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Thermal Diffusion in Binary Gas Mixtures and Intermolecular Forces*

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The available binary thermal diffusion data for a number of gas systems as a function of temperature and composition have been critically examined and interpreted using the kinetic theory of Chapman and Enskog. In the computation of the thermal diffusion factor α_T two familiar central intermolecular potentials, viz., Lennard-Jones (12–6) and modified Buckingham exp-six have been considered. The theoretical expressions for α_T employed are of known and tolerable accuracy so that the uncertainty associated on this account in many early interpretations is avoided in this study. The scope of work is confined mostly to inert gas mixtures as the kinetic theory is rigorously developed so far only for such systems. This comprehensive effort brings to light many interesting points. A general deficiency is realized in the available α_T data. Even for some systems where data exist as a function of composition, it is found that the composition range which is theoretically interesting is not investigated. This study also leads to the unpleasant prospect that some of the available data may be in error. Thus, many indications are provided for planning future work on α_T measurements. Further, the L–J (12–6) potential is found to be inadequate for representing the force field of these molecules and especially for such systems where He is one of the two components. To be specific, the choice of a repulsive index as twelve is found to be a bit large. The exp-six potential has succeeded in general to explain the α_T data of many of the systems discussed in this article.

I. INTRODUCTION

Since the prediction of the phenomenon of thermal diffusion in gases by Chapman,[1] and by Enskog,[2] and its experimental confirmation by Chapman and Dootson,[3] several efforts have been made to measure the thermal diffusion factor α_T both for isotopic as well as nonisotopic gas mixtures. Chapman[4] and others emphasized the importance of α_T in investigating the nature of intermolecular forces and this provided some incentive to the experimentalists for producing appropriate data. The various measurements of α_T reported till 1952 are given in the excellent monograph of Grew and Ibbs.[5] Recently, techniques have been improved[6] and also developed[7–9] which enable the determination of α_T very precisely. However, even among earlier measurements, the values reported by Atkins, Bastick, and Ibbs[10] on the composition dependence and by Grew[11] on the temperature dependence are fairly extensive and accurate. Most of the efforts[12–14] directed towards examining the adequacy of a particular potential energy function usually involved the computation of theoretical α_T values and their comparison with the experimental values. The reverse approach, that is the determination of the potential energy function from the knowledge of the thermal diffusion data was not in fashion till the work of Srivastava and Madan.[15,16] These methods were further refined and elaborated by Saxena,[17,18] and by Saxena and Srivastava.[19] In the work of Srivastava and Madan[15,16] as well as in the more recent work of Srivastava and Srivastava,[20] and Srivastava[21] only the first-approximation expression to α_T is used. The contribution of the second approximation to the determination of potential parameters was investigated[17–19] for a few systems and as such suspicion is raised[22] against the values of the potential parameters determined using the first-approximation expression for α_T.

A great advance in this direction was initiated by Mason,[23] who determined the higher approximations to α_T and studied the convergence for certain specialized types of binary mixtures. However, this work also did not help directly in assessing the magnitudes of higher approximations for actual gas mixtures which might have thrown some light on the appropriateness

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

[2] D. Enskog, Physik. Z. **12,** 56, 533 (1911); Ann. Phys. (N.Y.) **38,** 731 (1912); dissertation, Uppsala, 1917 (unpublished).

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[13] E. A. Mason, J. Chem. Phys. **23,** 49 (1955).

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

[17] S. C. Saxena, Indian J. Phys. **29,** 131 (1955).

[18] S. C. Saxena, Indian J. Phys. **29,** 453 (1955).

[19] S. C. Saxena and B. N. Srivastava, J. Chem. Phys. **23,** 1571 (1955).

[20] B. N. Srivastava and K. P. Srivastava, Physica **23,** 103 (1957).

[21] K. P. Srivastava, J. Chem. Phys. **26,** 579 (1957).

[22] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

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

of the earlier work based on the first-approximation expression to α_T. The situation for the case of isotopes was cleared rather soon. Saxena and Mason[24] tabulated the α_T values for heavy isotopes and the two particular cases of He and H_2 have also since been studied in detail by Saxena and Pardeshi.[25] The difficulty in the case of binary mixtures was essentially one of computational labor. This necessitated looking into the possibility of simplifying the rigorous expressions without loss of accuracy. Saxena and Dave,[26,27] Saxena, Dave, and Pardeshi,[28] and Saxena and Joshi[29–33] have derived such expressions starting from the rigorous expressions and making different types of approximations.

This article analyzes some of the available experimental α_T data in terms of either the rigorous theoretical expressions derived in the Chapman–Enskog theory[34] or their simpler versions[26–33] with a view to deriving information regarding the nature of intermolecular forces.

Table I. Lennard-Jones (12–6) potential parameters for gases and gas mixtures.[a]

Gas	ϵ/k (°K)	σ (Å)	Gas mixtures[a]	ϵ_{12}/k (°K)	σ_{12} (Å)
H_2	37.0	2.928	Xe–H_2	92.21	3.433
D_2	37.0	2.928	Xe–D_2	92.21	3.433
He	10.22	2.556	Xe–He	48.46	3.247
Ne	35.60	2.749	Xe–Ne	90.45	3.343
Ar	119.8	3.405	Xe–Ar	165.9	3.671
Kr	167	3.679	Kr–He	41.31	3.118
Xe	229.8	3.937	Kr–Ne	77.11	3.214
Rn	484	4.48	Rn–Ne	131.3	3.615
...	...	...	Rn–Ar	240.82	3.942

[a] Parameters for pure gases are those given by R. J. Lunbeck, thesis, Amsterdam, 1951 (unpublished) except for Kr and Rn. The krypton parameters of E. Whalley and W. G. Schnieder, J. Chem. Phys. **23**, 1644 (1955) and the Rn ones of B. N. Srivastava and S. C. Saxena, Physica **22**, 253 (1956) are listed. Parameters for the gas mixtures are derived from the corresponding pure gas values by adopting the geometric mean rule for ϵ_{12} and arithmetic mean rule for σ_{12}.

