DECEMBER 1 AND 15, 1942 PHYSICAL REVIEW VOLUME 62

The Coefficients of Thermal Diffusion of Neon and Argon and Their Variation with Temperature

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(Received June 24, 1942)

In the case of a mixture of two isotopic molecules, D, the coefficient of ordinary diffusion, and D_T, the coefficient of thermal diffusion, are related by the equation: $D_T/D=\alpha C_1C_2$, where C_1 and C_2 are the relative concentrations of the molecules, and α is the thermal diffusion constant. Experimental values of α for neon and argon in seven different temperature intervals from 90–720°K are given. For both gases it appears that α varies linearly with the logarithm of the absolute temperature. These results are compared with values obtained from viscosity data and measurements made on binary mixtures of the noble gases. There is poor agreement with values calculated from the Sutherland and Lennard-Jones 9,5 models. In particular, no negative values of α are observed in the neighborhood of the critical temperature of argon as the 9,5 model predicts.

INTRODUCTION

SUPPOSE we have a system consisting of two bulbs joined by a connecting tube. If the system is filled with a mixture of two gases, and if one of the bulbs is maintained at a higher temperature than the other, then it will be found upon analysis that the relative concentration of the heavier component will, in general, be greater in the cold bulb than in the hot bulb. In the case of isotopic molecules, the change in concentration at equilibrium can be expressed by means of the following equation:

$$\text{grad } C_1=-(\alpha C_1C_2/T)\text{ grad } T, \qquad (1)$$

where α is the thermal diffusion constant; C_1 is the relative concentration of the heavy component; C_2 is the relative concentration of the light component; T is the absolute temperature.

An experimental determination of the thermal diffusion constant of neon for three different temperature ranges was made by Nier.[1] His results showed a definite variation of the coefficient with temperature. Jones[2] has made an extensive theoretical investigation of the problem and has proved that such an effect is to be expected for both the Sutherland and the Lennard-Jones 9,5 molecular models. One of the many interesting implications of the latter model is the possibility of negative values for the coefficient at temperatures in the neighborhood of the critical temperature.

The following considerations initiated the work to be presented here. In the first place, it was desirable to measure α over a large number of different temperature intervals so as to determine, if possible, the relationship between α and T. In the second place it was possible to test the predications of Jones' theory, as regards the negative coefficient, in the case of argon whose critical temperature is 151°K. Neon which has a very large value of α serves as a good comparison gas.

I. APPARATUS

The twin-bulb method described by Nier[3] was employed here in unmodified form. To establish the desired temperature gradients electric furnaces were used in the high temperature ranges and constant temperature baths at the low temperatures. The temperature of the connecting tubes and stopcocks was kept constant by means of a specially constructed circulating water bath.

The mass spectrometer used for analyzing the gas samples was similar to one described by Nier[4] for routine gas analysis. A 60° magnetic analyzer was used. Positive ions were formed by electron impact of the gas at low pressure and the ion currents were measured with an electrometer tube amplifier. The voltages for the various components of the apparatus were supplied by specially designed electronic regulating

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[1] A. O. Nier, Phys. Rev. **57**, 338 (1940).

[2] R. Clark Jones, Phys. Rev. **59**, 1019 (1941).

[3] A. O. Nier, Phys. Rev. **56**, 1009 (1939).

[4] A. O. Nier, Rev. Sci. Inst. **11**, 212 (1940).

devices. No storage batteries were used. This was a unique feature of the mass spectrometer.

II. RESULTS

A. Argon

Argon has three isotopes[5] of mass 36, 38, and 40. The percent abundances are 0.307, 0.061, and 99.632, respectively. The concentration of A^{38} is so small that it can be neglected. The initial pressure in the system was 40 cm Hg. The hot and cold bulbs were allowed to come to equilibrium twelve times, and after each equilibrium condition was attained, the hot bulb was evacuated.

