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A CONTRIBUTION TO THE UNDERSTANDING OF THE EQUATION OF STATE OF GASES AT HIGH TEMPERATURE AND DENSITIES

Max Klein
National Bureau of Standards

March 1967

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ARNOLD ENGINEERING DEVELOPMENT CENTER
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NOTICES

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FOREWORD

The research reported herein was sponsored by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 61445014, Task Number 895102, Project Number 8951. The work was done by the National Bureau of Standards, Washington, D. C., under Delivery Order No. (40-600)65-22, and the manuscript was submitted for publication on March 21, 1967.

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This technical report has been reviewed and is approved.

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ABSTRACT

Intermolecular potential functions and certain means by which they can be obtained from experiment have been studied as the first step in the evaluation and development of a high density equation of state. The second virial coefficient has been found to be a poor method for reduced temperatures (on the (12,6) scale) greater than 2.0 while transport coefficients were found to be poor in the range $1.5 < T^* \ (12,6) < 5.0$.

Experimental second virial coefficient data have been fitted to 40 intermolecular potential functions for each of 15 substances. That such data taken in the range $T^* \ (12,6) > 2.0$ cannot serve as a means for determining the potential function is clearly demonstrated. Also indicated is the result that such data in the range $T^* \ (12,6) < 2.0$ cannot be used for determining more than three potential parameters.

The Percus-Yevick theory has been investigated and appears to be as applicable to air as it is to argon. The theory has been found to be sensitive to the choice of the intermolecular potential function.

The effect improving the potential functions has on the NBS tables of equilibrium properties of gases at high temperatures has been investigated and found to be generally small although changes of approximately 2% were obtained at the highest densities.

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I. INTRODUCTION

The main purpose of the work under this contract has been a theoretical investigation of certain high density statistical mechanical theories with an aim to their application to systems of aerodynamic interest. These theories assume prior knowledge of the pair potential function. It was necessary, therefore, to start this work with an investigation of the ways in which one obtains a knowledge of this function for any given system. This investigation of potential functions, originally envisioned as a small part of this contract, had to be expanded considerably as new paths of investigation developed. The study of the pair potential function, in fact, became a major part of the work carried out under this contract. This has resulted in an increased understanding of intermolecular potential functions and of the means available for their determination. This understanding has a usefulness far beyond the needs of this contract since the calculation of all thermodynamic and transport properties of fluids on the basis of fundamental statistical mechanical theory always depends on prior knowledge of the intermolecular pair potential function. In fact, the results of such calculations can be modified drastically when changes are made in the potential functions used.

We have attempted in this work to pursue several avenues of research simultaneously. Considerable emphasis has been placed on theoretical studies of the usefulness of certain thermodynamic properties as probes of potential functions. A study of the second virial, Joule-Thomson, viscosity and diffusion coefficients and their first derivatives was completed and has already appeared as a formal publication[1] (included as an appendix). That work has been extended considerably to include the study of the sensitivity of the simultaneous fit of equilibrium and transport data to the potential function. The simultaneous fit of the viscosity and second virial coefficient has been studied in some detail. The following are other property pairs for which we have less detailed results at this time:

a. the second virial and diffusion coefficients
b. the Joule-Thomson and diffusion coefficients
c. The joule-Thomson and viscosity coefficients
d. the viscosity and diffusion coefficients

For years, the literature has been filled with conjectures on the subject of the sensitivity of the simultaneous fit of equilibrium and transport properties to the potential function. All such work has been based on results of fits to experimental data. As a result, all necessarily suffer from a lack of clarity due to the effects of experimental uncertainties, and what is more important, inconsistencies between the two kinds of experiments. This has, in fact, resulted in total disagreement among a number of workers. Some have felt this to be a sensitive probe of the potential while others have taken the opposite view. Our approach, as before, has been to deal with this question on a strictly theoretical basis. We determine what is, in principle, the sensitivity to the potential function of this simultaneous fit to these two kinds of data. The results are presented in accompanying graphs and will be discussed below. These results, being entirely independent of experimental precision, will continue to hold as experimental techniques are refined and precision improved. Our results can be used for fundamental predictions in that we can make definite statements on the temperatures at which the properties are very insensitive to the potential. It follows, then, that at such temperatures, more refined experimental techniques cannot yield further knowledge of the potential function.

Another part of our research effort has been applied to the study of actual fits of experimental second virial coefficient data to a large number of potential functions. These are specific illustrations of the application of our theoretical results to real data. In addition, some very interesting new insights into the entire problem of potential functions resulted from these fits. These will be discussed below. In the particular case of the constituents of air, these fits have an additional purpose in that they also serve to define the best potential functions for use both in the high temperature tables and in the correlation of data in the experimental range. These latter functions were also used, as described below, in an assessment of certain high density theories and in a determination of the sensitivity of an equilibrium calculation to the potential function. The results of all of the fits are presented in the accompanying tables and graphs.

We have also done a study of the applicability of the Percus-Yevick theory[2] to gases made up of non-spherical molecules. There appear to be three main reasons why such a theory might be less applicable to non-spherical systems. First, the present form of the Percus-Yevick theory requires the use of a spherically symmetric potential function. It is possible that this may not be a serious problem since one expects an averaging of the actual potential over all interparticle orientations to be a reasonable procedure. In other words, one expects there to be an effective spherical potential to associate with the molecules for use in the theory. A second reason is that the theory is based on an assumption of pair-wise potential additivity. Deviations from additivity might be larger for the non-spherical molecules. Again, there might be an effective spherical potential which averages this effect for the purposes of the theory. The third reason is more basic, and while important for both spherical and non-spherical molecules, might conceivably be of a different magnitude for one kind of molecule as compared to the other kind. This objection is that the theory, though based on a summation of a certain infinity of terms in the full density series, neglects another infinity of terms. The effect of this neglect, and hence the success or failure of the application of such a theory to particular systems (e.g., air) can be judged only by the results of comparisons with experiment. Since such theories depend on prior knowledge of the potential function, we have first sought an understanding of how such functions can be obtained. This accounts for the strong emphasis placed by us on the potential function aspect of this contract.

Despite all of these possible objections, theories such as the Percus-Yevick are far superior to any other means available for the extrapolation required at the temperatures of interest in aerodynamic application at moderate to high densities. Work on such theories is complicated by the problems involved in the solution of the appropriate non-linear integral equations by numerical means. This has the result of reducing the rate of progress significantly.

As indicated above, the ultimate purpose of the investigation of potential functions is to provide the best possible input data for aerodynamic calculations and to attempt to provide a sound theoretical understanding of both these data and the methods used to obtain them. In the interest of maintaining the connection between our work and the NBS effort in calculating tables of the properties of air and its constituents, we have investigated the effect on the equilibrium properties of nitrogen of changing the N_2-N_2 intermolecular potential function. Our results are discussed below.

II. PRELIMINARY RESULTS FROM THE STUDY OF THE SENSITIVITY OF THE SIMULTANEOUS FIT OF THE SECOND VIRIAL COEFFICIENT AND VISCOSITY DATA TO DIFFERENCES IN THE INTERMOLECULAR POTENTIAL FUNCTION +

In our previous work[1], we have shown that equating the value of certain thermodynamic properties for a given potential function to their values for a second potential results, for each property, in a single equation in two unknowns. The unknowns are the ratios of the potential parameters ε/k and σ which guarantee equality of the property for the two potentials. Given a similar equation for a second function of each property, one would have a pair of equations in the two unknowns, the solution of which would lead to their complete determination. Previously, we took for this second function of the thermodynamic property its derivative with respect to the temperature. Thus, for example, we equated the second virial coefficient and its first derivative for a pair of potentials. For reasons previously outlined[1], we always took the (12,6) function as one of the two potential functions and used it as a reference potential. We solved the pair of equations in the parameter ratios as a function of the (12,6) reduced temperature. The results obtained have been discussed in considerable detail in the published work[1]. In that work we formed pairs of equations by equating, for the two potentials, the following pairs of functions:

1. the second virial coefficient plus its first derivative
2. the Joule-Thomson coefficient and its first derivative
3. the viscosity and its first derivative
4. the diffusion coefficient and its first derivative

Instead of basing the calculation on the equality of a property and its first derivative, one can base it on the equality of two properties. We have done this recently for the following pairs of properties:

1. the second virial coefficient and the viscosity
2. the second virial and diffusion coefficients
3. the Joule-Thomson coefficient and the viscosity
4. the Joule-Thomson and diffusion coefficients
5. the viscosity and the diffusion coefficient

In this section of this report we discuss some preliminary results obtained from the simultaneous equality of the second virial coefficient and the viscosity. Results which have been obtained for the other pairs in the above list have not been studied sufficiently for reporting at this time.

If $B(T)$ represents the experimental second virial coefficient at the temperature T and if $B^*(T^*)$ represents the reduced second virial coefficient for some potential function $\phi(R)$, then

$$B(T) = b_o B^*(T^*)$$

where $T^* = T / \varepsilon/k$ and $b_o = \frac{2\pi}{3}N\sigma^3$, ε/k and σ being the potential

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\+ In collaboration with Dr. H. Hanley of the Boulder Laboratories of NBS parameters and N Avogadro's number. If, in the spirit of our earlier work, we equate the second virial coefficient for two potential functions then

$$(b_o)_1 B_1^* (T_1^*) = (b_o)_2 B_2^* (T_2^*)$$

or
$$B_1^* (T_1^*) = \left(\frac{\sigma_2}{\sigma_1}\right)^3 B_2^* \left(T_1^* \frac{\epsilon_1}{\epsilon_2}\right) \tag{1}$$

This represents a single equation for the two unknowns ϵ_2/ϵ_1 and σ_2/σ_1.

If, now, $\eta(T)$ represents the experimental viscosity, then

$$\eta(T) = \frac{A}{\sigma^2 \Omega^{(2,2)*}(T^*)}$$

where A is a quantity which will not concern us, σ is a potential parameter, and $\Omega^{(2,2)*}$ (T^*) are the collision integrals associated with the viscosity for a particular potential function $\phi(R)$. If, now, we equate the viscosity for two potential functions, then

$$\sigma_1^2 \Omega_1^{(2,2)*}(T_1^*) = \sigma_2^2 \Omega_2^{(2,2)*}(T_2^*)$$

or
$$\Omega_1{}^{(2,2)*}(T_1^*) = \left(\frac{\sigma_2}{\sigma_1}\right)^2 \Omega_2{}^{(2,2)*}(T_1^* \epsilon_1/\epsilon_2) \tag{2}$$

again a single equation in the same pair of ratios ϵ_2/ϵ_1 and σ_2/σ_1.

Requiring that the second virial coefficients and viscosities be equal simultaneously is equivalent to requiring equations (1) and (2) to be satisfied simultaneously. Elimination of the ratio σ_2/σ_1 between the two equations results in the single equation

$$\frac{B_1^*(T_1^*)}{\left[\Omega_1{}^{(2,2)*}(T_1^*)\right]^{3/2}} = \frac{B_2^*(T_1^*\epsilon_1/\epsilon_2)}{\left[\Omega_2{}^{(2,2)*}(T_1^*\epsilon_1/\epsilon_2)\right]^{3/2}} \tag{3}$$

Note that for each potential function, one needs to compute the quantity

$$Q^*(T^*) = \frac{B^*(T^*)}{\left[\Omega^{(2,2)*}(T^*)\right]^{3/2}}$$

Given two tables of this quantity, one for each of two potential functions, one can solve (3) in the manner described by us, in the appendix, for the solution of equation (3) there.

The quantity $Q^*(T^*)$ is shown in Figure 1 for several potential functions. For each potential, this quantity changes sign at the Boyle temperature. One has, therefore, to exercise the same caution as was previously required (see appendix). As before, this sign change creates no problem.

Results obtained for the solution of (3) for the (12,6) potential and each of the exp-6 functions appear in Figures 2a and 3. Results for the Kihara potential appear in Figure 2b. These figures also contain the results for the properties B, $T\frac{dB}{dT}$ as reported earlier[1] (see Figures 6 and 7 of appendix). These results illustrate very clearly the difficulty involved in determining the proper potential functions to use in aerodynamic calculations. According to Figure 2a, one can barely distinguish between the (12,6) potential and any of the exp-6 functions studied if the data is entirely in the range $1.5 \le T^*_{12,6} \le 10.0$. Distinctions can certainly not be made if the range of temperatures is further restricted to $1.5 \le T^*_{12,6} \le 5.0$. This is even true for the simultaneous fit to the properties B, η, $T\frac{dB}{dT}$. Almost all experimental data lies within the second (narrower) range. For nitrogen, for example, these temperature ranges correspond to $150°K \le T \le 1000°K$ and $150°K \le T \le 500°K$. Clearly, one can have considerable difficulty in choosing between potential functions based on available experimental data.

Figure 2 can be considered to illustrate the information available. Figure 3, on the other hand, illustrates the information needed. This covers the much more extensive range $0 \le T^*_{12,6} \le 50$, the upper limit now corresponding to 5000°K for nitrogen, not a high temperature for aerodynamic applications. According to the curves of Figure 3, it is exceedingly easy to distinguish between the potential functions at the higher temperatures. What this means is that calculations based on the use of each of these potentials will yield quite different results at such temperatures. Clearly, the intermolecular potential functions associated with a given substance must be very carefully chosen if the application is to a calculation at aerodynamic temperatures.

We have already shown[1] that the simultaneous fit of the viscosity and its first derivative can be a sensitive probe of the potential function. In particular, it appeared that the fit of such data simultaneously below $T^* = 1.5$ and above $T^* = 5.0$ might serve to define the potential function. It was felt at the time that this sensitivity might have been due to the requirement on the simultaneous equality of both the viscosity and its first derivative. The results presented here are entirely compatible with the results of the appendix and show that the sensitivity is inherent in the viscosity itself. According to Figures 2 and 3, a potential function with more than three parameters appears to be needed. With such a potential function, one might be able to find parameters which fit the data simultaneously at $T^* < 1.5$ and $T^* > 5.0$. This question is of the utmost importance and is the subject of continuing research.

It is possible, however, that this requirement is more stringent than necessary for aerodynamic applications. Thus, it is clear from Figures 2 and 3 that the value $\alpha \cong 15.5$ will simultaneously reproduce the second virial and viscosity data for the (12,6) function over the whole temperature range $1.5 \le T^*_{12,6} \le 50$ and possibly to still higher temperatures. The fact that the lower temperature data (i.e., $T^*_{12,6} < 1.5$) is not reproduced may not be of any consequence in such applications. Before drawing any conclusions along these lines, one needs to do these calculations for other families of functions of which the (12,6) is not a member. If this conclusion is supported, then, clearly, the fit of viscosity data at temperatures $T^*_{12,6} > 5.0$ would be enough to determine the potential functions needed in aerodynamic calculations. Any conclusions of this kind would need to be followed by actual fits to such data as exist. Where data do not exist, one could point to the need for further experimental work.

In summary and to illustrate our results, suppose that the system of aerodynamic interest were such that its intermolecular potential function were the (12,6) function and that there were available to us only the exp-6 family of functions. This is analogous to the actual situation since the "actual" potential of a given substance is unknown to us but there are available only a limited number of reasonable functions to try. At ordinary temperatures, any one of the exp-6 functions might properly describe the properties of the hypothetical system of interest. At high temperatures, however, these properties would be only poorly described unless one happened to use the potential corresponding to $\alpha = 15.5$. There is clearly not enough information available at the lower temperatures on which to base the choice $\alpha = 15.5$. This difficulty is compounded further if one includes the fact that at low temperatures one needs to use the value $\alpha = 13.5$ for describing the properties involved.

One aspect of the problem has yet to be investigated. That is, the effect of basing the comparisons on spherically symmetric potentials when many of the actual potentials of interest are not spherically symmetric. An initial investigation of this will involve the fitting of actual data to potentials in a manner to be determined after further study.

III. THE DETERMINATION OF POTENTIAL FUNCTIONS FROM THE FIT OF EXPERIMENTAL SECOND VIRIAL COEFFICIENT DATA

We have fitted experimental second virial coefficient data to those calculated for various potential functions both in order to illustrate how some of our earlier results[1] apply to actual experimental data and to determine potential functions and their parameters for our study of high density theories. We present here results for fifteen substances, chosen in order to cover a variety of molecular shapes. The data for each substance was fitted to over 40 different potential functions. Such a formidable task clearly called for an automatic procedure; hence a computer program was developed. The numerical procedure adopted will be outlined but will not be discussed in detail.

The potential functions can be written in reduced form by dividing lengths by a characteristic length and energies by a characteristic energy[3]. This enables one to calculate the second virial coefficient also in reduced form. This, in turn, leads to a universal second virial coefficient table for each potential. The theoretical second virial coefficient for any given substance and a particular potential function is obtained by inserting into such a table the characteristic length and energy appropriate to that substance for that potential function. In this way one can calculate a set of theoretical second virial coefficients to match a given set of experimental data. Thus, for each experimental point, one will have a corresponding theoretical point and a deviation, Δ, of theory from experiment. Because of experimental error and since one does not know the precise potential function to use, it is always impossible to match exactly a set of experimental data with $\Delta = 0$ for each point. Clearly, at each experimental point, the magnitude of Δ is a measure of the goodness of fit to that point. It is general practice to use a quantity such as

$$\bar{\Delta} = \frac{1}{n}\left[\Sigma\Delta_i^2\right]^{1/2}$$

where the summation is over all of the experimental points, as a measure of the overall goodness of fit.

Now, for a given potential and a given set of experimental data, $\bar{\Delta}$ will depend on the choice of the parameters used (i.e., the characteristic length and energy). $\bar{\Delta}$ will be least, by definition, for the best values for this pair of parameters. We have found such a best pair of values for over 40 potentials for each of fifteen substances. Our method was based on the following:

If the characteristic length is designated σ and the characteristic energy ϵ/k, then $\bar{\Delta} = \bar{\Delta}\ (\epsilon/k, \sigma)$ described a surface in a space for which ϵ/k and σ are (e.g.) the X and Y axes and $\bar{\Delta}$ the Z axis. A given set of experimental data will have a $\bar{\Delta}$ surface associated with each potential function which one chooses to use. The best fit to the data for any potential function will be obtained with that pair of parameters $\epsilon/k, \sigma$

which are the coordinates of the minimum of the $\overline{\Delta}$ surface. It is this pair of parameters which we seek. Our computer program was designed to perform a surface minimization of $\overline{\Delta}$ with respect to $\epsilon/k,\sigma$. The details of the method will not be described. The results obtained with the computer program appear in Table 1.

As mentioned earlier, we shall first use these fits to illustrate the meaning of our earlier theoretical results.[1] According to our theoretical results, the second virial coefficient is very insensitive to the potential function for reduced temperatures above $T^*_{(12,6)} = 2.0$. Furthermore, we see that, although the second virial coefficient can be expected to be a sensitive probe of the potential at higher temperatures, this sensitivity certainly does not manifest itself below $T^*_{(12,6)} = 10.0$. On the other hand, we have shown that below $T^*_{(12,6)} = 2.0$, the second virial can be sensitive to differences in the potential function. Now, for argon, the characteristic energy in temperature units is, for the (12,6) function, $\epsilon/k = 120°K$. Thus, we see that for $240°K \le T \le 1200°K$, the second virial coefficient cannot be used as a probe of the potential function while for $T^* < 240°K$, it is at least potentially sensitive (subject to the size of the experimental errors).

We shall use the fits of three sets of experimental data for argon as illustrations. These are the 1958 data of Michels et al which cover the range $133.15°K \le T \le 273.15°K$, the 1949 data of Michels et al which cover $273.15°K \le T \le 423.15°K$, and the 1953 data of Whalley et al in the range $273.15°K \le T \le 873.15°K$. In terms of reduced units, these cover the ranges $1.11 \le T^*_{12,6} \le 2.28$, $2.28 \le T^*_{12,6} \le 3.53$, and $2.28 \le T^*_{12,6} \le 7.29$. Thus, the first of these is in a range for which the second virial coefficient is potentially sensitive while the others lie entirely in an insensitive temperature range.

Table 2 serves as the basis for our discussion. The differences in the sensitivity of each set of data are read across Table 2 for each potential. It is clear that the lowest temperature data is more sensitive than the high temperature data. The variations within each column have to do with the extent to which the potential has been varied. This will be discussed from another point of view below.

Our point here with respect to the differences in sensitivity below and above $T^*_{(12,6)} = 2.0$ is more strongly illustrated in Tables 1a-1c by the absence of a clear minimum for the higher temperature data. In other words, the moderately large values of the ratios in the second column of Table 2 are not taken as ratios to a value of $\overline{\Delta}$ at a meaningful minimum but to a value which happens to be smallest. For the (m,6) data in the second column, the indications are that a minimum, if any, will appear at a value of m close to the physically meaningless value $m = 6$ (for which the potential vanishes).

Clearly, it is absolutely impossible to assign a potential function and its parameters to argon based entirely on the high temperature data. Unfortunately, even to this day, the (12,6) function and its parameters, as obtained from the high temperature data reported by Michels et al prior to 1958, are taken to give a correct representation of the intermolecular potential function for argon. Such a representation suffers horribly on two accounts. First of all, the data is entirely in the temperature range for which one cannot distinguish among the functions. Secondly, an analysis of the low temperature data, where distinctions can be made, shows the (12,6) to be incorrect.

A more subtle conclusion of our theoretical work was that, given a potential function, together with a family of functions of which the given function is not a member, one can find a member of this family which would reproduce the second virial coefficient for the given function over a range of temperature which starts from very low temperatures and goes to very high temperatures. We specifically showed this to be true for the (12,6) potential as the given function. This conclusion would seem to say that the second virial coefficient is a three-parameter object as far as the potential function is concerned.

In order to examine this aspect of our conclusion more closely, we have plotted the ϵ/k and b_0 values obtained for each potential function for a representative number of substances. These are presented in Figure 4 for the various substances. It seems clear that, in almost every case, if one were able to remove experimental error, the data for all potentials, with the exception of the physically unreasonable square well, would fall on one curve. Furthermore, the point which represents the (12,6) function corresponds, in families of potentials for which the (12,6) is not a member, to that function which was found in our earlier work to reproduce the second virial coefficient of the (12,6) over a large temperature range. In order to make certain that we are talking about the same fits, we have also plotted ϵ/k versus $\bar{\Delta}$ for the various potentials. These are presented in Figures 5a et seq. for the same substances. Here again, all points, except for those for the square well, tend to lie on one curve. This is particularly true in the vicinity of the minimum value of $\bar{\Delta}$ which, after all, is the most physically meaningful part of these curves. Such differences as there are, appear to be, in almost every case, smaller than the uncertainties which one might assign on reasonably based estimates of experimental precision. It would thus appear that by fitting experimental second virial coefficient data to theoretical values for any "reasonable" three-parameter family of potentials one obtains the same information about the potential function of the experimental system. A corollary of this is that the same best fit will be found within every such family, and in fact, for the same parameters.

CO_2 appears to be an exception to this, although one cannot be certain since the minima in the $\bar{\Delta}$ versus ϵ/k curves have not been reached. A reasonable extrapolation of the curves leads to relatively large differences among some of the curves at the place where the minimum is indicated, however. It should be noted that even for CO_2 the curves for the exp-6 and (m,6) families essentially coincide, it being only the Kihara and (12,n) families which produce separated curves. Now these latter two families have in common the same repulsive exponent (m = 12). This may mean that a value m = 12 for the repulsive exponent is sufficiently unrealistic so that, in each case, the other parameter (γ for the Kihara, and n for the 12,n), is unable to compensate for it. On the other hand, it is possible that the separation of the curves is an indication of a need for a fourth parameter. This is not unreasonable for a highly non-spherical molecule like CO_2. In any event, further investigations are called for.

It should be noted again that the $\bar{\Delta}$ versus ϵ/k curves for the other substances for the (12,n) function differ only slightly from the equivalent curves associated with the other families. We mention again that this is particularly true at the minimum. This greatly restricts one's ability to determine the proper value of n and then to use the remaining deviations to determine an additional parameter (e.g., the repulsive exponent m). The $\bar{\Delta}$ versus ϵ/k curves for the different families are, in fact, so close together that we are inclined to think that it is not possible to determine the additional parameter m, after having determined n. This would reinforce the statement in our earlier work to the effect that the second virial coefficient was a three-parameter object (ϵ/k, σ and one other).

Nevertheless, the results for the (12,n) family of functions are still very interesting. There seems to be the vague indication of a relationship between the fit of the second virial coefficient data and the proper attractive exponent, n. Thus, the best fit for the rare gases is obtained for n = 7. This could indicate either the need for an attraction made up of the combination of an inverse 6th power and an inverse 8th power or it could indicate that n = 6 is the best choice, the difference in $\bar{\Delta}$ between n = 6 and n = 7 being statistically insignificant. The data for systems with more non-spherical molecules are generally best fit by still larger values of n. This one could ascribe to the need for higher moments, i.e., the addition of an inverse 10th power attraction.

Exceptions to this general behavior are seen for nitrogen (and hence air) and for ethane, the data for both of these being best fit by the virials for n = 7.

This general behavior is probably fortuitously associated with the use of the repulsive exponent m = 12. In our previously reported work[1], we found the second virial coefficient to be quite insensitive to the attractive exponent for $T^* > 2.0$. The sensitivity indicated below $T^* = 2.0$ could not be properly evaluated in that work since all comparisons were with respect to the (12,6) function which is a member of the (12,n) family. Further research is in progress to determine the sensitivity, if any, of the low temperature second virial coefficient data to the attractive exponent.

Mention has been made of the variations within a given column of Table 2 and its relation to the extent of variation of the potential function. This relationship can be seen in Figures 4. Thus, for example, the variation of γ for the Kihara potential between $\gamma = 0.1$ and 0.6 traces out the entire parabola. The variation of the parameter α from $\alpha = 16$ to $\alpha = 19$ for the exp-6 function, on the other hand, traces out a much smaller part of the parabola. The same is true for each of the other families of potentials, a different part of the common parabolas of Figure 4 being traced out in each case. Since the same parabola applies in each case, it follows that the minimum $\overline{\Delta}$ is the same for each family of functions. The maximum (and hence the value in each column) is different in each case, depending on how far up the common parabola a given family goes. Thus, $\alpha = 12$ represents a lower starting point than does $m = 9$; hence, the $(m,6)$ ratio is larger than is the exp-6.

IV. A STUDY OF THE APPLICABILITY OF THE PERCUS-YEVICK THEORY TO SYSTEMS OF DIATOMIC MOLECULES

We have solved the non-linear integral equation associated with the Percus-Yevick theory numerically for three potential functions along with equivalent isotherms in order to study the sensitivity of that theory to reasonable changes in the intermolecular potential function. The potential functions used were all of the Lennard-Jones (m,6) type. We have chosen the particular values $m = 12$, 18, and 24. The choice of the values $m = 18$ and 24 was dictated by our interest in a comparison with experimental data for argon and air. According to our fits of the second virial coefficient data, $m = 18$ is a proper choice for argon while $m = 24$ is a proper choice for air. The (12,6) function was also included since that function was used for almost all of the interactions in the NBS air and argon calculations[4,5,6].

Let us first consider the results for the (12,6) potential function. We have solved the Percus-Yevick integral equation for that potential function at a reduced temperature of $T^* = 2.74$. This can be taken as corresponding to $T = 328.15°K$ for argon (based on the old value of $\varepsilon/k = 119.8°K$) and to $T = 273.15°K$ for air. Our discussion will be based on Figure 6. There are seven equations of state in that diagram. Two of these are experimental, one for argon and one for air. Of the remaining five, three are associated with the first few terms of the virial series. Now, the ideal gas equation of state is just $\frac{PV}{RT} = 1$, hence that appears as a horizontal straight line for unit ordinate. The addition of the second virial coefficient, which is the first correction for non-ideality, converts the equation of state to $\frac{PV}{RT} = 1 + B\rho$, still a straight line but no longer horizontal. Now, for the (12,6) function, the Boyle temperature, i.e., that temperature which $B = 0$, is above $T^* = 2.74$, hence, for $T^* = 2.74$, $B < 0$. Therefore, except for very low densities ($\rho^* < .1$), including the second virial coefficient results in an equation of state which is far inferior to the ideal gas equation of state.