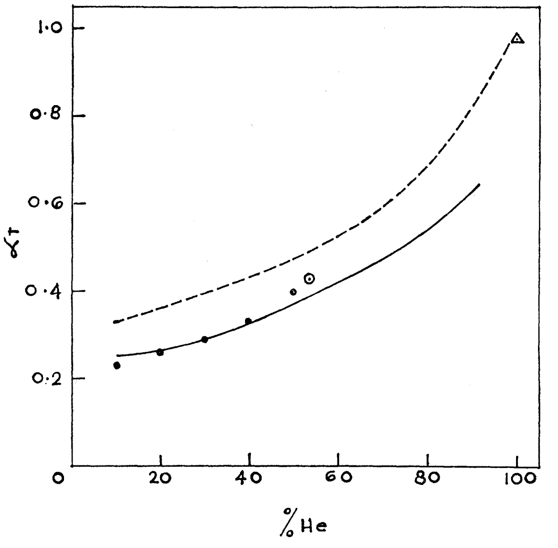

Fig. 1. Composition dependence of α_T for the He–Xe system at 326°K. Experimental data: ● Atkins *et al.*; ⊙ Grew; △ Heymann and Kistemaker. Theoretical curves: — exp-six; - - - L-J (12–6) potentials.

The discussion is confined mostly to mixtures of noble gases for the theory rigorously applies only to such systems.

We consider only two types of potential energy functions which have proved very successful[22] in correlating and explaining the various properties of gases. These are the familiar Lennard-Jones (12–6) potential,

$$\Phi(r)=4\epsilon[(r_0/r)^{12}-(r_0/r)^6], \tag{1}$$

$$\Phi(r)=\frac{\epsilon\alpha}{\alpha-6}\left[\frac{6}{\alpha}\exp\left\{\alpha\left(1-\frac{r}{r_m}\right)\right\}-\left(\frac{r_m}{r}\right)^6\right]. \tag{2}$$

Here, $\Phi(r)$ represents the interaction potential energy at the molecular separation r, ϵ the depth of the potential energy minimum, α a parameter which determines the steepness of the repulsive part of the potential energy, r_0 and r_m are the values of r for which the potential energy is zero and minimum, respectively.

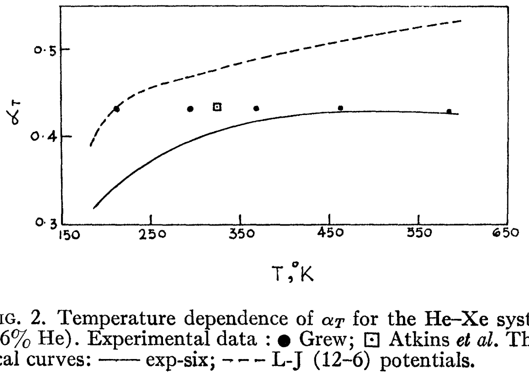

Fig. 2. Temperature dependence of α_T for the He–Xe system (53.6% He). Experimental data : ● Grew; ⊡ Atkins *et al.* Theoretical curves: —— exp-six; - - - L-J (12–6) potentials.

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

[25] S. C. Saxena and P. A. Pardeshi, Indian J. Phys. **35**, 55 (1961); **36**, 13 (1962).

[26] S. C. Saxena and S. M. Dave, Rev. Mod. Phys. **33**, 148 (1961).

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[28] S. C. Saxena, S. M. Dave, and P. A. Pardeshi, Can. J. Phys. **40**, 1608 (1962).

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[31] S. C. Saxena and R. K. Joshi, J. Phys. Soc. (Japan) **18**, 702 (1963).

[32] R. K. Joshi and S. C. Saxena, Z. Naturforsch. **19a**, 314 (1964).

[33] S. C. Saxena and R. K. Joshi, Physica **29**, 207 (1963); Indian J. Phys. **37**, 479 (1963).

[34] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1952).

Table II. Exponential-six potential parameters for gases and gas mixtures.[a]

Gas	ϵ/k (°K)	r_m (Å)	α	Gas mixture	ϵ_{12}/k (°K)	$(r_m)_{12}$ (Å)	α_{12}
H_2	37.3	3.337	14.0	Xe–H_2	110.1	3.739	13.31
D_2	37.3	3.337	14.0	Xe–D_2	110.1	3.739	13.31
He	9.16	3.135	12.4	Xe–He	52.3	3.650	12.55
Ne	38.0	3.147	14.5	Xe–Ne	121.8	3.574	13.45
Ar	123.2	3.866	14.0	Xe–Ar	178.5	4.108	13.44
Xe	231.2	4.450	13.0	He–Ar	33.4	3.488	13.21
				He–Ne	18.71	3.143	13.46

[a] These parameters are those given by E. A. Mason, J. Chem. Phys. 23, 49 (1955).

