He and Li$^+$ as compared to the CS functions, the results for the polarizability get worse as we go from the CS to the 0S1 approximation. Thus the 0S1 functions, in general, are quite extended, which is clearly demonstrated by the extremely large polarizability of H$^-$ ion.

We have also calculated the polarizability of H$^-$ when the unperturbed wave function is 0S2, but only in the Henrich's approximation. This approximation is not expected to be serious because 0S2 gives a very good value for the energy of H$^-$. First of all, we find from Table I that α is drastically lowered as we go from 0S1 to 0S2. Secondly, a relatively simple three-parameter unperturbed wave function 0S2 gives a value of the polarizability of H$^-$ which is a significant improvement over all the previous calculations except the one due to Schwartz.[10]

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Methods for Determining the Second Virial Coefficient of a Gas from Speed-of-Sound Data*

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Two methods of analyzing speed-of-sound data in gases to obtain the second virial coefficients $B(T)$ are compared. The older method, which assumes a form for the temperature dependence of B, is shown to correspond to finding an exact solution to an approximate differential equation for B, while a method recently proposed by Bruch solves the exact equation, but in an approximate manner. Examination of the errors in each method indicates that the first method is preferable.

Keesom and Van Itterbeek[1] showed that if the square of the speed of sound, W, in a gas at a temperature T is expanded in powers of the pressure p, such that

$$W^2 = W_0^2[1 + (2/RT)f(T)p + \cdots] \ , \tag{1}$$

where W_0 is the speed of sound in an ideal gas and R is the gas constant, then the coefficient of the linear term can be related to the second virial coefficient $B(T)$ by

$$f(T) = B(T) + \frac{2}{3}\,T\,\frac{dB(T)}{dT} + \frac{2}{15}\,T^2\,\frac{d^2B(T)}{dT^2} \ . \tag{2}$$

Unfortunately, the functional form of $f(T)$ is not known, so Eq. (2) cannot be solved directly to yield $B(T)$. The usual procedure has been to assume a functional form for $B(T)$ involving arbitrary coefficients and to use Eq. (2) to define a corresponding functional form for $f(T)$. The coefficients are then obtained by curve-fitting the experimental values of $f(T)$.

Recently, Bruch[2] proposed avoiding the imposition of a functional form by using the formal solution of the differential equation, Eq. (2), integrating numerically, and determining the two integration constants by fitting to two independently known values of $B(T)$. In so doing he criticized the former method as not making explicit use of the solution of the homogeneous equation. Also, he attributed apparent discrepancies between results of such a fitting and PVT values at the low-T end of the range involved to neglect of this term. We shall show here that (i) Bruch's criticism of the curve-fitting method is invalid, and (ii) use of Bruch's method is, as he suspected, rendered impracticable by the unrealistic requirements on the accuracy needed in the data used.

In discussing the first point it is important to emphasize that since the functional form of $f(T)$ is not theoretically known, Eq. (2) is only a mathematical relationship between the unknown $f(T)$ and $B(T)$, and we do not, in fact, know the form of the actual differential equation satisfied by $B(T)$. Bruch proceeds on the basis that we know numerical values for $f(T)$ at certain T values, and writes down the formal solution of Eq. (2), considered as a differential equation, as

$$\begin{aligned} B(T) &= B_{\text{homogeneous}} + B_{\text{particular}} \\ &= \frac{\alpha(\tau)}{T^2}\cos\left[\left(\frac{7}{2}\right)^{1/2}\ln\frac{T}{\tau}+\phi(\tau)\right] \\ &\quad + \frac{15}{(14)^{1/2}}\frac{1}{T^2}\int_{\tau}^{T} dt\, tf(t)\sin\left[\left(\frac{7}{2}\right)^{1/2}\ln\frac{T}{t}\right], \end{aligned} \tag{3}$$

where α and ϕ are the integration constants and are functions of τ, since the particular integral chosen will be different for every choice of the range of integration. Since $f(T)$ is only known numerically at a limited number of points, an approximation to the integral is obtained by numerical integration, and α and ϕ then fitted from previously known values in the range $\tau \leq t \leq T$. That is, one obtains an approximate solution to the correct differential equation, the accuracy of the approximation depending upon the adequacy of the data used.

