Isotopic Thermal Diffusion Factors for Helium and Neon at Low Temperatures*†

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Herrn Professor Dr. Klaus Clusius *zum 60. Geburtstag gewidmet*

With an all-metal "swing separator" having unique features, thermal diffusion factors α_T for He^3/He^4 and Ne^{20}/Ne^{22} have been measured with improved accuracy down to average gas temperatures $\bar{T}=136$ °K. For helium α_T is 0.0696 ± 0.0010 at 136 °K, dropping gradually to 0.0651 ± 0.0010 at 313 °K. These data, plus measurements by Van der Valk and de Vries at somewhat higher temperatures, agree best with values predicted by an exp-six intermolecular potential with $\varepsilon/k=9.16$ and $\alpha=12.7$. We are extending these helium measurements down to $T=4$ °K for the lower temperature, to detect if possible quantum corrections to the intermolecular potential. For neon α_T increases from 0.0166 ± 0.0010 at 136 °K to 0.0233 ± 0.0020 at 310 °K, considerably higher than our previously reported values. These T. D. factors for neon are in good agreement with values calculated from an exp-six potential with $\varepsilon/k=46.0\pm0.6$ and $\alpha=13$.

The variation of isotopic thermal diffusion factors α_T with temperature is most accurately measured with a relatively simple apparatus, the "Trennschaukel" or swing separator, first described by Clusius and Huber [1] and used for precision measurements of this factor for a binary gas mixture. Extension of this technique to isotopic mixtures was made by Moran and Watson [2] in this laboratory, with measurement of α_T for each of the noble gases over a range of temperature higher than $\bar{T}=236$ °K. These measurements were extended here to somewhat lower temperatures [3] for He, Ne, and Ar. From a number of indications, however, it became evident that many of our measured values of α_T were too low, by 10 per cent or so, because of questionable features of the equipment as well as the procedures. We believe that all of these errors have been eliminated in the research reported herein.

In order to attain the full cascading effect theoretically possible from the swing-separator concept, it is essential that an isothermal region be maintained at the top and bottom of each tube. Also, these regions must be large enough so that the only interchange of gas between tubes during the swinging process involves gas solely from these isothermal end regions. Since it is mandatory that these top and bottom temperatures be held constant, fast experiments are preferable to slow ones. The equilibrium time for the entire series of n tubes varies as n^2, and hence there is a positive advantage in employing as small a number of tubes as possible. It must also be remembered, however, that the total change in concentration ΔC varies directly as n.

Inspection of reference [2] will show that in this earlier research with a 22-tube, all-metal apparatus many features and procedures were carefully considered. It is now clear, however, that the amount of gas displaced in each swing was too close to the volume of the isothermal end regions, making it possible for some gas from the non-isothermal regions to be transported between tubes. Also, since the Monel-metal tubes were only 7 cm in total length and of wall thickness 1 mm, the temperature gradient was probably too severe to thermally isolate the two isothermal regions. As for glass swing-separators [3], we now conclude that it is in practice unduly difficult, with n fairly large, to maintain all of the upper tube regions at the same constant temperature.

It is true that the thermal diffusion factor α_T is independent of the concentrations C_1 and C_2 of the two isotopes in the binary mixture. But since we employ the relation

$$[\Delta C]_{1n}/n[C_1\,C_2]_{\text{initial}}=\alpha_T \ln (T_2/T_1), \qquad (1)$$

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[1] K. Clusius and M. Huber, Z. Naturforschg. **10 a**, 230 [1955].
[2] T. I. Moran and W. W. Watson, Phys. Rev. **109**, 1184 [1958].
[3] S. C. Saxena, J. G. Kelley, and W. W. Watson, Phys. Fluids **4**, 1216 [1961].

for which it is assumed that the sum of the products $C_1 C_2$ for all n tubes is $n[C_1 C_2]_{\text{initial}}$, the least error is introduced if $C_1 = C_2 = 0.5$, since $C_1 C_2$ varies only slightly from tube to tube if the concentrations are near equality. Also, since the product $C_1 C_2$ is a maximum for this $50-50\%$ mixture, ΔC is also maximized for the given conditions. A third advantage of using a $50-50\%$ mixture of the two isotopes is that the relative abundance measurements with the mass spectrometer are the most accurate because it is then not necessary to change sensitivity scales, the base line for the mass peaks is the same, etc. In the earlier work in this laboratory the two concentrations were never close to equality.