II. THEORETICAL FORMULAS FOR α_T

The rigorous Chapman–Enskog[34] theory expresses α_T as the ratio of infinite determinants. This expression is finally put in the form of an infinite series by two alternative procedures. One is due to Chapman and Cowling,[34] and the other to Kihara[35] which has been further extended by Mason.[23] Thus, we get two sets of rigorous formulas for α_T, one on each approximation scheme. These rigorous expressions have been further simplified[26–33] by applying different criteria to rigorous α_T expressions for different types of binary mixtures. A critical review of these formulas is given by Saxena and Joshi.[36] For the sake of brevity we do not reproduce here the relevant expressions. It is however pertinent to quote two inferences of this study[36] which are relevant to our present work: (1) in general, for binary mixtures while dealing with the temperature and composition dependence of α_T, one can use with enough accuracy the doubly approximated formula derived by Saxena and Joshi[31] on the Kihira approximation scheme; (2) if the binary mixture contains the heavier component in trace, formulas derived by Saxena and Dave[26] are appropriate. In the next section we interpret the α_T results for actual binary systems.

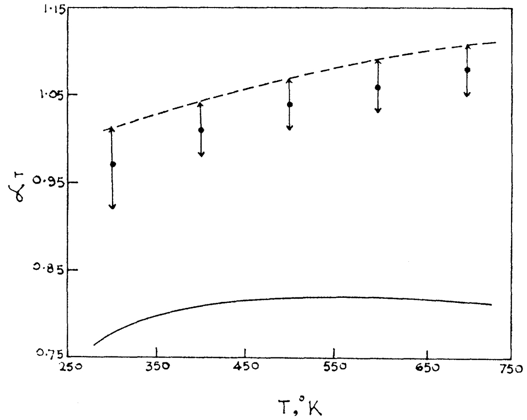

Fig. 3. The legend is same as in Fig. 2 except Xe is in trace and experimental points are of Heymann and Kistemaker.

III. COMPARISON OF THEORETICAL AND EXPERIMENTAL α_T VALUES

We will discuss the experimental α_T data of Atkins, Bastick, and Ibbs[10] on the composition dependence, and of Grew,[11] and Heymann and Kistemaker[7] on the temperature dependence. The latter workers have used binary systems where radioactive Xe in trace has always been used as one of the components. We also consider some of the results of Ghozlan,[37] and of Grew and Mundy.[38] The former workers[37] have used binary mixtures containing radioactive Kr in trace, while the latter[38] radioactive Rn in trace. The data of different workers on the same system are considered together and are compared with theory with a view to deriving information regarding the nature of intermolecular forces. The potential parameters used in these calculations are those given in Tables I and II.

The experimental data for the He–Xe system of Atkins *et al.*[10] are plotted in Fig. 1. The points of Grew[11] and Heymann and Kistemaker[7] are also shown. The data of Atkins *et al.*[10] and of Grew[11] are definitely consistent though nothing very definite can be said about the point of Heymann and Kistemaker[7] because of the uncertainty involved in the large extrapolation. Calculated curves both according to the L-J (12–6) and exp-six potentials are also shown in the figure and are based on the doubly approximated formulas given by Saxen and Joshi.[31] The estimated accuracy of these curves is approximately one percent. The experimental values are in good agreement with the computed values in the case of exp-six potential. The L-J (12–6) values are systematically greater than the experimental values and by an amount which is much larger than the uncertainty in the data.

The experimental data for the He–Xe system of

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

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[37] A. I. Ghozlan, Ph.D. thesis, Amsterdam, 1963 (unpublished); A. I. Ghozlan and J. Kistemaker, Kernenergie 4, 287 (1962).

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

Grew[11] and the point of Atkins *et al.*[10] along with the two sets of calculated values as a function of temperature are shown in Fig. 2. The accuracy of these theoretical curves which are again based on the doubly approximated formulas[31] is within a couple of percent. Here also, as in Fig. 1, the exp-six potential predicts the values satisfactorily except at low temperatures where quantum effects may be important,[39] while the (12–6) potential overestimates the α_T values. The data of Heymann and Kistemaker[7] as a function of temperature for this system are plotted in Fig. 3. Values on both the potentials are calculated according to the following formula[40]:

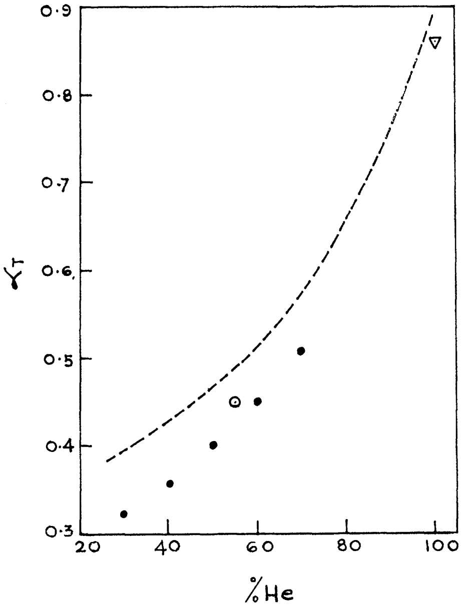

FIG. 4. Composition dependence of α_T for He–Kr system at 326°K. Experimental data: ● Atkins *et al.*; ⊙ Grew; ▽ Ghozlan and Kistemaker, calculated curve on L-J (12–6) potential.

$$[\alpha_T']_2=[\alpha_T]_1(1+K), \qquad (3)$$

where

$$K=(c/21)[\tfrac{1}{2}c+2d(1-M)]. \qquad (4)$$

Here c and d are as defined by Saxena and Dave.[26] The accuracy of these curves is better than 2%. The measurements of Fig. 3 refer to approximately the same temperature range as Fig. 2. Surprisingly enough, we find in Fig. 3 that the L-J (12–6) values are in good agreement with the experimental values while the exp-six values are much smaller. Thus, the inference which can be derived from Fig. 3 is inconsistent with the one that follows from an examination of Figs. 1 and 2. One possible way out of this inconsistency is to assume the experimental α_T values of Heymann and Kistemaker[7] to be systematically larger than the true values. We can then conclude that only the exp-six potential is capable of representing the force field of this system while the L-J (12–6) potential is not. This inference is in agreement with that of Mason and Rice[41] for the He–He interaction, and of Weissman, Saxena, and Mason[40] for the He–Ar system. No such possibility which may suggest the data of Heymann and Kistemaker[7] to be systematically larger than the true values follows from their work. The discussion given later on some other systems of these workers, however, substantiates this viewpoint and has encouraged us to advance this possibility. We also show later on that the reason for the L-J (12–6) values to be systematically larger than the experimental values lies in the choice of a large value (twelfth) for the repulsive force index in the potential. This is too steep a potential to represent He–Xe interaction. This analysis also suggests the need of more data as a function of composition

