THE TRANSPORT PROPERTIES OF GASES AND GASEOUS MIXTURES. II[1,2]

JOSEPH O. HIRSCHFELDER, R. BYRON BIRD, AND ELLEN L. SPOTZ

Naval Research Laboratory, University of Wisconsin, Madison, Wisconsin

Received October 25, 1948

The intermolecular forces are determined for collisions between both like and unlike molecules from experimental measurements of certain transport properties. From these forces other transport properties and the second virial coefficients for pure gases and gaseous mixtures may be calculated as a function of temperature. In most cases the agreement with experiment is excellent. Only thermal conductivity remains anomalous, and this is due to the transfer of energy from the translational to the internal degrees of freedom. A large number of numerical examples are given for viscosity, self-diffusion, ordinary diffusion, and thermal diffusion for pure substances and mixtures. The extrapolations of our equations to very high temperatures are often more reliable than the direct experimental measurements. The relations are given for multicomponent as well as binary mixtures. Formulae are given for all of the transport properties in terms of the integrals presented in a previous paper (7). This treatment assumes that the energy of interaction of two colliding molecules is the sum of an energy of repulsion varying inversely as the twelfth power of the separation and an energy of attraction varying as the inverse sixth power. The viscosities for seven-component industrial flue and fuel gas mixtures up to 1300°K. are readily calculated and shown to agree with available experimental data.

I. INTRODUCTION

The transport coefficients of simple non-polar gases are dependent upon the forces between the molecules involved. In a previous paper (7) we evaluated all of the collision integrals required in the calculations for the transport coefficients. These integrals were tabulated for eighty-four temperature levels, embracing a very wide range.

The potential energy function for the molecular interaction which was employed is that of the form

$$E(r) = 4\epsilon\,[-(r_0/r)^6 + (r_0/r)^{12}] \tag{1}$$

in which r is the molecular separation, ϵ is the maximum energy of attraction, and r_0 is the collision diameter for low-energy head-on collisions. When the force constants are known, it is possible to predict any of the transport properties by the use of the collision integrals; conversely, the transport coefficients provide a very effective means for the determination of the force constants ϵ and r_0.

---

[1] Presented at the Symposium on Thermodynamics and Molecular Structure of Solutions, which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 114th Meeting of the American Chemical Society, Portland, Oregon, September 13 and 14, 1948.

[2] This work was carried out under Contract NOrd 9938 with the Bureau of Ordnance of the United States Navy.

II. DETERMINATION OF THE INTERMOLECULAR FORCE CONSTANTS

At the present time there is a decided dearth of accurate experimental data both for the transport properties and also for the determination of the second virial coefficients of simple gases and their mixtures. On this account, the values of ϵ and r_0 are by no means uniquely specified and must be altered as more precise experimental data become available. Not until more and better measurements have been obtained will it be reasonable to examine and interpret deviations of the actual energy of interaction from the form shown in equation 1.

TABLE 1A

Force constants between like molecules

FORCE CONSTANTS DETERMINED FROM VISCOSITY DATA			REFERENCE FOR VISCOSITY DATA	FORCE CONSTANTS DETERMINED FROM SECOND VIRIAL COEFFICIENT		REFERENCE FOR SECOND VIRIAL COEFFICIENT
Gas	ϵ/k	r_0		ϵ/k	r_0	
	°K.	Å.		°K.	Å.	
Air	97.0	3.617	(a)	99.2	3.522	(c)
H_2	33.3	2.968	(a)	37.02	2.92	(d, e)
N_2	91.46	3.681	(a)	95.9	3.72	(f)
CO_2	190	3.996	(a)	185	4.57	(g)
N_2O	220	3.879	(a)	189	4.59	(g)
NO	119	3.470	(a)	131	3.17	(g)
CH_4	136.5	3.882	(a)	142.7	3.81	(g)
O_2	113.2	3.433	(a)	117.5	3.58	(f)
CO	110.3	3.590	(a)	95.33	3.65	(e)
A	124.0	3.418	(b)	119.5	3.41	(h)
Ne	35.7	2.80	(b)	35.7	2.74	(h)
He	6.03	2.70	(b)	6.03	2.63	(h)

(a) H. L. Johnston and K. E. McCloskey: J. Phys. Chem. **44**, 1038 (1939).
(b) H. L. Johnston and E. R. Grilly: J. Phys. Chem. **46**, 948 (1942).
(c) L. Holborn and H. Schultze: Ann. Physik **47**, 1089 (1915).
(d) J. DeBoer and A. Michels: Physica **5**, 945 (1938); **6**, 97 (1939).
(e) J. Corner: Proc. Roy. Soc. (London) **58**, 737 (1946).
(f) J. O. Hirschfelder and W. E. Roseveare: J. Phys. Chem. **43**, 15 (1939).
(g) J. O. Hirschfelder, F. T. McClure, C. F. Curtiss, and D. W. Osborne: NDRC Report A116.
(h) R. A. Buckingham: Proc. Roy. Soc. (London) **A168**, 264 (1938).

We have already discussed (7) the calculation of force constants between pairs of similar molecules from viscosity data for pure gases. In table 1 are tabulated values of ϵ/k and r_0 so obtained. There are also shown some force constants which are estimated from critical and boiling-point data. These values were obtained using the following approximate relations (which follow from the Lennard-Jones and Devonshire theory of gases and liquids (11; also 2)):

$$\epsilon/k \doteq 0.75T_c \tag{2}$$

$$\epsilon/k \doteq 1.39T_b \tag{3}$$

$$r_0 \doteq (8.33 \times 10^7)(V_c)^{1/3} \tag{4}$$

TABLE 1B

Force constants between like molecules

GAS	r_0 FROM VISCOSITY DATA	ϵ/k FROM VISCOSITY DATA	ϵ/k FROM BOILING POINT	ϵ/k FROM CRITICAL TEMPERATURE	r_0 FROM CRITICAL VOLUME	REFERENCE FOR VISCOSITY DATA
	Å.	°K.	°K.	°K.	Å.	
Xe	4.051	230	228	192	4.04	(i)
C_2N_2	4.38	339	352	301		(i)
AsH_3	4.06	281	303			(i)
CH_2Cl_2	4.759	406	435			(j)
Kr	3.61	190	169	158	3.96	(i)
Cl_2	4.115	357	332	313	4.15	(j)
Br_2	3.859	400	461	431		(k)
COS	4.13	335	310	284		(i)
I_2	4.982	550	637	620		(j)
CCl_4	5.881	327	487	417	5.42	(i)
HgI_2	5.625	698	872			(j)
$SnBr_4$	6.666	465	660			(j)
CS_2	4.438	488	445	410		(p)
$HgBr_2$	5.414	530	827			(j)
CH_3Cl	3.375	855	346	312	4.29	(j)
$CHCl_3$	5.430	327	581	402	5.11	(i)
HCl	3.305	360	261	243	3.69	(m)
SO_2	4.290	252	366	323	4.15	(n)
$SnCl_4$	4.540	1550	538	444	5.88	(j)
$CH\equiv CH$	4.221	185	263	232	4.02	(l)
$CH_2{=}CH_2$	4.232	205	235	212	4.19	(i)
C_2H_6	4.418	230	257	229	4.36	(i)
C_3H_8	5.061	254	321	278		(i)
n-C_4H_{10}	4.997	410	379	320		(l)
i-C_4H_{10}	5.341	313	366	305		(l)
n-C_5H_{12}	5.769	345	431	353	5.64	(p)
n-C_6H_{14}	5.909	413	475	381	5.97	(p)
n-C_8H_{18}	7.451	320	555	427	6.56	(i)
n-C_9H_{20}	8.448	240	589			(i)
Cyclohexane	6.093	324	491	416	5.65	(p)
C_6H_6	5.270	440	491	442	5.30	(i)
CH_3OH	3.585	507	470	385	4.08	(p)
C_2H_5OH	4.455	391	489	387	4.59	(p)

(i) Landolt-Börnstein: *Physikalisch-Chemische Tabellen.*

(j) H. Braune and R. Linke: Z. physik. Chem. **A148**, 195 (1930).

(k) A. O. Rankine: Proc. Roy. Soc. (London) **88**, 582 (1913).

(l) T. Titani: Bull. Chem. Soc. Japan **5**, 98 (1930).

(m) M. Trautz and A. Narath: Ann. Physik **79**, 637 (1926).

(n) M. Trautz and R. Zink: Ann. Physik **7**, 427 (1930).

(p) T. Titani: Bull. Chem. Soc. Japan **8**, 255 (1933).

in which k is Boltzmann's constant, r_0 is the low-velocity collision diameter expressed in Ångströms, T_c is the critical temperature, V_c is the critical volume in cubic centimeters, and T_b is the boiling point. By means of these approximate relations it is possible to estimate the transport properties as well as the second virial coefficients without any direct experimental data.

The values given in table 1, which are calculated from the viscosity data, should be quite good for those spherical non-polar gases whose interaction can be represented fairly well by the above-mentioned potential function. There are included in the table, however, a number of gases which certainly do not meet these qualifications. While we realize that the calculation of these values is not strictly justified on the bases of the polarity and/or the non-spherical shape of many of the molecules listed, we have set forth these force constants in the hope that they may be of some use in the estimation of the various transport properties until the theory can be extended to include these special cases. Also, these figures give some qualitative ideas as to the size of the molecules and the strength of the interaction forces.

The force constants determined from viscosity seem unreasonable for carbon tetrachloride, stannic bromide, stannic chloride, methyl chloride, carbon disulfide, mercuric iodide, and mercuric bromide. In the case of the tetrahalides, this is somewhat surprising because of their symmetric nature. The carbon disulfide discrepancy can be due to its cigar shape. The mercury halides are quite polar.

