N 62 71055

NASA TN D-481

NASA TN D-481

IN-72

[illegible]

TECHNICAL NOTE

D-481

COLLISION INTEGRALS FOR A MODIFIED STOCKMAYER POTENTIAL

By Eugene C. Itean, Alan R. Glueck, and Roger A. Svehla

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON January 1961

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNICAL NOTE D-481

COLLISION INTEGRALS FOR A MODIFIED STOCKMAYER POTENTIAL

By Eugene C. Itean, Alan R. Glueck,
and Roger A. Svehla

E-791

CO-1

SUMMARY

Collision integrals were calculated for the modified Stockmayer potential $E(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6 - \delta(\sigma/r)^3]$, which may be applied to polar molecules. It was assumed that the colliding molecules maintain their same relative orientation during the encounter. Calculations of the integrals were made for a large reduced temperature range and for a range of δ from 0 to 10. The results agree with other work on nonpolar interactions ($\delta = 0$). However, for polar interactions, the only previously published calculations have been found to be in error and do not agree with this work.

Assuming that the molecules interact as alined dipoles of maximum attraction, values for σ, ϵ, and δ were determined for various polar molecules by a least squares fit of experimental viscosity data. Satisfactory results were obtained for slightly polar molecules, but not for more highly polar molecules such as NH_3 or H_2O. Therefore, it appears that the assumed model of molecules interacting at all times as alined dipoles of maximum attraction is not satisfactory for estimating transport properties of polar molecules.

INTRODUCTION

Coefficients of viscosity, thermal conductivity, and diffusion are needed in heat- and mass-transfer calculations. Equations for calculation of these transport properties have been developed from kinetic theory in terms of collision integrals, quantities that describe the interaction between colliding molecules. When these integrals are known it is possible to predict transport properties at elevated temperatures. Values of these integrals (ref. 1, pp. 1126-1180) have been calculated assuming various interaction potentials. However, these integrals are specifically for nonpolar molecules. In many cases a polar gas such as H_2O, NH_3, or HCl is of interest, and the predictions would be in error if these integrals were used, because the polar character of the gas is ignored.

The Lennard-Jones potential of interaction for spherically symmetric nonpolar molecules (ref. 1, p. 32), given in equation (1), is a well-known potential that has been successfully used for correlating transport properties of many nonpolar gases:

$$E(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where $E(r)$ is the potential energy of interaction, r is the intermolecular distance between colliding molecules, ϵ the maximum energy of attraction, and σ the value of r where the potential energy of interaction is zero. For low-velocity encounters, σ can be considered the collision diameter of the molecule. (All symbols are defined in appendix A.) These relations are shown in figure 1.

For polar molecules, an equation similar to equation (1) has been proposed by Stockmayer (ref. 2), given in a modified form in equations (2) and (3):

$$E(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3}\, g(\theta_1,\theta_2,\varphi) \tag{2}$$

$$g(\theta_1,\theta_2,\varphi) = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \varphi \tag{3}$$

Stockmayer actually proposed this equation using an arbitrary exponent S, instead of 12 as given in equation (2). But written in the preceding form it can be considered a Lennard-Jones potential modified to include the forces between two point dipoles. The angles θ_1 and θ_2 are the angles of inclination of the dipoles with the intermolecular axis, μ is the dipole moment of the molecule, and φ is the azimuthal angle between the dipoles. This is shown in figure 2. However, the molecular constants σ and ϵ do not have quite the same significance as in equation (1). They now represent constants that would be obtained from the interaction of a polar and a nonpolar molecule.

Define the parameter δ as follows:

$$\delta \equiv \frac{\mu^2}{4\epsilon\sigma^3}\, g(\theta_1,\theta_2,\varphi) \tag{4}$$

Using this definition, equation (2) may be rewritten as follows:

$$E(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \delta\left(\frac{\sigma}{r}\right)^{3}\right] \tag{5}$$

Equation (5) is the form of the equation that Krieger (ref. 3) used to obtain collision integrals for polar molecules. In order to simplify calculations, Krieger suggested letting $g(\theta_1,\theta_2,\varphi)$ in equation (4) equal +2, corresponding to alined dipoles of maximum attraction. This assumes the dipoles have sufficient time to orient before collision. For this assumption, equation (4) becomes

$$\delta = \frac{\mu^2}{2\epsilon\sigma^3} \tag{6}$$

For the purpose of calculating the collision integrals using equation (5), no specific orientation of the colliding molecules need be assumed. If it is only assumed that the molecules maintain their same relative orientation during the encounter, then $g(\theta_1,\theta_2,\varphi)$ becomes a constant, and it is possible to assign constant values of δ. Krieger performed his calculations for positive δ values. Since a wider range of parameters was desired, and because of a lack of smoothness of Krieger's results, collision integrals for positive values of δ were recalculated.

The calculation of the integrals requires three integrations. The first is to obtain the angles of deflection, the second the collision cross sections, and the third the collision integrals. These three integrals (ref. 1, pp. 525 - 527), based on equations given by Chapman and Cowling (ref. 4), are given in the next section.

The collision integrals evaluated were the $\Omega^{(2,2)*}$ and the $\Omega^{(1,1)*}$ integrals. These are the ones used in evaluating first approximations to the coefficients of viscosity, thermal conductivity, and diffusion of pure gases. The significance of the superscripts is indicated in the following section. Other integrals such as $\Omega^{(1,2)*}$, $\Omega^{(1,3)*}$, or $\Omega^{(2,3)*}$ could be calculated in a similar manner. These are used in higher approximations or for mixtures. But the approximate nature of the potential assumed does not warrant their use.

The transport property equations for pure gases (ref. 1, pp. 528-539) are given here for convenience:

$$[\eta_1]\times10^7 = \frac{266.93\sqrt{MT}}{\sigma^2\Omega^{(2,2)*}} \tag{7}$$

$$[D_1]\times10^7 = \frac{0.0026280\sqrt{T^3/M}}{p\sigma^2\Omega^{(1,1)*}} \tag{8}$$

where

D	self-diffusion coefficient, cm^2/sec
k	Boltzmann's constant, ergs/$^{\circ}$K
M	gas molecular weight, g/mole
p	pressure, atm
T	temperature, $^{\circ}$K
η	viscosity, g/(cm)(sec)
σ	collision diameter, angstroms
$\Omega^{(1,1)*}, \Omega^{(2,2)*}$	collision integrals from table II evaluated at reduced temperature, $T^* = kT/\epsilon$

No equation is given for thermal conductivity, because, for polyatomic molecules, the equation is complicated by the interconversion of translational and internal energy. In polar molecules, additional configurational effects are involved (refs. 5 and 6).

DERIVATION AND EVALUATION OF COLLISION INTEGRALS

Equations of Motion

The general equations of motion for a two-body system in polar coordinates, consisting of two identical colliding molecules A and B, and describing the motion of A relative to B, are as follows:

$$\frac{m}{2} r^2 \dot{\theta} = \frac{m}{2} bg \tag{9}$$

$$\frac{1}{4} m(r^2 \dot{\theta}^2 + \dot{r}^2) + E(r) = \frac{1}{4} mg^2 \tag{10}$$

where g is the relative velocity before the encounter at $r = \infty$, b is the distance of nearest approach in the absence of any interactions, m is the mass of each particle, r is the intermolecular separation, and $E(r)$ is the potential function given in equation (5). These relations are illustrated in figure 3.

If time is eliminated between equations (9) and (10), the resulting equation is

$$d\theta = \frac{dr}{r}\left[\frac{r^2}{b^2} - 1 - \frac{4r^2 E(r)}{mg^2 b^2}\right]^{-(1/2)} \tag{11}$$

Integrating from $r = a$ to $r = \infty$, where a is the distance of closest approach, results in the expression for the angle θ_m, the angle of θ for $r = \infty$:

$$\theta_m(g,b,\delta) = \int_a^\infty \frac{dr}{r}\left[\frac{r^2}{b^2} - 1 - \frac{4r^2E(r)}{mg^2b^2}\right]^{-(1/2)} \tag{12}$$

Since $dr/d\theta = 0$ at $r = a$, equation (11) becomes

$$\frac{a^2}{b^2} - 1 - \frac{4a^2E(a)}{mg^2b^2} = 0 \tag{13}$$

which determines the lower limit a. Knowing θ_m as a function of g and b, the cross section for transport can be found from the relation (ref. 1, p. 525)

$$Q^{(l)}(g,\delta) = 2\pi \int_0^\infty (1 - \cos^{(l)} \chi)b\ db \tag{14}$$

where l is a positive integer, and

$$\chi = \pi - 2\theta_m \tag{15}$$

as shown in figure 3.

