PREPARATION OF A GENERALIZED CHART FOR THE DIFFUSION COEFFICIENTS OF GASES AT HIGH PRESSURES*

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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[5,12] 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[9,25]. Therefore modifications[10,21,22] of Enskog-Thorne's theory, and other theories[7,17,18,20,36] 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[27] 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[16] was constructed from limited amounts of experimental data on the self-diffusion coefficients of carbon dioxide. Berezhnoi and Usmanov[3] 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 $DP/(DP)^\circ$ is correlated to the reduced temperature and pressure, where $(DP)^\circ$ 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[5] the binary-diffusion coefficient at high pressure is given by the following equations:

$$D_{12}n = (D_{12}n)^\circ / \chi_{12} \qquad (1)$$

$$\chi_{12} = 1 + (1/8)b_1\rho_1(8 - 3\sigma_1/\sigma_{12}) + (1/8)b_2\rho_2(8 - 3\sigma_2/\sigma_{12}) \qquad (2)$$

$$b_1\rho_1 = (2/3)\pi n_1\sigma_1^3, \quad b_2\rho_2 = (2/3)\pi n_2\sigma_2^3 \qquad (3)$$

where $n = n_1 + n_2$. When diffusion component 1 is present only as a trace and σ_1 is nearly equal to σ_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

System[a]	x[b]	T_r	P_r	N[c]	Dev.[d] in the SB chart [%]	Dev.[d] in the present chart [%]	
H_2–H_2		1.67–2.72	0.08–7.8	e)	1.7–2.5	3.0–4.2	11, 19)
CH_4–CH_4		0.99–1.61	0.02–4.37	e)	1.0–15.4	1.3–4.5	35)
CH_4–CH_4		0.98–1.85	0.02–8.73	67	2.8–16.9	1.2–7.0	8)
CTH_3–CH_4		1.43–1.69	0.02–6.55	25	7.6–13.7	7.5–11.1	13)
CTH_3–CH_4		1.56–1.82	0.33–5.45	24	3.5–6.6	1.3–2.1	31)
$^{15}N^{14}N$–N_2		2.32	0.60–2.69	6	1.1	0.1	2)
$^{13}CO_2$–CO_2		0.96	0.21–0.71	10		5.2	2)
$^{14}CO_2$–CO_2		0.97–1.04	0.01–1.78	64	39.6	4.8–28.0	33, 26)
$^{14}CO_2$–CO_2		0.90–1.23	0.08–2.18	37	12.9–14.8	1.9–11.8	25)
$^{14}CO_2$–CO_2		0.98–1.15	0.21–3.43	62	10.6–11.1	1.8–5.5	28)
^{37}Ar–Ar		2.14	1.42–6.06	10	3.1	1.6	23)
^{85}Kr–Kr		1.47	0.13–4.20	9	5.2	1.6	9)
^{85}Kr–N_2		2.44	0.54–12.2	9	4.1	5.0	9)
^{85}Kr–C_2H_4		1.09	0.28–2.24	8	13.1	6.3	9)
^{85}Kr–Ar		2.04	0.15–8.54	6	4.4	2.4	9)
^{85}Kr–CO_2		1.01	0.08–0.80	7	16.8	2.0	9)
CTH_3–Ar		1.97–2.30	0.31–5.20	34	0.8–2.3	0.6–2.0	32)
CTH_3–CO_2		0.98–1.15	0.21–3.43	24	5.8–10.8	2.2–8.3	31)
$^{14}CO_2$–CH_4		1.56–1.82	0.33–5.45	30	3.9–10.5	1.2–1.9	30)
$^{14}CO_2$–Ar		1.97–2.30	0.31–5.20	32	2.4–4.9	1.4–2.7	29)
$^{14}CO_2$–(CO_2+CH_4)	0.75	1.08–1.17	0.61–3.40	16	16.0–20.3	14.2–14.6	14)
	0.50	1.20–1.31	0.67–3.79	18	9.7–10.9	11.7–13.6	14)
$^{14}CO_2$–(CO_2+H_2)	0.790	1.24–2.41	0.40–3.58	19	5.3–12.9	1.4–5.3	6)
	0.432	2.00–2.41	0.43–5.06	15	1.0–3.0	0.2–1.0	6)
	0.266	2.77–3.36	0.92–7.41	13	0.6–1.3	0.0–1.0	6)
	0.064	5.30–6.41	0.99–9.83	16	2.2–2.4	0.7–0.9	6)
$^{14}CO_2$–(CO_2+C_3H_8)	0.797	1.08–1.30	0.11–2.33	9	5.5–7.2	3.5–5.5	6)
	0.559	0.93–1.12	0.13–2.75	11	18.2	3.8–9.8	6)
	0.230	0.88–1.05	0.12–1.55	9	10.3	2.6–4.3	6)
CTH_3–(CO_2+CH_4)	0.478	1.22–1.42	0.26–4.25	27	6.4–8.8	2.4–2.6	31)
CTH_3–(CO_2+Ar)	0.281	1.73–2.02	0.27–4.55	23	2.8–3.5	4.9–6.4	32)
	0.503	1.31–1.53	0.25–4.13	23	3.7–7.3	2.8–5.6	32)
	0.755	1.12–1.31	0.23–3.75	20	5.2–12.0	2.2–3.5	32)
$^{14}CO_2$–(CO_2+CH_4)	0.269	1.34–1.57	0.28–4.70	26	5.1–7.9	1.1–1.6	30)
	0.478	1.22–1.42	0.26–1.42	24	9.4–10.2	2.6–3.4	30)
	0.757	1.08–1.26	0.23–3.78	29	8.4–13.9	1.3–20.7	30)
$^{14}CO_2$–(CO_2+Ar)	0.281	1.73–2.02	0.27–4.55	28	0.6–1.7	1.3–3.4	29)
	0.503	1.31–1.53	0.25–4.13	23	8.6–9.3	2.0–3.0	29)
	0.755	1.12–1.31	0.23–3.75	23	8.9–13.1	2.0–5.4	29)

