

VARIOUS APPROXIMATIONS FOR THE ISOTOPIC THERMAL DIFFUSION FACTOR. I. APPLICATION TO HELIUM ISOTOPES

S. C. SAXENA AND P. A. PARDESHI

CHEMISTRY DIVISION, ATOMIC ENERGY ESTABLISHMENT TROMBAY, BOMBAY, INDIA

(Received, September 8, 1960)

ABSTRACT. Various formulæ for the isotopic thermal diffusion factor have been reviewed and a new formula has been derived. Numerical calculations have been performed for the particular case of He^3 - He^4 in a region where quantum effects are negligible. These calculations establish the relative adequacy of a comparatively simpler formula advanced by us and will be useful to interpret the recent experimental results of Saxena, Kelley and Watson on the thermal diffusion factor as a function of temperature.

1. INTRODUCTION

Knowledge of the thermal diffusion factor for helium isotopes is important, for thermal diffusion has been used by McInteer, Aldrich and Nier (1948) and Schuette, Zucker and Watson (1950) to enrich He^3 despite its extremely low abundance ($1.3 \times 10^{-4}\%$) in natural helium and still lower abundance for well helium. Measurements of the isotopic thermal diffusion factor, α_T , as a function of temperature are also important to investigate the intermolecular forces. Moran and Watson (1958) measured the thermal diffusion factor for He^3 - He^4 in the temperature range 233°K to 571°K by using an elegant apparatus "Trennschaukel" introduced by Clusius and Huber (1955). Recently Saxena, Kelley and Watson (1960) have extended these measurements to still lower temperatures. These measurements show a much steeper temperature dependence for α_T than given by the existing theoretical expressions. Approximate quantum mechanical calculations of α_T by Saxena (1960) reveal that the quantum corrections are negligible even at the lowest temperature (233°K). Thermal diffusion factor like other transport properties, emerges from the theory as the ratio of infinite determinants, Chapman-Cowling (1953). There are two alternative procedures developed separately by Chapman and Cowling (1953) and by Kihara (1949) to expand these infinite determinants into infinite convergent series. The use of varying number of terms of these series lead to the various approximations on the two schemes. As Moran and Watson (1958) compared their experimental results only with an approximate formula, valid more rigorously for a mixture of heavy isotopes, it would be interesting to explore the possibility of this anomaly

in the use of an inadequate theoretical expression. The purpose of the present paper is to evaluate α_T for He³-He⁴ according to the expressions derived on the two approximation schemes. This will establish the relative usefulness and limitations of the various formulae. A new formula has been derived on the Kihara approximation scheme, taking into consideration terms containing upto the second power of the reduced mass.

2. GENERAL FORMULAE FOR THE ISOTOPIC THERMAL DIFFUSION FACTOR

The Chapman-Enskog kinetic theory of gases expresses the m -th Chapman-Cowling approximation for α_T as follows:

$$[\alpha_T]_m = \frac{5}{2} [X_1 \dot{X}_2 A_{00}^{(m)}]^{-1} \left[X_1 A_{01}^{(m)} \left(\frac{M_1 + M_2}{2M_1} \right)^{\frac{1}{2}} + X_2 A_{0-1}^{(m)} \left(\frac{M_1 + M_2}{2M_2} \right)^{\frac{1}{2}} \right]. \quad (1)$$

Here X_1 and X_2 are the mole fractions of the two components of molecular weights M_1 and M_2 respectively. The quantity $A^{(m)}$ represents a determinant of $(2m+1)$ order, the general term of which is a_{ij} where i and j range from $-m$ to $+m$ including zero. The minor of $A^{(m)}$ obtained by deleting the row and column containing a_{ij} , is denoted by the symbol $A_{ij}^{(m)}$. To the first approximation, Eq.(1) can be written into the following convenient form:

$$[\alpha_T]_1 = \frac{(6C^* - 5)(X_1 S_1 - X_2 S_2)}{X_1^2 Q_1 + X_2^2 Q_2 + X_1 X_2 Q_{12}}, \quad \dots \quad (2)$$

where

$$S_1 = \left[\frac{M_1}{M_2} \left(\frac{2M_2}{M_1 + M_2} \right)^{\frac{1}{2}} A^* - \frac{4M_1 M_2 A^*}{(M_1 + M_2)^2} - \frac{15M_2(M_2 - M_1)}{2(M_1 + M_2)^2} \right],$$

$$Q_1 = \left[\frac{2}{M_2(M_1 + M_2)} \left(\frac{2M_2}{M_1 + M_2} \right)^{\frac{1}{2}} A^* \left\{ \left(\frac{5}{2} - \frac{6}{5} B^* \right) M_1^2 + 3M_2^2 + \frac{8}{5} M_1 M_2 A^* \right\} \right],$$

and

$$Q_{12} = \left[15 \left(\frac{M_1 - M_2}{M_1 + M_2} \right)^2 \left(\frac{5}{2} - \frac{6}{5} B^* \right) + \frac{4M_1 M_2 A^*}{(M_1 + M_2)^2} \left(11 - \frac{12}{5} B^* \right) + \frac{8}{5} \frac{(M_1 + M_2)}{(M_1 M_2)^{\frac{1}{2}}} A^{*2} \right].$$