In this work the only cross sections of interest are $Q^{(1)}(g)$ and $Q^{(2)}(g)$. Equation (14) then becomes

$$Q^{(1)}(g,\delta) = 2\pi \int_0^\infty (1 + \cos 2\theta_m)b\ db \tag{16a}$$

$$Q^{(2)}(g,\delta) = 2\pi \int_0^\infty (1 - \cos^2 2\theta_m)b\ db \tag{16b}$$

From the cross sections, the final collision integrals can be computed (ref. 1, p. 525) by

$$\Omega^{(l,s)}(T,\delta) = \sqrt{\frac{kT}{\pi m}} \int_0^\infty e^{-\gamma^2} \gamma^{2s+3} Q^{(l)}(g)\ d\gamma \tag{17}$$

where s is a positive integer, and

$$\gamma^2 = \frac{mg^2}{4kT} \tag{18}$$

The collision integrals calculated were $\Omega^{(1,1)}(T)$ and $\Omega^{(2,2)}(T)$.

Introduction of Dimensionless Parameters

As an aid to computation, the variables can be put in dimensionless form, utilizing the characteristic quantities ϵ and σ Define the following dimensionless quantities:

$$r^{*} = r/\sigma \tag{19}$$

$$b^{*} = b/\sigma \tag{20}$$

$$E^{*} = E(r^{*})/\epsilon = 4(r^{*-12} - r^{*-6} - \delta r^{*-3}) \tag{21}$$

Letting

$$g^{*2} = mg^{2}/4\epsilon \tag{22}$$

$$T^{*} = kT/\epsilon \tag{23}$$

and using the values of $Q^{(l)}$ and $\Omega^{(l,s)}$ for a rigid sphere (ref. 1, p. 525)

$$Q^{(l)}_{\text{rigid sphere}} = \left[1 - \frac{1}{2}\,\frac{1 + (-1)^{l}}{1 + l}\right]\pi\sigma^{2} \tag{24}$$

$$\Omega^{(l,s)}_{\text{rigid sphere}} = \sqrt{\frac{kT}{\pi m}}\,\frac{(s + 1)!}{2}\,\left[Q^{l}\right]_{\text{rigid sphere}} \tag{25}$$

then equations (12), (14), and (17) become in reduced form (ref. 1, p. 527)

$$\theta_{m}(g^{*},b^{*},\delta) = \int_{a^{*}}^{\infty} \frac{dr^{*}}{r^{*}}\left(\frac{r^{*2}}{b^{*2}} - 1 - \frac{r^{*2}E^{*}}{g^{*2}b^{*2}}\right)^{-1/2} \tag{26}$$

$$Q^{(l)*}(g^{*},\delta) = \frac{Q^{(l)}}{Q^{(l)}_{\text{rigid sphere}}} = \frac{2}{\left[1 - \frac{1}{2}\,\frac{1 + (-1)^{l}}{1 + l}\right]}\int_{0}^{\infty} (1 - \cos^{(l)}\chi)b^{*}\,db^{*} \tag{27}$$

$$\begin{aligned}\Omega^{(l,s)*}(T^{*},\delta) &= \frac{\Omega^{(l,s)}}{\Omega^{(l,s)}_{\text{rigid sphere}}}\\ &= \frac{2}{(s + 1)!T^{*s+2}}\int_{0}^{\infty} e^{-(g^{*2}/T^{*})}\,g^{*2s+3}\,Q^{(l)*}(g^{*})dg^{*}\end{aligned} \tag{28}$$

In particular,

$$Q^{(1)*}(g^*,\delta) = 2\int_0^\infty (1 + \cos 2\theta_m)b^*\, db^* \tag{29a}$$

$$Q^{(2)*}(g^*,\delta) = 3\int_0^\infty (1 - \cos^2 2\theta_m)b^*\, db^* \tag{29b}$$

$$\Omega^{(1,1)*}(T^*,\delta) = \frac{1}{T^{*3}}\int_0^\infty e^{-(g^{*2}/T^*)}\, g^{*5}\, Q^{(1)*}(g^*)dg^* \tag{30a}$$

$$\Omega^{(2,2)*}(T^*,\delta) = \frac{1}{3T^{*4}}\int_0^\infty e^{-(g^{*2}/T^*)}\, g^{*7}\, Q^{(2)*}(g^*)dg^* \tag{30b}$$

Integration Technique

Angle of deflection integral. - The angle of deflection integral is

$$\theta_m(g^*,b^*,\delta) = \int_{a^*}^\infty \frac{dr^*}{r^*}\left(\frac{r^{*2}}{b^{*2}} - 1 - \frac{r^{*2}E^*}{g^{*2}b^{*2}}\right)^{-1/2} \tag{26}$$

In order to simplify the numerical integration, the change of variable $\rho \equiv 1/r^*$ is used in equation (26) to give

$$\theta_m(g^*,b^*,\delta) = \int_0^A \left[\frac{b^{*2}}{1 - b^{*2}\rho^2 + \frac{4}{g^{*2}}(-\rho^{12} + \rho^6 + \delta\rho^3)}\right]^{1/2} d\rho \tag{31}$$

where $A(= 1/a^*)$ is the smallest positive root of the denominator of the integrand of equation (31):

$$\frac{4}{g^{*2}}(-\rho^{12} + \rho^6 + \delta\rho^3) - b^{*2}\rho^2 + 1 = 0 \tag{32}$$

Equation (32) has either three or one positive roots (by Descartes' rule of signs), so that finding the smallest root proves to be a problem in some cases. Figure 4 shows a typical example of this function for $g^* = 0.5$, $\delta = 1$, and various values of b^*.

To find the proper root of equation (32), an iterative procedure (Uspensky's method, ref. 7) is used with the initial estimate $A = 1/b^*$. This is a good estimate for sufficiently large b^*, and also for all $b^* < 1$, since an examination of equation (32) shows that A is greater than unity for all $b^* < 1$. However, in certain cases where b^* is not much greater than 1, a minimum above the ρ-axis exists for equation (32) in the vicinity of the initial estimate $\rho = 1/b^*$ (e.g., $b^* = 3$ in fig. 4). In this situation Uspensky's method does not converge but oscillates about the minimum. This situation can be detected by the fact that the first derivative becomes positive during this oscillation. When this occurs a new estimate of $A > 1$ is made so that the first derivative of equation (32) is negative, and the iterative procedure is continued. This root-finding procedure has been successful in all cases attempted in this work.

Once the proper root has been found, the angle of deflection integral can be evaluated. It should be noted that a pole exists at the upper limit A. However, it is a half-order pole if A is a single root, and can be handled by fitting the function to a polynomial of the form $(a_0 + a_1x + \cdot \cdot \cdot + a_nx^n)/x^{1/2} = f(x)$ in the vicinity of the pole. The remainder of the integral is well behaved and is accurately evaluated using the Gaussian numerical integration procedure (ref. 8).

Referring to figure 4, it is seen that a double root of equation (32) is possible (in this example at $b^* = b_0^*$, where $b_0^* \cong 3.6$). The integral now no longer has a half-order pole at A, but rather a pole of order 1, which leads to an integral whose value approaches ∞. Thus, for values of b^* near b_0^*, the molecules orbit around each other an indefinite number of times before separating. The occurrence of a double root is not possible for all values of the parameter g^*. For every value of δ there exists a value $g_0^*(\delta)$, such that for all $0 < g^* \leq g_0^*$ there exists a $b_0^*(g^*,\delta)$, where equation (32) has a double root, and the phenomenon of "orbiting" occurs. For all $g^* > g_0^*$ no positive value of b^* exists such that equation (32) has a double root, and orbiting cannot occur. Values of $g_0^{*2}(\delta)$ are given in table I.