Inspection of Eq. (1) also indicates that for a constant value of $T_2 - T_1$ the variation of $\ln(T_2/T_1)$ with the average $\bar{T}$ of the two temperatures is most severe at low temperatures. Therefore the variation of α_T with $\bar{T}$ is always more pronounced in the low-temperature range. Measurement of α_T at the lowest temperatures should thus be most favorable for determining the parameters of the intermolecular potential and for indicating most clearly the limitations of a given model.

Experimental Features

Guided by these thoughts, we constructed the 4-tube swing-separator shown schematically in Fig. 1. The tubes are stainless steel, 2 cm I.D. and 0.010 inch wall thickness. The interconnecting capillaries are also stainless steel, 1.5 mm I.D. The 15-cm long tubes are imbedded to a depth of 3 cm at each end, with good thermal contact, into a large block of electrolytic copper. This makes the volume of the isothermal region at each tube end about 9 cm³, while the volume of gas displaced by the gas pump is from 1 to 2 cm³. The 9-cm tube length between the copper blocks diminishes the temperature gradient, and these lengths are jacketed with asbestos to isolate them thermally into the system. For constant-temperature baths in the low-temperature range, a sheet-copper pan is soft-soldered around the upper copper block, while the lower block is immersed into liquid nitrogen, etc., in a large dewar.

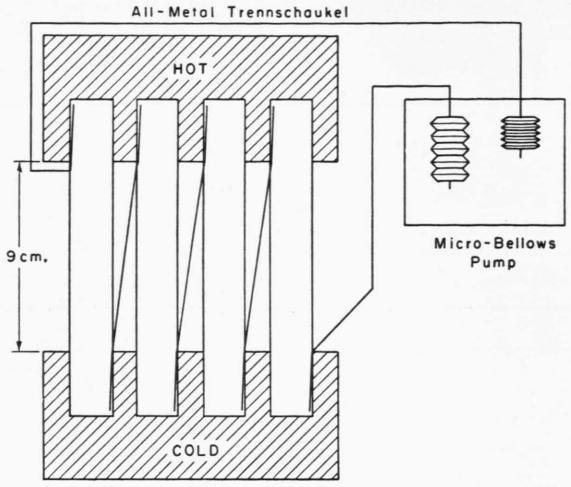

Fig. 1. Schematic of the swing separator. The four tubes and the capillary connections are stainless steel. The shaded areas are large copper blocks.

For the gas swinging the micro-bellows pump working push-pull with a full period of 30 sec is an improvement over the rocking mercury-filled U-tube. This period was chosen with consideration of the calculation of Saxena and Mason [4] that the equilibrium time is about 10 sec for a single tube of comparable dimensions. Since the total equilibrium time is increased not only by this slow swing period but also by our enlarged ratio of the isothermal volume in the tube to the gas displacement volume, rough calculation indicated an equilibrium time of about 2 hours. Actually, for all the results reported below we have analyzed gas samples to 5 or 6 hours for assurance that the equilibrium value of ΔC was being measured. In all cases we have used about a $50-50\%$ mixture of He^3/He^4 or Ne^{20}/Ne^{22} at about 15 cm of Hg pressure.

Results for Helium and Neon

In Tables 1 and 2 we give the observed changes in concentration ΔC from operation of this 4-tube swing separator at six different average temperatures $\bar{T}$ in the range from 136 °K to 313 °K for Ne^{20}/Ne^{22} and for five values of $\bar{T}$ in the same range

T_2 °K	T_1 °K	$\bar{T}$ °K	$(\Delta C)\%$	α_T	α_0
195	77	136	6.43 ± 0.06	0.0696	0.488 ± 0.011
273	77	175	8.65 ± 0.11	0.0688	0.482 ± 0.006
273	195	234	2.20 ± 0.08	0.0657	0.460 ± 0.024
344	273	309	1.46 ± 0.09	0.0637	0.446 ± 0.017
351	273	312	1.63 ± 0.09	0.0651	0.456 ± 0.017

Table 1. Isotopic Thermal Diffusion in Helium (50% He^3, 50% He^4) with a Four-Tube Swing Separator.

