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The Coefficient of Thermal Diffusion of Methane

ALFRED O. NIER
Department of Physics, University of Minnesota, Minneapolis, Minnesota

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According to the theories of Enskog and Chapman, if a mixture of two gases is confined in a vessel in which there exists a temperature gradient a concentration gradient of the gases should also exist. The effect is confirmed for the isotopic gases $C^{12}H_4$ and $C^{13}H_4$ and the coefficient of thermal separation for methane has been determined. As the value found for this coefficient is somewhat less than that arbitrarily assumed by Furry, Jones and Onsager in their theory on carbon isotope separation by thermal diffusion, the attainable separation factor for a given length column would be materially lower than that computed.

ENSKOG[1] in 1911 and Chapman[2] in 1917 showed from theoretical considerations that if a mixture of two gases was confined in a vessel in which there existed a temperature gradient one should also expect to find a gradient in the relative concentrations of the two constituents. The theory predicted that, in general, the heavier molecules would tend to move toward the cooler part of the vessel and vice versa. The concentration gradient increases until such a value is reached that the effect of thermal diffusion is just matched by the opposing effect of ordinary diffusion. The theory predicts that the coefficient of thermal diffusion vanishes for molecules interacting with a force varying with the inverse fifth power of the separation and is a maximum for rigid elastic spheres.

Experimental confirmation of the phenomenon was made by Chapman and Dootson[3] who obtained partial separations of mixtures of hydrogen and carbon dioxide in a vessel consisting of two bulbs maintained at different temperatures and joined by a connecting tube. Further experiments[4] demonstrated the existence of the effect in other gases as well.

The recent experiments of Clusius and Dickel[5] and other investigators[6] indicate that by using a tall column consisting of concentric cylinders at different temperatures and confining a gas in the annular space between the cylinders, the combination of the convection currents and thermal diffusion effect give rise to an appreciable isotopic separation in the gas. Furry, Jones and Onsager[7] and Waldmann[8] have discussed the theory of the operation of such a column and the former group have worked out an example in which they considered the possibility of separating the carbon isotopes by using methane gas. As no numerical value for the coefficient of thermal diffusion for methane was available, Furry, Jones and Onsager tentatively assumed a value and made their computations.

The purpose of the present investigation was to make a direct experimental determination of this coefficient. As was pointed out by Furry, Jones and Onsager, a determination of the thermal diffusion coefficient is not only of practical value in designing columns for the separation of isotopes, but also a knowledge of its value for isotopic gases should yield valuable information about the nature of the intermolecular forces in the gas in question, without the complications that arise if one studies mixtures of dissimilar gases.

APPARATUS AND PROCEDURE

The apparatus used in the present experiments consisted of two 100-cc bulbs joined by a connecting tube 7 cm long and 8.5 mm inside diameter. A three-way stopcock which had a hole 2 mm in diameter and 1.5 cm long was part of

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[1] D. Enskog, Physik. Zeits. **12**, 56, 533 (1911).

[2] S. Chapman, Phil. Trans. **A217**, 115 (1917).

[3] S. Chapman and F. W. Dootson, Phil. Mag. **33**, 248 (1917).

[4] For a complete list of these, up to 1937, see T. L. Ibbs, Physica **4**, 1133 (1937). For recent work on rare gas mixtures, Atkins, Bastick and Ibbs, Proc. Roy. Soc. **A172**, 142 (1939).

[5] K. Clusius and G. Dickel, Naturwiss. **26**, 546 (1938); **27**, 148 (1939).

[6] See review paper, H. S. Taylor, Nature **144**, 8 (1939).

[7] W. H. Furry, R. Clark Jones and L. Onsager, Phys. Rev. **55**, 1083 (1939).

[8] Waldmann, Naturwiss. **27**, 230 (1939).