Cross-section integrals. - The cross-section integrals, equations (29a) and (29b), can be easily evaluated for $g^* > g_0^*(\delta)$ by dividing the integral into two parts:

(a) 0 to b_R^*

(b) b_R^* to ∞

where for all $b^* \geq b_R^*$, it has been found empirically that θ_m can be well approximated by

$$\theta_m(b^*, g^*, \delta) \cong \frac{\pi}{2} + \frac{4\delta}{g^{*2}b^{*3}} \tag{33}$$

That is to say, θ_m approaches $\pi/2$ asymptotically as $b^* \rightarrow \infty$.

The first region is evaluated numerically using the Gaussian integration procedure. The second region is evaluated by substituting equation (33) for θ_m, expanding $\cos 2\theta_m$ in a Maclaurin series, and integrating equations (29) analytically. Dropping all terms after the first nonvanishing term gives:

$$\int_{b_R^*}^{\infty} (1 + \cos 2\theta_m)b^* \, db^* \cong \frac{1}{2}\left(\frac{4\delta}{g^{*2}b_R^{*2}}\right)^2 \tag{34a}$$

$$\int_{b_R^*}^{\infty} (1 - \cos^2 2\theta_m)b^* \, db^* \cong \left(\frac{4\delta}{g^{*2}b_R^{*2}}\right)^2 \tag{34b}$$

When $g^* < g_0^*(\delta)$, orbiting occurs and the curve θ_m against b^* has a singularity at b_0^*. For this situation the integral was broken into five parts as in reference 9 (see fig. 5):

(a) 0 to b_M^*

(b) b_M^* to b_0^*

(c) b_0^* to b_N^*

(d) b_N^* to b_R^*

(e) b_R^* to ∞

Regions (a) and (d) are evaluated numerically as was done in the first case. Also, region (e) is evaluated as before by using equations (34). The regions (b) and (c), which are in the neighborhood of the singularity at b_0^*, are evaluated by curve-fitting θ_m against b^{*2} by an empirical equation of the form

$$\theta_m = a_0 + \frac{a_1}{b_0^{*2} - b^{*2}} \tag{35}$$

where a_0 and a_1 are constants.

If this substitution is made for θ_m in equations (29), the following results are obtained by integrating analytically:

$$\int_{b_M^{*2}}^{b_0^{*2}} (1 + \cos 2\theta)\,d(b^{*2}) = (b_0^{*2} - b_M^{*2}) \Bigg(1 + \cos 2\theta_M$$

$$- 2(\theta_M - a_0) \left\{(\cos 2a_0)\left[\mathrm{Si}(2\theta_M - 2a_0) - \frac{\pi}{2}\right] + (\sin 2a_0)\mathrm{Ci}(2\theta_M - 2a_0)\right\}\Bigg) \tag{36a}$$

$$\int_{b_M^{*2}}^{b_0^{*2}} (1 - \cos^2 2\theta)\,d(b^{*2}) = \frac{(b_0^{*2} - b_M^{*2})}{2} \Bigg(1 - \cos 4\theta_M$$

$$- 4(\theta_M - a_0)\left\{(\cos 4a_0)\left[\mathrm{Si}(4\theta_M - 4a_0) - \frac{\pi}{2}\right] + (\sin 4a_0)\mathrm{Ci}(4\theta_M - 4a_0)\right\}\Bigg) \tag{36b}$$

where

$$\mathrm{Si}(x) = \int_0^x \frac{\sin t}{t}\,dt$$

and

$$\mathrm{Ci}(x) = -\int_x^\infty \frac{\cos t}{t}\,dt$$

Similar results are obtained for the region from b_0^{*2} to b_N^{*2}.

Collision integrals. - The collision integrals are given by equations (30a) and (30b). The final integration that obtains the collision integral is divided into two parts:

(a) 0 to g_0^*

(b) g_0^* to g_R^*

The integral over both parts is evaluated numerically using Gaussian integration, the only difference being in the manner in which the cross sections $Q^{(l)*}$ are calculated. This has already been discussed. The integration is terminated at some $g^* = g_R^*$ where the integral from g_R^* to ∞ is negligible compared with the total integral. For all $T^* \leq 512$, g_R^* is less than 120.

DISCUSSION OF RESULTS

The results of the calculation of the collision integrals $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ are given in table II. The values extend over a large reduced temperature range from $T^* = 0.25$ to $T^* = 512$, and ten values of δ from 0 to 10. The T^* intervals were selected for ease in interpolation and for comparison with other work.

Results of this paper, Hirschfelder's values (ref. 1), Krieger's results (ref. 3), and Rowlinson's values (ref. 10) of $\Omega^{(2,2)*}$ for $\delta = 0$ showed agreement. Moreover, Hirschfelder's $\Omega^{(1,1)*}$ for $\delta = 0$ agreed with this work. However, for $\delta > 0$ the results of Krieger and this work do not agree. Values of collision integrals more than double Krieger's values were obtained at low T^*. At high T^* the discrepancy lessens because the effect of polarity decreases. A study of the goniometric variable method used by Krieger indicated an error in the limits of an integration, and that the transformation to goniometric variables is unfeasible when δ is greater than zero. Details are given in appendix B. The only other work for δ greater than zero is unpublished calculations by Mason and Monchick, which include negative values of δ as well as positive. Their results agree closely with the results of this paper.

DETERMINATION OF PARAMETERS

In order to determine the constants σ, ϵ/k, and δ for various molecules, Krieger assumed the molecules interacted as point dipoles of maximum attraction. He then selected two experimental viscosity data points for each molecule, and used equations (6) and (7) and his $\Omega^{(2,2)*}$ table in connection with the experimental data to determine the constants. His $\Omega^{(2,2)*}$ table extends over a range of T^* from 1 to 512 and a range of δ from 0 to 2 at intervals of 0.25. Of 12 molecules tested, water had the highest δ, with a value of 2.33. In general the constants seem reasonable.

The procedure to find the constants using the present $\Omega^{(2,2)*}$ table was the same as Krieger's method, except that a least squares fit of selected experimental viscosity data was used to determine the best overall constants for a molecule. Table III gives the constants (σ, ϵ/k, δ) obtained using the present $\Omega^{(2,2)*}$ table and experimental dipole moments (μ). Table IV gives the experimental viscosities used to obtain the constants of table III. It also contains viscosities calculated with these constants and $\Omega^{(2,2)*}$ values of this paper. The agreement between experimental and calculated data is good. The average deviation for all molecules is 0.5 percent, the largest average deviation being 1.2 percent for H_2S. The explanation for the relatively large deviation for H_2S is that the experimental data are not smooth. The constants, σ and ϵ/k, are different from those of nonpolar molecules; σ is larger and ϵ/k is smaller. This becomes more pronounced with increasing δ values.

No satisfactory results were obtained for more highly polar molecules such as NH_3 or H_2O using this least-squares technique. Independent hand calculations verified the computer results and indicated that extending the tables to larger values of δ would not help. Since the contribution of the dipole-dipole interaction term to the Stockmayer potential is small for slightly polar molecules, and becomes important for highly polar molecules, it appears that assuming $g(\theta_1,\theta_2,\varphi)$ equals +2 at all times is inadequate.

However, another possible method for obtaining the constants σ, ϵ, and δ would be to treat δ as a third parameter, independent of σ and ϵ. This would mean that no specific relative orientation is assumed during the encounter. Then, knowing the dipole moment of the molecule, it would be possible to calculate an effective $g(\theta_1,\theta_2,\varphi)$ for each molecule by equation (4).

Hornig (ref. 11) suggests using a combination of three types of interactions. Two are for resonant collisions, where the first has $g(\theta_1,\theta_2,\varphi)$ equal to some positive number between 0 and 2, and the second is $-g(\theta_1,\theta_2,\varphi)$. The magnitude of $g(\theta_1,\theta_2,\varphi)$ is calculated from a knowledge of the internal quantum numbers of the molecules. The third type of interaction is a nonresonant collision where the r^{-3} term disappears. Mathematically, this latter interaction is identical to the Lennard-Jones equation for the interaction of nonpolar molecules. Therefore, according to Hornig, the effect of the r^{-3} term on the potential can be attractive, repulsive, or nonexistent depending upon the type of interaction between the two molecules.

Using Hornig's approach, an effective $g(\theta_1,\theta_2,\varphi)$ for an interaction could then be calculated as a weighted average of the three types of interactions, where the weighting factor would depend upon the frequency of each type of collision. When collision integrals for negative δ values become available, it will be possible to try this approach.

