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In this case $\rho v = M$ is a constant and we have, after integration,

$$\rho v^2 = -p + \text{constant}.$$

Indicating the cold side of the flame by subscript "0" and hot side by "m" we have

$$\rho_m v_m^2 - \rho_0 v_0^2 = p_0 - p_m.$$

The velocity of sound in a gas is

$$c = (\gamma p / \rho)^{1/2}.$$

Using this to eliminate the ρ_0 and ρ_m we find

$$\frac{p_m}{p_0} = \frac{1 + \gamma(v_0^2/c_0^2)}{1 + \gamma(v_m^2/c_m^2)}.$$

The ratio of specific heats, γ , is only slightly larger than unity and in the case of ordinary flames the ratio v/c is small. Hence, p_m/p_0 never varies much from unity and we can ignore variations in the pressure throughout the flame.

To amplify this point, let us consider a typical case. A flame velocity of the order of 30 cm/sec. is usual. This is the velocity of the cold gas relative to the flame front. Since the temperature rises by a factor of about 10, the velocity of the hot gases relative to the flame front is about 300 cm/sec. The velocity of sound in gases at ordinary temperatures is about 3×10^4 cm/sec. The velocity of sound goes up as the square root of T and thus in the hot gases c is about 9×10^4 cm/sec. Taking $\gamma = 1.3$ these figures result in

$$p_m/p_0 = 1 + 1.69 \times 10^{-6} - 1.88 \times 10^{-6} = 1 - 1.71 \times 10^{-5}.$$

Thus the pressure drop through a flame at 1 atmos. pressure is about 0.01 mm of mercury.

It should be pointed out that although variations in the pressure are unimportant in this problem, in the case of a real three-dimensional flame the small variations may be important in determining the geometrical shape of the flame front.

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Self-Diffusion in Argon*

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The self-diffusion coefficient of argon was measured at five different temperatures between -183°C and 53.5°C by observing the diffusion of radioactive A^{41} into normal argon. The decrease in the observed diffusion coefficient caused by the larger mass of A^{41} was deduced and found to be 0.6 percent. The experimental values are compared with several theoretical calculations. In particular, it is shown that use for argon of an inverse power model ($V \propto r^{-\nu}$), with different values of ν ascribed to different temperature ranges, is not permissible since widely different values of ν at the same temperature can be obtained from different experimental data. The experimental figures agree very well with numerical calculations by Hirschfelder, Bird, and Spotz based on an interaction potential of the form $4E[-(r_0/r)^6 + (r_0/r)^{12}]$.

THE rate at which different gases intermingle is usually described by a diffusion coefficient which in general depends on the intermolecular force fields of the diffusing molecules. Enskog and Chapman have derived expressions which relate the value of the diffusion coefficient to these interaction potentials. A knowledge of the values of the coefficients thus enables something to be said about the forces between the diffusing molecules. For this purpose the case of self-diffusion—i.e., all molecules involved being the same—is much the most satisfactory to consider. Only a single type of interaction has to be considered; there is no variation of the coefficient with relative concentration; and the potential function involved, that between like molecules; is usually of greater interest, being also involved in the equation of state and in the coefficients of viscosity and thermal conductivity.

Of course, there is really no such thing as a self-diffusion coefficient for a gas. By definition a self-diffusion coefficient describes the interdiffusion of identical

molecules; but since the molecules are identical there is no way of following the course of the diffusion, and therefore no process actually takes place. Now suppose that the molecules of one of the gases differ only very slightly from those of the other gas—a good example would be molecules having the nucleus of one atom in a metastable state only a little above the ground state. The progress of these molecules through normal molecules could be followed, and if the mass of the molecule containing the metastable nucleus were increased only a very small amount, the diffusion coefficient thus measured could be identified with the self-diffusion coefficient calculated classically on the assumption that the origin of each molecule could be determined at any time.

This paper describes measurements at several temperatures of the diffusion of radioactive A^{41} through ordinary argon, which is more than 99 percent A^{40} . The difference in mass between these two molecules is of course quite appreciable, but the next section shows how the "true" self-diffusion coefficient of either isotope may be deduced from results in a case where the diffusing molecules differ only in mass.

