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Thermal Diffusion in Isotopic Gas Mixtures and Intermolecular Forces

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Available thermal diffusion data on He, Ne, Ar, Kr, Xe, H_2, N_2, O_2, CO, CH_4, NH_3, HCl of different workers have been discussed. This study has revealed the need and nature of the additional measurements which will be useful and is thus of help in planning new experiments. The problems of temperature assignment and composition dependence of the thermal diffusion factor α_T are examined. The adequacy of the theoretical α_T expression used while interpreting the experimental results is also given proper consideration. Comparison of the experimental data are made with the prediction of the rigorous Chapman–Enskog kinetic theory in conjunction with the three spherically symmetric potentials (Lennard-Jones 12–6, modified Buckingham exp-6, and Morse) for nonpolar gases, while a Stockmayer type 12-6-3 potential for polar gases. Reasonably satisfactory agreement is obtained even for polyatomic gases. The extent to which Chapman-Enskog theory in conjucntion with central force-field models may be expected to hold for polyatomic gases is investigated The up-to-date knowledge of the kinetic theory which takes into consideration inelastic molecular collisions is reviewed

I. INTRODUCTION

There have been many attempts in recent years to understand the phenomenon of thermal diffusion both theoretically and experimentally. These efforts primarily arose because of the large sensitivity of the thermal diffusion factor α_T to the nature of intermolecular forces and the importance of its knowledge in the design of thermal diffusion columns for separation purposes. Saxena and Mathur[1] and Saxena and Joshi[2] have recently given the status of our knowledge of the thermal diffusion of binary gas mixtures and the interesting results derived therefrom regarding the force-field between different molecules. This article examines the available α_T data on isotopic mixtures.

The formulation of the rigorous theory of thermal diffusion in gases was given by Chapman,[3] and its adequate description is given in the book of Chapman and Cowling.[4] In this work only the first approximation to α_T, $[\alpha_T]_1$, was discussed but since then Mason[5] and Saxena and Srivastava[6] have extended this work to include second as well as third approximations. These formulas, which are derived according to an approximation procedure described in detail by Chapman and Cowling,[4] will be referred after these authors. Kihara[7] and later Mason[5] developed another procedure for simplifying the infinite determinants which occur in α_T and gave a set of formulas which will be referred after these workers. All these expressions which are essentially for binary gas mixtures are considerably simplified for isotopic mixtures. However, for each isotope one has to choose the right expression for α_T to be able to interpret the experimental results with reliance. This point is discussed here at length when we consider the data on individual isotopes.

For either interpretation or computation of α_T from the rigorous expressions one needs the knowledge of the form of intermolecular potential. We consider in detail the L-J (12–6) and exp-6 potentials but also discuss for a few systems the Morse potential, recently introduced. These potentials can be written explicitly in terms of the potential parameters and the separation between the molecules. If $\phi(r)$ refer to the interaction potential energy between two molecules at a separation distance r then according to the L-J (12–6) potential[8]

$$\phi(r)=4\epsilon[(\sigma_0/r)^{12}-(\sigma_0/r)^6], \qquad (1)$$

for the modified Buckingham exp-6 potential,[5]

$$\phi(r)=[\epsilon\alpha/(\alpha-6)] \times[(6/\alpha)\exp\{\alpha[1-(r/\sigma_m)]\}-(\sigma_m/r)^6], \qquad (2)$$

and for the Morse potential,[9]

$$\phi(r)=\epsilon\{\exp\{-2(c/\sigma_0)(r-\sigma_m)]-2 \times\exp[-(c/\sigma_0)(r-\sigma_m)]\}. \qquad (3)$$

Here ϵ is the depth of the potential energy minimum and is equal to the maximum attractive energy which occurs at $r=\sigma_m$, σ_m, and σ_0 are the finite values of r for which $\phi(r)$ is minimum and zero, respectively, α is a parameter which measures the steepness of the repulsive limb, and c is also a similar parameter which controls the curvature at the minimum also.

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[1] S. C. Saxena and B. P. Mathur, Rev. Mod. Phys. **37**, 316 (1965).

[2] S. C. Saxena and R. K. Joshi, J. Sci. Ind. Res. (to be published).

[3] S. Chapman, Phil. Trans. Roy. Soc. (London) **A211**, 433 (1912); **A216**, 279 (1916); **A217**, 115 (1917); Proc. Roy. Soc. (London) **A93**, 1 (1916), **A177**, 38 (1941).

[4] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, New York, 1952), 2nd ed.

[5] E. A. Mason, J. Chem. Phys. **22**, 169 (1954); **27**, 75, 782 (1957).

[6] S. C. Saxena and B. N. Srivastava, J. Chem. Phys. **23**, 1571 (1955); S. C. Saxena, *ibid.* **24**, 1209 (1956).

[7] T. Kihara, *Imperfect Gases* (Asakura Bookstore, Tokyo, Japan, 1949) (English transl.: U.S. Office of Air Research, Wright-Patterson Air Force Base, Ohio); see also Rev. Mod. Phys. **25**, 831 (1953).

[8] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1964).

[9] S. E. Lovell and J. O. Hirschfelder, University of Wisconsin, Theoretical Chemistry Laboratory Report WIS-AF-21 (1962); see also D. D. Konowalow, M. H. Taylor, and J. O. Hirschfelder, Phys. Fluids **4**, 622 (1961).

We consider the experimental α_T data on the nonpolar gases He, Ne, Ar, Kr, Xe, H_2, N_2, O_2, CO, and CH_4 as a function of temperature and in the case of H_2 isotopes as a function of composition, also. We also review the data on the two polar gases HCl and NH_3. For nonpolar gases we have considered only the spherically symmetric potentials given by Eqs. (1)–(3) while for polar gases a Stockmayer type potential[10] recently worked out in detail by Monchick and Mason[11] is used. According to this potential[11]

$$\phi(r)=4\epsilon[(\sigma_0/r)^{12}-(\sigma_0/r)^6+\delta(\sigma_0/r)^3],$$

$$\delta=\tfrac{1}{4}\mu^*\zeta(\theta_1,\theta_2,\varphi),\qquad \mu^*=\mu/(\epsilon\sigma_0^3)^{\frac{1}{2}},$$

and

$$\zeta(\theta_1,\theta_2,\varphi)=2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\varphi,\quad (4)$$

where all the terms have the usual meaning.