For example, the ϵ/k value for stannic chloride which was calculated from viscosity data is far greater than that estimated from the formulae in equations 2 and 3. This discrepancy might suggest that stannic chloride molecules are associated in the vapor phase or are polar. Joel Hildebrand suggests that the chlorine atoms might stand out from the central tin atom like the quills of a porcupine. As a result, there is a large interchange of energy between translation and rotation during collisions. Chapman and Cowling show that the viscosity for such "perfectly rough" spheres may be anomalously large by as much as 14 per cent.

It is not surprising that the force constants for the hydrocarbons do not behave properly. In order to fit their second virial coefficients, it is necessary to use a form for the intermolecular energy involving three adjustable constants rather than two (9). We are trying to evaluate the collision integrals for this three-constant model and hope that it will prove suitable for the hydrocarbons.

There are some substances for which our force constants could not be obtained from the experimental viscosity data. They are listed in table 3, together with their Sutherland's constants and the temperature index of their viscosity. For these substances there is no possible choice of ϵ/k and r_0 which would lead to the observed temperature dependence. Their Sutherland's constants divided by the temperature or their temperature exponent, s, are generally larger than any values which can be interpreted in terms of our equations. This may be seen by comparing the values in table 3 with those in table 5. Obviously, our simple model of the intermolecular potential (designed for spherical non-polar molecules) does not apply in these cases. These molecules fall into the following classes:

A. Polar molecules: H_2O, NH_3, HBr, HCN, HI, $HgCl_2$

The energy of interaction of polar molecules is quite different from that of non-polar molecules. Stockmayer (14) has considered the interaction of two polar spherical molecules. He finds that, in addition to the interaction energy which we have assumed (equation 1), there is a term proportional to the product of the dipole moments, inversely proportional to the cube of the separation, and dependent on the orientation of the molecules. With this Stockmayer potential

TABLE 2

Force constants between unlike molecules

GAS PAIR	EXPERIMENTAL D_{12} MEASUREMENT	TEMPERATURE FOR D_{12}	ARITHMETIC MEAN r_{12} FROM VISCOSITY	GEOMETRIC MEAN ϵ_{12}/k FROM VISCOSITY	ϵ_{12}/k FROM D_{12}	ϵ_{12}/k FROM BINARY VISCOSITIES	REFERENCE FOR D_{12} DATA
	$cm.^2\ sec.^{-1}$	°K.	Å.	°K.	°K.	°K.	
He-A	0.641	273.2	3.059	27.3	24.5	30.1	(a)
H_2-O_2	0.697	273.2	3.201	61.4	58.2	59.8	(a)
H_2-N_2	0.674	273.2	3.325	55.2	47.8	60.4	(a)
	0.743	288.2			46.1		(b)
	0.76	293.2			47.7		(c)
H_2-CH_4	0.625	273.2	3.395	67.4	63.8	53.6	(a)
O_2-N_2	0.181	273.2	3.557	102	90.7	98.5	(a)
	0.22	293.2			67.7		(c)
O_2-CO	0.185	273.2	3.512	112	91.9	116	(a)
CO-N_2	0.192	273.2	3.636	100	68.2	104	(a)
CO_2-N_2O	0.096	273.2	3.938	204	183	190	(a)
H_2-CO	0.651	273.2	3.279	60.6	65.0		(a)
H_2-CO_2	0.550	273.2	3.482	79.5	76.0		(a)
	0.619	288.2			63.8		(b)
	0.60	293.2			88.4		(c)
H_2-N_2O	0.535	273.2	3.424	85.6	96.2		(a)
O_2-CO_2	0.139	273.2	3.715	147	115		(a)
	0.16	293.2			110		(c)
CO-CO_2	0.137	273.2	3.793	145	120		(a)
CO_2-N_2	0.144	273.2	3.839	132	93.3		(a)
	0.158	288.2			93.9		(b)
	0.16	293.2			100		(c)
CO_2-CH_4	0.153	273.2	3.909	161	126		(a)
H_2-A	0.77	293.2	3.193	64.3	64.1		(c)
A-N_2	0.20	293.2	3.550	107	83.8		(c)
A-O_2	0.20	293.2	3.426	119	95.2		(c)
A-CO_2	0.14	293.2	3.707	154	142		(c)
He-Ne			2.75	14.7		12.7	
Ne-A			3.11	66.5		68.9	

(a) S. Chapman and T. G. Cowling: *Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, Teddington (1939).

(b) L. E. Boardman and N. E. Wild: Proc Roy. Soc. (London) **A162**, 511 (1937).

(c) L. Waldman: Naturwissenschaften **32**, 223 (1944).

it is possible to fit the second virial coefficients for simple polar molecules with high precision. In order to predict the transport properties for polar molecules, the collision integrals should be evaluated for this same potential. The work involved is stupendous, but sooner or later it will have to be done.

The energy of interaction between polar and non-polar molecules is of the same form as the energy of interaction between two non-polar molecules. It is a surprising fact that the effect of the permanent dipole moment of the polar molecule is negligible in attracting the non-polar molecule (12). However, on this account we can treat such collisions as though they were between two non-polar molecules. Thus, in a forthcoming paper we shall consider the properties of gaseous mixtures in which one component is polar.

TABLE 3

Viscosity of anomalous gases

$$\eta \times 10^7 = c' T^s$$

$$\eta \times 10^7 = k_S T^{1/2}/[1 + (S/T)]$$

GAS	TEMPERATURE RANGE	c'	s	k_S	S	(S/T) SUTHERLAND CONSTANT DIVIDED BY TEMPERATURE IN MIDDLE OF RANGE	REFERENCE FOR VISCOSITY DATA
	°K.						
H_2O	300–400	2.039	1.079	140.2	459.4	1.313	(a)
	500–600	1.227	1.164	235.8	1051	1.911	
	600–700	1.598	1.123	244.4	1108	1.705	
NH_3	300–400	1.203	1.181	202.7	740.7	2.116	(a)
	500–600	2.576	1.053	189.4	684.3	1.244	
	600–700	5.207	0.9427	164.7	518.7	0.7980	
HI	300–400	6.889	0.9837	221.9	312.9	0.8940	(b)
	400–500	10.42	0.9152	229.4	334.4	0.7431	
HBr	300–400	5.004	1.040	245.3	376.2	1.075	(a)
HCN	300–400	0.7443	1.215	166.3	836.2	2.389	(a)
	500–600	1.131	1.144	185.4	999.1	1.817	
$HgCl_2$	500–600	1.521	1.180	351.6	1191	2.165	(a)
	600–700	4.841	1.000	248.1	656.5	1.010	
	750–850	3.406	1.057	314.1	982.8	1.229	
Zn	850–920	1.384	1.237	757.1	2374	2.682	(b)
	920–950	18.68	0.8554	338.9	557.0	0.5957	
Cd	750–850	5.390	1.048	475.5	1011	1.264	(b)
	850–900	9.836	0.9592	406.0	734.2	0.8391	
Hg	500–600	7.488	1.039	486.1	640.1	1.164	(b)
	700–800	8.793	1.018	552.0	776.4	1.035	
	800–900	8.827	1.018	595.7	892.6	1.050	
n-C_7H_{16}	350–450	2.163	0.9789	72.73	363.2	0.9080	(b)
	450–550	0.6715	1.172	133.1	1022	2.044	
F_2	50–150	3.237	1.170	244.7	246.9	2.469	(c)
	200–300	13.52	0.8793	170.7	139.3	0.5572	

(a) H. Braune and R. Linke: Z. physik. Chem. **A148**, 195 (1930).

(b) Landolt-Börnstein: *Physikalisch-Chemische Tabellen.*

(c) E. Kanda: Bull. Chem. Soc. Japan **12,** 463 (1937).

B. Metal vapors and valence-unsaturated molecules: Hg, Cd, and Zn

Valence-unsaturated molecules behave in a rather anomalous fashion. Sometimes their collisions follow one potential energy curve and sometimes another. At large separations, their van der Waals energy of attraction is perfectly normal. However, at shorter distances the energy of interaction depends very largely on the particular electronic state, which corresponds to the collision complex. According to quantum mechanics, there are well defined *a priori* probabilities that a collision will result in a particular electronic state.

The collision between two hydrogen atoms should serve to clarify this complicated situation. At large separations, the van der Waals energy of attraction is perfectly normal. However, at shorter distances the energy of interaction depends upon the spin orientations of the atoms (and the electronic state is determined by the spin orientations). In an arbitrary collision between two hydrogen atoms there is a chance of one in four that the collision will correspond to a singlet electronic state and a chance of three in four that the system will be in a triplet electronic state. The singlet corresponds to the normal H_2 molecule and has the force constants: $\epsilon/k = 51{,}000°K.$ and $r_0 = 0.5$ Å. The triplet state corresponds to the lowest excited state of the hydrogen molecule—a state in which the molecules repel each other except at the largest separations. The triplet state has the force constants:[3] $\epsilon/k = 3.8°K.$ and $r_0 = 3.5$ Å. Thus, in collisions between hydrogen atoms it is expected that one in four collisions will follow the potential curve corresponding to $\epsilon/k = 51{,}000°K.$ and $r_0 = 0.5$ Å., while the other three out of four collisions will follow the potential curve corresponding to $\epsilon/k = 3.8°K.$ and $r_0 = 3.5$ Å.

The metallic vapors mercury, cadmium, and zinc are not valence saturated, and it is to be expected that their collisions should be anomalous in the same sense as those of the hydrogen atoms. These metal vapor atoms are initially in the $^1S_0$ state, but their valence electrons are easily promoted during the course of collisions.