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DEPENDENCE OF DIFFUSION ON MASS OF DIFFUSING MOLECULES

Chapman and Cowling¹ give a first approximation for the coefficient of diffusion D of gas 1 into gas 2

$$D = \frac{3}{16} \frac{kT}{\mu n \Omega^{(1)}(1)}, \quad (1)$$

where

$$\Omega^{(1)}(q) = (kT)^{-q-1} \left(\frac{\pi}{\mu kT} \right)^{\frac{1}{2}} \int_0^\infty e^{-(w^2/kT)} w^{2q+3} dw \\ \times \int_0^\infty (1 - \cos^q \chi) b db, \quad (2)$$

$$w = (\mu/2)^{\frac{1}{2}} g.$$

μ = reduced mass of the system (molecule 1 + molecule 2),
 $= m_1 m_2 / (m_1 + m_2)$,
 g = relative speed of the colliding molecules before impact,
 n = total number of molecules per unit volume.

χ is the angle through which the relative velocity of the two colliding molecules is rotated by the collision for a given impact parameter b , and is given by the expression

$$\chi = \pi - 2b \int_{r_0}^\infty \frac{dr}{r \left(\left(1 - \frac{V(r)}{w^2} \right) r^2 - b^2 \right)^{\frac{1}{2}}}, \quad (3)$$

where r_0 is the largest real solution of

$$\left(1 - \frac{V(r_0)}{w^2} \right) r_0^2 = b^2, \quad (4)$$

and $V(r)$ is the potential function describing the interaction of molecules 1 and 2. It is to be noticed from Eqs. (2), (3), and (4) that for a given $V(r)$ the integral in $\Omega^{(1)}(q)$ depends only on the temperature, so that we can write

$$D = f(T) / n \mu^{\frac{1}{2}}, \quad (5)$$

$f(T)$ depending on $V(r)$. Thus from information on the diffusion of one isotope of a gas into another, $V(r)$ being the same no matter which isotope, we can calculate the correction to be applied to get the classical self-diffusion constant describing the process taking place with negligible difference in the molecular weights. Since Chapman and Cowling's first approximations to the transport coefficients are remarkably close² any corrections calculated from (5) will be almost exact.

Experimental data on the diffusion of hydrogen and deuterium can be used to check Eq. (5). Heath *et al.*³ found that the diffusion constant for deuterium into hydrogen $D_{HD} = 1.24$ cm²/sec. at 15°C and one atmos-

phere. From the data of Harteck and Schmidt⁴ we can find that the constant describing the diffusion of parahydrogen into orthohydrogen is $D_{HH} = 1.40$ cm²/sec. at the same temperature and pressure. This gives the experimental ratio $D_{HH}/D_{HD} = 1.40/1.24 = 1.13$. From Eq. (5) the calculated ratio is

$$D_{HH}/D_{HD} = (3/2)^{\frac{1}{2}} = 1.15,$$

agreeing with the experimental value to within the experimental error.

Inserting the appropriate figures in (5) we find that the "true" self-diffusion coefficient for A⁴⁰ can be obtained by multiplying the observed diffusion coefficient for the diffusion of A⁴¹ into A⁴⁰ by 1.006.

THE EXPERIMENTAL MEASUREMENTS

Measurement of D at Room Temperature

The measurement of D at room temperature has already been reported.⁵ A recalculation of the data leads to a slightly higher value for the diffusion constant of A⁴¹ into A⁴⁰, 0.425 ± 0.003 cm²/sec. at 32 cm Hg, 22°C. Using the well-established fact that D is proportional to n^{-1} and the isotope correction factor (1.006) we find

$$D = 0.180 \pm 0.001 \text{ cm}^2/\text{sec.}$$

at 76.0 cm Hg, 22°C, for A⁴⁰. The error given is the probable error calculated from the scatter of the data.

