64

THERMAL CONDUCTIVITY AND FORCE BETWEEN LIKE MOLECULES

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ABSTRACT. The Chapman-Enskog kinetic theory of non-uniform gases, as applied to the phenomenon of thermal conductivity, has been utilised to evaluate the intermolecular force constants, by assuming the Lennard-Jones 12 : 6 interaction potential for inert gas molecules. The temperature variation of thermal conductivity gives the force constant ε of the Lennard-Jones function, while r_0 is found by actual substitution. To test the adequacy of the model the transport coefficient have been calculated by utilising these potential parameters, and compared with the observed values over an extensive range of temperatures. It is found that the agreement between theory and experiment is quite satisfactory showing thereby the adequacy of the 12 : 6 model and correctness of the values assigned to the force constants. The important quantity $\lambda/\eta c_v$ has been calculated theoretically for various temperatures and pressures and is found to vary only slightly with temperature but considerably with pressure. The Enskog theory of dense gases has been applied to the particular case of argon and the results compared with the observed values.

1. INTRODUCTION

The Chapman-Enskog kinetic theory of gases expresses the transport coefficients in terms of a set of collision integrals which have been evaluated for various empirically chosen potential fields. Amongst these, the Lennard-Jones 12:6 model and the modified Buckingham (Exp-Six) model are the most realistic, though the relative appropriateness of the latter still awaits confirmation. The property most sensitive and hence suitable for the determination of potential parameters is the coefficient of thermal diffusion, but its usefulness is limited owing to the difficulty of obtaining accurate experimental data. The three elementary transport coefficients are almost equally sensitive for the determination of intermolecular field, though viscosity is usually preferred for this purpose in view of the greater accuracy attainable in its experimental determination. Recently, Kannuluik and Carman (1952) have made an accurate determination of the coefficient of thermal conductivity of inert gases over an extensive range of temperatures which are particularly useful in case of Krypton and Xenon where viscosity data are not sufficiently extensive. The aim of the present paper is to utilise the temperature dependence of thermal conductivity to evaluate the force constants, and to test the appropriateness of the Lennard-Jones 12 : 6 model to represent the molecular interactions of rare gases.

2. FORMULAE AND METHOD OF CALCULATION

According to the Lennard-Jones 12 : 6 model, the potential energy of molecular interaction is given by

$$E(r) = 4\varepsilon[(r_0/r)^{-12} - (r_0/r)^6] \qquad \ldots (1)$$

where r_0 is the separation for which the energy of interaction is zero and ε is the value of the maximum negative energy. From Chapman and Enskog theory the third approximation to the coefficient of thermal conductivity $[\lambda]_3$ of a single gas, as shown by Hirschefelder, Bird and Spotz (1948), can be written in the form

$$[\lambda]_3 \times 10^5 = \frac{2.6693(MT)^{\frac{1}{2}} f_\lambda^{3}}{r_0^2\, \Omega^{(2,2)*}} \cdot \frac{5}{2} C_v \qquad \ldots (2)$$

Here M is the molecular weight of the gas, T the absolute temperature, C_v the specific heat at constant volume and the quantities f_λ^{3} and $\Omega^{(2,2)*}$ are functions of kT/ε and have been tabulated by Hirschefelder, Bird and Spotz (1948). It is convenient to put

$$kT/\varepsilon = T^* \qquad \ldots (3)$$

where T^* is called the reduced temperature. Making use of the observed dependence of thermal conductivity on temperature, we have developed here the following two simple graphical methods to evaluate the potential parameters.

First Method

A graph of $T^{\frac{1}{2}}/\lambda$ was plotted against T (Fig. 1) to smoothen the data and to test their self-consistency which further gave us a number of additional points for calculation. Now from