Hildebrand, Wakeham, and Boyd (6) have determined the interaction potential between mercury atoms from a study of the experimental Menke distribution function for liquid mercury. They found that the mercury atoms are so "squishy" that it is necessary to use the inverse ninth rather than the inverse twelfth power to describe their energy of repulsion. This use of the smaller power might correspond to our view that collisions between mercury atoms are a statistical mixture of two sorts—those with large ϵ/k and small r_0 (corresponding to the ground state of Hg_2) and those with small ϵ/k and large r_0 (corresponding to an excited state of Hg_2). If we try to fit Hildebrand, Wakeham, and Boyd's potential with an inverse twelfth power, we obtain the force constants $\epsilon/k = 1522$ and $r_0 = 2.5$ Å. If we insert these force constants into equation 6 we calculate values for the viscosity of mercury as shown in table 4. There is a considerable discrepancy between the calculated and the observed values of the viscosity. It

---

[3] Rough quantum-mechanical calculations by J. O. Hirschfelder (unpublished).

will be interesting to find out whether this discrepancy is due to the two types of collisions or just to the natural "squishiness" of these particular atoms.

C. Cigar-shaped molecules: n-heptane

The transport properties are not very sensitive to the shape of the molecules. However, if the ratio of the length to the diameter becomes too great, all of the physical properties are affected. Thus, the temperature dependence of the viscosity of *n*-heptane is greater than would be expected for spherical molecules.

D. Fluorine

We cannot guess why the temperature dependence of the viscosity of fluorine should be anomalous. Perhaps the experimental data should be checked. If it is substantiated, we would have to conclude that the forces between two fluorine molecules are of a different nature from those for any of the other halogens. This should have a bearing on fluorine chemistry.

TABLE 4

Viscosity of mercury

T	$\eta \times 10^7$ (CALCULATED)	$\eta \times 10^7$ (EXPERIMENTAL)*
°*K.*		
491	4945	4709
603	5943	5831
769	7466	7610
883	8551	8802

* Landolt-Börnstein: *Physikalisch-Chemische Tabellen.*

The force constants between pairs of dissimilar molecules could very easily be calculated from the coefficient of diffusion as a function of temperature, if these data were available. The expression for the coefficient of diffusion is independent of the force constants for the individual components; hence this particular transport property is exceedingly well-adapted to the calculation of the ϵ_{12} and r_{12} for pairs of unlike molecules. The *International Critical Tables* give values of the diffusion constant for a number of pairs of gases at a single temperature. Using these figures and making the fairly reasonable assumption that the collision diameter, r_{12}, is given by:

$$r_{12} = (r_1 + r_2)/2 \tag{5}$$

(here r_1 and r_2 are the individual collision diameters), we have calculated the values of ϵ_{12}/k for these molecule pairs. These results are displayed in table 2. It will be noticed that in many cases the values of ϵ_{12}/k can be fairly well approximated by the geometric mean of the ϵ_1/k and ϵ_2/k for the components involved. The values of ϵ_{12}/k determined from diffusion coefficients lead to values of the viscosity of mixtures which agree well with experimental data.

In table 2 we have omitted the consideration of D_{12} for D_2 diffusing through

H_2. The recent value of D_{12} given by Waldman (20) agrees perfectly with our expectation on the basis of the force constants already obtained from the viscosity of H_2. An older experimental value of D_{12} quoted by Chapman and Cowling was considerably in error.

III. THE COEFFICIENT OF VISCOSITY

In this and the following sections, the formulae for the various transport properties will be set forth and their application will be discussed. The formulae for the transport coefficients are essentially those of Chapman and Cowling (1) and are written here for convenience in terms of the transport integrals which are tabulated in table 1 of our preceding publication (7).

The coefficient of viscosity for a single gas is given by the relation:

$$\eta \times 10^7 = 266.93(MT)^{1/2} r_0^{-2} \mathrm{V}/[W^{(2)}(2)] \qquad (6)$$

where M is the molecular weight, T is the temperature in degrees K., r_0 is the low-energy collision diameter expressed in Ångströms, and $\mathbf{V}$ and $W^{(2)}(2)$ are slowly varying functions of kT/ϵ previously tabulated. We have already shown how this equation may be used to predict values of the viscosity. And to obtain the intermolecular force constants equation 6 is simply written for values of viscosities at two temperatures, the resulting two equations then being solved simultaneously for r_0 and ϵ.

The temperature dependence of viscosity is often expressed in terms of a Sutherland constant, S:

$$\eta = k_S T^{1/2}/[1 + (S/T)] \qquad (7)$$

Both k_S and S are supposed to be constants characteristic of the gas. Unfortunately, our relations show that this cannot be true over any large temperature range. If we require that at a particular temperature η and $d\eta/dT$ as determined from equation 7 agree with that determined from equation 6, it follows that S/T is the following function of ϵ/kT:

$$S/T = -(4 - \phi_1 - \phi_2 + \phi_3)/(3 - \phi_1 - \phi_2 + \phi_3) \qquad (8)$$

in which:

$$\phi_1 = W^{(2)}(3)/W^{(2)}(2) \qquad (9)$$

$$\phi_2 = 2\left[\frac{\mathrm{V} - 1}{\mathrm{V}}\right]\left[\frac{28W^{(2)}(2) - 17W^{(2)}(3) + 2W^{(2)}(4)}{7W^{(2)}(2) - 2W^{(2)}(3)}\right] \qquad (10$$

$$\phi_3 = 4\left[\frac{(\mathrm{V} - 1)^2}{\mathrm{V}}\right]\left[\frac{\begin{array}{r}[\frac{77}{8}W^{(2)}(2) + W^{(2)}(4)][4W^{(2)}(2) - W^{(2)}(3)] \\ + W^{(2)}(2)[6W^{(2)}(4) - W^{(2)}(5)] \\ - 2W^{(2)}(3)[5W^{(2)}(3) - W^{(2)}(4)]\end{array}}{7W^{(2)}(2) - 2W^{(2)}(3)}\right] \qquad (11)$$

A plot of S/T as a function of kT/ϵ is shown in figure 1 and values are given in table 5. This result is useful, since ϵ/k can be determined immediately from tabulated values of S. The double values of ϵ/kT for a given value of S need cause no concern, since we usually know whether a gas is above or below the critical point ($\epsilon/kT_c = 0.75$).

For some purposes it is more convenient to express the viscosity in terms of an equation of the form:

$$\eta = k'T^s \tag{12}$$

TABLE 5

Temperature dependence of Sutherland's constant and the temperature exponent, s

$$\eta = k_S T^{1/2}/[1 + (S/T)]$$
$$\eta = k'T^s$$

kT/ϵ	S/T	s	kT/ϵ	S/T	s
0.30	0.5538	0.8564	3	0.3669	0.7684
0.50	0.8786	0.9677	4	0.2829	0.7205
0.75	1.083	1.0200	5	0.2453	0.6970
1.00	1.012	1.0030	10	0.1857	0.6566
1.25	0.8660	0.9641	50	0.1697	0.6451
1.50	0.7443	0.9267	100	0.1681	0.6439
2.00	0.5466	0.8534	400	0.1680	0.6438
2.50	0.4331	0.8022			

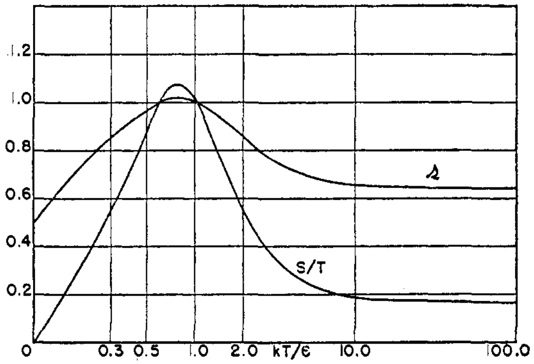

FIG. 1. Sutherland's constant (equation 7) divided by the temperature, S/T, and the temperature exponent, s (equation 12), plotted against kT/ϵ.

The exponent, s, may be determined as a function of ϵ/kT in a manner quite similar to the method used for the Sutherland constant above. It is not difficult to show that

$$s = (9/2) - \phi_1 - \phi_2 + \phi_3 \tag{13}$$

Values of s so determined are shown in table 5, and graphically in figure 1.

For the binary mixture, the formula for the first approximation to the viscosity has already become rather complicated:

$$\eta_{12} \times 10^7 = \frac{R_1 + R_2 + R_3 + (E/H_1) + (E/H_2)}{(R_1/H_1) + (R_2/H_2) + (E/H_1H_2) + (R_4/E)} \tag{14}$$

in which

$$R_1 = (x_1/x_2)(2/3 + AM_1/M_2) \tag{15}$$

$$R_2 = (x_2/x_1)(2/3 + AM_2/M_1) \tag{16}$$

$$R_3 = 2[(2/3) - A] \tag{17}$$

$$R_4 = 2A(M_1 + M_2)^2/3M_1M_2 \tag{18}$$

$$H_i = 266.93(M_iT)^{1/2}(r_i)^{-2}/(W^{(2)}(2; kT/\epsilon_i)) \qquad (i = 1, 2) \tag{19}$$

$$E = 37.75[(M_1 + M_2)^3T/(M_1M_2)]^{1/2}(r_{12})^{-2}/(W^{(1)}(1; kT/\epsilon_{12})) \tag{20}$$

Here x_i is the mole fraction of the i^{th} component; M_i is the molecular weight of the i^{th} component; the r_i and r_{12} are the low-velocity collision diameters measured in Ångströms; A is a function of the collision integrals and is tabulated as a function of kT/ϵ in our previous paper. The H_i are simply the first approximations to the viscosity of the i^{th} component.

Using the force constants between like molecules which were determined from viscosity data and those between dissimilar molecules which were determined from diffusion, we have calculated the viscosity of several binary mixtures. The diffusion data used to get the ϵ_{12}/k are those values tabulated in Chapman and Cowling (1). The experimental binary viscosity data listed are from Landolt–Börnstein, with the single exception of the H_2–N_2 data (18). The results of these computations are displayed in table 6 along with the experimental figures. It will be observed that the agreement is excellent in most cases. This is a nice illustration of the use of force constants obtained from one transport property in the calculation of another of the transport coefficients.