Thus, in addition to properly pooling together the data of different workers on a particular system and then interpreting it in terms of an adequate theoretical expression in conjunction with the intermolecular potentials discussed above, the endeavor here is also to throw some light on the composition dependence of α_T and on the problem of assigning a temperature to the measured α_T value. This detailed study automatically brings to light the deficiencies of the existing α_T data and the differences between the values of different experimentalists using different techniques in certain cases. This study is thus intended not only to be just a critical review but also a source of information for planning further α_T measurements. Grew and Ibbs[12] in their excellent monograph discussed the data which were available at that time. Since then many reliable and elaborate measurements have appeared, and also, theoretical expressions which are more accurate have been derived. The calculations of α_T on potentials of Eqs. (2)–(4) have also appeared only after their work. A new method of measuring α_T using a swing separator or Trennschaukel has also since been introduced. Reliable calculations of the composition dependence are possible only now and further some success has also been achieved during these years in assigning the temperature to measured α_T value more unambiguously than before. As contrasted with the earlier work of Grew and Ibbs,[12] this article covers new information from all these view points.

II. THEORETICAL EXPRESSIONS FOR α_T

To list here all the different rigorous and approximate formulas applicable to different isotopes would be a long story which we do not attempt. An extensive critical survey is given by Saxena and Joshi.[2] These formulas are also applicable to isotopes if we incorporate the obvious simplification that molecular interactions are now identical for all the molecular species. This implies to be more specific for a binary mixture that $\epsilon_{12}=\epsilon_{11}=\epsilon_{22}$, $(\sigma_m)_{12}=(\sigma_m)_{11}=(\sigma_m)_{22}$, $(\sigma_0)_{12}=(\sigma_0)_{11}=(\sigma_0)_{22}$, $\alpha_{12}=\alpha_{11}=\alpha_{22}$, and $C_{12}=C_{11}=C_{22}$. Further, the various Chapman–Cowling collision integrals[4] $\Omega_{ij}^{(l,n)*}$ will also have the same simplification, viz. $\Omega_{ij}^{(l,n)*}=\Omega_{ii}^{(l,n)*}=\Omega_{jj}^{(l,n)*}$. For the sake of convenience in reference and interpretation of results, we quote here the pertinent formulas.

Both according to Chapman–Cowling and Kihara–Mason approximation procedures, the first approximation to α_T is given by

$$[\alpha_T]_1=(6C^*-5)(x_1S_1-x_2S_2)(x_1^2Q_1+x_2^2Q_2+x_1x_2Q_{12})^{-1}.\quad (5)$$

The terms are as defined by Saxena and Joshi.[2] The defining relations for Q_i and Q_{12} are different for the two approximation procedures. For heavy isotopes, which are characterised by a small value of the proportionate mass difference $M=(M_1-M_2)/(M_1+M_2)$, M_1 and M_2 being the molecular weights of the two components, Eq. (5) has been expanded in powers of M and on the Kihara approximation scheme to give[13]

$$[\alpha_T']_1=[\alpha_0']_1M\{1-[5-3A^*/2(2A^*-5)]M(x_1-x_2)\},\quad (6)$$

where

$$[\alpha_0']_1=15(6C^*-5)/16A^*.\quad (7)$$

A^* and C^* are defined in Ref. 13. In Eq. (6) they[13] have neglected terms having powers of M greater than 2. Mason[5] has given the second approximation to α_T on the Kihara–Mason approximation procedure and is

$$[\alpha_T']_2=[\alpha_T]_1[1+K_1']+K_2'.\quad (8)$$

The defining relations for K_1' and K_2' are given by Mason.[5]

III. TEMPERATURE ASSIGNMENT TO THE MEASURED α_T VALUE

Even the most accurate thermal diffusion measurement has to solve the problem of temperature assignment in a unique manner before any adequate interpretation can be based on it. This evidently results from the fact that thermal diffusion measurements are done across a temperature gradient. The early practice has been to calculate the average value of α_T in the temperature range at which the two bulbs are maintained (T_1, T_2) and then calculate the corresponding temperature T_r, by the relation[14]

$$T_r=[(T_1-T_2)/T_1T_2]\ln(T_1/T_2).\quad (9)$$

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[10] W. H. Stockmayer, J. Chem. Phys. **9**, 398 (1941).

[11] L. Monchick and E. A. Mason, J. Chem. Phys. **35**, 1676 (1961).

[12] K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (Cambridge University Press, New York, 1952).

[13] S. C. Saxena and P. A. Pardeshi, Indian J. Phys. **35**, 55 (1961).

[14] H. Brown, Phys. Rev. **58**, 661 (1940).

Relation (9) implies that α_T varies as

$$\alpha_T = A - (B/T). \qquad (10)$$

Srivastava and Madan[15] have used different relations than (10) for temperature assignment, viz.

$$\alpha_T = A - (B/T) + (C/T^2), \quad \text{and} \quad \alpha_T = A + BT. \qquad (11)$$

Holleran[16] suggested that

$$\alpha_T = A + B \ln T, \qquad (12)$$

so that

$$T_r = (T_1 T_2)^{\frac{1}{2}}. \qquad (13)$$

Paul *et al.*[17] also have recently used the latter relation of Eq. (11) while interpreting their recent measurements on Ar; according to this one gets

$$T_r = (T_1 - T_2)/\ln (T_1/T_2). \qquad (14)$$

A somewhat better procedure is to make measurements for different values of the temperature of one bulb while keeping the other bulb temperature constant. Such measurements can yield the values of α_T as a function of temperature directly as indicated by Grew,[18] Grew, Johnson, and Neal,[19] Grew and Mundy,[20] Saxena and Mason,[21] and Weissman, Saxena, and Mason.[22]

Corbett and Watson[23] have suggested another way out of this problem of temperature assignment which has also the advantage that it tests the degree of agreement between theory and experiment at the same time. The procedure is based on an earlier suggestion of Srivastava and Madan.[15]

This problem of temperature assignment gets a happy solution in those *trennschaukel* measurements where the difference in the temperatures of the two end-bulbs is small, and as such the different procedures do not lead to any appreciably different values for T_r. Usually the average of T_1 and T_2 is taken as T_r.

In discussing the various measurements where different procedures have been employed for temperature assignment, the uncertainty due to this should be kept in mind. However, for future experiments on the two bulb method the procedure of Grew[18,21] is about the best, and in *trennschaukel* the temperature difference should be kept as small as possible.

IV. COMPOSITION DEPENDENCE OF α_T

To a fairly large extent α_T for isotopic mixtures is independent of the relative proportions of the constituents. This follows directly from theory. If the Eqs. (5) and (8) are expanded in increasing powers of M then the coefficient of M is always independent of the composition of the mixture. It is only in the coefficient of M^2, which is always small at least for most of the heavy isotopes, that the dependence on composition appears. Thus, *a priori* we would expect in H_2 and He isotopes only a relatively pronounced composition dependence. This aspect is discussed in detail in the next section. This point is also worth investigating experimentally for it offers one of the crucial tests of theory. Except in the case of hydrogen isotopes, no systematic investigations have ever been undertaken with this view point. It will, however, be worthwhile to plan such experiments specially in view of the results discussed in the next section where the theory predicts appreciable composition dependence in a few other cases also.