In summary, it is concluded that the ability to estimate transport properties of polar gases is still in doubt. However, two possible approaches to the solution of the problem have been mentioned that may eventually resolve the situation.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, August 12, 1960

E-791

APPENDIX A

SYMBOLS

A	$1/a^*$
a	distance of closest approach of colliding molecules
a_0, a_1	constants in empirical equation (35) for curve-fitting θ_m against b^{*2}
a^*	a/σ
b	distance of closest approach of colliding molecules in absence of any interactions
b^*	b/σ
b_M^*	lower limit for analytic integration of $Q^{(l)*}$ integrals in vicinity of orbiting
b_N^*	upper limit for analytic integration of $Q^{(l)*}$ integrals in vicinity of orbiting
b_R^*	numerical integration limit for $Q^{(l)*}$ integrals
b_0^*	value of b^* for which orbiting occurs
$Ci(x)$	$-\int_x^\infty \frac{\cos t}{t}\,dt$
D_1	first approximation to coefficient of diffusion
$E(r)$	interaction potential
E^*	$E(r^*)/\epsilon$
g	relative velocity between molecules at infinite separation before colliding
g^*	$(mg^2/4\epsilon)^{1/2}$
g_R^*	numerical integration limit for $\Omega^{(l,s)*}$ integrals
g_0^*	value of g^* such that orbiting does not occur for all $g^* > g_0^*$

k	Boltzmann's constant
M	molecular weight
m	molecular mass
p	pressure
$Q^{(l)}(g,\delta)$	collision cross section
$Q^{(l)*}(g^*,\delta)$	$Q^{(l)}/Q^{(l)}_{\text{rigid sphere}}$
r	intermolecular separation between colliding molecules
r^*	r/σ
$\mathrm{Si}(x)$	$\int_0^x \frac{\sin t}{t}\,dt$
T	temperature
T^*	kT/ϵ
γ	$(mg^2/4kT)^{1/2}$
δ	parameter in modified Stockmayer potential
ϵ	maximum energy of attraction between colliding molecules in absence of dipole forces
η_1	first approximation to coefficient of viscosity
θ	$\frac{1}{2}(\pi - \chi)$
θ_m	angle θ at infinite separation of colliding molecules
$\theta_1,\theta_2,\varphi$	angles describing relative orientation of two point dipoles
$\dot{\theta}$	first derivative of θ with respect to time
μ	dipole moment
ρ	$1/r^*$
σ	collision diameter
χ	angle of deflection in bimolecular collision

$\Omega^{(l,s)}(T,\delta)$	collision integral
$\Omega^{(l,s)*}(T^*,\delta)$	$\Omega^{(l,s)}/\Omega^{(l,s)}_{\text{rigid sphere}}$

APPENDIX B

INVALIDITY IN THE TRANSFORMATION TO GONIOMETRIC VARIABLES

In reference 3, the following statement is made on page 18: "The value of $b^* = 0$ (central collision), for which $2/a^{*6} = 1 + (1 + g^{*2})^{1/2}$, corresponds to the value $\beta = 0$." It can be shown that this is a true statement if, and only if, $\delta = 0$. To accomplish this, equations (26), (29), and (30) from reference 3, corresponding here to equations (B1), (B2), and (B3), respectively, are used:

$$\frac{b^{*2}}{a^{*2}} + \frac{4}{g^{*2}}\left(a^{*-12} - a^{*-6} - \delta a^{*-3}\right) = 1 \tag{B1}$$

$$g^* = \cot \gamma \qquad \left(0 \leq \gamma \leq \frac{\pi}{2}\right) \tag{B2}$$

$$2a^{*-6} = 1 + \frac{\cos \beta}{\sin \gamma} \qquad \left(0 \leq \beta \leq \frac{\pi}{2} + \gamma\right) \tag{B3}$$

where equations (B2) and (B3) are the defining equations for the transformation to the goniometric variables β and γ.

If $b^* = 0$ (the lower limit of the cross-section integrals), equation (B1) becomes

$$a^{*-12} - a^{*-6} - \delta a^{*-3} = \frac{g^{*2}}{4} \tag{B4}$$

Let a_0^* be the one positive real root of this equation. Then from equation (B3) the β corresponding to $b^* = 0$ is

$$\beta = \text{arc cos}\left[\left(2a_0^{*-6} - 1\right)\sin \gamma\right]$$

or

$$\beta = \text{arc cos}\left[(2a_0^{*-6} - 1)\Big/(g^{*2} + 1)^{1/2}\right] \tag{B5}$$

since $\sin \gamma = (g^{*2} + 1)^{-1/2}$ from equation (B2).

If $\delta = 0$, equation (B4) becomes

$$a^{*-12} - a^{*-6} = \frac{g^{*2}}{4} \tag{B6}$$

The solution of this equation leads to the result

$$a^{*-6} = \frac{1 \pm (1 + g^{*2})^{1/2}}{2}$$

and, since a_0^* is positive,

$$2a_0^{*-6} = 1 + (1 + g^{*2})^{1/2} \tag{B7}$$

If this quantity is substituted in equation (B5), the result is

$$\beta = \text{arc cos } 1$$

or

$$\beta = 0$$

When $\delta = 0$, $\beta = 0$ corresponding to $b^* = 0$.

Next, assume $\beta = 0$. Then from equation (B5),

$$(2a_0^{*-6} - 1)/(g^{*2} + 1)^{1/2} = 1$$

Solving for a_0^{*-6} and substituting in equation (B4) give

$$\left[\frac{(g^{*2} + 1)^{1/2} + 1}{2}\right]^2 - \frac{(g^{*2} + 1)^{1/2} + 1}{2} - \delta\left[\frac{(g^{*2} + 1)^{1/2} + 1}{2}\right]^{1/2} - \frac{g^{*2}}{4} = 0 \tag{B8}$$

which, after combining like terms, results in

$$\delta\left[\frac{(g^{*2} + 1)^{1/2} + 1}{2}\right]^{1/2} = 0 \tag{B9}$$

This implies either $\delta = 0$ or $(g^{*2} + 1)^{1/2} + 1 = 0$. Since the latter quantity is never zero for all real g^*, $\delta = 0$. Thus it has been shown that $\beta = 0$ corresponds to $b^* = 0$ if, and only if, $\delta = 0$. In reference 3 $\beta = 0$ is used for the lower limit of the cross-section integral for all δ. This is therefore incorrect.

However, even if the correct lower limit (eq. (B5)) for β had been used, the transformation to β (eq. (B3)) does not always lead to a real value for β corresponding to $b^* = 0$. An example will suffice to illustrate this fact. Take $\delta = 1$ and $g^* = \sqrt{40}$ and calculate β. Substituting in these values for g^* and δ and letting $a^{*-3} = C$, equation (B4) becomes

$$C^4 - C^2 - C - 10 = 0 \tag{B10}$$

The solution of equation (B10) for the one real, positive root is $C = 2$. Therefore, $2C^2 = 2a^{*-6} = 8$. Substituting this value in equation (B5) leads to the result

$$\beta = \text{arc cos}\,\frac{7}{\sqrt{41}}$$

Thus in this particular example, no real β corresponds to $b^* = 0$. Therefore, the transformation to the goniometric variable β by equation (B3) is not valid for $\delta \neq 0$.

REFERENCES

1. Hirschfelder, Joseph O., Curtiss, Charles F., and Bird, R. Byron: Molecular Theory of Gases and Liquids. John Wiley & Sons, Inc., 1954.

2. Stockmayer, W. H.: Second Virial Coefficients of Polar Gases. Jour. Chem. Phys., vol. 9, no. 5, 1941, pp. 398-402.

3. Krieger, F. J.: The Viscosity of Polar Gases. RM-646, The Rand Corp., July 1, 1951.

4. Chapman, Sydney, and Cowling, T. G.: The Mathematical Theory of Non-Uniform Gases. Second ed., Cambridge Univ. Press, 1952, p. 157.

5. Schäfer, K.: Über das Verhältnis des Warmeleitvermögens von Dipolgasen zu ihrer Viscosität. Zs. f. phys. Chem., Abt. B, Bd. 53, 1943, pp. 149-167.

