Thermal Diffusion and Transfer of Rotational Energy

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Separations by thermal diffusion in the mixtures $^{14}N^{15}N/^{14}N_2$ and $^{15}N_2/^{14}N_2$ have been made at average temperatures between 152 °K and 470 °K. The results are consistent with the Chapman–Enskog theory in sharp contrast to separations in isotopic CO mixtures [1]. From the difference in behaviour between CO and N_2 it is concluded that energy transfer between translation and rotation of the molecules is not responsible for the influence of isotopic substitution on the thermal diffusion factor.

In a previous paper on thermal diffusion of isotopic molecules [1] we presented results on mixtures of $^{14}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{16}O$. These experiments were done in thermal diffusion columns provided with a Dewar cooling jacket which enabled us to cover a wide temperature range by applying an ultra kryostat for cooling the outer jacket in some of the experiments. The behaviour of the CO molecules deviated from the Chapman–Enskog theory and could only be explained if unreasonably big differences in the potential parameters of the different isotopic molecules were chosen. We raised the question if inelastic collisions (tranfer of rotational energy) or the influence of the asymmetry in the potential energy on elastic collisions attributed mainly to the observed phenomenae.

Experimental Results

We have now compared the separations of the pairs $^{14}N^{15}N/^{14}N_2$ and $^{15}N_2/^{14}N_2$ in the same column. $^{15}N_2$ was obtained from the "Office national industriel de l'azote". It contained 10.3% $^{15}N_2$, 43.2% $^{14}N\,^{15}N$ and 46.5% $^{14}N_2$. This gas was diluted with natural N_2. The final mixture contained 0.6% $^{15}N_2$, 3.2% $^{14}N^{15}N$ and 96.2% $^{14}N_2$.

The experimental results are given in Table 1. In Table 2 the results are summarized and compared with calculated values.

The experiment at $\overline{T}=152$ was done in a swing-separator in order to extend the covered temperature range, $\overline{T}=(T_{\text{cold}}\,T_{\text{hot}})^{1/2}$. The other separations were done in a thermal diffusion column where we used $\overline{T}=T_{\text{cold}}+\frac{1}{4}(T_{\text{hot}}-T_{\text{cold}})$.

Temperature in °K	$q'(^{14}N^{15}N/^{14}N_2)$	$q(^{15}N_2/^{14}N_2)$	$\frac{\alpha'}{\alpha}=\frac{\ln q'}{\ln q}$
$T_{\text{cold}}=77$	1.0158	1.0297	0.532
$T_{\text{hot}}=303$	1.0166	1.0309	0.537
$\overline{T}=152$	1.0162	1.0290	0.559
$T_{\text{cold}}=208$	1.288	1.622	0.523
$T_{\text{hot}}=308$	1.330	1.743	0,514
$\overline{T}=235$	1.268	1.572	0.525
	1.307	1.662	0.527
	1.252	1.520	0.536
	1.284	1.600	0.532
	1.264	1.538	0.545
	1.296	1.630	0.531
$T_{\text{cold}}=203$	1.620	2.433	0.543
$T_{\text{hot}}=413$	1.763	2.923	0.529
$\overline{T}=260$	1.613	2.425	0.539
	1.760	2.880	0.534
	1.622	2.441	0.542
	1.781	2.914	0.539
	1.618	2.442	0.539
	1.772	2.847	0.547
	1.625	2.459	0.540
	1.783	2.903	0.543
$T_{\text{cold}}=273$	1.997	3.543	0.547
$T_{\text{hot}}=673$	2.023	3.605	0.550
$\overline{T}=370$	1.972	3.570	0.534
	1.990	3.349	0.570
	1.984	3.635	0.531
	1.978	3.624	0.530
	2.002	3.709	0.530
	2.032	3.830	0.528
	2.038	3.866	0.527
	1.996	3.727	0.525
	1.998	3.747	0.524
	1.997	3.677	0.531
	1.989	3.671	0.529
$T_{\text{cold}}=343$	1.69	2.68	0.532
$T_{\text{hot}}=848$	1.67	2.64	0.528
$\overline{T}=470$	1.66	2.63	0.524
	1.63	2.55	0.522

Table 1.

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[1] A. E. De Vries and A. Haring, Z. Naturforschg. **19 a**, 225 [1964].

T in °K	$\alpha'(^{14}N^{15}N/^{14}N_2)$ $\alpha(^{15}N_2/^{14}N_2)$		Ratio of experimental and theoretical value of α'/α
	experiment	theory	
152	0.543 ± 0.009	0.510	1.065 ± 0.018
235	0.529 ± 0.004	0.510	1.037 ± 0.018
260	0.540 ± 0.002	0.510	1.057 ± 0.010
370	0.535 ± 0.004	0.510	1.047 ± 0.027
470	0.527 ± 0.003	0.510	1.033 ± 0.006

Table 2.

Discussion

The observed value of $\alpha'(^{14}N\,^{15}N/^{14}N_2)$ is about 5% higher than the value calculated from the observed separation for the mixture $^{15}N_2/^{14}N_2$ by means of the KIHARA approximation[2]. The difference is independent of the temperature in sharp contrast to the behaviour of CO[1], and may even be due to the approximation which is used.

Now it is known from ultra-sonic experiments that for $^{14}N_2$ at room temperature about 1 in every 5 collisions is inelastic[3]. The energy transferred in these rotational jumps in general is not small with respect to the translational energy of the molecules: The rotational energy is given by $J(J+1)\hbar/2I$ (J = rotational quantum number, I = moment of inertia).

The energy transferred is at least

$$\{J(J+1) - J(J-1)\}\hbar^2/2I = 2J\cdot\hbar^2/2I .$$

The average kinetic energy of the molecules is $\frac{3}{2}RT$ per Mole, the average rotational energy of diatomic molecules is RT per Mole and so the fraction of the kinetic energy which is transferred at an inelastic collision as rotational energy is at least

$$\frac{2}{3}\cdot 2J/[J(J+1)] = 4/[3(J+1)].$$

For carbon monoxide and the asymmetric nitrogen molecules, where the most frequently occuring species has a rotational level of 7, this amounts to 1/6 or 17% of the translational energy. For the symmetric N_2 molecules $\Delta J = 2$ and the minimum fraction of the energy which is transferred is about twice as large, namely

$$\frac{2}{3}(4J+2)/[J(J+1)] \cong 36\% .$$

The transition probability for the asymmetric molecule $^{14}N\,^{15}N$ is larger than for $^{14}N_2$ and $^{15}N_2$ because transitions are now possible between all rotational levels, so that the level spacings are effectively reduced by a factor[4] of about 2.

The differences in rate of energy transfer as well as in the rotational level spacings between the isotopic CO molecules are considerably smaller than between the symmetric and the asymmetric N_2 molecules. The fact that nitrogen does not show the special behaviour which we observed for the different CO molecules therefore seems to indicate that the observed deviation from the CHAPMAN–ENSKOG theory is due to the influence of the position of the center of mass on the collisions rather than by a different rotational-translational energy transfer for the respective isotopic molecules.

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[2] J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD, Molecular Theory of Gases and Liquids, Chapman and Hall, London 1954, p. 609.

[3] J. G. PARKER, Phys. Fluids **2**, 449 [1959].

[4] K. TAKAYANAGI, Progr. Theor. Phys. Japan, Suppl. **25**, 1 [1963].