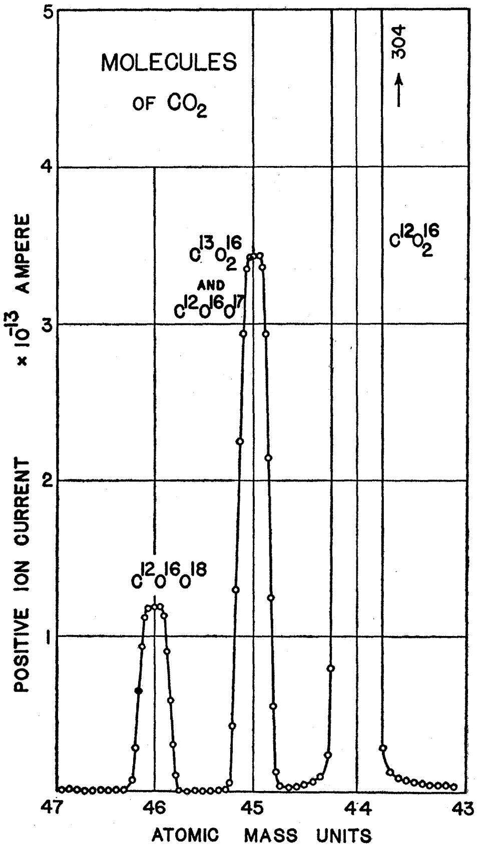

FIG. 1. Mass spectrum showing the most abundant molecular ions of CO_2 formed from carbon and oxygen isotopes. The experimental points are obtained by plotting positive ion current passing through the exit slit of the analyzer of the mass spectrometer as a function of the energy of ions while the magnetic field is held constant. As there is a definite relation between the energy and the mass of the ions collected, namely, energy x mass = a constant, the voltage scale can be readily changed to a mass scale as was done in the figure. The width of the peaks is, of course, caused by the finite width of slits used and imperfections in focusing.

the connecting tube. The system was evacuated and filled with methane to a pressure of approximately 60 cm. One bulb was placed in a water bath and the other in a furnace. After waiting a period of time at least three times the relaxation time of the system, the stopcock was turned and the hot bulb was evacuated. The stopcock was again turned, this time to allow the contents of the cold bulb to expand into the evacuated hot bulb. This process was repeated twelve times, so that in the end the change in concentration in the cold bulb was twelve times what it would have been for a single process. Of course the pressure decreased for succeeding runs, but as the effect measured should be practically independent of pressure, errors due to this score should be negligible compared to others in the experiment. The final gas remaining in the cold bulb was then analyzed with a mass spectrometer and the relative abundance of the carbon isotopes determined. The ratio obtained was compared with that for some of the original gas.

A calculation indicated that for methane at atmospheric pressure the relaxation time of the system was approximately one hour. As the coefficient of ordinary diffusion of methane varies inversely with the pressure, this time amounted to only a few minutes for the last few runs in the series of twelve. However, in all cases, at least one-half hour was allowed for a separation.

The mass spectrometer used for analyzing the gas samples consisted of a tube containing a 180° magnetic analyzer. Positive ions were formed by electron impact of the gas at low pressure. The analyzed ion currents were measured with an electrometer tube amplifier. The spectrometer tube was similar to one already described.[9] It differed mainly in that the slits S_1, S_2, and S_3 in Fig. 1 of reference 9 were 0.25, 0.23, and 0.90 mm wide, respectively. In order to insure freedom of difficulties with water vapor ($O^{16}H^+$ has the same mass as $C^{13}H_4^+$) the methane was burned to CO_2 in an excess of O_2. Heated $KClO_3$ was used as a source of O_2 and a platinum filament heated to approximately 1000°C caused the burning. The CO_2 was purified by condensation in a liquid-air trap while excess O_2 or unburned CH_4 were pumped off. Water vapor was later removed by placing dry ice on the trap which was originally immersed in liquid air. Fig. 1 shows a typical mass spectrum obtained for CO_2. The C^{13}/C^{12}

TABLE I. *Ratio of galvanometer deflections corresponding to ratio of mass* 45 *to mass* 44 *ion currents for three individual samples of* CH_4 *burned to* CO_2.