V. COMPARISON OF EXPERIMENTAL AND THEORETICAL α_T VALUES

We will now discuss individually the thermal diffusion data of different isotopic mixtures of various workers and assess their relative agreement. These results are also compared with the calculated theoretical values using the appropriate formula and according to different molecular potentials. This comparison will throw some light on the nature of intermolecular forces. This laborious work is not only supported but also receives preference from the well-known fact that thermal diffusion is very sensitive to the nature of molecular interactions.

Helium

The experimental values of α_T for this gas have been reported by McInteer, Aldrich, and Nier,[24] Moran and Watson,[25] Saxena, Kelley, and Watson,[26] Van der Valk and de Varies,[27] and Watson, Howard, Miller, and Schiffrin.[28] All these workers except the first one have used *trennschaukel* for determining α_T. Saxena and Joshi[29] have earlier pointed out that the measured α_T values of Moran and Watson[25] and Saxena *et al.*[26] may be smaller than the actual values due to a fault in the *trennschaukel* design. Very recently Joshi and Saxena[30]

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[15] B. N. Srivastava and M. P. Madan, J. Chem. Phys. **21**, 807 (1953).

[16] E. M. Holleran, J. Chem. Phys. **21**, 1901 (1953).

[17] R. Paul, A. J. Howard, and W. W. Watson, J. Chem. Phys. **39**, 3053 (1963).

[18] K. E. Grew, Proc. Roy. Soc. (London) **A189**, 402 (1947).

[19] K. E. Grew, F. A. Johnson, and W. E. J. Neal, Proc. Roy. Soc. (London) **A224**, 513 (1954).

[20] K. E. Grew and J. N. Mundy, Phys. Fluids **4**, 1325 (1961).

[21] S. C. Saxena and E. A. Mason, Mol. Phys. **2**, 379 (1959).

[22] S. Weissman, S. C. Saxena, and E. A. Mason, Phys. Fluids **4**, 643 (1961).

[23] J. W. Corbett and W. W. Watson, J. Chem. Phys. **25**, 385 (1956).

[24] B. B. McInteer, L. T. Aldrich, and A. O. Nier, Phys. Rev. **72**, 510 (1947).

[25] T. I. Moran and W. W. Watson, Phys. Rev. **109**, 1184 (1958).

[26] S. C. Saxena, T. G. Kelley, and W. W. Watson, Phys. Fluids **4**, 1216 (1961).

[27] F. Van der Valk and A. E. de Vries, J. Chem. Phys. **34**, 345 (1961).

[28] W. W. Watson, A. J. Howard, N. E. Miller, and R. M. Shiffrin, Z. Naturforsch. **18a**, 242 (1963).

[29] S. C. Saxena and R. K. Joshi, J. Chem. Phys. **37**, 1160 (1962).

[30] R. K. Joshi and S. C. Saxena, J. Sci. Ind. Res. (India) **24**, 21 (1965).

TABLE I. Potential parameters for pure gases.

Potential	L-J (12–6)		exp-6			Morse		
Parameters	ϵ/k	σ	α	ϵ/k	σ_m	C	ϵ/k	σ_m
Gas	(°K)	(°A)		(°K)	(°A)		(°K)	(°A)
He	10.22	2.556[a]	12.4	9.16	3.135[c]	6	8.55	2.687[g]
Ne	35.6	2.749[a]	14.5	38.0	3.147[c]	8	67.1	2.611[h]
Ar	119.8	3.405[a]	14.0	123.2	3.866[c]	5.7	120.0	4.461[i]
H_2	37.0	2.928[a]	14.0	37.3	3.337[c]			
N_2	96.0	3.730[a]	17.0	101.2	4.011[c]			
O_2	128.0	3.398[b]	17.0	132.0	3.726[e]			
CH_4	148.0	4.220[c]	14.0	152.8	4.206[c]			
			15.0	163.7	4.218[f]			
CO	110.0	3.590[d]	17.0	119.1	3.937[c]			

[a] R. J. Lunbeck, thesis, Amsterdam (1951).

[b] C. J. W. Raw and C. P. Elies, J. Chem. Phys. **28**, 1198 (1958).

[c] E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 525, 843 (1954).

[d] Reference 8.

[e] J. T. Vanderslice, E. A. Mason, and W. G. Maisch, J. Chem. Phys. **31**, 738 (1959).

[f] H. W. Schamp, Jr., E. A. Mason, A. C. B. Richardson, and A. Altman, Phys. Fluids **1**, 329 (1958).

[g] Reference 33.

[h] Reference 34.

[i] A. Saran, Indian J. Phys. **37**, 491 (1963).

worked out the detailed theory of *trennschaukel* operation and gave expressions for the calculation of various correction factors. They have also examined the probable uncertainties in the α_T values of different workers. They conclude that α_T values of Moran and Watson[25] are likely to be very much in error; Saxena *et al.*[26] data may be of relatively better accuracy as the additional corrections discussed in the later paper[30] are almost negligible for this case. Though Van der Valk[27] values are within reasonable accuracy, the values of Watson *et al.*[28] are again associated with some appreciable uncertainty arising from the fact that the connecting capillaries used in construction are somewhat wide, 1.5 mm. A careful knowledge of these facts is essential for a correct assessment of experimental data. We have thus dropped the data of Moran and Watson[25] from Fig. 1 and, also, the value of α_T at 136°K of Watson *et al.*[28] for there may be appreciable quantum corrections around such temperatures.[31] The uncertainties shown in the data of Fig. 1 are just the precision of the measurements claimed by the workers; it is not to be confused with the error which may still be larger. It is not possible to estimate it for the various corrections arising due to nonideal conditions of the *trennschaukel* design and operation have not been applied. Thus, within the scope of rather large uncertainty, it is possible to conclude that the various measurements are consistent with each other. However, the need to evolve a better set of α_T values as a function of temperature is apparent.

In Fig. 1 we also show the computed α_T values for the L-J (12–6), exp-6, and Morse potentials. The potential parameters used are those listed in Table I. Saxena and Pardeshi[13] have computed the theoretical α_T values for a mixture of He^3 and He^4 containing 5% He^3 and according to different formulas on the L-J (12–6) potential. They found the Kihara approximation scheme to yield the best results and that the second approximation formula differs from the first approximation by less than 1%. In view of this it will be quite accurate to use only the first approximation Kihara formula. Sample calculations were also performed by us for the case when the heavier component is in trace, and this revealed that the first approximation formula is accurate within about 2% in the temperature range 400°–800°K. Similar results were found for the exp-6 potential, also. We have, consequently, used the first approximation Kihara formula for our calculations on this system throughout. Calculated curves a, b, and c refer to the isotopic mixtures having 0%, 50%, and 100% of the heavier component, respectively, and refer to the L-J (12–6) potential. It is interesting to note that the theory predicts an appreciable composition dependence for α_T, the value increases as the proportion of the lighter component increases, the maximum vari-