It might be worth mentioning that the early NBS air calculation[4] was an ideal gas one. The equation of state was not simply a straight line due to the change in the number of moles as a result of chemical reactions. In other words, the equation of state was $\frac{PV}{RT} = n$ where $n = n\ (T,\rho)$ is the total number of moles. In later calculations[5], we have included the second virial coefficients of the constituents. The limit of the validity of an approximation which includes only the second virial correction is seen in Figure 6 to be approximately $\log \rho/\rho_0 \leq 2.0$. For this reason, our tables have been cut off near $\log \rho/\rho = 2.0$.

Figure 6 can be misleading if one uses it literally for a description of the situation at the temperatures of our air claculation. Since the temperatures included in those reports are above the Boyle temperature, $B > 0$, the straight line equation of state $\frac{PV}{RT} = 1 + B\rho$ is everywhere greater than unity. Thus, at such high temperatures, the second virial equation of state represents an improvement over the ideal gas at <u>all</u> densities, although a small one at high densities.

The addition of the third virial coefficient results in the equation of state $\frac{PV}{RT} = 1 + B\rho + C\rho^2$ containing two density corrections. Such an equation of state has some curvature. According to Figure 6, this results in a considerable improvement over both the ideal and second virial equations of state. Deviations from experiment are still quite large, however. At our reduced temperature of $T^* = 2.74$, the range of validity of an approximation containing the third virial coefficient would be, roughly, $\rho^* \leq .3$ which, for argon, is near 220 times normal density $(\log \rho/\rho_0 = 2.3)$.

This demonstrates the extreme difficulty which one rapidly encounters in attempting to extend our calculations as presently performed beyond the density $\log \rho/\rho_0 = 2.0$. The third virial coefficient describes interactions involving three particles at a time. Thus, for example, undissociated air considered to consist of molecular nitrogen, molecular oxygen, and argon would require the specification of six interactions as a function of temperature. This would increase to <u>fifteen</u> on the dissociation of the molecules and would increase still further on ionization. On the expenditure of this extraordinary amount of effort, one would find that one could increase the range of the calculation from $\log \rho/\rho_0 = 2.0$ only to $\log \rho/\rho = 2.3$.

Experience with the known hard sphere virial coefficients indicates that the higher virial coefficients will have still narrower density ranges. That is, as one increases the density one will find that one needs the fifth virial coefficient much sooner (in terms of the density increment) after the fourth virial coefficient than one needed the fourth after introducing the third. This gets progressively worse as one increases the density.

A further complication is introduced by the progressively larger number of particles required in the calculation of the higher virial coefficients. This makes the calculation become considerably more difficult very rapidly as the order of the virial coefficient increases. This difficulty is demonstrated by the paucity of published results. Third virial coefficients have been calculated for only a very small number of functions, the fourth for only the (12,6) (aside from the unrealistic hard sphere and square well) and the fifth for only the hard sphere.

In short, the extension beyond $\log \rho/\rho_0 = 2.0$ of the approach used by us in the calculation of tables of thermodynamic properties of air, nitrogen, and argon is practically impossible. This serves to emphasize the importance of seeking approximations like that of the Percus-Yevick theory.

The remaining two equations of state of Figure 6 are associated with the Percus-Yevick theory. The fact that there are two equations of state results from an inconsistency between two representations of the pressure. This, in turn, comes from the neglect of diagrams mentioned earlier. This inconsistency appears only in terms beyond the third virial coefficient. It is our present view that the equation of state labeled Z_p should be used since the calculation of thermodynamics functions consistent with it appears to be relatively straightforward.

The agreement of the Percus-Yevick equations of state with experiment for argon is exceedingly good. Even at a reduced density $\rho^* = .65$ (approximately 450 times normal), the deviation of Z_p from the argon experimental value is only 5%. The situation for air is less satisfactory, however. In that case, the deviation at $\rho^* = .65$ is roughly 30%. This is less than half the discrepancy from the ideal gas (75%) but roughly equal to that for the equation of state containing the third virial coefficient. An obvious source for this increased deviation in the case of air might be the use of an unsuitable potential function. According to Table 1 the (12,6) is a poor choice of potential for almost all experimental systems. In particular, for argon one should use the (18,6) potential while for air the (24,6) potential is most appropriate. The better fit of the argon data as compared with the air data in Figure 6 could easily be attributable to the fact that the (18,6) potential is more nearly like the (12,6) than is the (24,6) function.

Clearly, the next step in our study was to obtain the solutions to the Percus-Yevick integral equation for both the (18,6) for argon and (24,6) for air. Our results for the (18,6) potential function are contained in Figure 7. The calculation was carried out for isotherm $T^*_{(18,6)} = 2.0467$ in reduced units. This temperature was selected as equivalent to $T^*_{(12,6)} = 2.74$ on the basis of the ratio ϵ_1/ϵ_2 corresponding to the simultaneous fit, for the two potentials[1] for the pair of properties B^* and $T^* \frac{dB^*}{dT^*}$. This is clearly in agreement with our fits (see Table 1) of the second virial coefficient data to the second virial associated with the (18,6) potential.

It is clear from Figure 7, that the change from the (12,6) potential to the more reasonable (18,6) results in a considerable deterioration of the agreement between theory and experiment for argon at the higher densities. On the other hand, the agreement between theory and experiment for air is considerably enhanced in going from the (12,6) function to the (18,6).

Carrying the air comparison one step further to the more reasonable (for air) (24,6) function again results in a worsening of the agreement between theory and experiment at high densities (see Figure 8). It should be noted that at low densities ($\rho^* \leq .1$), at which the second virial coefficient is the major contributor, essentially the same agreement is obtained for all of the functions. This is in keeping with the results of our earlier work[1] in which we showed the second virial coefficient to be very insensitive to the potential function for $T^*_{(12,6)} < 2.0$.

One might argue that it would be proper to use the (12,6) function for argon and the (18,6) function for air since these result in quite good fits even at high density. This might be a reasonable procedure if one were only interested in fitting the experimental data at temperatures in the neighborhood of the isotherms used. Clearly one cannot use those potentials at low temperatures since one would certainly not get a good fit at low densities (and possibly at high densities as well). What the choice of the (18,6) for air and (12,6) for argon would do for the relationship between the calculated properties and the "actual" properties at aerodynamic temperatures would be impossible to say at this time due to the lack of experimental data at such temperatures. In short, the assignment of these potentials based on the behavior along the isotherms examined here would reduce the statistical mechanical theory to a completely empirical one which could not be extrapolated. The importance of extrapolation to high temperatures forces us to choose a potential function based on fundamental considerations and to insert that function into the best available theory.

We have begun an examination of a more consistent Percus-Yevick theory starting with an examination of the theory for hard spheres. The results obtained are in too preliminary a form to be reported at this time. Progress in this area has been hampered by a lack of time resulting from the need for continued intensive effort in the examination of intermolecular potential functions.

V. THE EFFECT ON THE CALCULATED EQUILIBRIUM PROPERTIES OF NITROGEN OF CHANGING TO AN IMPROVED POTENTIAL FUNCTION

We have, in recent years, produced a number of sets of tables of equilibrium properties of high temperature gases. The most recent of these go beyond the ideal gas approximation to the extent of including the effect of the second virial coefficient. The second virial coefficient accounts for the effect of interactions between pairs of molecules, depending explicitly, therefore, on the potential function assumed to describe the interaction between a given pair of molecules.

In the calculations on which our tables have been based, we have, almost exclusively, taken the Lennard-Jones (12,6) potential function for this description. According to the fits to second virial coefficient data reported herein, the (12,6) function is clearly a poor choice. While we cannot state a unique best choice on the basis of fits to such data, we can, nevertheless, determine the best member of a given family of functions. This is equivalent to assigning the best value to the third parameter which characterizes the family. Thus, according to Table 1, the best member of the (m,6) family to use for nitrogen would be that characterized by the value $m = 24$, which is considerably different from the $m = 12$ previously employed by us.

We have calculated a new set of second virial coefficients for the N_2-N_2 interaction based on the (24,6) potential function and have introduced these virial coefficients into the calculation of the equilibrium properties of nitrogen. It should be noted that the N-N and N-N_2 interactions have not been modified.

A comparison of the results of this calculation with the earlier work is presented in Figure 9 and in Table 3 for the density $\log \rho/\rho_0 = 2.0$.

According to Table 3, a very large change in the density correction results from changing the potential function in this way. The effect on the properties themselves is much less since these contain, in addition to the density correction, an ideal gas contribution which is independent of the potential function and hence unaffected by changes in it. It should be noted that the first density correction being examined is linear in the density. Therefore, the density corrections in Table 3 double on doubling the density to $\rho/\rho_0 = 200$ (i.e., $\log \rho/\rho_0 = 2.14$). The percent deviation associated with the total properties at 10,000°K actually more than double under these circumstances since the degree of dissociation decreases as does the ideal gas contribution. The first density correction then represents a larger part of the total property. On the other hand, the corrections decrease linearly with decrease in density (except for the effect of dissociation). Thus, the density corrections are reduced by a factor of 100 in going to normal density ($\log \rho/\rho_0 = 0.$) making their effect on the total properties essentially negligible at that density.

In this section of this report we have examined only the change which takes place in the first density correction to the ideal gas properties when a reasonable modification is made in the intermolecular potential function. At higher densities one would have to examine the effect on the higher virial coefficients associated with the higher order density corrections. This, we have, in effect, undertaken in our examination of the sensitivity of the Percus-Yevick equation to these same changes in the potential function. It should be remembered that the Percus-Yevick equation contains approximations to each of the virial coefficients. Results of this examination appear elsewhere in this report.

Our investigation has involved the modification of the N_2-N_2 interaction exclusively. It should be noted that estimates of the N-N_2 interaction are based on prior assumptions as to how to characterize the N_2-N_2 interactions. The N-N_2 interaction contributes significantly only in a narrow band in a temperature-density plot. This band is characterized by a dissociation sufficiently far advanced to produce a non-negligible mole fraction of N atoms but not sufficiently far advanced to reduce the number of molecules to too low a level.

From the results listed in Table 3, one can conclude that the equation of state of nitrogen previously published by us is good to better than a fraction of a percent with respect to improvement in the N_2-N_2 intermolecular potential function at densities below normal $(\log \rho/\rho_o = 0)$, to approximately 1% at 10 times normal density $(\log \rho/\rho_o = 1.0)$ and to 2% at 100 times normal density $(\log \rho/\rho_o = 2.0)$. Those properties whose density corrections depend on the derivatives of the second virial coefficient are considerably more accurate with respect to these improvements in the potential functions.

According to Table 1, the O_2-O_2 potential function should also be changed to the (24,6) function while the (18,6) potential should be used for argon. The effect of improving the functions used in the air calculation should, therefore, be no worse than that found for nitrogen.

VI. SUMMARY AND CONCLUSIONS

The study of high density statistical mechanical equations of state of a fluid has necessitated the prior investigation of intermolecular potential functions and of the means for the determination of such functions from experimental data. While this study of potential functions is far from complete, we have, nevertheless, come to a number of important conclusions. We have found second virial coefficient data at reduced temperatures above 2.0 on the (12,6) scale to yield no information on the potential function. The same is true of viscosity and diffusion coefficient data for reduced temperatures between 1.5 and 5.0 on the (12,6) scale.

Second virial coefficient data for reduced temperatures below 2.0 on this scale can certainly be used to determine three parameters in a potential function. There are vague indications that one might, in some instances, be able to determine an additional parameter.

The fit of viscosity and diffusion coefficient data might serve as a sensitive probe of the potential function provided such data is available both below $T^* = 1.5$ and above $T^* = 5.0$ on the (12,6) scale. We have shown the simultaneous fit of these properties and their first derivatives in these temperature ranges to be possibly quite sensitive. We have also found this to be true of the simultaneous fit of second virial coefficient and viscosity data. The extent of this sensitivity and whether or not it is a property of the individual physical properties is the subject of investigation at the present time. This investigation involves the actual fit of experimental data as well as the extension of our theoretical investigation to additional families of potential functions.

Our investigation of high density theories has thus far been limited to the Percus-Yevick theory. We have found that theory to be as applicable to a fluid of diatomic molecules like air as it is to a fluid of spherical molecules like argon. The effect on the theory of changing potential functions in a manner dictated by fits to the second virial coefficient is under investigation. We have already shown that improving the potential function has a strong effect on the equation of state. We have not determined, as yet, whether or not there are differences, at high densities, for potentials which produce equivalent second virial coefficients over a large temperature range. Our investigations in this area combined with our continuing work on the potential function should produce a balanced view of what one can accomplish with the combination of such high density theories and the tools available for the determination of potential functions required by them.

We have examined the effect improving the potential functions has on some of our tables of thermodynamic properties of gases. We have found that, while the virial corrections can be drastically altered by changing potential functions, the properties themselves are only slightly changed. The equation of state itself is affected in a non-negligible way only at the highest densities indicating that the tables will probably need to be redone only at a small number of the highest densities. Final results in this area must necessarily wait for final decisions as to the potential functions.

REFERENCES

1. Klein, Max, Journal of Research of the National Bureau of Standards 70A, 259 (1966), attached herewith as an Appendix.

2. Frisch, H. L. and Lebowitz, J. L., The Equilibrium Theory of Classical Fluids, W. A. Benjamine, Inc., New York, 1954.

3. Hirschfelder, J., Curtiss, C., and Bird, R. F., "The Molecular Theory of Gases and Liquids", John Wiley and Sons, New York, 1954.

4. Hilsenrath, J., Klein, M., Woolley, H. W., Tables of Thermodynamic Properties of Air Including Dissociation and Ionization From 1,500°K to 15,000°K, Report No. AEDC-TR-59-20, Arnold Engineering Development Center, Tennessee, 1959.

5. Hilsenrath, J. and Klein, M., Tables of Thermodynamic Properties of Air in Chemical Equilibrium Including Second Virial Corrections From 1500°K to 15,000°K, Report No. AEDC-TDR-63-161, Arnold Engineering Development Center, 1963. (Reissued under same title, as Report No. AEDC-TR-65-58).

6. Hilsenrath, J., Klein, M., and Messina, C., "The Thermodynamic Properties of Argon" (AEDC-TR-66-248), 1966.

TABLE 1a. ARGON* $\bar{B} = 12.09$

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	90.15	58.12	.376
		12	120.00	50.85	.379
		15	142.48	47.05	.382
		16	148.82	46.16	.383
		17	154.69	45.38	.383
		18	160.15	44.71	.384
		21	174.49	43.12	.386
		24	186.43	41.97	.387
		27	196.54	41.10	.389
		30	205.26	40.42	.389
		40	227.38	38.91	.392
Kihara	γ =	0.1	142.38	35.83	.381
		0.15	153.53	30.54	.381
		0.2	164.64	26.25	.382
		0.25	175.67	22.74	.383
		0.3	186.66	19.83	.383
		0.4	208.33	15.35	.384
		0.45	219.01	13.62	.384
		0.5	229.61	12.13	.385
		0.55	240.02	10.86	.385
		0.6	250.46	9.76	.385
		0.70	270.86	7.96	.386
exp-6	α =	12	104.90	86.04	.375
		13	115.31	79.20	.376
		14	124.36	74.21	.377
		15	132.50	70.44	.378
		17	146.49	64.89	.380
		19	158.33	61.02	.382
		30	201.57	50.65	.388
		40	224.86	46.69	.391
		50	240.96	44.40	.393
(12,n)	n =	4	41.41	66.91	.376
		5	83.52	55.97	.378
		6	120.00	50.85	.379
		7	151.27	47.67	.380
		8	178.33	45.45	.381
		9	202.06	43.80	.382
		10	233.05	42.51	.383
Square well	R =	1.2	358.80	31.06	.409
		1.4	186.00	33.71	.393
		1.6	114.27	34.98	.402
		1.8	76.57	35.68	.411
		1.9	64.07	35.90	.415
		2.0	54.26	36.10	.417
		2.2	40.02	36.38	.422

*E. Whalley, Y. Lupien, and W. G. Schneider
Can. J. Chem. 31, 722 (1953)

TABLE 1b. ARGON* $\bar{B} = 8.7557$

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	89.711	56.15	.0370
		12	119.58	49.41	.0382
		15	142.10	45.81	.0409
		16	148.46	44.95	.0419
		17	154.34	44.20	.0428
		18	159.82	43.55	.0439
		21	174.20	41.99	.0471
		24	186.16	40.84	.0500
		27	196.32	39.97	.0527
		30	205.06	39.27	.0552
		40	227.28	37.73	.0618
Kihara	γ =	.1	141.93	34.66	.0432
		.15	153.06	29.43	.0473
		.2	164.15	25.19	.0523
		.25	175.16	21.71	.0582
		.3	186.10	18.84	.0648
		.4	207.69	14.41	.0797
		.45	218.32	12.701	.0878
		.5	228.87	11.24	.0962
		.55	239.23	9.993	.1048
		.6	249.59	8.91	.1138
exp-6	α =	12	104.25	81.42	.0427
		13	114.67	75.44	.0424
		14	123.80	71.05	.0426
		15	131.95	67.63	.0431
		17	146.02	62.57	.0445
		19	157.88	58.96	.0460
		30	201.30	49.08	.0553
		40	224.69	45.21	.0617
		50	240.86	42.94	.0664
(12,n)	n =	4	41.18	67.03	.0518
		5	83.27	55.42	.0399
		6	119.58	49.41	.0382
		7	150.69	45.45	.0524
		8	177.60	42.56	.0719
		9	201.15	40.33	.0918
		10	222.01	38.53	.111
Square well	R =	1.2	356.25	22.75	0.3761
		1.4	185.705	30.63	0.1391
		1.6	114.45	34.74	.0500
		1.8	76.84	37.14	.0419
		1.85	70.21	37.58	.047
		1.9	64.35	37.98	.0524
		1.95	59.15	38.33	.0579
		2.0	54.51	38.65	.0631
		2.2	40.25	39.65	.0802

*A. Michels, H. Wijker, and H. Wijker
Physica 15, 627 (1949)

TABLE 1c. ARGON* $\bar{B} = 72.016$

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	84.16	66.36	.392
		12	115.06	54.76	.223
		15	140.10	47.76	.110
		16	147.50	45.96	.103
		17	154.53	44.34	.118
		18	161.22	42.87	.145
		21	179.57	39.19	.252
		24	195.79	36.28	.363
		27	210.25	33.93	.471
		30	223.14	32.04	.576
		40	254.82	28.35	.895
Kihara	γ =	.1	140.76	35.57	.102
		.15	154.72	28.79	.142
		.2	169.67	23.31	.245
		.25	185.82	18.83	.377
		.3	203.31	15.18	.539
		.4	238.05	10.18	.985
		.45	251.48	8.72	1.273
		.5	262.36	7.65	1.589
		.55	271.60	6.82	1.916
		.6	279.96	6.13	2.252
exp-6	α =	12	99.90	90.93	.271
		13	110.71	82.73	.220
		14	120.44	76.45	.173
		15	129.35	71.40	.134
		17	145.33	63.63	.102
		19	159.46	57.82	.144
		30	217.87	40.57	.535
(12,n)	n =	4	36.84	90.03	.723
		5	76.71	68.83	.499
		6	115.06	54.76	.223
		7	153.58	43.50	.166
		8	195.16	33.75	.539
Square well	R =	1.2	324.5	18.40	8.871
		1.4	210.27	19.75	2.842
		1.6	122.62	29.49	.422
		1.8	73.68	41.78	.196
		1.85	66.39	43.85	.272
		1.9	60.17	45.65	.339
		1.95	54.78	47.26	.399
		2.0	50.08	48.69	.452
		2.2	36.15	53.06	.610

*A. Michels, J. M. H. Levelt, and W. deGraaf Physica <u>24</u>, 659 (1958)

TABLE 1d. KRYPTON $\bar{B} = 173.50$

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	118.24	91.85	7.82
		12	165.15	78.05	4.90
		15	200.56	58.97	2.494
		16	209.55	56.86	1.903
		17	217.36	55.28	1.50
		18	224.16	54.08	1.38
		21	240.31	51.83	2.22
		24	252.36	50.62	3.38
		27	261.8	49.93	4.40
		30	269.80	49.388	5.274
		40	288.82	48.52	7.377
Kihara	γ =	.1	200.29	44.17	2.246
		.15	215.09	36.44	1.43
		.2	227.69	30.81	2.00
		.25	238.59	26.51	3.27
		.3	248.33	23.11	4.663
		.4	265.44	18.01	7.415
		.45	273.14	16.04	8.732
		.5	280.50	14.36	10.005
		.55			
		.6	294.04	11.66	12.41
		.7	306.56	9.593	14.645
exp-6	α =	12	140.87	121.95	6.00
		13	157.47	107.76	5.05
		14	172.2	97.29	4.16
		15	185.15	89.46	3.33
		17	206.04	79.16	1.99
		19	221.57	73.12	1.40
		30			
		40			
		50			
(12,n)	n =	4	51.02	135.78	12.792
		5	108.02	96.81	9.309
		6	165.15	78.05	4.90
		7	211.46	55.82	1.48
		8	238.34	51.51	4.48
		9			
		10			
Square well	R =	1.2	319.52	33.80	30.47
		1.4	219.0	37.68	13.59
		1.6	158.09	41.21	3.086
		1.8	107.04	51.85	4.51
		1.85	96.70	55.19	5.653
		1.9	87.64	58.34	6.66
		1.95	79.76	61.21	7.545
		2.0	72.84	63.90	8.32
		2.2	52.43	72.26	10.66

TABLE 1e. XENON $\bar{B} = 49.56$

		Potential	ε/k	b_0	$\bar{\Delta}$
(m,6)	m =	9	167.57	99.37	1.28
		12	224.11	85.71	.89
		15	267.01	78.15	.60
		16	279.15	76.32	.53
		17	290.41	74.71	.49
		18	300.91	73.29	.46
		21	328.53	69.87	.47
		24	351.57	67.32	.57
		27	371.15	65.34	.70
		30	388.04	63.76	.822
		40	431.02	60.20	1.169
Kihara	γ =	.1	266.80	58.88	.55
		.15	288.18	49.44	.47
		.2	309.57	41.80	.52
		.25	330.90	35.58	.68
		.3	352.17	30.45	.91
		.4	394.37	22.67	1.45
		.45	415.24	19.69	1.736
		.5	435.99	17.18	2.04
		.55	456.41	15.05	2.343
		.6	476.86	13.23	2.66
		.70	516.76	10.34	3.302
exp-6	α =	12	195.15	141.51	.94
		13	214.88	130.43	.84
		14	232.22	122.19	.74
		15	247.71	115.72	.66
		17	274.56	106.07	.53
		19	297.25	99.11	.47
		30	380.80	78.84	.786
		40	426.03	72.24	1.136
		50	457.35	67.79	1.393
(12,n)	n =	4	76.45	124.33	2.33
		5	155.26	99.78	1.65
		6	224.11	85.71	.89
		7	283.87	75.90	.49
		8	336.17	68.52	.99
		9	382.37	62.74	1.653
		10	423.50	58.11	2.290
Square well	R =	1.2	665.90	26.19	10.48
		1.4	356.39	43.67	3.40
		1.6	216.47	56.74	.68
		1.8	144.22	64.72	.98
		1.85	131.60	66.21	1.209
		1.9	120.50	67.52	1.42
		1.95	110.65	68.72	1.609
		2.0	101.90	69.78	1.78
		2.2	75.05	73.13	2.30

TABLE 1f. SECOND VIRIAL COEFFICIENT OF NITROGEN $\bar{B}$ = 47.88

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	70.74	81.28	2.99
		12	94.77	69.46	2.21
		15	112.98	62.92	1.58
		16	118.12	61.34	1.39
		17	122.88	59.95	1.22
		18	127.31	58.74	1.07
		21	138.94	55.82	.69
		24	148.59	53.66	.49
		27	156.74	52.01	.53
		30	163.75	50.70	.702
		40	181.38	47.80	1.335
Kihara	γ =	.1	112.80	47.43	1.44
		.15	121.78	39.72	1.03
		.2	130.70	33.51	.65
		.25	139.54	28.47	.44
		.3	148.27	24.35	.67
		.4	165.29	18.13	1.59
		.45	173.50	15.77	2.109
		.5	181.50	13.80	2.64
		.55	189.21	12.142	4.817
		.6	196.74	10.73	3.72
exp-6	α =	12	82.24	115.65	2.35
		13	90.66	106.17	2.13
		14	98.04	99.14	1.92
		15	104.64	93.63	1.72
		17	116.04	85.45	1.35
		19	125.66	79.58	1.04
		30	160.69	63.55	.628
		40	179.30	57.41	1.263
		50	192.01	53.88	1.757
(12,n)	n =	4	32.33	102.61	4.76
		5	65.70	81.61	3.60
		6	94.77	69.46	2.21
		7	119.79	61.08	.88
		8	141.31	54.95	.72
		9	159.83	50.35	1.850
		10	175.70	46.92	2.958
Square well	R =	1.2	244.58	26.44	15.04
		1.4	145.97	35.71	4.70
		1.6	91.54	45.10	.51
		1.8	61.44	51.69	2.38
		1.85	56.12	52.94	2.783
		1.9	51.42	54.07	3.14
		1.95	47.24	55.10	3.448
		2.0	43.54	56.00	3.73
		2.2	32.12	58.87	4.57

TABLE 1g. METHANE B = 63.00

		Potential	ϵ/k	b_0	$\bar{\Delta}$
(m,6)	m =	9	105.49	103.00	7.91
		12	143.25	84.15	6.02
		15	172.81	73.17	4.43
		16	181.26	70.49	3.96
		17	189.17	68.09	3.53
		18	196.53	66.00	3.12
		21	215.82	61.05	2.07
		24	231.64	57.54	1.33
		27	244.71	54.98	1.10
		30	255.63	53.07	1.384
		40	281.66	49.37	2.928
Kihara	γ =	.1	172.91	54.76	4.19
		.15	188.02	44.66	3.20
		.2	203.14	36.69	2.21
		.25	218.02	30.40	1.36
		.3	232.34	25.43	1.22
		.4	258.31	18.42	3.12
		.45	269.76	15.94	4.286
		.5	280.30	13.93	5.47
		.55	290.97	12.28	6.634
		.6	299.05	10.89	7.79
		.7	315.51	8.709	9.999
exp-6	α =	12	123.91	141.83	6.62
		13	137.16	128.37	6.03
		14	148.92	118.23	5.47
		15	159.55	110.19	4.94
		17	178.20	98.06	3.99
		19	194.06	89.37	3.15
		30	251.0	66.70	1.232
		40			
		50			
(12,n)	n =	4	47.10	140.09	11.52
		5	97.17	106.11	9.03
		6	143.25	84.15	6.02
		7	185.28	68.22	2.98
		8	221.87	57.23	1.23
		9	250.47	50.64	3.445
		10			
Square well	R =	1.2	343.32	26.29	25.60
		1.4	223.12	35.12	9.10
		1.6	142.54	48.46	1.42
		1.8	92.51	62.91	5.82
		1.85	83.99	65.70	6.632
		1.9	76.57	68.27	7.35
		1.95	70.06	70.51	7.975
		2.0	64.31	72.61	8.53
		2.2			