The expressions for S_2 and Q_2 are obtained from those of S_1 and Q_1 by an interchange of the subscripts for the molecular masses. Here the functions $\Omega^{(b,n)*}$ are the reduced Chapman-Cowling collision integrals and the functions A^* , B^* and C^* are ratios of $\Omega^{(b,n)*}$ and have been tabulated by Hirschfelder, Curtiss and Bird (1954) as a function of the reduced temperature. Second and higher

approximations are conveniently left in the determinant form of Eq. (1) for computational purposes.

For the case of heavy isotopes where the reduced mass, $\frac{M_1 - M_2}{M_1 + M_2}$, is small, Eq. (1) can be expanded in the powers of the reduced mass. Retaining terms only up to the first power of the reduced mass, one obtains;

$$[\alpha_T]_m = [\alpha_0]_m \left(\frac{M_1 - M_2}{M_1 + M_2} \right), \quad \dots \quad (3)$$

where $[\alpha_0]_m$ is dimensionless thermal diffusion factor and has been given by Mason (1954, 1957a) for $m = 1, 2$ and 3 . For $m = 1$, α_0 is given by

$$[\alpha_0]_1 = \frac{15(6C^* - 5)(2A^* + 5)}{2A^*(16A^* - 12B^* + 55)} \quad \dots \quad (4)$$

Expressions for m equal to 2 and 3 are rather lengthy and will not be repeated here.

Eq. (2) transforms into the following form for the case of heavy isotopes when one retains terms up to the second power of the reduced mass, M , (Chapman, 1941):

$$[\alpha_0]_1' = [\alpha_0]_1 [1 - \gamma M(X_1 - X_2)], \quad \dots \quad (5)$$

where

$$\gamma = \frac{3(5 - A^*)}{2(5 + 2A^*)} - \frac{2(12B^* + 5)}{(16A^* - 12B^* + 55)}.$$

It is interesting to note that $[\alpha_0]_1'$ is now dependent on the relative proportions of the two isotopes unlike Eq. (4).

Kihara (1949) developed an alternative scheme to expand these infinite determinants into convergent infinite series. This procedure is mathematically less straightforward than that of Chapman-Cowling but it has a more physical basis and gives simpler expressions at least in the earlier approximations. Recently, Mason (1957a) has elaborated and extended this procedure and has given the expression upto the second approximation for the thermal diffusion factor. The general formula for the m -th approximation to the thermal diffusion factor on Kihara scheme remains the same as given by Eq. (1) except that now a_{ij} have different meaning. The first approximation $[\alpha_T]_1$ is again given by Eq. (2) except that the Q 's are now defined as follows:

$$Q_1' = \left[\frac{2}{M_2(M_1 + M_2)} \left(\frac{2M_2}{M_1 + M_2} \right)^{\frac{1}{2}} A^* \left\{ M_1^2 + 3M_2^2 + \frac{8}{5} M_1 M_2 A^* \right\} \right],$$

and

$$Q_{12}' = \left[15 \left(\frac{M_1 - M_2}{M_1 + M_2} \right)^2 + \frac{32M_1M_2A^*}{(M_1 + M_2)^2} + \frac{8}{5} \frac{M_1 + M_2}{(M_1M_2)^{\frac{1}{2}}} A^{*2} \right] \quad \dots (6)$$

Using the extended Kihara scheme, Mason (1957a) gave the following formula for the second approximation to α_T :

$$[\alpha'_T]_2 = [\alpha_T]_1(1 + K'_1) + K'_2, \quad \dots (7)$$

where

$$K'_1 = h_3h_5 + h_4h_{-6} + h_{-3}h_{-5} + h_{-4}h_6, \quad \dots (8)$$

and

$$K'_2 = \frac{5}{2\bar{X}_1} \left(\frac{M_1 + M_2}{2M_2} \right)^{\frac{1}{2}} (h_{-1}h_{-5} + h_1h_6 - h_2h_4 + h_{-2}h_3) \\ - \frac{5}{2\bar{X}_2} \left(\frac{M_1 + M_2}{2M_1} \right)^{\frac{1}{2}} (h_1h_5 + h_{-1}h_{-6} - h_{-2}h_{-4} + h_2h_{-3}). \quad \dots (9)$$

In Eq. (7), $[\alpha_T]_1$ is given by Eq. (2) and the various h_K are similar to those given by Mason (1957a) except that the subscripts characterising the molecular species are all the same.

