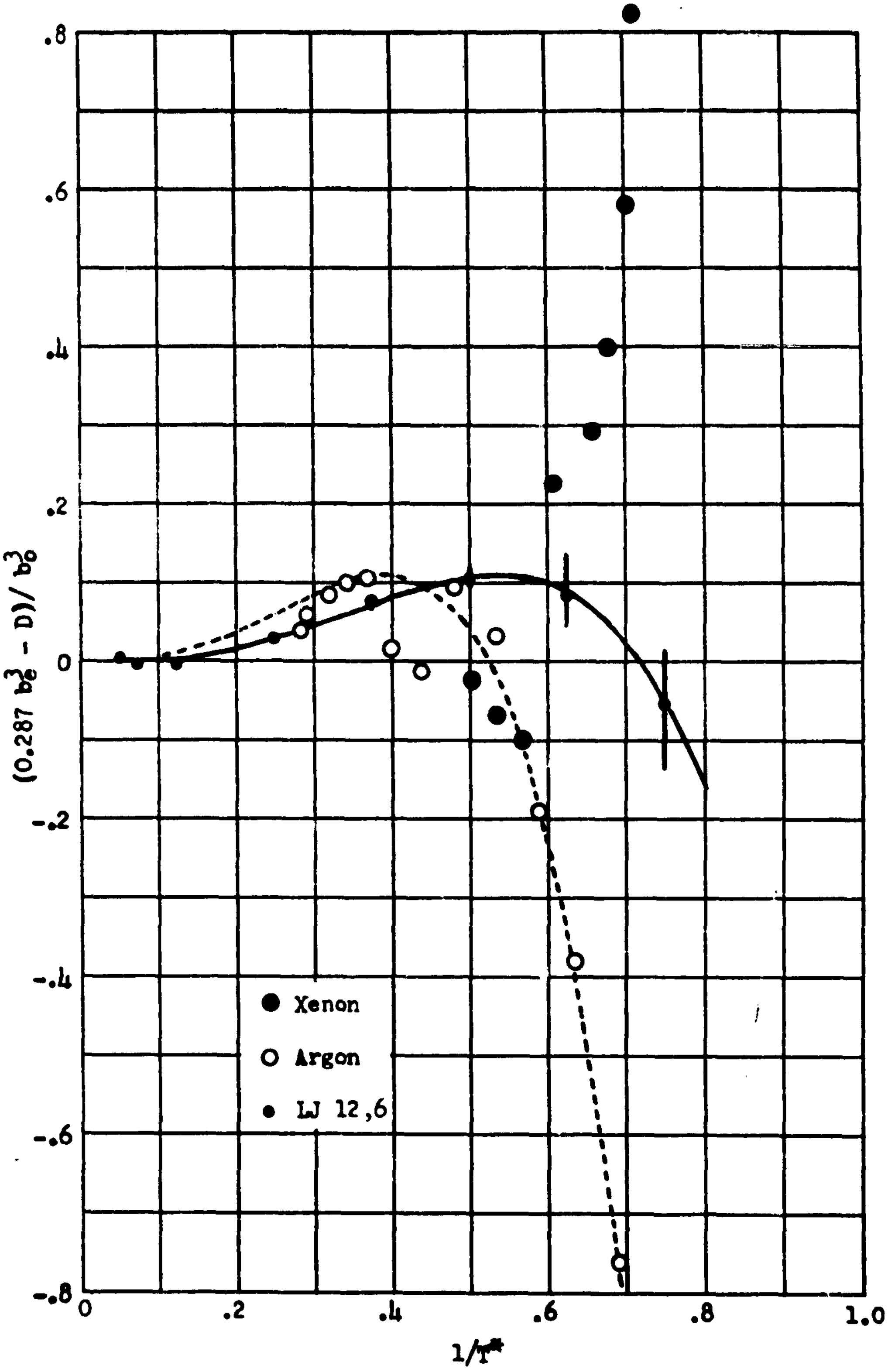

Fig. 6 - Fourth virial difference from effective rigid sphere gas.