6. Vines, R. G., and Bennett, L. A.: The Thermal Conductivity of Organic Vapors. The Relationship Between Thermal Conductivity and Viscosity, and the Significance of the Eucken Factor. Jour. Chem. Phys., vol. 22, no. 3, Mar. 1954, pp. 360-366.

7. Uspensky, J. V.: Theory of Equations. McGraw-Hill Book Co., Inc., 1948, p. 179.

8. Scarborough, James B.: Numerical Mathematical Analysis. The Johns Hopkins Press, 1930, pp. 131-139.

9. Hirschfelder, Joseph O., Bird, R. Byron, and Spotz, Ellen L.: The Transport Properties of Non-Polar Gases. Jour. Chem. Phys., vol. 16, no. 10, Oct. 1948, pp. 968-981.

10. Rowlinson, J. S.: The Transport Properties of Non-Polar Gases. Jour. Chem. Phys., vol. 17, no. 1, Jan. 1949, p. 101.

11. Hornig, James F.: A Semiclassical Theory of Molecular Collisions. Tech. Rep. ONR-10, Naval Res. Lab., Univ. Wisconsin, Sept. 2, 1954.

12. Maryott, Arthur A., and Buckley, Floyd: Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State. Circular 537, NBS, June 25, 1953.

13. Johnston, Herrick L., and Grilly, Edward R.: Viscosities of Carbon Monoxide, Helium, Neon, and Argon Between 80° and 300° K. Coefficients of Viscosity. Jour. Phys. Chem., vol. 46, no. 8, Nov. 1942, pp. 948-963.

14. Wobser, R., und Müller, Fr.: Die innere Reibung von Gasen und Dämpfen und ihre Messung im Höppler-Viskosimeter. Kolloid-Beihefte, Bd. 52, Nos. 6-7, 1941, pp. 165-276.

15. Trautz, Max, und Bauman, P. B.: Die Reibung, Wärmeleitung und Diffusion in Gasmischungen. II. - Die Reibung von H_2-N_2- und H_2-CO-Gemischen. Ann. Phys., Bd. 2, ser. 5, 1929, pp. 733-736.

16. Trautz, Max, und Ludewigs, Walter: Die Reibung, Wärmeleitung und Diffusion in Gasmischungen. VI. - Reibungsbestimmung an reinen Gasen durch direkte Messung und durch solche an ihren Gemischen. Ann. Phys., Bd. 3, ser. 5, 1929, pp. 409-428.

17. Trautz, Max, und Melster, Albert: Die Reibung, Wärmeleitung und Diffusion in Gasmischungen. XI. - Die Reibung von H_2, N_2, CO, C_2H_4, O_2 und ihren binären Gemischen. Ann. Phys., Bd. 7, ser. 5, 1930, pp. 409-426.

18. Trautz, Max, und Freytag, Adolf: Die Reibung, Wärmeleitung und Diffusion in Gasmischungen. XXVIII. - Die innere Reibung von Cl_2, NO und NOCl. Gasreibung während der Reaktion $2NO + Cl_2 = 2NOCl$. Ann. Phys., Bd. 20, ser. 5, 1934, pp. 135-144.

19. Trautz, Max, und Gabriel, Ernst: Die Reibung, Wärmeleitung und Diffusion in Gasmischungen. XX. - Die Reibung des Stickoxyds NO und seiner Mischung mit N_2. Ann. Phys., Bd. 11, ser. 5, 1931, pp. 606-610.

20. Ellis, C. P., and Raw, C. J. G.: High-Temperature Gas Viscosities. II. Nitrogen, Nitric Oxide, Boron Trifluoride, Silicon Tetrafluoride, and Sulfur Hexafluoride. Jour. Chem. Phys., vol. 30, no. 2, Feb. 1959, pp. 574-576.

21. Trautz, Max, und Winterkorn, Hans: Die Reibung, Wärmeleitung und Diffusion in Gasmischungen. XVIII. - Die Messung der Reibung an aggressiven Gasen (Cl_2,HJ). Ann. Phys., Bd. 10, ser. 5, 1931, pp. 511-528.

22. Trautz, Max, und Ruf, Fritz: Die Reibung, Wärmeleitung und Diffusion in Gasmischungen. XXVII. - Die innere Reibung von Chlor und von Jodwasserstoff Eine Nachprüfung der η-Messungsmethode für aggressive Gase. Ann. Phys., Bd. 20, ser. 5, 1934, pp. 127-134.

23. Harle, H.: Viscosities of the Hydrogen Halides. Proc. Roy. Soc. (London), ser. A, vol. 100, Jan. 2, 1922, pp. 429-440.

24. Braune, H., und Linke, R.: Über die innere Reibung einiger Gase und Dampfe. III. - Einfluss des Dipolmoments auf die Grösse Sutherlandschen Konstanten. Zs. phys. Chem., Abt. A, Bd. 148, no. 3, June 1930, pp. 195-215.

25. Titani, Toshizo: The Viscosity of Vapours of Organic Compounds. Chem. Soc. Japan, Bull. 8, Sept. 1933, pp. 255-276.

26. Vogel, Hans: Über die Viskosität einiger Gase und ihre Temperaturabhängigkeit bei tiefen Temperaturen. Ann. Phys., Bd. 43, ser. 4, Apr. 1914, pp. 1235-1272.

27. Smith, C. J.: On the Viscosity and Molecular Dimensions of Gaseous Carbon Oxysulphide (COS). Phil. Mag., vol. 44, Aug. 1922, pp. 289-292.

28. Titani, Toshizo: Viscosity of Vapours of Organic Compounds, I. Inst. Phys. Chem. Res. (Japan), vol. 8, 1929, pp. 433-460.

29. Van Cleave, A. B., and Maass, O.: The Variation of the Viscosity of Gases with Temperature Over a Large Temperature Range. Canadian Jour. Res., vol. 13, no. 3, Sept. 1935, pp. 140-148.

30. Rankine, A. O., and Smith, C. J.: On the Viscosities and Molecular Dimensions of Methane, Sulphuretted Hydrogen, and Cyanogen. Phil. Mag., vol. 42, Nov. 1921, pp. 615-620.

31. Trautz, Max, und Narath, Albert: Die innere Reibung von Gasgemischen. Ann. Phys., Bd. 79, ser. 4, Apr. 23, 1926, pp. 637-672.

TABLE I. - VALUES OF $g_0^{*2}(\delta)$

δ	$g_0^{*2}(\delta)$
0	0.80000
.25	1.02738
.5	1.26188
1.0	1.75000
1.5	2.26093
2.0	2.79221
2.5	3.34197
3.0	3.90874
3.5	4.49133
4.0	5.08872
4.5	5.70007
5.0	6.32464
7.5	9.62567
10.0	13.18494

