state of ^{147}Pm. However, in order to consider this choice a small deformation parameter is required. This is not reasonable compared to other deformation parameters in this region and one concludes that the NILSSON approach is not applicable here. Even if the additional freedom of non-axially symmetric shapes is allowed in accordance with the calculations of HECHT and SATCHLER[16], it is not possible to account for the spins and parities found in the present work. Finally, we may compare the level structure with the calculations of KISSLINGER and SORENSEN[17], in which the spectra of spherical nuclei with residual forces have been predicted. The main assumption of this theory is that the low-lying states of spherical nuclei can be treated in terms of two basic excitations, quasi-particles and phonons. For the most part these are treated as separate modes of motion. For even-even nuclei the lowest excitations are the phonons, and only these are treated in detail. For the odd-mass nuclei both of these modes of excitations are low in energy and are considered as well as their interactions. However, these calculations are not fully successful in predicting ^{147}Pm structure especially for the low-lying levels. These facts have been observed in the neighbouring ^{149}Pm nucleus.

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Composition Dependence of the Thermal Diffusion Factor in Binary Gas Mixtures

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The thermal diffusion factor, α_T, for the gas systems He—Ar, He—Ne, Ne—Kr and Ne—Xe is measured as a function of composition in a glass two bulb apparatus, operating with its hot and cold bulbs at 373.9° and 273.3 °K respectively. Gas samples are analysed with a sensitive and specially designed differential thermal conductivity analyser. The α_T data are compared with similar values of other vorkers and a smooth set is recommended. The data are further compared with the predictions of rigorous theory in conjunction with realistic intermolecular potentials. An approximate prediction of the theory concerning the composition dependence of α_T has been checked.

Many efforts have been made to measure the thermal diffusion factor α_T, for binary mixtures of gases and these are summarized by GREW and IBBS[1], and MASON, MUNN and SMITH[2]. SAXENA and MATHUR[3–5] have interpreted some of these data in a series of three articles. During these studies a need for a number of specialised investigations came into light. The present work is polarized towards such deficiencies and particularly deals with the composition dependence of α_T. The mixtures of noble gases have been investigated in view of the fact that the CHAPMAN–ENSKOG theory strictly applies only to such monatomic spherically symmetric molecules. The specific binary systems covered are He – Ar, He – Ne, Ne – Kr and Ne – Xe.

Experimental Procedure and Results

For our measurements the known two bulb thermal diffusion apparatus is used with the volumes $V_1 = 193.5$ cc and $V_2 = 30.3$ cc. The two volumes can be separated by a stopcock and the two bulbs

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[1] K. E. GREW and T. L. IBBS, Thermal Diffusion in Gases, Cambridge University Press, New York 1952.

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[4] S. C. SAXENA and B. P. MATHUR, Rev. Mod. Phys. **38**, 380 [1966].

[5] S. C. SAXENA and B. P. MATHUR, J. Sci. Indust. Res. India **25**, 54 [1966].

by a standard vacuum joint. The effective L/A is $380\ \mathrm{cm}^{-1}$ (L = length and A = area of the tube connecting the two bulbs). The upper bulb (volume V_1) is kept at 373.9 °K by circulating oil from a constant temperature bath through the jacket surrounding the bulb. The temperature in the thermostat is constant to ± 0.05 °C. The lower bulb is immersed in a mixture of ice and water. For the analysis of the gas samples a specially designed differential thermal conductivity analyser is used[6].

Let us consider a two-bulb convection free apparatus whose bulbs have volumes V_1 and V_2 and are maintained at temperatures T_1 and T_2 respectively, where $T_1 > T_2$. Further let us represent the mole fraction of the heavier component by x, and x_1 and x_2 are the values of x at the steady state in the bulbs V_1 and V_2 respectively. We now define, in common practice, the so-called separation factor Q such that,

$$Q = \frac{x_2(1-x_1)}{x_1(1-x_2)} . \qquad (1)$$

α_T can now be computed by the following relation:

$$\alpha_T = \ln Q / \ln (T_1/T_2) . \qquad (2)$$

The so computed α_T refers to an average temperature $\overline{T}$ between T_1 and T_2. Assuming α_T varies with temperature as $A-(B/T)$, Brown[7] showed that

$$\overline{T} = \frac{T_1 T_2}{T_1 - T_2} \ln \frac{T_1}{T_2} . \qquad (3)$$

If α_T is assumed to vary as $A-(B/T^2)$ we get[8]

$$\overline{T} = T_1 T_2 \sqrt{\frac{2 \ln (T_1/T_2)}{T_1^2 - T_2^2}} . \qquad (4)$$

