$$\frac{\Delta \bar{h}_i}{R} = \sum_{j=1}^{c-1} \left[1 + \left(\frac{\partial \ln \phi_i}{\partial \ln y_j} \right)_{T,P,y_{k \neq j}} \right] \left(\frac{\partial \ln y_j}{\partial 1/T} \right)_P - \sum_{j=1}^{c-1} \left[1 + \left(\frac{\partial \ln \gamma_i}{\partial \ln x_j} \right)_{T,P,x_{k \neq j}} \right] \left(\frac{\partial \ln x_j}{\partial 1/T} \right)_P \tag{20}$$

The phase rule allows c-2 composition variables to be fixed as temperature is varied at constant pressure, which would simplify the equation but would be experimentally awkward. As it stands Equation (20) requires a prohibitively large amount of experimental information for systems of more than two or perhaps three components.

CONCLUSION

At moderate vapor densities Equation (16), which includes the effect of vapor and liquid nonideality, permits a more accurate calculation of heats of solution than Equation (17), provided the experimental data are sufficiently accurate to warrant its use.

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NOTATION

B = second virial coefficient
f = fugacity
$\bar{h}$ = partial molar enthalpy
K = y/x
M = Henry's Law constant
P = total pressure
R = gas constant
$\bar{s}$ = partial molar entropy
T = absolute temperature
v = molar volume
$\bar{v}$ = partial molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
z = PV/RT
γ = liquid phase activity coefficient
μ = partial molar Gibbs free energy
ϕ = vapor phase fugacity coefficient

Subscripts

$i, j, 1, 2, k, c$ = component
1 = lighter component

Superscripts

l = liquid phase
g = vapor phase

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High Temperature Transport Properties of Gases; Limitations of Current Calculating Methods in the Light of Recent Experimental Data

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Requirements for satisfactory calculation of high temperature transport properties are discussed, with special emphasis on the role of the intermolecular potential. The determination of appropriate pair potentials from scattering of high energy neutral beams is described, and potentials obtained from helium, neon, argon, krypton, and xenon, each scattered by its own gas, are tabulated. Similar potentials are given for helium scattered by argon, nitrogen, methane, monofluoromethane, difluoromethane, trifluoromethane, and tetrafluoromethane; neon by argon; argon by hydrogen and nitrogen; atomic hydrogen by helium and hydrogen; and atomic deuterium by deuterium gas. Average potentials derived from suitable combinations of these experimental potentials are given for the like-particle systems of nitrogen, methane, monofluoromethane, difluoromethane, trifluoromethane, and tetrafluoromethane.

Results of calculations which use suitable and unsuitable potential functions are shown in tabulated form for the coefficient of viscosity, the coefficient of self-duffusion, and the isotopic reduced thermal diffusion ratio of argon and of nitrogen, and in graphical form for the coefficient of viscosity of xenon.

The rapidly increasing interest in the physics and chemistry of the upper atmosphere, combustion, detonation, and high-speed gas dynamics has focused attention on the lack of suitable information concerning gaseous transport properties at high temperatures. Direct measurements of these properties cannot usually be made at temperatures above about 1,000°K., and long range extrapolations from low temperatures are almost certain to be in serious error (*1*), since they incorrectly assume that the semiempirical potential functions which are suitable for the relatively large internuclear separations of importance at low temperatures will also be adequate at the smaller separations of importance at high temperatures. It is obviously worthwhile to see if it is possible to make accurate, direct calculations of transport properties at elevated temperatures.

A satisfactory calculation procedure must meet three necessary conditions:

1. The actual species present at the densities of interest must be known.
2. A suitable formal kinetic theory must exist which can be properly applied to the transport properties of these species.
3. Quantitative information must be available concerning the intermolecular

potentials of such species in the ranges of internuclear separation which are important at elevated temperatures.

In many instances the species present can be determined by actual equilibrium measurements or computed from statistical thermodynamics. Suitable formal kinetic theory relations have been developed for systems of atoms or molecules with force fields which may be assumed to be spherically symmetrical (*2, 3*). For the most part these relations are presently limited to gases at low or moderate densities (a limitation which is less serious at high temperatures than at low temperatures) and to transport properties for which contributions from internal degrees of freedom are not important: coefficients of viscosity, self-diffusion, mutual diffusion, thermal conductivity of monatomic gases, and thermal diffusion factors. In the case of these properties the assumption of spherically symmetrical force fields and the absence of effects associated with internal degrees of freedom appear to be quite well justified. Although the thermal conductivity of polyatomic gases (for which the internal degrees of freedom must be taken into account), the effects of spherical asymmetry, and the general problem of the transport properties of dense gases have been treated to some extent (*2* to *10*), a complete theory of these topics is still lacking.