Measurement of D at Other Temperatures

The apparatus used to measure D at other than room temperature is shown in Fig. 1 and was suggested by the apparatus used by Ney and Armistead.⁶ Two chambers each of about 100 cc volume were connected by a straight tube 0.475 cm diameter and 2.85 cm long drilled through a steel block containing a valve which could close off the connecting tube. The entire apparatus was set in a well-stirred bath held at the appropriate temperature, the valve being operated from outside the bath through a metal bellows. In use, with the valve closed one chamber was filled with tank argon, the other with argon containing A⁴¹, each at about one atmosphere pressure. The filling was done through capillaries with a total volume less than 1/20 percent of either chamber, making diffusion in and out of the filling tubes a negligible effect. Opening the valve allowed the gases to intermingle, the relative amount of A⁴¹ in either chamber at any time being determined by the ion current drawn to an insulated electrode inserted into each chamber. Radioactive material in one chamber did not cause an appreciable amount of ionization in the other because the steel block stopped all the 1.18 Mev β -rays from A⁴¹, the 1.37 γ -ray causing only a very small fraction of the ionization. A negligible amount of radiation

¹ S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, London, 1939), p. 165.

² See reference 1, p. 196. See also the last section of this paper.

³ Heath, Ibbs, and Wild, *Proc. Roy. Soc. A178*, 380 (1941).

⁴ P. Harteck and H. W. Schmidt, *Zeits. f. physik. Chemie B21*, 447 (1933).

⁵ F. Hutchinson, *Phys. Rev.* **72**, 1256 (1947).

⁶ E. P. Ney and F. C. Armistead, *Phys. Rev.* **71**, 14 (1947).

could pass through the connecting tube. The collecting voltage was 90 volts, well above the voltage necessary to collect essentially all the ions formed. The currents were in the range 10^{-11} – 10^{-12} amperes and were measured by the voltage drop across a 10^{11} ohm resistor. A null method was employed, a vacuum tube electrometer using a Western Electric D-96475 indicating when the variable reference voltage equaled the potential drop across the high resistance.

The voltage V due to the ion current from each electrode passing through the 10^{11} ohms was directly proportional to the average concentration \bar{c} of A^{41} in the corresponding chamber. Denoting the chamber to which a quantity refers by the subscripts 1 and 2

$$V_1 = \alpha_1 \bar{c}_1, \quad V_2 = \alpha_2 \bar{c}_2, \quad (6)$$

where α_1 and α_2 are constants. Now

$$\frac{d}{dt}(\bar{c}_1 \tau_1) = -\lambda \bar{c}_1 \tau_1 - AD(\partial c / \partial x), \quad (7)$$

where τ_1 is the volume of chamber 1, λ the radioactive decay constant, A the area of the connecting tube, and $\partial c / \partial x$ the concentration gradient along the axis of the connecting tube at the midpoint. A similar equation can be written for the other chamber and combining gives

$$\frac{d}{dt}(\bar{c}_1 - \bar{c}_2) = -\lambda(\bar{c}_1 - \bar{c}_2) - \left(\frac{A}{\tau_1} + \frac{A}{\tau_2} \right) D \frac{\partial c}{\partial x}. \quad (8)$$

A plausible assumption is that after the initial very steep gradients have passed away

$$\partial c / \partial x = \theta(\bar{c}_1 - \bar{c}_2), \quad (9)$$

where θ is a constant; for a very long thin tube θ would equal the reciprocal of the length of the tube. Substituting this in (8)

$$\frac{d}{dt}(\bar{c}_1 - \bar{c}_2) = -(\lambda + \beta)(\bar{c}_1 - \bar{c}_2) \quad \beta \equiv (A/\tau_1 + A/\tau_2)\theta D = KD, \quad (10)$$

or using (6) and integrating,

$$\ln \left(V_1 - \frac{\alpha_2}{\alpha_1} V_2 \right) = -(\lambda + \beta)t + \text{const.} \quad (11)$$

The ratio α_2/α_1 was determined to be 0.983 by filling both chambers with the same sample of radioactive argon (i.e., making $\bar{c}_1 = \bar{c}_2$), measuring the voltages corresponding to each chamber, and using Eq. (6). In a diffusion experiment V_1 and V_2 were measured as a function of time. Plotting $\log[V_1 - (\alpha_2/\alpha_1)V_2]$ against time as in Fig. 2, a straight line was obtained, from the slope of which the value of β could be found. λ was set equal to $1.041 \times 10^{-4} \text{ sec}^{-1}$, corresponding to a half-life of 110.8 minutes as determined by a special experiment.

