The thermal diffusion in binary gaseous mixtures under pressures, III: hydrogen-argon system

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THE THERMAL DIFFUSION IN BINARY GASEOUS MIXTURES UNDER PRESSURES, III

Hydrogen-Argon System

BY TADASHI MAKITA AND TOSHIHARU TAKAGI

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The thermal diffusion in the hydrogen-argon system has been measured at mean temperatures of 322.7~322.1 K and pressures up to 220 atm, by means of a "two-bulb" type apparatus reported previously. The effect of composition, temperature and pressure on the thermal separation and the thermal diffusion factor is discussed and compared with the results of the hydrogen-carbon dioxide system in earlier works. The results at the atmospheric pressure are also compared with a theoretical equation treated with both Lennard-Jones (12-6) and "Modified Buckingham" (exp-6) potentials.

There have been only a few studies of the thermal diffusion in gaseous system under high pressures, in spite of its importance for both practical use and theoretical treatment, as described in the author's review paper). The previous thermal diffusion measurements2,3) were made for the system of H2-CO2 at pressures up to 120 atm. In the present work, the H2-A system has been selected so that a comparison could be made with the results obtained for the H2-CO2 system, the mass ratio of the molecules in the two cases being closely similar.

The measurements are made in a "two-bulb" type apparatus in which the top chamber is kept at a hot temperature Ti and the bottom one at a low temperature Tb. At a steady-state condition where the separation due to thermal diffusion is balanced by the remixing effect of the ordinary diffusion, the thermal diffusion factor \( \alpha \) at a mean temperature \( \bar{T} \) is expressed as follows:

\[
\alpha(\bar{T}) = \frac{\Delta x}{x_1 x_2 \ln(T_i/T_b)}
\]

where \( x_1 \) and \( x_2 \) are mole fractions in feed of heavy and light components, respectively, and the thermal separation \( \Delta x \) is

\[
\Delta x = (x_1)_b - (x_1)_t = (x_2)_b - (x_2)_t
\]

where subscripts \( t \) and \( b \) show the top and bottom chambers, respectively, at the steady state, and Brown's expression4) is used for \( \bar{T} \):

\[
\bar{T} = \frac{T_i T_b}{T_i - T_b} \ln \frac{T_i}{T_b}
\]

References:
2) T. Makita, This Journal, 29, 47 (1960)
3) T. Makita, ibid., 29, 55 (1960)
In this investigation, the thermal separation and the thermal diffusion factor have been calculated by Eqs. (2) and (1), respectively, at the mean temperature assigned by Eq. (3).

**Experimental**

The experimental apparatus and procedures were described in details in the previous paper. The top chamber was maintained in a boiling liquid bath, that is, m-xylene for 138.8°C, water for 100.0°C and carbon tetrachloride for 76.7°C were used, and the bottom chamber in a water thermostat of 25.0 or 30.0°C.

The sample gases used were obtained from commercial sources and purified by passage through a trap of silica-gel. The purity of both gases was more than 99.9%. The gas mixtures were made up in large cylinders and were used at least in one week.

A mixture of the sample gases was introduced into the evacuated chambers of the thermal diffusion apparatus which had been kept at each definite temperature. If necessary, the gas mixture was compressed through a pressure-intensifier in which the pressure was transmitted by means of an oil-pump. After the gas mixture was allowed to attain to a steady state, the gas in each chamber was analysed. For the measurement at one condition, 3~4 runs were taken in about twice as long as time to attain to a steady state.

The composition of gas mixtures in feed and at equilibrium was determined both by chemical analysis and by use of a thermal conductivity bridge, which had been devised to obtain the accuracy within 0.02% of the composition.

**Results and Considerations**

The present experimental results are described and discussed on the effect of mean composition, temperature and pressure upon the thermal separation $dx$ and thermal diffusion factor $\alpha$.

**The effect of mean composition**

The thermal separation at the atmospheric pressure is plotted against the mean mole fraction of $H_2$, $x_2$, as isotherms of mean temperature in Fig. 1. It is found that the curves are a little more symmetrical than those obtained for the $H_2$--CO$_2$ system, and that the maximum separation is obtained near $x_2=0.55$--0.60 at the three temperatures. The composition of the maximum separation agrees with the results of Ibbs at $T=360^\circ$K and those of van Itterbeek et al. at $T=133.5^\circ$K, being independent on temperature.

At the atmospheric pressure, the thermal diffusion factors are the same at the three temperatures and are nearly coincident with the results of Ibbs at $T=360^\circ$K, as shown in Fig. 2. The $\alpha$ increases gradually with increasing $x_2$, and reaches a maximum near $x_2=0.9$. In this figure,

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4) H. Brown, Phys. Rev., 58, 661 (1940)
6) A. van Itterbeek and A. de Troyer, Physica, 16, 329 (1950)
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Fig. 1. Thermal separation versus mean mole fraction of \( \text{H}_2 \) diagram at the atmospheric pressure:

- \( T = 349.0^\circ \text{K}, \) \( \Delta T = 332.9^\circ \text{K}. \)
- \( T = 322.7^\circ \text{K} \)

Mean mole fraction of \( \text{H}_2, \alpha \)

![Graph](image)

Fig. 2. Thermal diffusion factor as a function of mean mole fraction at the atmospheric pressure:

- \( \Delta \) This work \( (T = 332.9^\circ \text{K}) \),
- \( \bullet \) Ibbs\(^5\) \( (T = 360^\circ \text{K}) \)
- Theoretical, (12-6) potential \( (T = 332.9^\circ \text{K}) \)
- Theoretical, (exp-6) potential \( (T = 332.9^\circ \text{K}) \)
- \( \text{H}_2-\text{CO}_2 \) system\(^2\) \( (T = 346.0^\circ \text{K}) \)

Mean mole fraction of \( \text{H}_2, \alpha \)

![Graph](image)

two theoretical curves are also plotted, which have been calculated from the first approximation of Kihara\(^1,7\) by means of both Lennard-Jones (12-6) and a modified Buckingham (exp-6) potentials\(^8,9\). The force constants used are shown in Table 1\(^10\). The theoretical values are not satisfactory for the present system, but the (exp-6) potential gives somewhat better results than

<table>
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<tr>
<th>Parameter</th>
<th>A</th>
<th>Lennard-Jones</th>
<th>mix.</th>
<th>( \text{H}_2 )</th>
<th>modified</th>
<th>Buckingham</th>
<th>mix.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_m ) (( \text{Å} ))</td>
<td>3.87</td>
<td>3.187</td>
<td>3.58</td>
<td>3.866</td>
<td>3.337</td>
<td>3.574</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon/k ) (( ^\circ \text{K} ))</td>
<td>119.3</td>
<td>37.0</td>
<td>66.44</td>
<td>123.2</td>
<td>37.3</td>
<td>69.7</td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>14.0</td>
<td>14.0</td>
<td>13.97</td>
<td></td>
</tr>
</tbody>
</table>

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the (12-6) one.

The results of the $\text{H}_2-\text{CO}_2$ system, which were shown as a dotted curve in Fig. 2, are steeper in slope than those of the $\text{H}_2-\text{Ar}$ system. However, these two curves cross each other near $x_r=0.45$. It would be interesting to mention that the same value for $\alpha$ is given for both systems near $x_r=0.45$, and argon molecules are as effective as carbon dioxide molecules at the atmospheric pressure, though there is the much difference between their properties.

The results under high pressures are shown in Figs. 3 and 4. It can be seen that both $\Delta x$

![Graph of Thermal Separation](image1)

![Graph of Thermal Diffusion Factor](image2)

and $\alpha$ increase gradually with increasing pressure at a constant composition, and that the pressure effect becomes larger with decreasing $x_r$. That is, the composition of maximum separation displaces toward left with increasing pressure as shown in Fig. 3, and the slope of $\alpha$ versus $x_r$ at 108.7 atm is contrary to that of 1.0 atm. Although the tendency is similar to the system of $\text{H}_2-\text{CO}_2$ reported previously, the discrepancy in quantity is very large between them. For instance, the ratio of $\alpha$ under 100 atm to $\alpha$ under 1 atm at a composition $x_r=0.3$ is about 6.8

12) E. W. Becker, *Z. Naturforch.*, 5a, 457 (1950)
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for H₂—CO₂ and only about 1.7 for the H₂—A system. This means that the difference in properties between CO₂ and A molecules becomes remarkable under high pressure, although it is not at 1 atm as described above.

The effect of temperature The plots of the thermal separation against ln(T₁/T₀) at a constant composition are found to be linear at the atmospheric pressure. According to Eq. (1), the slope should be x₁x₁, and χ at a constant composition is constant over the present temperature range. The experiments at low temperatures gave considerably lower values of χ. Some results are compared in Fig. 5, where it seems that χ is constant at mean temperatures above 250°K and decreases continuously at the lower temperatures.

The thermal separation of x₁=0.561 under pressures is plotted against ln(T₁/T₀) in Fig. 6. It can be seen that the relation is no longer straight under high pressures. And the thermal diffusion factor versus mean temperature diagram is also shown in Fig. 7, where χ under high pressures decreases continuously with increasing T. This tendency would be similar to the results obtained for the H₂—CO₂ system reported by Beckert.

The effect of pressure The gas mixture with the composition of x₁=0.561, which has been close to the composition of maximum separation at the atmospheric pressure, is used for the measurement of the effect of pressure up to 220 atm. The results are given in Fig. 8, where

![Fig. 1. Variation of thermal diffusion factor with mean temperature in H₂—A system at the atmospheric pressure:](image)
a part of the results in the H$_2$—CO$_2$ system obtained previously$^{2}$ is also plotted by a dotted curve. As seen in this Figure, $\alpha$ of the H$_2$—CO$_2$ system becomes remarkably large with increasing pressure, and, for instance, although the ratio of $\alpha$ at 1.15 atm to $\alpha$ at 1 atm was about 4.7 for the H$_2$—CO$_2$ system, that of $\alpha$ at 217 atm to $\alpha$ at 1 atm is only 1.8 for the H$_2$—A system. As the thermal diffusion is sensitive to the intermolecular force, the discrepancy between the two systems would be caused by the difference in properties between A and CO$_2$. The nature of interaction, which is the most important factor for the thermal diffusion under high pressure, has not been explained theoretically, and therefore now it would be reasonable to use the reduced state expression as a measure of the nature. And we must have more reliable experimental data for more systems.

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