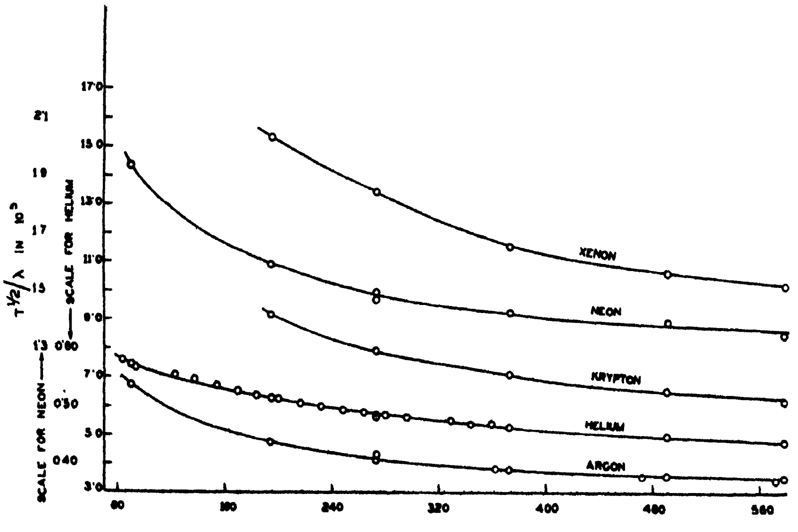

Fig. 1. Plots of $T^{\frac{1}{2}}/\lambda$ *Vs.* T.

equation (2) it follows that

$$[T^{\frac{1}{2}}/\lambda]_2/[T^{\frac{1}{2}}/\lambda]_1 = [\Omega^{(2,2)*}/f_\lambda^{3}\ ]_2/[[\Omega^{(2,2)*}/f_\lambda^{3}]_1 \tag{4}$$

The suffixes 1, 2 outside the square brackets refer to temperatures T_1 and T_2. Hirschfelder's tables were then utilised to give a plot of $\Omega^{(2,2)*}/f_\lambda^{3}$ against T^* and the values of $[\Omega^{(2,2)*}/f_\lambda^{3}]_2/[\Omega^{(2,2)*}/f_\lambda^{3}]_1$ were calculated from this plot for various initial values of $[kT/\epsilon]_1 = [T^*]_1$ for $[T^*]_2/[T^*]_1$ ratios equal to 1.5 and 2.0. These are plotted in fig. 2 against the corresponding initial values of $[T^*]_1$.

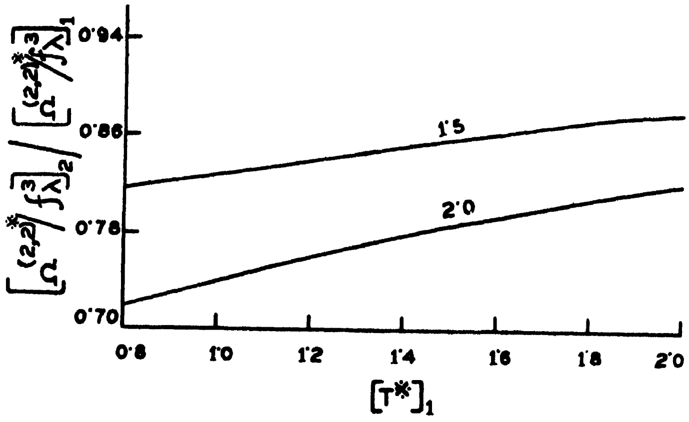

Fig. 2. Plots of $[\Omega^{(2,2)*}/f_\lambda^{3}]_2/[\Omega^{(2,2)*}//f_\lambda^{3}]_1$ *Vs.* $[T^*]_1$

From the observed thermal conductivity data plotted in figure 1, the ratio of the left hand side of equation 4 was found for different initial temperature T_1 for the same T or T^* (since they are proportional when ϵ is constant) ratios of 1.5 and 2.0, and the point representing the same value of the ordinate in fig. 2, on the appropriate $[\Omega^{(2,2)*}/f_\lambda^{3}]_2/[\Omega^{(2,2)*}/f_\lambda^{3}]_1$ ratio graph was noted and the corresponding abscissa read giving the value of $[T^*]_1$ corresponding to T_1. Knowing $[T^*]_1$ and T_1, ϵ was calculated by simple substitution. r_0 was then calculated by substituting this value of ϵ in equation 2 for some intermediate temperature.

In the above method a large temperature range has to be taken for high accuracy and therefore the values obtained for force parameters are average values over that interval. In view of the remarks of Keyes (1951), Whalley and Schneider (1952) and Srivastava and Madan (1953) regarding the temperature variation of ϵ and r_0, it was considered worthwhile to try a second method in which it is possible to obtain the force parameters at a single temperature, without averaging it over a large interval.