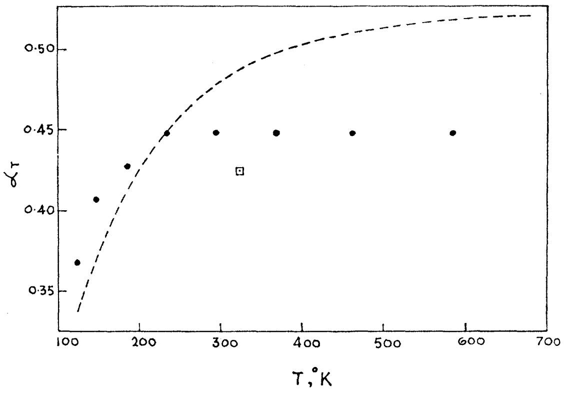

FIG. 5. Temperature dependence of α_T for He–Kr system (55.0% He). Experimental data: ● Grew; ⊡ Atkins *et al.*, calculated curve on L-J (12–6) potential.

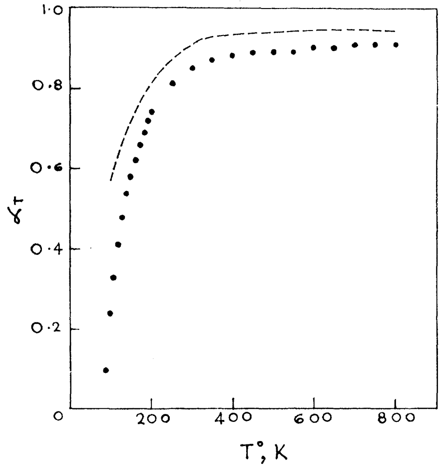

FIG. 6. The legend is same as in Fig. 5 except Kr is in trace and experimental points are of Ghozlan and Kistemaker.

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

[40] S. Weissman, S. C. Saxena, and E. A. Mason, Phys. Fluids **3**, 510 (1960).

[41] E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 522 (1954).

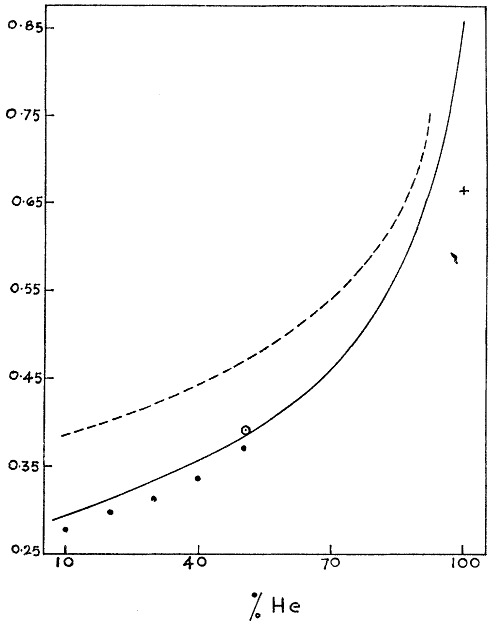

FIG. 7. Composition dependence of α_T for Ar–He system at 326°K. Experimental data: ● Atkins *et al.*; ⊙ Grew; + Saxena and Mason. Theoretical curves: —— exp-six; - - - L-J (12–6) potentials.

specially for higher proportions of the lighter component (He).

The experimental data for the He–Kr system as a function of composition[10] are shown in Fig. 4 along with the points of Grew,[11] and Ghozlan and Kistemaker.[37] Calculated values on the L-J (12–6) potential according to the doubly approximated formulas[31] are also plotted in this figure and are accurate to within a couple of percent. Computations were not performed for the exp-six potential for, as shown by Bahethi and Saxena,[42] this potential fails to correlate the various properties of Kr gas. Experimental data as a function of temperature of Grew[11] along with one point of Atkins *et al.*[10] are plotted in Fig. 5. The dashed curve is obtained in the same way as in Fig. 4 and its accuracy is approximately one percent above 200°K. From an examination of both these figures it follows that the experimental values of Grew[11] are somewhat larger than those of Atkins *et al.*[10] Further, the computed values are always larger than the experimental values if some allowance is made for quantum corrections at low temperatures, and if the dashed curve of Fig. 5 is shifted to the left so that the temperature after which α_T becomes almost constant coincides with the corresponding temperature for the experimental curve. The important point is that the theoretical constant α_T value is much larger than the constant experimental value.

The experimental α_T values of Ghozlan and Kistemaker[37] for this system where Kr is in trace are shown in Fig. 6 along with the computed curves on the L-J potential using Eqs. (3) and (4). The accuracy of the theoretical curve is around one percent. From Fig. 4 we also find that the data of Ghozlan *et al.*[37] are probably consistent with those of Atkins *et al.*[10] A careful study of Fig. 6 again confirms the same over-all picture obtained from the examination of Figs. 4 and 5. The agreement between theory and experiment improves at higher temperatures but still the calculated values are always larger than the experimental values. The large discrepancy at low temperatures may be of quantum origin. The reason for the failure of the L-J potential for this system in our opinion is again due to the choice of a large value, twelve, for the repulsive force index as in the case of the He–Xe system. This is explained later on.