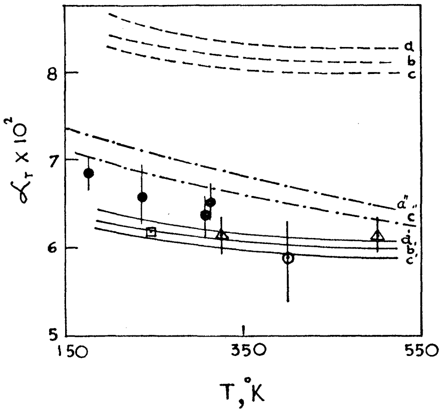

FIG. 1. Temperature dependence of α_T for the He^3–He^4 system. Experimental data: ⊙ McInteer *et al.*; ⊡ Saxena *et al.*; △ Van der Valk *et al.*; ● Watson *et al.* Theoretical curves: – – – L-J (12-6), a(x_1=0), b(x_1=0.5), c(x_1=1); —— exp-6, a′(x_1=0), b′(x_1=0.5), c′(x_1=1); –·–·– Morse potential, a″(x_1=0), c″(x_1=1).

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[31] S. C. Saxena, Physica **26**, 730 (1960).

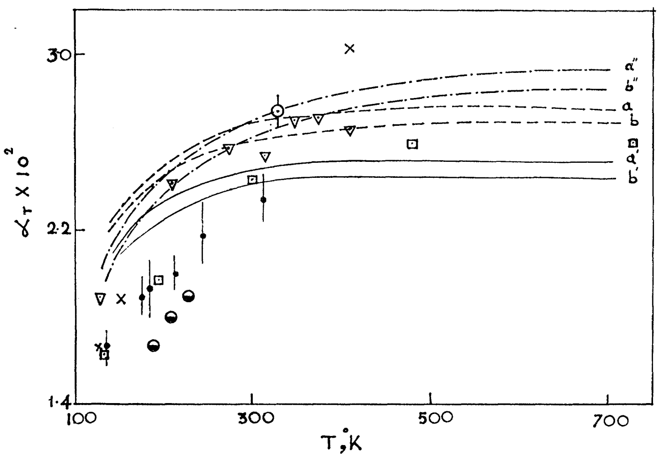

FIG. 2. Temperature dependence of α_T for the system Ne^{20}–Ne^{22}. Experimental points: × Nier; ⊙ Mann; ◒ Saxena *et al.*; ▽ Fischer; ⊡ Grew *et al.*; ● Watson *et al.* Calculated curves: --- L-J (12-6), a(x_1=0), b(x_1=0.5); —— exp-6, a′(x_1=0), b′(x_1=0.5); •——• Morse potential, a″(x_1=0), b″(x_1=0.5).

ation being 3%–4%. Thus, a carefully planned experiment having high precision can check this particular prediction of theory. At the moment even the precision of the available data is relatively more poor than the expected composition dependence. The measurements of Saxena *et al.*,[26] Van der Valk and de Varies,[27] Watson *et al.*,[28] and McInteer *et al.*[24] refer to 5%, 10%, 50%, and trace quantities of He^3, respectively. A somewhat apparent trend of the experimental data with varying composition does fall in line with the prediction of theory.

Only the exp-6 potential leads to a satisfactory agreement between theory and experiment if allowance is made for the fact that at low temperatures quantum corrections may be important. The Lennard-Jones as well as the Morse potentials over-estimate the α_T values. Thus, out of these three intermolecular potentials only the exp-6 potential is capable of correlating the equilibrium and nonequilibrium properties if one recalls the work of Mason and Rice.[32] Lennard-Jones (12–6) potential does not seem to be adequate enough to represent the force field of He. This is due to the choice of a higher force index twelve to represent the overlap part of the interaction; He molecules are much softer. This conclusion is also supported from the study of α_T data of binary mixtures involving He gas as one of the components by Saxena and Mathur.[1] In the case of the Morse potential, Bahethi and Saxena[33] found that a single set of potential parameters cannot explain both the equilibrium and nonequilibrium properties. This is further confirmed here for if we choose the second virial parameters much lower values of α_T are obtained. However, the set obtained from viscosity and found adequate to interpret thermal conductivity and diffusion is reasonable for α_T also. Consequently, this set of parameters is recommended for working on Morse potential while dealing with transport properties. This conclusion is in agreement with the finding of Bahethi, Gambhir, and Saxena,[34] who have studied the various properties of mixtures involving He with the Morse potential.

Neon

Isotopic thermal diffusion factor for Ne has been measured using the conventional two-bulb apparatus by Nier,[35] Stier,[36] Mann,[37] and Grew and Mundy[20]; and using a *trennschaukel* by Moran and Watson,[25] Saxena *et al.*,[26] Fischer,[38] and Watson *et al.*[28] As pointed out earlier by a number of workers,[39,40] and more recently by Grew and Mundy,[20] the data of Stier[36] are probably in error. We also exclude the data of Moran and Watson[25] for reasons already mentioned in connection with the discussion on He. These data are systematically smaller than the values of other workers. Rest of the data are plotted in Fig. 2. The α_T values of Grew and Mundy[20] and Watson *et al.*[23] refer to an approximately equimolar mixture of Ne^{20} and Ne^{22} while in other measurements samples of Ne used were having the natural isotopic abundance. In general, there is a very poor agreement between the data of different workers, and unfortunately, even the data obtained using the same technique present serious discrepancies and inconsistencies though the values of a worker as a function of temperature are smooth. It is not possible to pinpoint the source which can lead to simple explanations of the observed discrepancies. The need of a careful and accurate α_T measurement for this system as a function of temperature is still as essential as ever.

Convergence of the theoretical formulas for this system was judged on the basis of the formula applicable to mixtures of heavy isotopes. For L-J (12–6) and

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[32] E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 525 (1954).

[33] O. P. Bahethi and S. C. Saxena, Phys. Fluids **6**, 1774 (1963).

[34] O. P. Bahethi, R. S. Gambhir, and S. C. Saxena, Z. Naturforsch. (to be published).

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

[36] L. G. Stier, Phys. Rev. **62**, 548 (1942).

[37] A. K. Mann, Phys. Rev. **73**, 412 (1948).

[38] A. Fischer, Ph.D. thesis, Zurich (1959).

[39] E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 843 (1954).

[40] S. C. Saxena, Indian J. Phys. **29**, 587 (1955).

TABLE II. Calculated values of the $[\alpha_0']_1$ for the Morse potential.

