

yield of protons would be expected to differ from the yield of neutrons by a factor which increases with energy in the low energy region. This factor would shift a maximum in the yield curve toward higher energies. This shift does not occur for the second resonance at 1.02 Mev; but this second resonance is narrower and the proton is more energetic, so it is less affected by the potential barrier. This argument seems to be contradicted

by the fact that the first resonance is stronger than the second for proton emission; however, other differences in the states of the intermediate nucleus may affect the strength of a resonance. A third resonance at 1.35 Mev in the beta-ray curve corresponds to a state of Be^9 for which neutron emission is forbidden or at least is much weaker than for the other resonances at 0.65 and 1.02 Mev.

The Self-Diffusion Coefficient of Uranium Hexafluoride*

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A method is reported for measuring the self-diffusion coefficient of a vapor by observing with a mass spectrometer the rate at which material enriched in one isotope diffuses into normal material in an apparatus of known geometry. A value of ρD (where ρ is the density and D the diffusion constant) was obtained for uranium hexafluoride at 30°C. Knowledge of the viscosity together with the constants reported here allow calculation of the molecular force law.

IN the kinetic theory of transport phenomena ρD is a prominent factor whose value must be known. Heretofore its value has been determined from the coefficient of viscosity, η , on the basis of the equation $\rho D = \epsilon \eta$ where ϵ is at best an uncertain quantity. The following is a report of the measurement of ρD in which D is understood to be the diffusion coefficient for one gas diffusing into another where the only difference between the gases is their isotopic ratios.

This measurement represents an excellent approximation to the self-diffusion coefficient, which strictly speaking cannot be measured.¹ If one may speak of the self-diffusion of a gas whose molecules are composed of more than one isotope, one should probably define it as the

diffusion of one gas in which the isotopes are in their normal ratio into another with normal ratio. The ideal experiment to measure this would consist of tagging one group of molecules differently from the other group in such a way that the tagging would not affect the phenomenon of diffusion. If uranium hexafluoride slightly enriched in U^{238} and uranium hexafluoride slightly enriched in U^{235} diffuse into each other exactly as normal uranium hexafluoride diffuses into normal then isotopic concentration is just such an ideal tag. As can easily be seen the measurement of the changing concentration of one isotope as the diffusion takes place gives directly the changing concentration of one group in the mixture of both groups of molecules.

I. DESCRIPTION OF APPARATUS AND PROCEDURE

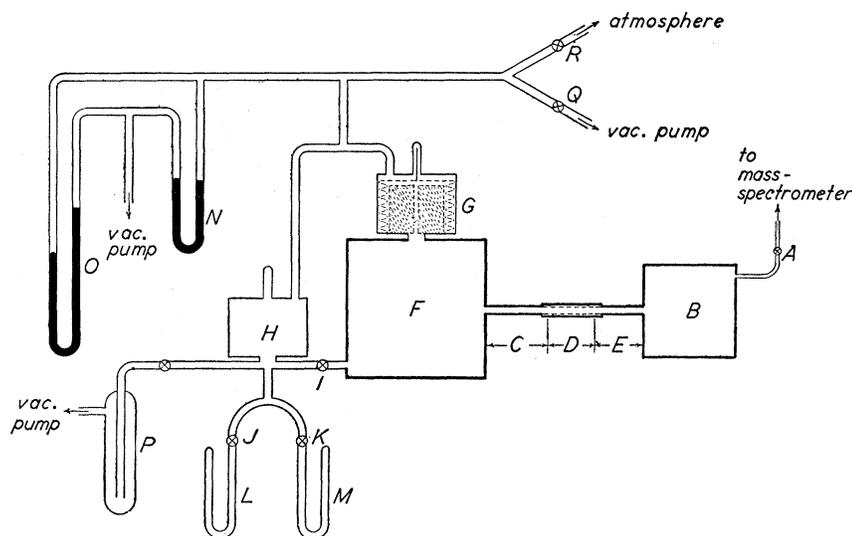
The apparatus is shown schematically in Fig. 1. The diffusion bulbs F and B were two coaxial copper cylinders of volumes 925 and 259 cubic centimeters, respectively. They were connected by the copper pipes C (length 6.80 cm; area

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¹ Rigorously the self-diffusion coefficient can be defined only for a gas composed of identical molecules, e.g., all U^{238}F_6 or all U^{235}F_6 .

FIG. 1. Schematic drawing of the diffusion apparatus (not to scale).