Much of the quantitative information about intermolecular potentials has been derived from macroscopic properties such as transport and virial coefficients of gases or sublimation energies and lattice spacings in crystals. Since these properties were measured at relatively low temperatures, the derived potentials cannot safely be used to calculate properties at elevated temperatures. Further because of the semiempirical nature of the analytical functions which represent the interaction potentials and the differences in the ranges of the interaction distances which contribute significantly to the various properties, it is frequently found that a potential deduced from measurements of one property is not adequate for accurate calculations of another. For these reasons, and because of the theoretical importance of the results, a program was begun many years ago (*11*) for measuring intermolecular potentials directly at small internuclear distances of systems of atoms and molecules in their ground states.

The basis of the method is a study of atomic and molecular collisions in which the initial relative velocities are great enough to involve the small interaction distances of interest. If the masses, initial speeds, final speeds, and direction of scattering are known for a colliding system, it is possible, by considering the collision dynamics of a two-body encounter, to determine the potential energy of interaction at the closest distance to which the two particles approach in the course of their trajectories (*12, 13*). Experimentally a controlled atomic or molecular beam of high-energy particles is scattered by atoms of molecules of room temperature gas, and the desired interaction information is deduced from the variations with energy of the total elastic scattering cross sections. For the range of beam energies which are used, about 200 to 2,000 electron v., and the geometries of the various apparatus which have been used, the experimentally derived potential lies in the approximate range of 0.1 to 10 electron v. Potentials of this magnitude are derived from highly repulsive forces which are a result of interpenetration of atomic or molecular electron shells at the small internuclear distances involved. (Most binary systems of nonreactive, nonpolar particles have maximum values of the attractive potential, at relatively large internuclear distances, of about 0.01 electron v.)

TABLE 1*a*. INTERMOLECULAR POTENTIALS FOR ATOM-ATOM SYSTEMS

System	$\phi(r) \times 10^{12}$ erg. (r in Å.)	Range, Å.	Literature cited
He-He	$4.62/r^{1.79}$ or $314 \exp(-4.21r^{1/2})$	0.52-1.02	*20*
	$7.55/r^{5.94}$	1.27-1.59	*21*
	$5.56/r^{5.03}$	0.97-1.48	*22*
Ne-Ne	$500/r^{9.99}$	1.76-2.13	*23*
Ar-Ar	$46.1/r^{4.33}$ or $3.66 \times 10^4 \exp(-6.88r^{1/2})$	1.37-1.84	*24*
	$1{,}360/r^{8.33}$	2.18-2.69	*25*
Kr-Kr	$255/r^{5.42}$	2.42-3.14	*26*
Xe-Xe	$1.13 \times 10^4/r^{7.97}$	3.01-3.60	*27*
He-Ar	$99.5/r^{7.25}$	1.64-2.27	*15*
	$35.5/r^{5.42}$	1.40-1.81	*31*
Ne-Ar	$1{,}010/r^{9.18}$	1.91-2.44	*16*
H-He	$3.75/r^{3.29}$	1.16-1.71	*28*

TABLE 1*b*. INTERMOLECULAR POTENTIALS FOR ATOM-MOLECULE SYSTEMS

System	$\phi(r) \times 10^{12}$ erg. (r in Å.)	Range, Å.	Literature cited
H-H_2	$70.8 \exp(-29.9r^2) + 6.07 \exp(-0.942r^2)$	0.27-0.68	29
Ar-H_2	$254/r^{6.28}$	1.81-2.36	32
D-D_2	$45.9 \exp(-5.17r^2)$	0.29-0.56	29
He-N_2	$119/r^{7.06}$	1.79-2.29	*14*
Ar-N_2	$1{,}210/r^{7.78}$	2.28-2.83	*14*
He-CH_4	$965/r^{9.43}$	1.92-2.37	*30*
He-CH_3F	$618/r^{8.34}$	2.00-2.47	*33*
He-CH_2F_2	$6.22 \times 10^4/r^{13.33}$	2.22-2.58	*33*
He-CHF_3	$6.50 \times 10^5/r^{15.43}$	2.33-2.63	*33*
He-CF_4	$9.90 \times 10^6/r^{17.51}$	2.43-2.74	*30*