T^*	C 3	4	5	5.5	6	8	10
1	−0.354	−0.152	0.0386	0.111	0.160	0.351	0.460
1.4	−0.271	−0.0313	0.101	0.152	0.201	0.370	0.466
2	−0.111	0.0741	0.208	0.264	0.307	0.421	0.514
3	0.0232	0.210	0.319	0.360	0.394	0.505	0.572
4	0.0783	0.266	0.378	0.419	0.452	0.545	0.608
6	0.123	0.309	0.419	0.461	0.496	0.590	0.647
8	0.126	0.320	0.434	0.475	0.509	0.605	0.664
10	0.115	0.320	0.437	0.480	0.515	0.611	0.670
20	0.0323	0.281	0.418	0.466	0.506	0.612	0.675
30	−0.0429	0.244	0.359	0.448	0.490	0.605	0.671
40	−0.107	0.212	0.376	0.432	0.477	0.597	0.668
50	−0.163	0.185	0.360	0.419	0.466	0.591	0.663
60	−0.214	0.162	0.344	0.407	0.457	0.586	0.659
70	−0.261	0.141	0.334	0.407	0.449	0.581	0.656
80	−0.305	0.122	0.322	0.455	0.441	0.577	0.654
90	−0.346	0.104	0.312	0.380	0.435	0.574	0.651
100	−0.386	0.0881	0.303	0.373	0.429	0.570	0.649
200	−0.707	−0.0345	0.237	0.321	0.386	0.548	0.635

exp-6 potentials the tabulations of Saxena,[41] Saxena and Mason,[42] and Srivastava[43] were used. For both the potentials the Kihara approximation formulas seem to be preferable, and the first-approximation expression is accurate within 1%. To investigate the composition dependence, we used Eq. (5) on the Kihara scheme. Calculations in the temperature range 100°–700°K revealed that for both the potentials α_T decreases as the proportion of the heavier component increases though in the range 50%–100%; the change is almost negligible while in the range 0%–50% the change is about 3%. Another interesting conclusion to which these calculations lead is the invalidity of Eq. (7) for this gas and the fact that one should use either Eq. (5) or Eq. (6) for precise estimation of α_T. Similar conclusions also follow for the Morse potential.

Computed values of α_T according to Eq. (5) and on the Kihara approximation scheme are also shown in Fig. 2 for all the three potentials when $X_1=0$ and 0.5. The agreement between theory and experiment is very poor and, due to the large scatter and widely different trends in the data of different workers, it is not possible to comment on the adequacy of any particular potential. The fact that the composition differs is of no help and the discrepancies become still more pronounced if one makes an attempt to reduce the data on the same composition.

Argon

Employing a two-bulb apparatus and a normal sample of Ar (0.307% Ar^{36} and 99.63% Ar^{40}) Stier[36] and Mann[37] have reported the α_T values. Moran and Watson,[25] Saxena *et al.*,[26] and Paul *et al.*[17] on the other hand exploited the *trennschaukel* and obtained the α_T values using isotopic mixture which contained 9.87%, 36.4%, and 50% of Ar^{36}. All the values except those due to Moran and Watson[25] are plotted in Fig. 3 as a function of temperature. The values are in reasonable agreement with each other though it is desirable to have a better set of values with less uncertainty in the individual values. Only such a set will be capable of uniquely answering the appropriateness of a molecular potential.

It was further established that for this case the simpler formulas obtained from the rigorous ones by expanding in powers of the proportionate mass differ-

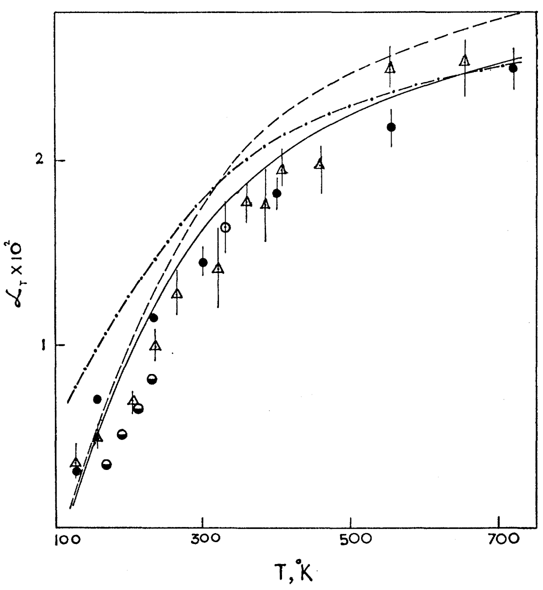

FIG. 3. Temperature dependence of α_T for the Ar^{36}–Ar^{40} system. Experimental points: ● Stier; ⊙ Mann; ⊖ Saxena *et al.*; △ Paul *et al.* Theoretical curves; – – – L-J (12-6); —— exp-6; –·–·– Morse potential.

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[41] S. C. Saxena, Proc. Phys. Soc. Japan **11**, 367 (1956).

[42] S. C. Saxena and E. A. Mason, J. Chem. Phys. **28**, 623 (1958).

[43] K. P. Srivastava, Indian J. Phys. **31**, 404 (1957).

ence are quite adequate and that there is no composition dependence. The tabulated values of α_0 of Saxena and Mason[42] were therefore used for L-J and exp-6 potentials. The Morse potential values were obtained from Eq. (7), which was found to be as adequate as Eq. (5) at least in the temperature range of Fig. 3, though it is likely to hold even for still higher temperatures. For future use we tabulate α_0 values according to Eq. (7) on this potential in Table II. The agreement between theory and experiment is best for the exp-6 potential while the other potentials fail either at low temperatures or at high temperatures.

Krypton and Xenon

There are practically no reliable data on Kr and Xe; Corbett and Watson[23] using the two-bulb apparatus were the first to report α_T data for Kr. Later Moran and Watson[25] employed *trennschaukel* to evolve α_T data for Kr and Xe. This latter set for Kr is inconsistent with the earlier values of Corbett and Watson.[23] Further, recently Saxena and Joshi[44] examined the α_T data of Moran and Watson[25] and came to the conclusion that probably these values are systematically low. Thus, unfortunately we have no reliable thermal diffusion data for these two gases and such data will be extremely useful for the proper understanding of the potential-field of these molecules.

Hydrogen

Thermal diffusion factors have been measured by a large number of workers[19,45–55] for the different isotopes of hydrogen both as a function of composition as well as temperature. We will, however, consider here only the data on H_2–D_2 system of Heath, Ibbs, and Wild[46] and Grew, Johnson, and Neal[19] on the composition dependence and of Murphy[48] and Grew, Johnson, and Neal[19] on the temperature dependence. These data are plotted in Figs. 4 and 5, respectively. In the latter case the values of Murphy[48] refer to 20% D_2 while those of Grew *et al.*[19] to 49.7% D_2. The two sets of measurements plotted in Fig. 4 are widely different, and an experimental determination to resolve this discrepancy would be very useful. The fact that Grew *et al.*[19] measurements refer to a slightly smaller temperature cannot explain the large difference in the values of the two groups of workers. Both groups have used the familiar two-bulb apparatus.

