Thermal diffusion in mixtures of the inert gases

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Measurements have been made of the separation produced by thermal diffusion in all the binary mixtures of the inert gases (except Kr-X and Rn mixtures) at temperatures ranging from −180 to 400° C. The temperature dependence of the thermal diffusion ratio, \( k_T \), and of \( R_T \) (where \( R_T = k_T / [k_T(\infty)]_1 \)) has been deduced. The results indicate that, in general, \( R_T \) increases with the temperature in the lower range and becomes constant at high temperatures. The constant value is first attained at a temperature which varies from mixture to mixture, but its magnitude is nearly the same for all mixtures. It corresponds with a repulsive force index of 11, if the molecules are treated as centres of repulsive force only.

The results have been compared with those calculated by R. Clark Jones (1940, 1941) for a gas mixture in which the two molecular species have identical force fields of the Lennard-Jones type, with repulsive force index \( \nu = 9 \) and attractive force index \( \nu' = 5 \). The theoretical results give \( R_T \) as a function of \( T / T_c \), where \( T_c \) is the critical temperature of the gas. This relation with the critical temperature is supported by the experimental results, though there are difficulties in the comparison due to the non-identical nature of the force fields in the experimental mixtures. It appears, however, that the observed behaviour could be explained by a Lennard-Jones model if the force indices were suitably chosen, and that a study of the temperature dependence of \( R_T \) in isotropic mixtures would enable the indices to be determined with some precision.

INTRODUCTION

The work to be described is an experimental investigation of the dependence on temperature of the thermal diffusion ratio \( k_T \) for the various combinations of the inert gases, and a comparison of the results with the theoretical ones of R. Clark Jones (1940, 1941) for molecules which have an attractive field superimposed on a repulsive field.

The thermal diffusion ratio \( k_T \) appears in the Chapman-Enskog equation relating the concentrations \( c_1, c_2 \) of the molecular species in a binary gas mixture in which a temperature gradient exists to the temperature

\[
\nabla c_1 = - \nabla c_2 = - k_T \cdot \nabla \log T.
\]

\( k_T \) is a complicated function of the masses, concentrations and force fields of the molecules. The effect of the fields enters in the form of integrals \( \Omega \) which may be considered as dimensionless collision cross-sections, and unless the two molecular species have identical fields of force, distinction must be made between the interactions of like and unlike molecules, that is, between \( \Omega_1, \Omega_2 \) and \( \Omega_{12} \). When the molecules have identical fields, as in mixtures of isotopes, only one type of interaction occurs. Chapman describes such molecules as ‘isotopic’, whether or not they are isotopes of the same element. Prior to Clark Jones’s work \( k_T \) had been evaluated only in the following special cases:

(i) for molecules interacting like rigid elastic spheres of different diameters \( \sigma_1, \sigma_2 \);
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(ii) for mixtures of isotopic molecules which are point centres of repulsive force $F$ varying inversely as the $\nu$th power of the distance $r$, i.e. $F = \kappa r^{-\nu}$.

In both these cases $k_T$ is independent of the temperature.

Experimental determinations of $k_T$ have been made for various gas mixtures (Ibbs & Grew 1931; Atkins, Bastick & Ibbs 1939, etc.; Grew 1941). A comparison of the experimental and theoretical values enables an estimate to be made of the force index $\nu$, assuming the interaction to be an inverse power repulsion. In many cases, however, the value of $k_T$ changes with temperature. This is an indication that an inverse power repulsion does not adequately represent the molecular fields, since for this type of interaction $k_T$ is theoretically independent of the temperature if the molecules are isotopic, and only slightly dependent otherwise (Chapman 1940).