The determination of force constants between dissimilar molecules from viscosity data of binary mixtures is not too difficult in principle. However, the existing data are apparently not sufficiently good to give worthwhile results.

The viscosity of multicomponent gas mixtures has been worked out by C. F. Curtiss and J. O. Hirschfelder (3). For a mixture of f components, the generalized viscosity may be expressed as follows:

$$\eta_{123\cdots f} \times 10^7 = \frac{\begin{vmatrix} J_{11} & J_{12} & J_{13}\cdots J_{1f} & 1 \\ J_{12} & J_{22} & J_{23}\cdots J_{2f} & 1 \\ J_{13} & J_{23} & J_{33}\cdots J_{3f} & 1 \\ \cdot & \cdot & \cdot \quad \cdot & \cdot \\ \cdot & \cdot & \cdot \quad \cdot & \cdot \\ \cdot & \cdot & \cdot \quad \cdot & \cdot \\ J_{1f} & J_{2f} & J_{3f}\cdots J_{ff} & 1 \\ 1 & 1 & 1\cdots 1 & 0 \end{vmatrix}}{|J_{ij}|} \tag{21}$$

in which $|J_{ij}|$ is the f^{th}-order determinant of the J_{ij}, the J_{ij} (for $i \neq j$) and J_{ii} being given by:

$$J_{ij} = +A_{ij} - B_{ij} \tag{22}$$

TABLE 6

Viscosity of binary mixtures

	VISCOSITY H_2–He						VISCOSITY H_2–C_2H_6				
T	%H_2........	0.0	55.20	60.69	69.18	100.0	%H_2........	0.0	45.00	85.15	100.0
°*K*.											
293	EX*....	1974	1317	1252	1166	875		909	987	993	876
	CG*....	1926	1318	1261	1175	876		909	986	1005	876
373	EX.....	2320	1551	1478	1383	1029		1142	1208	1189	1033
	CG.....	2244	1536	1470	1370	1021		1139	1213	1197	1021
473	EX.....	2715	1817	1728	1619	1211		1409	1467	1412	1213
	CG.....	2615	1790	1714	1596	1185		1401	1469	1411	1185
523	EX.....	2903	1939	1852	1732	1296		1526	1583	1511	1296
	CG.....	2790	1910	1828	1702	1265		1522	1588	1513	1265

	VISCOSITY CH_4–C_2H_6						VISCOSITY C_2H_6–C_3H_8				
T	%CH_4......	0.0	19.03	48.74	81.16	100.0	%C_2H_6...	0.0	15.26	25.63	43.27	100.0
°*K*.											
293	EX....	909	938	986	1046	1087		801	815	828	842	909
	CG.....	909	939	991	1053	1092		801	814	824	824	909
373	EX....	1142	1174	1226	1288	1331		1008	1025	1039	1058	1142
	CG.....	1139	1171	1226	1289	1327		1008	1025	1037	1058	1139
473	EX....	1409	1442	1496	1562	1603		1253	1272	1298	1313	1409
	CG.....	1401	1435	1490	1552	1588		1248	1268	1282	1307	1401
523	EX.....	1526	1560	1614	1682	1725		1363	1382	1401	1425	1526
	CG.....	1522	1556	1611	1674	1709		1360	1381	1396	1422	1522

	VISCOSITY CH_4–C_3H_8						VISCOSITY NO–N_2				
T	%CH_4......	0.0	16.59	36.17	63.16	100.0	%NO....	0.0	26.74	58.37	69.48	100.0
°*K*.											
293	EX.....	801	831	878	948	1087		1747	1778	1827	1833	1882
	CG.....	801	835	881	957	1092		1747	1787	1833	1849	1894
373	EX.....	1008	1042	1101	1182	1331		2084	2132	2209	2222	2272
	CG.....	1008	1047	1099	1183	1327		2086	2138	2201	2223	2284
473	EX.....	1253	1291	1355	1441	1603						
	CG.....	1248	1290	1347	1438	1588						
523	EX.....	1363	1403	1465	1553	1725						
	CG.....	1360	1404	1463	1556	1709						

* EX = experimental data; CG = calculated using a geometric mean ϵ/k; CD = calculated using an ϵ/k calculated from diffusion.

TABLE 6—*Continued*

VISCOSITY H_2–CO_2							VISCOSITY H_2–O_2						
T	%H_2......	0.0	19.93	41.29	78.50	100.0	%H_2....	0.0	18.35	39.45	60.30	78.08	100.0
°*K*.													
300	EX*....	1493	1501	1506	1370	891		2057	2019	1925	1784	1494	889
	CG*....	1493	1507	1508	1372	889		2064	2021	1934	1774	1524	889
	CD*....	1493	1509	1512	1379	889		2064	2024	1939	1782	1531	889
400	EX.....	1944	1945	1933	1713	1081		2568	2507	2381	2192	1858	1087
	CG.....	1920	1926	1913	1698	1065		2567	2506	2388	2178	1857	1065
	CD.....	1920	1928	1918	1703	1065		2567	2509	2394	2186	1865	1065
500	EX.....	2353	2353	2321	2026	1256		3017	2950	2790	2556	2158	1259
	CG.....	2301	2302	2275	1990	1228		3015	2940	2795	2541	2158	1228
	CD.....	2301	2303	2280	1998	1228		3015	2943	2802	2551	2168	1228
550	EX.....	5556?	2542	2506	2173	1341		3220	3147	2978	2733	2288	1381
	CG.....	2479	2478	2445	2130	1308		3224	3140	2986	2714	2302	1308
	CD.....	2479	2479	2450	2137	1308		3224	3146	2993	2721	2313	1308

VISCOSITY CO_2–N_2O							VISCOSITY O_2–CO					
T	%CO_2.....	0.0	40.24	60.33	80.97	100.0	%O_2....	0.0	23.37	42.01	77.33	100.0
°*K*.												
300	EX....	1488	1494	1495	1490	1493		1776	1841	1900	1998	2057
	CG.....	1489	1497	1498	1496	1493		1779	1880	1946	2034	2064
	CD.....	1489	1523	1524	1513	1493		1779	1844	1897	1998	2064
400	EX.....	1493?	1950	1950	1941	1944		2183	2268	2343	2482	2568
	CG.....	1936	1938	1934	1928	1920		2210	2328	2407	2521	2567
	CD.....	1936	1965	1961	1946	1920		2210	2292	2358	2485	2567
500	EX.....	2355	2365	2365	2358	2353		2548	2650	2741	2908	3017
	CG.....	2338	2332	2325	2314	2301		2593	2725	2817	2954	3015
	CD.....	2338	2361	2354	2332	2301		2593	2690	2768	2918	3015
550	EX.....	2555	2562	2564	2551	2556						
	CG.....	2525	2517	2508	2495	2479						
	CD.....	2525	2546	2537	2513	2479						

VISCOSITY C_2H_4–N_2							VISCOSITY H_2–N_2O					
T	%C_2H_4....	0.0	24.05	56.95	76.21	00.0	%H_2....	0.0	39.89	59.61	78.57	100.0
°*K*.												
300	EX.....	1781	1574	1308	1169	1033		1488	1481	1451	1348	891
	CG.....	1777	1562	1306	1176	1029		1489	1509	1483	1376	889
400	EX.....	2190	1956	1655	1491	1348		1943	1907	1849	1684	1081
	CG.....	2192	1946	1653	1501	1330		1936	1932	1876	1710	1065
500	EX.....	2560	2292	1963	1786	1622		2355	2292	2206	1990	1256
	CG.....	2556	2284	1961	1792	1602		2338	2311	2229	2009	1228
550	EX.....	2727	2453	2108	1921	1753		2555	2477	2376	2137	1341
	CG.....	2729	2444	2104	1927	1728		2525	2489	2392	2150	1308

* EX = experimental data; CG = calculated using a geometric mean ϵ/k; CD = calculated using an ϵ/k calculated from diffusion.

TABLE 6—*Continued*

VISCOSITY He-A						VISCOSITY H_2-CH_4						
T	%He......	0.0	38.20	49.06	100.0	%H_2....	0.0	28.08	48.55	60.22	92.23	100.0
°K.												
293	EX*....	2211	2291	2296	1973		1087	1099	1098	1086	955	876
	CG*....	2223	2305	2319	1926		1092	1102	1096	1083	952	876
	CD*....	2223	2314	2330	1926		1092	1105	1101	1088	955	876
373	EX.....	2684	2745	2750	2320		1331	1337	1328	1306	1132	1033
	CG.....	2688	2753	2757	2244		1327	1329	1313	1291	1115	1021
	CD.....	2688	2765	2774	2244		1327	1333	1318	1297	1119	1021
473	EX.....	3208	3250		2715		1603	1602	1587	1551	1338	1213
	CG.....	3205	3261	3257	2615		1588	1583	1557	1525	1300	1185
	CD.....	3205	3282	3285	2615		1588	1585	1561	1531	1303	1185
523	EX.....	3448	3488		2903		1725	1718	1699	1662	1423	1296
	CG.....	3443	3502	3496	2790		1709	1701	1670	1634	1389	1265
	CD.....	3443	3518	3516	2790		1709	1704	1675	1641	1393	1265

VISCOSITY A-Ne							VISCOSITY He-Ne					
T	%A.......	0.0	26.80	60.91	74.20	100.0	%He ...	0.0	26.59	56.24	76.21	100.0
°K.												
293	EX.....	3092	2808	2504	2401	2213		3092	2971	2702	2429	1941
	CG.....	3079	2805	2503	2401	2223		3079	2935	2675	2407	1926
373	EX.....	3623	3313	2990	2885	2693		3623	3479	3171	2846	2281
	CG.....	3602	3306	2988	2878	2688		3602	3428	3122	2805	2244
473	EX.....	4220	3890	3529	3413	3222		4220	4056	3702	3327	2672
	CG.....	4168	3862	3526	3410	3205		4168	3980	3633	3271	2615
523	EX.....	4501	4150	3793	3658	3460		4501	4310		3555	2853
	CG.....	4447	4127	3779	3656	3443		4447	4244	3875	3488	2790