In an apparatus of the above type the approach to steady state is characterised by a relaxation time, τ. The expression for τ is given by Saxena and Mason[9],

$$\tau = \frac{L}{A} \left[\frac{T_1}{V_1} + \frac{T_2}{V_2} \right]^{-1} \left[\frac{T}{D} \right]_{\mathrm{av}} , \qquad (5)$$

where

$$[T/D]_{\mathrm{av}} = (1/L) \int_0^L (T/D)\, \mathrm{d}z .$$

The five stable rare gases used in preparing the different gas mixtures are supplied by the British Oxygen Co. He, Ne and Ar are spectroscopically pure, Kr and Xe only 99 – 100 percent, the rest being Xe and Kr respectively.

The accurately prepared mixtures of the desired composition is filled in the two bulb apparatus at a pressure around 10 cm of mercury. Such low pressures were preferred specially in view of the small value of τ, in such cases. The computed values of τ from Eq. (5) are reported in Table 1. We have allowed the diffusion to proceed for a period of about six relaxation times before withdrawing the steady state sample from the hot bulb, while the cold bulb itself is removed and directly analysed. These two samples, the initial feed sample and a number of standard mixtures of known composition around the unknown ones are then analysed on the differential conductivity analyser. Thus, knowing the compositions of the mixtures in the hot and cold bulb, the separation factor Q and hence α_T can be easily evaluated. In Table 1 we report for all four binary systems such Q and α_T values as a function of composition. Also indicated are the values of the gas mixture-pressure at which the thermal diffusion run is made.

Gas pair	Pressure cm of Hg.	τ* hrs.	% He or Ne	% S	Q	α_T
He-Ar	11.5	0.56	58.9	2.95	1.129	0.390
			69.2	3.00	1.150	0.448
			77.5	2.70	1.165	0.490
He-Ne	10.0	0.35	28.0	1.95	1.103	0.315
			46.5	2.50	1.106	0.325
			64.5	2.35	1.109	0.332
Ne-Kr	13.3	1.90	41.0	2.15	1.094	0.287
			48.2	2.40	1.101	0.308
			69.0	2.30	1.111	0.335
			83.3	2.00	1.149	0.445
Ne-Xe	9.6	1.57	51.9	2.20	1.092	0.280
			55.9	2.30	1.097	0.296
			69.1	1.96	1.095	0.295
			84.8	1.37	1.111	0.335
			91.0	1.02	1.128	0.385

* The values refer to the pressures listed in column 2 of this table and not to a one common value.

Table 1. Experimental values of S, Q and α_T. Temperature of the hot bulb 373.9 °K. Temperature of the cold bulb 273.3 °K.

For all the four different gas pairs the difference in the thermal conductivity values of the two components is sufficiently large with the result that separations could be measured very accurately. The separation S, defined as the difference in the com-

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positions of a component in the two bulbs, for the gas systems of Table 1 varies between 1 to 3 percent. The actual values of S are reported in Table 1, column 5. Our analyser is capable of detecting and responding to changes in composition of the order of 0.025 percent. Thus, in the worst case in Table 1, for which the separation has a minimum value, we have an uncertainty of 2.5 percent. An error of the same order will, therefore, creep into the computed α_T values on this accord only. The error caused by temperature fluctuations is small. We estimate an overall uncertainty of about two percent in our smoothed α_T values. The α_T values of Table 1 can be assumed to correspond to the composition of the initial mixtures because in all cases the observed separation is small.

If we use Brown's formula we get an average temperature of 318.5 °K. The average temperature according to Eq. (4) is 317.1 °K. This value does not differ by any appreciable amount from that given by Brown's formula. We therefore continue to regard our α_T values consistently for all mixtures to refer to 318.5 °K. Thus, knowing the α_T values at specific composition and temperature we preceed to compare with the α_T data of the other groups and also with the predictions of the Chapman–Enskog theory.

Comparison with the Earlier Data

For each system the α_T values determined here will now be compared with the values available in the literature and obtained on a two-bulb apparatus of the same general design as employed here. We present this comparison graphically and consider each system individually. We attach some importance to this effort because in a few cases the available data have been suspected [3] and appreciable discrepancies occur in the data of different groups. In general our experiments are confined to such compositions where the available information is scarce. Unfortunately some interesting runs with specific compositions could not be made due to limited amount of gas available with us.