As a result of recent experimental work on thermal diffusion in mixtures of isotopes (Nier 1940), in which also a dependence of $k_T$ on temperature was observed, Clark Jones (1940, 1941) has treated theoretically thermal diffusion in isotopic mixtures in which the interaction includes an inverse power attraction superimposed on an inverse power repulsion, thus $F = \kappa r^{-\nu} - \kappa' r^{-\nu'}$ (Lennard-Jones's model). This model is on first consideration unpromising as a means of explaining the observed variation of $k_T$ with temperature, which is a decrease with decreasing temperature: it suggests, indeed, that the variation should be in the opposite direction. For, considering a repulsive field only, $F = \kappa r^{-\nu}$, it is seen that

$$\nu = -d \log F / d \log r.$$ 

This quantity Clark Jones calls the hardness function $\mu(\nu)$. For the Lennard-Jones model it is

$$\mu(\nu) = \nu + Q(\nu - \nu') + O(Q^2), \quad Q = \frac{\kappa'}{\kappa} r^{(\nu - \nu')}.$$ 

For values of $r$ less than $r_0$ (the value of $r$ at which the potential energy is a minimum), $Q$ is positive and less than unity, so that $\mu(\nu) > \nu$, and by an amount which decreases as $r$ decreases, that is, as the temperature increases. It would be expected then that $k_T$ would decrease with increasing temperature, contrary to what is observed. Clark Jones has shown that this is the case only at high temperatures; at lower temperatures the effect of the attractive field is to cause $k_T$ to decrease as the temperature falls, and even to change sign.

His fullest treatment is for an interaction in which the repulsive index $\nu = 9$, and the attractive index $\nu' = 5$, a model which was chosen because much of the numerical work had already been done. His results are shown graphically in figure 1. Here the ordinate $R_T$ is the ratio of $k_T$ for the particular model to the value for rigid elastic spheres $k_T(\infty)$. ($R_T$ is more conveniently discussed than $k_T$, since it is roughly independent of the concentrations of the molecular species and only slightly dependent on their masses, so that its value is determined mainly by the molecular fields.) The abscissa is the quantity $\epsilon / kT$, $\epsilon$ being the depth of the potential energy minimum, i.e.

$$\epsilon = \frac{\nu - \nu'}{(\nu - 1)(\nu' - 1)\kappa^{(\nu - 1)(\nu' - 1)}}.$$
and $k$ is the Boltzmann constant. Clark Jones has compared these theoretical values with some experimental values of $R_T$ obtained by Nier (1940) for mixtures of the isotopes $^{20}\text{Ne},^{22}\text{Ne}$, and $^{12}\text{CH}_4,^{13}\text{CH}_4$. The observed values are mean values over a wide temperature range, and the maximum value is considerably greater than the maximum theoretical value, presumably because the actual repulsive index is greater than 9. Despite these difficulties the comparison suggests that the observed variation of $R_T$ could reasonably be explained with the Lennard-Jones model, though the indices (9, 5) are not suitable, at least for neon.

![Graph](http:// rspa.royalsocietypublishing.org/)

**Figure 1.** The variation of $R_T$ with temperature for the (9, 5) model (Clark Jones). The abscissa is approximately $[T_c/T]^2$, where $T_c$ is the critical temperature of the gas.

As a result of this extension of the theory of the thermal diffusion effect further measurements of the variation of $R_T$ with temperature are desirable. These should preferably apply to isotopic mixtures, since in them only one type of interaction has to be considered. But, although for such mixtures the theoretical treatment is relatively simple, the experimental difficulties are large, and the work which is now described is a measurement of the thermal diffusion effect over a wide range of temperature in mixtures of the inert gases—which presumably form the next simplest case to that of isotopic mixtures.

Some measurements on mixtures of the inert gases have already been reported. Atkins et al. (1939) have examined all the binary combinations of He, Ne, A, Kr and X, but the effect was measured only for a temperature gradient from 15 to 100° C. Measurements over a range of temperature from 0 to $-180^\circ$ C were made by Ibbs & Grew (1931) for He-Ne, He-A and Ne-A mixtures. These indicated clearly that $R_T$ diminishes as the temperature falls. Since this work was done the inert gases have
come to be commercially obtainable in a pure state, and larger volumes may now be used than formerly. A modification of the original method has been made to permit measurements on one and the same mixture over a temperature range from \(-180\) to \(400^\circ\) C.