Saxena and Pardeshi[56] have made detailed calculations to determine the proper formula to be used for the different combinations of the isotopes of H_2. For H_2–D_2 mixtures, their computations which are according to the exp-6 potential suggest that the Kihara first approximation formula, Eq. (5), is accurate enough. In both Figs. 4 and 5, calculations of α_T are according to this expression and are for L-J (12–6) and exp-6 potentials. Comparison of theory and experiment does not lead to any preference for either of these two potentials as far as Fig. 4 is concerned, but on the basis of Fig. 5, exp-6 potential seems to be a better choice than the (12–6) potential. Not much importance can be attached to the values below 200°K because the magnitude of the quantum corrections is likely to be appreciable.[57] Due to the general failure of the Morse potential[58] in correlating the various properties of H_2, we have excluded it from our consideration.

Nitrogen

Mann[37] and Davenport and Winter[59] have reported the data for N_2 obtained on a two-bulb apparatus. These data are plotted in Fig. 6. Though the data of the two different groups of workers agree with each other, still there seem to be large uncertainties in the individual values as the points fail to lie on a smooth curve. Additional measurements are thus apparently needed.

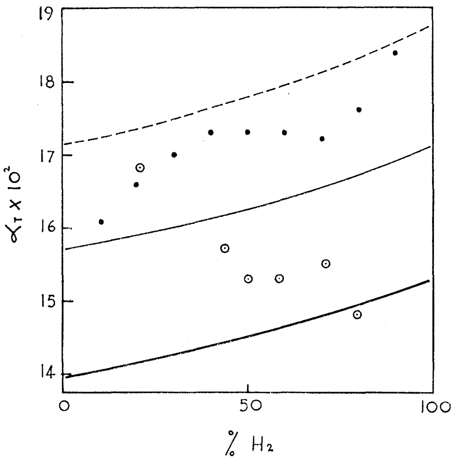

Fig. 4. Composition dependence of α_T for the H_2–D_2 system. Experimental points: ● Heath *et al.* (326°K); ⊙ Grew *et al.* (300°K). Calculated curves: - - - L-J (12-6); —— exp-6; **——** calculated from experimental diffusion and viscosity data.

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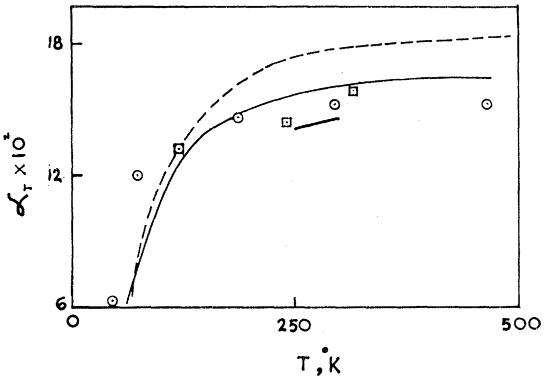

FIG. 5. Temperature dependence of α_T for the H_2–D_2 system. Experimental points: ⊡ Murphy (20% D_2); ⊙ Grew *et al.* (49.7% D_2). Theoretical curves: - - - L-J (12-6) (49.7% D_2); —— exp-6 (49.7% D_2); ━━ calculated from experimental diffusion and viscosity data.

On the basis of Eq. (5), numerical calculations indicated that there is no composition dependence of α_T and that the formula appropriate for mixtures of heavy isotopes is adequate. Calculated values shown in Fig. 6 are based on the tabulated values of Saxena and Mason[42] for the L-J potential and of Srivastava[43] for the exp-6 potential.

In view of the scatter in the experimental data, both the potentials seem to be equally good, though some preference can be attached to the L-J potential tentatively. Another point against the exp-6 potential lies in the use of the value of the parameter $\alpha = 17$, for this choice predicts no reversal in the thermal diffusion factor even at low temperatures which has been observed in a few other cases. For this reason, as pointed out by Madan,[60] the applicability of the exp-6 potential with the parameter α equal to 15 and greater is questionable.

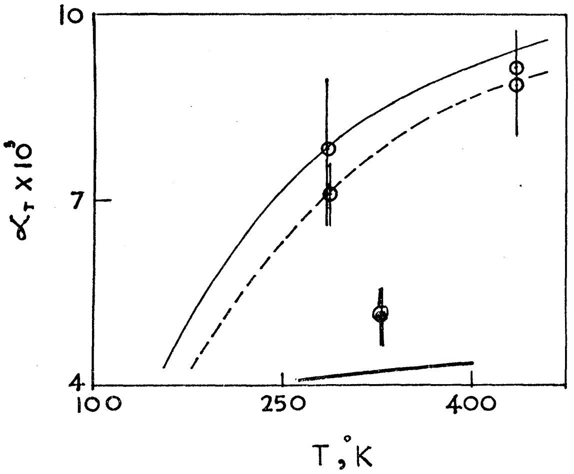

FIG. 6. Temperature dependence of α_T for the N_2^{28}–N_2^{29} system. Experimental data: ● Mann; ⊙ Davenport *et al.* Calculated curves: - - - - L-J (12-6); —— exp-6 potential; ━━ calculated from experimental diffusion and viscosity data.

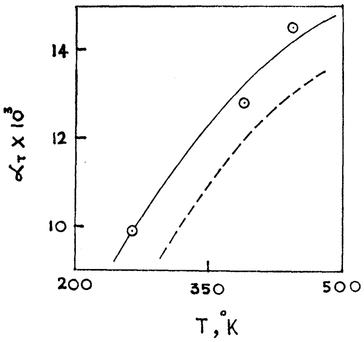

FIG. 7. Temperature dependence of α_T for the O_2^{32}–O_2^{34} system. Experimental points: ⊙ Whalley *et al.* Theoretical curves: - - - - L-J (12-6); —— exp-6 potential.

Oxygen

The only data of Whalley, Winter, and Briscoe[61] on the isotopes of oxygen are indicated in Fig. 7. They used a sample of oxygen 32 and 34 in which the latter was only 0.04% and employed a two-bulb apparatus. α_T values for oxygen are also found to be composition independent by actual calculation like nitrogen. The calculated values shown in Fig. 7 are therefore according to the tabulations of Saxena and Mason[42] for the L-J (12–6) potential and for the exp-6 potential these are according to the first approximation, Eq. (7), tabulated by Srivastava.[43] The existing limited data show preference for the exp-6 potential though in view of what has been said already in the case of N_2 it may be questionable to accept this conclusion. It seems highly desirable to have more extensive measurements of α_T so that more definite information regarding the potential field of this gas may be derived.

