A new generalized chart analogous to that of Slattery and Bird (SB chart) was prepared from the observed values of the self- and binary-diffusion coefficients of gases at high pressures. The deviation of the values produced by the new chart from those observed is 4.1% on the average, whereas that of the values produced by the SB chart is 7.9%. In addition the new chart gives the average of the values observed, whereas the SB chart gives lower values for most of the systems.

Introduction

Enskog-Thorne's theory for the diffusion coefficients of gases at high pressures is well-known, but comparison of the values resulting from it with observed values has shown unsatisfactory agreement. Therefore modifications of Enskog-Thorne's theory, and other theories have been proposed. However, they do not seem to give better agreement than Enskog-Thorne's theory.

To predict the properties of a substance under conditions where no satisfactory theoretical treatment can be applied, corresponding state arguments provide a practical method for making use of measured properties of other substances. Several generalized charts based on the principle of corresponding state have been prepared from experimental data for prediction of the diffusion coefficients of dense gases. The chart of Slattery and Bird was constructed from experimental viscosity and P-V-T data by means of Enskog’s theory, inasmuch as there were not enough high-density diffusion coefficient data available at that time for the preparation of a dimensionless graphical representation. The chart of Kennedy and Thodos was constructed from limited amounts of experimental data on the self-diffusion coefficients of carbon dioxide. Berezhnoi and Usmanov prepared a graph showing the correlation of the experimental self- and binary-diffusion coefficients to the entropy of systems. Of these charts Berezhnoi and Usmanov’s is best from the viewpoint of reproducing the observed values, but it is inconvenient to use for practical purposes, since the entropy must be estimated first. That of Kennedy and Thodos is for carbon dioxide only, and its application to other substances is difficult, since $D/D_C$ is correlated to the reduced temperature and pressure, where $D_C$ i.e. the diffusion coefficient at the critical point is unknown and cannot be estimated in most cases. On the other hand, that of Slattery and Bird (hereafter abbreviated to SB chart) is convenient to use, since $D/P/(DP)^0$ is correlated to the reduced temperature and pressure, where $(DP)^0$ is the value at 1 atm, which is known experimentally for many substances. However, agreement between calculated values and those observed is not sufficient.

The author attempted to prepare a new chart analogous to the SB chart using the observed values for the self- and binary-diffusion coefficients which have been reported up to the present time by not a few investigators.

Application of the SB Chart to the Binary-Diffusion Coefficients

According to Enskog-Thorne's theory the binary-diffusion coefficient at high pressure is given by the following equations:

$$D_{12}n = (D_{12}n)^0 / \chi_{13}$$  \hspace{1cm} (1)

$$\chi_{13} = 1 + (1/8)b_1n_1(8 - 3\sigma_1/\sigma_{13}) + (1/8)b_2n_2(8 - 3\sigma_2/\sigma_{13})$$  \hspace{1cm} (2)

$$b_1n_1 = (2/3)\pi n_1\sigma_1^2, \hspace{0.5cm} b_2n_2 = (2/3)\pi n_2\sigma_2^2$$  \hspace{1cm} (3)

where $n = n_1 + n_2$. When diffusion component 1 is present only as a trace and $\sigma_1$ is nearly equal to $\sigma_2$, Eq. (1) takes the following form:
Table 1 Comparison of the observed values with those produced by the SB chart and the present chart