**Experimental method**

In general, the method and procedure were the same as in the study of the effect in hydrogen-deuterium mixtures (Grew 1941). The analysis of the gas mixture before and after separation was made by a small thermal conductivity gauge to which a sample of gas of volume 0·2 to 0·4 c.c. was admitted from the diffusion apparatus by means of a special sampling cock. The diffusion vessel consisted of a large bulb \(A\), of volume 61·3 c.c., connected by a tube 9·5 cm. long and 3·6 mm. internal diameter to a small bulb \(B\) which formed part of a stopcock, as shown in figure 2. The volume of \(B\) was 2·6 c.c. Diffusion proceeded with the stopcock turned so that the short side tube \(C\) was in communication with the bulbs. Rotation of the cock then spilt the gas in \(C\) into the gauge for analysis.

The gas mixtures were prepared in known proportions in a burette attached to the apparatus and were then admitted to the evacuated bulbs. The pressure was adjusted to about 30 cm. of mercury at room temperature prior to the high-temperature measurements, and to about 70 cm. prior to the low-temperature measurements. This ensured that at high temperatures the pressure did not exceed atmospheric pressure, and at low temperatures there was sufficient gas in the side tube \(C\) for analysis. The separation was thus measured at pressures which varied with the temperature, but theoretically the separation is independent of the pressure and experiment has confirmed this (Grew 1945).

For high temperatures the bulb \(A\) was placed in an electric furnace. The support for the nichrome winding was a thick-walled copper tube on which there were supplementary windings at either end so that the region near the bulb could be brought to a uniform temperature. The low-temperature measurements were made in two ways. In the first method the bulb \(A\) (which was now brought below \(B\) by rotation about the ground-joint \(D\)) was surrounded by a copper cylinder, a little
longer than the bulb, on which a few turns of nichrome wire were wound to form a heating coil. The cylinder was supported inside a double-walled vessel of which the space between the walls could be evacuated. Surrounding this vessel was a vacuum vessel containing liquid oxygen. Temperatures from $-120$ to $-180^\circ$ C were thus readily maintained by adjustment of the heating current and of the vacuum between the walls of the inner vessel. In the second method, applicable between $-20$ and $-150^\circ$ C, the bulb was surrounded with pentane contained in a vacuum vessel, and cooled and maintained at constant temperature by addition of liquid oxygen or solid carbon dioxide. Manual control sufficed to keep the temperature constant to within $0.5^\circ$ C for the 45 min. or so required for equilibrium to be attained and the samples analyzed. Over the range of temperature common to both methods excellent agreement was obtained. In those cases in which the boiling-point of the gases permitted of it, the bulb was immersed in liquid oxygen for the lowest temperature.

Temperatures were measured by three copper-constantan couples placed close to the upper, middle and lower parts of the bulb $A$ respectively, so that the temperature variation over the bulb could be measured and a mean temperature found. Above $300^\circ$ C the variation was $4^\circ$ C; at low temperatures not more than $2^\circ$ C. The couple was calibrated frequently, using as reference points the boiling-point of oxygen, the freezing-point of mercury, and the boiling-points of water, naphthalene and benzophenone. The temperature of the water circulating about the small bulb was measured with a mercury thermometer. The temperature was controlled to within $0.5^\circ$ C.

Measurement of the separation. The difference in composition of the gas in the large bulb and in the small bulb when a temperature gradient exists in the connecting tube is termed the separation. Only the change in composition in the small bulb was measured, the separation being calculated from this and the relative volumes and temperatures of the two bulbs. Both bulbs were first brought to the same temperature and a sample of gas admitted to the gauge, which, as before (Grew 1941), formed one arm of a bridge across which the potential difference could be varied. The potential difference to balance the bridge for the uniform mixture was thus found. The large bulb was then brought to the required temperature, and after 20 min. or more a sample was withdrawn from the small bulb. From the change in potential difference required to balance the bridge and the slope of the potential difference-concentration curve, the change in composition of the gas in the small bulb was calculated. To ensure that equilibrium had been attained a second sample was taken later. The separation is then given by