SAMPLE	12A	11A	10A	12A–11A	12A–10A
Aug. 20	0.9087 .9017	0.9043 .8974	0.9080 .8997	0.0044 .0043	0.0007 .0020
Aug. 21	.9041 .9019 .9036	.9017 .8977 .9059	.9010 .9029 .9039	.0024 .0042 −.0023	.0031 .0010 −.0003
Average	0.9040	0.9014	0.9031	0.0026	0.0009
Grand average		0.9028			

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[9] A. O. Nier, Phys. Rev. **52**, 933 (1937).

ratio was determined by comparing the relative heights of the peaks corresponding to masses 45 and 44.

RESULTS

As a test to see whether or not the burning of the methane had any effect upon the C^{13}/C^{12} ratio, a preliminary experiment was performed. Three samples of methane gas, called 12A, 11A, 10A, were removed from the supply bulb and burned separately. The C^{13}/C^{12} ratio was measured for each of these. The results obtained are tabulated in Table I. Each of the numbers there given is the average of ten determinations and represents the *ratio of galvanometer deflections* corresponding to the 45 and 44 peaks. As the mass 45 ion current is only about one percent that for mass 44, different resistances in the grid circuit of the electrometer tube were used for the two ions and also the Ayrton shunt in the galvanometer circuit had different settings. Thus, to obtain the absolute C^{13}/C^{12} abundance ratio one would have to multiply the ratios recorded by a suitable factor, the numerical value of which is not important to us here, as we are interested only in fractional changes of the C^{13}/C^{12} ratio. In addition one would have to make a correction for the fact that the ion $C^{12}O^{17}O^{16}$ made a contribution of about seven percent to the 45 peak. Also a small correction (about one percent) for the background under the 45 peak would have to be made (See Fig. 1). As one is only interested in changes in relative abundance in these experiments, these background corrections are not important, provided they are constant. Every effort was made to study each sample under as nearly as possible the same conditions and thus insure constancy of background and other discriminatory effects. The same source of oxygen was used to burn each of the samples so that the correction due to $C^{12}O^{17}O^{16}$ would be the same in each case.

TABLE II. *Comparison of galvanometer deflection ratios for sample* 12*A of Table I and three samples which had been through the thermal diffusion process. Temperature: hot bulb* 455°C, *cold bulb* 23°C.

SAMPLE	12A	6A	8A	9A	6A–AVE 12A	8A–AVE 12A	9A–AVE 12A
Aug. 22	0.8992	0.9217	0.9194	0.9172	0.0190	0.0167	0.0145
	.9047	.9253	.9289	.9175	.0226	.0262	.0148
	.9041						
Average	.9027						
Aug. 24	.9057	.9291	.9392	.9238	.0201	.0302	.0148
	.9116	.9309	.9300	.9241	.0219	.0210	.0151
	.9098						
Average	.9090						
Aug. 25	.9092	.9283	.9290	.9246	.0193	.0200	.0156
	.9088						
Average	.9090						
Average of differences					0.0206	0.0228	0.0150
Grand average of differences =0.0195							

The procedure in obtaining the readings was to make ten determinations of the ratio, then to introduce the next sample and make ten determinations for this, etc. Thus the samples were introduced in the order 12A, 11A, 10A, 12A, etc., until all the readings given were obtained. As may be seen, the ratio varied somewhat from day to day, but as it is differences that one is interested in, this slight variation is not important.

TABLE III. *Comparison of galvanometer deflection ratios for sample* 12*A of Table I and three samples which had been through the thermal diffusion process. Temperature: Hot bulb* 300°C, *cold bulb* 23°C.

SAMPLE	12A	15A	14A	16A	15A–AVE 12A	14A–AVE 12A	16A–AVE 12A
Aug. 27	0.9145	0.9292	0.9303	0.9233	0.0164	0.0175	0.0105
	.9111						
Average	.9128						
Aug. 27	.8996	.9117	.9127	.9168	.0175	.0185	.0126
	.9043	.9161	.9187	.9176	.0119	.0145	.0144
	.9075	.9198	.9197	.9240	.0156	.0155	.0198
	.9047	.9184	.9229	.9442*	.0142	.0187	—
	.9050						
Average	.9042						
Average of differences					0.0151	0.0169	0.0143
Grand average of differences =0.0154							

* Value believed unreliable and hence discarded in final computations.