To get D from the experimental values of β four runs were made at room temperature as listed in Table I.

The values of β were corrected to 76.0 cm Hg pressure and 22°C by assuming that D , and hence β , varied inversely as the density and as $T^{1.8}$. This last correction was deduced from measurements of the variation of viscosity with temperature,⁷ and from the experimental data later obtained was found to be quite accurate enough for the small corrections involved. Each value of β thus obtained was divided by the value for D at room temperature, $0.180 \text{ cm}^2/\text{sec}$., giving the values of K listed in Table I. If θ is assumed equal to (tube

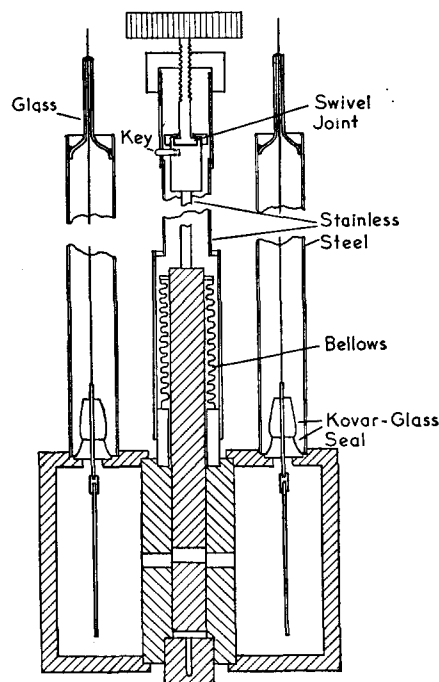


FIG. 1. Apparatus used to measure temperature variation of self-diffusion coefficient D .

length)⁻¹, K becomes $1.31 \times 10^{-3} \text{ cm}^{-2}$, showing that this assumption is not too bad an approximation.

If K were strictly a constant the diffusion coefficient at any temperature could be obtained by dividing the observed value of β by K . Actually, K might vary with temperature because (a) θ might involve D , which certainly varies with temperature, and (b) it depends on the dimensions of the apparatus, which also change with temperature.

Considering the second point first, it is easy to show, using the approximation given above for θ and the handbook values of the thermal expansion coefficients of the materials involved in the tube length, τ , and A , that K should be multiplied by the factor $[1 - 42 \times 10^{-6}(t - 22)]$, where t is the temperature in $^\circ\text{C}$. This correction was made for each point, although at no temperature used did it exceed one percent.

We can show that θ does not depend on D in the following way. The fundamental equation obeyed by c ,

⁷ See reference 1, p. 223.

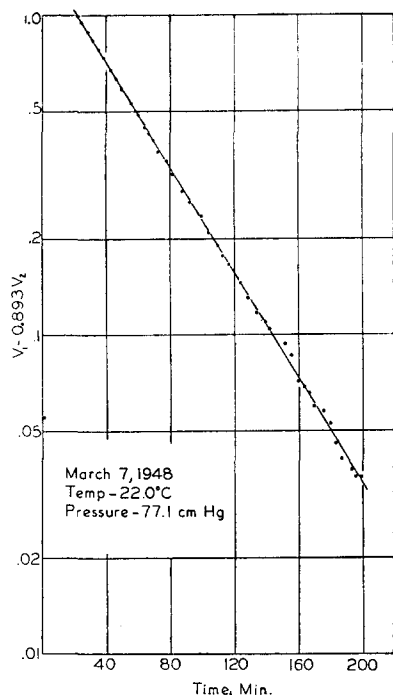


FIG. 2. Typical plot of experimental data for one run. The ordinate, proportional to the difference in A^{41} concentration in the two chambers, is plotted on a logarithmic scale. The scatter in the data is about that usually observed.

the concentration of A^{41} , is

$$\partial c / \partial t = D \nabla^2 c - \lambda c, \quad (12)$$

or writing $c \equiv g e^{-\lambda t}$, $u \equiv D t$,

$$\partial g / \partial u = \nabla^2 g. \quad (13)$$

Inserting the appropriate boundary conditions, the solution to this equation is

$$c = g(u) e^{-\lambda t}. \quad (14)$$

It is obvious that any dependence of θ on D must be through the parameter u . But the experimental data as exemplified by Fig. 2 show that β , and therefore θ , does not depend on time. θ , then, cannot depend on u , and so does not involve D .