TABLE 1h. CO_2 $\bar{B}$ = 94.51

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	138.38	138.01	1.102
		12	186.15	118.18	0.995
		15	223.05	106.90	0.905
		16	233.60	104.11	0.879
		17	243.45	101.65	0.855
		18	252.66	99.47	0.832
		21	277.12	94.14	0.771
		24	297.80	90.09	0.719
		27	315.59	86.89	0.674
		30	331.09	84.29	0.636
		40	371.26	78.27	0.538
Kihara	γ =	0.1	223.36	80.22	0.887
		0.15	242.41	66.84	0.827
		0.2	261.78	56.03	0.765
		0.25	281.48	47.20	0.700
		0.3	301.57	39.94	0.633
		0.4	343.14	28.87	0.492
		0.45	364.72	24.63	0.423
		0.5	387.11	21.03	0.357
		0.55	410.18	17.97	0.303
		0.6	434.68	15.33	0.273
		0.7			
exp-6	α =	12	162.36	194.19	1.0173
		13	178.99	178.80	0.986
		14	193.70	167.23	0.956
		15	206.93	158.08	0.928
		17	230.07	144.27	0.876
		19	249.86	134.21	0.829
		30	324.63	105.69	0.649
		40	366.68	94.04	0.548
		50	396.55	87.06	0.480
(12,n)	n =	4	62.09	176.85	1.337
		5	127.29	140.22	1.182
		6	186.15	118.18	0.995
		7	239.52	102.04	0.805
		8	288.76	89.28	0.623
		9	335.18	78.69	0.456
		10	380.03	69.54	0.322
Square well	R =	1.2	649.43	26.97	6.707
		1.4	339.67	45.84	0.363
		1.6	184.14	75.37	0.669
		1.8	118.93	90.64	0.992
		1.85	108.04	93.37	1.047
		1.9	98.54	95.80	1.094
		1.95	90.20	97.97	1.136
		2.0	82.83	99.91	1.174
		2.2	60.50	105.95	1.286

TABLE 11. ETHANE $\bar{B}$ = 142.62

		Potential	ε/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	152.18	171.03	0.950
		12	206.65	143.36	0.770
		15	249.89	127.00	0.637
		16	262.48	122.87	0.603
		17	274.35	119.17	0.574
		18	285.56	115.85	0.550
		21	315.90	107.54	0.505
		24	342.29	101.01	0.498
		27	365.62	95.69	0.518
		30	386.58	91.21	0.556
		40	444.04	80.20	0.737
Kihara	γ =	0.1	250.75	94.87	0.616
		0.15	274.09	77.77	0.551
		0.2	298.59	63.92	0.509
		0.25	324.36	52.62	0.505
		0.3	352.06	43.23	0.553
		0.4	415.76	28.73	0.824
		0.45	453.64	23.09	1.060
		0.5	492.83	18.66	1.407
		0.55	523.32	15.79	1.891
		0.6	545.1	13.91	2.490
		0.7	577.86	11.33	3.799
exp-6	α =	12	179.84	236.78	0.819
		13	198.85	216.56	0.765
		14	215.83	201.18	0.717
		15	231.26	188.89	0.674
		17	258.63	170.12	0.602
		19	282.47	156.22	0.550
		30	377.93	115.12	.540
		40	437.27	97.01	.712
		50	483.03	85.58	.906
(12,n)	n =	4	67.21	227.16	1.340
		5	139.14	176.12	1.074
		6	206.65	143.36	0.770
		7	271.61	117.96	0.536
		8	337.68	96.28	0.560
		9	411.28	76.11	0.913
		10	488.79	60.16	1.637
Square well	R =	1.2	638.0	42.57	16.77
		1.4	412.00	44.36	3.69
		1.6	213.29	83.05	0.521
		1.8	132.09	109.80	0.742
		1.85	119.41	114.39	0.824
		1.9	108.47	118.43	0.899
		1.95	98.96	122.02	0.966
		2.0	90.62	125.22	1.027
		2.2	65.71	135.07	1.215

TABLE 1j. CF_4 $\bar{B} = 40.64$

		Potential	ϵ/k	b_o	$\bar{\Lambda}$
(m,6)	m =	9	113.95	153.32	1.192
		12	151.90	134.49	1.091
		15	180.49	124.36	1.003
		16	188.55	121.94	0.978
		17	196.02	119.85	0.955
		18	202.96	118.00	0.934
		21	221.20	113.59	0.879
		24	236.37	110.35	0.835
		27	249.24	107.87	0.801
		30	260.33	105.87	0.733
		40	288.44	101.50	0.713
Kihara	γ =	0.1	180.22	94.07	0.965
		0.15	194.30	79.77	0.901
		0.2	208.32	68.17	0.839
		0.25	222.22	58.67	0.782
		0.3	236.02	50.82	0.735
		0.4	263.22	38.76	0.684
		0.45	276.58	34.10	0.686
		0.5	289.83	30.13	0.709
		0.55	302.83	26.74	0.750
		0.6	315.82	23.81	0.809
		0.7			
exp-6	α =	12	132.29	221.94	1.037
		13	145.55	205.43	1.025
		14	157.15	193.28	1.007
		15	167.50	183.82	0.987
		17	185.39	169.80	0.948
		19	200.45	159.80	9.912
		30	255.52	132.39	0.777
		40	285.16	121.64	0.717
		50	305.62	115.35	0.684
(12,n)	n =	4	52.40	184.10	1.624
		5	105.89	151.33	1.376
		6	151.90	134.49	1.091
		7	191.20	123.13	0.855
		8	225.11	114.82	0.719
		9	254.71	108.40	0.705
		10			
Square well	R =	1.2	444.73	58.45	3.760
		1.4	234.75	81.37	1.023
		1.6	145.39	93.60	0.807
		1.8	97.86	100.80	1.308
		1.9	82.03	103.31	1.503
		2.0	69.54	105.33	1.661
		2.2	51.39	108.36	1.896

TABLE 1k. SF6 $\bar{B}$ = 160.15

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	141.46	289.37	7.155
		12	189.81	248.88	6.768
		15	226.90	226.08	6.456
		16	237.47	220.45	6.366
		17	247.31	215.52	6.283
		18	256.50	211.16	6.206
		21	280.84	200.50	6.002
		24	301.28	192.47	5.833
		27	318.78	186.22	5.692
		30	333.99	181.11	5.572
		40	373.09	169.45	5.278
Kihara	γ =	0.1	227.04	169.91	6.387
		0.15	245.95	142.06	6.184
		0.2	265.06	119.54	5.975
		0.25	284.36	101.16	5.763
		0.3	303.90	86.01	5.552
		0.4	343.53	63.00	5.129
		0.45	363.73	54.19	4.928
		0.5	384.29	46.73	4.735
		0.55	405.04	40.40	4.558
		0.6	426.51	34.95	4.397
		0.70	470.61	26.29	4.156
exp-6	α =	12	165.54	409.20	6.832
		13	182.37	377.17	6.725
		14	197.23	353.18	6.622
		15	210.57	334.20	6.525
		17	233.81	305.74	6.348
		19	253.59	285.06	6.193
		30	327.60	226.91	5.613
		40	368.63	203.44	5.307
		50	397.45	189.51	5.106
(12,n)	n =	4	63.83	367.28	8.072
		5	130.45	292.64	7.468
		6	189.81	248.88	6.768
		7	242.76	217.32	6.102
		8	290.65	192.75	5.513
		9	334.61	172.80	5.016
		10	375.61	156.04	4.620
Square well	R =	1.2	670.5	52.29	15.918
		1.4	325.75	110.13	4.173
		1.6	185.89	161.72	5.673
		1.8	121.43	190.30	6.794
		1.85	110.53	195.34	6.998
		1.9	100.96	199.82	7.181
		1.95	92.51	204.05	7.343
		2.0	85.02	207.82	7.487
		2.2	62.30	219.18	7.937

TABLE 1l. PROPENE $\bar{B}$ = 249.36

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	154.39	307.06	2.167
		12	209.01	259.30	1.947
		15	251.93	231.46	1.763
		16	264.35	224.48	1.708
		17	276.01	218.25	1.656
		18	287.00	212.65	1.607
		21	316.52	198.81	1.473
		24	341.89	188.09	1.356
		27	364.07	179.44	1.254
		30	383.80	172.21	1.162
		40	436.81	154.64	.916
Kihara	γ =	0.1	252.63	173.16	1.726
		0.15	275.47	142.77	1.601
		0.2	299.13	118.20	1.467
		0.25	323.82	98.10	1.323
		0.3	349.72	81.52	1.167
		0.4	407.12	55.97	.813
		0.45	440.34	45.91	.609
		0.5	479.42	37.01	.340
		0.55	529.58	28.79	.296
		0.6	580.71	22.67	.818
		0.7	619.24	18.22	2.613
exp-6	α =	12	182.08	427.25	2.00
		13	201.10	391.79	1.935
		14	218.05	364.84	1.87
		15	233.39	343.40	1.813
		17	260.46	310.81	1.703
		19	283.90	286.76	1.604
		30	375.67	216.74	1.195
		40	430.63	186.57	.943
		50	472.04	167.55	.753
(12,n)	n =	4	68.51	403.20	2.614
		5	141.40	314.93	2.316
		6	309.01	259.30	1.947
		7	272.72	217.01	1.557
		8	335.24	181.78	1.152
		9	400.99	149.75	.721
		10	481.05	116.51	.291
Square well	R =	1.2	677.	70.51	19.91
		1.4	441.48	71.33	2.481
		1.6	212.47	155.59	1.254
		1.8	133.52	198.90	1.927
		1.85	120.89	206.42	2.034
		1.9	109.96	213.06	2.128
		1.95	100.41	219.01	2.209
		2.0	92.03	224.28	2.281
		2.2	66.88	240.57	2.497

TABLE 1m. AIR $\bar{B} = 48.29$

		Potential	ϵ/k	b_o	$\bar{\Delta}$
(m,6)	m =	9	74.03	75.58	1.086
		12	99.35	64.69	0.769
		15	118.75	58.58	0.507
		16	124.27	57.07	0.431
		17	129.41	55.76	0.360
		18	134.20	54.58	0.294
		21	146.88	51.75	0.133
		24	157.51	49.62	0.110
		27	166.59	47.95	0.215
		30	174.46	46.62	0.324
		40	194.58	43.58	0.615
Kihara	γ =	0.1	118.78	44.03	0.449
		0.15	128.62	36.75	0.276
		0.2	138.54	30.89	0.115
		0.25	148.52	26.11	0.151
		0.3	158.57	22.19	0.339
		0.4	178.78	16.25	0.768
		0.45	188.96	13.99	0.995
		0.5	199.14	12.09	1.23
		0.55	209.23	10.49	1.474
		0.6	219.38	9.133	1.728
		0.7	239.24	7.01	2.253
exp-6	α =	12	86.55	106.69	0.823
		13	95.38	98.18	0.734
		14	103.16	91.78	0.647
		15	110.15	86.75	0.565
		17	122.30	79.21	0.415
		19	132.64	73.74	0.283
		30	171.13	58.43	0.286
		40	192.27	52.33	0.585
		50	207.03	48.74	0.797
(12,n)	n =	4	33.47	96.36	1.806
		5	68.33	76.48	1.335
		6	99.35	64.69	0.769
		7	126.88	56.25	0.209
		8	151.56	49.77	0.374
		9	173.91	44.63	0.895
		10	194.19	40.50	1.392
Square well	R =	1.2	302.88	18.09	8.420
		1.4	165.72	29.32	2.278
		1.6	97.13	41.67	0.204
		1.8	63.74	49.18	0.801
		1.85	58.03	50.56	0.968
		1.9	53.02	51.79	1.114
		1.95	48.62	52.87	1.243
		2.0	44.70	53.89	1.357
		2.2	32.78	57.00	1.704

TABLE 2. THE RATIO OF THE LARGEST $\bar{\Delta}$ TO THE SMALLEST $\bar{\Delta}$ FOR THE ARGON DATA

Potential Family	[a]High T	[b]High T	[c]Low T
(m,6)	1.04	1.7	8.7
Kihara	1.01	2.6	22.0
exp-6	1.04	1.3	5.2
(12,n)	1.02	1.8	4.5
square well	1.07	9.2	45.3

[a] Whalley et al $2.28 \leq T^*_{12,6} \leq 7.29$

[b] Michels et al (1949) $2.28 \leq T^*_{12,6} \leq 3.53$

[c] Michels et al (1958) $1.11 \leq T^*_{12,6} \leq 2.28$

TABLE 3. THE EFFECT OF VARYING THE N_2-N_2 INTERMOLECULAR POTENTIAL FUNCTION ON THE EQUILIBRIUM PROPERTIES OF NITROGEN AT THE DENSITY $\log \rho/\rho_o = 2.0$

T°K	Δ(Z)	Δ(E/RT)	Δ(S/R)	Z	E/RT	S/R
		Based on the (24,6) Function				
2,000	.1604	-.0163	-.1768	1.1604	2.8810	23.528
5,000	.1642	-.00489	-.1593	1.1646	3.2574	26.725
10,000	.1673	-.01606	-.1512	1.2702	4.7445	30.774
		Based on the (12,6) Function				
2,000	.1480	-.00624	-.1418	1.1480	2.8911	23.551
5,000	.1423	-.0151	-.1271	1.1426	3.2785	26.766
10,000	.1438	-.0234	-.1204	1.2443	4.7387	30.785
		Percent Deviation of the (24,6) Results from the (12,6) Results				
2,000	8.4	73.9	-24.7	1.1	-0.3	-0.1
5,000	15.4	-61.0	-25.3	1.9	-0.6	-0.2
10,000	16.3	31.2	-25.6	2.1	0.1	-0.0

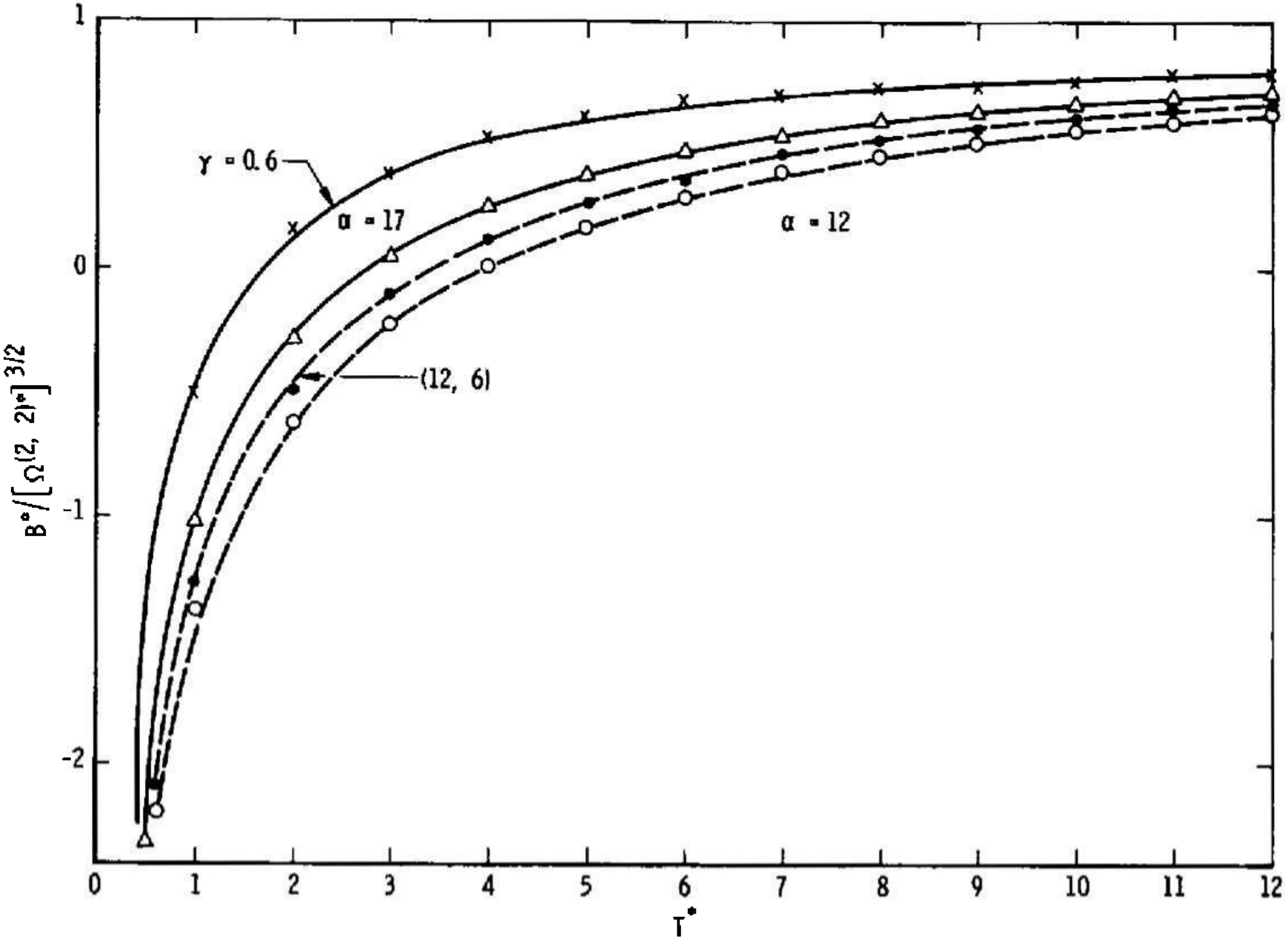

Figure 1 The Function $B^*/[\Omega^{(2,2)*}]^{3/2}$ as required in the Simultaneous Fit of Viscosity and Second Virial Coefficients

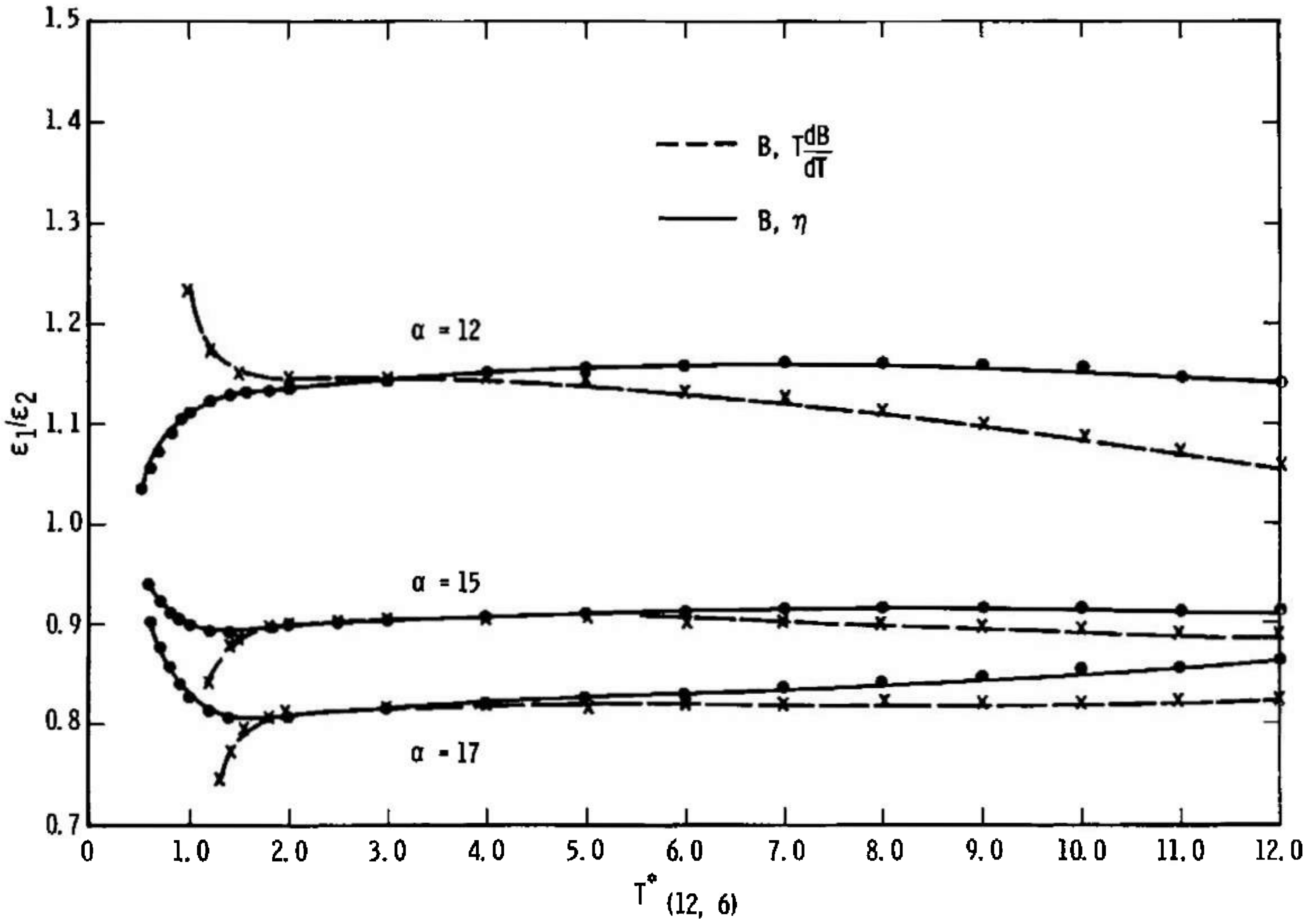

Figure 2a The Simultaneous Fit of the Pairs of Properties B and T $\frac{dB}{dT}$ as well as B and η for the (12,6) and exp-6 Functions to $T^*_{12,6} = 12.0$

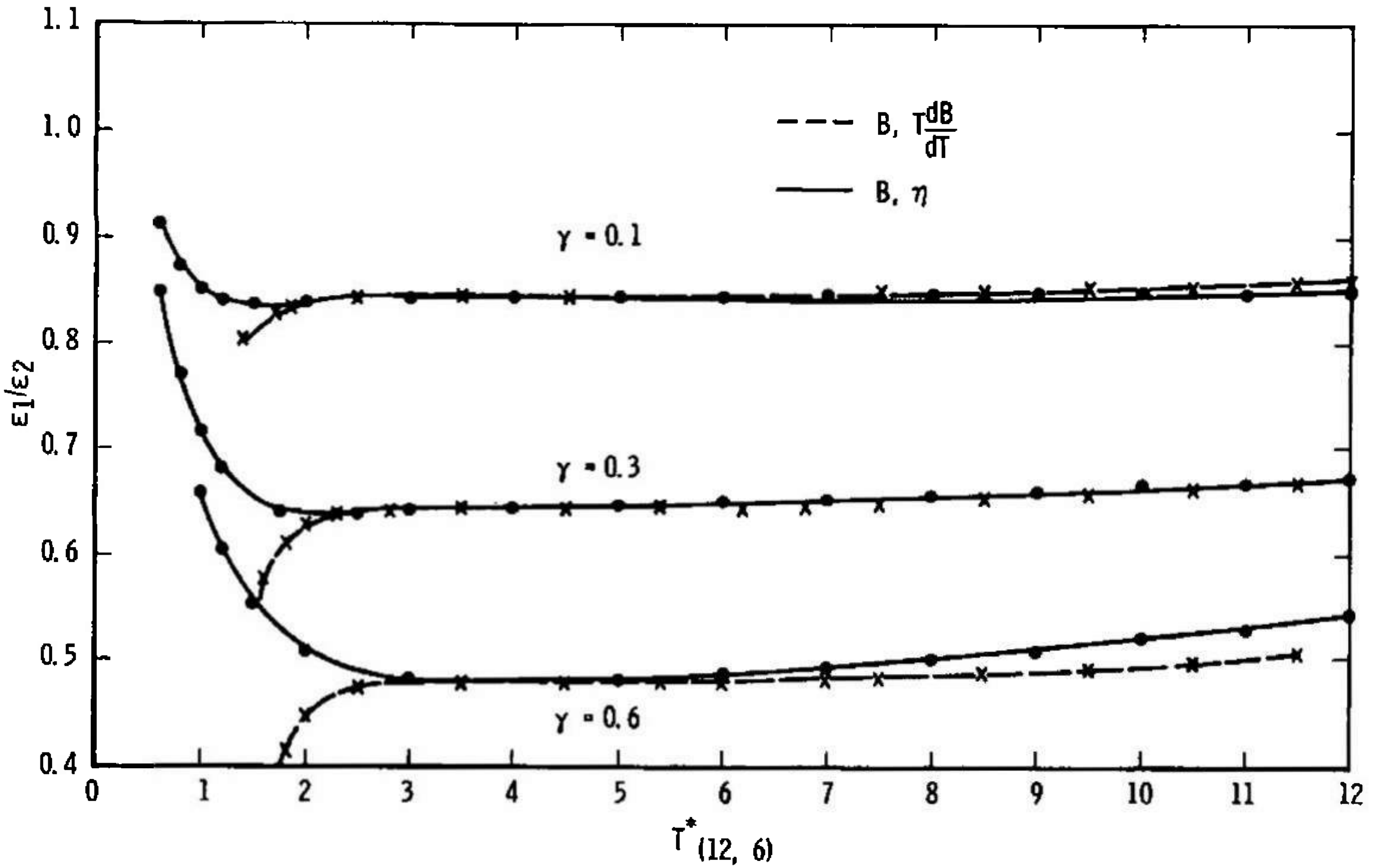

Figure 2b The Simultaneous Fit of the Pairs of Properties B and T $\frac{dB}{dT}$ as well as B and η for the (12,6) and Kihara Functions to $T^*_{12,6} \sim 12.0$

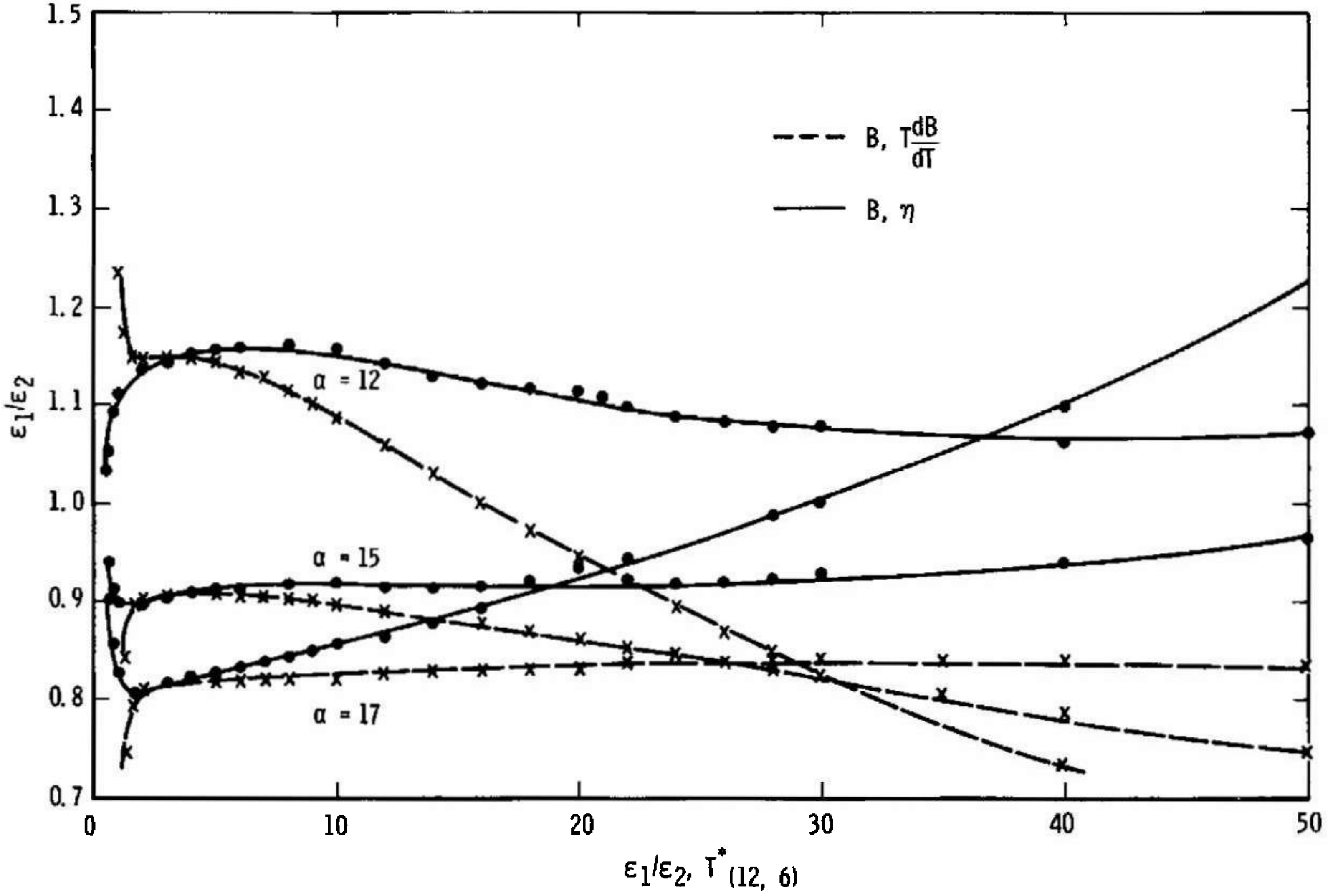

Figure 3 The Simultaneous Fit of the Pairs of Properties B and T $\frac{dB}{dT}$ as well as B and η for the (12,6) and exp-6 Functions to $T^*_{12,6}$ - 50