VISCOSITY H_2-Ne							VISCOSITY H_2-A					
T	%H_2......	0.0	25.20	46.09	77.15	100.0	%H_2....	0.0	29.42	44.57	65.15	100.0
°K.												
293	EX.....	3092	2782	2427	1684	875		2211	2140	2056	1857	875
	CG.....	3079	2763	2411	1670	876		2223	2140	2060	1860	876
373	EX.....	3623	3269	2845	1981	1029		2684	2586	2488	2238	1029
	CG.....	3602	3231	2820	1950	1021		2688	2576	2470	2219	1021
473	EX.....	4220	3807	3327	2319	1211		3208	3070	2948	2636	1211
	CG.....	4168	3741	3267	2263	1185		3205	3063	2929	2619	1185
523	EX.....	4501	4054	3540	2476	1296		3448	3310	3164	2826	1296
	CG.....	4447	3992	3487	2416	1265		3443	3287	3143	2808	1265

* EX = experimental data; CG = calculated using a geometric mean ϵ/k; CD = calculated using an ϵ/k calculated from diffusion.

TABLE 6—*Continued*

	VISCOSITY N_2-O_2						VISCOSITY CO-N_2						
T	%N_2......	0.0	24.08	58.93	78.22	100.0	%CO...	0.0	18.46	39.70	65.68	83.71	100.0
°*K*.													
300	EX*....	2057	1995	1894	1843	1781		1781	1782	1781	1775	1774	1776
	CG*....	2064	1994	1894	1839	1777		1779	1826	1855	1852	1823	1777
	CD*....	2064	2015	1921	1858	1777		1779	1778	1780	1780	1780	1777
400	EX.....	2568	2480	2345	2275	2190		2190	2186	2183	2191	2184	2183
	CG.....	2568	2475	2343	2272	2192		2210	2245	2279	2279	2252	2192
	CD.....	2568	2497	2372	2292	2192		2210	2196	2201	2205	2208	2192
500	EX.....	3017	2909	2741	2658	2560		2560	2560	2558	2549	2551	2548
	CG.....	3015	2901	2741	2654	2556		2593	2617	2656	2661	2636	2556
	CD.....	3015	2923	2768	2674	2556		2593	2564	2573	2582	2588	2556
550	EX.....	3220	3109	2932	2840	2727		2727	2721	2719	2722	2719	2714
	CG.....	3224	3100	2925	2833	2729		2771	2792	2834	2840	2814	2729
	CD.....	3224	3125	2956	2854	2729		2771	2737	2746	2757	2763	2729

	VISCOSITY C_2H_4-CO						VISCOSITY H_2-C_3H_8					
T	%C_2H_4....	0.0	26.32	43.54	80.62	100.0	%H_2....	0.0	37.04	78.82	92.25	100.0
°*K*.												
300	EX.....	1776	1553	1402	1135	1033		817	874	985	970	891
	CG.....	1779	1538	1399	1144	1029		819	892	995	980	889
400	EX.....	2183	1943	1763	1460	1342		1070	1130	1233	1194	1081
	CG.....	2210	1930	1768	1466	1330		1074	1152	1241	1194	1065
500	EX.....	2548	2279	2098	1760	1622		1308	1366	1459	1392	1256
	CG.....	2593	2279	2097	1757	1602		1309	1390	1462	1389	1228
550	EX.....	2714	2433	2240	1900	1753		1422	1478	1566	1485	1347
	CG.....	2771	2440	2249	1891	1728		1418	1499	1566	1482	1308

	VISCOSITY CO_2-C_3H_8						VISCOSITY N_2O-C_3H_8					
T	%CO_2.....	0.0	40.25	57.76	78.83	100.0	%N_2O..	0.0	20.16	58.29	79.82	100.0
°*K*.												
300	EX.....	817	1058	1174	1326	1493		817	926	1167	1326	1488
	CG.....	819	1033	1146	1304	1493		819	917	1145	1307	1489
400	EX.....	1070	1383	1533	1730	1944		1070	1213	1525	1725	1943
	CG.....	1074	1345	1487	1685	1920		1074	1201	1494	1703	1936
500	EX.....	1308	1670	1856	2093	2353		1308	1478	1854	2083	2355
	CG.....	1309	1627	1795	2026	2301		1309	1460	1811	2059	2338
550	EX.....	1422	1815	2010	2267	2556		1422	1610	2012	2271	2556
	CG.....	1418	1759	1939	2186	2479		1418	1581	1959	2227	2525

* EX = experimental data; CG = calculated using a geometric mean ϵ/k; CD = calculated using an ϵ/k calculated from diffusion.

TABLE 6—*Concluded*

VISCOSITY H_2–N_2

T	$\%H_2$.......	0.0	25.00	50.00	75.00	100.0
°K.						
82	EX*....	544	540	524	493	362
	CG*....	564	564	552	508	356
292	EX.....	1746	1700	1609	1396	882
	CG.....	1744	1699	1605	1393	874

VISCOSITY C_2H_4–O_2

T	$\%C_2H_4$....	0.0	13.06	41.45	77.03	100.0
°K.						
293	EX.....	2019	1854	1529	1198	1010
	CG.....	2027	1850	1521	1187	1007
323	EX.....	2181	2004	1658	1308	1107
	CG.....	2187	2001	1650	1294	1102
373	EX.....	2433	2243	1865	1479	1262
	CG.....	2440	2238	1855	1465	1254

VISCOSITY SO_2–CO_2

T	$\%SO_2$....	0.0	20.00	40.00	60.00	80.00	100.0
°K.							
289	EX....	1458	1428	1388	1346	1299	1243
	CG....	1443	1420	1397	1375	1353	1331

VISCOSITY CO_2–HCl

T	$\%CO_2$....	0.0	20.00	40.00	60.00	80.00	100.0
°K.							
291	EX....	1426	1453	1473	1483	1481	1464
	CG....	1422	1429	1435	1442	1448	1453

VISCOSITY air–CO_2

T	%Air.....	0.0	20.00	40.00	60.00	80.00	100.0
°K.							
290	EX....	1455	1523	1591	1660	1730	1797
	CG....	1448	1511	1578	1648	1722	1800

VISCOSITY air–HCl

T	%Air....	0.0	20.00	40.00	60.00	80.00	100.0
°K.							
290	EX....	1407	1535	1616	1693	1755	1794
	CG....	1415	1499	1582	1660	1734	1798

* EX = experimental data; CG = calculated using a geometric mean ϵ/k; CD = calculated using an ϵ/k calculated from diffusion.

$$J_{ii} = +A_{ii} - B_{ii} - \sum_{k=1}^{f} (x_k/x_i)(A_{ik} + B_{ik}M_k/M_i) \tag{23}$$

and the A_{ij} and B_{ij} are defined as:

$$A_{ij} = (0.017663)T^{-1/2}[r_{ij}]^2[W^{(1)}(1;\, kT/\epsilon_{ij})][M_iM_j/(M_i + M_j)^3]^{1/2} \tag{24}$$

$$B_{ij} = (0.0052988)T^{-1/2}[r_{ij}]^2[W^{(2)}(2;\, kT/\epsilon_{ij})][M_iM_j/(M_i + M_j)^3]^{1/2} \tag{25}$$

In table 7a are shown some experimental figures for the viscosity of a helium–neon–argon mixture; along with this data are given the calculated results obtained by using equation 21, letting $f = 3$. The force constants between like molecules which were used are those obtained from viscosity data; the force constants between unlike molecules which were used are those obtained by taking an arithmetic-mean collision diameter and a geometric-mean ϵ/k.

The methods presented here are well suited to the prediction of transport properties for such industrially important mixtures as flue and fuel gases. In table 7b we compare the experimentally observed values of the viscosity of flue and fuel gases with values calculated using equation 21, together with the force constants given in tables 1 and 2. The agreement in more than half of the examples is excellent; however, in some of the other mixtures there is a considerable discrepancy. This might be explained on the basis of small errors in the experimental gas analysis. In any case we believe that our calculated values have an inherent accuracy of within 0.5 per cent. The fact that some of these mixtures contained as many as seven components caused no computational difficulties.

In this report we do not consider quantum corrections, inasmuch as they are numerically small and negligible at any reasonable temperature ($T > 15$°K.).

TABLE 7A

Viscosity of ternary mixture of neon–argon–helium

T	VOLUME PER CENT			$\eta_{123} \times 10^7$ g./cm.-sec.	
	Ne	A	He	Calculated	Experimental[a]
°*K.*					
193	55.76	26.70	17.54	2718	2740
	31.93	32.13	35.94	2562	2569
	21.66	58.51	19.83	2429	2411
	21.89	23.82	54.29	2500	2504
373	55.76	26.70	17.54	3205	3237
	31.93	32.13	35.94	3025	3044
	21.66	58.51	19.83	2895	2886
	21.89	23.82	54.29	2938	2957
473	55.76	26.70	17.54	3752	3790
	31.93	32.13	35.94	3551	3574
	21.66	58.51	19.83	3425	3415
	21.89	23.82	54.29	3449	3470

Force constants used

LIKE MOLECULES			UNLIKE MOLECULES		
Molecule	r_i	ϵ_i/k	Molecule pair	Arithmetic mean r_{ij}	Geometric mean ϵ_{ij}/k
	Å.	°*K.*			
Ne	2.80	35.7	Ne–A	3.11	68
A	3.418	124.0	Ne–He	2.75	14
He	2.70	6.03	A–He	3.059	27

(a) M. Trautz and K. F. Kipphan: Ann. Physik **2**, 746 (1929).