TABLE 1*c*. INTERMOLECULAR POTENTIALS FOR MOLECULE-MOLECULE SYSTEMS

System	$\phi(r) \times 10^{12}$ erg. (r in Å.)	Range Å.	Literature cited
N_2-N_2	$954/r^{7.27}$	2.43-3.07	*14*
CH_4-CH_4	$9.03 \times 10^6/r^{15.47}$	2.56-3.16	*30*
CH_3F-CH_3F	$2.76 \times 10^{10}/r^{19.61}$	3.41-4.01	*33*
CH_2F_2-CH_2F_2	$1.83 \times 10^{13}/r^{24.71}$	3.33-3.93	*33*
CHF_3-CHF_3	$1.46 \times 10^{18}/r^{32.85}$	3.46-3.88	*33*
CF_4-CF_4	$1.87 \times 10^{22}/r^{39.27}$	3.58-3.88	*30*

The high energy beam particles originate in an ion source where electrons from a grounded filament are accelerated to an anode, at a potential of about + 40 v., through gas at about 0.1-mm. pressure, and produce positive ions by collision. A portion of these ions, which are confined in space by a cylindrical cathode at a potential of 0 to −200 v., are withdrawn from the arc plasma by an extraction electrode whose potential may be varied between −200 and −2,000 v. As these ions, accelerated to terminal velocities determined by the potential of the extraction electrode, pass through neutral gas

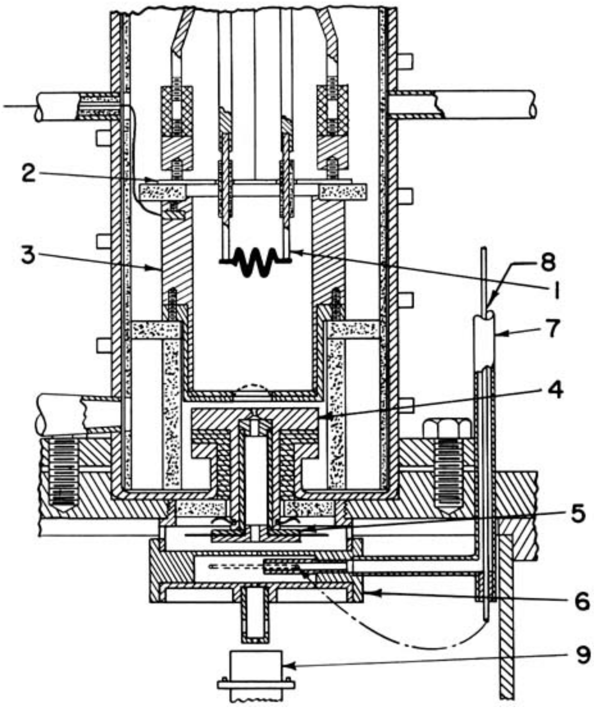

Fig. 1. Details of beam apparatus, 1. filament, 2. anode, 3. cathode, 4. extraction electrode, 5. condenser, 6. scattering chamber, 7. connection for measuring scattering pressure, 8. scattering gas inlet, 9. detector.

of their own species, charge transfer occurs. In this process a positive ion receives an electron from a neutral gas particle in the gas through which it passes without being deflected in the process of being neutralized. The fast positive ions which escape neutralization and the slow positive ions produced in the charge transfer are deflected out of the beam by parallel condenser plates. The remaining beam of high energy neutral particles is then scattered by passage through a layer of gas of known particle density. From the ratio of the scattered and unscattered axis intensities of the beam as measured by a suitable detector, the total elastic cross section at a specified beam energy can be obtained; from the variation of this cross section with energy, the intermolecular potential can be deduced. Figure 1 indicates the essential features of the apparatus.