Bruch contends that the curve-fitting method amounts to choosing the particular integral without considering explicitly the homogeneous solution. We now show that this contention is incorrect, and that choosing a form for B is, in effect, specifying an approximate differential equation for which the chosen form is the complete solution. This can be made clear by considering a form of solution frequently employed for curve-fitting in the past,

$$B(T) = A + C/T\,, \tag{4}$$

which in Eq. (2) gives

$$f(T) = A + \tfrac{3}{5}(C/T). \tag{5}$$

Suppose now that we have chosen expression (5) for $f(T)$, that we have obtained the coefficients by curve-fitting the experimental data, and now we wish to obtain $B(T)$ by solving the differential equation resulting from inserting this expression for $f(T)$ in Eq. (2). This Eq. (2), let us repeat, is now no longer the "true" one, but an approximation to it. Its formal solution is Eq. (3) where the particular integral can be obtained analytically, and is

$$\begin{aligned} B(T)_{\text{homogeneous}} &= \frac{\alpha(\tau)}{T^2}\cos\left[\left(\frac{7}{2}\right)^{1/2}\ln\frac{T}{\tau}+\phi(\tau)\right], \\ B(T)_{\text{particular}} &= A + \frac{C}{T} - \frac{\tau^2}{T^2}\cos\left[\left(\frac{7}{2}\right)^{1/2}\ln\frac{T}{\tau}+\psi(\tau)\right], \end{aligned} \tag{6}$$

where

$$\psi(\tau) = \tan^{-1}\left[-\left(\frac{2}{7}\right)^{1/2}\frac{(2A + C/\tau)}{(A + C/\tau)}\right].$$

Since physically $B(T)$ is a unique function of T and cannot be a function of the range over which measurements have been made, we must choose the integration constants to eliminate the dependence of the solution on τ. This can obviously be done, and we are left with the solution as Eq. (4). Note that in the case of this general solution the homogeneous term is nonzero and is thus not neglected in obtaining the solution. One could, of course, have chosen the particular integral as Eq. (4), and since the solution must be mathematically equivalent, the homogeneous term will then be given by the trigonometric combination of the cosine terms in the above solution. The new coefficient and phase angle can be obtained from the old and will result in the homogeneous term being identically zero. This seems to have been the case Bruch envisioned without realizing that the homogeneous term was not arbitrarily ignored in obtaining Eq. (4) as the complete solution. Thus the curve-fitting method is the equivalent of an exact complete (integration constants specified) solution of an approximate differential equation (2) for $B(T)$, and is limited in accuracy by the adequacy of the form chosen to represent the real behavior of $B(T)$ in the range of the measurements.

Bruch gives an example in which he takes a curve-fitting solution[3] to speed-of-sound data on He^4 for the range 2 K $\leq T \leq$ 10 K, compares its results to those from a fitting to PVT results near the low end of the range[4], and ascribes the apparent difference to a missing homogeneous term. Fitting values of α and ϕ and calculating a new B at 10 K with the resulting expression, he finds a 3% change. However, we have seen that the curve-fitting solution is a complete one with the constants already specified for the approximate differential equation solved, and it is mathematically inconsistent to impose another homogeneous term with another set of the constants to be fitted. Alternatively, this solution is *not* a particular integral of the true differential equation which would be required if the constants in the homogeneous solution are to be fitted to independent actual values of B and the range dependence eliminated. Thus Bruch was, in effect, adding a mathematically unjustifiable correction factor to account for the inadequacy of the chosen form to represent $B(T)$. In fact, Eq. (4) has been shown,[5] in the case of a Lennard-Jones (LJ) potential for He^4, to represent adequately only the Boltzmann part of $B(T)$ in the range of Bruch's example. At the low-T end of the range (2 K) it will not include the exchange contribution which would amount to about 3%. However, it is also the case that the two sets of measurements used in his example are actually