The quantum corrections would be expected to be larger for hydrogen than for any heavier molecules. The magnitude of this correction may be seen from a comparison of the viscosity of H_2 and D_2. If there were no quantum corrections, η_{H_2} would equal $(M_H/M_D)^{1/2}\eta_{D_2}$. This would be true regardless of the form for the energy of interaction as long as classical mechanics applies, but quantum corrections would introduce deviations. From table 8 it is seen that there is no appreciable deviation (nor quantum correction) down to 15°C. Similarly in the case of CH_4 and CD_4, where it is expected that $\eta_{CH_4} = (M_{CH_4}/M_{CD_4})^{1/2}\eta_{CD_4}$. Here,

TABLE 7B

Viscosity of multicomponent mixtures: industrial gases

COMPOSITION (VOLUME PER CENT)							TEMPERATURE	$\eta \times 10^7$ EXPERIMENTAL	$\eta \times 10^7$ CALCULATED	REFERENCE
CO_2	O_2	CO	H_2	CH_4	N_2	Heavier hydrocarbons				
							°K.			
8.6	2.3				89.1		293	1756	1761	(b)
13.3	3.9				82.8		293	1749	1765	(b)
6.2	10.7				83.1		293	1793	1789	(b)
10.4		28.5	1.6		59.5		293	1738	1798	(b)
10.80	2.00		2.20		85.00		300.5	1827	1792	(a)
							524.5	2715	2661	
							973	4117	4008	
							1279	4856	4753	
6.70	0.10	7.80	2.20		83.20		307.5	1842	1835	(a)
							519	2655	2653	
							975	4048	4019	
							1285	4808	4783	
6.40	3.00	0.30	0.70		89.60		314	1904	1856	(a)
							518	2706	2644	
							974.5	4113	4017	
							1287	4895	4777	
6.00	0.10	25.70	11.50		56.70		302	1823	1829	(a)
							526	2686	2696	
							976	4041	4042	
							1283	4777	4821	
10.6		29.8	3.9	0.3	55.4		293	1743	1794	(b)
8.9		30.7	3.3	0.4	56.7		293	1747	1797	(b)
8.7		32.8	1.5	0.2	56.8		293	1749	1802	(b)
3.70	0.30	27.10	9.50	1.60	57.80		300.5	1815	1816	(a)
							565.5	2819	2823	
							981	4045	4041	
							1282	4792	4803	
1.7	0.9	6.0	57.5	24.0	7.8	2.1	293	1262	1254	(b)
2.1	0.9	5.7	53.0	24.3	11.7	2.3	293	1304	1290	(b)
2.0	1.4	4.6	54.9	23.5	11.6	2.0	293	1310	1398	(b)
3.3	0.6	3.8	51.3	29.6	10.0	1.4	293	1332	1269	(b)
2.2	0.6	4.1	53.1	29.5	9.2	1.3	293	1306	1254	(b)
2.2	1.0	4.0	52.3	29.9	9.4	1.2	293	1307	1261	(b)
2.5	0.8	14.9	53.0	18.1	9.1	1.6	293	1355	1373	(b)
4.8	0.3	26.4	17.2	2.6	48.2	0.5	293	1714	1743	(b)
3.5	0.3	27.3	14.4	3.7	50.0	0.8	293	1712	1732	(b)
3.1	0.5	28.6	17.7	4.2	45.0	0.9	293	1715	1719	(b)

(a) Schmid: Gas- u. Wasserfach **85**, 92 (1942).

(b) F. Herning and L. Zipperer: Gas- u. Wasserfach **79**, 49–54, 69–73 (1936).

from the figures shown in table 8, there is no appreciable quantum correction indicated by the experimental data down to 90°K. Only in the cases of hydrogen and helium is it expected that the transport properties would show a small quantum correction above 15°K. In these two cases it appears probable that a part of our difficulty in obtaining a suitable fit with the experimental viscosity data may arise from small quantum corrections. The conclusions have been substantiated by the theoretical work of Uehling and Uhlenbeck (4, 16, 17) and Massey and Mohr (13).

TABLE 8

Viscosity of light and heavy methane and light and heavy hydrogen

T	$\sqrt{\frac{M_{H_2}}{M_{D_2}}}\,\eta_{D_2}$ (EXPERIMENTAL)	η_{H_2} (EXPERIMENTAL)[a]	η_{H_2} (CALCULATED)
°K.			
15	71	82	70
30	146	158	141
75	332	347	331
290	886	884	876

T	$\sqrt{\frac{M_{CH_4}}{M_{CD_4}}}\,\eta_{CD_4}$ (EXPERIMENTAL)	η_{CH_4} (EXPERIMENTAL)[b]	η_{CH_4} (CALCULATED)
°K.			
90	384	376	353
200	828	785	780
225	922	874	868
250	1013	961	955
275	1101	1039	1037
300	1095	1111	1115

[a] A. Van Itterbeek and O. Van Paemel: Physica **7**, 265 (1940).

[b] A. Van Itterbeek: Physica **9**, 831 (1940).

IV. THE COEFFICIENT OF DIFFUSION

The first approximation for the coefficient of diffusion is given by the following equation:

$$(D_{12})_1 = \frac{0.000929\,16\,T^{3/2}[(M_1 + M_2)/M_1M_2]^{1/2}}{p(r_{12})^2 W^{(1)}(1; kT/\epsilon_{12})} \tag{26}$$

in which D_{12} is the coefficient of diffusion in cm.^{2} sec.$^{-1}$, p is the pressure in atmospheres, and the M_i represent molecular weights. Note that the first approximation to the diffusion coefficient is independent of composition. This is no longer true in the case of the second approximation:

$$(D_{12})_2 = (D_{12})_1/(1 - \Delta) \tag{27}$$

Here Δ, a small quantity usually less than 0.03, is defined by

$$\Delta = 5(C - 1)^2(P_1x_1^2 + P_2x_2^2 + P_{12}x_1x_2)/(Q_1x_1^2 + Q_2x_2^2 + Q_{12}x_1x_2) \tag{28}$$

in which

$$P_1 = M_1^3[M_1 + M_2]^{-2}(2/3V_0)([D_{12}]_1/[\eta_1]_1)(273.16P/T) \tag{29}$$

$$P_2 = M_2^3[M_1 + M_2]^{-2}(2/3V_0)([D_{12}]_1/[\eta_2]_1)(273.16P/T) \tag{30}$$

$$P_{12} = [3(M_1 - M_2)^2 + 4M_1M_2A]/(M_1 + M_2)^2 \tag{31}$$

$$Q_1 = (P_1/M_1^2)(6M_2^2 + 5M_1^2 - 4M_1^2B + 8M_1M_2A) \tag{32}$$

$$Q_2 = (P_2/M_2^2)(6M_1^2 + 5M_2^2 - 4M_2^2B + 8M_1M_2A) \tag{33}$$

$$Q_{12} = \begin{bmatrix} 3(5 - 4B)(M_1 - M_2)^2/(M_1 + M_2)^2 \\ + 4AM_1M_2(11 - 4B)/(M_1 + M_2)^2 \\ + 2P_1P_2(M_1 + M_2)^4/M_1^2M_2^2 \end{bmatrix} \tag{34}$$

Here the x_i are mole fractions of the i^{th} component; the M_i are molecular weights; A, B, and C are functions of kT/ϵ_{12} tabulated previously; V_0 is the molar volume under standard conditions, i.e., 22,414.6 cc.; and $[\eta_1]_1$ and $[\eta_2]_1$ are calculated first approximations to the viscosity of the pure component given by the formula:

$$[\eta_i]_1 = 2.6693(10^{-5})(M_iT)^{1/2}/[(r_i)^2W^{(2)}(2; kT/\epsilon_i)] \tag{6$'$}$$

The possibility of getting good force constants between pairs of dissimilar molecules from equation 26 has already been mentioned. This equation could be written for two temperatures, inserting two diffusion measurements, and the resulting equations solved simultaneously for r_{12} and ϵ_{12}/k.

In the case of self-diffusion

$$M_1 = M_2 \qquad \epsilon_1 = \epsilon_2 = \epsilon_{12} \qquad r_1 = r_2 = r_{12}$$

and equations 26 and 27 reduce to the particularly simple forms for the first approximation to the coefficient of self-diffusion:

$$(D_{11})_1 = 0.0013140T^{3/2}/[pr_0^2W^{(1)}(1; kT/\epsilon)M^{1/2}] \tag{35}$$

and the second approximation is given by:

$$(D_{11})_2 = (D_{11})_1/(1 - \Delta) \tag{36}$$

in which Δ is defined simply as:

$$\Delta = 5(C - 1)^2/(11 - 4B + 8A) \tag{37}$$

and, as before, is a small correction factor.

The coefficients of self-diffusion may be calculated from our previously assigned values of the force constants without making any adjustments. The results are shown in table 9, along with experimental values. Harteck and Schmidt determined the self-diffusion coefficient for hydrogen by using ortho- and para-hydrogen. The self-diffusion coefficients for the other gases shown were determined using gases containing tracer isotopes. In all of these cases the agreement is very good between the experimental and calculated quantities. Additional experimental data would be very useful for purposes of comparison.

The available values for the coefficient of ordinary diffusion have been analyzed to give the force constants of table 2 for the interaction between dissimilar molecules.