The experimental results at different temperatures are given in Table II. The values of D given are corrected to 76.0 cm Hg in the same way as explained above. The point to be looked on with the greatest suspicion is of course the one at -183°C . Measurement here is more difficult than at the higher temperatures because D is so small that β is only a fraction of λ , and since it is the sum $\lambda + \beta$ which is directly measured, the percent error in D is high. In addition, chilling the valve to this temperature caused it to jam; it was ruined in the process of freeing it, and thus additional measurements were prevented. The error attached to it is that which might be expected in view of the scatter from run to run observed at other temperatures.

The errors listed for the mean values of D at the

other temperatures are the probable errors calculated by taking into account the spread in the data and the probable errors in the various parameters used in the calculations, including the value of D at room temperature. There was no way to estimate any systematic errors, the most important possibly being the effects of a small amount (believed less than 0.4 percent) of contaminating gases in the argon. The biggest part of the systematic error is probably in the value of D at room temperature, and since the relative changes in D with temperature are independent of this quantity, these relative changes are more accurate than the absolute values.

COMPARISON WITH THEORY

A quantity of much interest in the kinetic theory of gases is the dimensionless ratio $\epsilon \equiv \rho D / \eta$, where ρ is the density and η the viscosity of the gas. Table III gives the experimental values of ϵ taking the figures for ρ and η from the literature. The first approximation for this quantity given by kinetic theory is⁸

$$\epsilon = \frac{2}{3} \Omega^{(2)}(2) / \Omega^{(1)}(1), \quad (15)$$

where $\Omega^{(i)}(q)$ is given by (2).

If the interaction potential $V(r)$ of two colliding molecules is known, then D and ϵ can be calculated by using Eqs. (1), (2), (3), (4), and (15). $V(r)$ is not known exactly; however, by substituting various types of $V(r)$ into these equations and comparing the calculated with the experimental values of D and ϵ some idea can be obtained of the suitability of the assumed type of interaction potential.

Interaction Potential $V(r) = A/r^\nu$

A repulsive potential of this type has been much used in kinetic theory because it leads to expressions for the transport coefficients which can be handled analytically. Thus it can be shown⁹ that for this model at constant pressure $D \propto T^{s+1}$, $s = \frac{1}{2} + 2/(\nu - 1)$, and that ϵ lies between 1.2 and 1.551, depending on the value of ν , with no dependence on temperature. From the first relation it follows that a plot of $\log D$ against $\log T$ should yield a straight line. Figure 3 shows that this is not so, even in the high temperature region. Also, it is probable that the variation in ϵ with temperature for the first four

TABLE I. Experimental values of K .

Temperature °C	Pressure cm Hg	K cm^{-2}
22.0	76.4	1.212×10^{-3}
23.2	76.9	1.183
22.0	77.1	1.197
21.6	77.7	1.213
		mean $(1.201 \pm 0.005) \times 10^{-3}$

⁸ See reference 1, p. 198.

⁹ See reference 1, pp. 172, 248.

TABLE II. Experimental values of D .

Temperature °C	Pressure cm Hg	D (corrected) cm ² /sec.
53.5	77.9	0.2144
	77.5	0.2082
	77.2	0.2125
	mean	0.212±0.002
0	78.1	0.1568
	76.5	0.1590
	mean	0.158±0.002
-78.5	69.6	0.0835
	72.3	0.0844
	76.7	0.0820
	mean	0.0833±0.0009
-183	77.1	0.0277±0.0010

TABLE III. Experimental values of ϵ .

Temp. °C	D cm ² /sec.	ρ^a g/cm ³	η^b g/cm-sec.	ϵ
53.5	0.212	1.490×10 ⁻³	0.2435×10 ⁻³	1.30
22	0.180	1.650	0.2240	1.32
0	0.158	1.783	0.2104	1.34
-78.5	0.0833	2.508	0.1555	1.34
-183	0.028	5.75	0.0765	2.1

^a Calculated from the density at STP given by the International Critical Tables (1933) and the compressibility data given by L. Holborn and J. Otto, *Zeits. f. Physik* **30**, 320 (1924). Density at -183° from data by Mathias, Onnes, and Crommelin, *Com. Phys. Lab. Leiden*, No. 131a (1912) and C. A. Crommelin, *Com. Phys. Lab. Leiden*, No. 138c (1913).