a) Except for H_2–H_2 and CH_4–CH_4 systems, the first gas is present only as a trace. Second gas is the base gas. If the base gas is a mixture, it was shown in the parentheses.

b) The mole fraction of carbon dioxide in the mixed base gas is given.

c) The number of experimental values.

d) Dev. is the arithmetic average of the absolute values of the deviation of the values produced by the charts from those observed.

e) The numerical values were not given. $(DP)_R$-values were estimated from the curves or the experimental equations.

$$D_{12}P/(D_{12}P)^\circ = (D_{12}P)_R = z_2/\chi_2 \tag{4}$$

$$\chi_2 \doteqdot 1 + (5/8)b_2\rho_2 \tag{5}$$

Here χ_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[5], then gives Eq. (7).

$$\eta_2/\eta_2^\circ = b_2\rho_2[(1/b_2\rho_2\chi_2) + 0.8 + 0.7614b_2\rho_2\chi_2] \tag{6}$$

$$(D_{12}P)_R = (\eta_2/\eta_2^\circ)z_2[1 + 0.8b_2\rho_2\chi_2 + 0.7614(b_2\rho_2\chi_2)^2]^{-1} \tag{7}$$

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 $(D_{12}P)_R$, 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 simple gas having pseudocritical constants. Therefore it may be expected that $(D_{1m}P)_R$ is also predicted by use of the SB chart, where $(D_{1m}P)_R$ is $D_{1m}P/(D_{1m}P)^\circ$.

In comparison of the values produced by the SB chart with those observed, $(DP)^\circ$ 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]:

$$T_c' = x_1 T_{c1} + x_2 T_{c2} \tag{8}$$

Ref.

○	28	■	9
●	29	▣	8
◐	30	▨	35
◑	31	△	11,19
⊗	32	▲	2
□	25	▽	23
■	6	▼	13,14,33,34
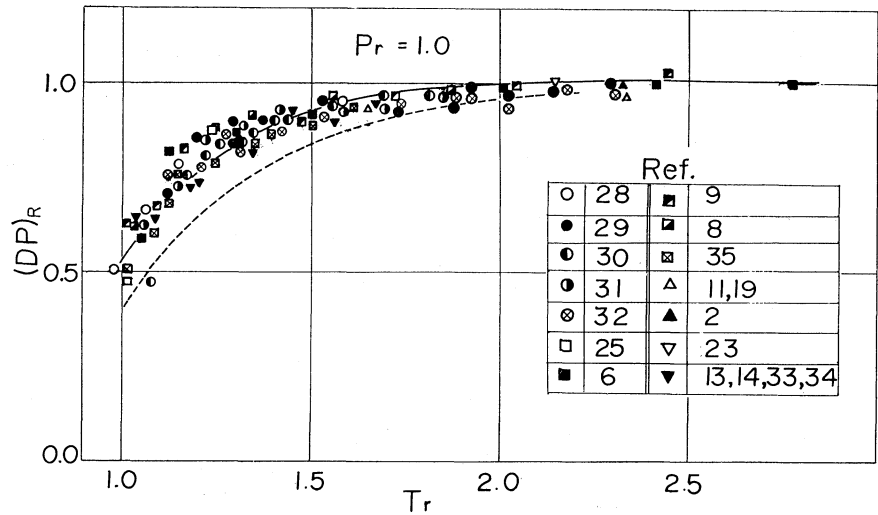
——— : calculated by Eq. (10)
------ : produced by the SB chart