A summary of intermolecular potentials obtained directly from the scattering of high energy neutral beams is given in Table 1*a* and Table 1*b*, where the atom-molecule potentials are averages with respect to all possible orientations in space of the scattering molecule relative to the atomic beam particle. If it is assumed that interatomic forces are additive and that a single scattering molecule has an essentially fixed orientation in space during the brief period of collision with the high velocity beam particle, then it is possible to calculate apparent interatomic potentials which may then be used to calculate average molecule-molecule interactions (*14*). The molecule-molecule interactions in Table 1*c* have been calculated in this manner.

The potential functions in Table 1 may be reclassified into two groups: those for systems of like particles, and those for systems of unlike particles. The first group is used for the calculation of properties of one-component systems, coefficients of viscosity, thermal conductivity, and self-diffusion: the second for the calculation of properties of systems of more than one component, mutual and multicomponent diffusion coefficients, thermal diffusion factors, viscosities, and thermal conductivities of binary and multicomponent mixtures. In the event that potentials for unlike systems are not available from direct measurements, they can be synthesized from appropriate like particle potentials by use of combination rules. Some of these rules have been suggested on the basis of semitheoretical considerations, others on the basis of experimental test (*15* to *17*). In this way transport properties of many gas mixtures may be calculated by making effective use of the potential functions of a relatively small number of like particle systems.

Once an accurate intermolecular potential in the appropriate range of internuclear distance is available, the calculation of most transport properties for normal atomic and molecular species is relatively straightforward. A discussion of the fundamental statistical mechanical and kinetic theory relations (*1*) and numerical results for a number of transport properties and virial coefficients of the rare gases, nitrogen, and helium-argon mixtures have been published (*18*). The calculation procedure may be summarized as follows:

1. Properties up to about 1,000°K. are calculated from potential energy functions which are valid at relatively large internuclear separations. Parameters of such functions, derived from low-temperature properties, have been tabulated by Hirschfelder, Curtiss, and Bird (3) who also present an excellent treatment of the theory of gaseous transport and equilibrium properties.

2. High-temperature properties, usually in the range 5,000° to 15,000°K., are calculated directly from beam potentials such as those listed in Table 1.

3. Intermediate range properties, approximately 1,000° to 5,000°K., are calculated from potentials which are blends or combinations of functions valid at large internuclear distances with those derived from the beam experiments. These blended potentials, in forms suitable for calculation of gas

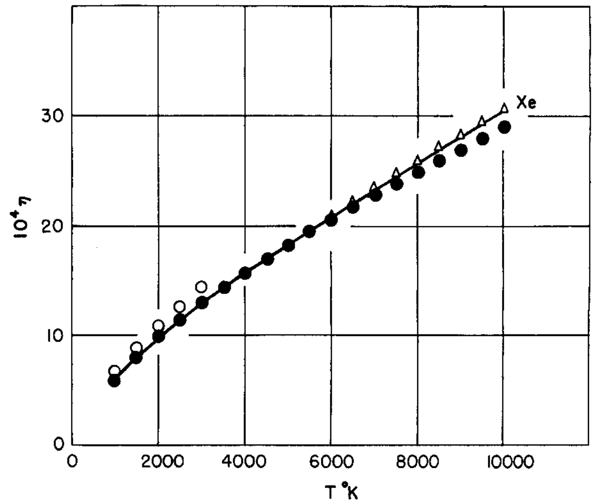

Fig. 2. Viscosity of xenon at elevated temperatures.

TABLE 2. HIGH-TEMPERATURE TRANSPORT PROPERTIES OF ARGON

Temp., °K.	$10^4[\eta]_1$, g. cm.$^{-1}$ sec.$^{-1}$ A	Beam	Best	$10^4\rho[D_{11}]_1$, g. cm.$^{-1}$ sec.$^{-1}$ A	Beam	Best	$[k_T{}^*]_1$ A	Beam	Best
1,000	5.5	5.6	5.4	7.1	8.1	7.2	0.56	0.41	0.48
5,000	15.2	18.6	18.3	20.6	26.6	25.4	0.57	0.41	0.41
15,000	30.7	42.0	41.8	42.0	60.1	60.0	0.57	0.41	0.40

properties, reproduce reasonably well the characteristics of the beam potentials while retaining, as much as possible, the positions and magnitude of the minima in the functions suitable for low-temperature properties.

4. Final values of a specified property are obtained by smoothing the values obtained in the separate ranges mentioned above.