[4] S. C. Saxena and E. A. Mason, Mol. Phys. **2**, 264 [1959].

T_2 °K	T_1 °K	$\bar{T}$ °K	$(\Delta C)\%$	α_T	α_0
195	77	136	1.46 ± 0.08	0.0166	0.349 ± 0.020
273	77	175	2.27 ± 0.05	0.0189	0.397 ± 0.020
293	77	185	2.44 ± 0.07	0.0193	0.415 ± 0.029
347	77	212	2.81 ± 0.05	0.0200	0.420 ± 0.018
294	195	245	0.85 ± 0.05	0.0217	0.456 ± 0.030
351	273	312	0.57 ± 0.04	0.0233	0.489 ± 0.028

Table 2. Isotopic Thermal Diffusion in Neon (50% Ne^{20}, 50% Ne^{22}) with a Four-Tube Swing Separator.

for He^3/He^4. Each of these values of ΔC is the average of the mass spectrometer analyses of 4 to 6 gas samples drawn from each end of the equipment from 3 to 6 hours after the start. We also list the top (T_2) and bottom (T_1) temperature from each run, the value of α_T calculated using Eq. (1), and the value of the reduced thermal diffusion factor α_0 defined as

$$\alpha_T = \alpha_0 [(M_1 - M_2)/(M_1 + M_2)]. \qquad (2)$$

It is these α_0 values that are plotted in Figs. 2 and 3. The vertical error bars for each observation give the standard deviation as judged from the spread of the individual determinations involved in each average ΔC.

The product $C_1 C_2$ is 0.2489 for the He^3/He^4 mixture and 0.2495 for the Ne^{20}/Ne^{22} mixture, both close to the maximum possible for a binary mixture. The curves drawn in the Figures are calculated fits from assumed exp-six molecular potentials as explained below.

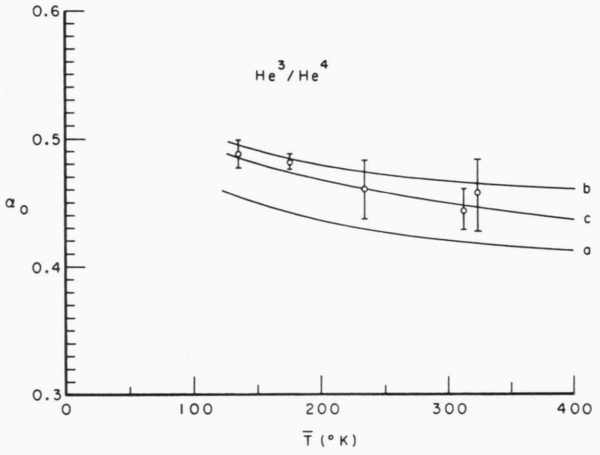

Fig. 2. Variation of the reduced thermal diffusion factor α_0 with temperature for He^3/He^4. The five points with vertical error bars are experimental values. Curve a is calculated for an exp-six potential with $\alpha=12$, curve b is exp-six with $\alpha=13$, curve c is a pure exponential potential.

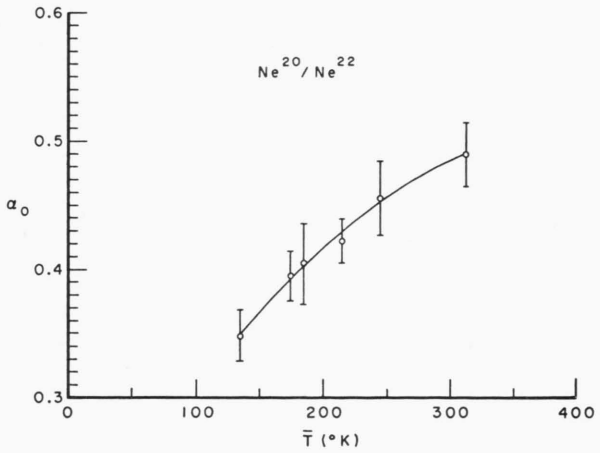

Fig. 3. Variation of the reduced thermal diffusion factor α_0 with temperature for Ne^{20}/Ne^{22}.