For the case heavy isotopes, α'_T can again be put in the form of Eq. (3), where $[\alpha'_0]_1$ is now given by the following simpler form:

$$[\alpha'_0]_1 = \frac{15(6C^* - 5)}{16A^*}. \quad \dots (10)$$

The second approximation $[\alpha'_0]_2$ can be written in the following form:

$$[\alpha'_0]_2 = [\alpha_0]_1(1 + K'_0). \quad \dots (11)$$

Here $[\alpha_0]_1$ is given by the Eq. (4) and K'_0 is a correction factor given by Mason (1957a).

Using Kihara's scheme for approximating transport coefficients, we have worked out the following first approximation to the thermal diffusion factor for a mixture of heavy isotopes in which terms containing upto the second power of the reduced mass have been retained:

$$[\alpha'_0]_{1'} = [\alpha_0]_1 \left\{ 1 - \frac{(5 - 3A^*)}{2(2A^* + 5)} M(X_1 - X_2) \right\}. \quad \dots (12)$$

This formula is slightly simpler than the one given by Eq. (5) and as shown in the next section, is very useful for the accurate evaluation of α_T of isotopic mixtures

where M is not quite small. Such isotopic mixtures are the mixtures of helium and hydrogen isotopes.

3. CALCULATION OF THE THERMAL DIFFUSION
[FACTOR FOR HELIUM

Detailed calculations for the thermal diffusion factor of helium have been performed on both the approximation schemes, according to the various formulae discussed in the previous section. The results of this calculation are tabulated in Table I and refer to the following $L-J(12-6)$ law for intermolecular force:

$$E(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (13)$$

Here $E(r)$ is the potential energy of the two molecules at a separation distance r and σ is the molecular separation for which the interaction energy is zero. ϵ is the value of the maximum negative potential energy. The various collision integrals required for these calculations are tabulated by Hirschfelder, Curtiss and Bird (1954).* In those calculations of Table I where the system has been treated as a binary mixture of He^3 and He^4 , we have chosen arbitrarily the concentration of He^3 as 5%, a value close to the one used in the work of Moran and Watson (1958). Further, these calculations were performed on a desk calculator and have been subjected to only spot-checking.

TABLE I

Calculated values of the isotopic thermal diffusion factor for Helium

Chapman-Cowling approximation scheme					Kihara approximation scheme				
T^*	$[\alpha_T]_1^{mix}$	$[\alpha_T]_1^{iso}$	$[\alpha_T]_1^{iso}$	$[\alpha_T]_2^{mix}$	$[\alpha_T]_1^{mix}$	$[\alpha_T]_1^{iso}$	$[\alpha_T]_1^{iso}$	$[\alpha_T]_2^{mix}$	$[\alpha_T]_2^{iso}$
5	0.0671	0.0695	0.0677	0.0690	0.0702	0.0718	0.0707	0.0694	0.0716
7	0.0724	0.0751	0.0732	0.0747	0.0742	0.0759	0.0747	0.0755	0.0779
9	0.0744	0.0788	0.0753	0.0760	0.0779	0.0797	0.0785	0.0778	0.0803
20	0.0767	0.0794	0.0774	0.0803	0.0802	0.0820	0.0808	0.0809	0.0832
40	0.0768	0.0794	0.0774	0.0801	0.0802	0.0820	0.0808	0.0808	0.0832
60	0.0764	0.0791	0.0771	0.0799	0.0799	0.0816	0.0805	0.0804	0.0827
80	0.0763	0.0789	0.0769	0.0796	0.0797	0.0814	0.0803	0.0805	0.0826
100	0.0761	0.0787	0.0767	0.0794	0.0795	0.0812	0.0800	0.0800	0.0829
200	0.757	0.0781	0.0762	0.0784	0.0790	0.0806	0.0795	0.0797	—

*It may be pointed out that there is a misprint in the value of the collision integ al $\Omega^{(1,1)}$ * for $T^* = 100$. It should read as 0.5170 instead 0.5130.