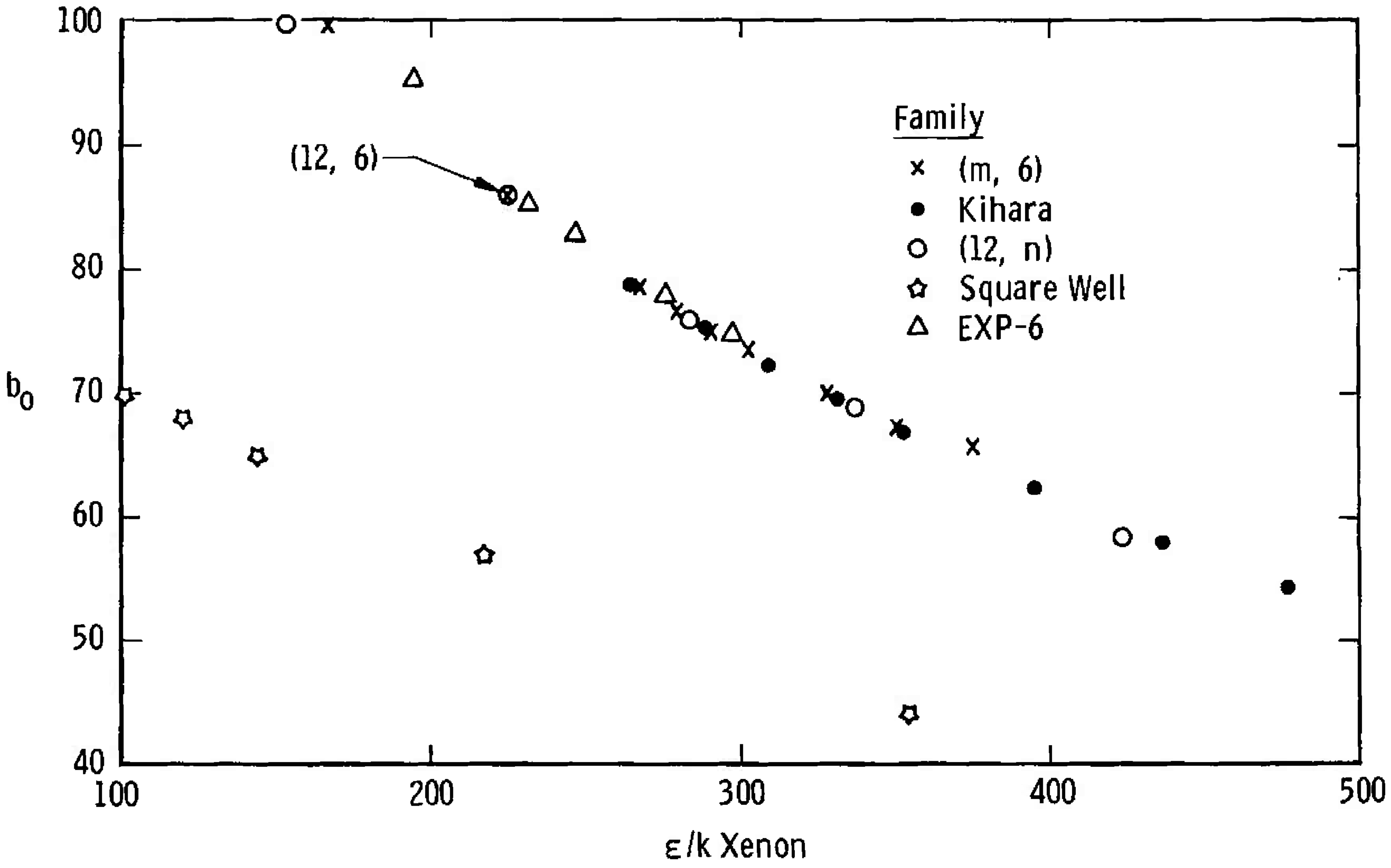

Figure 4a The Best Values of ϵ/k and b_o for Xenon

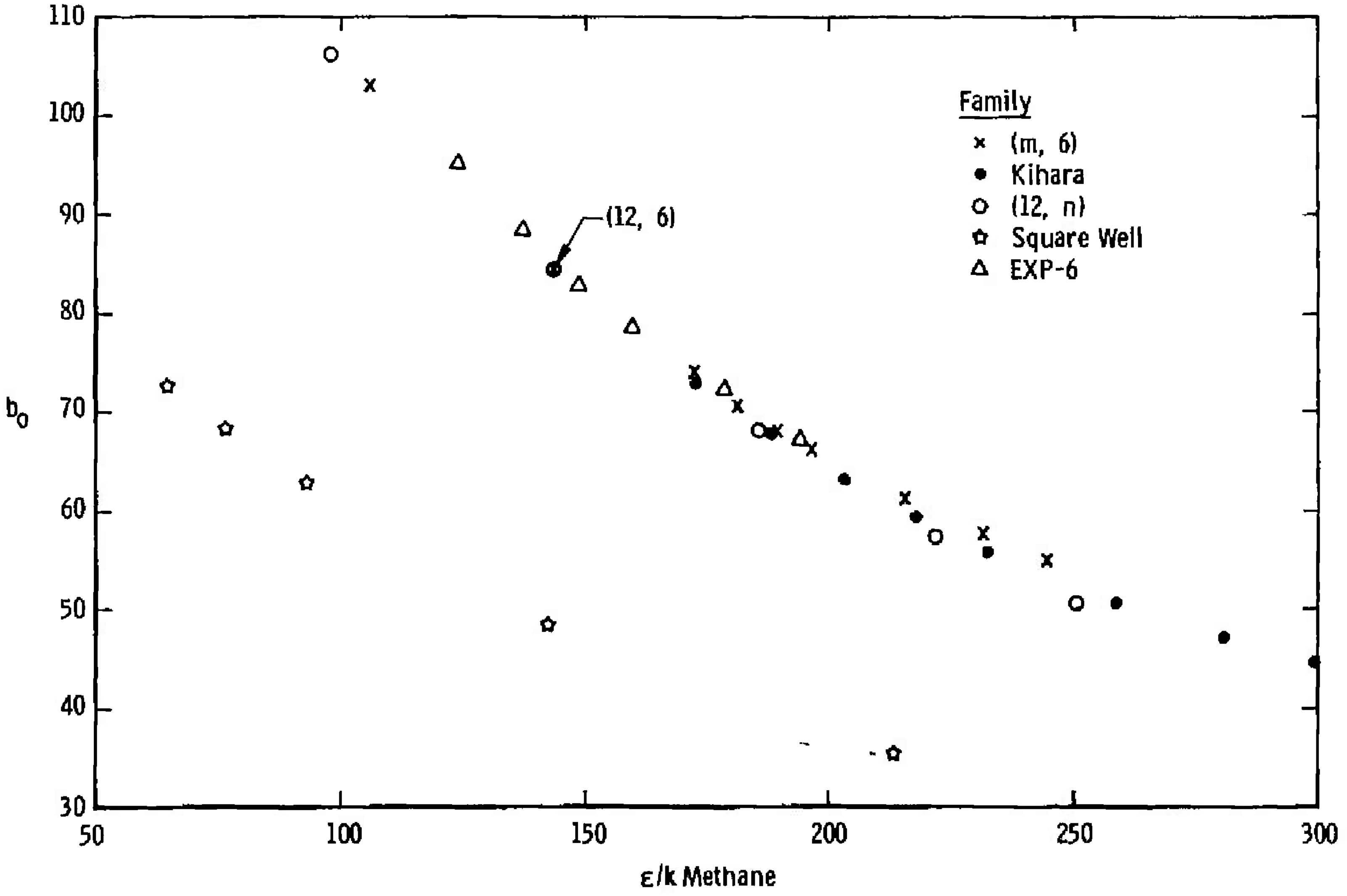

Figure 4b The Best Values of ϵ/k and b_o for Methane

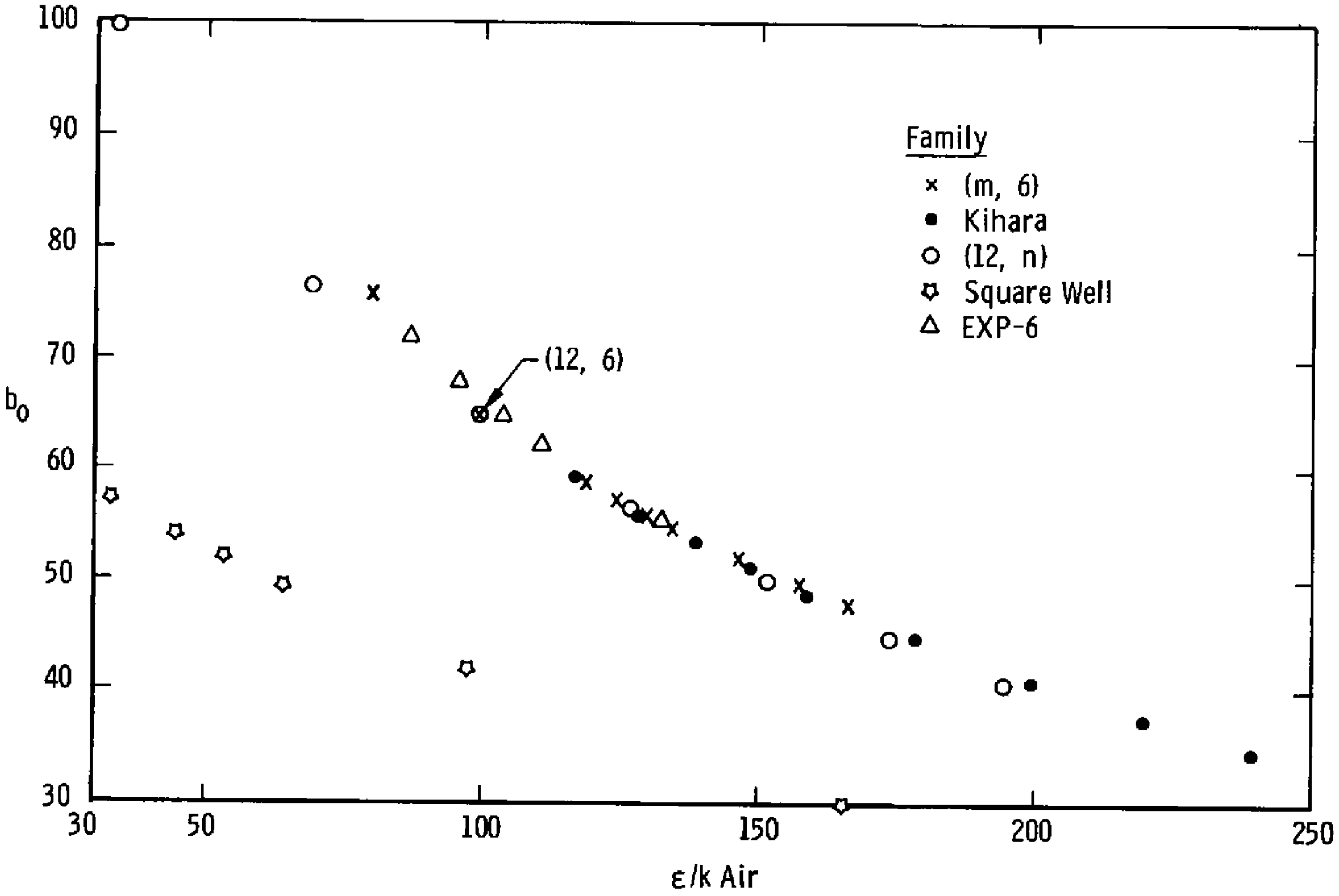

Figure 4c The Best Values of ε/k and b_0 for Air

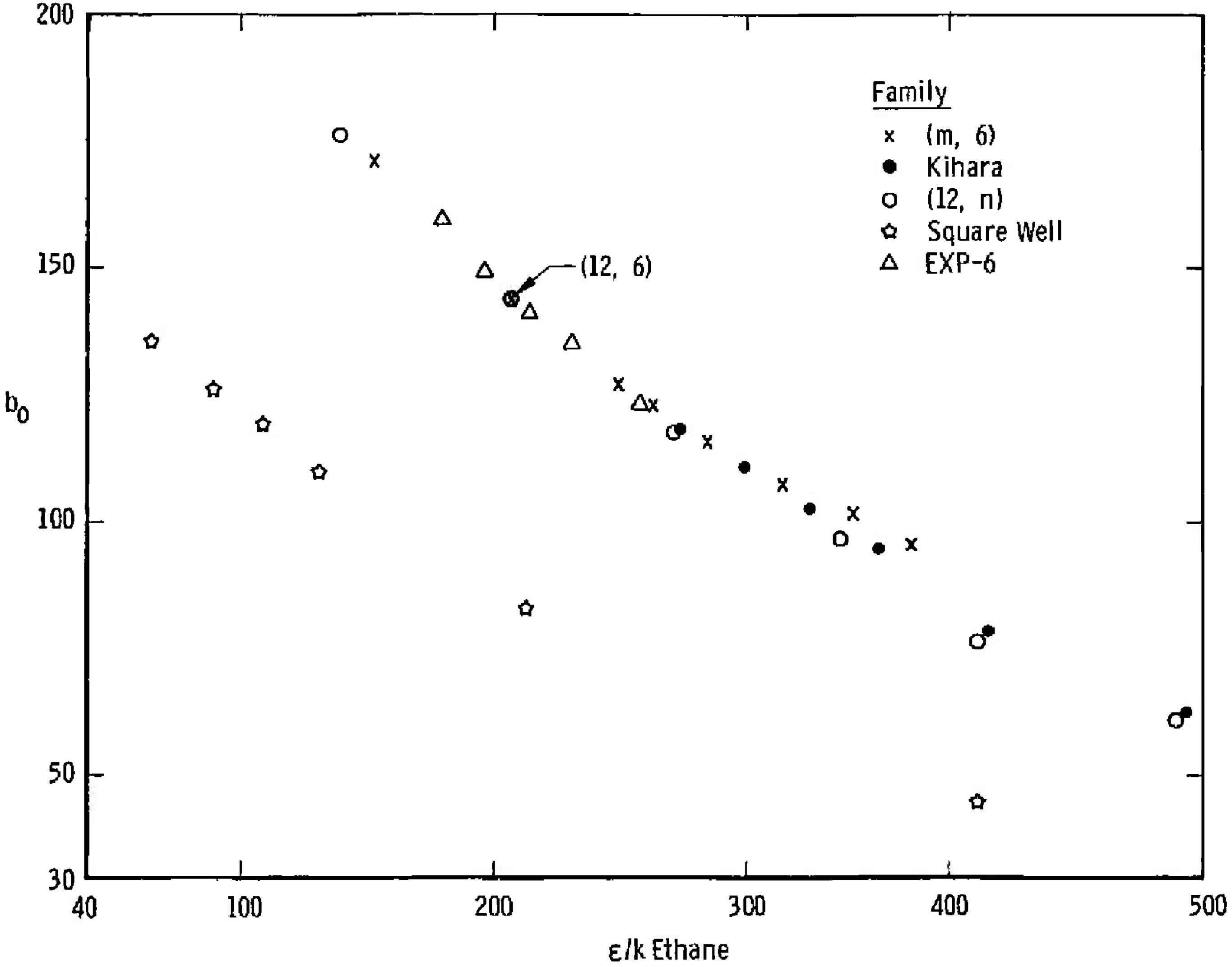

Figure 4d The Best Values of ε/k and b_0 for Ethane

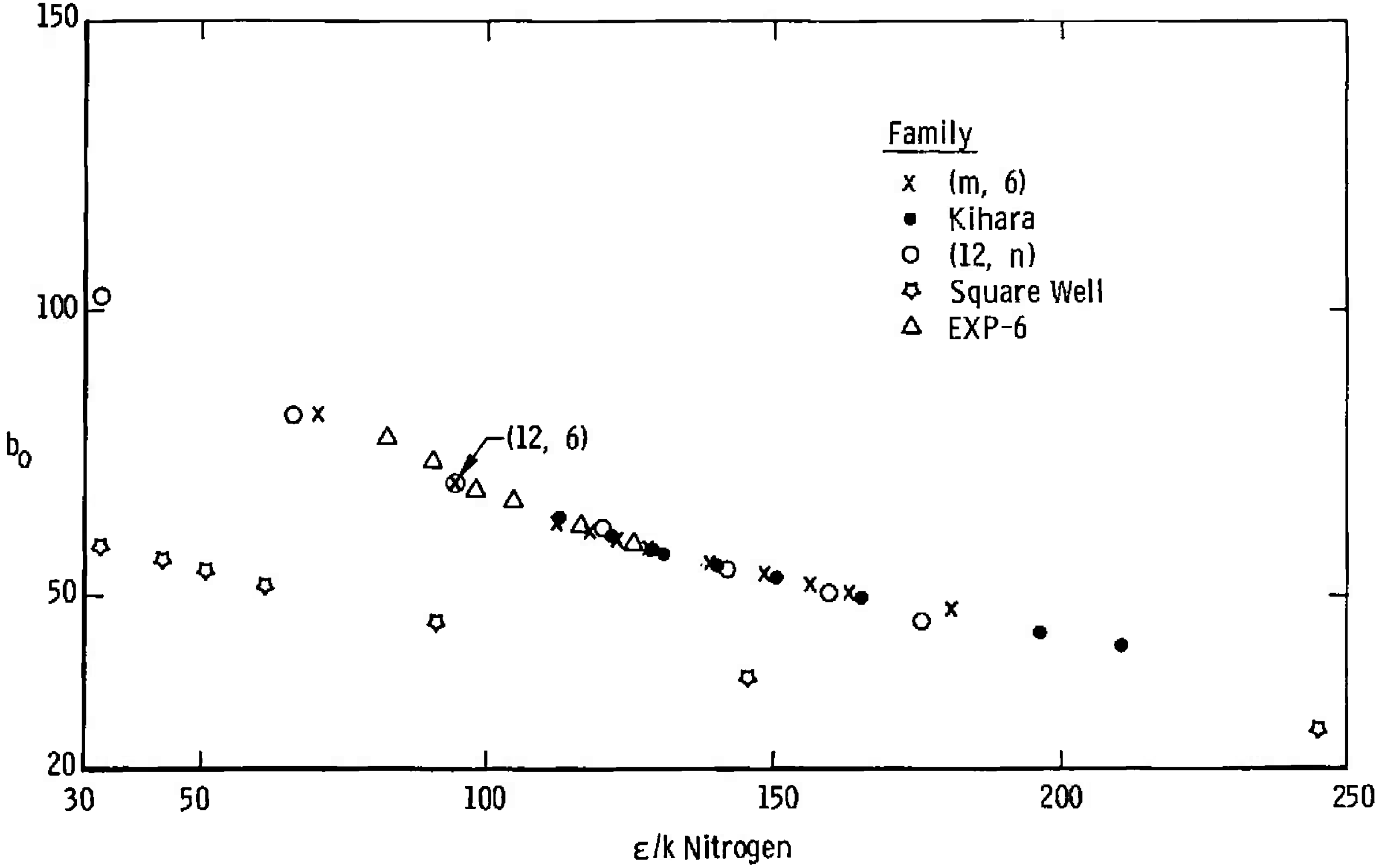

Figure 4e The Best Values of ε/k and b_o for Nitrogen

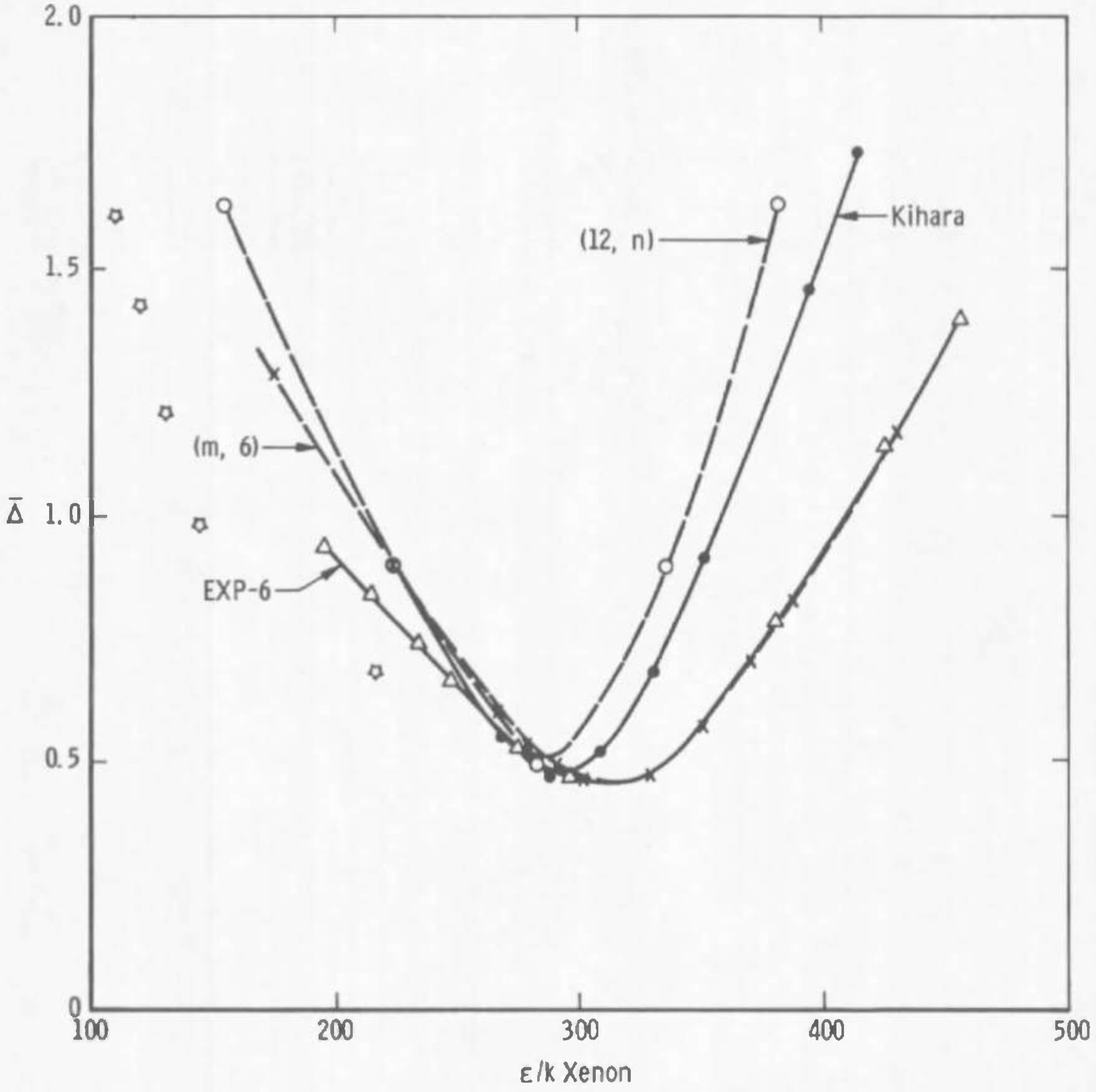

Figure 5a The Minimum Deviation $\bar{\Delta}$ versus the Corresponding Value of ε/k for Xenon

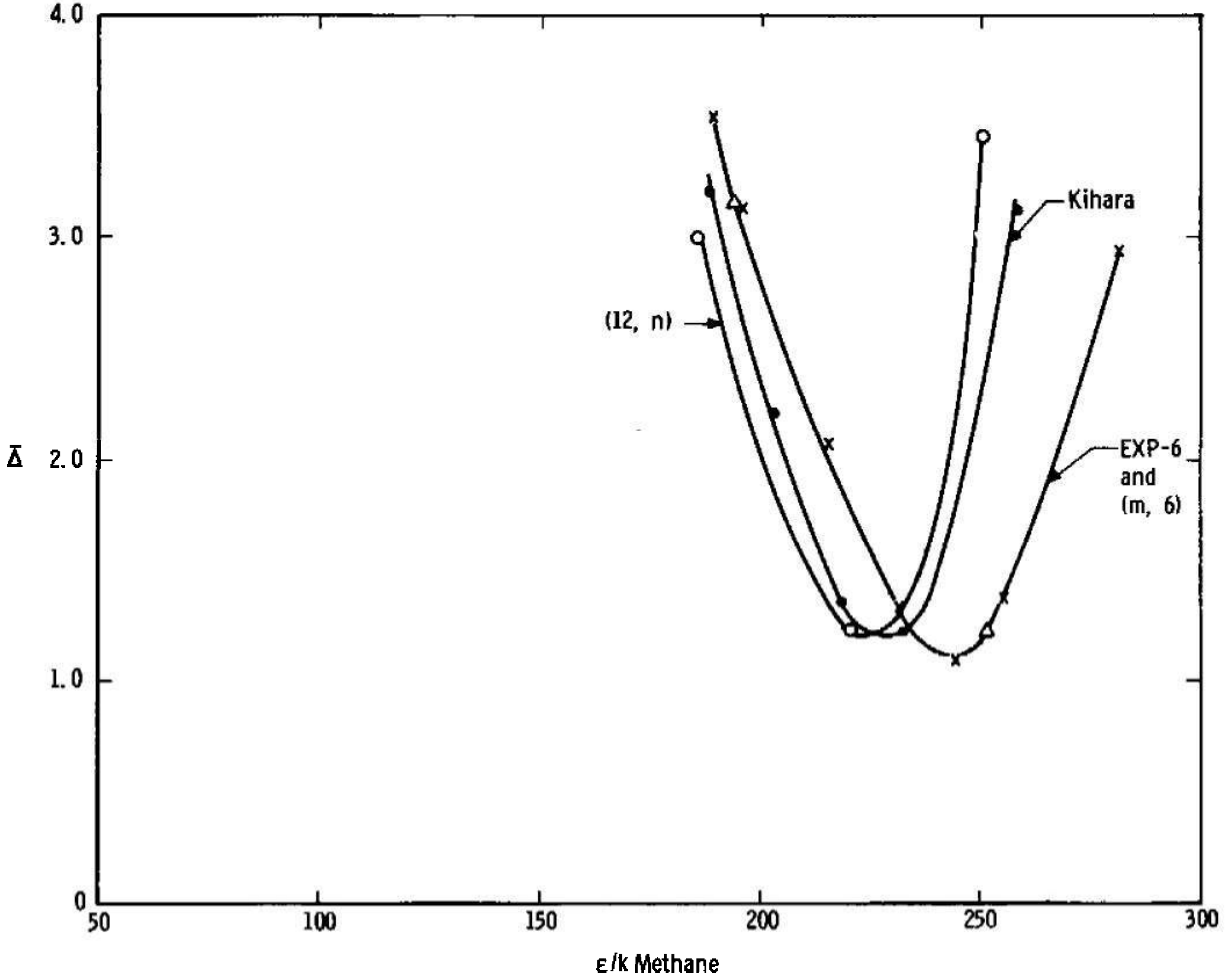

Figure 5b The Minimum Deviation $\overline{\Lambda}$ versus the Corresponding Value of ϵ/k for Methane