In a mixture containing f components the concept of diffusion may be generalized (8). If U_i is the average velocity of molecules of the i^{th} species relative to U, the mass average velocity of the gaseous mixture, then rigorously:

$$U_i = (n^2/\rho n_i) \sum_{k=1}^{f} m_k \, d_{ik} \operatorname{grad} x_j \tag{38}$$

where

$$n = \sum_{k=1}^{f} n_k = p/(RT) \tag{39}$$

s the total number of moles of gas in a cubic centimeter. The d_{ij} are not the usual diffusion constants for binary mixtures, D_{ij}, but the two are very closely related, in the general case by:

$$d_{12} = -\frac{\rho n_1}{m_2} \left[\frac{ \begin{vmatrix} 0 & A_{23} & A_{24} \cdots \\ A_{32} & 0 & A_{34} \cdots \\ A_{42} & A_{43} & 0 \cdots \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix} + \begin{vmatrix} A_{12} & A_{13} & A_{14} \cdots \\ A_{32} & 0 & A_{34} \cdots \\ A_{42} & A_{43} & 0 \cdots \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix} }{ \begin{vmatrix} 0 & A_{12} & A_{13} & A_{14} \cdots \\ A_{21} & 0 & A_{23} & A_{24} \cdots \\ A_{31} & A_{32} & 0 & A_{34} \cdots \\ A_{41} & A_{42} & A_{43} & 0 \cdots \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix} } \right] \tag{40}$$

Here the coefficients in the determinant are

$$A_{ik} = (n_i n_k/D_{ik}) + (n_k m_k/m_i) \cdot \sum_{s \neq i}^{f} (n_s/D_{is}) \tag{41}$$

The other d_{ij} may be obtained from the final form of the d_{12} by permuting the indices or from equation 40 by suitable modifications of the determinants in the numerator. This generalized formula may be obtained also from the work of Hellund and Uehling (5).

For the binary mixture

$$d_{12} = D_{12} \tag{42}$$

and for ternary mixtures:

$$d_{12} = D_{12} \left[1 + \frac{n_3 \left(\frac{m_3}{m_2} D_{13} - D_{12} \right)}{n_1 D_{23} + n_2 D_{13} + n_3 D_{12}} \right] \tag{43}$$

TABLE 9

The coefficient of self-diffusion

GAS	T	P	D_{11}		REFERENCE FOR EXPERIMENTAL VALUES
			Calculated	Experimental	
	°K.	atm.	cm.²/sec.	cm.²/sec.	
Hydrogen	273	1	1.243	$1.28_5 \pm 0.002_5$	(a)
	85	1	0.167	0.172 ± 0.008	(a)
	20.4	1	0.01043	0.00816 ± 0.0002	(a)
Krypton	293	1	0.093	$0.093 \pm 0.004_5$	(b)
Xenon	293	1	0.055	$0.044 \pm 0.002_2$	(b)
Neon	293	1	0.491	0.473 ± 0.002	(c)
Argon	295	0.4211	0.422	0.423 ± 0.003	(d)
Nitrogen	293	1	0.198	0.200 ± 0.008	(e)
Methane	292	0.00811	26.38	26.32 ± 0.73	(f)
Hydrogen chloride	295	1	0.127	0.1246	(g)

(a) P. Harteck and H. W. Schmidt: Z. physik. Chem. **21B**, 447 (1933).
(b) W. Groth and P. Harteck: Z. Elektrochem. **47**, 167 (1941).
(c) W. Groth and E. Sussner: Z. physik. Chem. **193**, 296 (1944).
(d) F. Hutchinson: Phys. Rev. **72**, 1256 (1947).
(e) E. B. Winn: Phys. Rev. **74**, 698 (1948).
(f) E. B. Winn and E. P. Ney: Phys. Rev. **72**, 77 (1947).
(g) H. Braune and F. Zehle: Z. physik. Chem. **49B**, 247 (1941).

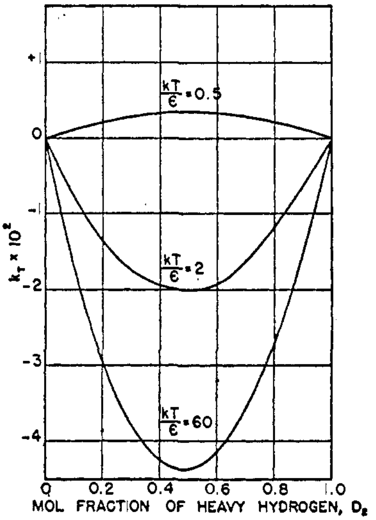

FIG. 2. The calculated thermal diffusion ratio for separation of a mixture of hydrogen and deuterium. Note the change in sign of k_T at low temperatures, an effect which has been experimentally observed for some substances.

V. THE THERMAL DIFFUSION RATIO

Since the second approximation to the thermal diffusion ratio involves very complicated algebra, only the first approximation will be set forth here. It is:

$$k_T = 5x_1x_2(C - 1)(S_1x_1 - S_2x_2)/(Q_1x_1^2 + Q_2x_2^2 + Q_3x_1x_2) \tag{44}$$

in which

$$S_1 = \frac{M_1}{5}\left(\frac{r_1}{r_{12}}\right)^2 \left[\frac{2(M_1 + M_2)^3}{M_2}\right]^{1/2} \left[\frac{W^{(2)}(2; kT/\epsilon_1)}{W^{(1)}(1; kT/\epsilon_{12})}\right] - 3M_2(M_2 - M_1) - 4AM_1M_2 \tag{45}$$

$$S_2 = \frac{M_2}{5}\left(\frac{r_2}{r_{12}}\right)^2 \left[\frac{2(M_1 + M_2)^3}{M_1}\right]^{1/2} \left[\frac{W^{(2)}(2; kT/\epsilon_2)}{W^{(1)}(1; kT/\epsilon_{12})}\right] - 3M_1(M_1 - M_2) - 4AM_1M_2 \tag{46}$$

$$Q_1 = \frac{1}{5}\left(\frac{r_1}{r_{12}}\right)^2 \left[\frac{2(M_1 + M_2)}{M_2}\right]^{1/2} \left[\frac{W^{(2)}(2; kT/\epsilon_1)}{W^{(1)}(1; kT/\epsilon_{12})}\right] \cdot [6M_2^2 + (5 - 4B)M_1^2 + 8AM_1M_2] \tag{47}$$

$$Q_2 = \frac{1}{5}\left(\frac{r_2}{r_{12}}\right)^2 \left[\frac{2(M_1 + M_2)}{M_1}\right]^{1/2} \left[\frac{W^{(2)}(2; kT/\epsilon_2)}{W^{(1)}(1; kT/\epsilon_{12})}\right] \cdot [6M_1^2 + (5 - 4B)M_2^2 + 8AM_1M_2] \tag{48}$$

$$Q_3 = \left[3(M_1 - M_2)^2(5 - 4B) + 4AM_1M_2(11 - 4B) + \frac{4}{25}\left(\frac{r_1r_2}{r_{12}}\right)^2 \cdot \left[\frac{(M_1 + M_2)^3}{(M_1M_2)^{1/2}}\right]\left[\frac{W^{(2)}(2; kT/\epsilon_1)W^{(2)}(2; kT/\epsilon_2)}{W^{(1)}(1; kT/\epsilon_{12})}\right]\right] \tag{49}$$

Here the M_i are the molecular weights of the i^{th} species; the x_i are mole fractions; the A, B, and C are functions of kT/ϵ_{12} previously tabulated; and the r_1, r_2, and r_{12} are low-velocity collision diameters in Angströms. When the thermal diffusion of isotopes is under consideration, equation 44 may be used where the S's and the Q's have the more simple form:

$$S_1 = AM_1[(2/M_2)^{1/2} - 4M_2] - 3M_2(M_2 - M_1) \tag{50}$$

$$S_2 = AM_2[(2/M_1)^{1/2} - 4M_1] - 3M_1(M_1 - M_2) \tag{51}$$

$$Q_1 = A(2/M_2)^{1/2}[6M_2^2 + (5 - 4B)M_1^2 + 8AM_1M_2] \tag{52}$$

$$Q_2 = A(2/M_1)^{1/2}[6M_1^2 + (5 - 4B)M_2^2 + 8AM_1M_2] \tag{53}$$

$$Q_3 = 4A^2(M_1M_2)^{-1/2} + 3(M_1 - M_2)^2(5 - 4B) + 4AM_1M_2(11 - 4B) \tag{54}$$

A graph of k_T *versus* composition for light and heavy hydrogen calculated with the above formula is shown in figure 2. The force constants for a mixture of isotopes are the same as those for the pure substance. It is interesting to note that these theoretical values predict the change in sign in the thermal diffusion coefficient which have been found to occur at low temperatures. At very low temperatures the thermal diffusion is so small that no practical use can be made of this inversion.

Experimental data are generally reported as the ratio, R_T, of the thermal diffusion ratio, k_T, to the corresponding value for rigid spherical molecules. While the calculated and experimental k_T are functions of temperature for real molecules, k_T for rigid spheres is independent of temperature, and it is computed using the rigid spheres quantities:

$$A = 0.4, \quad B = 0.6, \quad C = 1.2, \quad W^{(1)}(1) = \tfrac{1}{2}, \quad \text{and } W^{(2)}(2) = 1 \qquad (55)$$

TABLE 10

Thermal diffusion of gases

GAS MIXTURE	CONCENTRATION	T	R_T (CALCULATED)	R_T (EXPERIMENTAL)	REFERENCE
		°*K.*			
He–Ne	53.8 % He	585.2	0.71	0.64	(a)
		233.2	0.70	0.64	
		117.2	0.68	0.58	
He–A	51.2 % He	585.2	0.73	0.66	(a)
		233.2	0.71	0.63	
		117.2	0.63	0.55	
He–Xe	53.6 % He	585.2	0.75	0.66	(a)
		233.2	0.70	0.66	
Ne–A	51.2 % Ne	585.2	0.66	0.57	(a)
		233.2	0.52	0.48	
		117.2	0.27	0.28	
Ne–Xe	54.2 % Ne	585.2	0.66	0.66	(a)
		233.2	0.44	0.46	
A–Xe	56.4 % A	585.2	0.51	0.45	(a)
		233.2	0.15	0.15	
H_2–D_2		333	0.63	0.50	(b)
Ne^{20}–Ne^{22}		357	0.62	0.60	(c)
A^{36}–A^{40}		620	0.55	0.47	(c)
$C^{12}H_4$–$C^{13}H_4$		274	0.29	0.49	(b)
$N^{14}H_3$–$N^{15}H_3$		308	0.08	0.11	(d)
CH_4–H_2		506	0.68	0.67	(e)
O_2–CO_2		735	0.61	0.63	(e)
CO–CO_2		725	0.60	0.40	(e)
H_2–He		284	0.53	0.41	(b)
H_2–CO_2		596	0.70	1.03	(e)

(a) K. E. Grew: Proc. Roy. Soc. (London) **189,** 402 (1947).
(b) B. F. Murphy: Phys. Rev. **72,** 836 (1947).
(c) L. G. Stier: Phys. Rev. **62,** 548 (1942).
(d) W. W. Watson and D. Woermley: Phys. Rev. **63,** 184 (1943).
(e) N. G. Schmahl and J. Schewe: Z. Elektrochem. **46,** 210 (1940).