Second Method :

Taking logarithms of equations (2) and (3), we obtain

$$\log\,[T^{\frac{1}{2}}/\lambda\times10^5] = \log\,[\Omega^{(2,2)*}/f_\lambda^3]+2\log r_0+\log\,[6.6733M^{\frac{1}{2}}C_v] \qquad \ldots \quad (5)$$

and

$$\log T = \log T^*+\log \epsilon/k \qquad \ldots \quad (6)$$

From equations (5) and (6) it is seen that a plot of the experimental quantity $\log\,[T^{\frac{1}{2}}/\lambda\times10^5]$vs. $\log T$ should be superposable on the theoretical curve of log $[\Omega^{(2,2)*}/f_\lambda^3]$vs. $\log T^*$ only by the parallel translation of the axes. Further r_0 can be directly determined by the amount of translation parallel to $T^{\frac{1}{2}}/\lambda$ sxis, and ϵ/k by the amount of translation parallel to the T axis. Such curves are shown in fig. 3 for the case of Neon. The details of superposing the two curves are given by Srivastava and Srivastava (1956) and the author is thankful to them for allowing him to see their manuscript in advance of publication.

The second method gives the average value of ϵ over a much shorter interval than the first method and may therefore be theoretically preferable to the latter but practically the graphical computation becomes less accurate and the values therefore become less reliable than those given by the first method.

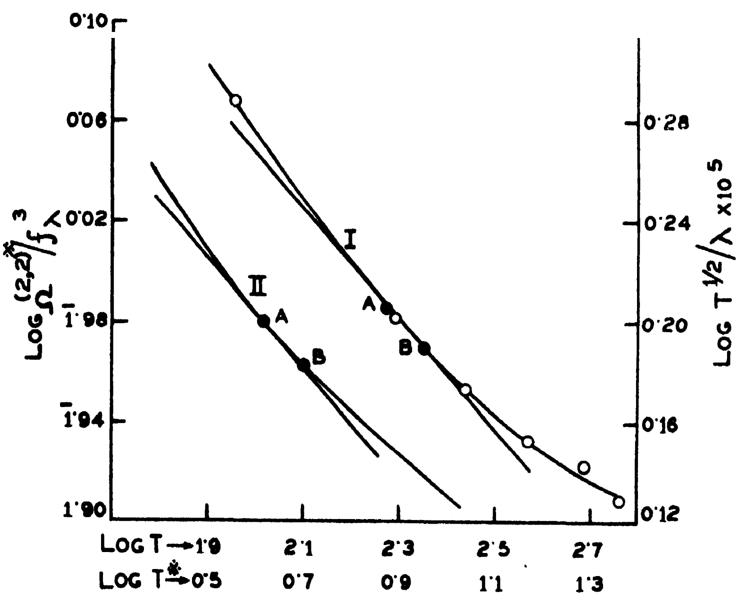

Fig. 3. Curve I for neon represents the plot of $\log\,[T^{\frac{1}{2}}/\lambda\times10^5]$ *Vs.* $\log T$. while curve II is the theoretical plot of $\log\,[\Omega^{(2,2)*}/f_\lambda^3]$ *Vs.* T^*

3. EVALUATION FROM EXPERIMENTAL DATA

The thermal conductivity of inert gases at 0°C has been reported by a number of workers, viz. Eucken (1911), Weber (1917, 1927), Dickens (1934), and Kannuluik and Martin (1934). Ubbink and Haas (1943), Johnston and Grilly (1946), Keyes (1951, 1954) have measured the thermal conductivity of some of the inert gases at various temperatures. The recent measurements of Kannuluik and Carman (1952) on the five rare gases over an extensive temperature range are the most useful for our present purpose. The thermal conductivity data of these workers have been utilised in evaluating the force constants and are plotted in fig. 1.

Adopting the first method explained above we have computed the values of the potential parameters for various temperature intervals both in the low and high temperature ranges for inert gases. These results are recorded in Table I.