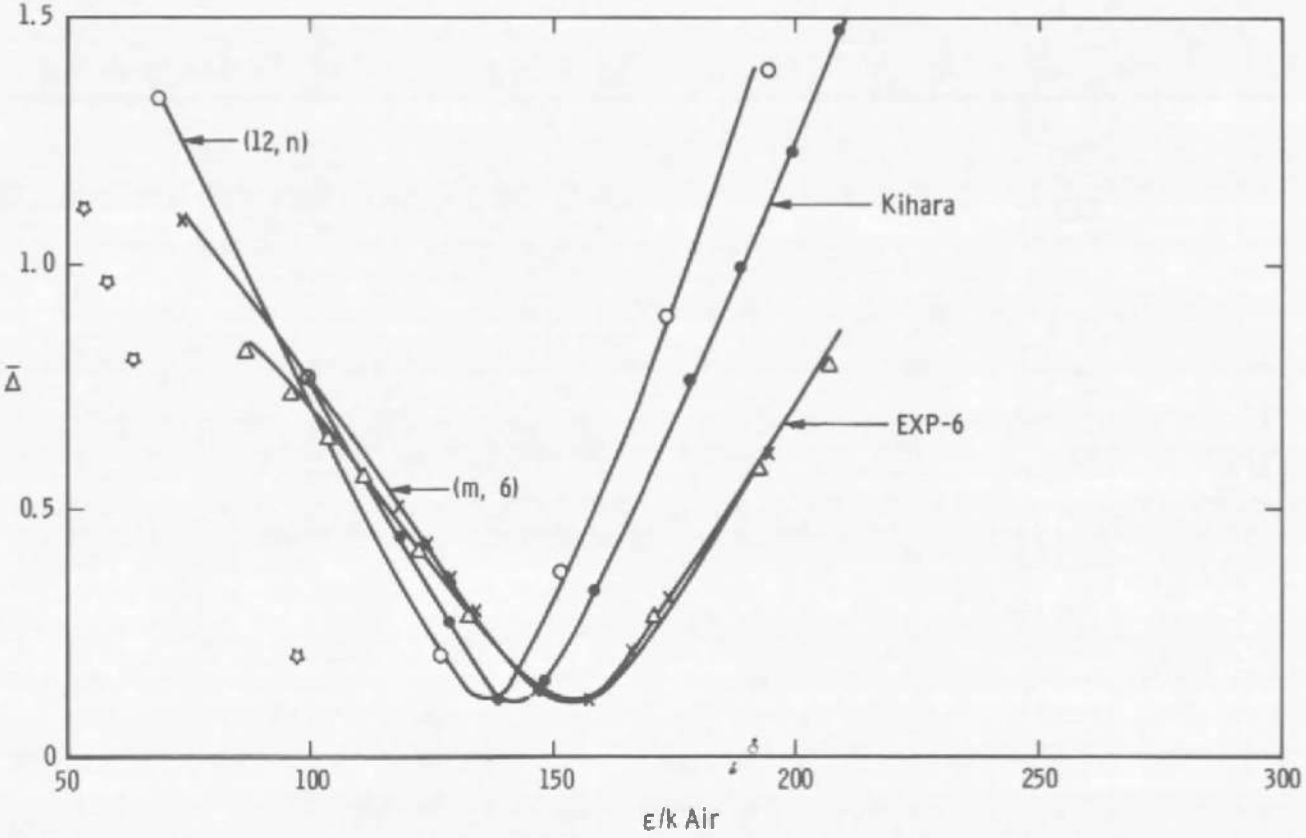

Figure 5c The Minimum Deviation $\bar{\Delta}$ versus the Corresponding Value of ϵ/k for Air

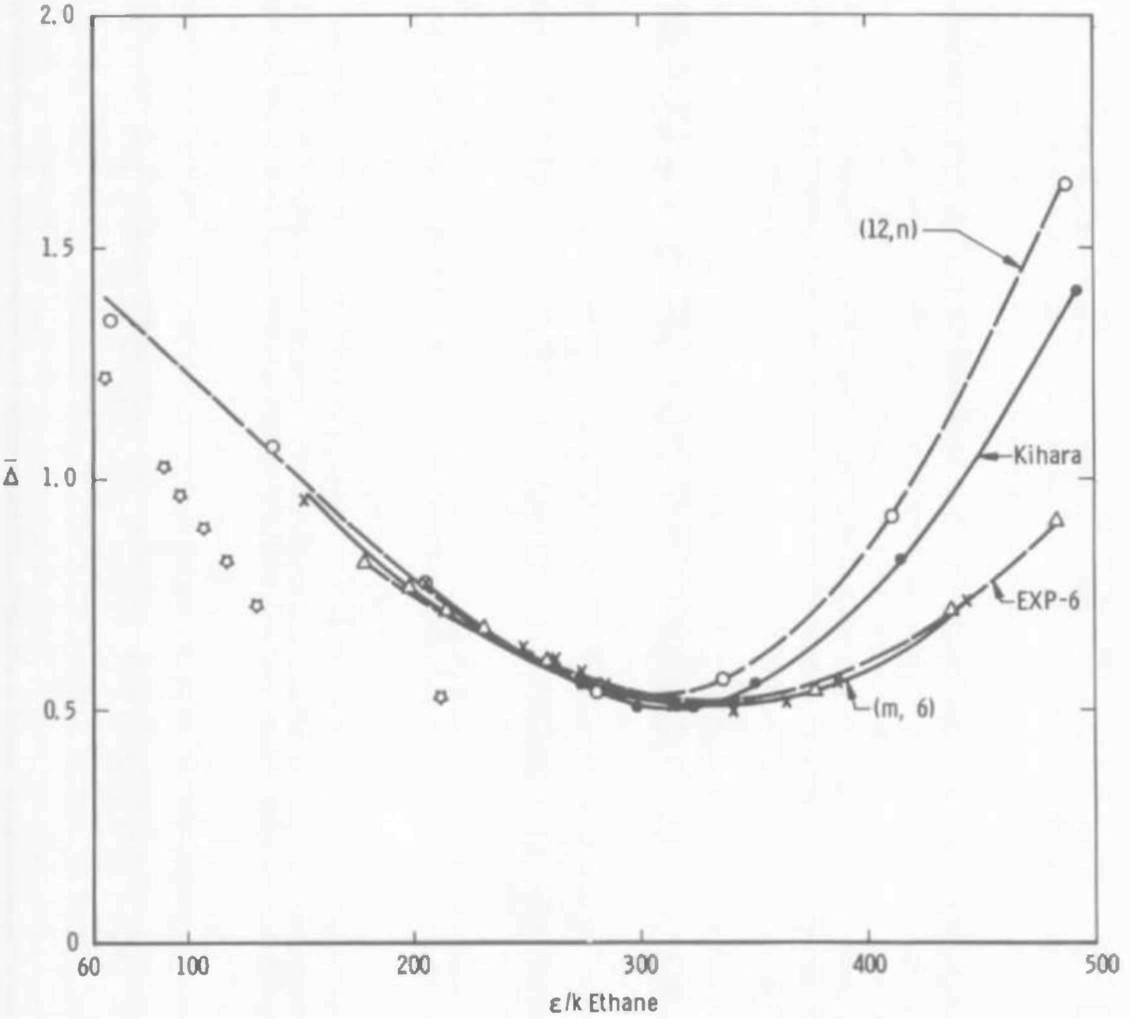

Figure 5d The Minimum Deviation $\bar{\Delta}$ versus the Corresponding Value of ε/k for Ethane

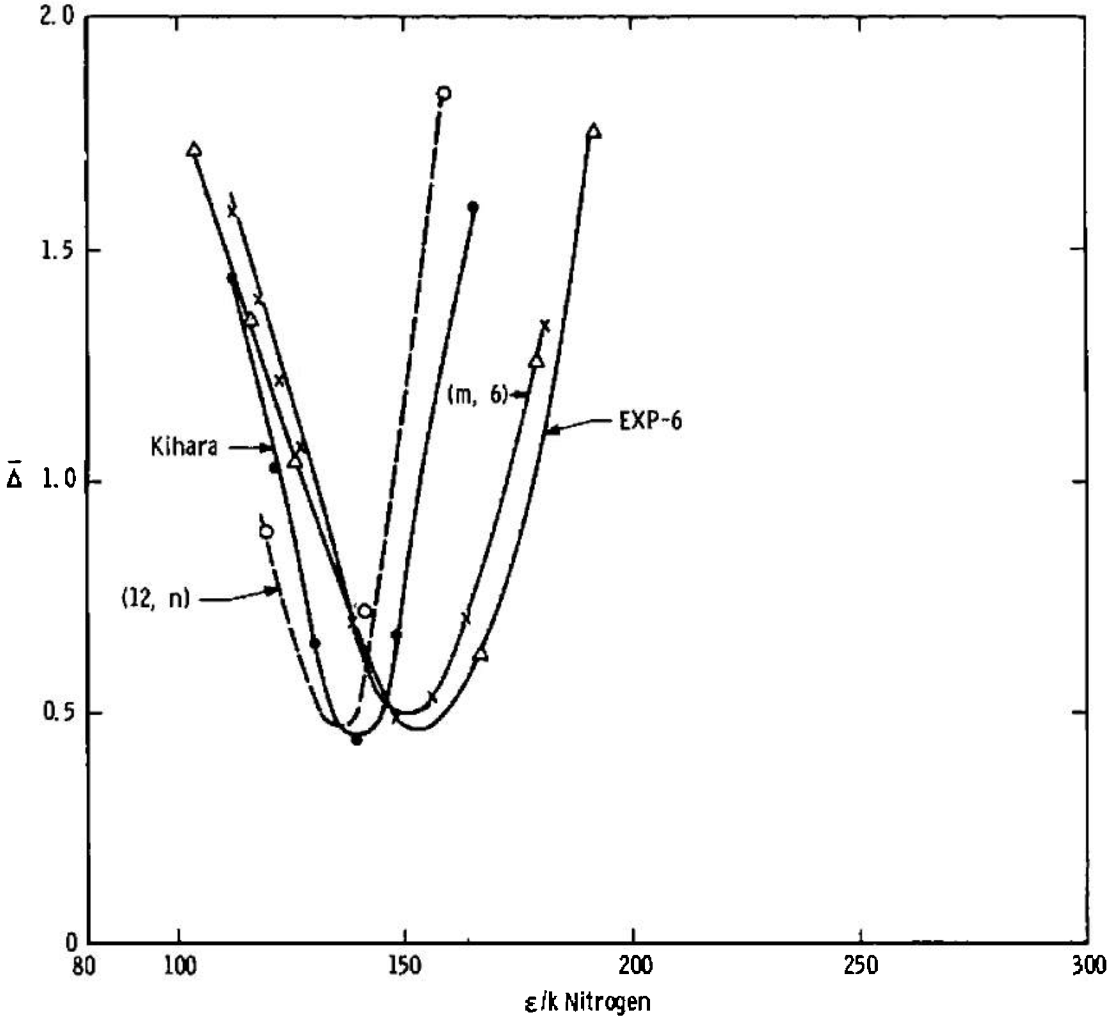

Figure 5e The Minimum Deviation $\bar{\Delta}$ versus the Corresponding Value of ϵ/k for Nitrogen

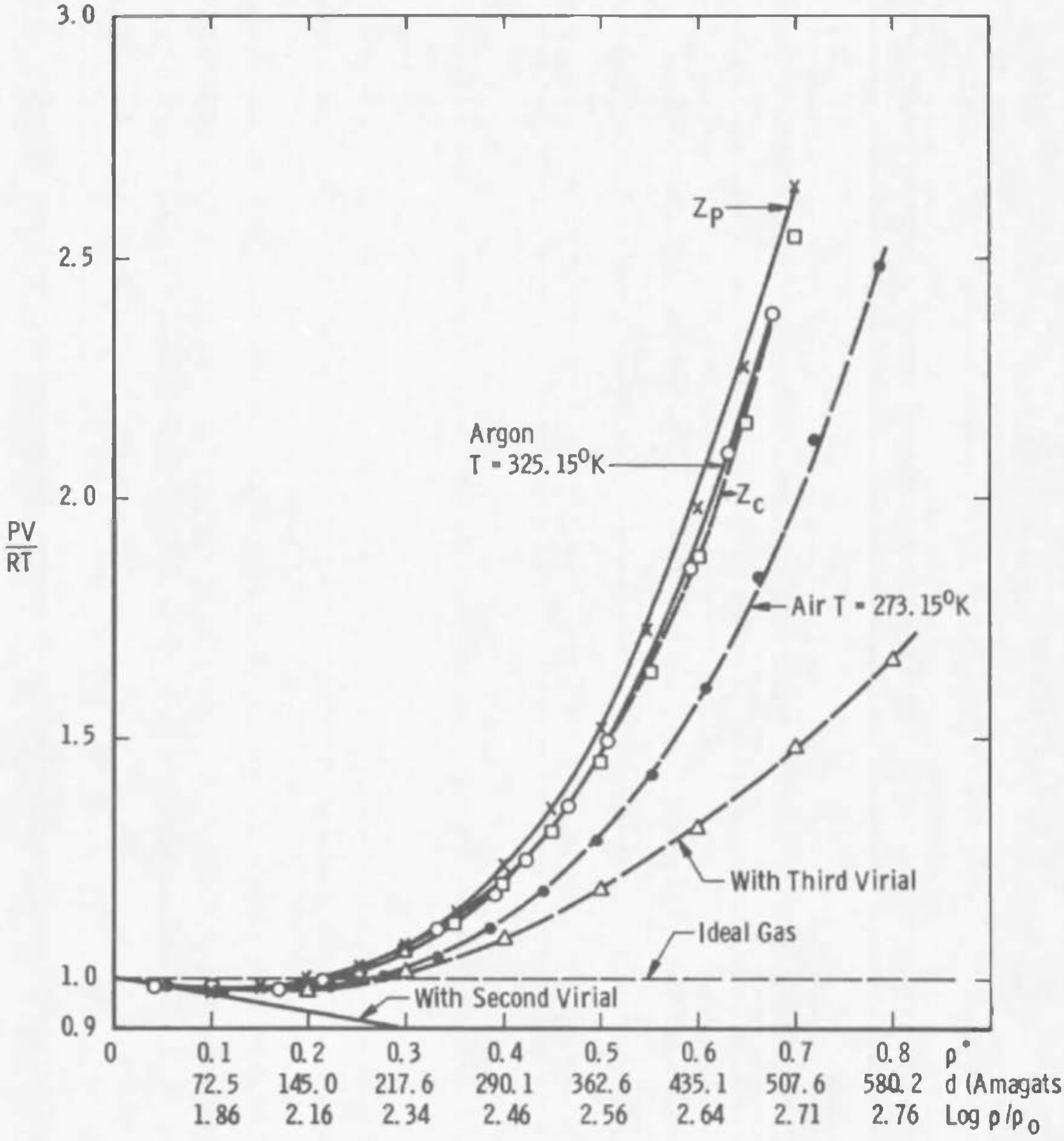

Figure 6 The Percus-Yevick Equations of State for the (12,6) Potential Function at $T^*_{12,6} = 2.74$ as compared with Experimental Data for Air and Argon

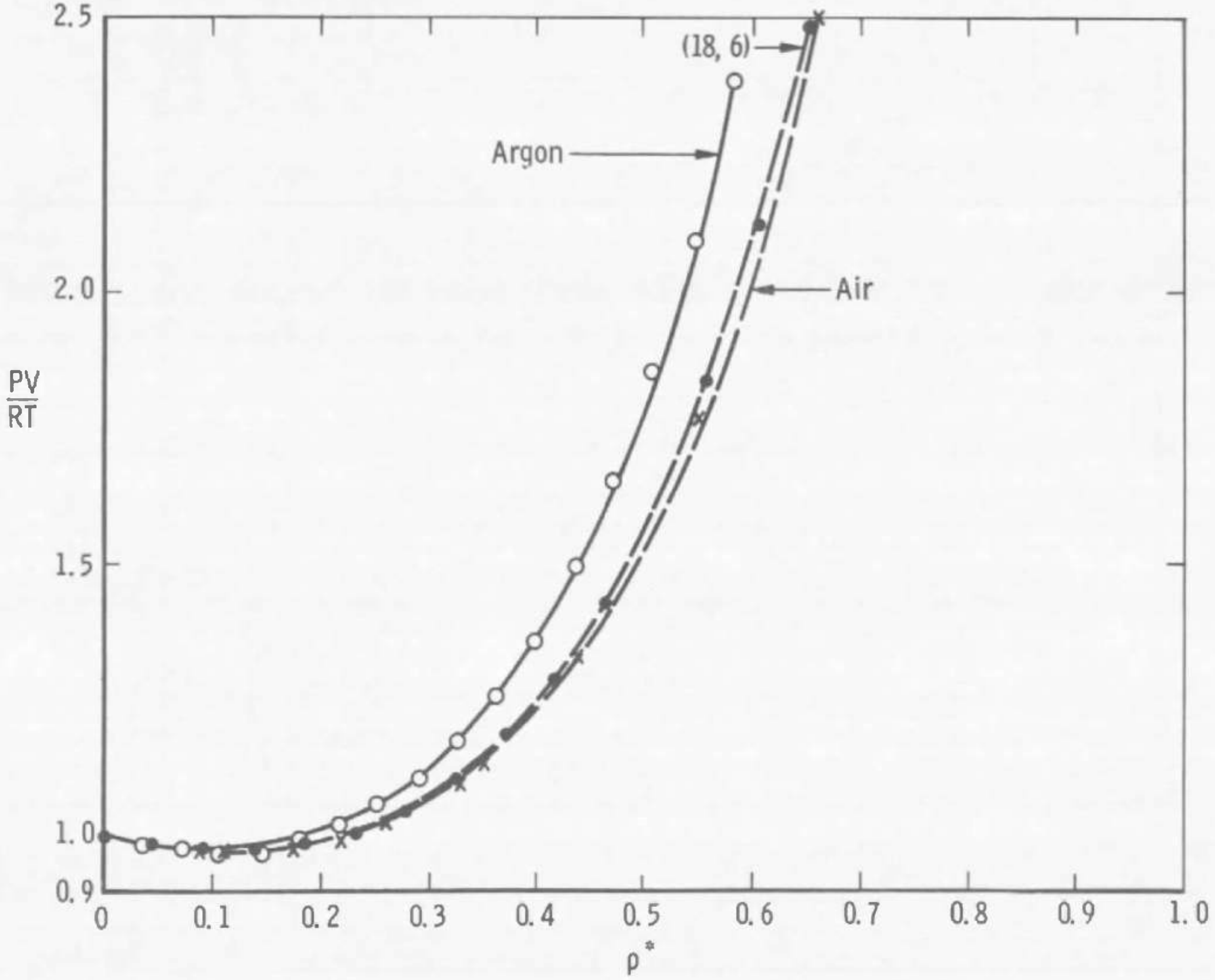

Figure 7 The Percus-Yevick Equations of State for the (18,6) Potential Function at $T^*_{18,6} = 2.0467$ as compared with Experimental Data for Air and Argon

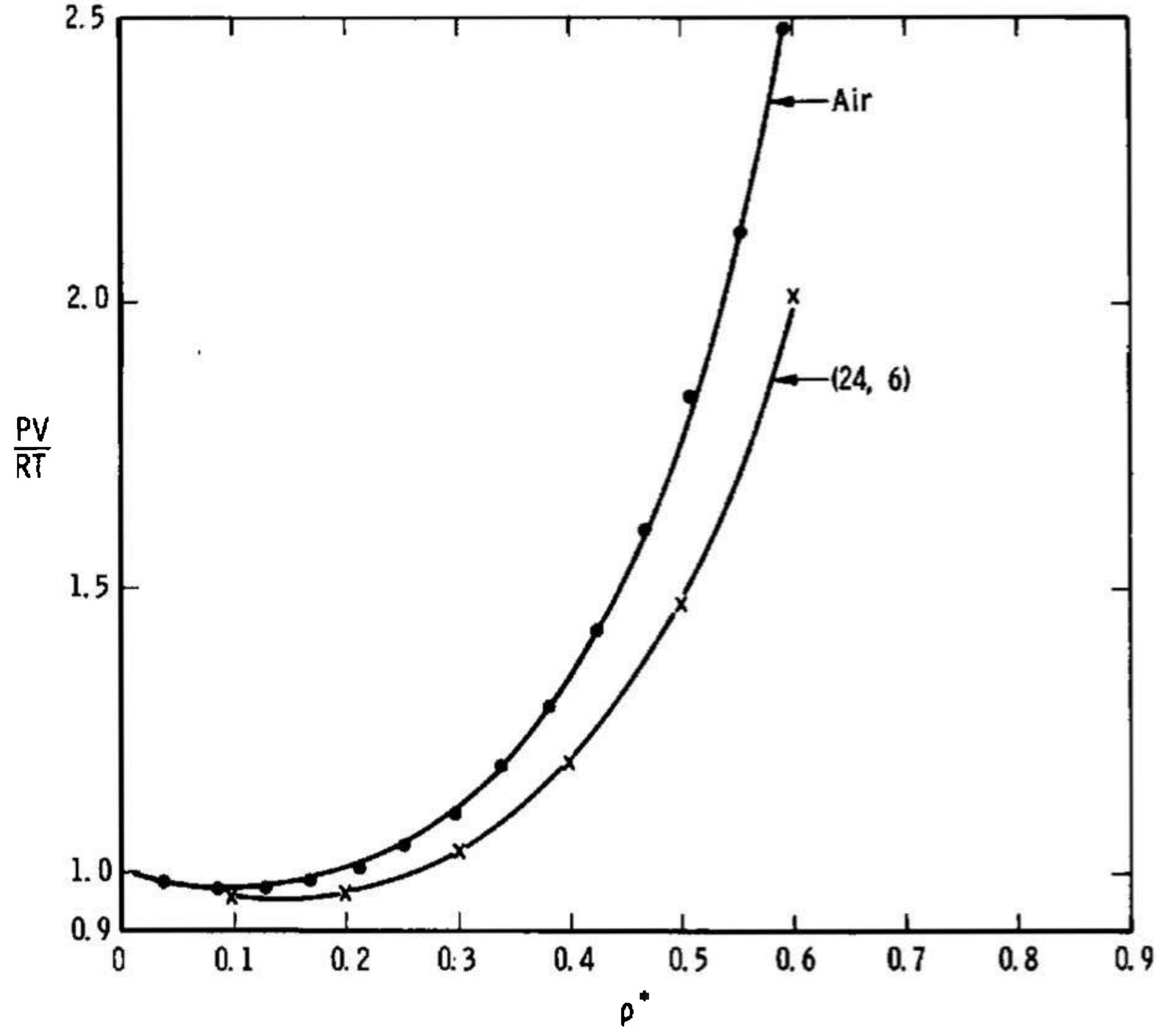

Figure 8 The Percus-Yevick Equations of State for the (24,6) Potential Function at $T^*_{12,6}$ = 1.732 as compared with Experimental Data for Air

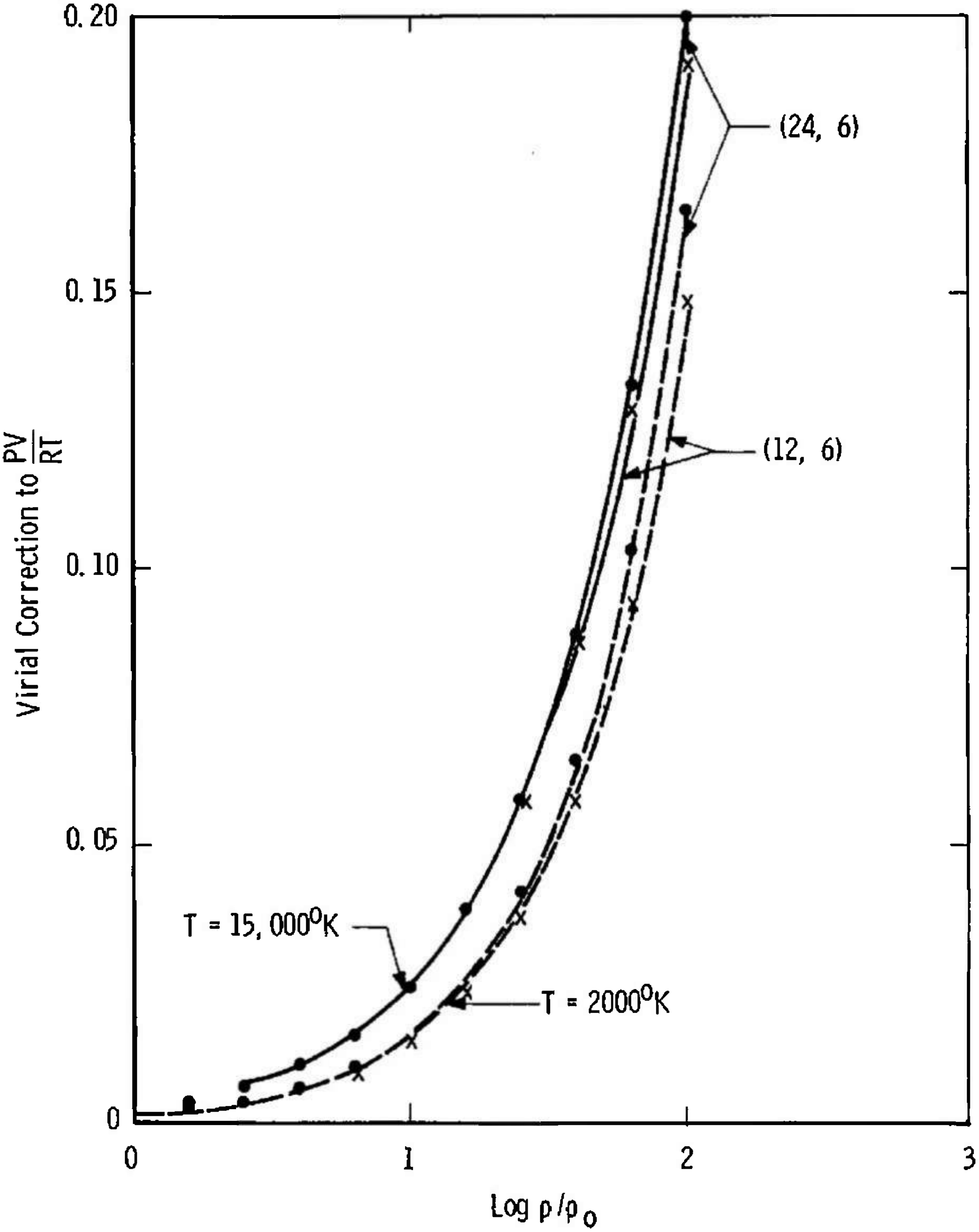

Figure 9 The Effect on the Virial Correction to the Equation of State of Improving the N_2–N_2 Intermolecular Potential Function

APPENDIX

THE DETERMINATION OF INTERMOLECULAR POTENTIAL FUNCTIONS FROM MACROSCOPIC MEASUREMENTS*+

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ABSTRACT

The second virial, adiabatic Joule-Thomson, viscosity, and diffusion coefficients predicted for a number of potentials are compared with those predicted for the (12,6) potential. A quantitative picture, as a function of temperature, is obtained of the ability of each property to act as a probe of the potential function. The transport properties are found to be the most sensitive probes, the Joule-Thomson coefficient next, and the second virial coefficient least, the last property being essentially useless in the range $2.0 < T^* < 8.0$ on the (12,6) reduced temperature scale.