TABLE II. - COLLISION INTEGRALS

(a) $\Omega^{(1,1)*}$

T^*	$\Omega^{(1,1)*}$ for δ of -									
	0.0	0.25	0.50	1.00	1.50	2.00	3.50	5.00	7.50	10.00
0.25	2.8620	4.5027	6.1857	9.3646	12.2534	14.9085	21.8997	27.9376	36.5864	44.1961
.30	2.6475	4.0726	5.5299	8.2948	10.8258	13.1617	19.3388	24.7006	32.4749	39.2127
.35	2.4669	3.7360	5.0312	7.4907	9.7515	11.8455	17.4041	22.2453	29.3133	35.4827
.40	2.3130	3.4612	4.6338	6.6599	8.9093	10.8127	15.8829	20.3103	26.8004	32.5157
.45	2.1806	3.2302	4.3060	6.3485	8.2286	9.9775	14.6503	18.7403	24.7512	30.0775
.50	2.0651	3.0323	4.0289	5.9231	7.6650	9.2860	13.6282	17.4368	23.0447	28.0340
.55	1.9645	2.8603	3.7899	5.5616	7.1889	8.7025	12.7646	16.3345	21.5987	26.2945
.60	1.8761	2.7093	3.5810	5.2491	6.7801	8.2025	12.0237	15.3882	20.3555	24.7945
.65	1.7980	2.5756	3.3963	4.9751	6.4241	7.7681	11.3801	14.5654	19.2734	23.4862
.70	1.7288	2.4565	3.2316	4.7321	6.1103	7.3866	10.8149	13.8423	18.3217	22.3338
.80	1.6118	2.2537	2.9500	4.3179	5.5798	6.7449	9.8666	12.6277	16.7215	20.3933
.90	1.5172	2.0879	2.7179	3.9759	5.1452	6.2233	9.0998	11.6443	15.4241	18.8182
1.00	1.4398	1.9504	2.5237	3.6875	4.7801	5.7878	8.4648	10.8292	14.3477	17.5102
1.20	1.3211	1.7368	2.2177	3.2261	4.1955	5.0951	7.4687	9.5511	12.6568	15.4537
1.40	1.2537	1.5799	1.9893	2.8730	3.7444	4.5621	6.7161	8.5890	11.3816	13.9012
1.60	1.1679	1.4606	1.8134	2.5946	3.3841	4.1352	6.1215	7.8342	10.3804	12.6810
1.80	1.1166	1.3674	1.6746	2.3702	3.0894	3.7838	5.6356	7.2228	9.5703	11.6927
2.00	1.0754	1.2929	1.5628	2.1861	2.8441	3.4890	5.2281	6.7148	8.8993	10.8733
2.20	1.0415	1.2320	1.4712	2.0329	2.6372	3.2378	4.8796	6.2838	8.3329	10.1812
2.40	1.0132	1.1815	1.3951	1.9038	2.4606	3.0215	4.5769	5.9118	7.8472	9.5877
2.60	.9890	1.1390	1.3308	1.7939	2.3084	2.8334	4.3109	5.5863	7.4251	9.0722
2.80	.9682	1.1027	1.2761	1.6993	2.1762	2.6684	4.0747	5.2980	7.0540	8.6197
3.00	.9500	1.0714	1.2289	1.6173	2.0605	2.5229	3.8635	5.0403	6.7245	8.2186
3.50	.9131	1.0092	1.1354	1.4537	1.8266	2.2251	3.4209	4.4985	6.0386	7.3883
4.00	.8846	.9627	1.0664	1.3322	1.6503	1.9970	3.0700	4.0646	5.4947	6.7356
4.50	.8617	.9266	1.0134	1.2389	1.5135	1.8177	2.7855	3.7076	5.0486	6.2054
5.00	.8428	.8976	.9714	1.1654	1.4049	1.6739	2.5507	3.4083	4.6736	5.7633
5.50	.8267	.8737	.9374	1.1060	1.3169	1.5565	2.3542	3.1537	4.3524	5.3868
6.00	.8129	.8536	.9091	1.0572	1.2443	1.4592	2.1878	2.9346	4.0734	5.0608
7.00	.7898	.8214	.8647	.9818	1.1322	1.3079	1.9225	2.5776	3.6107	4.5208
8.00	.7712	.7965	.8313	.9264	1.0501	1.1965	1.7218	2.3004	3.2419	4.0882
9.00	.7556	.7763	.8050	.8839	.9876	1.1115	1.5657	2.0799	2.9409	3.7319
10.00	.7422	.7596	.7836	.8502	.9384	1.0448	1.4415	1.9012	2.6909	3.4323
11.00	.7306	.7453	.7658	.8228	.8989	.9912	1.3408	1.7541	2.4805	3.1768
12.00	.7202	.7329	.7506	.8000	.8663	.9473	1.2578	1.6313	2.3013	2.9562
16.00	.6878	.6955	.7062	.7367	.7784	.8301	1.0359	1.2964	1.7940	2.3130
20.00	.6641	.6692	.6765	.6973	.7260	.7622	.9091	1.1014	1.4847	1.9039
24.00	.6454	.6492	.6544	.6696	.6907	.7174	.8279	.9759	1.2802	1.6250
32.00	.6173	.6194	.6226	.6317	.6445	.6609	.7303	.8262	1.0317	1.2763
40.00	.5963	.5977	.5998	.6059	.6145	.6256	.6734	.7409	.8894	1.0720
50.00	.5760	.5769	.5782	.5824	.5880	.5955	.6282	.6751	.7808	.9144
64.00	.5542	.5548	.5556	.5585	.5618	.5666	.5879	.6189	.6904	.7830
80.00	.5352	.5355	.5360	.5381	.5401	.5433	.5576	.5787	.6283	.6939
100.00	.5168	.5169	.5173	.5188	.5198	.5219	.5315	.5458	.5799	.6257
128.00	.4970	.4971	.4973	.4983	.4988	.5001	.5061	.5153	.5376	.5681
200.00	.4630	.4630	.4630	.4635	.4635	.4640	.4666	.4706	.4807	.4949
256.00	.4450	.4450	.4450	.4453	.4453	.4456	.4471	.4496	.4560	.4651
300.00	.4338	.4338	.4338	.4340	.4339	.4341	.4353	.4370	.4418	.4487
400.00	.4142	.4141	.4141	.4142	.4141	.4142	.4149	.4158	.4185	.4225
512.00	.3980	.3979	.3979	.3979	.3979	.3979	.3983	.3988	.4004	.4029

TABLE II. - Concluded. COLLISION INTEGRALS

(b) $\Omega^{(2,2)*}$

T*	$\Omega^{(2,2)*}$ for δ of -									
	0.0	0.25	0.50	1.00	1.50	2.00	3.50	5.00	7.50	10.00
0.25	3.0303	4.5079	6.0258	8.8682	11.4260	13.7547	19.8484	25.1364	32.9424	38.9667
.30	2.8413	4.1279	5.4332	7.9028	10.1493	12.2037	17.5907	22.2624	29.1768	35.1536
.35	2.6774	3.8359	4.9897	7.1762	9.1854	11.0323	15.8858	20.0958	26.3160	31.8686
.40	2.5319	3.5980	4.6414	6.6079	8.4282	10.1110	14.5446	18.3927	24.0691	29.1682
.45	2.4015	3.3962	4.3573	6.1503	7.8156	9.3642	13.4569	17.0120	22.2515	26.9569
.50	2.2843	3.2201	4.1180	5.7731	7.3088	8.7448	12.5538	15.8658	20.7450	25.1212
.55	2.1789	3.0635	3.9112	5.4559	6.8822	8.2216	11.7896	14.8963	19.4717	23.5714
.60	2.0842	2.9228	3.7290	5.1842	6.5177	7.7732	11.1787	14.0635	18.3786	22.2426
.65	1.9989	2.7952	3.5659	4.9478	6.2024	7.3843	10.3632	13.3390	17.4279	21.0881
.70	1.9222	2.6790	3.4184	4.7392	5.9265	7.0436	9.4691	12.7018	16.5920	20.0737
.80	1.7904	2.4753	3.1598	4.3843	5.4651	6.4741	9.2260	11.6303	15.1866	18.3692
.90	1.6824	2.3032	2.9396	4.0897	5.0918	6.0161	8.5287	10.7611	14.0469	16.9875
1.00	1.5930	2.1568	2.7495	3.8379	4.7803	5.6381	7.9605	10.0393	13.1006	15.8406
1.20	1.4552	1.9232	2.4386	3.4235	4.2811	5.0448	7.0712	8.9038	11.6124	14.0372
1.40	1.3552	1.7476	2.1971	3.0928	3.8894	4.5918	6.4056	8.0465	10.4876	12.6747
1.60	1.2801	1.6125	2.0061	2.8216	3.5679	4.2269	5.8870	7.3738	9.6021	11.6026
1.80	1.2220	1.5064	1.8525	2.5956	3.2968	3.9217	5.4692	6.8309	8.8836	10.7328
2.00	1.1758	1.4214	1.7274	2.4051	3.0643	3.6602	5.1230	6.3829	8.2872	10.0105
2.20	1.1382	1.3521	1.6241	2.2431	2.8627	3.4320	4.8289	6.0063	7.7829	9.3991
2.40	1.1071	1.2949	1.5378	2.1042	2.6863	3.2308	4.5739	5.6845	7.3506	8.8738
2.60	1.0808	1.2468	1.4648	1.9843	2.5312	3.0518	4.3491	5.4056	6.9754	8.4166
2.80	1.0583	1.2061	1.4026	1.8801	2.3939	2.8915	4.1482	5.1605	6.6467	8.0146
3.00	1.0388	1.1711	1.3491	1.7889	2.2719	2.7473	3.9667	4.9427	6.3560	7.6580
3.50	.9997	1.1021	1.2435	1.6054	2.0203	2.4439	3.5784	4.4868	5.7573	6.9198
4.00	.9699	1.0514	1.1660	1.4680	1.8265	2.2039	3.2596	4.1200	5.2901	6.3421
4.50	.9463	1.0124	1.1071	1.3623	1.6739	2.0108	2.9921	3.8137	4.9123	5.8769
5.00	.9268	.9815	1.0609	1.2790	1.5518	1.8533	2.7645	3.5514	4.5974	5.4935
5.50	.9104	.9563	1.0237	1.2120	1.4523	1.7230	2.5687	3.3229	4.3285	5.1708
6.00	.8962	.9352	.9931	1.1572	1.3701	1.6141	2.3991	3.1215	4.0940	4.8944
7.00	.8728	.9017	.9456	1.0731	1.2433	1.4436	2.1214	2.7824	3.7003	4.4412
8.00	.8538	.8760	.9103	1.0120	1.1507	1.3174	1.9054	2.5084	3.3782	4.0795
9.00	.8380	.8554	.8829	.9656	1.0806	1.2213	1.7341	2.2835	3.1072	3.7794
10.00	.8244	.8383	.8607	.9292	1.0259	1.1460	1.5962	2.0965	2.8752	3.5233
11.00	.8125	.8238	.8423	.8998	.9822	1.0858	1.4833	1.9395	2.6744	3.3004
12.00	.8019	.8112	.8267	.8756	.9466	1.0366	1.3898	1.8064	2.4989	3.1037
16.00	.7684	.7730	.7814	.8094	.8517	.9073	1.1387	1.4352	1.9791	2.5011
20.00	.7436	.7461	.7511	.7688	.7966	.8339	.9959	1.2149	1.6453	2.0901
24.00	.7241	.7254	.7285	.7403	.7598	.7863	.9055	1.0729	1.4185	1.7965
32.00	.6942	.6944	.6957	.7012	.7123	.7274	.7988	.9046	1.1384	1.4150
40.00	.6717	.6714	.6719	.6738	.6816	.6911	.7380	.8103	.9774	1.1856
50.00	.6498	.6493	.6493	.6484	.6545	.6603	.6905	.7389	.8554	1.0073
64.00	.6262	.6256	.6253	.6223	.6275	.6307	.6486	.6790	.7553	.8590
80.00	.6054	.6048	.6043	.6007	.6049	.6066	.6175	.6370	.6879	.7596
100.00	.5851	.5845	.5840	.5805	.5837	.5845	.5907	.6030	.6362	.6848
128.00	.5633	.5628	.5623	.5595	.5614	.5616	.5646	.5717	.5919	.6227
200.00	.5256	.5251	.5247	.5232	.5236	.5233	.5231	.5257	.5332	.5459
256.00	.5056	.5052	.5048	.5038	.5037	.5033	.5023	.5038	.5078	.5152
300.00	.4931	.4927	.4924	.4915	.4913	.4909	.4895	.4907	.4932	.4983
400.00	.4710	.4708	.4705	.4699	.4696	.4692	.4677	.4682	.4690	.4714
512.00	.4528	.4526	.4523	.4519	.4516	.4512	.4499	.4500	.4500	.4511