As is evident in the consistent differences in columns 12A–11A, and 12A–10A, slight discriminations are introduced in burning and manipulating the separate samples. However, as we note by comparing the averages, the individual sample averages agree to better than 0.2 percent with the grand average. These data also indicate to what extent it is possible to reproduce readings with a mass spectrometer of the sort employed.

The procedure employed in analyzing the samples which had been through the thermal diffusion process was similar to that described above. In Table II are recorded the data obtained when the hot and cold bulb temperatures were 455°C and 23°C, respectively. Three separate runs were made. The samples are designated as 6A, 8A, and 9A. Sample 12A (ordinary methane from Table I) was used as a standard for comparison. For the data in Table III the hot and cold bulb temperatures were 300°C and 23°C, respectively. Three samples, 15A, 14A, and 16A were obtained under these conditions, and 12A was again used as a standard.

The results clearly indicate that as a result of the existence of the phenomenon of thermal diffusion a slight, but definite, change in relative abundance of the carbon isotopes takes place.

COMPUTATION OF COEFFICIENT OF THERMAL SEPARATION

For the equilibrium condition in the present experiment we may write

$$D \text{ grad } C_2 = -\frac{D_T}{T} \text{ grad } T, \tag{1}$$

where D is the coefficient of self-diffusion of methane, D_T the coefficient of thermal diffusion, T, the absolute temperature and C_2 the concentration of the molecule $C^{13}H_4$ in the gas. C_1 is the concentration of $C^{12}H_4$ and $C_1+C_2=1$. Upon integrating (1) we arrive at the result:

$$C_2{}^0 - C_2{}^1 = \frac{D_T}{D} \log \frac{T_1}{T_0}, \tag{2}$$

where $C_2{}^0$ and $C_2{}^1$ represent the concentrations C_2 in the bulbs (0) and (1) and T_0 and T_1 the respective temperatures of the two bulbs. According to Enskog's[7] treatment of the problem of thermal diffusion, D_T/D in the case of isotopes reduces to the simple, approximate form:

$$D_T/D = k_T = \alpha C_1 C_2, \tag{3}$$

where α is a constant; k_T is called the coefficient of thermal separation.

If m_0 and m_1 represent the respective masses of gas in the two bulbs, then

$$m_0 T_0 = m_1 T_1. \tag{4}$$

Also, to express the fact that there is conservation of $C^{13}H_4$ during the diffusion process we may write

$$m_0 C_2{}^0 + m_1 C_2{}^1 = (m_0 + m_1) C_2. \tag{5}$$

Then, by suitable algebraic manipulations between Eqs. (3), (4) and (5), we arrive at the result:

$$\alpha = \frac{(C_2{}^0 - C_2)}{C_2} \cdot \frac{1}{C_1} \cdot \frac{T_1/T_0 + 1}{\log T_1/T_0}. \tag{6}$$

For $T_1 = 455 + 273°\text{K}$, $T_0 = 23 + 273°\text{K}$ (data Table II)

$$\frac{C_2{}^0 - C_2}{C_2} = \frac{0.0195 + 0.0012}{0.9 \times 0.92 \times 12} = 0.0021. \tag{7}$$