^b H. L. Johnston and E. R. Grilly, *J. Phys. Chem.* **46**, 948 (1942). Viscosity at 53.5°C from A. O. Rankine, *Proc. Roy. Soc.* **84**, 181 (1910).

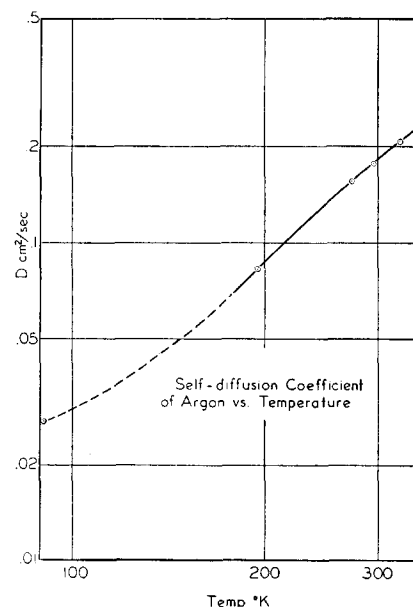
points as given in Table III is real. Thus this assumed interaction potential does not agree well with experiment.

Because this form of interaction potential leads to comparatively simple analytical expressions for the transport coefficients, attempts to extend its use are often made by assuming that equations based on it are valid over small temperature ranges, an "effective ν " being used as an index of the manner in which the molecular interaction varies with separation. For example, from the variation of D or η with temperature in the vicinity of 15°C it can be readily calculated that either variation corresponds to a ν of about 8. Thus argon would be regarded as a "soft" molecule whose interaction field at room temperature could be approximated by a potential varying as r^{-8} . But the effective value of ν could just as well be calculated from the value found for ϵ (=1.33), which gives ν equal to 16! $\nu=8$ corresponds to $\epsilon=1.45$, which differs from the experimental value by much more than the margin of error. We conclude that the common method of retaining this simple molecular model and defining an "effective ν " which varies with the temperature is not a valid procedure and can sometimes lead to incorrect results.

The Sutherland Model

Sutherland used as his model of two colliding gas molecules a system consisting of two elastic spheres with a weak attractive field varying as $r^{-\nu'}$ between them. With this assumption it is found that¹⁰ $D \propto T^{5/2}/(T+S_D)$, where S_D is a constant depending on the fields, and $\epsilon=1.2(1+[S_\eta-S_D]/T)$, S_η being another constant obtained from the variation of viscosity with temperature. Taking¹¹ $S_\eta=142$, Table IV compares the experimental and calculated values of D and ϵ with $S_D=115$.

The good fit between experimental and calculated values (except at -183°C) does not mean that the simple Sutherland model can be taken as a literal picture of an argon molecule. From the derivation of the Sutherland equations it can be seen that S_D and S_η are each equal to the potential energy of two argon molecules in contact multiplied respectively by functions $i_1(\nu')$, $i_2(\nu')$ tabulated by Chapman and Cowling.¹⁰ From the values of S_D and S_η , as well as their difference as determined by the values of ϵ , it can be determined that the attractive potential field falls off more rapidly than r^{-10} , perhaps as r^{-16} , which is much more rapid than can be understood on physical grounds. Furthermore, the calculated attractive potential energy of two molecules in contact is greater than the mean thermal energy of a molecule at 500°C, which would lead one to expect aggregation of molecules at temperatures where none is observed. The Sutherland equation is perhaps best regarded as a simple interpolation formula.

FIG. 3. Log-log plot of D against temperature.

¹⁰ See reference 1, p. 184.

¹¹ M. Trautz and H. E. Binkley, *Ann. d. Physik* **5**, 561 (1930); A. O. Rankine, *Proc. Roy. Soc.* **84**, 181 (1910).

TABLE IV. Calculation of D and ϵ on Sutherland model.