where appreciable. Experimental indications as to this difference quantity are also shown, based on observational data as reported by Michels for argon [13] and xenon [14]. The data were reduced to dimensionless form using accepted values of Lennard-Jones parameters. The failure of the experimental fourth virials to agree closely with calculated values is naturally not surprising in view of the well known similar failure in the case of the third virial coefficient. Of particular interest is the closeness with which the difference appears to approach zero even for values of $1/T^*$ that are only moderately small. The solid curve in Fig. 6, approximating the calculated values of Boys and Shavitt, is given by

$$(0.287b_e^3 - D)/b_o^3 = 2.8T^{*-3} - 3.9T^{*-4}.$$

It seems uncertain whether the function should be slightly positive rather than negative near $T^* = 10$. The sign of the deviation in this region could be affected by a 5 per cent change of the virial coefficient itself. In view of the large uncertainty in experimental fourth virials, this uncertainty may be quite tolerable for the theoretical prediction. A dashed curve is also shown for the trend of some of the values reported for argon. It is represented by $(0.287b_e^3 - D)/b_o^3 = 7.2T^{*-3} - 13.8T^{*-4}$. In Fig. 7 are shown the similar fifth virial differences based on the reported virials of Michels for argon and xenon. The dashed curve is represented by

$$(0.111b_e^4 - E)/b_o^4 = 7.5T^{*-5}.$$

No theoretical values are available for comparison.

GAS MIXTURES

Problems in extrapolations to high temperatures arise because of the many new constituents that are added by chemical decomposition of the gas at the high temperature. With a large number of constituents, the full number of interaction virials theoretically present becomes enormous, particularly when higher order virials are taken into consideration. The virial equation of state for one mole of a gas mixture of s constituents may be indicated in beginning form in terms of mole fractions, x_i, as

$$PV/RT = 1 + \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} x_\alpha x_\beta B_{\alpha\beta}/V + \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} \sum_{\gamma=1}^{s} x_\alpha x_\beta x_\gamma C_{\alpha\beta\gamma}/V^2 + \dots \quad . \qquad (20)$$