In columns 2, 3, 4 and 5 of Table I are recorded the values of the different approximations to α_T as a function of the reduced temperature ($T^* = kT/\epsilon$) according to Chapman-Cowling scheme; while the columns 6, 7, 8, 9 and 10 report the results on Kihara scheme. Values of α_T listed in columns 2 and 3 of Table I have been obtained according to the Eqs. (2) and (4) respectively. The two sets of values differ appreciably and reveal the fact that for Helium, terms involving only first power of the reduced mass are not enough; a result previously pointed out by Winter (1950). It is, therefore, interesting to consider terms involving still higher powers of M . Chapman (1941) derived an expression, Eq. (5), which takes into account the terms upto the second power of M . Calculated values according to this formula are given in column 4 of Table I. It will be seen that these values are appreciably different ($\approx 2.4\%$) from $[\alpha_T]_1^{iso}$ but are in good agreement with the $[\alpha_T]_1^{mix}$ values ($\approx 0.9\%$). Values of $[\alpha_T]_2$ computed according to Eq. (1) with $m = 2$ are shown in column 5. These values are approximately 4% higher than the $[\alpha_T]_1^{mix}$ values, establishing thereby that the convergence of the series is fast enough and the error involved, because of the neglect of the third and higher approximations, is small. This inference is very welcoming in view of the fact that the higher approximations will involve evaluation of seven and higher order determinants and can be safely avoided till we considerably improve the precision and accuracy of the measurements. It is also very interesting to note that $[\alpha_T]_1^{iso}$ values are in better agreement with the $[\alpha_T]_2^{mix}$ values than the $[\alpha_T]_1^{mix}$ values. The authors therefore feel that the simple formula for α_T as given by Eq. (5) is preferable to the complicated form of Eq. (2) and still more complicated form as given by Eq. (1).

Results obtained using similar approximations, but on Kihara scheme are listed in columns 6, 7, 8 and 9, and are seen to follow the same qualitative trend. In column 10 are tabulated for comparison the results obtained from a formula which considers terms upto the second approximation but retains only the first power of reduced mass, Saxena and Mason (1958). These values of $[\alpha'_T]_2^{iso}$ are systematically higher than the $[\alpha'_T]_2^{mix}$ values. As the convergence for the Kihara approximation scheme is still faster than that of Chapman-Cowling, we are of the opinion that the neglect of the second power of the reduced mass is much more serious. A critical examination of all the values obtained on Kihara approximation scheme again leads to the same conclusion that the values obtained by using the simpler formula, Eq. (12), which considers terms upto the second power of reduced mass, is preferable to the rest of all, both for accuracy and simplicity.

A critical examination of the various approximations for α_T on the two approximation schemes for realistic intermolecular potentials and for a few mathematically simple systems, was done by Mason (1957a and 1957b). Mason (1957b) considered three types of mixtures viz. (1) Lorentzian, (2) Quasi-Lorentzian and (3) Heavy isotopic mixtures. Unfortunately our system is not identical to any of these

but resembles to (3) in as much as all the interactions are identical but the two masses differ considerably. Our numerical calculations of Table I reveal that Kihara approximation scheme is preferable to Chapman-Cowling and is in conformity with the conclusions of Mason (1957b) for mixtures of heavy isotopes.

4. CONCLUSIONS

Our numerical calculations for α_T of helium isotopes establish that Kihara approximation procedure is better than that of Chapman and Cowling. With He³ present in trace, a simple formula derived, treating the mixture of He³ and He⁴ as a heavy isotopic mixture but retaining terms up to the second power of the reduced mass, will yield results within the range of experimental error. This formula is also preferable in view of comparative simplicity and accuracy.

ACKNOWLEDGMENT

The authors are thankful to Dr. J. Shankar for his kind interest and making available to us all the facilities.

REFERENCES

- Chapman, S., 1941, *Proc. Roy. Soc.*, **A177**, 38.
Chapman, S. and Cowling, T. G., 1953, *The Mathematical Theory of Non-Uniform gases*, Cambridge University Press, England.
Clusius, K. and Huber, M., 1955, *Z. Naturforsch.*, **10A**, 230.
Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., 1954, *The Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York.
Kihara, T., 1949, *Imperfect Gases*, originally published in Japanese (Asakusa Book Store, Tokyo) and translated into English by the U.S. office of Air Research, Wright-Patterson Air Force Base, Chap. 6; see also 1953, *Revs. Modern Phys.*, **25**, 831.
Mason, E. A., 1954, *J. Chem. Phys.*, **22**, 169.
Mason, E. A., 1957a, *J. Chem. Phys.*, **27**, 75.
Mason, E. A., 1957b, *J. Chem. Phys.*, **27**, 782.
McInteer, B. B., Aldrich, L. T., and Nier, A. O., 1948, *Phys. Rev.*, **74**, 946.
Moran, T. I., and Watson, W. W., 1958, *Phys. Rev.*, **109**, 1184.
Saxena, S. C., 1960, unpublished calculations.
Saxena, S. C., Kelley, T. G. and Watson, W. W., 1960, In course of publication.
Saxena, S. C., and Mason, E. A., 1958, *J. Chem. Phys.*, **28**, 623.
Schuette, O. F., Zucker, A. and Watson, W. W., 1950, *Rev. Sci. Instr.*, **21**, 1016.
Winter, E. R. S., 1950, *Trans Faraday Soc.*, **46**, 81.