Table 10 shows some values of R_T (calculated) and R_T (experimental). For those gas pairs for which diffusion data were available, ϵ_{12}/k obtained from diffusion (see table 2) were used; otherwise, it was necessary to employ the geometric mean of the ϵ/k for the single components. For all of the gas pairs, r_{12} was taken to be the arithmetic mean of the r_0 for each of the two components. Force constants for ammonia were obtained from second virial coefficient data.

Since the concentration gradient which results from thermal diffusion is opposed by ordinary diffusion, a steady state is reached after a certain time interval. Van Itterbeek, Van Paemel, and Van Lierde (19) have measured thermal diffusion in gas mixtures at low temperatures as per cent change in composition at the steady state $\Delta\gamma$, which may also be calculated from the following integral:

$$\Delta\gamma = \int_{T_1}^{T_2} k_T \, \mathrm{d} \ln T \tag{56}$$

This integration was performed numerically, making use of equation 44 for k_T, for the gases and temperatures in table 11, where the experimental and calculated values of $\Delta\gamma$ may be compared.

TABLE 11

Thermal diffusion in gas mixtures

$\Delta\gamma$ = change in per cent H_2

GAS MIXTURE	AVERAGE VOLUME PER CENT H_2	T_1	T_2	$\Delta\gamma$ (EXPERIMENTAL)[a]	$\Delta\gamma$ (CALCULATED)
		°K.	°K.		
H_2-Ne	35.6	290.4	90.2	6.9	7.1
	50.9	290.4	90.2	8.2	8.2
	66.7	290.4	90.2	7.7	7.9
H_2-CO	39.7	293.3	90.2	5.6	5.9
	51.7	293.3	90.2	6.6	6.7
	73.7	293.3	90.2	5.7	6.4
H_2-He	32.3	291.7	90.2	3.4	3.8
	50.5	291.7	90.2	4.6	4.2
	65.4	291.7	90.2	3.7	3.7
H_2-N_2	40.9	292.1	64.4	7.6	8.1
	50.8	292.1	64.6	8.4	9.0
	78.0	292.1	64.4	6.3	8.1
H_2-O_2	33.8	293.6	90.2	4.0	5.7
	48.2	293.6	90.2	5.5	7.1
	73.7	293.6	90.2	5.3	6.9

[a] A. Van Itterbeek, O. Van Paemel, and J. Van Lierde: Physica **13**, 231 (1947).

VI. THE COEFFICIENT OF THERMAL CONDUCTIVITY

For a single gas the coefficient of thermal conductivity, λ, through the second approximation is given in terms of the viscosity, η, and the specific heat at constant volume, C_v, by the relation:

$$\lambda = (H\eta/\mathrm{V}M)[C_v + (9/4)R] \tag{57}$$

Here R is the usual gas constant per mole, M is the molecular weight, and H and V are functions of kT/ϵ previously tabulated. The ratio H/V is very close to unity. The factor $[C_v + (9/4)R]$ depends upon the Eucken assumption that, during a collision, thermal equilibrium is established between the translational and internal degrees of freedom in the molecule. The experimental values of λ determined by Johnston and coworkers (10, 15) provide an opportunity to check the validity of this equation. Table 12 shows the comparison of the observed *versus* the calculated value of $(H/V) = (\lambda M/\eta)[C_v + (9/4)R]^{-1}$. The agreement is fairly good in the case of helium, where there are no internal degrees of freedom. In all other cases the discrepancies are large. This indicates that the Eucken assumption is not valid; hence equation 57 must be modified so as to take into account the difficulty of transferring energy from translation to rotation and vibration. The time lag in the specific heat is another indication of this difficulty. At very high temperatures, such as occur in combustions, the molecules behave more classically, and equation 57 should apply.

Until the discrepancies in the Eucken assumption are settled, there seems little advantage in trying to apply the complicated Chapman–Enskog relationships for the heat conductivity of gaseous mixtures. Instead, we shall employ equation 57, using the viscosity and specific heat of the mixture to estimate the heat conductivity.

TABLE 12

Thermal conductivity

GAS	H/V	100°K.	200°K.	300°K.
He	Experimental[a]	0.9933	0.9897	0.9733
	Calculated	1.0042	1.0043	1.0045
CH_4	Experimental[a]	0.9676	1.0258	1.0675
	Calculated	1.0000	1.0002	1.0009
NO	Experimental[a]		0.9504	0.9974
	Calculated		1.0004	1.0013
CO_2	Experimental[a]		0.8788	0.9479
	Calculated		1.0001	1.0003
O_2	Experimental[a]	0.9529	1.0042	1.0320
	Calculated	1.0000	1.0005	1.0015
Air	Experimental[b]	0.9499	1.0022	1.0107
	Calculated	1.0001	1.0008	1.0019

(a) H. L. Johnston and E. R. Grilly: J. Chem. Phys. **14**, 233 (1946).

(b) W. J. Taylor and H. L. Johnston: J. Chem. Phys. **14**, 219 (1946).

Unfortunately, accurate experimental measurements of heat conductivity are very difficult to obtain, so that there is no possibility of developing a more satisfactory empirical formulation at the present time.

The authors wish to express their appreciation to Dr. C. F. Curtiss for allowing them to set forth the generalized viscosity and diffusion equations in this paper, and for valuable assistance throughout the course of the work. The wide scope of the present report was made possible by the efforts of a computing group, under the direction of Ruth Shoemaker. In this connection we wish to thank Mary Nordling, Doris Jayne, Phyllis Rood, Phyllis Rhoades, Marjorie Leikvold, and Ted Mesmer.

The authors also wish to thank the Navy Bureau of Ordnance for their financial support under Contract NOrd 9958.

One of the authors, R. Byron Bird, desires to acknowledge the financial help which he has received from the Wisconsin Alumni Research Foundation.

REFERENCES

(1) CHAPMAN, S., AND COWLING, T. G.: *Mathematical Theory of Non-Uniform Gases.* Cambridge University Press, Teddington (1939).

(2) CORNER, JACK: Trans. Faraday Soc. **35,** 711 (1939); **35,** 1 (1939).

(3) CURTISS, C. F., AND HIRSCHFELDER, J. O.: "The Kinetic Theory of Multicomponent Systems of Gases" (University of Wisconsin, July, 1947), CF-727; to be submitted to The Journal of Chemical Physics for publication.

(4) HELLUND, E. J., AND UEHLING, E. A.: Phys. Rev. **54,** 479 (1938); **56,** 818 (1939).

(5) HELLUND, E. J., AND UEHLING, E. A.: Phys. Rev. **56,** 818 (1939).

(6) HILDEBRAND, J. H., WAKEHAM, H. R. R., AND BOYD, R. N.: J. Chem. Phys. **7,** 1094 (1939).

(7) HIRSCHFELDER, J. O., BIRD, R. B., AND SPOTZ, E. L.: J. Chem. Phys. **16,** 968 (1948).

(8) HIRSCHFELDER, J. O., AND CURTISS, C. F.: "The Theory of Propagation of Flames. Part I" (University of Wisconsin), CF-957; to be submitted to the Journal of Chemical Physics for publication.

(9) HIRSCHFELDER, J. O., MCCLURE, F. T., AND WEEKS, I. F.: J. Chem. Phys. **10,** 201 (1942).

(10) JOHNSTON, H. L., AND GRILLY, E. R.: J. Chem. Phys. **14,** 233 (1946).

(11) LENNARD-JONES, J. E., AND DEVONSHIRE, A. F.: Proc. Roy. Soc. (London) **A165,** 1 (1938); **A163,** 53 (1937).

(12) LONDON, F.: Trans. Faraday Soc. **33,** 8 (1937).

(13) MASSEY, H. S. W., AND MOHR, C. B. O.: Proc. Roy. Soc. (London) **A141,** 434 (1933); **A144,** 188 (1934).

(14) STOCKMAYER, W. H.: J. Chem. Phys. **9,** 398, 863 (1941).

(15) TAYLOR, W. J., AND JOHNSTON, H. L.: J. Chem. Phys. **14,** 219 (1946).

(16) UEHLING, E. A.: Phys. Rev. **46,** 917 (1934).

(17) UEHLING, E. A., AND UHLENBECK, G. E.: Phys. Rev. **43,** 552 (1933).

(18) VAN ITTERBEEK, A., VAN PAEMEL, O., AND VAN LIERDE, J.: Physica **13,** 88 (1947).

(19) VAN ITTERBEEK, A., VAN PAEMEL, O., AND VAN LIERDE, J.: Physica **13,** 231 (1947).

(20) WALDMAN, L.: Naturwissenschaften **32,** 223 (1944).