$$ s = s' \left(1 + \frac{V_1 T_2}{V_2 T_1} + \theta \right), $$

where $s' = \text{change in composition in the small bulb}; V_1 = \text{volume of small bulb}; V_2 = \text{volume of large bulb}; T_1 = \text{temperature of small bulb}; T_2 = \text{temperature of large bulb}$, and $\theta = \text{a correction term for the gas in the connecting tube}$. $\theta$ is a function of the volumes of the connecting tube and large bulb and of the temperatures $T_1$ and
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$T_2$. In finding $\theta$ it was assumed that the temperature gradient in the connecting tube was uniform and that $k_T$ could be regarded as constant throughout the gas in the tube. Both assumptions were sufficiently valid for the calculation of the correction. $\theta$ increases with the temperature $T_2$; at the highest temperatures used its value was 0·013.

It is estimated that in mixtures containing He or Ne, the error of a measurement of the percentage separation is $\pm$ 0·03. The gauge is less sensitive for A-Kr and A-X mixtures, and here the error may be $\pm$ 0·05.

Preparation of the gases. The inert gases used were all supplied by the British Oxygen Co. The helium, neon and argon were spectroscopically pure. The krypton was of German origin and stated to contain 1% xenon. No attempt was made to purify this gas. The xenon was produced in the U.S.A., and, as its purity was not given, the gas was fractionated. The gauge readings for the various fractions indicated that the gas contained a small amount of impurity—about 2% if it was krypton and a smaller amount if it was a lighter gas. The residue, which alone was used in the diffusion measurements, contained without doubt only a negligible amount of impurity.

Results

The values of the separation, when plotted against $\log T_2/T_1$ ($T_1$ = the constant temperature of the small bulb, $T_2$ = the varying temperature of the large bulb), yield in some cases and over a limited range of temperature $T_2$ a straight line, indicating that the fundamental equation

$$dc = k_T d(\log T)$$

may be integrated as if $k_T$ were constant, to give the separation

$$s = c_2 - c_1 = k_T \log T_2/T_1$$

(where $c_1$, $c_2$ are the concentrations at temperatures $T_1$, $T_2$). In general, however, the linear relation between the separation and $\log T_2/T_1$ does not hold if $T_1$ is sufficiently reduced, and it is necessary to consider the interpretation of the separation $-\log T_2/T_1$ curve in this case.

$k_T$ is a function of the concentration, and for some types of molecular field of the temperature also. If the separation is not too large the dependence on concentration may be ignored and $k_T$ regarded as a function of temperature only. Then

$$s = c_2 - c_1 = \int_{T_1}^{T_2} k_T d(\log T) \quad \text{and} \quad ds = \int_{T_1}^{T_1+dT_1} k_T d(\log T),$$

since $T_1$ is constant in this method of experiment. Hence

$$ds = k_T d(\log T_2).$$

The slope of the separation $-\log T_2/T_1$ curve at any point is therefore a measure of $k_T$ at the temperature $T_2$ corresponding to that point.

The assumption made here that $k_T$ may be considered as independent of the concentration in the range of separation involved is questionable, as the separation
amounts in some of the mixtures examined to 10%. It is, however, not easily avoided, and its effect was therefore minimized. First, the mixtures used were those containing nearly equal proportions of the two components and for which therefore the variation of $k_T$ with composition is small. Secondly, each observed separation was corrected so that it applied to a mixture of mean composition the same as that of the original uniform mixture. In the form of apparatus used, most of the change in composition occurs in the small bulb. This causes the mean composition of the gas in the connecting tube to vary with the separation attained, and consideration shows that there is an apparent decrease in $k_T = ds/d(\log T_s)$ as $T_s$ increases, since in all cases the proportion of the lighter component was less than that for maximum value of $k_T$. The reverse effect would occur if the change in composition occurred in the large bulb. For equal changes in composition in the two bulbs, that is, for constant mean composition of the gas in the connecting tube, the separation $-\log T_2/T_1$ curve should be linear. Each value of the separation was therefore corrected so that it applied to a mixture of mean composition equal to that of the original mixture. For this purpose use was made of the curves showing the separation as a function of the composition (for constant temperature ratio) given by Atkins et al. (1939). It is these corrected values which are recorded and from which the values of $k_T$ were derived. That this treatment is satisfactory is shown by the fact that for those mixtures in which $k_T$ is expected to be independent of temperature (for example, He-Ne except at very low temperatures) the separation $-\log T_2/T_1$ plot is a straight line even though the separation amounts to 8% or more. The apparent variation of $k_T$ in other cases is therefore a temperature effect.