For the Ar – He system the experimental data available are of Atkins, Bastick and Ibbs [10], Grew [11], and Saxena and Mason [8]. The measurements of Grew and the ones of Saxena and Mason were made at only one composition but as a function of temperature. We got α_T at 318.5 °K by interpolating their values. Atkins et al. determined α_T as a function of composition but at 326 °K. We have not made any effort to reduce their values to our working temperature, because of the fact that at these temperatures the temperature dependence of α_T is very small [11]. All the data are plotted in Fig. 1. The measurements of all groups are in reasonable agreement with each other. The continuous curve is a compromised plot through the experimental points giving equal weight to all. The α_T values read from this curve over the whole composition range and at conveniently spaced values of composition are recorded in Table 2. We recommend their use being the most reliable and consistent set.

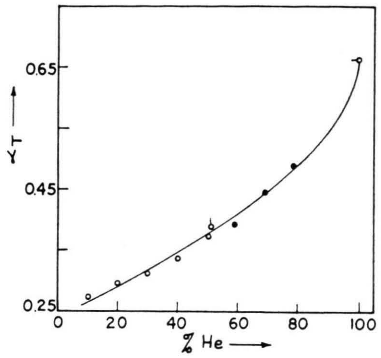

Fig. 1. Composition dependence of α_T for the Ar—He system. Experimental data: ○ Atkins et al., $\overset{|}{\circ}$ Grew, –○ Saxena and Mason, ● Present results. — Smooth experimental curve.

In Fig. 2 we show plotted, the α_T values for the He – Ne system as determined by us, Atkins et al. [10] and the interpolated value from the data of Grew [11]. The data of Atkins et al. are systematically greater than the other values while our results agree well with the single point from Grew. The discrepancy consistently increases as the percentage of He in the mixture increases. We have drawn a smooth curve through the different points, ignoring completely the data of Atkins et al., which we certainly feel are in error. The values in Table 2 are taken from the smooth curve.

The various α_T values for the Ne – Kr system as obtained in the present work, by Atkins et al. [10], and by Grew [11] are plotted in Fig. 3. Here, contrary

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[10] B. E. Atkins, R. E. Basiick, and T. L. Ibbs, Proc. Roy. Soc. London **A 172**, 142 [1939].

[11] K. E. Grew, Proc. Roy. Soc. London **A 189**, 402 [1947].

Gas pair	α_T	%He 10	30	50	70	85	100
He-Ar	Exptl.	0.265	0.317	0.377	0.447	0.515	0.665
	Calc.	0.295	0.332	0.382	0.457	0.530	0.638
	Exp-six	(+1.0)	(+4.5)	(+1.3)	(+2.2)	(+2.8)	(−4.2)
	Calc.	0.380	0.420	0.467	0.540	0.615	0.735
	12−6	(+30.2)	(+24.5)	(+19.2)	(+17.2)	(+16.7)	(+9.5)
He-Ne	α_T	%He 30	40	50	60	70	
	Exptl.	0.315	0.319	0.323	0.329	0.337	
	Calc.	0.314	0.316	0.324	0.335	0.348	
	Exp-six	(−0.3)	(−1.0)	(+0.3)	(+1.8)	(+3.2)	
Ne-Kr	α_T	%Ne 40	50	60	70	80	
	Exptl.	0.284	0.294	0.310	0.346	0.410	
	Calc.	0.270	0.290	0.313	0.345	0.382	
	12−6	(−5.1)	(−1.4)	(+0.3)	(−0.3)	(−7.3)	
Ne-Xe	α_T	%Ne 20	40	60	80	90	
	Exptl. Curve I	0.250	0.270	0.297	0.345	0.387	
	Exptl. Curve II	0.180	0.225	0.280	0.350	0.400	
	Calc. Exp-six	0.200	0.220	0.225	0.317	0.380	
	Calc. 12−6	0.215	0.255	0.310	0.390	0.450	

* The quantities in braces are the percentage deviations of the computed α_T values from the corresponding experimental data.

Table 2. Comparison of experimental (smooth) and calculated α_T values as a function of composition at $T=318.5$ °K *.

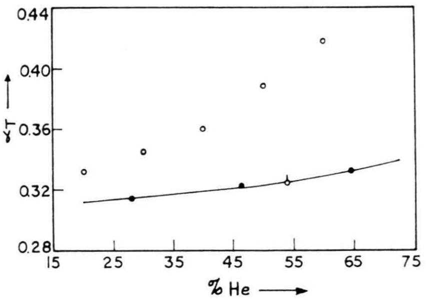

Fig. 2. Composition dependence of α_T for the He−Ne system, and the rest of the legend is same as in Fig. 1.