0.3215 cm²) and *E* (length 6.78 cm; area 0.3238 cm²) and by the Neoprene tubing, *D*, of area 0.2714 cm². In order to obtain different relaxation times, the length of the Neoprene was made 2.08 cm in six of the runs and 6.10 in two of them. Connected to bulb *F* is a null type sylphon pressure gauge *G*. The pressure above the sylphon could be made equal to the pressure in the bulbs by operating valves *R* and *Q* to obtain a null reading of the indicator needle which was observed in a microscope field. The neutralizing pressure was read on the mercury manometer *N* and the oil manometer *O*, the latter being capable of showing a pressure change of 0.06 mm Hg.

Material from bulb *B* was drawn through the adjustable capillary leak *A* into the ion source of the mass spectrometer. The leak *A* and the valve *I* add negligible volumes to the diffusion bulbs.

The system used for purifying the samples and filling the bulbs was connected to them through the valve *I*. This system consisted of a pressure gauge *H* and a manifold to which samples could be connected at *L* and *M*. The diffusion system was submerged in a 12-gallon water bath which was equipped with a vigorous stirrer and with a cover to minimize evaporation. A Beckman thermometer was placed beside each bulb.

Measurements of the dimensions of the apparatus were straightforward with the exception of the cross section of the Neoprene tube (*D*). This cross section was decreased by the pressure

on the outside and by the thin uranium hexafluoride reaction coating on the inside. Both of these effects were measured. The Neoprene used did not undergo any continuous reaction with uranium hexafluoride.

In order to establish that the samples were pure after admission to the diffusion bulbs, and that they remained pure throughout the course of an experiment, the impurity peaks were examined in the mass spectrometer. Samples with impurities less than one percent by volume were obtained for the experiment.

A certain amount of material was drawn by the mass spectrometer. This withdrawal causes some mass flow from *F* to *B*. An upper limit to this effect was determined by the following test. A sample of uranium hexafluoride was admitted to the diffusion bulbs. The pressure in the bulbs and the intensity of the ion peaks in the spectrometer were made the same as those used in the diffusion runs. After a careful reading on the gauge (*G*) had been obtained, the Neoprene (*D*) was pinched and left closed for 15 hours. If there had been a rate of withdrawal of such magnitude as to affect the measurement of the diffusion constant by as much as one percent there would have been an instantaneous and observable change at the gauge (*G*) upon unpinching *D*. No change was noted.

Before making any diffusion runs, the entire apparatus was pretreated. When it was necessary to replace some part of the apparatus, the pre-

treatment was repeated before more runs were made. A vacuum was maintained in the bulbs when runs were not being made.

In making the runs, samples were attached at *L* and *M* and purified. One sample had been enriched in $U^{238}F_6$, the other in $U^{235}F_6$. The first sample was then admitted to the diffusion system (through valve *I*) to a pressure of 1 cm of mercury. The Neoprene (*D*) was then pinched bulb *F* was pumped out and filled to 1 cm with material from the second sample. The character of the first sample was then the character of the material in bulb *B* at the start of the diffusion. Only moderate care was taken to remove traces of the first sample from *F* and from the walls of the purifying system before introducing the second sample. The presence of a slight amount of the first sample in *F* would not affect the calculation of ρD , but would merely reduce the over-all concentration change measured. Before starting the diffusion the Neoprene tube was unpinched for 10 seconds in order to assure equal pressures in *F* and *B*. (*A*) was opened and peaks were brought into the mass spectrometer; the Neoprene was unpinched, and the diffusion started. Continuous measurement of the 235/238 ratio was made in the mass spectrometer by the null method.² This consists essentially of balancing a fraction of the 238 current against the 235 current, and reading this fraction on a voltage divider. Readings were taken every ten minutes for a period of two to three hours, the relaxation time of the system. The resolution of the mass spectrometer remained good throughout the runs. The Beckmann thermometers showed temperature agreement to better than 0.01°C rise of one bulb over the other per hour. A variation of the order of ten times this could have been tolerated without affecting the accuracy of the measurement.

At the end of the relaxation time the leak *A* was closed and the peaks in the mass spectrometer dropped to their residual value. A standard sample was measured before and after the diffusion run. This permitted correction of the diffusion points for apparatus drift. This

² A. O. Nier, E. P. Ney, and M. G. Inghram, "Null method for the comparison of two ion currents in a mass spectrometer," Chicago Meeting of the American Physical Society, June 22, 1946.

correction was, on the average, about 4 percent of the total change measured in the diffusion run. Careful measurements of the pressure in the bulbs were made before and after the runs.