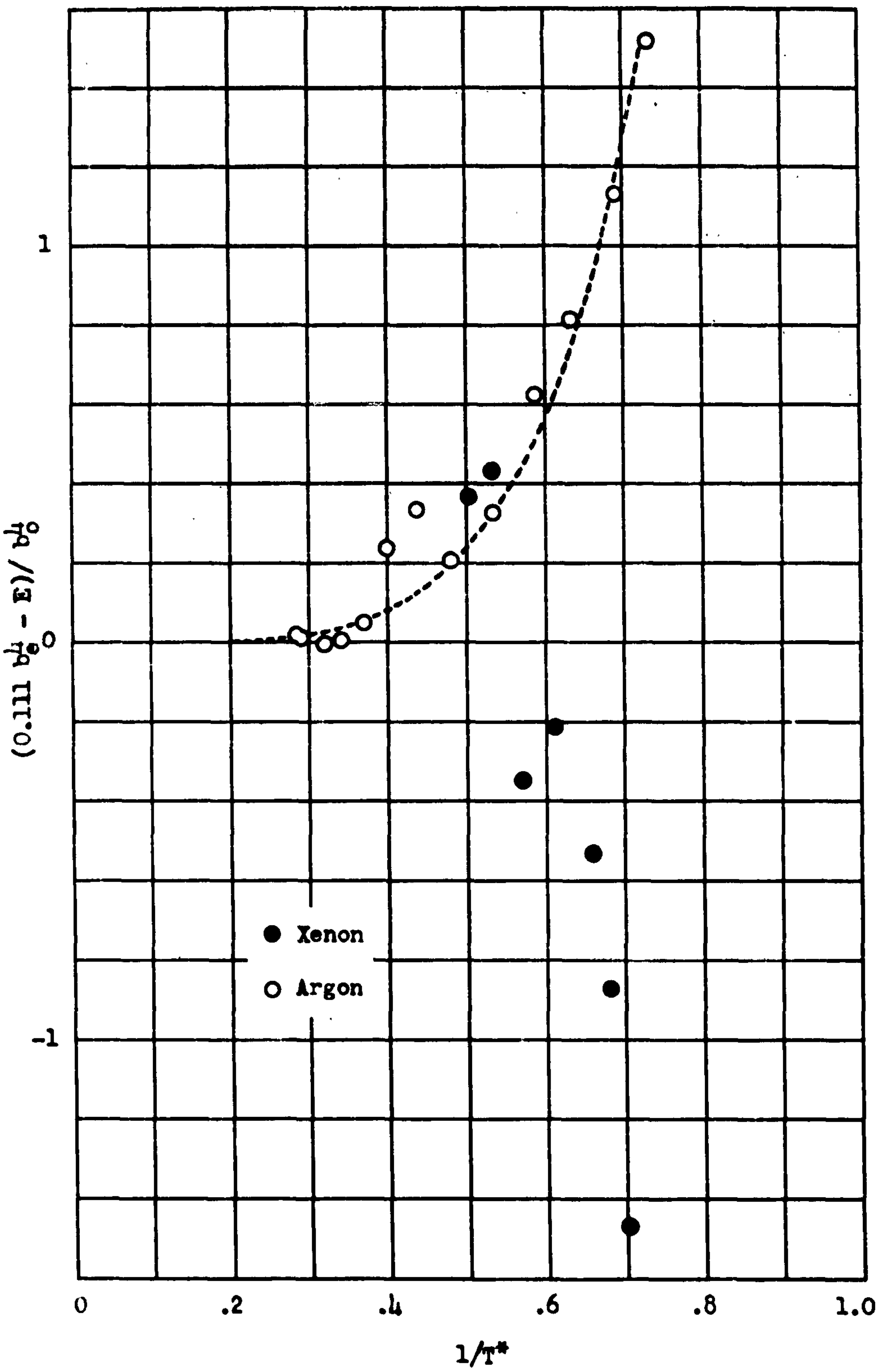

Fig. 7 – Fifth virial difference from effective rigid sphere gas.

or completely by

$$PV/RT = 1 + \sum_{n=2}^{\infty} n! \sum_{(i)} \left(\prod_{\alpha=1}^{s} \frac{x_\alpha^{n_\alpha}}{n_\alpha!} \right) B_{n(i)} V^{1-n} \tag{21}$$

where the interior summation is over all combinations with $\sum n_\alpha = n$ and the quantity $B_{n(i)}$ is the interaction n^{th} virial for the particular set of molecules enumerated by the indices α of the multiplier. The number of these interaction virials is evidently the same as the number of cross terms in the corresponding multinomial expansion, since in fact the multipliers of the virials are precisely identical with these. This has suggested the use of a very simple mixture rule for those higher order virial coefficients that have become positive in the high temperature domain. For these, it is proposed that the general term in the series for PV/RT be taken as

$$B_n V^{1-n} = [\sum x_\alpha (B_{n,\alpha})^{1/n}]^n V^{1-n}.$$

It is not proposed that this rule be used for second virials, for which well established combination rules exist for the estimation of molecular-pair parameters.

For virials that are of much higher order, it seems certain that verification would not be readily feasible either from theory or from the study of presently available experimental virials. In the single case of third virials, in 1943 I made some interaction virial calculations that appear relevant to this question. The results were regarded as failing to accomplish their intended purpose of predicting hydrogen-nitrogen interaction third virials accurately, but this failure can be adequately explained by the following: no quantum corrections were introduced, a large tabular interval of 0.2 in r/σ was used, the experimental third virials with which they were compared are difficult to infer from experimental data, and it seems uncertain that the Lennard-Jones 12, 6 average-force potentials are applicable. The portion of the results that pertained to pure substance resembled the later more accurate results of Bird, Spotz, and Hirschfelder [8] in that they indicated a different high temperature trend than had been given graphically by Montroll and Mayer [15]. In spite of the appreciable inaccuracy in my results, it seems likely that relative magnitudes are significant for questions of practical mixture rules.

The computational problem was to evaluate

$$C/b_o^2 = -6\int_0^\infty f_1\rho_1 d\rho_1 \int_0^\infty f_2\rho_2 d\rho_2 \int_{|\rho_2-\rho_1|}^{\rho_2+\rho_1} f_3\rho_3 d\rho_3 \qquad (22)$$

in which

$$f_i = \exp\left\{ -\frac{4\varepsilon_i}{kT}\left[\rho_i^{-12} - \rho_i^{-6}\right]\right\} - 1$$