TABLE I

Helium

Temp. Range °K	ϵ/k in °K	r_0 in A°	Temp. Range °K	ϵ/k in °K	r_0 in A°
100—200	6.6	2.728	250—375	7.8	2.670
140—210	6.1	2.727	250—500	8.3	2.657
150—225	6.4	2.715	275—550	9.1	2.643
200—300	7.0	2.694			
Mean	6.5	2.716	Mean	8.4	2.657

Neon

Temp. Range °K	ϵ/k in °K	r_0 in A°	Temp. Range °K	ϵ/k in °K	r_0 in A°
100—200	35.7	2.815	250—375	47.1	2.738
140—210	40.9	2.776	250—500	47.2	2.737
140—280	41.2	2.773	300—450	48.0	2.735
150—225	41.3	2.774	350—525	50.0	2.725
150—300	42.9	2.769			
200—300	43.0	2.760			
Mean	40.8	2.776	Mean	48.1	2.734

TABLE I (*contd.*)

Argon

Temp. Range °K	ϵ/k in °K	r_0 in A°	Temp. Range °K	ϵ/k in °K	r_0 in A°
100– 200	109.9	3.497	250—375	130.0	3.389
140—210	116.6	3.452	250—500	128.9	3.386
140—280	120.7	3.425	300—450	132.8	3.373
150—225	117.2	3.442	350—525	133.1	3.370
150—300	121.9	3.419			
200—300	122.3	3.421			
Mean	118.1	3.443	Mean	131.2	3.379

KRYPTON

Temp. Range °K	ϵ/k in °K	r_0 in A°
200—400	156.6	3.732
250—375	161.3	3.710
250—500	166.7	3.698
350—525	179.0	3.650
Mean	165.9	3.698

XENON

Temp. Range °K	ϵ/k in °K	r_0 in A°
200—400	217.0	4.014
250—375	217.4	4.014
250—500	211.9	4.032
350—525	218.8	4.017
Mean	216.3	4.019

Next the second method as explained above was utilised to determine ϵ/k and r_0, and the values so obtained are given in Table II.

TABLE II

Gas	Temp.°K	ϵ/k in °K	r_0 in A°
Helium	290	7.5	2.688
Neon	225	44.7	2.748
Argon	200	118.9	3.436
Krypton	365	163.3	3.699
Xenon	375	215.3	4.021

The values of the force constants computed here from thermal conductivity are compared in Table III with the values obtained by the other workers from viscosity and self-diffusion. The two sets of values obtained from thermal conductivity are consistent among themselves, and agree also with the values calculated from other transport properties if we take into account the temperatures to which they refer and the relative experimental errors involved in the determination of transport coefficients.

TABLE III

Force Constants for like molecules

Gas	From Viscosity[1]				From Viscosity[2]		From self-diffusion[3]		From Thermal Conductivity[4]					
	Low Temp.		High Temp.						Low Temp.		High Temp.		Second Method	
	ε/k °K	r_0 A°	ε/k °K	r_0 A°	ε/k °K	r_0 A°	ε/k °K	r_0 A°	ε/k °K	r_0 A°	ε/k °K	r_0 A°	ε/k °K	r_0 A°
He	—	—	—	—	10.22	2.576	—	—	6.5	2.716	8.4	2.657	7.5	2.688
Ne	41.0	2.769	—	—	35.7	2.80	49.2	2.659	40.8	2.776	48.1	2.734	44.7	2.748
A	112.0	3.483	126.2	3.414	124.0	3.418	125.5	3.384	118.1	3.443	131.2	3.379	118.9	3.436
Kr	—	—	—	—	120	3.61	—	—	—	—	165.9	3.698	163.3	3.699
Xe	—	—	—	—	230	4.051	—	—	—	—	216.3	4.019	215.3	4.021

[1] Srivastava, B. N. and Madan, M. P., 1952a, *Proc. Nat. Acad. Sci.*, **21**, III–VI, 254.
[2] Hirschfelder, J. O., Bird, R. B. and Spotz, E. L., 1948, *J. Chem. Phys.*, **16**, 968.
[3] Srivastava, B. N. and Madan, M. P., 1952b, *Phil. Mag.*, **7**, 43, 968.
[4] Present work.