Fig. 1 Plots of $(DP)_R$ vs. T_r

$$P'_c = x_1 P_{c1} + x_2 P_{c2} \qquad (9)$$

For hydrogen the modified critical constants proposed by Newton[24] were used in place of the experimental values. The results are shown in **Table 1** along with comparisons of the self-diffusion coefficients. The calculated values by the SB chart are lower than those observed in most cases, and the average deviation is 7.9%.

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 $(D_{12}P)_R$ and $(D_{1m}P)_R$ 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 $(DP)_R$

* In the preceeding section it was shown that the SB chart may be applied to the prediction of $(DP)_R$ when $n_1 \ll n_2$, and $\sigma_1 \doteqdot \sigma_2$. However, the deviation of the SB chart from observed values does not depend on the difference between σ_1 and σ_2. Therefore, in preparing the new chart the observed values were used without regard to the difference between σ_1 and σ_2.

Table 2 Constants in Eqs. (10) and (11)

P_r	$(DP)_{R,l}^{a)}$	A	B	C	E
0.1	1.01	0.038042	1.52267	0.0	
0.2	1.01	0.067433	2.16794	0.0	
0.3	1.01	0.098317	2.42910	0.0	
0.4	1.01	0.137610	2.77605	0.0	
0.5	1.01	0.175081	2.98256	0.0	
0.6	1.01	0.216376	3.11384	0.0	
0.8	1.01	0.314051	3.50264	0.0	
1.0	1.02	0.385736	3.07773	0.141211	13.45454
1.2	1.02	0.514553	3.54744	0.278407	14.00000
1.4	1.02	0.599184	3.61216	0.372683	10.00900
1.6	1.02	0.557725	3.41882	0.504894	8.57519
1.8	1.03	0.593007	3.18415	0.678469	10.37483
2.0	1.03	0.696001	3.37660	0.665702	11.21674
2.5	1.04	0.790770	3.27984	0.0	
3.0	1.05	0.502100	2.39031	0.602907	6.19043
4.0	1.06	0.837452	3.23513	0.0	
5.0	1.07	0.890390	3.13001	0.0	

a) $(DP)_{R,l}$ is the $(DP)_R$ at $T = \infty$.

vs. P_r isotherms with T_r as a parameter, by using the critical temperature and pressure of the base gas. In case the base gas was a mixture, the pseudocritical temperature and pressure determined by Eqs. (8) and (9) were used.

(3) $(DP)_R$ vs. P_r isotherms were converted into $(DP)_R$ 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:

$$(DP)_R = (DP)_{R,l}(1 - AT_r^{-B})(1-f) \qquad (10)$$

$$f = CT_r^{-E} \qquad (11)$$

The constants A, B, C, and E were determined by using the method of least squares, as shown in **Table 2**. Here, the $(DP)_{R,l}$ is the $(DP)_R$ at $T_r = \infty$, and was estimated from the shape of $(DP)_R$ 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
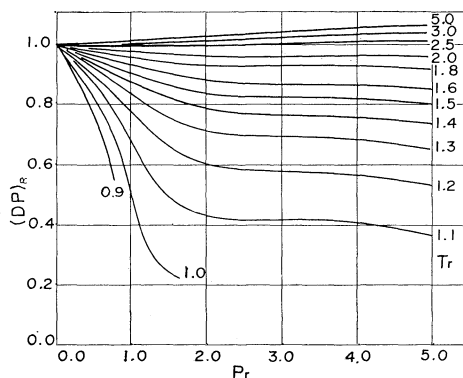
Fig. 2 Generalized chart for the self- and binary-diffusion coefficients of gases at high pressures

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 $(DP)_R$-values produced by this chart from those observed, as shown in Table 1, is 4.1% on the average for 102 $(DP)_R$ vs. P_r 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 $(DP)_R$ at the same P_r and T_r were scattered, for example, by ± 3–18% around the average values at $P_r=1$, 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