Carbon Monoxide

Thermal diffusion data of Davenport and Winter[59] for α_T of CO obtained on a two-bulb apparatus are displayed in Fig. 8. There is a large amount of un-

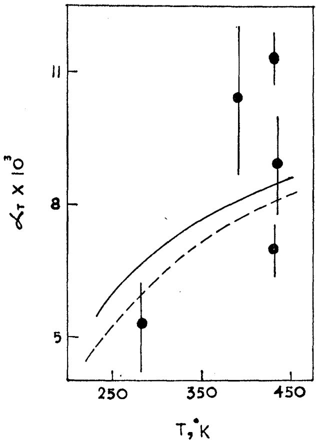

FIG. 8. Temperature dependence of α_T for the $C^{12}O^{16}$–$C^{13}O^{16}$ system. Experimental points: ● Davenport *et al.* Calculated curves: - - - - L-J (12-6); —— exp-6 potential.

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[61] E. Whalley, E. R. S. Winter, and H. V. A. Briscoe, Trans. Farday Soc. 45, 1085 (1949).

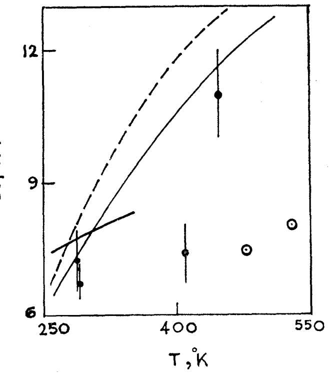

Fig. 9. Temperature dependence of α_T for the $C^{12}H_4$–$C^{13}H_4$ system. Experimental points: ⊙Nier; ● Davenport *et al*. Calculated curves: ---- L-J (12-6); —— exp-6 potential; ▬▬ calculated from experimental diffusion and viscosity data.

certainty as well as inconsistency in these measurements. α_T for this system was also found to be composition independent, and the theoretical curves for the two potentials in this case also were obtained in the same way as for N_2 and O_2, viz., on the basis of the tabulations of Saxena and Mason[42] and Srivastava.[43] The values of the two potentials do not differ much from each other as compared to the uncertainty in the individual values. Consequently, it is not possible to infer conclusively about the superiority of one potential over the other. Any definite conclusion must therefore await the availability of more reliable and elaborate measurements of α_T.

Methane

The quasi-spherical molecule methane has very often been found appropriate for interpretation on the basis of spherically symmetric potentials in conjunction with the theory of Chapman–Cowling based on elastic collision of molecules. Nier[62] and Davenport and Winter[59] have reported the α_T data obtained on the two-bulb type apparatus and these are shown in Fig. 9. Unfortunately, the two sets of measurements are not in agreement even if we keep in mind the large scatter of the various points and their individual uncertainties. Like practically all other gases new careful measurements are needed for this system also.

Based on the first approximation formula of Kihara for α_T, [Eq. (5)], sample calculations in this temperature range (according to the exp-6 potential) predicted that the composition dependence is small, and it remains always less than a percent within the two extreme limits of composition. Consequently, for both the potentials the tabulations of Saxena and Mason[42] were used, and the values so obtained are also shown in Fig. 9. Due to large uncertainties in the experimental data, it is hard to conclude anything definite on the adequacy of theory though exp-6 potential may be a better choice for expressing the behavior of this gas bears out from Fig. 9 to some extent. The two sets of available exp-6 potential parameters lead to identical results in the temperature range of Fig. 9.

Ammonia and Hydrogen Chloride

So far we have discussed only the nonpolar gases. Meager data are available for the two polar gases NH_3[63] and HCl[64] obtained on the two-bulb apparatus. Unfortunately, the uncertainty in these values is so great that no precise interpretation is possible. The best that has been obtained so far on the calculation of the transport properties of polar gases theoretically is the work of Monchick and Mason.[11] They assume a potential of the type of Eq. (4) and determine the two parameters ϵ and σ_0 from viscosity while the third parameter δ is so adjusted in the process of determining the potential parameters that it satisfies the relation

$$4\epsilon_0\sigma_0^3\delta_{\max}=2\mu^2. \qquad (15)$$

Within rather large uncertainty in the experimental data, it is hard to say anything definite and indeed Monchick and Mason[11] found reasonable agreement. Consequently, at the moment our knowledge of α_T of polar gases is very poor, and it would be a great help to obtain reliable measurements of the thermal diffusion factor.

VI. DISCUSSION OF RESULTS

In the previous section we have discussed in detail the experimental data of three inert gases, viz., He, Ne, and Ar. These gases, which are composed of monatomic spherically symmetric molecules, are most appropriate for interpretation in terms of the Chapman–Enskog kinetic theory in conjunction with central force models. Saxena, Kelley, and Watson[26] have confirmed this expectation also by expressing α_T as a function of only measurable quantities. However, a critical study of the behavior of these gases tends to suggest that most probably the exp-6 potential is the best of all the known potential functions for purposes of correlating and predicting the properties. The need of a consistent set of precise α_T values as a function of temperature is an urgent one. Investigations of the composition dependence of α_T also hold enough curious promise in a few cases. Obviously the measurements should also extend to other inert gases. It is also very likely that a reliable set of α_T values at low temperatures for He may prove to be of great value in throwing light on the nature and magnitude of quantum corrections.

We have also considered five of the simple diatomic molecules, viz., H_2, D_2, N_2, CO, and O_2. The data of α_T for these gases are also analysed on the basis of Chapman–Enskog kinetic theory. As these molecules possess rotational and vibrational modes,[65] the whole procedure is open to objection. The underlying confidence has been the usual experience of the success achieved by this theory in the description of the various equilibrium

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and nonequilibrium properties of polyatomic gases. Incentive to this approach has also been added by the indirect support advanced by Weissman, Saxena, and Mason[22,66] from the study of α_T for mixtures involving polyatomic gases. They[66] expressed the binary α_T expression in favor of such quantities which are experimentally known and showed that within the uncertainties of the experimental data it is possible to correlate the mixture properties of some gas pairs involving polyatomic molecules even on the basis of Chapman–Enskog theory and central interatomic potentials. As shown by Saxena, Kelley, and Watson,[26]

$$A^* = (\tfrac{5}{6})(\rho D/\eta), \tag{16}$$

and

$$(6C^* - 5) = 2[2 - (\partial \ln D/\partial \ln T)_p]. \tag{17}$$

Here ρ, D, η, and p represent the density, diffusion, viscosity, and pressure of the gas, respectively. Let us further assume that Eq. (7) is accurate enough to represent α_0 for these gases. This, as will be seen later, is not a bad approximation in view of the large uncertainty that gets associated with the calculation of α_0 on the basis of Eq. (7) in conjunction with Eqs. (16) and (17). Also Eq. (7) has been shown to be accurate enough for all these gases except the isotopes of H_2. One can therefore compute α_0 easily if the coefficients of diffusion, viscosity, and the slope of ln D vs ln T curve at a fixed pressure be known at that temperature. We now report the results so obtained for all these five gases.