TABLE IV

Viscosity of gases ($\eta\times 10^7$ in gm.cm^{-1} sec^{-1})

Temp. °K	Helium		Neon		Argon	
	ηobs.(*a*)	ηcalc.	ηobs.(*a*)	ηcalc.	ηobs.(*a*)	ηcalc.
80	821	815	1198	1173	688	657
100	947	935	1435	1412	839	824
120	1068	1055	1646	1631	993	992
140	1182	1176	1841	1832	1146	1154
160	1290	1281	2026	2021	1298	1312
180	1395	1379	2204	2199	1447	1464
200	1496	1484	2376	2368	1594	1612
220	1595	1597	2544	2529	1739	1754
240	1692	1663	2708	2683	1878	1832
260	1789	1751	2867	2835	2014	2022
280	1888	1849	3021	2979	2145	2150
300	1987	1935	3173	3128	2270	2283
800	3840(*b*)	3639	5918(*b*)	5911	4621(*c*)	4706
1000	4455(*b*)	4214	6800(*b*)	6878	5302(*c*)	5472
1200					5947(*c*)	6172
1500					6778(*c*)	7088

(*a*) Johnston, H. L. and Grilly, E. R., 1942, *Journal of Physical Chemistry*, **46**, 948.
(*b*) Trautz, M. and Zink, R., 1930, *Annalen der Physik*, **7**, 427.
(*c*) Vasilesco, V., 1945, *Annales de Physik* (Paris), series 11, **20**, 292.

Temp. °K	Krypton(*d*)	
	ηobs.	ηcalc.
273.2	2334	2334
283.8	2405	2418
289.5	2459	2460
373.2	3063	3059

Temp. °K	Xenon(*e*)	
	ηobs.	ηcalc.
289.7	2235	2336
293	2260	2361
400	3009	3136
450	3351	3468
500	3652	3789
550	3954	4094

(*d*) Landolt-Börnstein, Physikalich--Chemische tabellen.
(*e*) Trautz, M. and Heberling, R., 1934, *Ann. Physik.*, (5), **20**, 118.

4. CALCULATION OF TRANSPORT COEFFICIENTS

A knowledge of the force constants immediately enables one to predict any transport property. These calculated values can then te compared with the observed values and this comparison enables us to decide about the suitability of the molecular interaction law. With this idea we have given below such comparison for viscosity and thermal diffusion. The former has been chosen in view of the greater experimental accuracy involved in its determination and the latter due to its greater sensitiveness to molecular model. For viscosity from table 4 we find that the agreement between theory and experiment is excellent for Neon and Krypton, but for the remaining gases some discrepancies are apparent. For Helium the disagreement between theory and experiment is not much at low temperatures and may presumably be due to quantum effects. At high temperatures however, the differences are more and this is due to the fact that helium molecules are 'softer' than indicated by the 12:6 potential and the inverse twelfth power repulsion is too steep for helium. Mason and Rice (1954a) has found a comparatively better fit for exp—six potential. The measured values of Vasilesco (1945) at high temperatures for Argon are relatively lower than the calculated values, this implies an extremely steep repulsion energy at close distances of approach of the two molecules. The experiments by Amdur and Mason (1954) on the scattering of high velocity argon beams in argon gas give no indication of such a steep repulsion. It is therefore, likely that the experimental values are lower and further experiments will be helpful in clarifying this point. The calculated values of Xenon are always higher than the experimental ones, this may be due to the errors in the determination of thermal conductivity or viscosity and requires experimental confirmation. Since this gas is difficult to obtain pure, it is possible that some light gas impurities were present. Similar discrepancies for Argon and Xenon occur in the exp-six model (Mason & Rice, 1954b).

Experimental values of R_T, the thermal separation ratio has been reported by A. O. Nier (1940), L. G. Stier (1942) and A. K. Mann (1948) for Argon and Neon by measuring the thermal separation of isotopic mixtures between two temperatures T_1 and T_2. An experimental value is thus a mean over the entire temperature interval, but it has been shown by Brown (1940) that such a mean value is equal to the actual value at an intermediate temperature T_r given by

$$T_r = \frac{T_1 T_2}{T_2 - T_1} l_n \; T_2/T_1 \qquad \dots \quad (7)$$

and for our present purpose we have used this expression.