<table>
<thead>
<tr>
<th>System*</th>
<th>$x^{(b)}$</th>
<th>$T^*_P$</th>
<th>$P^*_P$</th>
<th>$N^{(c)}$</th>
<th>Dev. $^{(d)}$ in the SB chart [%]</th>
<th>Dev.$^{(d)}$ in the present chart [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$-H$_2$</td>
<td>1.67-2.72</td>
<td>0.08-7.8</td>
<td>e)</td>
<td>1.7-2.5</td>
<td>3.0-4.2</td>
<td>11, 19</td>
</tr>
<tr>
<td>CH$_4$-CH$_4$</td>
<td>0.99-1.61</td>
<td>0.02-4.37</td>
<td>e)</td>
<td>1.0-15.4</td>
<td>1.3-4.5</td>
<td>35</td>
</tr>
<tr>
<td>CTH$_3$-CH$_4$</td>
<td>0.98-1.85</td>
<td>0.02-8.73</td>
<td>25</td>
<td>7.6-13.7</td>
<td>7.5-11.1</td>
<td>13</td>
</tr>
<tr>
<td>CTH$_3$-CH$_4$</td>
<td>1.43-1.69</td>
<td>0.02-6.55</td>
<td>24</td>
<td>3.5-6.6</td>
<td>1-3.2</td>
<td>31</td>
</tr>
<tr>
<td>$^{15}$N$_2$-N$_2$</td>
<td>2.32</td>
<td>0.60-2.69</td>
<td>6</td>
<td>1.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>$^{13}$CO$_2$-CO$_2$</td>
<td>0.97-1.04</td>
<td>0.01-1.78</td>
<td>64</td>
<td>39.6</td>
<td>4.8-28.0</td>
<td>33, 26</td>
</tr>
<tr>
<td>$^{14}$CO$_2$-CO$_2$</td>
<td>0.90-1.23</td>
<td>0.02-1.43</td>
<td>37</td>
<td>12.9-14.8</td>
<td>1.9-11.8</td>
<td>25</td>
</tr>
<tr>
<td>$^{85}$Kr-CO$_2$</td>
<td>0.98-1.15</td>
<td>0.21-3.43</td>
<td>62</td>
<td>10.6-11.1</td>
<td>1.8-5.5</td>
<td>28</td>
</tr>
<tr>
<td>$^{15}$N$_2$-H$_2$</td>
<td>2.14</td>
<td>2.8-6.06</td>
<td>61</td>
<td>3.0-4.2</td>
<td>1.2-1.9</td>
<td>2</td>
</tr>
<tr>
<td>$^{15}$N$_14$N-N$_2$</td>
<td>0.99-1.57</td>
<td>0.02-8.73</td>
<td>6</td>
<td>1.1</td>
<td>1.6</td>
<td>2</td>
</tr>
<tr>
<td>$^{14}$CO$_2$-H$_2$</td>
<td>0.97-1.04</td>
<td>0.01-1.78</td>
<td>64</td>
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<td>33, 26</td>
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<td>$^{13}$CO$_2$-CO$_2$</td>
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<td>0.02-6.55</td>
<td>25</td>
<td>7.6-13.7</td>
<td>7.5-11.1</td>
<td>13</td>
</tr>
<tr>
<td>$^{14}$CO$_2$-H$_2$</td>
<td>1.56-1.82</td>
<td>0.33-5.45</td>
<td>24</td>
<td>3.5-6.6</td>
<td>1-3.2</td>
<td>31</td>
</tr>
</tbody>
</table>

\[ D_{12} P/(D_{12} P)^P = (D_{12} P)_{P} = \frac{z_{2}}{z_{2}} \] (4)

\[ \chi_{2} = 1 + (5/8)b_{2}p_{2} \] (5)

Here $\chi_{2}$ cannot be obtained in a simple way. However, it may be replaced by the viscosity, which has been measured accurately for many systems. Division of Eq. (4) by Eq. (5), Enskog’s theoretical equation for the viscosity of dense gases, then gives Eq. (7).

\[ (D_{12} P)_{P} = (\gamma_{2}/\gamma_{2})z_{2}[1 + 0.8b_{2}p_{2} + 0.7614(b_{2}p_{2})]^{-1} \] (6)

(7)

Eq. (7) has the same form as the equation used for the preparation of the SB chart. Therefore it can be seen that the SB chart may be applied to the prediction of $(D_{12} P)_{P}$, when diffusion component 1 is present only as a trace, and the collision diameters of component 1 and 2 are nearly the same.

In case a trace of gas 1 diffuses in a mixture, the diffusion coefficient of the trace of gas 1 with the mixture, $D_{1m}$, may be treated as a binary-diffusion coefficient, if the mixture is regarded as a single gas having pseudocritical constants. Therefore it may be expected that $(D_{1m} P)_{P}$ is also predicted by use of the SB chart, where $(D_{1m} P)_{P}$ is $D_{1m} P/(D_{1m} P)^P$.