Several methods were used to obtain the value of the concentration after complete mixing (C^∞).

In five of the runs C^∞ was measured 20 hours after the start of the experiment by making an analysis of the material in the diffusion bulbs (i.e., comparing the 235/238 ratio with that of standard material); in two of the runs C^∞ was obtained by pumping the material out of the bulbs into a copper trap and making a routine analysis of this; and in one of the runs C^∞ was obtained by calculation from the known initial values of the concentration in bulbs *F* and *B*. Of course, in all cases C^∞ could be thus calculated, and this was done as an added check. The agreement was found to be within the accuracy of measurement.

In six of the runs the diaphragm in the sylphon gauge (*G*) was pressed against the inside plug of the gauge by admitting air above it. The diaphragm thus acted as a valve closing off the main volume of the sylphon gauge from bulb *F*. In these instances the calculations were made on the basis of the two-bulb problem. In two of the runs the diaphragm of the sylphon gauge was forced against the upper stop of the gauge by pumping a vacuum through the valve *Q*. The volume of the sylphon gauge then communicated with the bulb *F* throughout the experiment. The calculations for this case was made on the basis of the three-bulb problem (described later).

II. THEORY

The following is a list of symbols to be used in developing the theory:

C_2^t = concentration in grams/cc of $U^{235}F_6$ in bulb *B* at time "*t*"

C_1^t = concentration in grams/cc of $U^{235}F_6$ in bulb *F* at time "*t*"

D = coefficient of diffusion in $cm^2/sec.$

V_2 = volume of bulb *B* in cc

V_1 = volume of bulb *F* in cc

l = effective length of connecting tube

A = effective area of connecting tube

C^∞ = equilibrium value of the concentration after complete mixing

$$\begin{aligned}
 V_0 &= V_1 + V_2 \\
 \gamma &= \frac{DA}{l} \left[\frac{V_0}{V_1 V_2} \right] \\
 \beta &= \frac{DA}{l} \left[\frac{V_0 C^\infty}{V_1 V_2} \right] \\
 \alpha &= \frac{D}{\sum_j (l_j/A_j)} \left[\frac{(V_0 + Al)}{(V_1 + Al/2)(V_2 + Al/2)} \right].
 \end{aligned}$$

The simplest case of the diffusion problem will be worked out first and the necessary corrections will be calculated later.

The assumptions made in the simple theory are:

(A) The concentration gradient in the connecting tube is linear.

(B) The concentration gradient is all in the connecting tube.

(C) The volume of the connecting tube is negligible compared with the volume of the bulbs.

Under these conditions we can write the equation for Q , the rate of transfer of $U^{235}F_6$ by diffusion:

$$Q = -DA \text{ grad} C. \quad (1a)$$

Because of assumptions A and B above:

$$Q = -(DA/l)(C_2^t - C_1^t). \quad (1b)$$

The rate of transfer in terms of the time is given by:

$$Q = V_2 \delta C_2^t / \delta t. \quad (2)$$

Equating (1) and (2), we obtain the differential equation

$$\delta C_2^t / \delta t = -(DA/lV_2)(C_2^t - C_1^t). \quad (3)$$

In view of the relation (4) between C_1^t and C_2^t , we can write Eq. (5) using β and γ as previously defined.

$$V_2 C_2^t + V_1 C_1^t = V_0 C^\infty, \quad (4)$$

$$\delta C_2^t / \delta t = -\gamma C_2^t + \beta. \quad (5)$$

We also have the boundary condition:

$$C_2^t = C_2^0 \text{ at } t=0. \quad (5a)$$

The solution of (5) subject to the boundary condition is:

$$C_2^t = C^\infty + (C_2^0 - C^\infty)e^{-\gamma t}. \quad (6)$$

Equation (6) is the solution of the diffusion equation for the simple case. In order to apply it to our experiment it is necessary to modify it

by making proper corrections for assumptions A , B , and C .

The assumption of a linear concentration gradient enters in the above as a substitution of $A(C_2 - C_1)/l$ for $A \cdot \text{grad} C$. Since the concentration gradient is linear in each element of length l_j with cross section A_j ; l/A must be taken to mean $\sum_j l_j/A_j$, which is the equivalent single l/A for the connecting tube.