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	[—]

⟨Subscripts⟩

c	= critical property
l	= limiting value
m	= mixture
r, R	= properties reduced with critical one and with that at 1 atm

⟨Superscripts⟩

$'$	= pseudocritical property
$\circ$	= property at 1 atm
1,2	= component 1 and 2

Literature Cited

1) Balenovic, Z, M. N. Myers, and J. C. Giddings: *J. Chem. Phys.*, **52**, 915 (1970)
2) Becker, E. W. and W. Vogell: *Z. Naturforsch.*, **8a**, 686 (1953)
3) Berezhnoi, A. N. and A. G. Usmanov: *Teor. Osn. Khim. Tekhnol.*, **2**, 820 (1969)
4) Berry, V. J., Jr. and R. C. Koeller: *AIChE J.*, **2**, 273 (1960)
5) Chapman, S. and T. G. Cowling: "The Mathematical Theory of Non-uniform Gases", Cambridge Univ. Press, London (1960)
6) Chou, C. and J. J. Martin: *Ind. Eng. Chem.*, **49**, 758 (1957)
7) Davis, H. T. and K. D. Luks: *J. Chem. Phys.*, **69**, 869 (1965)
8) Dawson, R., F. Khoury and R. Kobayashi: *AIChE J.*, **16**, 725 (1970)
9) Durbin, L. and R. Kobayashi: *J. Chem. Phys.*, **37**, 1643 (1962)
10) Dymond, F. H. and B. J. Alder: *ibid.*, **52**, 923 (1970)
11) Hartland, A. and M. Lipsicas: *Phys. Rev.*, **133**, A665 (1964)
12) Hirschfelder, J. O., C. F. Curtiss and R. B. Bird: "Molecular Theory of Gases and Liquids", John Wiley & Sons Inc., New York (1954)
13) Jeffries, Q. R. and H. G. Drickamer: *J. Chem. Phys.*, **21**, 1358 (1953)
14) Jeffries, Q. R. and H. G. Drickamer: *ibid.*, **22**, 436 (1954)
15) Kay, W. B.: *Ind. Eng. Chem.*, **28**, 1014 (1936)
16) Kennedy, J. K. and G. Thodos: *AIChE J.*, **7**, 625 (1961)
17) Longuet-Higgins, H. C. and J. A. Pople: *J. Chem. Phys.*, **25**, 884 (1956)
18) Longuet-Higgins, H. C. and J. P. Valleau: *Mol. Phys.*, **1**, 284 (1958)
19) Lipsicas, M. J.: *J. Chem. Phys.*, **36**, 1235 (1962)
20) Luks, K. D., M. A. Miller and H. T. Davis: *AIChE J.*, **12**, 1079 (1966)
21) McConalogue, D. J. and E. McLaughlin: *Mol. Phys.*, **16**, 501 (1969)
22) McLaughlin, E.: *J. Chem. Phys.*, **50**, 1254 (1969)
23) Mifflin, T. R. and C. O. Bennett: *ibid.*, **29**, 975 (1958)
24) Newton, R. H.: *Ind. Eng. Chem.*, **27**, 302 (1954)
25) O'Hern, H. A., Jr. and J. J. Martin: *ibid.*, **47**, 2028 (1955)
26) Robb, W. L. and H. G. Drickamer: *J. Chem. Phys.*, **19**, 1504 (1951)
27) Slattery, J. C. and R. B. Bird: *AIChE J.*, **4**, 137 (1958)
28) Takahashi, S. and H. Iwasaki: *Bull. Chem. Soc. Japan*, **39**, 2105 (1966)
29) Takahashi, S.: *ibid.*, **41**, 1573 (1968)
30) Takahashi, S. and H. Iwasaki: *Bull. Chem. Res. Inst. Non-Aqueous Solutions, Tohoku Univ.*, **20**, 27 (1970)
31) Takahashi, S.: *Bull. Chem. Soc. Japan*, **45**, 2074 (1972)
32) Takahashi, S.: *ibid.*, **47**, 1342 (1974)
33) Timmerhaus, K. D. and H. G. Drickamer: *J. Chem. Phys.*, **19**, 1242 (1951)
34) Timmerhaus, K. D. and H. G. Drickamer: *ibid.*, **20**, 981 (1952)
35) Trappeniers, N. J. and H. H. Oosting: *Physics Letters*, **23**, 445 (1966)
36) Valleau, J. P.: *J. Chem. Phys.*, **44**, 2626 (1966)