For H_2 the diffusion data[67] are available in the temperature range 85°–293°K, and these lead to a linear plot between ln D and ln T with a slope of 1.73 over the entire range. This, in conjunction with the viscosity data,[68] leads to α_T values on the basis of Eqs. (5), (16), and (17) as shown in Fig. 5 with a heavy solid line. These values are in reasonable agreement with the direct measured values. Similarly to check the composition dependence calculations were performed again using Eq. (5) along with Eqs. (16) and (17). These α_T values are shown in Fig. 4. These values are in better agreement with the data of Grew *et al.*[19] the discrepancies in the composition range 0%–50% of H_2 are rather serious. Thus, though on the basis of Figs. 4 and 5, it seems that the data of Grew *et al.*[19] is probably relatively more accurate than Heath *et al.*[46] still, even these data are not fully explained on the basis of Chapman–Enskog theory. A careful study suggests a precise redetermination of α_T values, and further the Chapman–Enskog theory is reasonably well competent to correlate the existing data specially in view of the large associated uncertainty in them.

For N_2 the diffusion data have been reported[69] in the temperature range 77°–350°K, and these lead to a constant value of 1.86 for $\partial \ln D/\partial \ln T$. Viscosity data[68] are also available, and when all these are used to compute α_0 according to Eqs. (7), (16), and (17), we get the values shown in Fig. 6 by the heavy solid line. The general large scatter, and the strangeness in the α_T value at 326°K offer some difficulty in interpretation. We can make two general observations. Firstly, the values indirectly obtained from diffusion and viscosity data are smaller than the directly observed values, and secondly, the observed temperature dependence of α_T data is much more pronounced than suggested by the indirect α_T values. Partly, this pronounced disagreement is due to the lack of accurate diffusion data which reflects in our inability to determine $\partial \ln D/\partial \ln T$ with enough precision on which α_T sensitively depends. However, the good agreement of the computed α_T values with the directly measured values is not, in our opinion, fortuitous, and in view of all that has been said above, we may conclude that the assumption of a central force-field is reasonably satisfactory for correlating the properties of this gas at least over the limited temperature range of our investigation. This tentative conclusion may require some modification when α_T data become available at higher temperatures where internal degrees will play a more pronounced role.[65]

An indirect check is further possible regarding the conclusion drawn for N_2 on the basis of CO data. Unfortunately this possibility is seriously handicapped by the lack of diffusion data for CO. Nevertheless, the similarity in the nature and the degree of agreement obtained between theory and experiment for this molecule (Fig. 8) with that for N_2 (Fig. 6) tend to support and substantiate the conclusion drawn in the case of N_2. Diffusion and α_T data at extended temperatures both for N_2 and CO will be of great assistance in further investigating with reliance the possibility of interpreting these simple gases on the basis of central force-field potentials.

O_2 is also an interesting gas for a study of this type. Diffusion data[69] for this gas are available in the temperature range 77°–353°K. The data exhibit enough internal consistency and ln D vs ln T was again found to be a linear plot in this temperature range, surprisingly enough, with a slope of two. On the basis of this, α_T value will be zero or at least very small in this temperature range. Direct measurements (Fig. 7) contradict this prediction. Thus, if reliance could be placed on the accuracy of diffusion data, one would doubt about the applicability of Chapman–Enskog theory to this gas. On the other hand, Fig. 7 shows a reasonably good agreement between theory and experiment. Further, since the indirectly generated α_T values are generally smaller than the directly measured values, we may tentatively conclude that the situation as regards this

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gas may be essentially the same as for the other diatomic gases considered here.

We may try a similar procedure for CH_4 because of its quasi-spherical nature. Diffusion data[70] for this gas are available again for the temperature range of 77°–353°K which lead to a constant value of 1.84 for $\partial \ln D/\partial \ln T$. This information in conjunction with the viscosity data[68] and Eqs. (7), (16), and (17) lead to α_T values shown in Fig. 9. The agreement with the directly obtained values can definitely be regarded as satisfactory in view of the large scatter of the thermal diffusion data. Consequently, in this limited temperature range, the correlation of the various properties of this gas on the basis of Chapman–Enskog theory seem to be possible.

On the whole we find that only approximate success is possible in the attempt to interpret the properties of complicated polyatomic molecules on the basis of Chapman–Enskog kinetic theory. Good success has been achieved here for the data considered are limited in temperature range and in most cases are of poor accuracy. The interpretation at high temperatures is likely to suffer more as rotational and vibrational modes will add appreciably to the energy of the molecule. Adequate solution of this difficulty lies in the development of the rigorous kinetic theory of nonspherical molecules. Curtiss and his collaborators[71] have contributed towards this complicated task. They have developed the kinetic theory based on classical mechanics of nonspherical molecules and specialized it for certain shapes of the molecules. Unfortunately, the detailed calculations have not yet been performed to a stage where application to actual systems is possible. A formal quantum-mechanical kinetic theory taking into account the inelastic nature of the molecular collisions has also been developed for pure gases by Wang Chang and Uhlenbeck[72] and de Boer.[73] Taxman[74] also has given the classical theory for such systems as an extension of the Chapman–Enskog kinetic theory. All these approaches[72–74] lead to expressions for the transport coefficients in terms of certain integrals, the solution of which appear almost hopelessly difficult. Recently Mason and Monchick[75] have indicated a practical way of evaluating these integrals and have derived expressions for the transport properties of pure gases. This theory indicated an appreciable correction for the case of thermal conductivity only. Saxena, Saksena, and Gambhir[76] have also developed a theory for the thermal conductivity of polyatomic gases, and the results apparently are similar to those obtained by Mason and Monchick.[75] Recently Monchick, Yun, and Mason[77] have given a formal kinetic theory of polyatomic gas mixtures by extending the Wang Chang and Uhlenbeck theory to mixtures. They have derived expressions for the various properties including α_T but the form is still not appropriate for actual numerical calculations. We hope that they will simplify these expressions also as for pure gases,[75] and then the interpretation of data may be possible. The interesting result that they have derived[77] which is relevant for our present discussion is that α_T is likely to be seriously affected by the presence of internal degrees of freedom. No quantitative indication can be made except their calculations for the specialized case of a "dusty gas" which indicate that the values obtained from the Chapman–Enskog theory will be reduced, a trend which is indicated by the indirect calculations of α_T, also. The work on the development of the properties of mixtures of polyatomic gases is rather limited and the only two efforts are in the area of thermal conductivity by Hirschfelder[78] and Saxena, Saksena, Gambhir, and Gandhi.[79]

The prospect of achieving only limited success in explaining α_T data of nonspherical molecules on the basis of Chapman–Enskog theory of spherical molecules has started accumulating in recent years. Becker *et al.*[80] were the first to plan suitable experiments using isotopic–isobaric systems. Work in this direction has also been continued by Schirdewahn *et al.*[53] and Slieker.[55] The former workers[53] have suggested an empirical formula derived on the basis of dimensional analysis which has also received some support from the measurements of Slieker.[55] However, much still remains to be done to make this entirely empirical approach reliable and we hope rigorous theories may provide a lead.

ACKNOWLEDGMENT

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