The nature of the results obtained by the blending of potential functions and the overall smoothing of calculated values is shown well in Figure 2 where the viscosity of xenon, calculated as described above, is plotted against the temperature. The low-temperature points (open circles), calculated from

$$10^{12}\phi(r) = 12{,}100\exp(-2.92r) - 460/r^6 \text{ erg. } (4.2\text{Å.} < r < 4.8\text{Å}) \tag{1}$$

have been deliberately extrapolated to 3,000°K. to illustrate the error introduced by extrapolating the low-temperature potential beyond the limits of its validity. The intermediate points (closed circles) have been extended to 10,000°K. for the same purpose. The deviation of these latter points from the smooth curve at the very high temperatures is a direct consequence of the procedure for blending potentials to obtain a function which is best suited for the intermediate range. In the case of xenon the blended function was

$$10^{12}\phi(r) = 31{,}200\exp(-3.05r) - 570/r^6 \text{ erg. } (3.5\text{Å.} < r < 3.8\text{Å.}) \tag{2}$$

The high-temperature points (open triangles) were calculated from the xenon-xenon beam potential in Table 1*a* and would continue to fall on the smooth curve if the figure were extended to 15,000°K. To be sure, at this temperature xenon at moderate pressure would be extensively ionized and excited, and there might be few instances where the viscosity of a pure gas of ground state xenon at 15,000°K. would be of interest. Nevertheless the calculation procedures and principles are still applicable. In the case of helium or neon, ionization at 10,000° or even 15,000°K. is not significant, and the viscosity of ground state molecules has physical reality.

Further examples of the nature of the errors produced by the use of inappropriate potential functions are shown in Tables 2 and 3. First approximation values of the coefficient of viscosity, the coefficient of self-diffusion, and the isotopic reduced thermal diffusion ratio have been calculated from two different potentials, along with smoothed best values obtained as in the case of xenon. The potentials *A* and *B* are of the Lennard-Jones (12-6) type whose parameters, derived from relatively low-temperature measurements of the viscosities of argon and nitrogen, have been taken from Hirschfelder, Curtiss, and Bird (3). The actual functions may be written in the form of

$$[\text{Ar}-\text{Ar}(A)]\ 10^{12}\phi(r) = 1.74 \times 10^5/r^{12} - 109/r^6 \text{ erg. } (3.6\text{Å.} < r < 4.8\text{Å.}) \tag{3}$$

$$[\text{N}_2-\text{N}_2(B)]\ 10^{12}\phi(r) = 3.13 \times 10^5/r^{12} - 126/r^6 \text{ erg. } (3.7\text{Å.} < r < 4.5\text{Å.}) \tag{4}$$

The quantity $\rho[D_{11}]_1$ has been entered in the tables rather than $[D_{11}]_1$, since the former quantity, like $[\eta]_1$, is independent of density for dilute gases.

It is apparent from Tables 2 and 3 that the features of the behavior of the viscosity of xenon shown graphically in Figure 2 are reproduced in argon and nitrogen not only with respect to viscosity but also with respect to other transport properties, namely self-diffusion, thermal diffusion, and, of course, the translation portion of the thermal conductivity which is simply related to the viscosity through the specific heat at constant volume. Equilibrium properties, such as virial coefficients, are also sensitive to the proper choice of potential functions. In fact at relatively low temperatures, where the contribution of the attractive portion of the intermolecular potential is important, the differences between values of the second virial coefficient calculated from different potential functions tend to be very much greater than for most transport properties.

For purposes of reference an appendix has been included which contains the basic kinetic theory relations for the type of calculations shown in Tables 2 and 3. Because of the importance of the intermolecular potential in equilibrium as well as transport properties relations for $B(T)$ have also been included.

Although the exact formulas for the transport properties of a dilute gas mixture are quite complex (*2, 3, 34*), the same principles and restrictions apply as in the case of a pure, dilute gas. This is because, in addition to the properties of the pure components, the only other quantities which are needed are those which refer to all possible pairs of components of the mixture. These binary parameters are calculated in the same manner as the corresponding quantities in a one-component system provided that suitable potential functions are available to describe interactions between the various unlike particle systems. Convenient empirical approximations for calculating viscosities and translational thermal conductivities have been proposed by Wilke (*35*) and by Mason and Saxena (*36*), respectively. These approximate relations, which predict values in good agreement with those obtained from rigorous kinetic theory expressions, have the advantage of requiring only properties of the pure components at the temperature of the mixture. A detailed discussion of the above points relating to mixtures, together with computational examples, has been given elsewhere (*18*). These numerical examples, interpreted in the light of the points made in the present paper, confirm the statement that the calculation of transport properties of dilute gas mixtures presents no serious problems beyond those encountered in dilute pure gases.