In figure 4, we have plotted the observed and calculated values of R_T using Kihara's (1949) expression as a function of T_r. The agreement for Argon is good while for Neon it is bad. The continuous increase of R_T for Neon at high temperatures implies a very steep repulsion and is supported neither by the data on any other transport coefficient nor by results obtained from the scattering of beams of high velocity Neon atoms by Neon gas (Amdur and Mason, 1955). Mason and Rice (1954b) have also found a similar disagreement for the exp-six model and further measurement of R_T for Neon at high temperatures would seem to be desirable

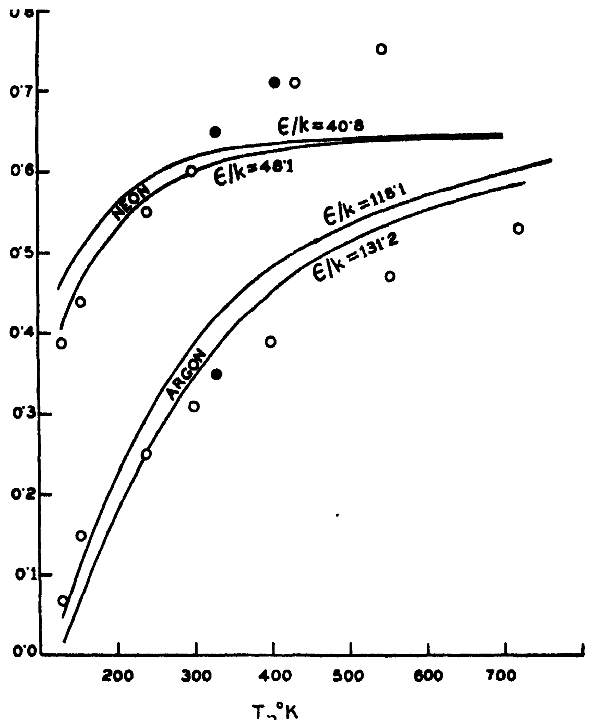

Fig. 4. Values of R_T versus T_r

The thermal conductivity values were also found to be reproduced within ±1%; while the departure of the calculated values from the observed values for self diffusion was more or less within the range of experimental errors except for the case of Xenon where a single data of one worker is available and is believed to be much in error (Mason and Rice 1954b).

5. TEMPERATURE AND PRESSURE DEPENDENCE OF $\lambda/\eta C_v$

A very interesting relationship connecting the heat conductivity, viscosity and specific heat at constant volume which follows from the kinetic theory of gases is

$$\lambda = F\eta C_v \qquad \cdots (8)$$

where F depends upon the nature of interaction between the molecules. No theoretically exact expression for F has been obtained in case of polyatomic gases and usually an empirical suggestion of Eucken is utilised. We shall therefore confine our discussion to monatomic gases only where rigorous expressions can be obtained from theory.

Temperature dependence of F

Chapman and Cowling (1952) have shown that whatever be the nature of interaction between the molecules, $[F]_1$, the first approximation to F, is always equal to 5/2 for all spherically symmetrical non-rotating molecules and the second approximation $[F]_2 \geqslant 5/2$. Numerical calculations for special molecular models suggest that F increases as successive degrees of approximation are taken into account and that the limiting value is only slightly greater than 5/2. It is further shown that both for rigid sphere model as well as for inverse power model F is independent of temperature. On the former model $[F]_4$ is equal to 2.522, while for the latter

$$[F]_2 = \frac{5}{2}\left[1+\frac{(\upsilon-5)^2}{4(\upsilon-1)(11\upsilon-13)}+\dots\right]\Big/\left[1+\frac{3(\upsilon-5)^2}{2(\upsilon-1)(110\upsilon-113)}+\dots\right] \qquad (9)$$

where υ is the force index

A slight variation of F with temperature is found if molecular attractions are taken into account. The two useful models taking into account molecular attractions are the Lennard-Jones 12 : 6 model and the modified Buckingham Exp-Six model. In the latter the potential energy $E(r)$ is

$$E(r) = \frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha}\, e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6\right] \qquad \dots \quad (10)$$

where ϵ is the depth of potential energy minimum, r_m is position of minimum and α a parameter which is a measure of the steepness of repulsion energy. On both these models $[F]_3$ can be shown to be given by the expression—

$$[F]_3 = 5f_\lambda^3/2f_\eta^3 \qquad \dots \quad (11)$$

f_λ^3 and f_η^3 are given by Mason (1954) for his Exp-Six model. Table 5 gives the values of $[F]_3$ for both these models and shows that there is only a slight dependence of F on temperature and is well within the limits of errors involved in the determination of λ and η. Kannuluik and Carman (1952) found no systematic change in the value of F with temperature from their experimental investigations of thermal conductivity of gases. On the other hand, Keyes (1954) by suitably assessing all the data for λ and η available in the literature has shown that there is a slight decrease in F with temperature. However, the present errors involved in the measurement of λ and the inconsistencies in the reported values of the different experimenters, does not permit any definite conclusion on the point.

