The Temperature Dependence of the Self-Diffusion Coefficients of Argon, Neon, Nitrogen, Oxygen, Carbon Dioxide, and Methane*

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The self-diffusion coefficients of A, Ne, N_2, O_2, CO_2, and CH_4 have been measured as functions of the temperature: A, Ne, N_2, and O_2 in the range -196°C to 80°C, CO_2 in the range -78.5°C to 80°C, and CH_4 in the range -183°C to 80°C. The experimental figures have been compared with values calculated on the assumption that the molecular interaction potential is of the form

$$V(r)=4\epsilon[-(r_0/r)^6+(r_0/r)^{12}].$$

With the exception of the lowest point for methane, all figures are in essential agreement with theory.

I. INTRODUCTION

A QUANTITY of considerable interest in the kinetic theory of gases is the coefficient of self-diffusion, which may be defined as a measure of the rate at which a group of gas molecules diffuses into another group composed of identical molecules. It is somewhat difficult to ascribe physical meaning to the process of self-diffusion under this definition, since, as long as the molecules are identical, there is no way of following the process, and hence no process really exists. However, if it be hypothesized that some of the molecules are tagged in such a way that the tagging does not affect the diffusion, then it would be possible actually to observe self-diffusion. Although such a method of tagging cannot exist, there are several devices by which good approximations to the self-diffusion coefficient of a gas may be obtained.

The most important of these devices involves the use of a tracer isotope, in which the mass of the molecule differs only slightly from the mass of the normal molecule. If a stable isotope be used as the tracer, then the diffusion process may be observed with a mass spectrometer; on the other hand, if it be a radioactive isotope, ordinary methods for the detection of radioactivity provide a means for watching the diffusion.

The interdiffusion of gases in general depends, among other factors, on the force fields of the diffusing molecules. Expressions which relate the coefficients of diffusion to these interaction potentials have been derived by Chapman and Cowling.[1] These relations and a knowledge of the values of the coefficients thus make it possible to infer something concerning the nature of the forces between the diffusing molecules.

The case of self-diffusion is by far the more attractive to consider, since only interactions between like molecules are involved. Also, the intermolecular potential for identical molecules is of the greater interest, since it is likewise involved in expressions for the other transport coefficients, as well as in the equation of state.

In the theory of Chapman and Cowling, the transport coefficients are expressed in terms of a set of collision integrals, $\Omega^l(n)$, the values of which depend upon the form chosen for the intermolecular potential function. It is practicable to evaluate these integrals analytically only for a few simple molecular models, such as const./r^n, n a positive integer, which have little or no real physical basis.

Recently Hirschfelder, Bird, and Spotz[2] carried out the numerical evaluation of a number of these integrals for the more realistic form of the potential function,

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

where r is the separation between the molecules, r_0 is the separation for which the energy of interaction is zero, and ϵ is the energy difference between the separated molecules and the molecules in the configuration for which they have the maximum energy of attraction.

The results are tabulated as the values of the functions $W^l(n;x)$, which are related to the $\Omega^l(n)$ of Chapman and Cowling by

$$\Omega^l(n)=r_0^2[2\pi kT/\mu]^{\frac{1}{2}}W^l(n;x), \quad (2)$$

where $x=\epsilon/kT$, k is the Boltzmann's constant, and μ is the reduced mass of the colliding molecules.

In the present paper are reported the results of the experimental determination of the self-diffusion coefficients of argon, neon, nitrogen, oxygen, carbon dioxide, and methane as functions of the temperature, stable isotopes being used as the tracers. These results are compared with the values calculated from the following expression for the first approximation to the self-diffusion coefficient, D_{11}, derived by Hirschfelder *et al.* in a later paper,[3] using the potential model of Eq. (1) and the basic theory of Chapman and Cowling:

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

where p is the pressure in atmospheres, and M is the

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[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1939).
[2] Hirschfelder, Bird, and Spotz, J. Chem. Phys. **10**, 968 (1948).
[3] Hirschfelder, Bird, and Spotz, Chem. Rev. **44**, 205 (1949).

molecular weight. The second approximation to D_{11} is given by

$$(D_{11})_2=(D_{11})_1/(1-\Delta). \quad (4)$$

For all of the temperatures used in this work Δ is a very small quantity, and the difference between the first and second approximations is less than the experimental error.