To be assured of equilibrium conditions the relaxation time t_{re} must be known. An approximate calculation shows that this is given by the following formula:

$$t_{re}=\frac{1}{\left(\dfrac{AD}{lV}\right)\left(\dfrac{T_h+T_c}{T_c}\right)}, \tag{2}$$

where A is the average cross section of the connecting tube; D is the coefficient of ordinary diffusion; l is the length of the connecting tube; V is the volume of one of the bulbs; T_h is the temperature of the hot bulb; T_c is the temperature of the cold bulb. Since D is given approximately by

$$D=1.4\eta/\rho, \tag{3}$$

where η is the viscosity of the gas and ρ is its density, it is seen that t_{re} is directly proportional to ρ. Thus the relaxation time decreases with each run. In all cases a time five times the relaxation time was allowed for each run, with thirty minutes for the minimum time. By running two different samples of gas under identical conditions but with different relaxation times, an experimental check was obtained.

TABLE I. Values of the coefficient of thermal diffusion of argon in seven different temperature ranges.

Temp. range°K	T_r°K	$\Delta(A^{36}/A^{40})$[b]	α	R_T
90–195	129	0.94%	0.00315 ± 10%	0.07 ± 10%
90–296	154	2.38%	0.0709 ± 5%	0.15 ± 5%
195–296	238	1.94%[a]	0.0116 ± 5%	0.25 ± 5%
195–495	300	4.68%	0.0146 ± 5%	0.31 ± 5%
273–623	400	5.22%	0.0182 ± 5%	0.39 ± 5%
455–685	555	3.32%	0.0218 ± 5%	0.47 ± 5%
638–833	720	2.73%[a]	0.0250 ± 5%	0.53 ± 5%

[a] Ten repeated runs; in all other cases 12.

[b] This number is the average of a total of sixteen readings on two different samples. In some cases three different samples were used.

For accurate analysis of the gas in the mass spectrometer the background under the A^{36} peak must be zero, or one must be able to correct for it. Also a sufficient number of readings of the relative abundance must be taken to ensure a small probable error. Background may be due to poor resolution in the instrument causing a tailing out of the high intensity peak, as well as to residual impurities in the instrument itself or in the sample to be analyzed. A^{36} and A^{40}, whose relative mass difference is ten percent, were completely resolved by the mass spectrometer.

Equation (1) may be rewritten in the form:

$$\alpha=[(C_2{}^0-C_2)/nC_2C_1]\frac{(T_1/T_0)+1}{\ln(T_1/T_0)}, \tag{4}$$

where T_1 is the temperature of the hot bulb; T_0 is the temperature of the cold bulb; C_2 is the concentration of A^{36} in the cold bulb; $C_2{}^0$ is the concentration of A^{36} in the normal argon; C_1 is the concentration of A^{40} in normal argon; n is the number of runs. Since $(C_2{}^0-C_2)/C_2$ represents the fractional change in the relative abundance of the argon isotopes in the concentrated argon sample relative to normal argon this ratio can be obtained from measurements of the relative abundances A^{36}/A^{40} in both the concentrated and normal argon samples. The procedure employed was first to make ten determinations of the ratio for the concentrated sample, then to introduce the normal argon sample and make ten determinations for this; averaging these ratios, taking the difference and dividing by the average ratio of the normal argon one obtains the factor $(C_2{}^0-C_2)/C_2$. Ten separate values were obtained in this way and a grand average taken.

This average, however, cannot be substituted directly in (4) since a correction has to be made for the gas in the connecting tube which is not at the temperature T_0. When the volume of the connecting tube and the volumes of the bulbs were taken into account, the results given in Table I were obtained for argon. The values in column three represent the average of at least

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[5] A. O. Nier, Phys. Rev. **50**, 1041 (1936).

two determinations. In most cases three separate determinations were made.

It is obvious that α increases with the temperature. However, since α is measured over a temperature interval we are faced with the problem of assigning a proper temperature to the measured value. Harrison Brown[6] has shown that the proper temperature T_r is given by

$$T_r = (T_1 - T_0)/T_1 T_0 \cdot \ln (T_1/T_0). \tag{5}$$

This is an adequate approximation for small temperature differences.