The He–Ar system, like the two previous systems, is one of those for which enough experimental data are available. Saxena and Mason[9] have reported the α_T data as a function of temperature for this system with Ar in trace. Weissman, Saxena, and Mason[40] have interpreted these data and arrived at the conclusion that L-J (12–6) potential is inadequate and that inverse twelfth power repulsion is too steep for He–Ar interaction. They[40] also found the exp-six potential to yield α_T values in good agreement with the experimental values. It will be interesting to see how far these conclusions are substantiated by the two other sets of measurements.

Composition dependence data of Atkins *et al.*[10] as well as the points of Grew,[11] and of Saxena and Mason[9] are shown in Fig. 7. The different measurements seem to be in reasonable agreement. Computed values are according to the doubly approximated expressions[31] and the convergence error though negligible for the exp-six curve assumes an appreciable magnitude, a couple of percent on the average, for the L-J curve. The agreement between theory and experiment is satisfactory for the exp-six curve while in the case of L-J potential

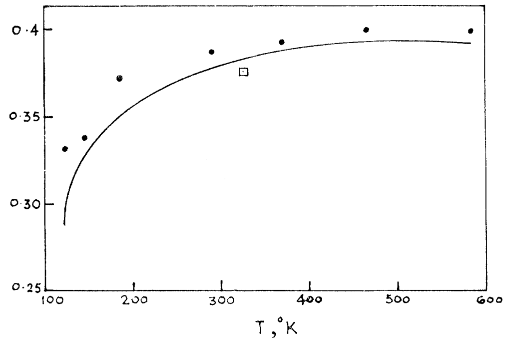

FIG. 8. Temperature dependence of α_T for Ar–He system (51.2% He). Experimental data: ● Grew; ⊡ Atkins *et al.*, calculated curve on exp-six potential.

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[42] O. P. Bahethi and S. C. Saxena, Indian J. Pure Appl. Phys. **3**, 12 (1965).

the calculated values are systematically larger than the experimental values. The experimental data of Grew[11] as a function of temperature are plotted in Fig. 8 along with the computed curve again according to the doubly approximated expressions,[31] on the exp-six potential. The theoretical curve which is accurate to within 1% above 200°K is in satisfactory agreement with the experimental points. Sample calculations on the L-J potential again showed the same trend of yielding higher values than the experimental ones. Thus, we find that the inference derived earlier by Weissman, Saxena, and Mason[40] regarding the force field of this system is confirmed, and that all the three sets of measurements lead to one consistent conclusion.

For all these three systems (He–Xe, He–Kr, and He–Ar) it is possible to show that the reason for the failure of the L-J (12–6) potential is not due to the combination rules used to determine the unlike parameters from the parameters of pure gases but is basic to the choice of the model. The argument[40] is as follows:

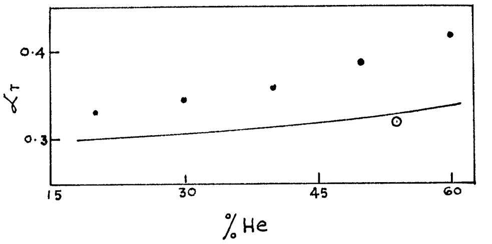

FIG. 9. Composition dependence of α_T for He–Ne system at 326°K. Experimental data: ● Atkins *et al.*; ⊙ Grew, calculated curve on exp-six potential.

For these systems it is possible to cast the expression for $[\alpha_T']_2$ in the following form:

$$[\alpha_T']_2=[\alpha_T]_1(1+g_2)=(6C^*-5)g_1(1+g_2). \quad (5)$$

The quantity $(6C^*-5)$ increases with increasing reduced temperature until it becomes very nearly constant at high values of the reduced temperature. At such high temperatures both g_1 and g_2 are approximately temperature-independent so that the constant $[\alpha_T']_2$ value is essentially controlled by the value of the factor $(6C^*-5)$. The height of the plateau is determined by the steepness of repulsion energy; a "hard" repulsion giving rise to a high plateau value of $(6C^*-5)$ and a soft repulsion to a low value.[40,22] It was found, as can also be seen from the Figs. 2, 3, 5, and 6, that the theoretical value of the plateau is much larger than the experimental value. The only way to bring them into agreement would be to lower the power twelve in the repulsion energy. The obvious implication is that the twelfth power repulsion is too "hard" for these systems. A similar conclusion has been previously drawn for the system He–He [41] and He–Ar.[40]

The data for the He–Ne system of Atkins *et al.*[10] are plotted in Fig. 9, and of Grew[11] in Fig. 10. To see the relative consistency of these two sets of data we have shown on each plot the point of the other measurement. The points of Grew[11] are considerably lower than those of Atkins *et al.*[10] Further, the measurements of Grew[11] clearly indicate that the experimental values have attained a constant value and the height of the plateau is much smaller than can be guessed on the basis of the *Atkins et al.*[10] measurements. Also shown in these figures are the calculated curves on the exp-six potential using the doubly approximated expressions.[31] The accuracy of the curve in Fig. 9 is approximately 3% while in Fig. 10 it is better than 2% above 200°K. The agreement between theory and experiment, while poor in the case of Fig. 9, is good in Fig. 10. In view of our general experience about the failure of the L-J potential for mixtures involving combinations of He with other noble gases, calculations were not performed on this potential. Further, if weight is put on this inference it follows immediately that the data of Atkins *et al.*[10] for the He–He system are systematically larger than the correct values. This analysis thus strongly suggests that α_T values for this system be measured as a function of composition at several temperatures to clarify the existing discrepancy.