The values of the quantities ϵ and r_0 involved in the expression for D_{11} can be determined from experimental measurements of the second virial coefficient. As a result of the numerical evaluation of the integrals in the expression given by Chapman and Cowling for the coefficient of viscosity, using the 6–12 potential model of Eq. (1), the values of ϵ and r_0 for pure gases can also be obtained from viscosity data. This has been done for a number of gases, including those reported here, by Hirschfelder *et al.*[3] The figures so obtained are found to be in close agreement with those computed from equation of state data.

II. APPARATUS

The apparatus in which the diffusions were carried out is illustrated schematically in Fig. 1. The diffusion system is patterned after a device originated by Ney and Armistead,[4] and consists of two identical cylindrical brass bulbs, A and B, having volumes of 357 cm^3, which are mounted on a common axis and connected through a cylindrical brass tube, C. The connecting tube has a length of 8.006 cm and an inside diameter of 0.3250 cm, uniform to 0.0003 cm. The diffusions were performed by placing a sample of the normal gas in one bulb and a sample enriched in a tracer isotope in the other. Mixing then occurred by diffusion through the connecting tube, so that the isotopic consistency of the gas in either bulb varied with time.

These bulbs differ from earlier diffusion set-ups in that there is no isolating stopcock in the connecting tube, nor are there any valves in the filling lines immediately at the bulbs. This construction was chosen so that no difficulty would be encountered in the operation of necessary valves when the apparatus was immersed in a bath of extreme temperature.

The absence of a stopcock in the connecting tube necessitated the use of a somewhat more complicated filling system than would otherwise have been required. The bulbs are connected through copper filling capillaries to two Hoke toggle valves, F and G, mounted just outside of the temperature bath, E. The volume of the capillaries is less than 0.3 percent of the total volume of the bulbs, so that only a very small correction is needed to account for the effect of diffusion into and out of the capillary ends. The Hoke valves are set up side by side and connected together with a link so that they may be operated either individually or simultaneously.

[4] E. P. Ney and F. Armistead, Phys. Rev. **71**, 14 (1947).

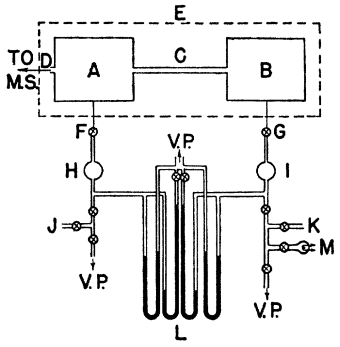

FIG. 1. Schematic diagram of the diffusion apparatus.

To fill the bulbs, samples are attached by means of grinds at J and K, and the entire system evacuated to a pressure less than 10^{-3} mm Hg, the pressure being indicated by a thermistor gauge attached at M. Evacuation is accomplished by a fore pump connected to the points $V.P.$ Valves F and G are closed, and the samples are admitted to the filling reservoirs H and I, each of which is a glass bulb having a volume of 225 cm^3. The sample pressures are matched by means of the comparison manometers, L, consisting of two mercury and two oil manometers. The oil manometers are mounted side by side, as shown, and are filled with Octoil, which, at room temperature, gives a magnification over mercury of 14.90 ± 0.03. When the samples are at the proper pressure, the toggle valves are snapped open simultaneously, and the samples in reservoirs H and I flow into bulbs A and B respectively. If the sample pressures have been chosen sufficiently near each other, then the observed equilibrium concentration of the tracer isotope is just that which is computed from the initial concentrations in the two samples, with an isolating stopcock assumed to be located at the midpoint of the connecting tube. This indicates that, for equal reservoir pressures, very little initial mixing occurs.

As soon as the equilibrium pressure is attained, within a few seconds after filling, the temperature and pressure are recorded, the toggle valves closed, and the diffusion allowed to proceed. A continuous analysis of the gas in bulb A is performed with a 60° Nier-type mass spectrometer, the bulb being connected to the spectrometer vacuum system through a fixed capillary leak, D. Since the initial concentrations of the tracer isotope in the two bulbs are not required for a calculation of the diffusion coefficient, any convenient time shortly after the start of the diffusion run may be taken as the time zero, and subsequent points measured from this reference. The final concentration of the tracer, after complete mixing, must be known, however. With an isolating stopcock in the connecting tube it is possible to compute this equilibrium concentration from a knowledge of the initial concentrations in the two bulbs. In the present apparatus, on the other hand, each run must be allowed to proceed to equilibrium, and the final concentration then measured. In theory, infinite time is required for complete mixing. Actually,

TABLE I. D_{11} for A^{40}.