The point has been made that the range of validity of the interaction potential determines the range of temperature in which reliable calculations of transport properties may be made. In most cases $\phi(r)$ behaves somewhat like a step function, namely in a single collision it has a significant magnitude over a small range of r near a minimum value r_0, but diminishes very rapidly as r increases. Since $\phi(r_0)/\overline{E}$, where $\overline{E}$

TABLE 3. HIGH-TEMPERATURE TRANSPORT PROPERTIES OF NITROGEN

Temp., °K.	$10^4[\eta]_1$, g. cm.$^{-1}$ sec.$^{-1}$ B	Beam	Best	$10^4\rho[D_{11}]_1$, g. cm.$^{-1}$ sec.$^{-1}$ B	Beam	Best	$[k_T{}^*]_1$ B	Beam	Best
1,000	4.0	3.8	4.0	5.4	5.5	5.2	0.57	0.35	0.58
5,000	11.5	13.2	12.8	15.6	19.1	17.7	0.57	0.35	0.41
15,000	23.1	30.9	30.9	31.7	44.8	43.5	0.57	0.35	0.35

is the average initial kinetic energy of relative motion in all the binary collision trajectories of the system, largely determines the temperature to be assigned to a given calculated transport value, the close correspondence between the range of the potential and the range of temperature follows. This concept has been expressed in quantitative form by Le Fevre (37) who shows that for calculations of the coefficient of viscosity with a potential of the form $\phi(r) = K/r^s$

$$\phi(r_o) = kT \tag{5}$$

where r_o is identified as the equivalent hard sphere diameter which at the temperature T gives the same value of the viscosity as the actual inverse power potential. Equation (5) holds within about 6% and is essentially unchanged when different potential forms are used, or when other transport properties at elevated temperatures are considered. Thus in experiments on the scattering of high velocity neutral particles it is the range of the derived potential energy and not the range of the kinetic energy of the beam which fixes the proper interval of temperature for the calculations of transport properties. For example if beam particles with kinetic energies between 100 and 1,000 electron v. are elastically scattered through a relative angle of about 10^{-3} radians, the range of the deduced interaction potential will be between 0.1 and 1.0 electron v. From Equation (5) it is seen that the appropriate range of temperature for calculating transport properties is 1,000° to 10,000°K. and not temperatures (which would be about 1,000 times larger) incorrectly associated with the beam energies.

It is interesting to examine the possibility of extending the type of calculation of transport properties of ground state species to systems which include excited species, ions, and dissociative atomic species. The author thinks that if it were possible to determine the appropriate potential functions for all important species in the states which contribute significantly to the properties in question, the additional problem of obtaining the appropriate statistical mechanical and kinetic theory relations might not be prohibitive.

Interaction potentials for ion-atom or ion-molecule systems are probably easier to determine experimentally than those for uncharged systems, since ion beams of high intensity in the desired energy range are not difficult to produce and the detection problem is simpler than for high-energy neutrals. There are many examples of experiments of this type in the literature (38).

Potentials involving reactive atomic species may be deduced from experiments in which atomic beams of particles such as hydrogen, oxygen, etc. are scattered either by stable atoms or by molecules. The atomic hydrogen-helium, atomic hydrogen-hydrogen, and atomic deuterium-deuterium systems in Table 1 are examples in point. These experiments yield directly atom-molecule potentials which are required for the calculation of properties involving interactions between unlike particles, such as the mutual diffusion coefficient, and properties of mixtures. In addition, by combining results of such experiments with those of the appropriate stable particle systems, for example helium-helium, hydrogen-hydrogen, etc., it is possible to obtain experimental interaction information about unstable atom-atom systems of the type atomic hydrogen-atomic hydrogen, atomic oxygen-atomic oxygen, etc.