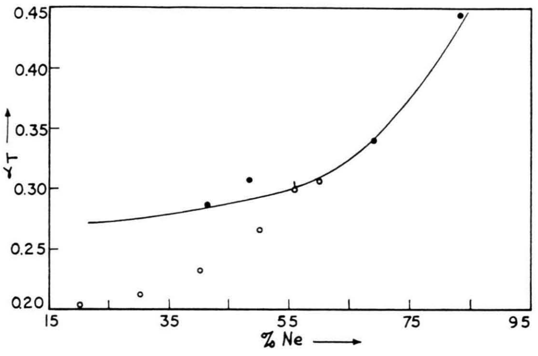

Fig. 3. Composition dependence of α_T for the Ne−Kr system, the remaining legend is same as in Fig. 1.

to the He − Ne system, the discrepancy between our values and the ones by Atkins et al., increases with decreasing percentage of Ne. We have consequently neglected their values while drawing the curve. Again the values in Table 2 are taken from the smooth curve.

The various available α_T values for the Ne − Xe system are shown in Fig. 4. Apart from the present measurements the values belong to Atkins et al. [10], Grew [11], and Heymann and Kistemaker [12]. The latter

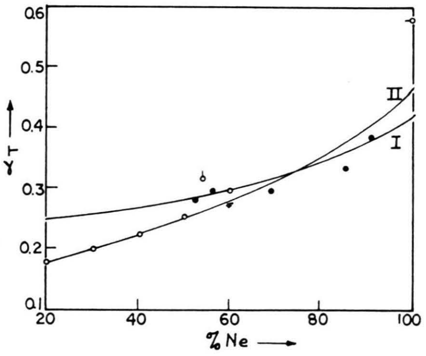

Fig. 4. Composition dependence of α_T for the Ne−Xe system. Experimental data: –o Heymann and Kistemaker, and rest of the legend is same as in Fig. 1.

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[12] D. Heymann and J. Kistemaker, Physica **25**, 556 [1959].

value is obtained by interpolating at the desired temperature from the original data. Unfortunately, the different measurements are in poor agreement with each other. The single point of Heymann and Kistemaker[12] seems to be greater than the value obtained from the trends evident in the figure. This possibility has been earlier indicated by us[3] and is conclusively confirmed here. Even after ignoring this point it is not possible to pass a single smooth curve through the remaining experimental points. We have therefore passed two alternative curves. The results are recorded in Table 2. A careful re-examination of this system would be useful.

Comparison with Theory

We now compare our smooth α_T values with the predictions of Chapman–Enskog theory in conjunction with the two popular intermolecular potentials for nonpolar spherically symmetric molecules. These are the modified Buckingham exp-six potential:

$$\Phi(r) = \frac{\varepsilon}{1-(6/\alpha)} \left[(6/\alpha) \exp \alpha \left(1 - \frac{r}{r_{\mathrm{m}}}\right) - \left(\frac{r_{\mathrm{m}}}{r}\right)^6 \right], \quad \text{for } r > r_{\max} \tag{6}$$

and

$$\Phi(r) = \infty , \qquad \text{for } r \leqq r_{\max} .$$

and the (12-6) Lennard–Jones potential:

$$\Phi(r) = 4\,\varepsilon [(r_0/r)^{12} - (r_0/r)^6] . \tag{7}$$

In a recent review Saxena and Joshi[13] have summarized the different explicit expressions for α_T to be used for computation and indicated by specific calculations the accuracy to be associated with a particular expression for α_T. Here we have employed the doubly approximated formula on the Kihara scheme. The expression in the commonly used notation is,

$$[\alpha_T']_2 = [\alpha_T]_1 (1 + K_1') + K_2', \tag{8}$$

where

$$K_1' = \frac{C_{12}^{\;2}}{C_{11}\, C_{22}} + \frac{C^2{}_{-1-2}}{C_{-1-1}\, C_{-2-2}} \tag{9}$$

and

$$K_2' = -\frac{-5}{2\sqrt{2}\, x_1} \left(\frac{1+M}{M}\right)^{1/2} \left[\frac{a_{0-2}\, C_{-1-2}}{C_{-1}{-}_1\, C_{-2-2}}\right] - \frac{5}{2\sqrt{2}\, x_2} (1+M)^{1/2} \left[\frac{a_{0-2}\, C_{-1-2}}{C_{11}\, C_{-2-2}}\right]. \tag{10}$$

Here $M = (M_2/M_1)$, and the expressions for the various C_{ij} and a_{ij} are compiled in the article of Saxena and Joshi[13]. The parameters (ε/k, r_{m} and α) for the exp-six and (ε/k and r_0) for the $L-J(12-6)$ potentials used by us are those listed by Saxena and Mathur[3].