Since in our experiment, the l/A for the bulbs was one-half of one percent of the l/A for the connecting tube the assumption that the gradient is all in the connecting tube is justified providing a small end correction is made. For the purpose of making this correction, we assume that the conditions at the ends of the connecting tube are the same as they would be if the bulbs had infinite volumes. The magnitude of the correction for the analogous electrical case has been shown by Rayleigh³ to be an effective increase in the length of the tube at each end by about 0.82 times the radius. This additional length is considered only in $\sum_j l_j/A_j$. It can also be shown by a method similar to that of Loschmidt⁴ that the concentration gradient in the connecting tube is set up in a time of the order of $\frac{1}{2}$ minute, with our geometry.

The connecting tube has a volume that can not be neglected. Because of the symmetry of the connecting tube about the point of pinching the Neoprene connector, the average concentration in the connecting tube (\bar{C}_L) is at any time the mean of the concentrations at the ends of the connecting tube.

$$\bar{C}_L = \frac{1}{2}(C_1^t + C_2^t). \quad (7)$$

Equation (4) must then be replaced by:

$$V_2 C_2^t + V_1 C_1^t + \bar{C}_L Al = (V_0 + Al) C^\infty. \quad (8a)$$

And using (7) and grouping terms, (8a) becomes:

$$(V_2 + Al/2) C_2^t + (V_1 + Al/2) C_1^t = (V_0 + Al) C^\infty. \quad (8b)$$

Equation (6) can be made consistent with this condition if one replaces in γ , V_1 by $(V_1 + Al/2)$, V_2 by $(V_2 + Al/2)$, and V_0 by $(V_0 + Al)$.

³ See Maxwell, *Electricity and Magnetism* (Oxford, 1892), p. 434; Lord Rayleigh, *Theory of Sound* (The MacMillan Company, 1878), Vol. II, pp. 291-295.

⁴ Loeb, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1934), pp. 268-272.

The quantity which embodies all of the above corrections, and which will replace γ , will be called α .

$$\alpha = \frac{D}{\sum_j (l_j/A_j)} \left[\frac{(V_0 + Al)}{(V_1 + Al/2)(V_2 + Al/2)} \right]. \quad (9)$$

The equation which describes the diffusion is then:

$$\frac{C^\infty - C_2^t}{C^\infty - C_2^0} = e^{-\alpha t}. \quad (10)$$

The constant $1/\alpha$ is the relaxation time of the system.

As was mentioned earlier, in some cases the diffusion was allowed to proceed with the sylvon gauge open to the adjacent bulb. The solution for the three-bulb problem will be indicated here. We use the same notation which we used previously with the addition of:

l_2/A_2 = effective l/A between sylvon gauge and bulb F .

V_3 = volume of sylvon gauge (G).

C_3^t = concentration of $U^{235}F_6$ in (G) at time " t ."

The equations which must be satisfied are:

$$V_2 \frac{\delta C_2^t}{\delta t} = \frac{DA}{l} (C_1^t - C_2^t), \quad (11a)$$

$$V_1 \frac{\delta C_1^t}{\delta t} = \frac{DA_2}{l_2} (C_3^t - C_1^t) + \frac{DA}{l} (C_2^t - C_1^t), \quad (11b)$$

$$C_3^t = \frac{(V_1 + V_2 + V_3)C^\infty - V_1 C_1^t - V_2 C_2^t}{V_3}. \quad (11c)$$

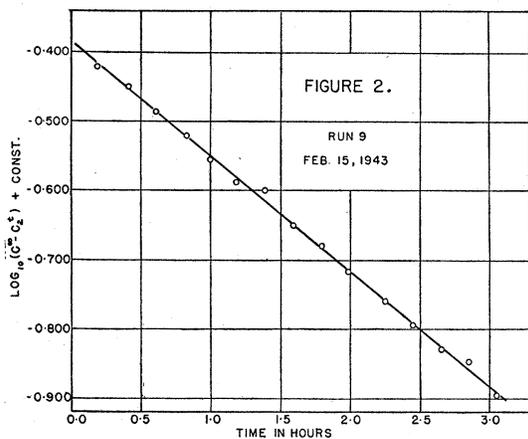


FIG. 2. Graph of $\log_{10}(C^\infty - C_2^t)$ as a function of the time. The slope of the least squares solution, together with the geometrical constants gives the diffusion coefficient.