When the first measurements were made it was observed that α varied linearly with $\ln T_r$. This is shown by the lower curve in Fig. 1. The empirical equation for this curve is

$$R_T = 0.25 \ln (T_r/86.9). \tag{6}$$

Here R_T is the ratio of the experimentally determined value of α to that calculated for hard spheres by means of Enskog's formula:

$$\alpha = 105/118 (M_2 - M_1)/(M_2 + M_1), \tag{7}$$

where the M's are the relative masses of the two molecular species.

The results presented in Table I can be compared with values obtained for binary mixtures of the noble gases and those deduced from viscosity data. Table V gives the results obtained by Atkins, Bastick, and Ibbs[7] from measurements made in binary mixtures of the noble gases. In all cases the temperature range was 273–373°K. This corresponds to $T_r = 314$°K. The value of R_T for A-Ne is 0.54; that for A-Kr is 0.19. Since the hardness of argon is between that of neon and krypton it would be expected that the value of A-A would be between 0.19 and 0.54. From Fig. 1 it is seen that the value for R_T is 0.325, which is in good agreement.

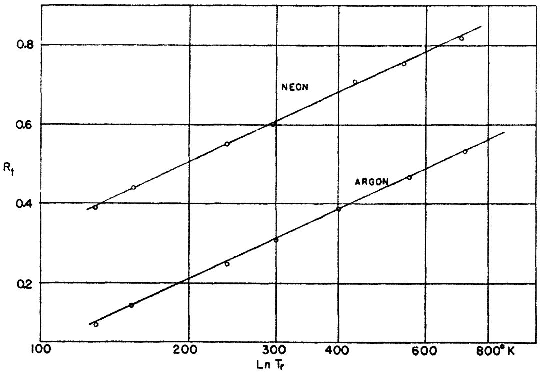

FIG. 1. The dependence of R_T for neon and argon on the temperature.

TABLE II. Comparison of various values of R_T for argon.

T_r	R_T (Meas.)	$R_T(n)$ (Viscosity)	$R_T(c)$ (Suth.) $C=142°$	R_T (L-J 9,5) $\epsilon/k=124°$
129	0.07			−0.44
154	0.15		0.04	−0.31
238	0.25	0.18	0.27	0.01
300	0.31	0.34	0.38	0.17
400	0.39	0.41	0.51	0.33
555	0.47	0.47	0.60	0.47
720	0.53	0.53	0.68	0.53

If the viscosity of a gas varies as T^n, it can be shown[2] that

$$R_T \cong 1.7(1-n). \tag{8}$$

Trautz[8] has given the experimentally determined values of n for argon as a function of temperature. From these and Eq. (8), values of $R_T(n)$ were calculated and compared in Table II with those measured by thermal diffusion. The agreement is much better than was expected.

We are now in a position to compare the results with the predication of the Sutherland and Lennard-Jones 9,5 models. According to Jones[2] R_T can be written in terms of the constant C which appears as the Sutherland constant for viscosity data and this results in the expression

$$R_T \cong \frac{1-0.98(C/T)}{1+0.92(C/T)}. \tag{9}$$

TABLE III. Values of the coefficient of thermal diffusion of neon in seven different temperature ranges.

Temp. range°K	T_r°K	$\Delta(\mathrm{Ne}^{22}/\mathrm{Ne}^{20})^c$	$\alpha \pm 5\%$	$R_T \pm 5\%$
90–195	129	$3.92\%^b$	0.0162	0.39
90–296	154	$6.08\%^b$	0.0187	0.44
195–296	238	$2.62\%^a$	0.0233	0.55
195–490	298	$5.47\%^b$	0.0254	0.60
302–645	432	$5.33\%^b$	0.0302	0.71
460–638	545	$2.10\%^b$	0.0318	0.75
621–819	712	$2.34\%^a$	0.0346	0.82

[a] Five repeated runs.
[b] Four repeated runs.
[c] The number given is the average of a total of ten determinations on two different samples.

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[6] Harrison Brown, Phys. Rev. **58**, 661 (1940).

[7] B. E. Atkins, R. E. Bastick, and T. L. Ibbs, Proc. Roy. Soc. **A172**, 142 (1939).