Interactions involving excited species are no doubt the most difficult to determine. Two approaches seem feasible. The first is applicable only to metastable species and involves the scattering, in the usual manner, of a beam containing a mixture of ground state and metastable particles or, if possible, only metastable particles. This method is limited by the difficulty of obtaining sufficiently high intensities of metastable atoms or molecules and by the small number of such species which have sufficiently long lifetimes (greater than about 10^{-6} sec.) to permit their extraction from the source and scattering before de-excitation occurs. The second approach involves the scattering of stable ground state particles such as helium or argon through scattering gas which contains known concentrations of excited, metastable, ionized, or dissociative atomic species. The concentrations of such species could be varied by changing the temperature of the scattering gas, by irradiating it with light of known intensity and spectral character, or by passing a suitable discharge through it. Experiments of this type would not be easy either to perform or to interpret correctly, but the obvious importance of interactions involving these unusual species and the difficulty of obtaining the information by other means appear to justify serious consideration of the type of experiments suggested. In fact exploratory studies of this nature have been recently started by the author and his co-workers.

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The author wishes to express his deep appreciation to the many graduate students and postdoctoral associates with whom he has had the pleasure of working since he produced his first high energy neutral beam about 1936. Without their contributions the quantitative determination of intermolecular potentials at close internuclear distances and the successful application of the results to problems of high temperature gas properties would not have been possible.

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NOTATION

A^* = ratio of reduced collision integrals, Equation ($A7$)
$A^{(1)}(s)$, $A^{(2)}(s)$ = dimensionless constants
b = impact parameter in binary collision
b^* = reduced impact parameter, Equation ($A11$)
$B(T)$ = second-virial coefficient
$B^*(T^*)$ = reduced second-virial coefficient, Equations ($A13$), ($A14$)
C^* = ratio of reduced collision integrals, Equation ($A8$)
$[D_{11}]_1$ = self-diffusion coefficient, first approximation
g = initial relative speed
g^* = dimensionless ratio, Equation ($A10$)
k = gas constant per molecule
$[k_{T^*}]_1$ = isotopic reduced thermal diffusion ratio, first approximation
K = parameter of inverse power potential function
l = index, Equation ($A5$)
M = molecular weight
n = index, Equation ($A4$)
N = Avogadro's number
r = internuclear separation
r_m = parameter of potential function (position of potential minimum)
r^* = reduced internuclear separation = r/r_m
r_o^* = reduced distance of closest approach = r_o/r_m
$Q^{(l)*}(g^*)$ = reduced transport cross section defined by Equation ($A5$)
R = gas constant per mole
s = parameter of inverse power potential function
T = absolute temperature, °K.
T^* = reduced temperature, Equation ($A9$)

Greek Letters

α = parameter of potential function
ϵ = parameter of potential function (magnitude of potential minimum)
$[\eta]_1$ = viscosity coefficient, first approximation
μ = reduced mass of colliding particles
ρ = mass density of molecules
σ = parameter of potential function (position of zero of potential)
$\phi(r)$ = intermolecular potential at internuclear separation r

$\phi^*(r^*)$ = reduced intermolecular potential

$\chi(g^*, b^*)$ = relative angle through which initial relative velocity is turned by collision

$\Omega^{(l,n))*}(T^*)$ = reduced collision integral, Equation (*A*4)

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APPENDIX

The potentials represented by Equations (1) to (4) may conveniently be written in the following forms for purposes of calculations based on tabulations such as those found in Hirschfelder, Curtiss, and Bird (*3*):

Modified Buckingham (exp-6) potential:

$$\phi(r) = \frac{\epsilon}{1 - 6/\alpha}\left\{\frac{6}{\alpha}\exp\left[(1 - r/r_m)\right] - (r_m/r)^6\right\} \qquad r \geqslant r_{\max}$$

$$\phi(r) = \infty \qquad r \leq r_{\max}$$

Lennard-Jones (12-6) potential:

$$\phi(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right]$$
$$= \epsilon\left[(r_m/r)^{12} - 2(r_m/r)^6\right]$$

The parameter α permits variation of the steepness of the repulsive portion of the potential, and $r_{\max}$ is the value of r where $\phi(r)$ has a spurious maximum. In most cases the potentials derived from scattering experiments have been represented by an inverse power point repelling model

$$\phi(r) = K/r^s$$

where K and s are not functions of r.