With the boundary conditions:

$$C_2 = C_2^0; \quad (12a)$$

$$C_1 = C_3 = C_1^0 = C_3^0; \text{ when } t=0. \quad (12b)$$

The solution of Eqs. (11) and (12) has for one of our numerical cases the form:

$$\frac{C_2^t - C^\infty}{C_2^0 - C^\infty} = 0.966 \exp(-9.49Dt \times 10^{-5}) \\ + 0.034 \exp(-16.45Dt \times 10^{-5}).$$

If in Eqs. (11) $C_3^t = C_1^t$, the equations reduce to the two-bulb case, for which the corresponding numerical solution is:

$$\frac{C_2^t - C^\infty}{C_2^0 - C^\infty} = \exp(-9.72 \times 10^{-5} Dt).$$

The value of D as calculated assuming a two-bulb problem, when the diffusion actually follows the three-bulb equations can be shown to be too small by approximately 0.8 percent.

III. CALCULATIONS AND RESULTS

The time derivative of the logarithm of $|C^\infty - C_2^t|$ gives (from (10)):

$$\frac{\delta}{\delta t} \log_e |C^\infty - C_2^t| = -\alpha.$$

The slope of the plot of $\log_e |C_2^t - C^\infty|$ against time thus gives $-\alpha$. A graph of $\log_{10}(C^\infty - C_2^t)$ against time is shown in Fig. 2. The line indicated was obtained by the method of least squares. The C_2^t of the theory was obtained from the 235/238 ratio measured in the mass spectrograph.

The quantity D/α was calculated from the measured geometric constants (9). The diffusion constant was then obtained by multiplying this D/α by the experimental α obtained from the least-squares solution.

In order to know ρD (where ρ is the density), ρ was calculated assuming the ideal gas law to hold. This assumption has been shown to be justified at one centimeter pressure and room temperature.

The results obtained are presented in Table I. As is indicated, half of the runs were made with C_2^t decreasing, and half with C_2^t increasing. Calling Δ the concentration difference between

TABLE I. Observational results.

Run	Date made	Cm Hg pressure	Temp.	Two-bulb or three-bulb	C ₂ ^t increasing or decreasing	Concentration difference	Geometry	(ρD) _{30°} * micropoises
5	Nov. 10, 1942	1.08 cm	27.6°C	III bulb	decreasing	Δ	A	235
6	Nov. 16, 1942	0.94	23.9°	III	increasing	Δ	A	215
7	Nov. 25, 1942	1.08	27.4°	II	increasing	Δ	A	254
8	Feb. 12, 1943	1.09	26.4°	II	decreasing	4 Δ	A	238
9	Feb. 15, 1943	1.10	26.2°	II	increasing	4 Δ	A	234
10	Feb. 18, 1943	1.11	26.2°	II	decreasing	4 Δ	A	237
11	Feb. 25, 1943	1.07	27.2°	II	decreasing	4 Δ	B	244
12	March 1, 1943	1.08	26.9°	II	increasing	4 Δ	B	215

Average (ρD)_{30°} = 234 micropoises

* The value of (ρD)_{30°} was calculated from ρD at the temperature measured (for example from (ρD)_{27.6°}) by utilizing the known temperature ϵ dependence of viscosity. This was justified because of the smallness of the correction.

the bulbs at the start of runs 5, 6, and 7, the concentration difference between the bulbs at the start of runs 8, 9, 10, 11, and 12 was about 4 Δ . The average ρD was the same for both of these conditions. This indicates that there is no memory effect in the mass spectrograph which would keep it from following the changes in concentration at the proper rate. Geometry A indicates that the Neoprene (D) was 2.08 centimeters long, geometry B means that the Neoprene was 6.10 centimeters. The values of ρD corrected to 30°C are shown in the last column of Table I. The average value for (ρD)_{30°} was 234 \pm 3 micropoises. The cumulative error in the measurement of the geometrical constants is about 3 percent. The error in measuring the pressure is less than one percent. In view of this:

$$(\rho D)_{30^\circ} = 234 \pm 9 \text{ micropoises.}$$

Knowledge of ρD makes it possible to determine ϵ in the theoretical relation $\rho D = \epsilon \eta$, where η is the viscosity coefficient. This ϵ is of peculiar interest in that a value for the force field ex-

ponent of the molecule may be deduced from it. According to classical theory ϵ should range from 1.200 for hard sphere molecules to 1.54 for molecules interacting as the inverse fifth power of their separation.

The value of the ratio of ρD to η at 30°C is 1.31. This gives for the molecular force law $F = \text{const.}/r^{20}$.

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