TABLE III. - FORCE CONSTANTS FOR POLAR MOLECULES

Molecule	σ	ϵ/k	δ	μ, Debyes (ref. 12)
CO	3.668	93.8	0.010	0.112
NO	3.469	120.0	.016	.15
HI	4.264	252.5	.033	.42
$CHCl_3$	5.513	256.7	.086	1.013
COS	4.396	209.3	.100	.70
HBr	3.858	161.2	.251	.80
CH_3OCH_3	4.796	123.1	.450	1.30
CH_2Cl_2	5.323	121.3	.488	1.57
H_2S	4.034	88.4	.529	.92
C_2H_5OH	5.296	47.8	1.456	1.69
HCl	4.164	23.6	2.477	1.079

TABLE IV. - EXPERIMENTAL AND CALCULATED VISCOSITIES

Temperature, °K	$\eta \times 10^6$ Experimental	Reference	$\eta \times 10^6$ Calculated (a)
		CO	
90.28	60.43	13	60.582
131.47	86.50		87.979
159.23	103.10		105.110
211.27	132.67		134.323
256.00	156.75		156.898
305.77	181.11		179.892
293.2	175.3	14	174.267
313.2	184.2		183.165
333.2	192.8		191.794
353.2	201.2		200.180
371.2	208.5		207.536
195.2	126.1	15	125.675
238.0	148.9		148.058
290.3	173.9		172.953
373.6	208.6		208.504
424.2	228.3		228.279
473.4	246.7		246.494
523.1	263.5		264.053
291.1	175.0	16	173.316
324.3	186.9		187.986
373.4	208.6		208.423
423.7	228.1		228.089
474.2	247.1		246.783
523.3	263.6		264.123
294.9	175.3	17	175.034
399.9	218.3		218.927
500.2	254.8		256.059
550.1	271.4		273.286
		COS	
273.2	113.5	27	113.514
288.2	120.0		119.984
373.2	155.4		155.402
		NO	
373.0	227.2	18	226.617
423.0	247.4		249.157
473.0	268.2		270.452
523.0	287.0		290.709
576.0	307.0		311.225
293.1	188.2	19	187.316
323.1	203.2		202.613
373.1	227.2		226.663
423.1	249.2		249.201
473.1	270.4		270.494
523.1	288.5		290.749
293.2	188.2	14	187.368
313.2	198.6		197.643
333.2	208.5		207.609
353.2	218.1		217.290
371.2	226.7		225.779
374.0	222.3	20	227.081
422.8	253.6		249.070
465.7	265.9		267.412
520.4	283.1		289.679
575.0	313.0		310.846
623.1	332.9		328.747
677.3	348.3		348.197
681.2	355.9		349.570
723.5	361.9		364.244
771.5	384.2		380.456
826.7	401.7		398.581
873.0	415.2		413.397
922.0	434.7		428.729
974.2	447.2		444.701
1023.2	454.8		459.383
1077.9	475.3		475.445
1174.8	498.6		503.132
1281.5	530.5		532.611
		HI	
293.6	185.7	21	185.207
369.7	231.0		232.667
422.2	263.1		263.615
471.7	292.2		291.944
524.1	322.8		320.460
293.2	185.5	22	184.951
323.2	201.8		203.969
373.2	231.6		234.786
423.2	262.7		264.395
473.2	292.4		292.778
523.2	318.9		319.980
293.8	187.3	23	185.335
373.4	240.4		234.907
		$CHCl_3$	
293.3	100.1	24	99.458
382.8	128.1		130.913
496.2	166.2		168.356
525.6	175.6		177.570
547.6	182.7		184.333
602.6	200.6		200.766
618.5	207.4		205.395
394.5	135.7	25	134.914
434.5	149.1		148.357
462.3	157.9		157.480
491.9	167.4		166.992
523.2	177.6		176.825
552.6	186.8		185.855
580.7	194.7		194.303
273.1	94.4	26	92.211
		HCl	
294.2	143.4	31	143.360
327.2	160.0		160.606
372.2	183.2		183.275
427.2	209.3		209.632
473.2	230.3		230.617
523.2	253.0		252.408
285.7	139.7	23	138.633
373.5	183.8		183.916
		CH_3OCH_3	
292.7	90.9	28	90.136
313.2	98.4		97.028
333.2	104.4		103.672
353.2	110.9		110.229
373.2	116.7		116.692
393.2	122.8		123.058
216.25	65.84	29	63.995
232.00	70.30		69.402
249.77	75.52		75.502
264.49	79.74		80.543
273.03	82.47		83.458
284.87	86.24		87.484
291.27	88.30		89.652
296.06	89.94		91.270
		CH_2Cl_2	
295.2	99.08	24	98.647
373.3	126.7		125.971
492.2	166.7		167.162
531.9	179.8		179.758
582.6	195.6		195.282
		H_2S	
273.2	116.8	(Corrected) 30	117.359
290.2	124.4		125.022
373.2	160.1		160.641
273.2	115.4	3	117.359
293.2	130.0		126.361
		C_2H_5OH	
403.4	117.3	25	117.346
443.9	129.3		129.217
465.0	135.5		135.242
490.7	142.1		142.436
524.9	151.9		151.772
551.4	158.5		158.826
581.9	167.0		166.761
		HBr	
291.9	183.5	23	183.500
373.4	236.5		236.500

[a] Calculated from equation (7) using constants from table III and collision integrals of table II.