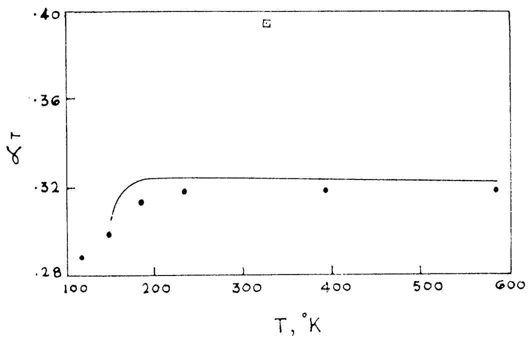

FIG. 10. Temperature dependence of α_T for He–Ne system (53.8% He). Experimental data: ● Grew; ⊡ Atkins *et al.*, calculated curve on exp-six potential.

The Ar–Xe system is of particular interest for besides enough experimental data, detailed theoretical

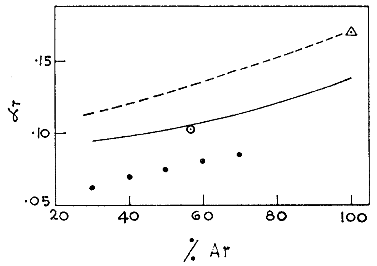

FIG. 11. Composition dependence of α_T for Ar–Xe system at 326°K. Experimental data: ● Atkins *et al.*; ⊙ Grew; △ Heymann and Kistemaker. Calculated curves: —— exp-six; - - - L-J (12–6) potentials.

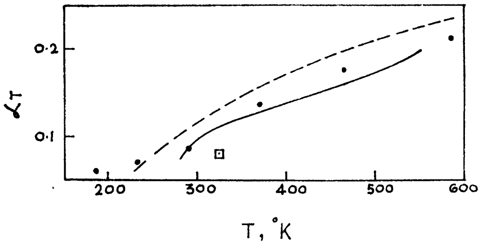

Fig. 12. Temperature dependence of α_T for Ar–Xe system (56.4% Ar). Experimental data: ● Grew; ⊡ Atkins *et al.* Theoretical curves: —— exp-six; - - - L-J (12–6) potentials.

calculations, are also available for this system. The experimental data as a function of composition of Atkins *et al.*,[10] and as a function of temperature of Grew,[11] and of Heymann and Kistemaker[7] are plotted in Figs. 11, 12, and 13, respectively. Nothing definite can be said about the relative consistency of the data of Heymann and Kistemaker[7] with the other measurements mainly because of the large flexibility involved in the extrapolation, Fig. 11. On the other hand, Figs. 11 and 12 clearly indicate that the data of Grew[11] is in disagreement with that of Atkins *et al.*,[10] the latter measurements suggesting always smaller values than the former. Additional measurements with a view to resolve this discrepancy would be very useful.

It was found[36] that for this system, the Chapman–Cowling formulas are somewhat preferable. Therefore in all three cases we have shown the calculated values on both the potentials according to the rigorous second-approximation expression of the Chapman–Cowling scheme.[34,23] The accuracies of these curves are very high and for temperatures above 200°K these can be relied upon within 1% in most of the cases. A study of all the three figures suggests a preference for the exp-six potential, although even the (12–6) potential does not fail for this system as badly as for most of the other systems considered so far.

Measurements for the Ne–Xe system of Atkins *et al.*,[10] Grew,[11] and Heymann and Kistemaker[7] are plotted in Figs. 14, 15, and 16, respectively. Certain discrepancies in the relative agreement between the different sets of measurements are apparent. The experimental values are compared with the calculated values on the L-J (12–6) and exp-six potentials in Figs. 14 and 16 and with only the exp-six potential in Fig. 15. The calculated curves in Figs. 14 and 15 are according to the doubly approximated expressions,[31] and according to the expression for $[\alpha_T']_2^C$ of Saxena and Dave[26] in Fig. 16. The accuracies of the curves obtained on the L-J potential are in general better than those of exp-six potential. In the former case it is always better than 1% while in the latter it is 2–3% in Figs. 14 and 15, while in Fig. 16 it is rather large, the difference between the second and first approximation is about 12% on the average.

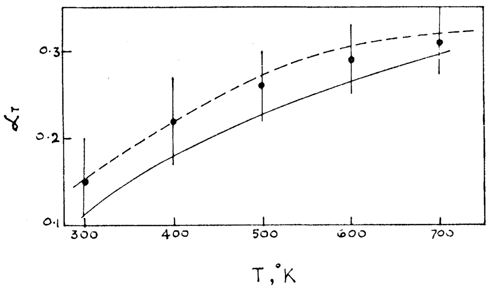

Fig. 13. The legend is same as in Fig. 12 except Xe is in trace and experimental points are of Heymann and Kistemaker.

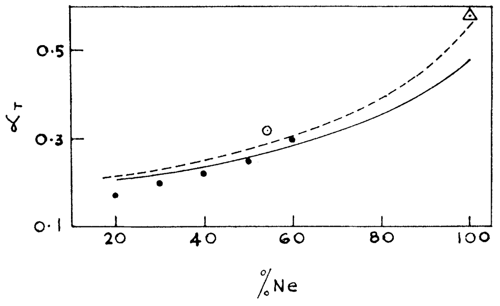

Fig. 14. Composition dependence of α_T for Ne–Xe system at 326°K. Experimental data: ● Atkins *et al.*; ⊙ Grew; △ Heymann and Kistemaker. Theoretical curves: —— exp-six; - - - L-J (12–6) potentials.