The results are summarized in table 1, where the values of the separation at definite values of $-\log T_2/T_1$ are given for the nine mixtures examined.* $R_T$ is the ratio of $k_T$ (determined from the slope of the separation $-\log T_2/T_1$ curves) to $k_T(\infty)$, this being the theoretical value of $k_T$ for the same mixture assuming that the molecules interact like rigid elastic spheres of diameters equal to those deduced from the viscosity of the pure gases. Expressions for $k_T(\infty)$ have been given by Atkins et al. (1939). The value of $R_T$ given in the last column is that found by Atkins et al. for a mixture of the same composition; it is a mean value in the range 15 to 100°C. There is reasonably good agreement except in the case of He-Ne. The difference between the present value for this mixture of 0.64 and Atkins et al. value of 0.80 is much greater than the experimental error. The cause of this discrepancy is unknown. In case the gases used had been inadvertently contaminated during manipulation, new supplies were obtained and further measurements made. The following are the results:

<table>
<thead>
<tr>
<th>mixture</th>
<th>% He</th>
<th>$k_T$</th>
<th>$k_T(\infty)$</th>
<th>$R_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36.8</td>
<td>0.070</td>
<td>0.104</td>
<td>0.67</td>
</tr>
<tr>
<td>2</td>
<td>53.8</td>
<td>0.080</td>
<td>0.124</td>
<td>0.64</td>
</tr>
<tr>
<td>3</td>
<td>62.5</td>
<td>0.078</td>
<td>0.125</td>
<td>0.62</td>
</tr>
</tbody>
</table>

* The method of analysis was not sufficiently sensitive to measure reliably the small separation in Kr-X mixtures.
<table>
<thead>
<tr>
<th>mixture</th>
<th>([k_r(\infty)]_1)</th>
<th>(\log_{10} T_2/T_1)</th>
<th>(t_2^\circ C)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
<th>(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He-Ne</td>
<td>0.124</td>
<td>53.8% He</td>
<td>0.58</td>
<td>0.60</td>
<td>0.63</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He-A</td>
<td>0.151</td>
<td>51.2% He</td>
<td>0.55</td>
<td>0.56</td>
<td>0.61</td>
<td>0.63</td>
<td>0.63</td>
<td>0.64</td>
<td>0.65</td>
<td>0.66</td>
<td>0.66</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He-Kr</td>
<td>0.166</td>
<td>55.0% He</td>
<td>0.55</td>
<td>0.61</td>
<td>0.64</td>
<td>0.67</td>
<td>0.67</td>
<td>0.67</td>
<td>0.67</td>
<td>0.67</td>
<td>0.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He-X</td>
<td>0.163</td>
<td>53.6% He</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne-A</td>
<td>0.084</td>
<td>51.2% Ne</td>
<td>0.28</td>
<td>0.36</td>
<td>0.44</td>
<td>0.48</td>
<td>0.52</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne-Kr</td>
<td>0.132</td>
<td>53.0% Ne</td>
<td>0.30</td>
<td>0.34</td>
<td>0.40</td>
<td>0.47</td>
<td>0.55</td>
<td>0.59</td>
<td>0.61</td>
<td>0.64</td>
<td>0.53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne-X</td>
<td>0.152</td>
<td>54.2% Ne</td>
<td>0.43</td>
<td>0.46</td>
<td>0.49</td>
<td>0.54</td>
<td>0.60</td>
<td>0.66</td>
<td>0.66</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-Kr</td>
<td>0.079</td>
<td>53.5% A</td>
<td>0.12</td>
<td>0.18</td>
<td>0.24</td>
<td>0.33</td>
<td>0.47</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-X</td>
<td>0.116</td>
<td>56.4% A</td>
<td>0.13</td>
<td>0.15</td>
<td>0.18</td>
<td>0.29</td>
<td>0.37</td>
<td>0.45</td>
<td>0.45</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1**