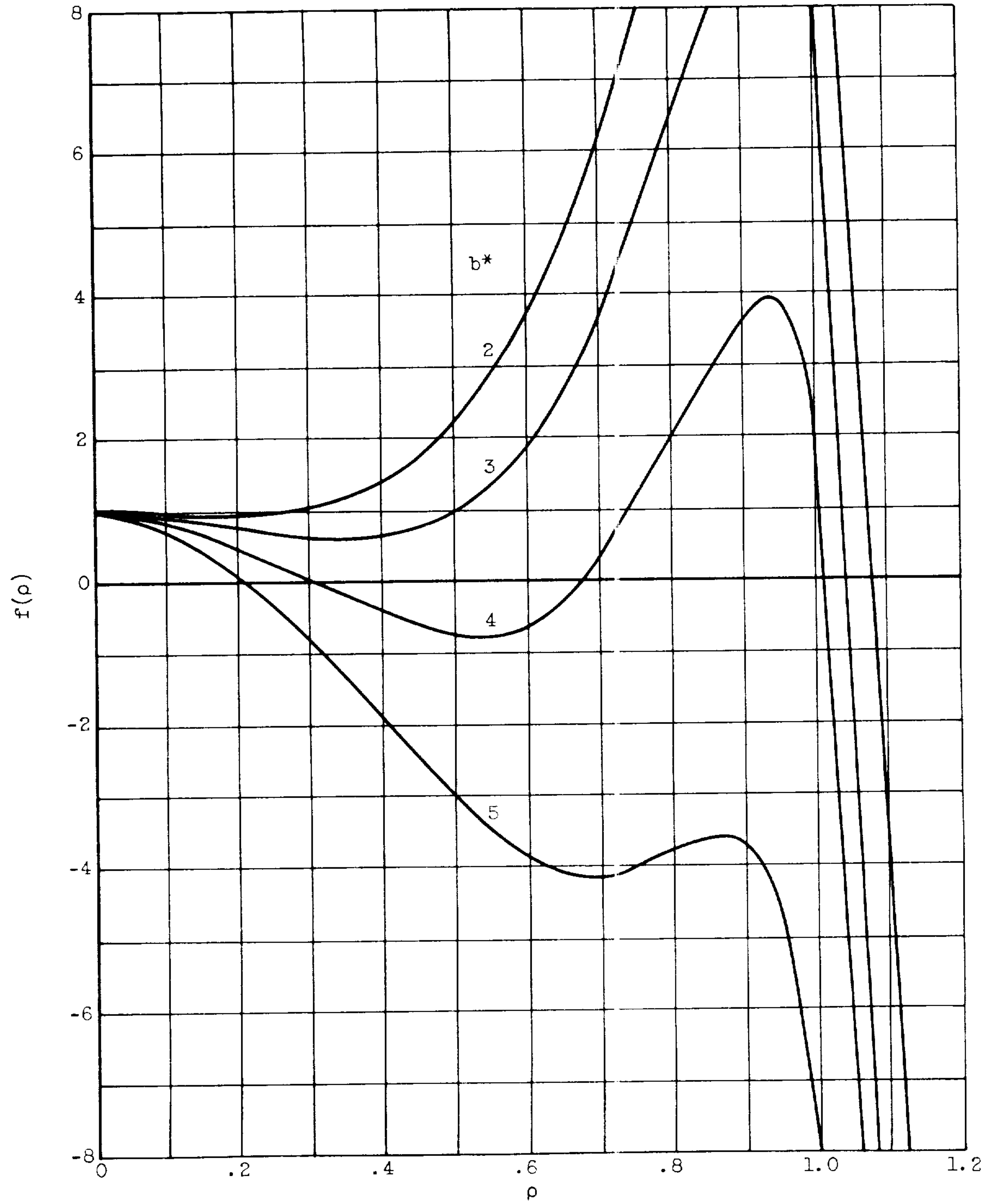

Figure 4. - The function $f(\rho) = (4/g^{*2})(-\rho^{12} + \rho^6 + \delta\rho^3) - b^{*2}\rho^2 + 1$ for $g^* = 0.5$, $\delta = 1$, and various values of b^*.

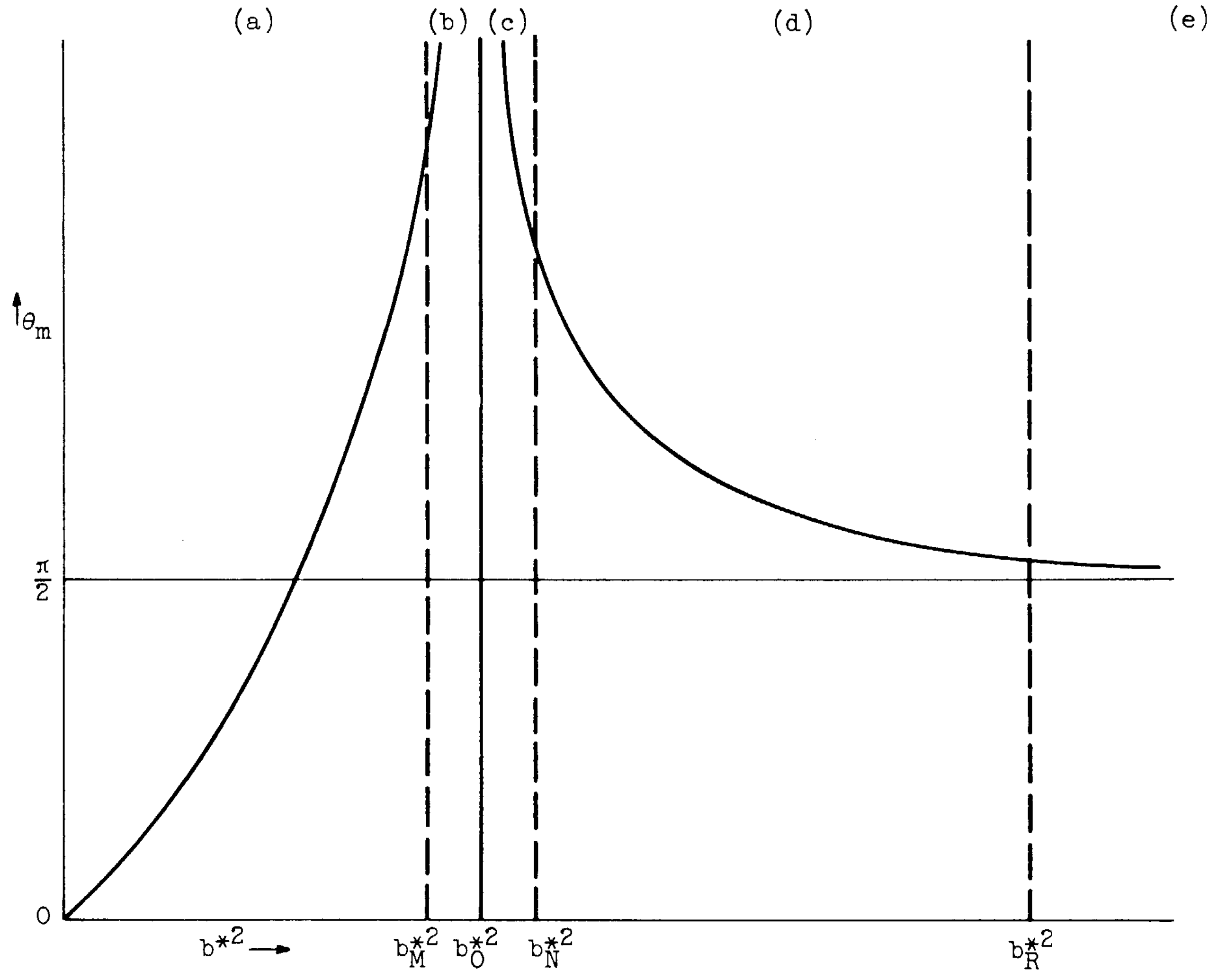

Figure 5. - Angle θ_m in vicinity of orbiting.