Temperature °C	D_{11}, cm²/sec. Theory	Experiment Present work	Experiment Hutchinson
80.0	0.246	0.249 ±0.003	···
53.5	0.213	—	0.212 ±0.002
22.0	0.178	0.178 ±0.003	0.180 ±0.001
0	0.154	0.156 ±0.002	0.158 ±0.002
−78.5	0.0822	0.0830±0.0011	0.0833±0.0009
−183.0	0.0178	0.0180±0.0003	0.0277±0.0010
−195.5	0.0134	0.0134±0.0002	···

however, the error becomes unmeasurably small if the equilibrium concentration determination is made after about seven relaxation times have elapsed. With the temperatures and pressures used, the relaxation time of the system varied from one to three hours for the gases studied in this program.

All of the tracer isotopes used were concentrated by separation of the normal gas in thermal diffusion columns. The purity of the samples was quite good, being in no case less than 99 percent.

Each value tabulated for D_{11} for each gas is the unweighted mean of four runs at that temperature. In two runs of each set, the concentration of the tracer isotope in bulb A increased with time; in the other two runs, it decreased. With the exception of the methane runs at −183.0°C, the four results were always in excellent agreement.

The precision measures assigned to the tabulated results are the most probable errors computed from the scatter of the data over the four runs and from the various known experimental errors.

In calculation of the diffusion coefficients at the various temperatures, account was taken of the effect of the thermal expansion of the apparatus. The correction of the geometrical constant was in no case as large as one percent.

The figure actually measured in this study is the coefficient of diffusion of the tracer isotope into the normal isotope, D_{12}. Although in most cases this is a good approximation to the true self-diffusion coefficient, D_{11}, it would nonetheless seem worth while to calculate D_{11} from D_{12}. Hutchinson has shown[5] that the self-diffusion coefficient of a gas can be obtained from the coefficient of diffusion of one isotope into another

TABLE II. D_{11} for Ne^{20}.

Temperature °C	D_{11}, cm²/sec. Theory	Experiment
80.0	0.668	0.703 ±0.005
25.0	0.504	0.516 ±0.005
0	0.435	0.452 ±0.003
−78.5	0.246	0.255 ±0.004
−195.5	0.0492	0.0492±0.0004

[5] F. Hutchinson, J. Chem. Phys. **17**, 1081 (1949).

TABLE III. D_{11} for $N^{14}N^{14}$.

Temperature °C	D_{11}, cm²/sec. Theory	Experiment Present work	Experiment Reference 6
80.0	0.273	0.287 ±0.009	···
25.0	0.203	0.212 ±0.005	0.219±0.009
0	0.174	0.185 ±0.006	···
−78.5	0.0946	0.104 ±0.002	···
−195.5	0.0161	0.0168±0.0003	···

by the following relation:

$$D_{11}=[2M_2/(M_1+M_2)]^{\frac{1}{2}}D_{12}, \quad (5)$$

where M_1 and M_2 are the masses of the two isotopes. The figures given for D_{11} in the accompanying tables were obtained from the observed D_{12} by means of this equation.

III. RESULTS

A. Argon

The results for argon, referred to 760 mm Hg pressure, are given in Table I. These results were obtained by observing the diffusion of argon having a 36/40 ratio of 0.051 into tank argon, which is more than 99 percent A^{40}.

The figures recorded in Table I were obtained by multiplying the observed coefficient of diffusion by the mass correction factor of 0.9736.

For purposes of comparison, the results of Hutchinson,[5] obtained from the diffusion of radioactive A^{41} into A^{40}, are reproduced here. It should be mentioned that his result at −183°C is the figure for one run only, after which run the apparatus was damaged, thus precluding further work at this temperature.

B. Neon

The results for neon, referred to 760 mm Hg, are given in Table II. These were obtained by allowing neon having a 22/20 ratio of 0.31 to diffuse into pure Ne^{20}. The coefficients are given as D_{11} for Ne^{20}, the observed figures being multiplied by the mass correction factor 1.0235.