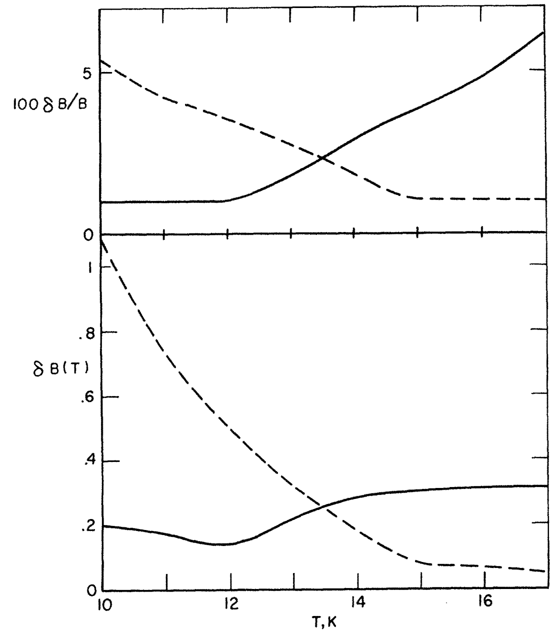

FIG. 1. Percent uncertainty $100\delta B/B$ and the uncertainty δB implied by a 1% uncertainty in the values of $B(T)$ used to determine α and ϕ. Case 1 is shown as the solid curve, and case 2 is shown as the dashed curve. The uncertainties are relative to $B(T)$ shown in Fig. 2.

in agreement within their estimated experimental errors.

Let us now turn to the second point and examine the effect of errors in the data used on the results obtained by Bruch's method. It is apparent that the problem of obtaining a good value for the particular integral in Eq. (3) will be quite acute, since $f(T)$ is only known approximately [it is obtained by curve-fitting data to an Eq. (1) at each T value] and usually at a relatively small number of points. In addition, the values of $f(T)$ are weighted in the integral by the range used and not by consideration of experimental accuracy – a statistically unsatisfactory situation. However, we will assume here that the integral can be obtained to as high an accuracy as desired and consider the effect only of uncertainty in the independently known values of B used to determine α and ϕ. For this purpose we will again employ a model where

$$B(T) = 17 - 375/T \tag{7}$$

and thus

$$f(T) = 17 - 225/T \tag{8}$$

over the temperature range $10\ \mathrm{K} \le T \le 17\ \mathrm{K}$. The coefficients used here are similar to those found for He in the range $11\ \mathrm{K} \le T \le 20\ \mathrm{K}$.[3] Only $f(t)$ will be considered as given, and Eq. (7) will be used only to obtain our "known" values of B, i.e., $B(10) = -20.50$ and $B(12) = -14.25$ for case 1 (solid curve, Fig. 1), and $B(15) = -8$, $B(17) = -5.06$ for case 2 (dashed curve, Fig. 1). Using these values to fix α and ϕ when $\tau = 10$ will of course enable us to calculate values of $B(T)$ agreeing exactly with Eq. (7). Now assume an error of ± 1% in these known values, a very conservative error indeed in experimental terms. Figure 1 displays the percent uncertainty in B and the magnitude of the uncertainty in B over the whole range which is thus introduced. Equation (7) is displayed in Fig. 2. One sees that the process introduces systematic errors which propagate and even amplify over the entire range considered, and are dependent on the range and the particular points fitted. Thus, in Bruch's method all the errors introduced are of an unknown nature and would be extremely difficult to estimate in actual cases. The method also suffers from the fact that it is not an independent determination of B but requires other measurements.

In the curve-fitting method, the form used can be based on experience with virial coefficients, considerations of physical reasonableness, or analysis of values calculated from model intermolecular-potential functions. Values of $f(T)$ can be weighted in the fitting by experimental considerations, and errors in the data are averaged out in the process rather than propagated over the range. Finally, probable error in the results can be estimated by comparing results for different assumed functional forms. Therefore we assert that this method is still preferable for obtaining second virial coefficients from speed-of-sound data. With either procedure, extrapolation outside the temperature range of the data is not justified.