TABLE V

Values of $[F]_3$ as a function of T^*

T^*	Lennard-Jones 12 : 6 model	Modified Buckingham Exp-Six Model			
		$\alpha=12$	$\alpha=13$	$\alpha=14$	$\alpha=15$
0.10	—	2.5025	2.5025	2.5027	2.5025
0.30	2.5020	2.5020	2.5023	2.5025	2.5025
0.50	2.5003	2.5003	2.5003	2.5003	2.5005
0.75	2.5000	2.5003	2.5000	2.5000	2.5000
1.00	2.5003	2.5003	2.5000	2.5000	2.5000
1.25	2.5003	2.5003	2.5000	2.5000	2.5003
1.50	2.5005	2.5003	2.5005	2.5008	2.5008
2.0	2.5017	2.5013	2.5013	2.5018	2.5018
2.5	2.5032	2.5023	2.5028	2.5030	2.5033
3.0	2.5045	2.5033	2.5040	2.5043	2.5048
4.0	2.5067	2.5052	2.5058	2.5063	2.5067
5.0	2.5080	2.5063	2.5070	2.5075	2.5078
10	2.5102	2.5080	2.5088	2.5095	2.5099
50	2.5112	2.5083	2.5093	2.5097	2.5108
100	2.5112	2.5093	2.5105	2.5104	2.5112
200	2.5112	2.5104	2.5120	2.5114	2.5125
400	2.5112	—	—	—	—

Pressure dependence of F

To investigate the pressure dependence of F, one has naturally to go into the dense gas theory, which unfortunately so far is quite undeveloped. The main difficulty in the development of kinetic theory for condensed systems is that one must understand certain aspects of three molecule and higher order collissions. For rigid spherical molecules, however, it is theoretically impossible for three or more molecules to collide at exactly the same moment. Hence for this particular case, Enskog developed a complete theory by suitably modifying the dilute gas theory and taking into account the collisional transfer of momentum and energy. The formulae for λ and η of a dense gas made of rigid spherical molecules are

$$\eta/\eta^0 = b_0/V[1/y+0.8+0.761y) \tag{12}$$

$$\lambda/\lambda^0 = b_0/V([1/y+1.2+0.755y] \tag{13}$$

Here λ^0 and η^0 are the values of λ and η respectively at normal densities, i.e. zero pressure values and

$$y = PV/RT-1 = b_0/V+0.6250(b_0/V)^2+0.2869(b_0/V)^3+0.115(b_0/V)^4+\dots\ \dots \tag{14}$$

where $b_0 = 2/3\, \pi n \sigma^3$ and σ is the molecular diameter. In the region of low and moderate densities y is given by the equation 4, while in the high density region probably the best equation of state for rigid sphere is obtained from the radial distribution function by Kirkwood, Maun and Alder (1950).

Hence for a dense gas made of rigid spherical molecules

$$\frac{\lambda\eta^0}{\lambda^0\eta} = \frac{F}{F^0} = \frac{[1/y+1.2+0.755y]}{[1/y+0.8+0.761y]} \qquad \ldots \ (15)$$

and if F^0 be taken as 2.522, the value characteristic of rigid spherical molecules, then

$$F = 2.522[1/y+1.2+0.755y]/[1/y+0.8+0.761y] \qquad \ldots \ (16)$$

Columns 3 and 4 of table 6 give the values of F/F^0 and F respectively for corresponding b_0/v and y. For b_0/v upto 0.30 equation 14 has been utilised to calculate y while for higher densities the table given by Hirschfelder, Curtiss and Brid (1954) has been used. It is seen that F/F^0 decreases both at low and high pressures, the maximum being attained round about $y = 0.3535$.