The factor 12 arises from the fact that in the experiment the process was repeated twelve times in order to enlarge the effect. The factor of 0.92 arises because only ninety-two percent of the 45 peak is associated with C^{13}. The remaining eight percent is due to $C^{12}O^{17}O^{16}$ and background. As the sample 12A was 0.0012 higher than the average of the three samples in Table I, we have corrected for this by adding 0.0012 to the 0.0195. As $(C_2{}^0 - C_2)/C_2$ represents the fractional change in the relative abundance of the carbon isotopes, we may use the data in Table II directly inasmuch as the numbers there recorded are proportional to the relative heights of the 45 and 44 peaks in the mass spectrometer. For normal carbon $C_2 \cong 0.011$[10] and $C_1 \cong 1$. Thus, substituting in (6), we arrive at the result:

$$\alpha = 0.0080. \tag{8}$$

Likewise, from the data in Table III we obtain the value:

$$\alpha = 0.0074. \tag{9}$$

As a first approximation for elastic spheres Enskog's[7] results give

$$\alpha = (105/118)(M_2 - M_1)(M_2 + M_1)$$

where the M's are the relative masses of the two types of molecules. In the case of methane this gives

$$\alpha = 0.027. \tag{10}$$

The writer's results are thus in rough accord with the results of experiments with dissimilar molecules where, except for the rare gases, the experimental values of α are less than half the theoretical values.

The consistency of the data leads one to believe

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[10] A. O. Nier and E. A. Gulbransen, J. Am. Chem. Soc. **61**, 697 (1939).

that the values in (8) and (9) are each accurate within perhaps ten percent. Although one would expect α to increase slightly with temperature, it is doubtful whether the apparent variation observed here is significant.

For want of any experimental data on the value of α for methane, Furry, Jones and Onsager aribtrarily assumed a value of 0.0106 for this quantity. In view of the present results it appears that a separation factor of only about one-third as great as computed would be obtained for the particular carbon isotope separating column proposed by these authors.

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Fluctuations, Thermodynamic Equilibrium and Entropy

EDWIN C. KEMBLE
Harvard University, Cambridge, Massachusetts

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To eliminate exceptions to the second law due to fluctuation phenomena, etc., the following changes are necessary. First we must state the laws of thermodynamics in terms of Gibbsian ensembles rather than of individual systems. Second we must sharpen our conception of the experimental procedure required for producing states of thermodynamic equilibrium. It will not suffice to isolate the system and wait. We must have the positive stirring action of thermal contact with a thermostat. Using the new definition of thermal equilibrium we can place statistical mechanics on a more satisfactory footing by showing that the thermostat experimental procedure leads to the canonical ensemble and maximizes v. Neumann's microscopic entropy. (Details of this proof appear in succeeding paper.) Difficulties with his macroscopic definition of entropy are avoided by showing that his original microscopic definition is satisfactory when used in conjunction with a proper operational definition of thermodynamic equilibrium. In conclusion the second law of thermodynamics is derived from quantum statistics on the basis of the microscopic definition of entropy.

IT IS customary to regard fluctuation phenomena as minor violations of the second law of thermodynamics marking the limits of validity of the law.[1] It is also customary to regard thermodynamics as a branch of physics applicable only to matter in bulk. Thus the concept of temperature is usually considered to be meaningless when applied to a single molecule. These two limitations on the scope of thermodynamics are, of course, really one, since it is the very large fluctuations in the behavior of microscopic systems that have led to the exclusion of such systems from the domain of this branch of physics. Statistical mechanics affords a point of view from which the dogma of the second law for macroscopic systems and the existence of fluctuations are both intelligible. It is well recognized, however, that the phenomenological point of view of classical thermodynamics has its own advantages. Hence a restatement of the laws of thermodynamics—especially the second—in such form as to eliminate the apparent exceptions is *prima facie* desirable. Such a restatement has been proposed by G. N. Lewis.[2] In this paper I offer an alternative procedure for reaching the same goal which has the advantage that it closely preserves the form of the original statement of the second law.

Although this procedure is from an experimental point of view extremely plausible, the

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[1] See, for example, P. S. Epstein's *Textbook of Thermodynamics* (New York, 1937), pp. 385–6 and accompanying references.

[2] G. N. Lewis, J. Am. Chem. Soc. **53**^{2}, 2578 (1931). A general idea of Lewis's proposal will be gleaned from the following statement of his cardinal postulate. "When a given content is partitioned between two systems, the ratio of the specific probabilities of any two partitions of this content depends solely upon the nature of the two systems and upon the respective contents."