with ρ_i representing r_i/σ_i where σ_i is a parameter selected to be consistent with the appropriate $(b_o)_i = (2\pi/3)N\sigma_i^3$. In the evaluation, the integral of $f_3\rho_3$ with respect to ρ_3 from 0 to $|\rho|$ was calculated tabularly at close intervals and tabulated at 0.2 intervals for negative as well as positive values of ρ. Values of $f_2\rho_2$ (here taken the same as the function $f_3\rho_3$ since only a binary mixture was being considered) were tabulated on a separate computation sheet for the same positive ρ_2 arguments as had been used for ρ_3. Then this second computation sheet was placed adjacent to the $\int_0^{|\rho|} f_3\rho_3 d\rho_3$ table at such a level that the $\rho_2 = 0$ entry in a first placement was adjacent to a forthcoming value for ρ_1 and, in a second placement was adjacent to the negative of the same forthcoming value for ρ_1. For each placement the product of the adjacent functions was formed and numerically integrated from $\rho_2 = 0$ to a region of negligible further contribution at large ρ_2. The difference between the two integrals gave

$$y(\rho_1) = \int_0^\infty f_2\rho_2 d\rho_2 \int_{|\rho_2-\rho_1|}^{\rho_2+\rho_1} f_3\rho_3 d\rho_3.$$

Products of $y(\rho_1)$ with $f_1\rho_1$ were then formed and numerically integrated taking $f_1\rho_1$ either identical with $f_3\rho_3$ and $f_2\rho_2$ to treat three like molecules or suitably modified but for the same r values to pertain to the interaction between two like molecules when $f_3\rho_3$ and $f_2\rho_2$ pertain to the two identical interaction functions between the unlike molecule and either of the two like molecules.

The force constants used for H_2 and N_2 were based on numbers reported by Lennard-Jones [16] in 1931. For the N_2-H_2 interaction the usual pair mixture rule gave 46 cm^3/mole for b_o and 54.3°K for ε/k, but the latter was changed to 56°K in improving the fit of the rather irregular experimental results for the interaction second virial. The evaluations were made with kT/ϵ for the two like interactions at 1, 1.5, 2, 2.5, 3, 4, 6, and 10. This gave so-called interaction third virials from 56 to 560°K and so-called hydrogen and nitrogen third virials from 30.8°K to 308°K and 96°K to 960°K, respectively.

The calculated results are shown in Fig. 8. No experimental points are shown. The dashed lines indicate the predictions of the proposed mixture rule

$$C_{ijk} = C_{iii}^{1/3} C_{jjj}^{1/3} C_{kkk}^{1/3} . \tag{23}$$

The dotted lines show predictions of a more complicated rule* recently recommended by Amdur and Mason [17]. Though their rule may be more reliable in general, we wish to make the following points in favor of the rule here proposed. In the region of comparison in the present instance it appears to predict about as reliably as the other rule; it is a much simpler rule; and it is easily extended to all higher order mixture virials in the high temperature region; and finally, it gives the dependence of complete higher virials on mole fraction composition in such a simplified form as to even eliminate completely the need for explicit evaluation of the interaction virials themselves.

$$^*C_{ijk} = \frac{1}{15}\Big[\sigma_{ij}^6 + \sigma_{ik}^6 + \sigma_{jk}^6 + 18\sigma_{ij}^2\sigma_{ik}^2\sigma_{jk}^2 + 16(\sigma_{ij}^3\sigma_{ik}^3 + \sigma_{ij}^3\sigma_{jk}^3 + \sigma_{ik}^3\sigma_{jk}^3)$$

$$- 9\sigma_{ij}^4(\sigma_{ik}^2 + \sigma_{jk}^2) - 9\sigma_{ik}^4(\sigma_{ij}^2 + \sigma_{jk}^2) - 9\sigma_{jk}^4(\sigma_{ij}^2 + \sigma_{ik}^2)\Big]$$

where $\sigma_{ij} = \frac{1}{2}(C_{iii}^{1/6} + C_{jjj}^{1/6})$, $\sigma_{ik} = \frac{1}{2}(C_{iii}^{1/6} + C_{kkk}^{1/6})$

and $\sigma_{kj} = \frac{1}{2}(C_{kkk}^{1/6} + C_{jjj}^{1/6})$.

For a binary mixture the 13 terms reduce to 3.