Discussion

These values of α_T and α_0 are the first data on the variation of the thermal diffusion factor for helium at these low temperatures. Extrapolation of the indicated trend of our measurements to somewhat higher temperatures shows fair agreement with the measurements of VAN DER VALK and DE VRIES [5] for He^3/He^4. In the range of overlapping temperatures our values of α_0 for neon average about 10% higher than those of MORAN and WATSON [2]. CLUSIUS has indicated [6] that Ne^{20}/Ne^{22} α_T values obtained in his laboratory also are about 10% higher than those reported here earlier. We may assume, then, that these observations of α_T vs T which we now present are close to the correct values.

Since thermal diffusion, particularly in the low-temperature range, is the transport property most sensitive to the law of intermolecular force, we should calculate the parameters of the potential best

[5] F. VAN DER VALK and A. E. DE VRIES, J. Chem. Phys. **34**, 345 [1961].

[6] Private communication.

fitting these new measurements. The two most commonly used potentials are the exp-six potential:

$$\Phi(r) = \varepsilon\,\alpha(\alpha-6)^{-1}[(6/\alpha)\exp\{\alpha(1-r/r_m)\} - (r_m/r)^6] \quad (3)$$

and the LENNARD–JONES $(12-6)$ potential:

$$\Phi(r) = 4\,\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (4)$$

Here $\Phi(r)$ is the potential energy of the two molecules separated by a distance r, ε is the depth of the potential energy minimum, and r_m and σ are the distance parameters for which the potential energy is minimum and zero, respectively. For the calculation we use the values of α_0 computed by SAXENA and MASON [7] as a function of temperature for several conceivable α's, and draw plots of $\log \alpha_0$ vs $\log T^*$, where T^* is the reduced temperature, $k\bar{T}/\varepsilon$. This yields a family of curves, one for each value of α for Eq. (3), and a single curve for Eq. (4). Then a plot of the experimental quantity $\log\left(\frac{M_1+M_2}{M_1-M_2}\right)\alpha_T$ vs $\log T$ should be superposable on one of the theoretical curves of $\log \alpha_0$ vs $\log T^*$ by simple translation along the T axis. The amount of translation gives ε/k. It is easy in this way to choose the theoretical curve best fitting the experimental points, and hence to determine the parameter α of Eq. (3).

This comparison yields the interesting conclusion that for the LENNARD–JONES $(12-6)$ potential there is no choice of ε/k that will fit the data. The exp-six potential gives a good fit, however, as already noted in reference [3], but our new measurements lead to revised potential parameters. For helium the α of Eq. (3) should be 12.7, and ε/k is 9.16 °K, while for neon the α parameter is 13.0 and ε/k is (46.0 ± 0.6) °K.

The curves a, b, and c in Fig. 2 for He^3/He^4 are identical with those in Fig. 7 of reference [3]. Curve a represents the calculated α vs $\bar{T}$ relation using an exp-six potential with $\alpha = 12$, curve b is for exp-six with $\alpha = 13$, and curve c is based on a purely exponential potential. One sees by interpolation that a curve based on an exp-six potential with $\alpha = 12.7$ would be a fairly good fit. It is just impossible to reproduce the observed α_0 vs $\bar{T}$ trend for He^3/He^4 with any curve based on a LENNARD–JONES potential.

For helium there is no evidence here for any quantum effects, even at $\bar{T} = 136$ °K. Since it would be interesting to have experimental data on quantum corrections at the lowest attainable temperatures (reference [3]), we have prepared a one-tube stainless steel apparatus which we shall operate with the lower end at or below 4 °K. Calculation indicates that the ΔC should be measurable, using $50-50\%$ He^3/He^4 in this single-tube, because of the favorable $\ln(T_2/T_1)$ term in Eq. (1) when T_1 is so low. It will be surprising if quantum corrections do not appear.

Our hearty congratulations to Professor CLUSIUS on this occasion of his 60th birthday. We wish him many years to come of productive research in his fine institute.

[7] S. C. SAXENA and E. A. MASON, J. Chem. Phys. **28**, 623 [1958].