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INTRODUCTION

Statistical mechanics provides a molecular foundation for thermodynamics. This results in the expression of thermodynamic properties as functionals of the intermolecular potential functions of the constituent molecules. In principle, given the potential function appropriate to a given system one can calculate all of the thermodynamic properties of that system merely by turning the computational crank. In practice, matters are not so simple both because the relationships to be evaluated are enourmously complicated and because the potential functions are not known with sufficient accuracy.

The most accurate of the statistical mechanical expressions contain N-body potential functions $(N \sim 10^{23})$ which are impossibly difficult to calculate. Simplifying assumptions can be made which often, as in the virial expansion, result in a power series in some parameter (e.g., the density) whose coefficients depend on lower order N-body potentials $(N = 2,3,\ldots)$. Since even the three-body potential is exceedingly difficult to calculate, the assumption of pairwise potential additivity must generally be included. With this assumption, the thermodynamic properties, in the statistical mechanical expressions, can be made to depend on only the pair potential function. Most theories for the further simplification of the complicated expressions proceed from this point on the assumption that the pair potential function is known. These theories result in simpler, but generally still complicated, relationships between the thermodynamic properties and the potential function. The evaluation of such theories can be a formidable task. All too often their final evaluation is obscured [1] considerably by the fact that pair potential functions are, in practice, only imperfectly known.

The intermolecular potential function together with a sufficiently accurate theory can be used to extrapolate far beyond the bounds of available experimental data [2] something which is not possible using completely empirical methods. Such extrapolations are very strongly dependent on the potential function and can be considerably in error when the wrong potential function is used.

Clearly the determination of accurate intermolecular potential functions is of some importance. In this work we have sought to understand some of the methods generally used to determine such functions, particularly with respect to the question of the uniqueness of the potentials obtained. A lack of uniqueness exists when a set of experimental data for a given property can be correlated equally well using the appropriate theory and any of two or more potential functions. When a lack of uniqueness exists, it becomes necessary to attempt to determine if there is a lack of sensitivity inherent in the theoretical quantity itself or if it is lack of experimental precision which makes it possible to fit the data equally well with two or more theoretical curves. These are equivalent to the following two questions. First, how well can the property of interest, in principle, distinguish among potential functions and, second, how well can it distinguish among such functions at the present time, given present day experimental precision. The answer to the first question is a permanent one while the answer to the second one changes as experimental technique is refined, approaching the first answer in the limit of zero experimental error. We have restricted ourselves to the first question and discuss the second one only in passing mainly to place our results in a practical light. The answer to the first question is of considerable practical importance since it points out where refined experimental techniques will not produce more information about the potential function.

In principle the pair potential functions can be calculated in an a priori fashion using quantum mechanics by calculating the potential energy of two molecules as a function of nuclear separation. Since one needs to consider all the electrons in each molecule, this is also an intractable N-body problem, N now being the total number of electrons involved. This leaves one no alternative but to turn the problem around and determine the potential, in some manner, from experiment. In practice, the procedure is reduced to a semi-empirical one. A functional form is assumed for the potential whose choice is based, in part, on theoretical arguments. In this form are included parameters whose values (and hence the detailed potential) are to be determined from experiment. The parameter determination is made by substituting the potential into statistical mechanical expressions for some macroscopic property and comparing the result with experiment [3]. Best results are to be expected when the theory is one whose dependence on the pair potential is strongly based as is the case, for example, in the low density limit of certain theories.

In this paper we shall discuss the use of the zero-density viscosity, diffusion, and adiabatic Joule-Thomson coefficients and the second virial coefficient as ways of obtaining the potential parameters. For each of these, the pair potential appears in the integrand of an expression for the macroscopic property. This suggests that, given enough experimental data of sufficient accuracy, one might be able to invert the theoretical expressions and determine the potential as a unique functional of the experimental data. For the second virial coefficient, however, Le Fevre and Keller and Zumino [4] have shown that the potential is not determined uniquely by the data, even in principle. In this work we demonstrate this lack of uniqueness quantitatively for particular potentials. We show there to be a lack of uniqueness for each of the macroscopic properties considered, although it is somewhat less pronounced for the transport properties than for the equilibrium properties. For each property, the lack of uniqueness is found to be more pronounced in one temperature range than in another. Strong positive statements can then be made about the temperatures at which experiments designed largely to determine potential functions should not be performed for particular substances. We are also able to show the simultaneous fit of certain of these properties to be sensitive to differences in the potential function.

THE COMPUTATIONAL METHOD

Because of its relative simplicity, we shall use the second virial coefficient to illustrate the details of the computation. The other properties are handled in essentially the same manner. We shall restrict the discussion to two parameter potentials. This is no real restriction since a three-parameter potential can be treated as a family of two parameter potentials, one for each value of the third parameter.

The second virial coefficient is related to the potential function, φ, by the relation [3]

$$B(T) = b_o\, B^*(T^*) = b_o \int_0^\infty \left[\exp\left(-\frac{\varphi^*(r^*)}{T^*}\right) -1\right] r^{*2}\, dr^* \qquad (1)$$

where $b_o = \frac{2\pi N\sigma^3}{3}$, $T^* = kT/\varepsilon$, $\varphi^* = \varphi/\varepsilon$, and $r^* = r/\sigma$. Here, as usual, σ is a characteristic length related to φ and ε is the depth of the potential well. N is Avogadro's number. For a given potential, a given T, and in the left-hand side, a given experimental value of B at that T, (1) contains only the two unknowns σ and ε. In this work, in place of experimental $B(T)$ values, we supply to the left-hand member of (1) the second virial coefficient for a potential function other than the one appearing in the right-hand side. Thus, if the subscripts 1 and 2 refer to the two potentials, (1) becomes

$$B(T) = (b_o)_1\, B_1^*(T_1^*) = (b_o)_2\, B_2^*(T_2^*)$$

or

$$B_1^*(T_1^*) = \frac{(b_o)_2}{(b_o)_1} \int_0^\infty \left\{\exp\left(-\frac{\varphi_2^*(r^*)}{T_2^*}\right) -1\right\} r^{*2}\, dr^*$$

where $B_1^*(T_1^*)$ is a functional of $\varphi_1^*(r^*)$. Now $T_1^* = kT/\varepsilon_1$ and $T_2^* = kT/\varepsilon_2$

hence, for a given T, $T_2^* = \frac{\varepsilon_1}{\varepsilon_2} T_1^*$ so that

$$B_1^*(T_1^*) = \frac{(b_o)_2}{(b_o)_1} \int_0^\infty \left\{\exp\left(-\frac{(\varphi_2^*(r^*)\varepsilon_2}{T_1^*\varepsilon_1}\right) -1\right\} r^{*2}\, dr^* \qquad (2)$$

This is an equation containing two unknowns, namely, the ratios $\frac{\varepsilon_2}{\varepsilon_1}$ and $(b_o)_2/(b_o)_1$. These ratios are completely determined, given another equation connecting some other functional of the potential for the two potentials. We have taken, for this second functional, the first derivative of B with respect to the logarithm of T [5]. We thus determine, <u>at each temperature</u>, that pair of ratios, ϵ_2/ϵ_1 and $(b_o)_2/(b_o)_1$ which results in the equality, for the two potentals, of both the second virial coefficient and its first derivative with respect to the logarithm of the temperature. Ordinarily, the ratios are different at different temperatures, hence we shall actually determine their temperature dependence. By dividing the equation which represents the requirement of equality of the first derivatives by that representing the equality of the second virial coefficients themselves, one obtains a single equation for the equality of the logarithmic derivatives. The working equation becomes

$$\frac{d \ln B_1^*(T_1^*)}{d \ln T_1^*} = \frac{d \ln B_2^*(T_2^*)}{d \ln T_2^*} \tag{3}$$

This is a single implicit equation in the ratio ϵ_2/ϵ_1, the dependence on $(b_o)_2/(b_o)_1$ being removed in the process of differentiating the logarithm.

On the substitution of the set of values $B_1^*(T_1^*)$ in the left-hand member, (2) becomes a family of curves for the ratio ϵ_2/ϵ_1, as a function of the ratio $(b_o)_2$ $(b_o)_1$, one curve for each value of T_1^* [7]. These can also be used for obtaining information about the potential function [8], although the results so obtained cannot be easily presented in a manner suitable for our purposes. We have therefore used a different approach.

We have computed, for each of a number of potentials, B^* and $B'^* = T^* \left(\frac{dB^*}{dT^*}\right)$ and from these

$$S = \frac{T^*}{B^*}\frac{dB^*}{dT^*} = \frac{B'^*}{B^*} = \frac{d \ln B^*}{d \ln T^*}.$$

These are used to solve (3) in the following way. Each value of T_2^* has associated with it a value S_2. Using inverse interpolation, the value of T_1^* is found for which $S_1 = S_2$. The ratios ϵ_2/ϵ_1 and $(b_o)_2/(b_o)_1$ are then computed simply from

$$\frac{\epsilon_2}{\epsilon_1} = \frac{T_1^*}{T_2^*} \quad \text{and} \quad \frac{(b_o)_2}{(b_o)_1} = \frac{B_2^*(T_2^*)}{B_1^*(T_1^*)}$$

This procedure can be illustrated graphically with the help of Figures 1 and 2. These contain plots of S for the second virial coefficient [9] versus the logarithm of the reduced temperature for several representative potential functions. Temperatures below the Boyle temperature appear in Figure 1, those above that temperature in Figure 2. Note that the S values for each potential are plotted against the logarithm of the reduced temperature <u>for that potential</u>. Equation (3) is solved graphically at each T_1^* by measuring the horizontal distance between the ordinate associated with T_1^* on curve 1 and the same ordinate on curve 2. This distance is then just

$$\log T_2^* - \log T_1^* = \log(T_2^*/T_1^*) = \log(\epsilon_1/\epsilon_2).$$

It should be noted that where there are values of S_2 greater than the maximum S_1 value, solution of (3) is impossible. This occurs (see Figure 1) for the (9,6) potential compared to the (12,6).

Note that both the value and slope of B_1^* are fit by B_2^* at T_1^*. It follows, therefore, that B_2^* will actually produce a relatively good fit to B_1^* in a small neighborhood around T_1^* for the parameter ratio obtained by solving (3) at T_1^*. Furthermore, when this ratio is found to be independent of T_1^* over a range of values of T_1^*, B_2^* provides an excellent fit to B_1^* over that range.

In this calculation, the Boyle temperature serves as a natural dividing point between two temperature ranges. Since B is zero at that temperature, the derivatives in (3) are not defined. Furthermore, since B changes sign while $\frac{dB}{dT}$ does not, S also changes sign. Hence, values of S taken from temperatures above the Boyle temperature for one potential cannot possibly be made to fit those taken from below it for the other potential. Therefore, we have treated these two ranges separately coming as close to the Boyle temperature as desired from either side.

As mentioned in the introduction, the zero density adiabatic Joule-Thomson, viscosity, and diffusion coefficients are also considered here. These are also treated as outlined above. The equation (3) for each of these is replaced in turn by the requirement that the quantities $\frac{d \ln [\mu C_p^{(0)}]}{d \ln T^*}$ for the adiabatic Joule-Thomson coefficient, $\frac{d(\ln \eta T^{*-1/2})}{d \ln T^*}$

for the viscosity, and $\frac{d \ln[DT^{*-3/2}]}{d \ln T^*}$ for the diffusion coefficient by equal for the two potentials. Now [3] $\mu^* C_p^{(o)} = T^* \frac{dB^*}{dT^*} - B^* = B'^* - B^*$ so that the connection between this quantity and the potential function is essentially the same as between the second virial coefficient and the potential. From this last, $T^* \frac{d}{dT^*} [\mu C_p^{(o)}] = B''^*$ and

$$\frac{d \ln [\mu C_p^{(o)}]}{d \ln T^*} = \frac{B''^*}{B'^* - B^*}$$

where $B''^* = T^{*2} \frac{d^2 B^*}{dT^{*2}}$. Here, as with the second virial coefficient, there is a temperature which divides the calculation into two parts. Now, however, the zero density inversion temperature (defined by $B'^* = B^*$) plays the role previously played by the Boyle temperature.

The connection between the viscosity and diffusion coefficients and the intermolecular potential function is contained in the so-called collision integrals [3]

$$\Omega^{(\ell,s)*}(T^*) = \frac{2}{(s+1)!\, T^{*(s+2)}} \int_0^\infty e^{-g^{*2}/T^*} g^{*(2s+2)} Q^{(\ell)*}(g^*)\, dg^*$$

where

$$Q^{(\ell)*}(g^*) = \frac{2}{1-\frac{1}{2}\,\frac{1+(-1)^\ell}{1+\ell}} \int_0^\infty (1 - \cos^\ell \chi)\, b^*\, db^*$$

with the intermolecular potential function being contained in the equation for the scattering angle

$$\chi\,(g^*,b^*) = \pi - 2b^* \int_{r_m^*}^\infty \frac{dr^*/r^*}{\sqrt{1 - b^{*2}/r^{*2} - \phi(r^*)/g^{*2}}}$$

r_m^* being the distance between a pair of molecules at the time of closest approach.

In terms of these, the zero density viscosity and diffusion coefficients can be written [3]

$$\eta T^{*\,-1/2} = \frac{C_a}{\Omega^{(2,2)*}(T^*)} \quad , \quad DT^{*\,-\frac{3}{2}} = \frac{C_b}{\Omega^{(1,1)*}\,(T^*)}$$

where C_a and C_b are constants whose precise values are of no particular interest here. It can be easily shown that

$$\frac{d \ln \Omega^{(\ell,j)*}}{d \ln T^*} = (j+2) \frac{\Omega^{(\ell,j+1)*}}{\Omega^{(\ell,j)*}} - (j+2).$$

From this it follows that, for the viscosity, equation (3) is replaced by the requirement that $4 \frac{\Omega^{(2,3)*}}{\Omega^{(2,2)*}} - 4$ be equal for the two potentials. For the diffusion coefficient, on the other hand, the quantity $3 \frac{\Omega^{(1,2)*}}{\Omega^{(1,1)*}} - 3$ must be equal for the potentials. Since η and D are each non-zero, there is no dividing temperature analogous to the Boyle temperature for these properties. The S values corresponding to these properties are plotted in Figs. 3 and 4.

The macroscopic properties of most experimental systems have been correlated using the (12,6) potential function [10]. As a result ϵ/k values for that potential can be found in the literature for just about all possible systems of interest. Furthermore, it has been shown that, for very many substances, a very simple relationship exists between the ϵ/k value for the (12,6) potential and the temperatures for the critical and normal boiling points for that substance [3,10,11]. As a result, good first guesses for the ϵ/k values for the (12,6) potential can be made for any system for which either the critical temperature or normal boiling point is known. For these reasons we have chosen to compare each potential with the (12,6) function using the reduced temperature for the latter as the reference temperature T_1^*. The conversion to real experimental temperatures for any system merely requires multiplication by the (generally available) ϵ/k value of the (12,6) potential for that system.

RESULTS

The Second Virial Coefficient

Our results for the second virial coefficient are given in Figs. 5-8 as plots of the ratios ϵ_2/ϵ_1 versus the Lennard-Jones (12,6) reduced temperature. Figure 11 contains plots of the ratio $(b_o)_2/(b_o)_1$. The potential functions considered are the following:

(1) The (m,n): $$\phi^*(r^*) = \frac{\phi(r)}{\epsilon} = \left\{\frac{1}{\frac{n}{m}^{\frac{m}{m-n}} - \frac{n}{m}^{\frac{n}{m-n}}}\right\}\left[\left(\frac{1}{r^*}\right)^m - \left(\frac{1}{r^*}\right)^n\right]$$

where $r^* = r/\sigma, \sigma$ is that value of r for which $\varphi^* = 0$.

(2) The Kihara: $$\phi^*(r^*) = \infty,\ r^* \leq \gamma^*$$
$$\phi^*(r^*) = 4\left[\left(\frac{1}{r^*-\gamma^*}\right)^{12} - \left(\frac{1}{r^*-\gamma^*}\right)^6\right],\quad r^* > \gamma^*$$

where $r^* = \frac{r}{\sigma-2a}$ and $\gamma^* = \frac{2a}{\sigma-2a}$, a being the core radius.

(3) The Exp-6: $$\phi^*(r^*) = \frac{1}{1 - 6/\alpha}\left[\frac{6}{\alpha}\exp\left(\alpha(1-r^*)\right) - \left(\frac{1}{r^*}\right)^6\right]$$

where $r^* = r/r_m$, r_m being that value of r for which $\varphi^* = -1$

(4) The Square Well:

$$\varphi^*(r^*) = \infty,\ r^* \leq 1$$

$$\varphi^*(r^*) = -1,\ 1 \leq r^* \leq R^*$$

$$\varphi^*(r^*) = 0,\ r^* \geq R^*$$

where $r^* = r/\sigma$.

Figure 5 contains results for the (m,6) and square well potentials, while results for the exp-6 and Kihara potentials are contained in Figs.

6 and 7. Results for the (12,n) appear in Figure 8. Each curve represents the comparison between a potential and the (12,6) potential, the subscript 2 always referring to the former potential. For each curve there is a smooth transition through the Boyle temperature indicating that the singularity in S at that temperature presents no problem. There exists, for each potential, a temperature range around the Boyle point such that in that range ϵ_2/ϵ_1 is essentially independent of T^*. This means that, for temperatures in that range, the (12,6) and the potential with which it is compared are equivalent [12]. In fact, each curve is flat to such an extent in this range that a choice cannot be made between the (12,6) potential and the one with which it is compared based on experimental second virial coefficient data taken entirely within the range, even when these data are obtained with an impossibly high precision. What is particularly striking is that there is a single temperature range in which all the curves are flat. This range becomes exceedingly large if one does not include the square well potential in the comparisons. Obviously, there is a reduced temperature regime in which the second virial coefficient is particularly useless as a probe of the potential function. What these results show specifically is that the second virial coefficient cannot be used in this range to distinguish among any of the members of the (m,6), exp-6, Kihara, (12,n), and square well families of potentials. The list would presumably have been broadened had we considered other classes of functions.

Of considerable interest are the results obtained when the (12,n) potentials are compared with the (12,6). The curves obtained for these are essentially the same as those for the (m,6) emphasizing the fact that the second virial coefficient cannot be used to determine the exponent of the attractive part of the potential. The requirement that the attractive exponent be 6 is, rather, a restriction placed on the potential based on a priori information, at least for the second virial coefficient. Thus, we see that the second virial coefficient is determined by the general shape of the potential and not necessarily by its details. This has previously been demonstrated formally by Le Fevre [4] and by Keller and Zumino [4]. They showed that all potentials for which the sum of a certain pair of integrals, one over the repulsive part and one over the attractive part, were equal yielded the same second virial coefficient. A special case of their result is that all potentials with the same repulsive part and whose attractive parts have the same width as a function of depth (i.e., but whose bowls are possible displaced laterally) yield the same second virial coefficient.

At temperatures outside the flat portion, the ratio ϵ_2/ϵ_1 is no longer constant. Below $T^* = 2.0$ a particularly rapid variation is indicated. The origin of this rapid variation can be seen in Fig. 1 to be due to large differences in the slopes of the corresponding S curves for equal values of the ordinate. According to Fig. 1, there are also potentials for which there is a temperature range in which there are S values larger than the maximum S value of the (12,6) potential. The (9,6) function is an example. In such cases, solution of (3) is impossible. In other words, no ratio ϵ_2/ϵ_1 exists by means of which one can obtain simultaneous equality of both B and $T \frac{dB}{dT}$ for the two potentials.

The existence of a rapid variation of ϵ_2/ϵ_1 with T^* at low temperatures would seem to indicate a very strong sensitivity, at such temperatures, to differences in the potential functions. Inability to solve (3) indicates an even stronger sensitivity to such differences. However, the sensitivity indicated applies strictly to exact data and the exact simultaneous fit of B and $T \frac{dB}{dT}$. As the requirement on the exactness of the fit is relaxed, the sharpness of the variation of ϵ_2/ϵ_1 with T^* is reduced. The introduction of these uncertainties in effect replaces each S curve of Fig. 1 by an area bounded by two S curves. One has then to compare two broadly defined S areas rather than two sharply defined S curves. This can make an overlap of ordinates possible near the maximum of the (12,6) curve and hence make solution of (3) possible where it previously was not. Furthermore, in comparing the two S areas one has the possibility of choosing the two S curves, one within each area, whose slopes are most nearly alike. This could result in a reduction in the rapid variation of ϵ_2/ϵ_1 with T^* at low temperatures. For application to inherently imprecise experimental data, the low temperature region therefore becomes a much less sensitive probe of the potential than is indicated in Fig. 5. That is, an approximate fit to an accuracy compatible with experimental error might be possible where an exact fit, as indicated by Figs. 1 and 5, is impossible or, at best, difficult.

There is another, more fundamental reason why the rapid variation of ϵ_2/ϵ_1 with T^* at low temperatures does not necessarily mean a sensitivity to differences in the potential functions. In this calculation, we have required the equality of both the second virial coefficient and its slope for the two potentials. This applies a much more stringent condition on the functions than is required in the correlation of experimental data. In the latter case, it is asked only that the theoretical values of B(T) come as close as possible to the experimental ones. Nothing is asked of the slope of the second virial coefficient. Clearly two functions may each fit the data within experimental precision, yet their slopes may disagree by considerably more than the precision of the present calculation.

On the other hand, the fact that we place such strong conditions on the potential enables us to make strong statements where the second virials and their first derivatives for the potentials are essentially indistinguishable from each other. Obviously where our calculations cannot distinguish between potentials, a correlation which makes use of experimental data will be able to distinguish between them to a much lesser extent. Clearly, therefore, experiments designed to measure the second virial coefficient for purposes of learning something about the potential function should never be carried out above $T^* = 2.0$ on the (12,6) scale. In fact, existing data in that range should not be included in a determination on potential parameters since such data will supply experimental error without supplying any discrimination and so will reduce, for example, the ratios of the standard deviations obtained from fits of different potentials. This reduced temperature is easily converted to real temperatures for a particular substance given the ϵ/k value for the (12,6) potential for that substance. For example, for argon, the data must have been taken at $T < 240°K$ while for xenon, the corresponding requirement is $T < 450°K$.

It is clear from Figures 5 and 6 that in each class (i.e., square well, exp-6, etc.) there exists a potential for which the ratio ϵ_2/ϵ_1 is essentially independent of T^* even at low temperatures. For the exp-6 this occurs for α slightly larger than 13. For the square well, it occurs for R^* approximately equal to 1.82. One expects this also to be true for other classes of three parameter potential classes of which the (12,6) is not a member. That is, there will exist a member of each such class which is equivalent to the (12,6) in predicting the second virial coefficient over a large temperature range including low temperatures. Since the (12,6) potential function was chosen as the reference potential in an entirely arbitrary fashion, there is no need to restrict this result to it. Thus, one can actually state that given any potential function, it is possible to find in every three parameter family of functions of which it is not a member, a potential function with which one can obtain a classical second virial coefficient whose value and slope differ from those calculated with the given potential by an amount much less than the best available experimental precision over a temperature range starting at extremely low temperatures and extending to temperatures will above experimental conditions for almost all substances. In short, the second virial coefficient is seen to be at best a three parameter quantity with regard to the potential function and any attempt to use functions with more parameters necessarily leads to redundancies. This is presumably what is behind the inability to obtain unique parameters in recent attempts to determine the potential function from second virial coefficient data using many parameter potential functions.

As expected, deviations from this can occur at high temperatures. That is, where the repulsive parts of the potentials differ sufficiently in character, the high temperature region can be used to choose among different classes. Thus a choice can be made between the extremely different (12,6) and square well potentials if the data covers a range above $T^* = 7.0$ on the (12,6) temperature scale. A choice between the somewhat less different exp-6 and (12,6) potentials, on the other hand, requires data at $T^* > 10.0$ on the same scale. These are very high temperatures for most substances. For argon this latter requirement is $T > 1200°K$ while for xenon it is $T > 2250°K$.

The ratio $(b_o)_2/(b_o)_1$ for the second virial coefficient behaves in essentially the same way as does ϵ_2/ϵ_1. There is, therefore, no need to discuss its behavior separately.

Attempts to select, from several functions, a potential function for a particular system have sometimes been based on fits to second virial coefficient data which lie almost entirely within the flat portions of

Figs. 5-8. Examples are the correlations of Whalley and Schneider [13] and of Mason and Rice [14]. In Table I we have reproduced the standard deviations obtained by Whalley and Schneider for several potential functions. Note that only in the case of xenon, where half of the points lie outside the flat portions of Figs. 5-8, is there a strong discrimination among the potential functions. For the krypton data, one certainly has no basis for the selection of one potential over another while for argon the choice is, at best, a marginal one.

From our results one can also see the futility of basing the choice of a potential function on the basis of the best fit of experimental data to a single two parameter function. To demonstrate this, let us take as an experimental system that system whose intermolecular potential function is exactly the (12,6) function. Figure 6 then represents an attempt to fit the "experimental" second virial coefficients to those predicted for the exp-6 potential. The best fit is obtained for that potential which gives the most nearly flat curve in Fig. 6. According to that figure, this best fit occurs for a value of α slightly greater than 13. The potential function defined by that value of α and the pair of parameters which give this best fit can then be associated with our "experimental" system and possibly used as such in other theories. Suppose now that instead of doing fits for a series of values of α we had just done the fit for a single value of α. Clearly, for every value of α, a pair of parameters exists which gives the best fit to the "experimental" data for that value of α. However, the potential represented by that value of α and this pair of parameters could not in general be associated with the experimental system unless the application is to a theory only weakly dependent on the potential, since the second virial coefficient associated with that function does not properly represent the low temperature second virial coefficient data. It is clear from Fig. 6, therefore, that one must take the best fit of experimental data to a series of two parameter potentials (here the family of functions generated by varying the third parameter, α) before assigning a particular potential to the experimental system. Unfortunately, the literature is full of fits of data to single potential functions, particularly to the (12,6) potential. Quite often the resulting potential has been used as the intermolecular potential functions for particular systems in evaluations of theories [15]. According to our results one must be suspicious of conclusions as to the relation between the particular theory and experiment, based on such work, unless the theory is known to depend only weakly on the potential function.

THE ZERO DENSITY ADIABATIC JOULE-THOMSON COEFFICIENT

This quantity is obtained directly as the zero density limit of experimental free expansion data. To obtain the second virial coefficient, on the other hand, one must first, in some manner, differentiate the experimental P-V-T data with respect to the density and then take the zero density limit. As a result, given the same experimental precision, one obtains the latter with much less precision than the former. This is not a real advantage for the free expansion data at the present time, however, since such data can be obtained only with a precision orders of magnitude below that possible in P-V-T work, particularly at low densities.

The adiabatic Joule-Thomson coefficient depends both on the second virial coefficient and its first derivative. Clearly, where two second virial coefficients, one for each of two potentials, are indistinguishable over an extended temperature range, their first derivatives are also indistinguishable, at least for temperatures near the center of this range. Furthermore, this will be true for exactly the same parameter ratios. Differences which occur for the second virial coefficients near the edge of this temperature range necessarily appear as larger differences in their derivatives. Thus, one expects the range of equivalence for two potentials to be smaller for the zero density Joule-Thomson coefficient than it is for the second virial coefficient. Results of this quantity are contained in Figs. 7 and 8. As expected, the range of equivalence of the potentials is shorter. It should be remembered that, since our method involves equating a property and its first derivative, equivalence here includes the second derivative of the second virial coefficient.