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The apparent dependence of $R_T$ on the composition is, at least in its direction, in accord with theoretical predictions for molecules exerting an inverse power repulsion (Chapman 1940, p. 58). The higher value of 0.80 is supported by Blüh, Blüh & Puschner (1937); on the other hand, values of $R_T$ deduced from the viscosity of the pure gases (Clark Jones 1940, p. 116) favour the lower value found in the present work.

**Discussion of results**

The results confirm the earlier ones (Ibbs & Grew 1931) in that they show that in general $R_T$ decreases as the temperature falls. In some mixtures, such as He-Ne, $R_T$ is constant over almost the whole temperature range; in A-Kr $R_T$ shows a continuous variation over the whole range. Other mixtures show a more or less extended temperature range in which $R_T$ is constant, and below this a range in which $R_T$ diminishes as the temperature falls. It is a reasonable conclusion that this behaviour would be shown by all the mixtures were the temperature range sufficiently extended. The constancy of $R_T$ over a range of temperature indicates that the molecules are, in that range, behaving as if they exerted repulsive forces only.

*The maximum value of $R_T$ and the corresponding force index.* It is remarkable that, although the temperature at which $R_T$ first becomes constant varies widely from mixture to mixture, the value of $R_T$ when constant, that is, the maximum value—$R_T$(max.), is much the same for all mixtures, viz. about 0.64. Thus the change in $R_T$ in passing from one to another of the inert gas mixtures, observed by Atkins et al. (1939), is now seen to be an accident of the temperature range to which their measurements were restricted. It appears that at sufficiently high temperatures $R_T$ would be nearly the same for all.

Assuming that, at high temperatures, the molecules behave like centres of repulsive force only, $F = kr^{-\nu}$, an estimate can be made of the force index $\nu$ by comparing the experimental value of $R_T$(max.) with the theoretical values of $R_T$ for different values of $\nu$. A difficulty arises in the comparison, however, in that theoretical values of $R_T$ are known exactly only for the special case of a mixture in which the ratio of the molecular masses is very large and the concentration of the heavier molecule tends to unity (the Lorentzian case).* In the general case only the ratio of the first approximations to $k_T$, $[k_T(\nu)]_1/[k_T(\infty)]_1$, is known, whereas the theoretical value of $R_T$ is more properly given by $k_T(\nu)/[k_T(\infty)]_1$ (where $k_T(\nu)$ is the exact value of $k_T$) to correspond with the experimental value of $R_T$ defined as

$$k_T\text{(experimental)}/[k_T(\infty)]_1.$$  

For small values of the mass ratio and of $\nu$ the error of the first approximation is small, but it increases to about 23% in the Lorentzian case with $\nu = \infty$. In the

* Values of $\nu$ have sometimes been estimated from theoretical values of $R_T$ for this special case, but more recent work (Grew 1941) has shown that this leads to considerable error, and the procedure here adopted is preferable.
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absence of an exact knowledge of the variation of the error, it may be assumed that it increases linearly with the proportionate mass difference defined by

\[ M = (m_1 - m_2)/(m_1 + m_2). \]

The error has been estimated for the case \( M = 0 \) and for \( \nu = 5, 9, 13, 17, \infty \) (Grew 1941, p. 397), and it is known in the Lorentzian case (\( M = 1 \)) for these same values of \( \nu \). Linear interpolation thus gives the error for intermediate values of \( M \) and \( \nu \). Then using Chapman’s (1940, p. 58) data, curves can be drawn showing \( R_T \) as a function of \( \nu \) for various values of \( M \). From these curves the values of \( \nu \) shown in table 2 were found to correspond with the experimental values of \( R_T \). As the mixtures are not isotopic, \( \nu \) derived in this way must be regarded as a mean of \( \nu_1, \nu_2, \nu_{12} \). The possible error of 0.01 in \( R_T \) introduces an uncertainty of 0.4 in the values of \( \nu \).