C. Nitrogen

The results for nitrogen, at 760 mm Hg, are given in Table III. The tracer molecule used was $N^{14}N^{15}$, the sample enrichment being such that the 29/28 ratio was

TABLE IV. D_{11} for $O^{16}O^{16}$.

Temperature °C	D_{11}, cm²/sec. Theory	Experiment
80.0	0.279	0.301 ±0.004
25.0	0.206	0.232 ±0.006
0	0.176	0.187 ±0.003
−78.5	0.0944	0.104 ±0.002
−195.5	0.0154	0.0153±0.0002

TABLE V. D_{11} for $C^{12}O^{16}O^{16}$.

Temperature °C	D_{11}, cm²/sec. Theory	Experiment
80.0	0.149	0.153 ±0.003
25.0	0.109	0.113 ±0.002
0	0.0918	0.0974±0.0007
−78.5	0.0475	0.0500±0.0003

0.031. The mass correction applied to the observed D_{12} is 1.0087.

The room temperature value of D_{12} for $N^{14}N^{15}$ into $N^{14}N^{14}$ was reported earlier[6] from work with another apparatus. The data have been recalculated, and the mass correction factor applied, to give the result which is compared to the room temperature figure for D_{11} found in the present work.

D. Oxygen

The results for oxygen, referred to 760 mm Hg, are listed in Table IV. The tracer molecule was $O^{16}O^{18}$, the isotopic enrichment by thermal diffusion giving a 34/32 ratio of 0.56. The mass correction factor applied to the observed values of the diffusion coefficient to obtain those given in the table is 1.0151.

E. Carbon Dioxide

The diffusion coefficients for carbon dioxide, referred to 760 mm Hg, are given in Table V. The tracer molecules were those of mass 45, and were principally $C^{13}O^{16}O^{16}$, although a small amount of $C^{12}O^{17}O^{16}$ was present. Since the theory takes no account of internal degrees of freedom, but treats the molecules as point masses surrounded by spherically symmetrical potentials, no differentiation between the two mass 45 molecules can be made.

The tracer sample was enriched to a 45/44 ratio of 0.038. The heavy CO_2 was not prepared directly by thermal diffusion; rather, it was obtained from $BaCO_3$ enriched in C^{13}, which had in turn been prepared from methane enriched in $C^{13}H_4$ by thermal diffusion.

The mass correction factor applied to the observed figures to obtain D_{11} is 1.0056.

F. Methane

The results for methane, referred to 760 mm Hg, are given in Table VI. The tracer used was $C^{13}H_4$, the sample having a 17/16 ratio of 0.042. The mass correction factor of 1.0151 was applied to the observed figures to obtain those listed for D_{11}.

[6] E. B. Winn, Phys. Rev. **74**, 698 (1948).

TABLE VI. D_{11} for $C^{12}H_4$

Temperature °C	D_{11}, cm²/sec. Theory	Experiment Present work	Reference 7
80.0	0.293	0.318 ±0.006	···
25.0	0.215	0.240 ±0.004	0.234±0.006
0	0.183	0.206 ±0.005	···
−78.5	0.0968	0.0992±0.0006	···
−183.0	0.0187	0.0266±0.0023	···

The room temperature figure for D_{12} for $C^{13}H_4$ and $C^{12}H_4$ has already been reported.[7] The data have been recalculated, and the mass correction factor applied, to give the value set forth here. It should be mentioned that the results for nitrogen and methane reported in references 6 and 7 were obtained with the same apparatus at the University of Virginia.

From Table VI it can be seen that the agreement between the observed and calculated values of D_{11} at the lowest temperature is not as close for methane as for the other five gases studied. Some difficulty was encountered in making the runs at −183.0°C, since, to obtain a reasonable relaxation time, pressures of 4 to 5 mm Hg were required. This resulted in the $C^{13}H_4^+$ peak being only a small part of the mass 17 peak, with the result that accurate figures for the methane 17/16 ratio could not be obtained. Despite the unduly large precision measure which must be assigned to the result, however, the D_{11} from each one of the four runs made at this temperature differed significantly from the calculated value.

On the whole, the experimental values agree fairly well with those computed from the theory. With the exception of methane, the agreement is especially good at the lowest temperature.

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[7] E. B. Winn and E. P. Ney, Phys. Rev. **72**, 77 (1947).