Temperature °C	D , cm ² /sec.		ϵ	
	calc.	expt.	calc.	expt.
53.5	0.214	0.212	1.30	1.30
22	0.179	0.180	1.31	1.32
0	0.156	0.158	1.32	1.34
-78.5	0.0837	0.0833	1.37	1.34
-183	0.018	0.028	1.6	2.1

Interaction Potential $V = Ae^{-ar} - Cr^{-6} - Dr^{-8} - Er^{-10}$

Amdur¹² has recently calculated the transport coefficients for various gases, including argon, using the more realistic potential given above. The parameters a , A , C , D , E , were derived from theoretical calculations of the polarizability of atoms and from the equation of state of argon. This potential is much too complicated to yield analytic expressions for the transport coefficients, and Amdur uses approximation methods to obtain his numerical results. The calculated values of D are compared with experiment in Table V. The computed values are about twenty percent low, which is a somewhat larger difference between theory and experiment than is found for the coefficients of viscosity and thermal conductivity. The reason for these discrepancies could lie either in the values chosen for the parameters describing the interaction potential or in the approximations made in solving for the transport coefficients.

Interaction Potential $V = 4E[-(r_0/r)^6 + (r_0/r)^{12}]$

Hirschfelder, Bird, and Spotz¹³ have selected a potential of this form, the term in r^{-6} being the Van der Waals attraction, that in r^{-12} being a good empirical fit to calculated repulsions due to overlapping electron clouds. This potential was used as the basis for a complete numerical integration to obtain values of the integrals $\Omega^{(i)}(q)$, said to be accurate to one part in 300. For argon, the most accurate values for E and r_0 , $E = 124.0k$, and $r_0 = 3.418A$, can be obtained from the variation of viscosity with temperature, and agree excellently with values deduced from the equation of state of argon. The calculated D 's in Table VI, obtained by using these values of E and r_0 , agree very well with experiment. Thus this form of potential is consistent with this diffusion data. It is significant that no arbitrary constants have been adjusted to fit this particular set of figures.

Since Hirschfelder *et al.* have calculated a number of the $\Omega^{(i)}(q)$ it is also possible to compute the second approximation to D , equal to the first approximation given by Eq. (1) multiplied by $1/(1-\Delta)$. For the case under consideration, where the two molecular species

TABLE V. Amdur's calculated values for D .

Temperature °C	D , cm ² /sec.	
	calc.	expt.
17	0.133	0.175
-3	0.118	0.155
-83	0.0650	0.0794

TABLE VI. Hirschfelder's calculated values of D .

Temperature °C	D , cm ² /sec.		Δ
	calc.	expt.	
53.5	0.213	0.212	0.0029
22.0	0.178	0.180	0.0024
0.0	0.154	0.158	0.0018
-78.5	0.0820	0.0833	0.0007
-183.0	0.0178	0.028	0.0001

have almost the same molecular weight, the expression for Δ given by Chapman and Cowling¹ can be simplified to

$$\Delta = \frac{5(C-1)^2}{11-4B+8A}, \quad (16)$$

where A , B , and C are functions of the $\Omega^{(i)}(q)$ as given by Chapman and Cowling. The column labelled Δ in Table VI gives the calculated value of this correction. A point of interest is the smallness of Δ , the correction added in the second approximation; the implication is that the first approximation is a very good one.

The calculated values of D at -183°C deviate in every case much more from experiment than do calculated values of the viscosity¹⁴ at the same temperature. Thus it is not too easy to ascribe the discrepancy in D at low temperatures to quantum effects, etc. Indeed, it throws definite suspicion on this measurement at -183°C ; nevertheless, there is no indication in the data taken at this point that there was anything wrong, and no reason for taking this run any less seriously than the others except for the somewhat higher percentage error due to the smallness of β compared with λ .

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¹² I. Amdur, J. Chem. Phys. **16**, 190 (1948).

¹³ Hirschfelder, Bird, and Spotz, J. Chem. Phys. **16**, 968 (1948).

¹⁴ See, for example, reference 1, p. 228; H. L. Johnston and E. R. Grilly, J. Phys. Chem. **46**, 948 (1942); W. Licht, Jr. and D. G. Stechert, J. Phys. Chem. **48**, 23 (1944).