Table 2. Values of the proportionate mass ratio \( M \), of \( R_T \) and of the corresponding force index \( \nu \)

<table>
<thead>
<tr>
<th>mixture</th>
<th>He-Ne</th>
<th>He-A</th>
<th>He-Kr</th>
<th>He-X</th>
<th>Ne-A</th>
<th>Ne-Kr</th>
<th>Ne-X</th>
<th>A-Kr</th>
<th>A-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M )</td>
<td>0.67</td>
<td>0.82</td>
<td>0.91</td>
<td>0.94</td>
<td>0.33</td>
<td>0.61</td>
<td>0.73</td>
<td>0.36</td>
<td>0.53</td>
</tr>
<tr>
<td>( R_T (\text{max.}) )</td>
<td>0.64</td>
<td>0.66</td>
<td>0.67</td>
<td>0.66</td>
<td>0.57</td>
<td>0.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu )</td>
<td>11.0</td>
<td>10.9</td>
<td>10.8</td>
<td>10.5</td>
<td>10.9</td>
<td>11.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus in the six mixtures for which values can be stated \( \nu \) is close to 11. This suggests that, in so far as they can be represented by an inverse power repulsion, that is, at high temperatures, the fields of the inert gas atoms are alike in having the same, or nearly the same, force index and differ only in the force constant.

The variation of \( R_T \) with temperature. Reference has already been made to Clark Jones’s (1940, 1941) calculation of \( R_T \) for the Lennard-Jones molecular field, which includes an inverse power attraction superimposed on a repulsive force: thus \( F = \kappa r^{-\nu} - \kappa' r^{-\nu'} \). The calculated values refer to the special case of \( \nu = 9, \nu' = 5 \). \( R_T \) is given as a function of a quantity \( \epsilon/kT \), where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, and \( \epsilon \) is the minimum potential energy of two interacting molecules. According to Lennard-Jones and Devonshire, \( \epsilon \) is related to the critical temperature \( T_C \) of the gas—\( \epsilon = kT_C \), or better \( \epsilon = kT_C/1.22 \) (cf. Fowler & Guggenheim 1939, p. 345). Using this latter relation, the curve marked (9, 5) of figure 3a, b has been drawn, representing \( R_T \) as a function of \( \log T/T_C \). The curve (9, \( \infty \)) is that for a molecule which exerts a repulsive force only, with index 9. In both cases the values of \( R_T \) apply to an isotopic mixture in which \( M \) is small. Also, \( R_T \) is here the ratio of the first approximations \( [k_T(9, 5)]_1/[k_T(\infty)]_1 \).

To compare the experimental results with these theoretical ones some assumption must be made about the ‘critical temperature’ to be assigned to the gas mixtures since they are not isotopic. Clark Jones gives reasons for taking as the critical temperature \( T_C \) of a mixture the mean proportional of the critical temperatures of the two components. If this is done the following values are found:

<table>
<thead>
<tr>
<th>mixture</th>
<th>He-Ne</th>
<th>He-A</th>
<th>He-Kr</th>
<th>He-X</th>
<th>Ne-A</th>
<th>Ne-Kr</th>
<th>Ne-X</th>
<th>A-Kr</th>
<th>A-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_C ) °K</td>
<td>15</td>
<td>27.5</td>
<td>32.5</td>
<td>38</td>
<td>81.5</td>
<td>96</td>
<td>112</td>
<td>178</td>
<td>209</td>
</tr>
</tbody>
</table>
The experimental values of $R_T$ at temperature $T$ ($T = T_2$ of table 1) may now be plotted against $\log T/T_C$. But as $R_T$ (max.) is not the same for all the mixtures, partly because of the dependence on the mass ratio, the maximum values of $R_T$ for each mixture (except A-Kr, A-X, for which a constant value of $R_T$ is not reached) have first been made equal to 0·63 and the other values changed in proportion. These are the values shown in figure 3a, b.