[8] M. Trautz and H. Binkele, Ann. d. Physik **5**, 561 (1930).

Viscosity data may be fitted rather well by a value of $C=142°\text{K}$. With this value of C the values of $R_T(c)$ are given in Table II. The agreement with experiment is poor.

In the case of the 9,5 model the agreement is no better than was obtained by the simpler Sutherland model.[9] However, in this case a more reasonable value of (ϵ/k), $(124°k)$, was used. In the case of the Sutherland model $(\epsilon/k)=823°\text{K}$ which is about five times the critical temperature.

B. Neon

Neon has three isotopes Ne^{20}, Ne^{21}, Ne^{22} with percent abundances[10] of 90.00, 0.27, and 9.93, respectively. What was said concerning argon applies here equally well except for the following considerations: (1) Since the value of R_T for neon is much greater than for argon the separation per run is larger. Only four or five runs are required in order to obtain an appreciable separation. (2) For this reason the initial pressure of the gas can be much lower (22 cm Hg). Also neon has a smaller density and greater viscosity than argon. Therefore, the relaxation time is much smaller. (3) No background difficulties in analysis were encountered with neon. The isotope ratio measured is $\sim 1/10$ as compared with 1/300 for argon. (4) Since the percent separation was larger than in the case of argon the average of only five differences was taken instead of ten. The results for neon are given in Table III and in Fig. 1. The empirical relation is

$$R_T=0.25 \ln (T_r/26.6). \tag{10}$$

TABLE IV. Comparison of various values of R_T for neon.

T_r	R_T (Meas.)	$R_T(n)$ (Viscosity)	$R_T(c)$ (Suth.) $C=60°$	$R_T(9,5)^a$ (L-J 9,5) $\epsilon/k=42.5°$
129	0.39		0.38	0.36
154	0.44		0.46	0.45
238	0.55		0.61	0.62
244*	0.56*	0.59		
298	0.60		0.76	0.66
333*	0.63*	0.62		
423*	0.69*	0.64		
432	0.71		0.81	0.71
498*	0.73*	0.64		
545	0.75			
712	0.82		0.85	0.73

* These values are obtained from the graph in Fig. 1.

TABLE V. Values of R_T for mixtures of the noble gases over the temperature range 0–100°C.

	Ne	A	Kr	Xe
He	0.80	0.65	0.63	0.59
Ne		0.54	0.51	0.43
A			0.19	0.17
Kr				0.08

These results check excellently with those obtained by Nier[1] for 129, 154, and 426°K. His values of R_T for these temperatures are 0.39, 0.44, and 0.71, respectively.

From the results obtained by Atkins, Bastick, and Ibbs we see that R_T for Ne-Ne should have a value between 0.80 and 0.54. This corresponds to a value of T_r equal to 314K. From Fig. 1 we obtain the value 0.62 which is consistent with their results.

In Table IV we have compared the experimental values of R_T for neon with those calculated from viscosity measurements, the Sutherland model with $C=60°$, and the 9,5 Lennard-Jones model.

From the empirical equation for argon it is seen that R_T is zero at 86.9°K. By the Lennard-Jones model this should occur at 220°K. Hence, negative values of R_T should be obtained for 129°K, 154°K. Experimentally the values of R_T at these temperatures are 0.07 and 0.151.

In Fig. 1 the effect of the greater hardness of neon is clearly demonstrated. The significance of the fact that both curves have the same slope is not immediately evident. However, since neon and argon are both spherically symmetrical and monatomic it might be expected that curves for all gases of this type will have the same slope, the difference in hardness being taken care of by the "characteristic temperature."

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the continued interest and helpfulness of Professor Alfred O. Nier under whose guidance this work was performed.

Thanks are also due to Messrs. E. F. Greinke, R. Thorness, and D. R. Miller for help and advice of a technical nature, and to my wife, Valorus Stier, for help in the preparation of the manuscript.

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[9] A complete description of the calculations is too lengthy to be presented here. The reader is advised to refer to Jones' paper, reference 2.

[10] Vaughan, Williams, and Tate, Phys. Rev. **46**, 327 (1934).