An over-all study of the three figures does not lead to a very satisfactory conclusion. Neither of the potentials seem to reproduce adequately the composition dependence and the agreement between theory and experiment gets still worse if some weight is given to the points of Grew,[11] and of Heymann and Kistemaker[7] in Fig. 14. Figure 16 suggests a preference for the (12–6) potential, though exp-six values may be in better agreement with the experimental values if still

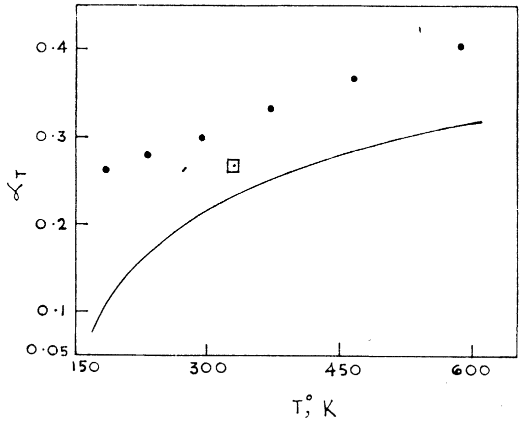

Fig. 15. Temperature dependence of α_T for Ne–Xe system (54.2% Ne). Experimental data: ● Grew; ⊡ Atkins *et al.* Calculated curve on exp-six potential.

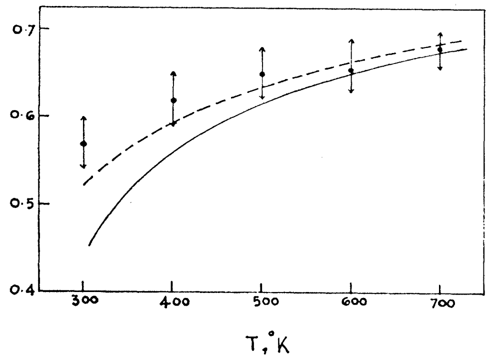

FIG. 16. The legend is same as in Fig. 15 except Xe is in trace and experimental points are of Heymann and Kistemaker. Theoretical curves: —— exp-six; - - - L-J (12–6) potentials.

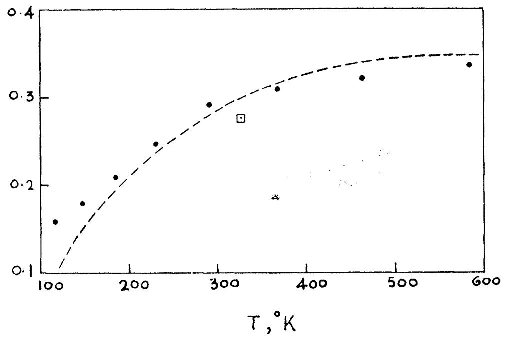

FIG. 18. Temperature dependence of α_T for Ne–Kr system (53.0% Ne). Experimental data: ● Grew; ⊡ Atkins *et al.*, calculated curve on L-J (12–6) potential.

higher approximations are considered. This conclusion is in contradiction with the inferences of Figs. 14 and 15 where exp-six values fail to reproduce the experimental values.

This analysis thus clearly suggests the need for more careful measurements for this system, and also that probably the force field for even these simple molecules cannot be adequately described by such simple potential forms. This latter inference also receives support from the elaborate analysis of the thermal-conductivity data by Saxena and Gandhi.[43]

The experimental data for the Ne–Kr system of Atkins *et al.*[10] giving the composition dependence and of Grew[11] giving the temperature dependence are shown in Figs. 17 and 18, respectively. Calculated values which are on the L-J (12–6) potential are according to the doubly approximated expressions,[31] and are accurate to within 3%. It is interesting to note that the theory predicts the temperature dependence satisfactorily but fails to reproduce the composition dependence. We feel that this is due to the fact that the two sets of measurements are not consistent with each other. If we assume that the theory is correct then the agreement in the case of Fig. 17 will improve if we systematically change the points of Atkins *et al.*[10] to pass through the point of Grew.[11] It may be pointed out that in view of the studies on the various systems presented here we are unable to think of the possibility that the theory gives the right temperature dependence but fails to reproduce the composition dependence. We suggest additional measurements be taken to resolve the discrepancy posed by the existing two sets of measurements.

Measurements on H_2–Xe and D_2–Xe systems of Heymann and Kistemaker[7] are plotted in Figs. 19 and 20, respectively. These systems are interesting as the force fields of H_2 and D_2 are expected to be the same and therefore one can check the internal consistency of these data. This was done[26] by comparing the ratio $\alpha_T(H_2\text{–Xe})/\alpha_T(D_2\text{–Xe})$ obtained from theory and experiment as a function of temperature. The two sets of values agree within the limits of experimental uncertainty. Computed α_T values for both the potentials based on Eqs. (3) and (4) are also shown in these figures and are accurate to within 1%.

In both cases the observed values are in good agreement with the computed values on the (12–6) poten-

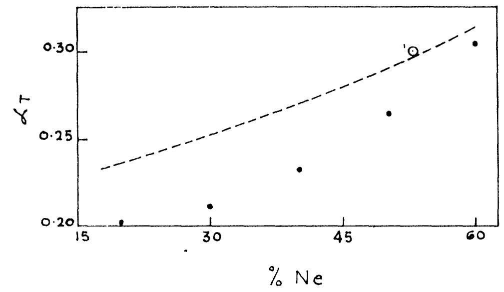

FIG. 17. Composition dependence of α_T for Ne–Kr system at 326°K. Experimental data: ● Atkins *et al.*; ⊙ Grew. Calculated curve on L-J (12–6) potential.