In Table 2 the calculated values for α_T are reported. It should be mentioned that at the temperatures of our measurements the corrections due to quantum effects are negligible and the classical expressions employed to describe the phenomenon are good enough. Further the operating pressures are such that the basic and fundamental assumption of kinetic theory of binary collisions holds very well. Thus, for such molecules the theoretical interpretation of the α_T data in terms of the potentials of Eqs. (6) and (7) is not only reasonable but is precise enough for detailed conclusions specially in view of the extreme sensitivity of thermal diffusion to interaction potential. We now attempt such a study for individual systems.

For the Ar – He system the computed values are in good agreement with the experimental values only for the exp-six potential. In the case of (12 – 6) potential the disagreement is pronounced and much more than can be explained on the basis of the experimental uncertainties. This conclusion of course is not new and this view has been presented over and over again by different workers. For the He – Ne system therefore we do not use the (12 – 6) potential at all for our numerical calculations and restrict ourselves to the exp-six potential. The values so obtained and reported in Table 2 are in excellent agreement with the experimental results. For Kr, the difficulty to approximate its intermolecular potential reasonably well be any simple form is well known. In an article by Bahethi and Saxena[14], this strange problem has been discussed. They conclude that the exp-six potential is inadequate and if the choice for the potential is to be confined only to simpler forms, the (12 – 6) potential is reasonably good. We therefore report in Table 2 the computed values for the Ne – Kr system for the (12 – 6) potential only. It is interesting as well as encouraging to note that the agreement between theory and experiment is good. The α_T values as obtained for the two potentials for Ne – Xe system are reported in the last two rows of

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[13] S. C. Saxena and R. K. Joshi, J. Sci. Indust. Res. India **24**, 518 [1965].

[14] O. P. Bahethi and S. C. Saxena, Indian J. Pure Appl. Phys. 3, 12 [1964].

Table 2. For this system unfortunately it has not been posible to present an undisputed and unique set of experimental values as for others. In Table 2 consequently, we report two sets which differ appreciably from each other particularly at the end where the proportion of Ne in the mixture is small. Within the margin of this rather large uncertainty in the experimental data we find that theory is good enough for estimating the facts. We hope to improve upon this uncertainty.

Composition Dependence of α_T

In recent years efforts have been made to develop a simple theory for the multicomponent thermal diffusion[15]. An important piece of information which emerged out of this investigation and which is of relevance for the work presented in this paper consists in the suggestion that for a binary system the plot of α_T vs. molefraction of a component should be linear. This prediction of simple theory has been further elaborated on the basis of rigorous Chapman–Enskog theory by Mason, Weissman, and Wendt[16], who have also tried to confirm it by the available experimental α_T data for six different systems. We examine this particular prediction for the four systems studied in this paper. In Fig. 5, we plot α_T^{-1} vs. percentage of the lighter component in the mixture. In all four cases it is possible to approximate the experimental points on the basis of a linear plot. However, the quantitative agreement is not as good as one would expect though on the scale of the plot of Fig. 5 it is not very much evident. We therefore feel that this inference of simple theory is qualitatively dependable and is approximately correct also. Any precise quantitative deduction on its basis will be a little too much and due caution has to be taken in such interpretations.

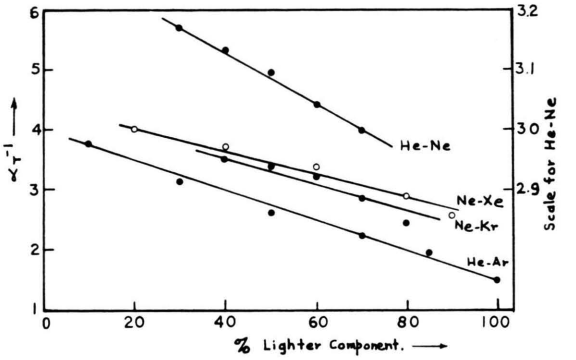

Fig. 5. Composition dependence of α_T .

Acknowledgements

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[15] M. F. Laranjeira, Physica **26**, 409, 417 [1960]. — M. F. Laranjeira and J. Kistemaker, ibid. **26**, 431 [1960].

[16] E. A. Mason, S. Weissman and R. P. Wendt, Phys. Fluids **7**, 174 [1964] ; see also E. A. Mason and F. J. Smith, J. Chem. Phys. **44**, 3100 [1966].