The expressions, to the first approximation, for the coefficient of viscosity, the coefficient of self-diffusion, and the isotopic reduced thermal diffusion ratio, as obtained from solutions of the Maxwell-Boltzmann equation of transport for dilute gases, are as follows:

$$[\eta]_1 = \frac{5}{16N}\left(\frac{MRT}{\pi}\right)^{1/2}\frac{1}{r_m{}^2\Omega^{(2,2)*}(T^*)} \qquad (A1)$$

$$[D_{11}]_1 = \frac{3}{8N}\left(\frac{MRT}{\pi}\right)^{1/2}\frac{1}{\rho r_m{}^2\Omega^{(1,1)*}(T^*)} \qquad (A2)$$

$$[k_T{}^*]_1 = \frac{15}{16}\frac{(6C^* - 5)}{A^*} \qquad (A3)$$

where

$$\Omega^{(l,n)*}(T^*) = \frac{2}{(n+1)!(T^*)^{n+2}}\int_0^\infty e^{-g^{*2}/T^*}g^{*2n+3}Q^{(l)*}(g^*)\,dg^* \qquad (A4)$$

$$Q^{(l)*}(g^*) = \frac{2}{\left[1 - \dfrac{1+(-1)^l}{2(1+l)}\right]}\int_0^\infty(1 - \cos^l\chi)b^*\,db^* \qquad (A5)$$

$$\chi(g^*, b^*) = \pi - 2b^*\int_{r_o{}^*}^\infty\left[1 - b^{*2}/r^{*2} - \phi^*(r^*)/g^{*2}\right]^{-1/2}dr^*/r^{*2} \qquad (A6)$$

$$A^* = \Omega^{(2,2)*}(T^*)/\Omega^{(1,1)*}(T^*) \qquad (A7)$$

$$C^* = \Omega^{(1,2)*}(T^*)/\Omega^{(1,1)*}(T^*) \qquad (A8)$$

$$T^* = kT/\epsilon \qquad (A9)$$

$$g^{*2} = \frac{1}{2}\mu g^2/\epsilon \qquad (A10)$$

$$b^* = b/r_m \qquad (A11)$$

$$\phi^*(r^*) = \phi(r)/\epsilon \qquad (A12)$$

$r_o{}^*$ = smallest positive root of $[1 - \phi^*(r_o{}^*)/g^{*2}]\ r_o{}^{*2} = b^{*2}$.

The second virial coefficient is related to the intermolecular potential by the equation

$$B^*(T^*) = -\frac{1}{T^*}\int_0^\infty r^{*3}\frac{d\phi^*(r^*)}{dr^*}e^{-\phi^*(r^*)/T^*}\,dr^*$$
$$= -3\int_0^\infty r^{*2}\left[e^{-\phi^*(r^*)/T^*} - 1\right]dr^* \qquad (A13)$$

where

$$B^*(T^*) = \frac{B(T)}{\dfrac{2}{3}\pi N r_m{}^3} \qquad (A14)$$

In the case of the potential form $\phi(r) = K/r^s$ the relations for the transport coefficients and $B(T)$ are somewhat more compact, in some cases of closed analytical form. The results may be summarized as follows:

1. In Equation (*A*1) $r_m{}^2\Omega^{(2,2)*}\ (T)^*$ is replaced by $\frac{1}{2}\left(\frac{sK}{kT}\right)^{2/s}\Gamma(4 - \frac{2}{s})$ $A^{(2)}(s)$ where $A^{(2)}(s)$ is a dimensionless constant whose values have been tabulated (*3, 19*).

2. Comparison of Equations (*A*1) and (*A*2) leads to the simple relation $\rho[D_{11}]_1/[\eta]_1 = 6A^*/5$. For the inverse power potential $A^* = \left(\frac{3}{2} - \frac{1}{s}\right) A^{(2)}(s)/A^{(1)}(s)$, where $A^{(1)}(s)$ is a tabulated constant similar to $A^{(2)}(s)$ (*3, 19*).

3. The expression for A^* which appears in $[k_T{}^*]_1$ has been given above. The new relation for C^* is simply $C^* = 1 - (2/3s)$.

4. The expression for $B(T)$ is given in closed form by $B(T) = \frac{2\pi N}{3}\left(\frac{K}{kT}\right)^{3/s}\Gamma\left(\frac{s-3}{3}\right)$.