THE ZERO DENSITY VISCOSITY AND DIFFUSION COEFFICIENTS

The ϵ_2/ϵ_1 ratios for the zero density viscosity and diffusion coefficients are contained in Figs. 6, 7, 9, and 10. The ratios $(b_o)_2/(b_o)_1$ for several potentials are presented in Fig. 11. In Fig. 7, for the Kihara potential, there is no curve for either of these properties which approaches that of the second virial coefficient in flatness. The ratio ϵ_2/ϵ_1, can be called independent of T^* only in a very narrow temperature region about the maximum of the curve. Figure 9 (which is drawn to a different scale) does indicate an increasing degree of flatness with increasing γ. This occurs for relatively high temperature, $T > T_B$, however. This demonstrates the strong role played by the bowl of the potential function in determining the transport properties. For any given potential function, there is a temperature above which the transport properties are entirely dependent on the repulsive part of the potential function. Now, for the Kihara potential function, the position of the hard sphere cut-off moves to larger values of r as γ increases. Therefore, the temperature at which the properties for the Kihara potential become those for a hard sphere should decrease with increasing γ. According to Fig. 9, this is compensated for by the changes produced by the modification of the bowl with increasing γ. The net result is a set of properties (e.g., for $\gamma = 0.6$) more nearly like those for the $\gamma = 0$ (i.e., (12,6)) potential at the highest temperaturees of Fig. 9. Further proof of the strong effect produced by the bowl can be seen in the behavior at low temperatures. At such temperatures, the repulsive part has a very minor effect on the properties. Therefore, the rapid variation in the dependence of ϵ_2/ϵ_1, with T^* as a function of γ at low temperatures is an indication of the marked effect of the bowl on these properties.

The curves in Fig. 10 are most flat for T^* approximately equal to 2.0. It is interesting to note that there is a value of α for which the curve is quite flat at low temperatures as well. This occurs for α slightly larger than 13 for both properties. It should be noted that the corresponding ratio is very close to unity. Furthermore, for essentially the same value of α, a flat curve with essentially the same ordinate obtained down to low temperatures for the second virial coefficient. Note that, unlike the case of the second virial coefficient, for these properties the curve for that value of α is not flat to very high temperatures. For these properties, a significant departure from unity occurs at $T^* = 5.0$, not an impossibly high temperature for many systems. There is a tendency for the curves to flatten out at high temperatures for a value of α larger than 15 under which conditions the curves show a marked deviation from flatness at quite low temperatures. This behavior shows that it may be possible to distinguish between the (12,6) potential and all members of the family of exp-6 functions given experimental transport data of sufficient accuracy which includes both temperature ranges $T^* < 2.0$ and $T^* > 5.0$ on the (12,6) scale. For argon this requires that there be data for $T < 240°K$ and $T > 600°K$ while for xenon $T < 450°K$ and $T > 1225°K$. These conditions are met for argon but not for xenon, at the present time.

It is clear from these results that the diffusion and viscosity coefficients are potentially more sensitive probes of the potential function than either the second virial or Joule-Thomson coefficients given experimental data covering a sufficiently large temperature range. One might not have expected this since the latter properties are more simply related to the potential function than are the former. One might have expected a quantity like the second virial coefficient which is related to the potential function through a single integration to be much more sensitive to differences in that function than one like the transport properties which are connected by three integrations, particularly when the functional dependence in the integrand is also more indirect for the latter than it is for the former.

It must be remembered that the requirement here has been that both the value and slope of the properties be equal for the two potentials. It is possible that some of the apparent sensitivity found for the transport properties comes from the requirement on the slope. Whether or not this disappears when one asks only for a match to the property, as is done in a correlation, bears further study. Again one can state that a lack of uniqueness found in this calculation will not disappear on the application to experimental data. Therefore, one must have data present in the temperature ranges mentioned if one is even to have a chance to discriminate between potential functions.

The slope of the ϵ_2/ϵ_1 versus T^* curve, for a given potential, is essentially the same for both the viscosity and diffusion coefficients. On this basis, the two quantities are equally effective when used individually. As we shall see in the next section, however, there is a difference between them in sensitivity to changes in the potential function. That difference makes the simultaneous fit of the two properties potentially a sensitive tool for finding the potential function.

THE SIMULTANEOUS FIT TO MORE THAN ONE PROPERTY

Figures 6, 7, 9, and 10 contain plots of the ratio ϵ_2/ϵ_1 for more than one property. With the help of these one can examine the effect the requirement of a simultaneous fit to two or more properties and their first derivatives has on the lack of uniqueness in the potential function. Figure 9 is particularly informative in this regard. Note that in that diagram, the curves for both the viscosity and diffusion coefficients for $\gamma = 0$ would be straight lines parallel to the abscissa at $\epsilon_2/\epsilon_1 = 1.0$. As γ deviates from zero, however, each curve begins to deviate from a straight line, particularly at low temperatures. Furthermore, the curves for the diffusion coefficient separate from those for the viscosity until, by $\gamma = 0.6$, the curves are quite widely separated. The lack of uniqueness associated with the flatness of the curves for the separate properties would be extended to the simultaneous fit to the pair of properties and their derivatives were the two curves essentially flat at the same value of the ordinate. However, the increase in the separation of the curves with γ (i.e., with increased deviation from the (12,6) reference potential) demonstrates a strong sensitivity of the simultaneous fit to changes in the potential function. This sensitivity is much stronger than that of the individual properties in the range $T^* > 4.0$. Whether or not it is more sensitive than the behavior for $T^* < 4.0$ would require an examination of detailed fits to data.

Figure 10 contains the same kind of information for the exp-6 function. Here the changes that occur at low and intermediate temperatures are much smaller while those at high temperatures are much more pronounced. There appears to be a value of α for which the curves both have a flat range and are essentially superimposed at high temperatures. However, for that value of α, the low temperature data still serves as a discriminant. In this case the simultaneous use of both properties and their derivatives does not appear to add any discrimination beyond that available with either property of itself. Note that the curves for the two properties exchange relative positions when one goes from $\alpha = 12$ to $\alpha = 17$. Increasing α beyond 17 would presumably result in further separation.

Figure 7 contains plots for all of the properties for the Kihara potential. These curves necessarily each form a straight line parallel to the abscissa with ordinate 1.0 for $\gamma = 0$. Increasing γ causes them to separate as in Figure 9 for the two transport properties. It is interesting to note that the change in separation between the curves for diffusion and second virial coefficients at intermediate temperatures is not uniform. Thus, for $T^* \cong 3.0$, the diffusion curve for $\gamma = 0.1$ lies above that for the second virial coefficient, for $\gamma = 0.3$ they are superimposed in a small region around $T^* = 3.0$, while for $\gamma = 0.4$ the diffusion curve lies below. Thus, as γ is increased from 0. to 0.1, the second virial curve "moves" more rapidly while for $\gamma > 0.1$ the reverse is true.

That we have, in this section, examined the simultaneous fit of four properties cannot be emphasized too strongly. Thus, for example, the simultaneous equality of the second virial coefficient and its first derivative is equivalent to the simultaneous equality of the second virial coefficient and the zero density Joule-Thomson coefficient. We have here considered situations in which, in addition to this, we have asked that (e.g.) the viscosity and its first derivative also be equal at the same temperature and for the same two potentials. Again it is possible that the ability to discriminate among potentials discussed here for this kind of simultaneous fit may disappear when the requirement is that only a pair of properties be equal.

CONCLUSIONS

We have investigated the use of the second virial coefficient as well as the zero density Joule-Thomson, viscosity, and diffusion coefficients as probes for the intermolecular potential function. We have found the second virial coefficient to be particularly poor in this regard in the temperature range $2.0 < T^* < 7.0$ on the Lennard-Jones (12,6) reduced temperature scale. The Joule-Thomson coefficient has been found to be somewhat better particularly in the lower part of this range. Considerably better were the transport coefficients, i.e., the viscosity and diffusion coefficients. It is clear from our results that these last coefficients can be sensitive probes of the potential function given experimental data covering a sufficiently large temperature range.

Further comparisons of this kind between the transport coefficients for the (12,6) potential function and those for other potential functions are clearly called for, particularly for classes of potentials of which the (12,6) is not a member. In particular, one would like to find such classes of functions as exist which contain a member whose transport properties can be fit to those of the (12,6) over an extensive temperature range. This will require the calculation of collision integrals for these various functions. In some cases tables do exist [16,17] which, unfortunately, contain too few points in the temperature region of interest. It is hoped that these will be extended shortly.

These calculations will be extended to include the thermal diffusion ratio and, possible, the quantum corrections to certain of these properties.

As regards the relationship between our results and experiment with present day precision, the fact that our results apply precisely to experiment only in the limit of very high precision actually strengthens our conclusions in regard to <u>lack</u> of uniqueness while conclusions regarding uniqueness are weakened. That is, where we did not find it possible to use a macroscopic property to distinguish between potential functions under our conditions, it certainly would not be possible to use this property for this purpose under less precise experimental conditions. On the other hand, our ability in other circumstances to distinguish among potentials (e.g., using second virial coefficient data for $T^*\ (12,6) < 2.0$) may be due in part to the fact that we have required a precise fit, something not possible with experimental data. It may likewise be due to the inclusion here of a requirement that the first derivative of the property be equal for the two potentials. More precise statements in this latter case await the result of fits to actual data.

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REFERENCES (for APPENDIX only)

1. M. Klein, J. Chem. Phys. 39, 1367 (1963).

2. J. Hilsenrath and M. Klein, Tables of Thermodynamic Properties of Air from 1500 °K to 15000 °K, Report AEDC TR-65-58 Arnold Engineering Development Center, Tullahoma, Tennessee.

3. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, The Molecular Theory of Liquids and Gases, John Wiley and Sons, New York, 1954.

4. J. B. Keller, and B. Zumino, J. Chem. Phys. 30, (1959); J. E. Le Fevre, Heat Division Paper 129 (1957), Mechanical Engineering Research Laboratory, East Kilbride, Glasgow, Scotland.

5. Note that equating the second virial coefficients and their first derivatives is equivalent to equating, for the two potentials, the first density correction to PV/RT and simultaneously requiring the first density corrections to the internal energy, U/RT, to be equal for the same two potentials [6]. The author is indebted to Mr. Lester Haar for pointing this out.

6. The requirement on the internal energy can be replaced by an equivalent requirement on the zero density Joule-Thomson coefficient.

7. One can also associate each curve of the family of curves with T_2^* or, for that matter, with the experimental temperature T.

8. M. Klein, Ph.D. thesis, 1962, University of Maryland.

9. Note that S is dependent on T^* and contrary to the statement in J. O. Hirschfelder, C. F. Curtiss, and E. M. Spotz, Chem. Rev. 44, 205 (1949), (see also p. 566 ref. 3) is not the exponent in the representation $B(T^*) = AT^{*t}$.

10. e.g., R. A. Svehla, NASA-TRR-132 (1962); see also reference 2.

11. C. J. G. Raw, J. South African Chemical Institute VII, 96 (1954).

12. As regards the second virial coefficient and hence low density P-V-T data, this weakens considerably one of the restrictions of the law of corresponding states in this temperature range. Thus, at these temperatures, one needs to place only mild restrictions on the form of the potential function.

13. E. Whalley and W. G. Schneider, J. Chem. Phys. 23, 1644 (1955).

14. E. A. Mason and W. E. Rice, Jr., J. Chem. Phys. 22, 843 (1954).

15. e.g., L. Verlet and D. Levesque, Physica 28, 1124 (1962); J. deBoer, J. M. H. van Leeuwen, and J. Groenevelt, Physica 30, 2265 (1964); J. G. Kirkwood, V. A. Lewison, and B. J. Alder, J. Chem. Phys. 20, 929 (1952); G. Casanova, and A. Levi, Physica 30, 937 (1964).

16. F. J. Smith and R. J. Munn, J. Chem. Phys. 41, 3560 (1964).

17. S. G. Brush and J. D. Lawrence, Report UCRL-7376 Lawrence Radiation Laboratory, Livermore, California.

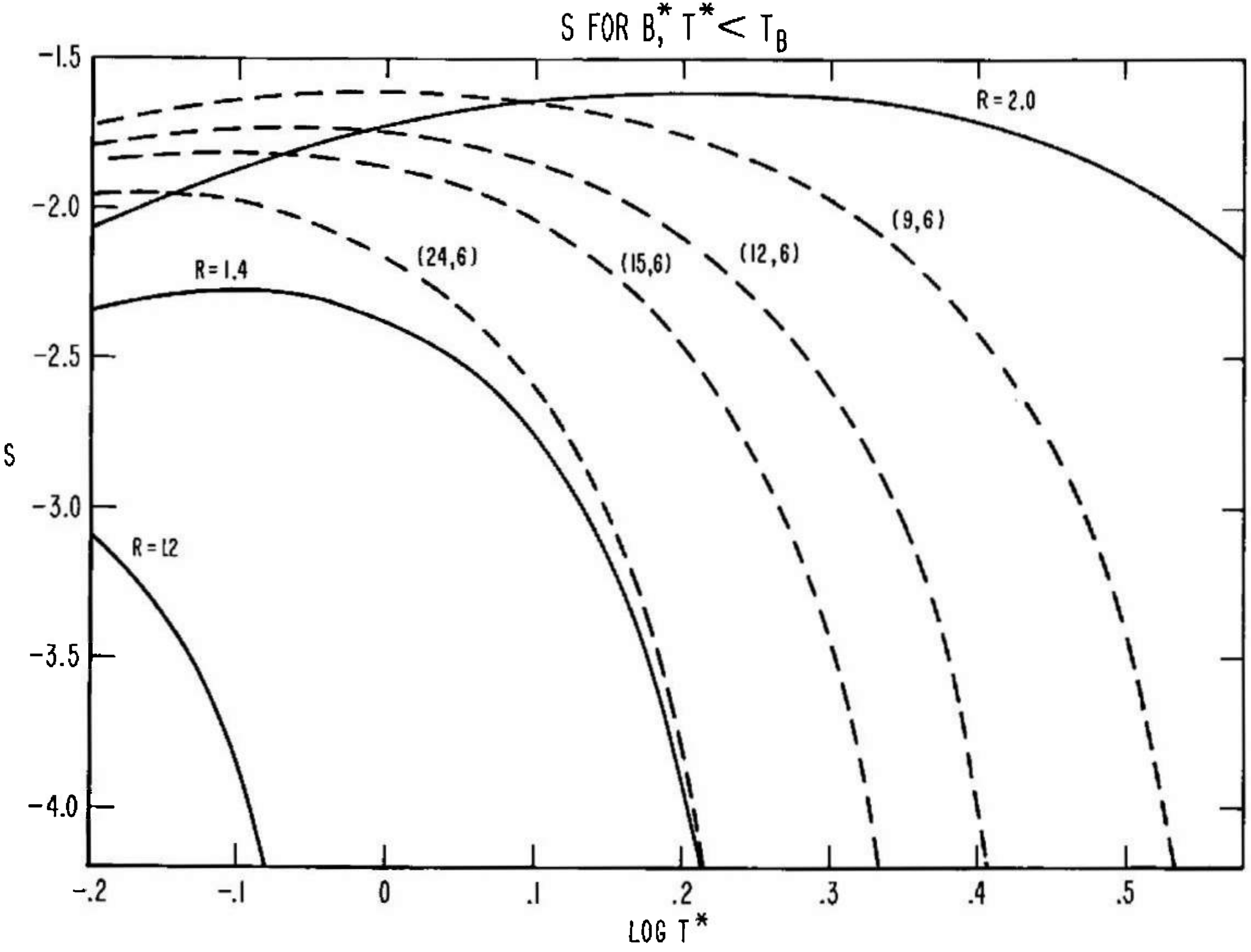

Figure 1 S for the Second Virial Coefficient of Several Potentials, T* less than the Boyle Temperature

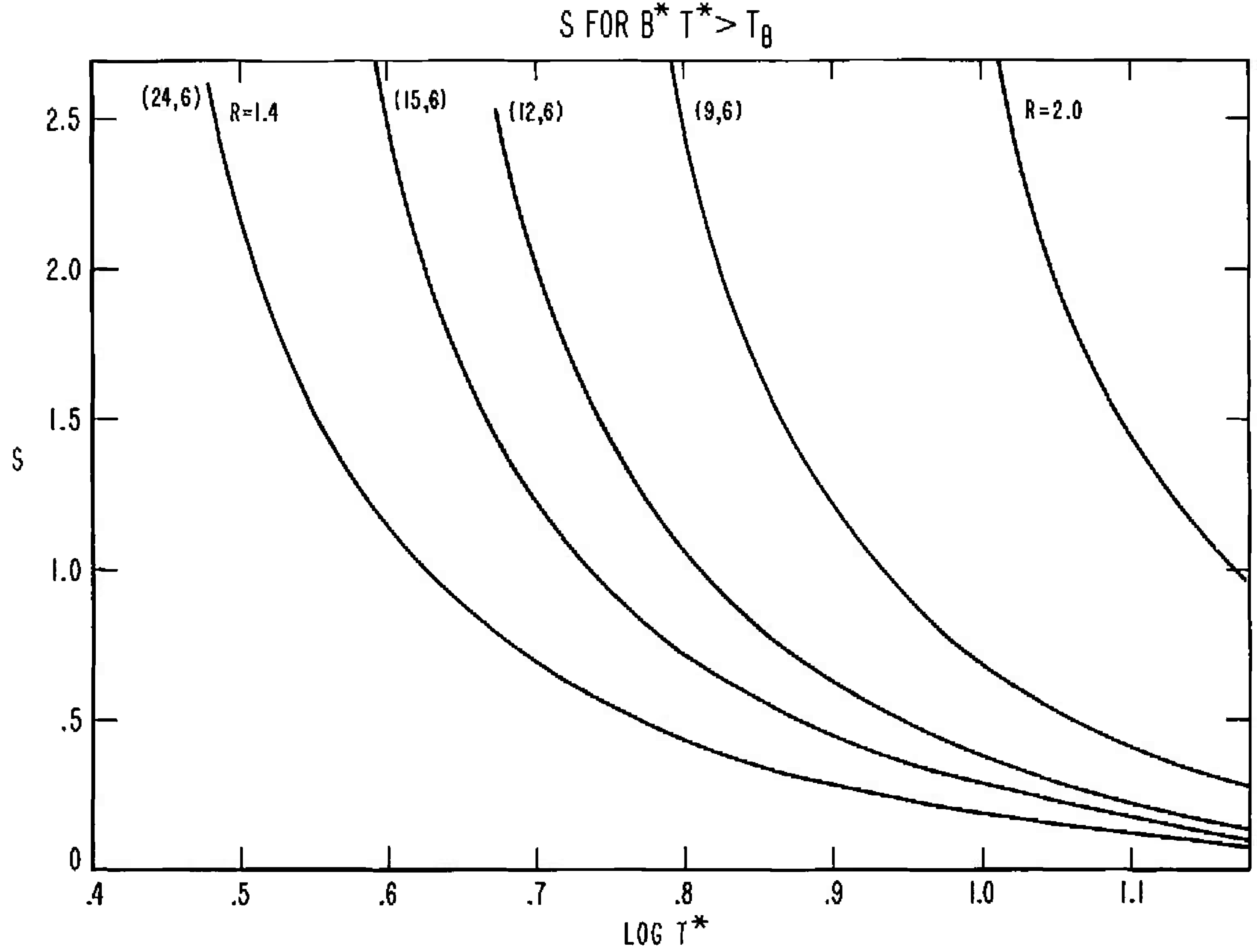

Figure 2 S for the Second Virial Coefficient of Several Potentials, T^* Greater than the Boyle Temperature

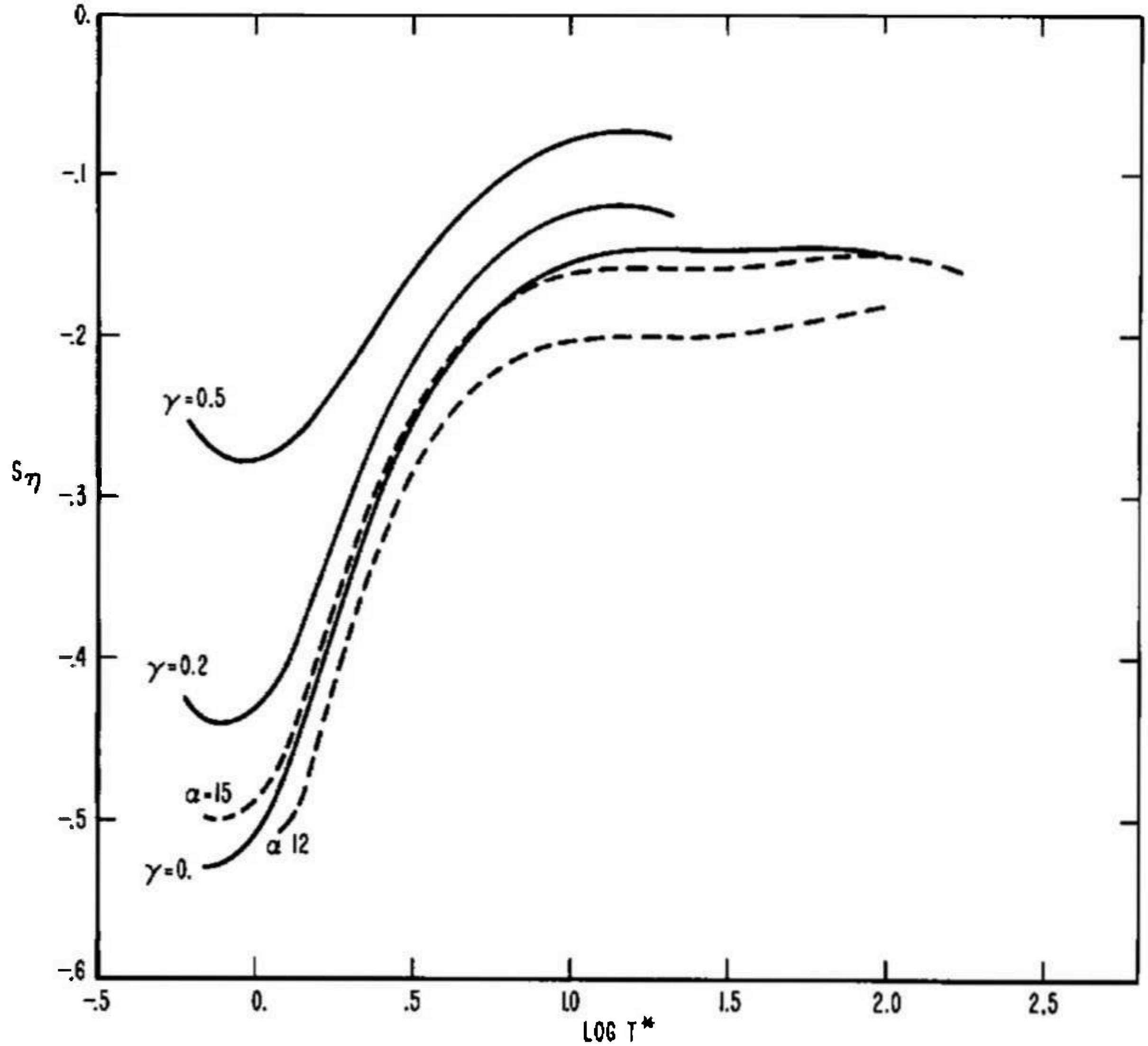

Figure 3 S for the Viscosity Coefficient of Several Potentials

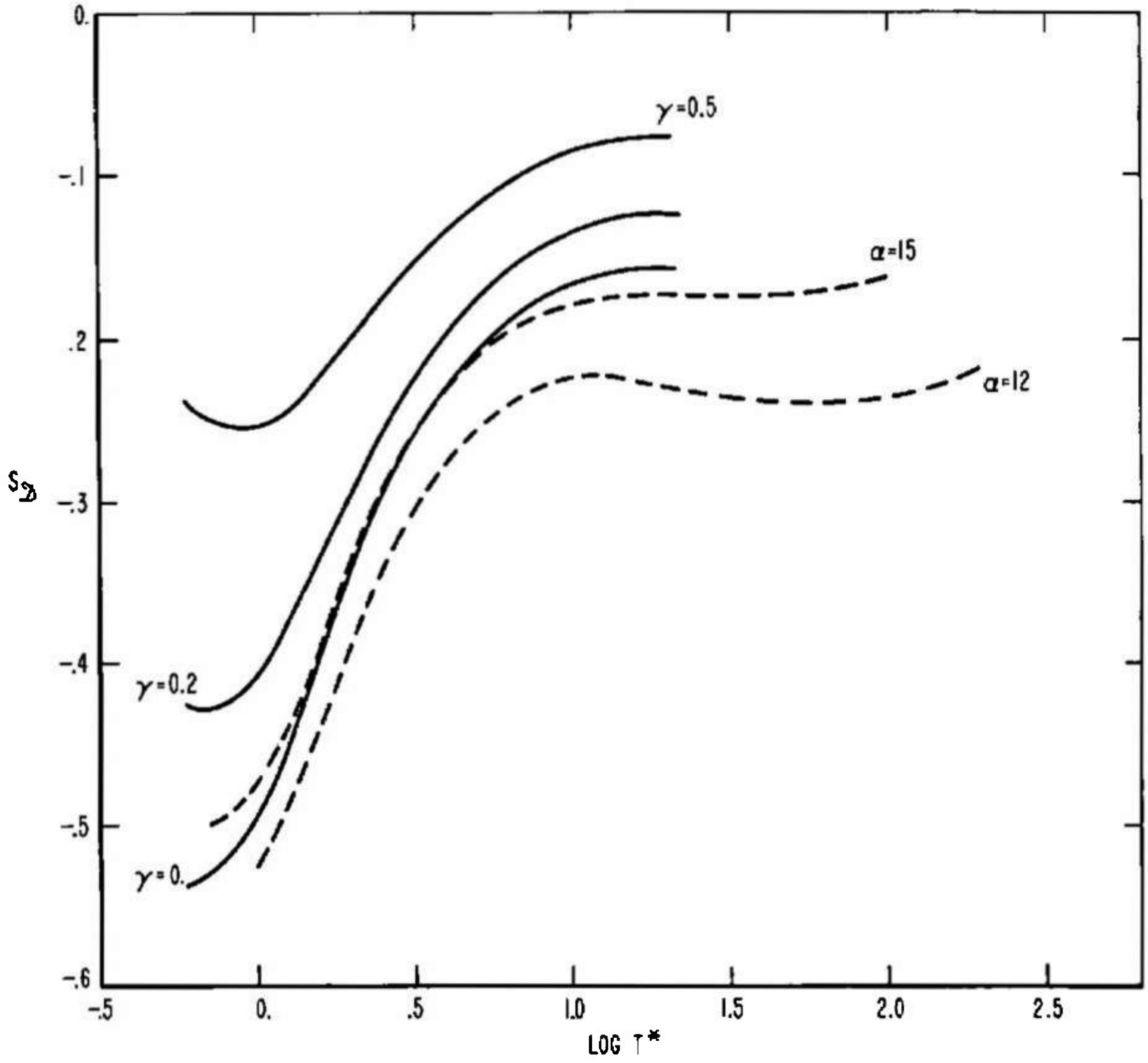

Figure 4 S for the Diffusion Coefficient of Several Potentials

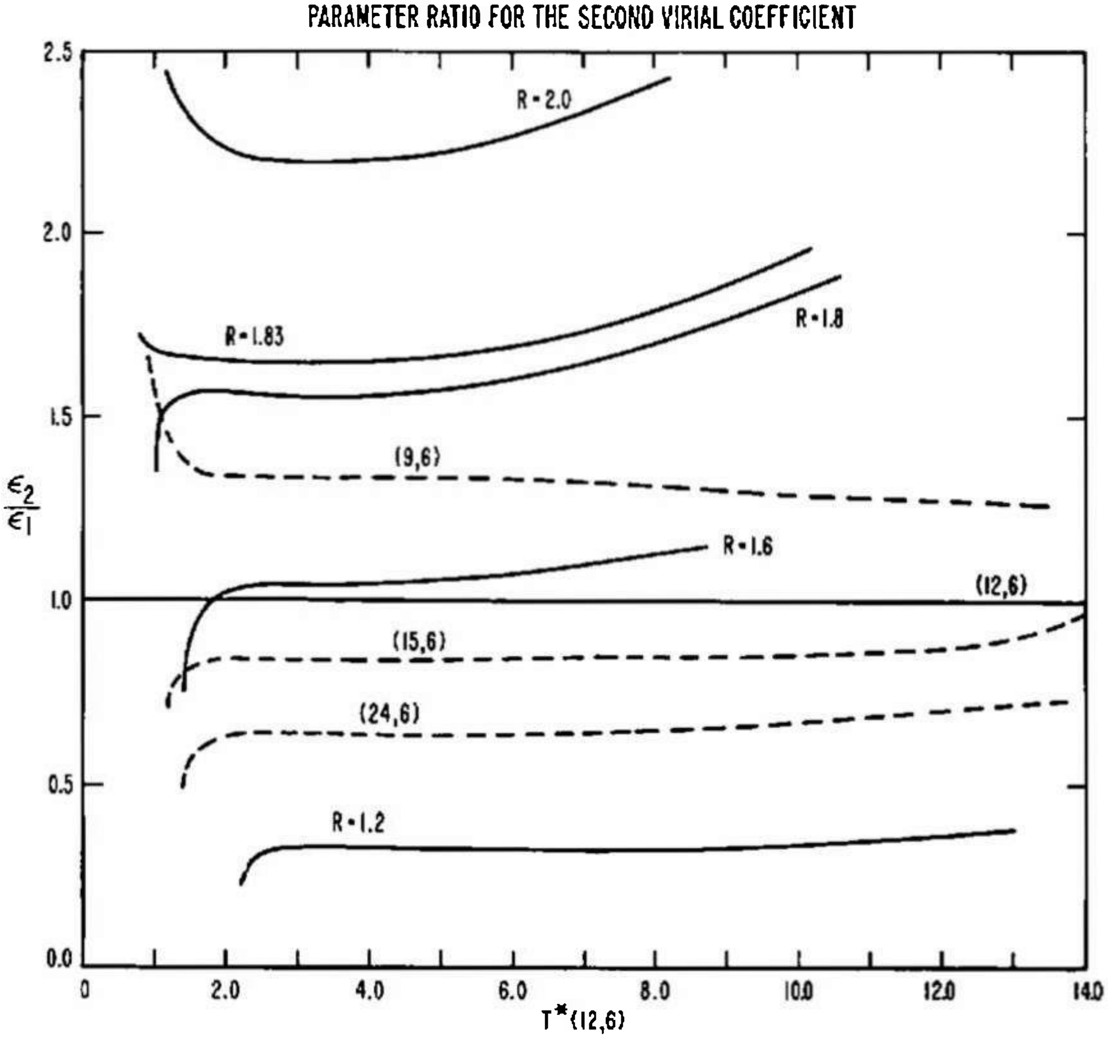

Figure 5 The Parameter Ratios ϵ_2/ϵ_1 for the Second Virial Coefficients of the (m,6) and Square Well Potentials with Respect to the (12,6) Potential. Note Particularly the Flatness of the Curves for the (m,6) Potentials