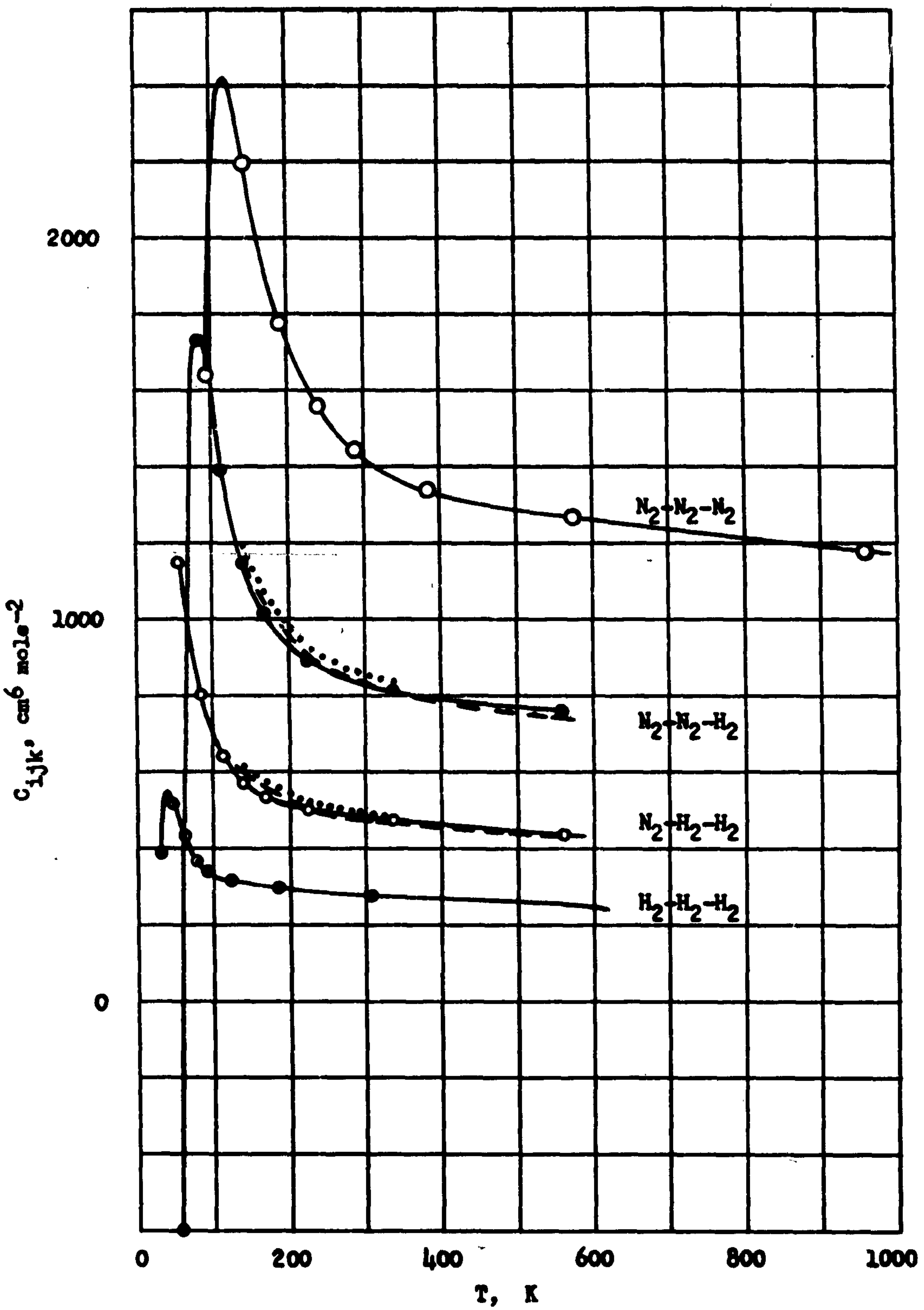

Fig. 8 – Classical LJ 12,6 third virials using early N_2 and H_2 force constants. Dotted curves by rule of Amdur and Mason. Dashed curves by rule of present paper.

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The calculation of thermodynamic properties of gases at high temperature using ion solution theory is analyzed in regard to various details. Earlier work based on rigid sphere ions is enlarged on briefly. An extension to a more general case of realistic pair interactions is also obtained. With Debye screened ionic interactions, a study is made of effects of repulsions and of both continuum and bound states for ionic attractions; simple approximate representations

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