TABLE VI

Values of F/F^0 as a function of b_0/v.

b_0/v	y	F/F^0	F† $= \lambda/\eta C_v$
0.01	0.0101	1.004	2.532
0.05	0.0516	1.020	2.572
0.10	0.1066	1.039	2.620
0.15	0.1651	1.057	2.666
0.20	0.2275	1.074	2.709
0.25	0.2940	1.090	2.749
0.30	0.3649	1.104	2.785
0.3535	0.44	1.292	3.258
0.6250	0.91	1.152	2.906
0.8511	1.39	1.152	2.905
1.047	1.89	1.140	2.876
1.224	2.40	1.127	2.842
1.377	2.91	1.114	2.809
1.527	3.43	1.103	2.781
1.664	3.93	1.093	2.757
1.805	4.44	1.085	2.736
1.934	4.95	1.078	2.718
2.058	5.46	1.071	2.702
2.160	5.99	1.066	2.688

† Here also C_v stands for 3R/2JM.

6. THERMAL CONDUCTIVITY OF MODERATELY DENSE ARGON GAS

Recently Keyes (1954) has reported the thermal conductivity data for argon at some moderate pressures. In order to be able to compare his experimental values with those given by equation 13 it is necessary to specify b_0 and V. By correlating the experimental pressure with the Beattie-Bridgeman equation of state,

$$PV^2 = RT(1-C/VT^3)(V+B_0-bB_0/V)-A_0(1-a/V) \qquad \ldots \quad (17)$$

the corresponding V can be easily determined. The values of the constants A_0, B_0, a, b and C for argon are given by Beattie and Bridgeman (1928) and we have utilised their values except for C, the relation

$$C = 0.0236(A_0^3/R^3B_0^2) \qquad \ldots \quad (18)$$

was preferred following Hirschfelder and Roseveare (1939). Assuming the value of σ for argon as 3.379A, b_0 comes out to be 48.67 c.c./mole. This value is in good agreement with the value 49.10 c.c./mole calculated from Beattie Bridgeman costants and can be taken as sufficiently accurate and reliable. Thus determining b_0 and V, λ/λ^0 has been calculated and compared with the observed values in table 7. It will be seen that the absolute agreement between $[\lambda/\lambda^0]$ calc. and $[\lambda/\lambda^0]$obs. it not very good and that the latter is always higher than the former. This discrepancy may be due (1) the non-realistic nature of the rigid sphere model and (II) the experimental errors involved in the determination of λ/λ^0.

TABLE VII

Thermal Conductivity of Argon at moderate pressures

Pressure in atm.	Temperature in °K	Volume in litros	b_0/V calc. 12 : 6	$[\lambda/\lambda^\circ]$ obs.	$[\lambda/\lambda^\circ]$ calc.
12.4	363.13	2.39825	0.020294	1.032	1.012
19.5	363.13	1.52350	0.031947	1.042	1.019
11.1	473.13	3.50346	0.013892	1.020	1.008
17.0	473.13	2.28964	0.021257	1.023	1.013
12.0	573.13	3.93093	0.012381	1.028	1.007
17.0	573.13	2.77826	0.017518	1.022	1.010

Further b_0 can also be evaluated directly from the dense gas theory by adopting the following procedure. From equation 13 it follows that λ/λ^0 is only a function of b_0/V and hence we can find that b_0/V and thereafter b_0 or σ which gives the absolute agreement with the $[\lambda/\lambda^0]$obs. value. In actual practice it was found that different choices for pressure and temperature gave widely different values for b_0 ranging from $b_0 = 87$ to $b_0 = 179$. This again leads to the same conclusion that either the $[\lambda/\lambda^0]$obs. values are wrong or this simple theory is inadequate. Very accurate measurements are required to arrive at a definite conclusion on the point.

From equation (15) we have

$$[\eta/\eta^0] = F^0/F[\lambda/\lambda^0] \qquad \ldots \quad (19)$$

Substituting the observed values for λ/λ^0 in equation 19, we have computed the corresponding η/η^0 and these values are recorded in column 3 of Table VIII Column 4 of table 8 gives the values of η/η^0 as calculated from equation 13.

TABLE VIII

Values of η/η^0 for Argon

Pressure in atm.	Temperature in °K	η/η^0 from eqn. 19	η/η^0 from eqn. 12
12.4	363.13	1.024	1.004
19.5	363.13	1.029	1.007
11.1	473.13	1.014	1.003
17.0	473.13	1.014	1.004
12.0	573.13	1.023	1.002
17.0	573.13	1.015	1.003

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