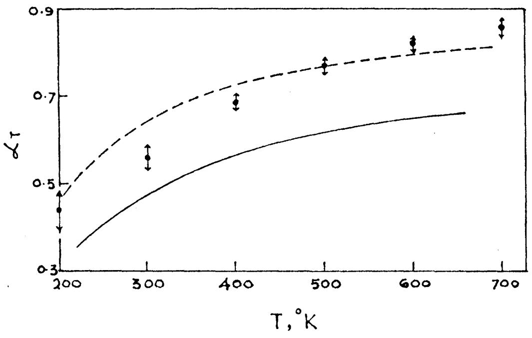

FIG. 19. Temperature dependence of α_T for H_2–Xe system, Xe in trace. ● experimental points of Heymann and Kistemaker. Theoretical curves: —— exp-six; - - - L-J (12–6) potentials.

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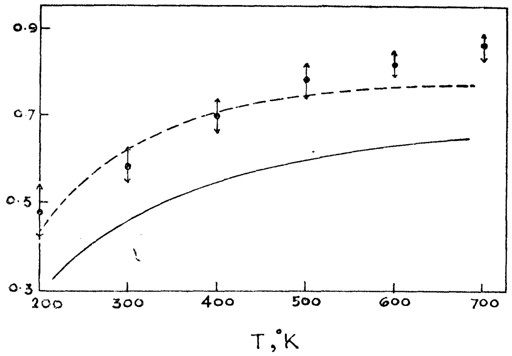

FIG. 20. The legend is same as in Fig. 19 except it refers to D_2–Xe system, Xe in trace.

tial while the exp-six values are smaller. This result is in essential disagreement with the conclusion of Mason and Rice[41] who found the exp-six potential a better choice for H_2 then the (12–6) potential. If we assume that these data are correct then the fault may be essentially in applying the Chapman–Enskog theory, which strictly applies to spherically symmetric molecules, to hydrogen or its combination with other inert gases. As this simple theory does succeed usually in correlating the various properties of simple polyatomic molecules, as shown in the case of H_2 by Mason and Rice,[41] we are tempted to suggest a redetermination of α_T for these systems. It may also be, as observed by us earlier, that the experimental data are systematically greater than the correct values. However, nothing very definite can be said as the thermal diffusion factor, like thermal conductivity, is also very sensitive to the internal degrees of freedom.[44]

Recently, Grew and Mundy[38] have reported α_T data for several systems as a function of temperature and we will consider here their results on Ne–Rn and Ar–Rn. In both cases Rn is present in trace quantities. Their experimental α_T values as a function of temperature along with the calculated values on the L-J (12–6) potential according to Eqs. (3) and (4) are recorded in Table III. In these calculations we have used the potential parameters given by Srivastava and Saxena[45,46] which are also listed in Table I. The estimated accuracy of the theoretical values is very high and is always better than 1%. This estimate does not include any uncertainty arising because of the parameters. For both systems the experimental values are much smaller than the computed values. The estimated uncertainty of the experimental results is 15–20%. The theoretical values are also somewhat uncertain because the potential parameters utilized in computation were obtained[45,46] by an indirect method. Still we feel that the large discrepancy between theory and experiment cannot be attributed to the uncertainty in the determination of potential parameters. Similar calculations have also been performed by Grew and Mundy[38] on the exp-six potential. Their computed $[\alpha_T]_1$ values are also much larger than the experimental values and the differences are more than can be accounted by the accuracy claimed for the measurements. Thus, the choice of the potential also cannot improve the agreement between theory and experiment though the procedure adopted for evaluating the potential parameters is somewhat empirical. More careful and elaborate measurements are essential for deriving any definite conclusion.

So far we have interpreted the experimental thermal diffusion data on the L-J (12–6) and exp-six potentials only. Another intermolecular potential of the Morse type[47] has been recently suggested by Konowalow, Taylor, and Hirschfelder[48] for discussing gas properties.[49] Lovell and Hirschfelder[50] have computed the various transport properties collision integrals. Saxena and Gambhir[51] have extended this potential for gaseous mixtures and since then it has been further tested.[52–55] These investigations do not encourage one to anticipate any distinctive merit for this potential than what has already been achieved by the exp-six potential. Further work done on this potential in our laboratory[56] for gas mixture properties which are accurately known confirms this viewpoint, so it does not seem worthwhile to interpret α_T data on this potential.

In the light of the foregoing detailed discussion on various systems it is possible to derive the following general conclusions:

TABLE III. Computed and experimental values of α_T for the Ne–Rn and Ar–Rn systems as a function of temperature.

Ne–Rn			Ar–Rn		
T (°K)	$[\alpha_T']_2$	α_T (exptl)	T (°K)	$[\alpha_T']_2$	α_T (exptl)
195	0.30	0.20	339	0.15	0.14
309	0.59	0.26	537	0.34	0.19
490	0.80	0.32	851	0.48	0.28

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(a) There seems to be a general deficiency in the experimental data giving the composition dependence of α_T specially towards the end of the decreasing proportion of the heavier component.

(b) For all the gas systems involving He as one of the components it turns out that the L-J (12–6) potential is inadequate. The fault lies in the choice of the exponent twelve to represent the overlap part of the potential energy. However, there seems to be no immediate need to undertake the laborious computations of the transport-properties collision integrals for an $(n-6)$ potential, n being less than 12, for the exp-six potential succeeds well in representing the interactions.

(c) This analysis also suggests a redetermination of α_T for a few systems at definite compositions and temperatures. It is hoped that these results will act as a great aid in reconciling several discrepancies posed by the existing data.

(d) Interpretation of α_T data on a few systems involving simple polyatomic gases may also be undertaken with a view to understanding the role of internal degrees of freedom in the phenomenon of thermal diffusion.