![Figure 3a](image1.png)

**Figure 3a, b.** $R_T$ as a function of $\log T/T_C$. Experimental values $\circ \times$ etc. (9, 5): Clark Jones's theoretical values. (9, $\infty$): for repulsive field only, index 9. Broken curve: a reference curve for comparison of figures 3a, b and 4.

It is apparent from the curves that:

(1) The experimental values of $R_T$ are higher than the theoretical value for the same value of $\log T/T_C$. In particular, the maximum experimental value is greater
Thermal diffusion in mixtures of the inert gases

than the maximum theoretical value, and since in this temperature range the attractive field has little effect, the discrepancy is an indication that the repulsive force index in these mixtures is greater than 9. It has, indeed, already been estimated to be 11 when a repulsive field only is assumed to be operative. This value would be somewhat smaller for a Lennard-Jones field, for Clark Jones's results show that in this temperature range the effect of the attractive field is to increase $R_T$ above the value for the repulsive field only.

(2) In some cases, such as Ne-A, the form of the experimental curve is strikingly similar to that of the theoretical curve. More frequently, however, $R_T$ changes less rapidly at the lowest temperatures than at the intermediate ones, so that the experimental curve becomes convex to the temperature axis. The explanation of this behaviour may perhaps be given when there are available theoretical data for force indices other than $(9, 5)$. It is a reasonable supposition, however, that as $\nu'$ increases above 5, $R_T$ changes sign, if it does so at all, at progressively lower temperatures. As a probable value of $\nu'$ is 7, this would explain the fact that the experimental results give no indication of $R_T$ becoming negative.

![Figure 4](http://rspa.royalsocietypublishing.org/)

**Figure 4.** Stier's experimental values for Ne isotopes and for A isotopes. Broken curve: as in figure 3.

(3) The experimental curves are coincident (except at the lowest temperatures) to a degree which is significant when the range of the 'critical temperature' and the method by which it was calculated are taken into consideration. The formal relation between $R_T$ and the critical temperature brought out by Clark Jones has therefore this much experimental support.

*The variation of $R_T$ in isotopic mixtures.* It is interesting to compare with these results for non-isotopic mixtures the measurements of $R_T$ in the isotopic mixtures Ne$^{20}$-Ne$^{22}$ and A$^{36}$-A$^{40}$ made by Stier (1942). The curves of figure 4 show Stier's values of $R_T$ as a function of $T/T_C$. The A values, and the Ne values too in the
low-temperature range, conform satisfactorily with the others, when it is remembered that the mass ratio $M$ in these cases is only 0·05 and $R_T$ may in consequence be 10 to 20% smaller than for the non-isotopic mixtures with their larger mass ratio. The persistent increase of $R_T$ at the higher temperatures in the case of the Ne isotopes is unexpected.

In spite, then, of the difficulty introduced into their interpretation by the non-isotopic nature of the mixtures, it seems that the experimental results could be satisfactorily explained with molecular fields of the Lennard-Jones type if the force indices were suitably chosen. The results suggest, indeed, that the measurement of the temperature variation of $R_T$ in isotopic mixtures would permit of the determination of both indices $\nu, \nu'$, with some precision. A knowledge of these values combined with the treatment of the second virial coefficient due to Lennard-Jones (1931) and Buckingham (1938) would enable the force constants $k, k'$ to be determined, and the molecular fields would then be completely known. Further progress depends on the provision of more experimental data for isotopic mixtures, and of theoretical data for molecular fields with values of $(\nu, \nu')$ other than (9, 5).

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References

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