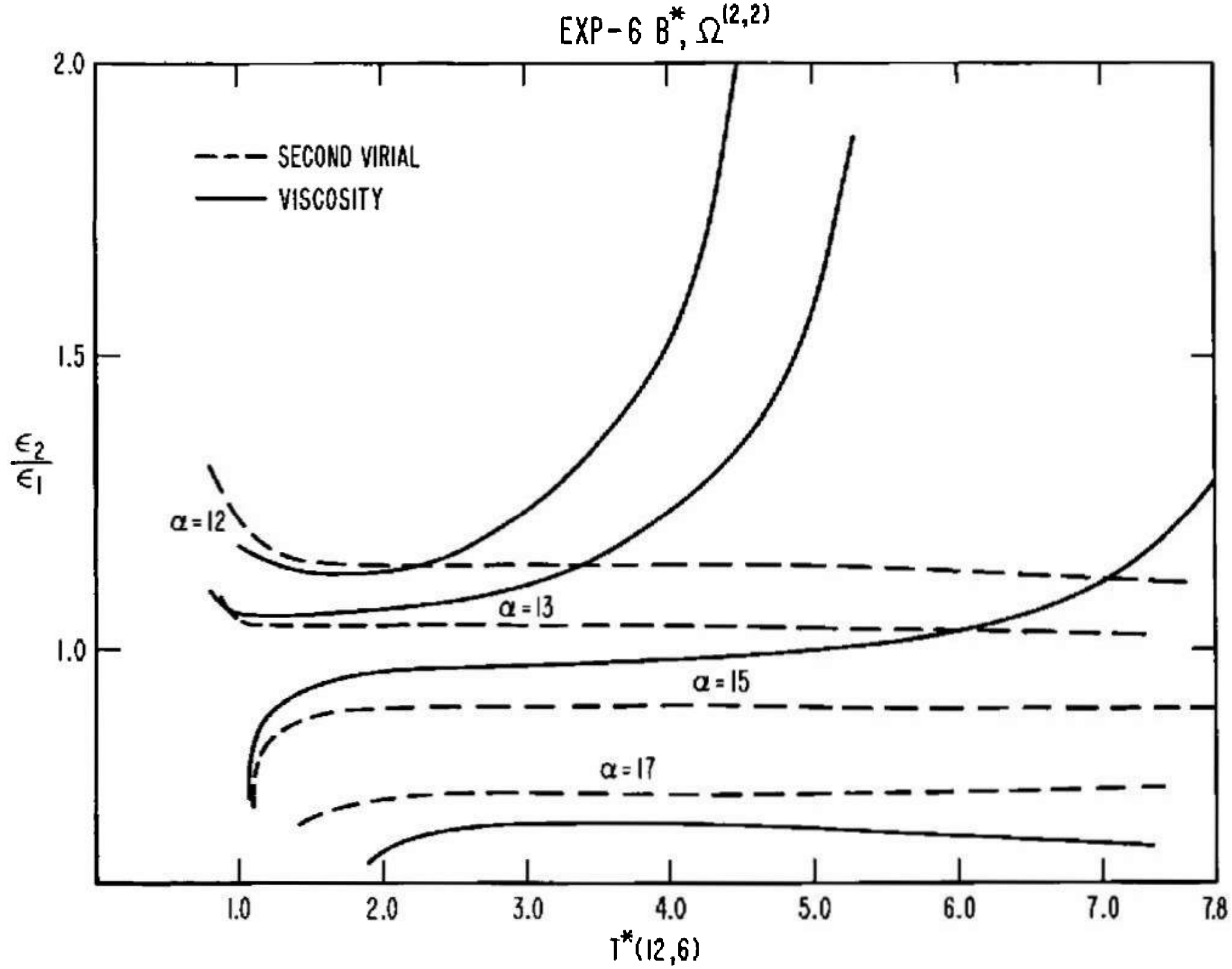

Figure 6 The Parameter Ratios ϵ_2/ϵ_1 for both the Second Virial and Viscosity Coefficients of the exp-6 Potential with Respect to the (12,6) Potential. Note that the Former are Flat while the Latter are not Flat

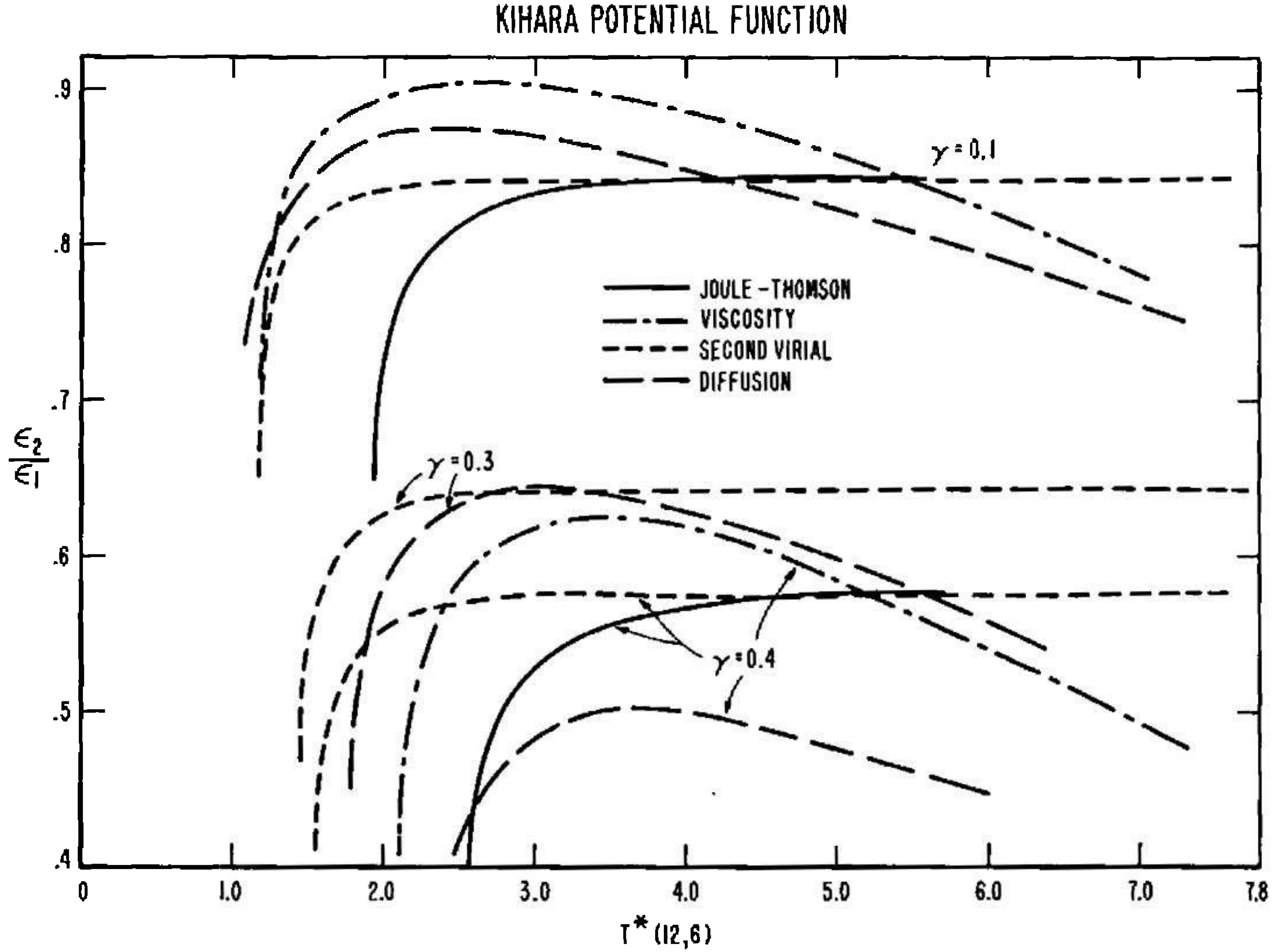

Figure 7 The Parameter Ratios ϵ_2/ϵ_1 for all Four Properties for the Kihara Potential with Respect to the (12,6) Potential. Note the Absence of any Single Ratio for which both the Equilibrium and Transport Properties are Flat

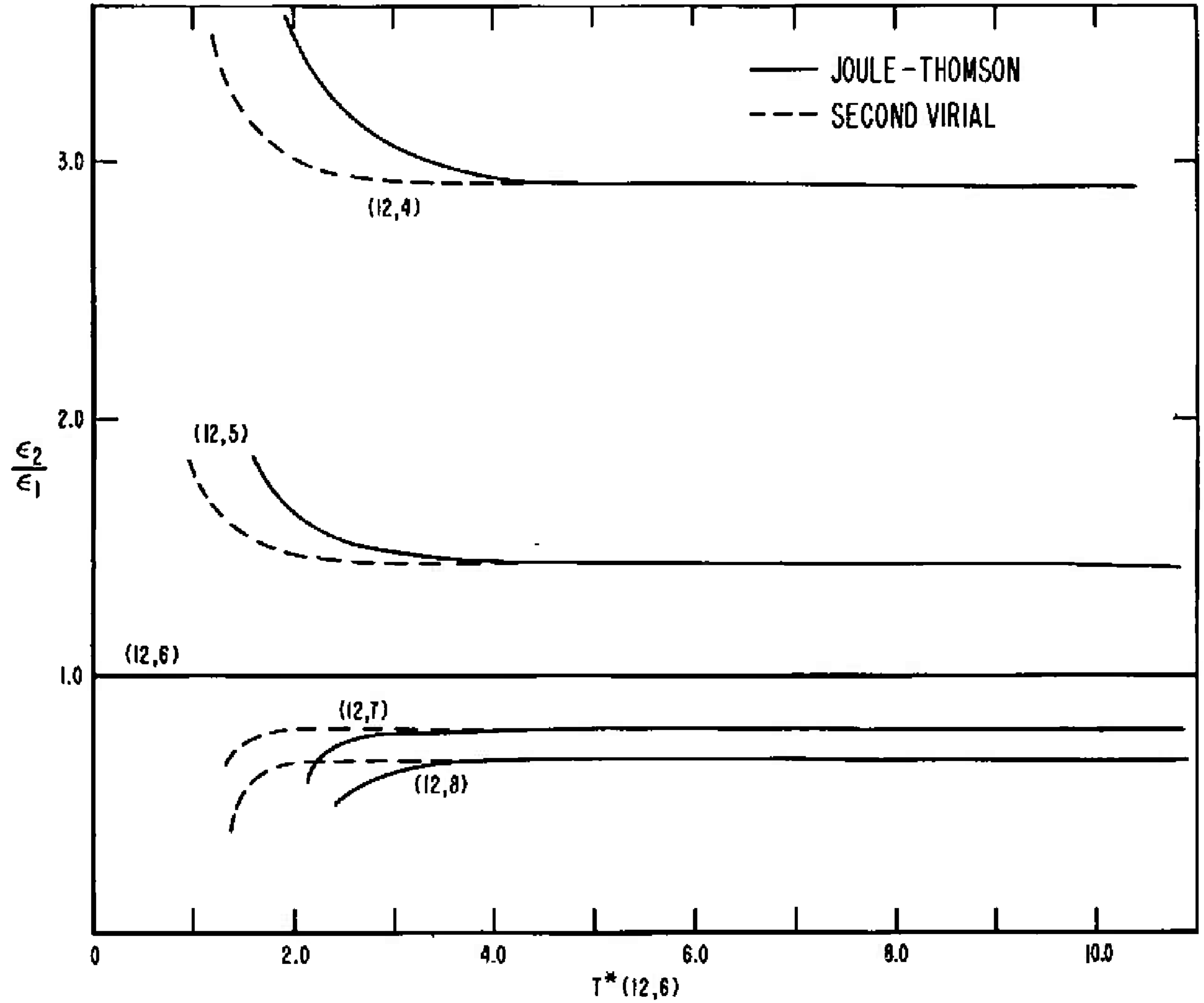

Figure 8 The Parameter Ratios ϵ_2/ϵ_1 for both the Second Virial and Joule Thomson Coefficients for the (12,n) Potential with Respect to the (12,6) Potential. Note that for Temperatures above the Boyle Point all Curves are Flat Making it Impossible to Select a Value of n at such Temperatures

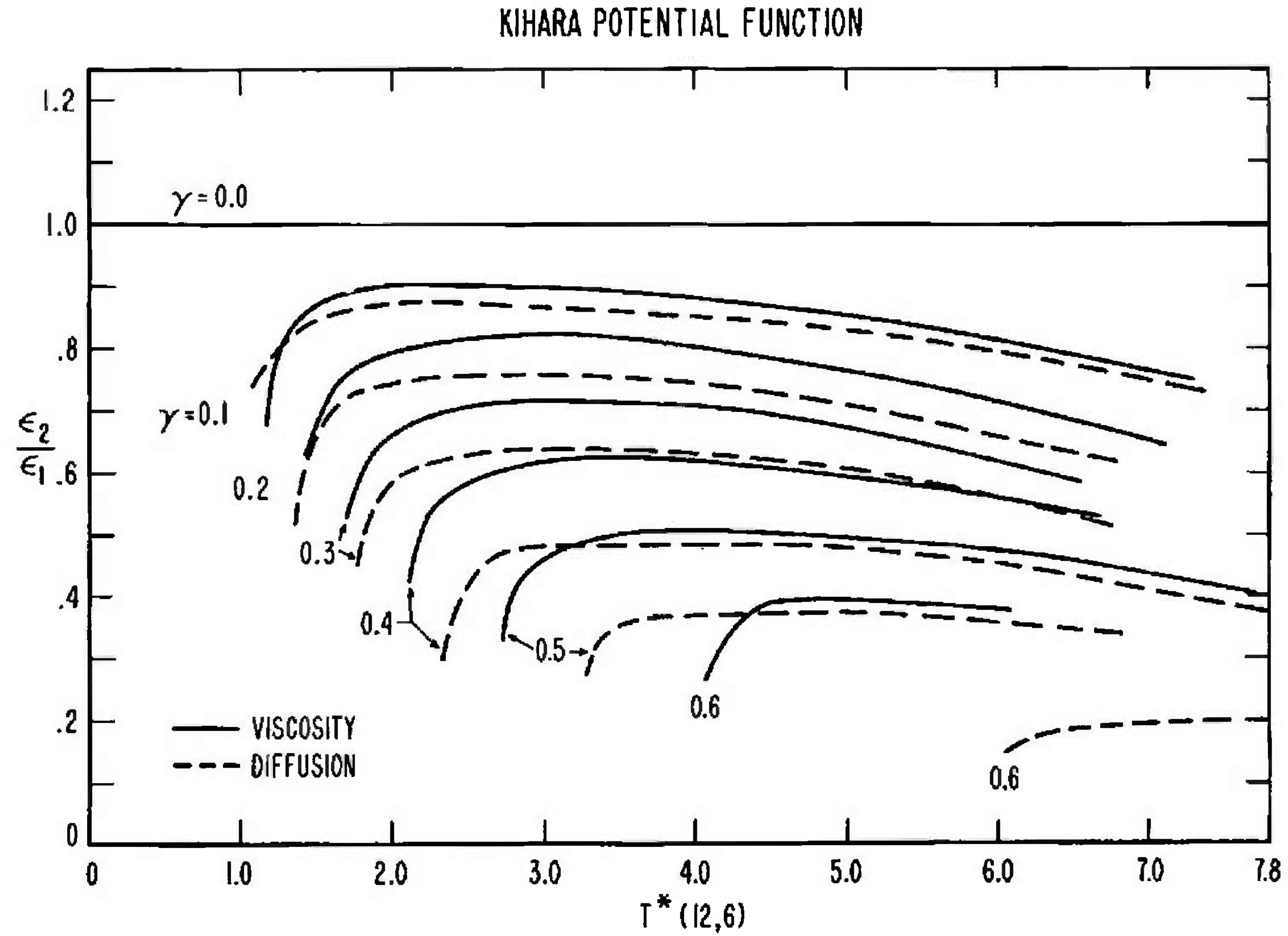

Figure 9 The Parameter Ratios ϵ_2/ϵ_1 for the Diffusion and Viscosity Coefficients for the Kihara Potential Function with Respect to the (12,6). Notice the Increasing Flatness with Increasing γ for T* Large

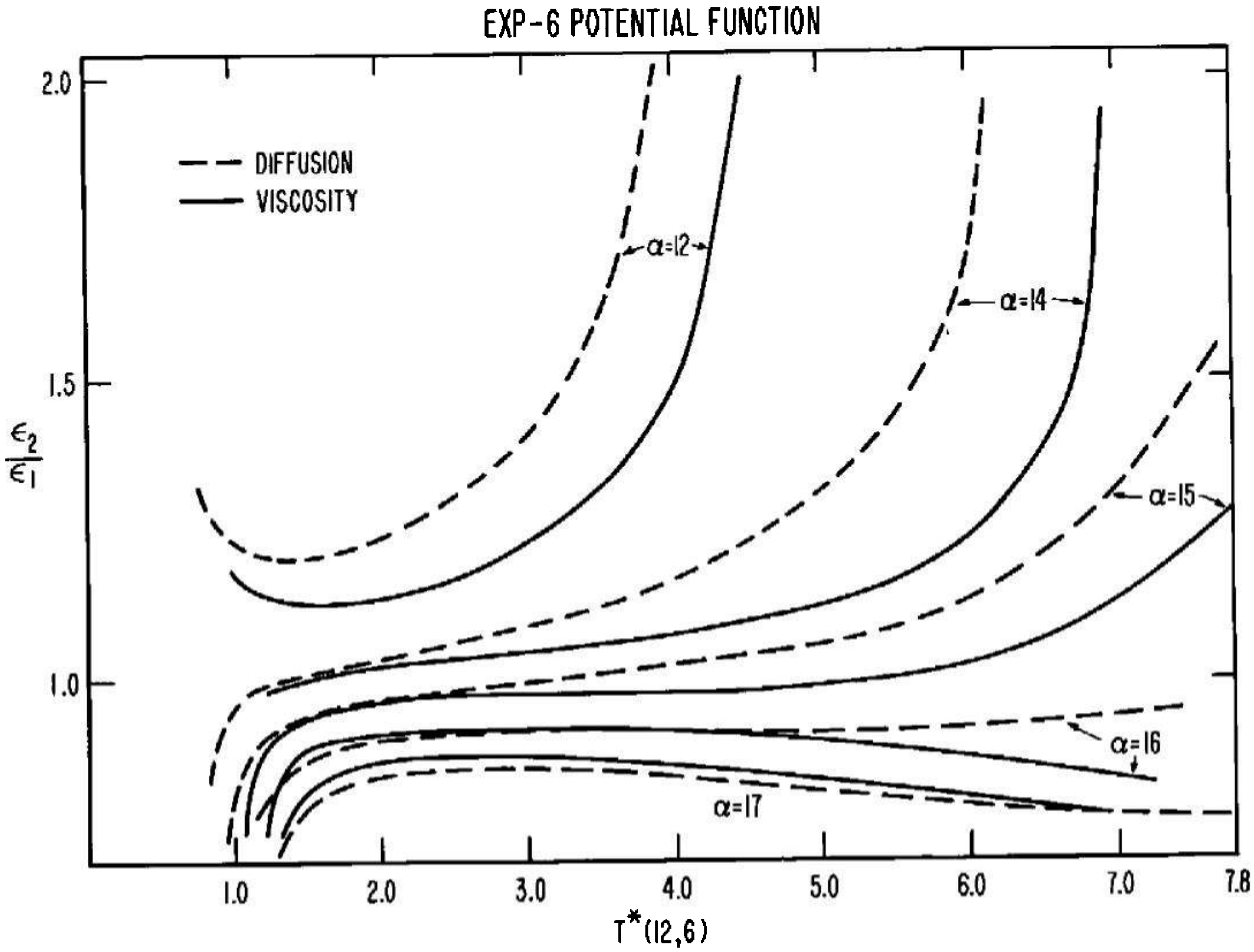

Figure 10 The Parameter Ratios ϵ_2/ϵ_1 for the Diffusion and Viscosity Coefficients for the exp-6 Potential with Respect to the (12,6) Potential

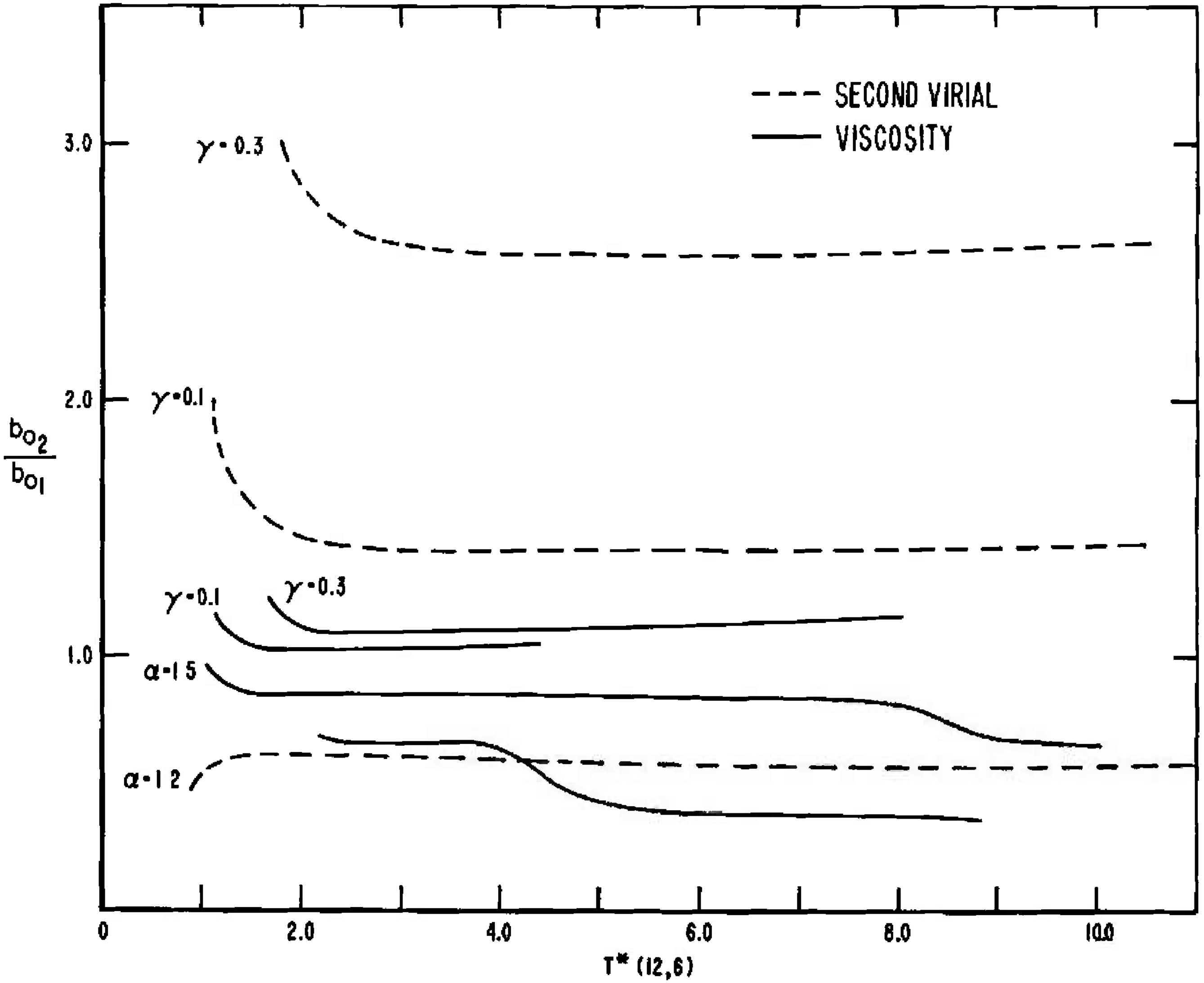

Figure 11 The Parameter Ratios $(b_o)_2/(b_o)_1$ for the Kihara and exp-6 Potentials with Respect to the (12,6)

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13 ABSTRACT

Intermolecular potential functions and certain means by which they can be obtained from experiment have been studied as the first step in the evaluation and development of a high density equation of state. The second virial coefficient has been found to be a poor method for reduced temperatures (on the (12, 6) scale) greater than 2.0 while transport coefficients were found to be poor in the range $1.5 < T^* (12, 6) < 5.0$. Experimental second virial coefficient data have been fitted to 40 intermolecular potential functions for each of 15 substances. That such data taken in the range $T^* (12, 6) > 2.0$ cannot serve as a means for determining the potential function is clearly demonstrated. Also indicated is the result that such data in the range $T^* (12, 6) < 2.0$ cannot be used for determining more than three potential parameters. The Percus-Yevick theory has been investigated and appears to be as applicable to air as it is to argon. The theory has been found to be sensitive to the choice of the intermolecular potential function. The effect improving the potential functions has on the NBS tables of equilibrium properties of gases at high temperatures has been investigated and found to be generally small although changes of approximately 2% were obtained at the highest densities.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
equation of state						
gases						
high temperatures						
high density						
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2 Gases - - Equation of State

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