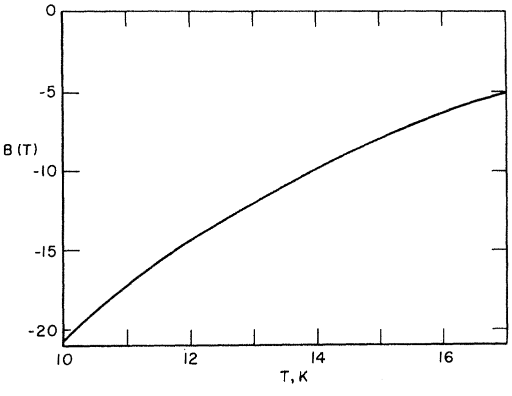

FIG. 2. The virial coefficient $B(T) = 17 - 375/T$.

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Uniqueness Problem in Indirect Determinations of the Second Virial Coefficient*

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Procedures which derive the second virial coefficient of a gas from the acoustic second virial coefficient or the Joule-Thomson coefficient are discussed. Model calculations with realistic helium intermolecular potentials are presented. The validity of a procedure which does not directly face the uniqueness problem is tested.

I. INTRODUCTION

This note is in part an addendum to a previous work,[1] presenting model calculations which illustrate points made there. It is also a comment on a critique[2] of that work.

The uniqueness problem which is discussed occurs when data for the acoustic second virial coefficient $f(T)$ or Joule-Thomson (JT) coefficient $\mu(T)$ are used to generate values of the second virial coefficient $B(T)$. This occurs when such data are used to test the accuracy of existing data for $B(T)$ or when values of $B(T)$ are needed for other purposes and direct determinations do not exist. It need not occur in the testing of model intermolecular potentials, since f, μ, or B can each be calculated directly from the model. This has sometimes been done.[3,4]

Section II contains the formulation of the problem, and Sec. III contains the model calculations. Conclusions and discussion of other work are given in Sec. IV.

II. FORMULATION

The acoustic second virial coefficient $f(T)$ and the JT coefficient $\mu(T)$ of a dilute gas are expressed in terms of the second virial coefficient $B(T)$ by these equations[1,4]:

$$\mu(T)=\left(T\frac{dB}{dT}-B\right)\Big/C_P \ , \qquad (1)$$

$$f(T)=B+(\gamma-1)T\frac{dB}{dT}+\frac{(\gamma-1)^2}{2\gamma}T^2\frac{d^2B}{dT^2} \ . \qquad (2)$$

γ is the ratio of ideal-gas specific heats, T is the absolute temperature, and C_P is the ideal-gas specific heat at constant pressure. In this work, the specific choice $\gamma=\frac{5}{3}$ is made, and the calculations are for helium. Treated as inhomogeneous differential equations for $B(T)$, these have solutions[1,4]

$$B(T)=a_\tau T+T\int_\tau^T\frac{dt}{t^2}\mu(t)C_P \ , \qquad (3)$$

$$B(T)=(\alpha(\tau)/T^2)\cos[(\tfrac{7}{2})^{1/2}\ln(T/\tau)+\phi(\tau)] + \frac{15}{(14)^{1/2}}\frac{1}{T^2}\int_\tau^T dt\,t f(t)\sin[(\tfrac{7}{2})^{1/2}\ln(T/t)] \ . \qquad (4)$$

Equation (3) is valid also for temperature-dependent C_P.

The quantities a, α, and ϕ are constants which in usual solutions of differential equations are determined by boundary conditions. The specification of these quantities is the mathematical form of the uniqueness problem for determination of B from f or μ. Calculations with realistic intermolecular potentials which support an earlier discussion of this topic[1] are presented in Sec. III. The JT coefficient provides an example of the phenomenon discussed for $f(T)$.

In contrast to Eqs. (3) and (4), the curve-fitting method, which has been used[5,6] for $f(T)$ and might be attempted for $\mu(T)$, assumes a finite series for $B(T)$:

$$B=\sum_{n=0}^{\eta} b_n T^{-n} \ ; \qquad (5)$$

and a corresponding series for f or μ:

$$f=\sum_{n=0}^{\eta} f_n T^{-n}, \quad \mu=\sum_{n=0}^{\eta}\mu_n T^{-n} \ . \qquad (6)$$

The coefficients f_n or μ_n are determined by a fit to