In comparison of the values produced by the SB chart with those observed, $(D P)_{H}$ was found by extrapolation of high-pressure experimental results to 1 atm, and the pseudocritical temperature and pressure were determined from the following relations proposed by Kay$^{15}$:

\[ T_{c} = x_{1}T_{c1} + x_{2}T_{c2} \] (8)
Preparation of a New Generalized Chart for the Self- and Binary-Diffusion Coefficients

Although the agreement between the values produced by the SB chart and those observed is not good, the results shown in Table 1 suggest that \((D_{12}P)\) and \((D_{1m}P)\) may be correlated to \(T_r\) and \(P_r\). Therefore it was attempted to prepare a new generalized chart by correlating the observed values to \(T_r\) and \(P_r\). The source of available data\(^*\) at present, the system, the experimental conditions, and the number of experimental values are listed in Table 1. Although most of the observed values lie in the \(T_r\) range 0.95–5.0, and in the \(P_r\) range 0.1–9, the values for the Kr–He system obtained by Durbin et al.\(^9\) are at \(T_r=50\), and those obtained by Balenovic et al.\(^1\) are in the \(P_r\) range 10–41. Being far from most of the other data in the experimental conditions, these values are not included in Table 1.

The data listed in Table 1 were treated as follows:

1. The quantity \(DP\) was plotted against \(P\) with \(T\) as a parameter, and \((DP)\) was obtained by extrapolation. Thus, one hundred and two isotherms were obtained.

2. \(DP\) vs. \(P\) isotherms were converted into \((DP)\) vs. \(T_r\) plots with \(P_r\) as a parameter. For example, such plots for \(P_r=1.0\) are shown in Fig. 1. The smoothed curves for these plots were approximated by the following equation:

\[
(DP)_{T=\infty} = (DP)_{T_r=\infty} \left(1 - AT_r\right) \left(1 - f\right)
\]  

\[
f = CT_r^E
\]

The constants \(A\), \(B\), \(C\), and \(E\) were determined by using the method of least squares, as shown in Table 2. Here, the \((DP)_{T=\infty}\) is the \((DP)\) at \(T_r=\infty\), and was estimated from the shape of \((DP)\) vs. \(T_r\) curves. The values calculated by Eq. (10) are, for example, shown in Fig. 1 with the solid line. As can be seen from Fig. 1, Eq. (10) seems to be satisfactory. For comparison, the values produced by the SB chart were used without regard to the difference between \(\sigma_1\) and \(\sigma_2\).
Fig. 2 Generalized chart for the self- and binary-diffusion coefficients of gases at high pressures

are shown in Fig. 1 with the dashed line.

A new chart prepared by use of Eq. (10) is shown in Fig. 2. The deviation of the (DP)B-values produced by this chart from those observed, as shown in Table 1, is 4.1% on the average for 102 (DP)B vs. P, isotherms, whereas the deviation of those produced by the SB chart is 7.9% on the average for 94 isotherms. In this connection it must be noted that experimental values of (DP)B at the same P and T were scattered, for example, by ±3-18% around the average values at P=1, as shown in Fig. 1. In addition the new chart gives the average of those observed, whereas the SB chart gives lower values for most of the systems. Therefore this new chart seems to be the most reliable at the present time for predicting the self-diffusion coefficients and the diffusion coefficients of traces of gases at high pressures.

Acknowledgment

The author wishes to express his deep gratitude to Professor Hiroji Iwasaki for his kind direction and encouragement throughout this work.

Nomenclature

A, B, C, E = constants of Eqs. (10) and (11) [-]
b = quantity defined by Eq. (3) [1/g-mol] D = diffusion coefficient [cm²/sec] f = correction factor in Eq. (10) [-] n = number of molecules in a unit volume [cm⁻³] P = pressure [atm] T = temperature [K] z = compressibility factor [-] η = viscosity [g/cm·sec] ρ = molar density [g/mol/L] σ = collision diameter [cm] χ = correction factor depending on pressure [-] c = critical property l = limiting value m = mixture r, R = properties reduced with critical one and with that at 1 atm

Subscripts

° = property at 1 atm 1,2 = component 1 and 2

Superscripts

' = pseudocritical property

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