Diffusion in Compressed Binary Gaseous Systems

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Apparatus is described for experimentally determining diffusion coefficients in dense-gas systems to pressures of 15,000 lb./sq. in. abs. Tests were made with the hydrogen-nitrogen and methane-ethane systems at 104°, 139°, and 171°F. to 10,000 lb./sq. in. abs. and with the nitrogen-methane and nitrogen-ethane systems at 104°F. to 2,500 lb./sq. in. abs. In all cases it was found that diffusion coefficients predicted on the basis of the Lennard-Jones model with Thorne's dense-gas correction diverged below the experimental data in the high-density region. Coefficients predicted from the Slattery-Bird reduced-state correlation showed better agreement with the experimental data. The temperature dependence of the results is better described by the exponential form for liquids than by the form of the dense-gas theory.

Fundamental physical data relating to molecular transport in gases at pressures above 1 atm. are not generally available. There is a growing need for such data for direct industrial application. Studies of gaseous diffusion at high pressures also provide data which can be used to evaluate the various theoretical relations available for predicting transport properties of dense gases. Not only do such comparisons aid the fundamental understanding of molecular interaction, but they are useful in demonstrating the accuracy of methods for predicting transport properties in regions for which no data are available.

A few studies have been made of diffusion in compressed gases, and the results compared with predictions based on the Chapman-Enskog (*1*) dense-gas theory. Drickamer and coworkers (*2, 3, 4*) have published self-diffusion coefficients for carbon dioxide at pressure up to 15,000 lb./sq. in. abs. The data indicate that in regions of high density the dense-gas approximation is not adequate for the prediction of the self-diffusion coefficient of carbon dioxide. It was concluded that at pressures above about 3,000 lb./sq.in.-abs. (density above about 1.3 lb. mole/cu.ft) the temperature dependence is more nearly described by the exponential form characteristic of liquids than by the Chapman-Enskog equations. O'Hern and Martin (*5*) have further studied self-diffusion in carbon dioxide at pressures to 3,000 lb./sq.in.abs. using a different experimental technique. Their results disagree even more with the theoretical predictions, and their opinion is that the diffusion coefficients published by Drickamer and co-workers are low.

Results for self-diffusion in methane were reported by Jeffries and Drickamer (*6*). Coefficients agreed with dense-gas predictions wthin about 10 to 20% at pressures to about 4,500 lb./sq.in.abs. Their measurements with mixtures of carbon dioxide and methane (*7*) over the same pressure range also show good agreement with theory, except near the critical point of carbon dioxide.

Studies of diffusion in a ternary system at pressures to 4,000 lb./sq.in.-abs. were reported by Chou and Martin (*8*). The results show that the diffusion of traces of radioactive carbon dioxide in mixtures of unlabeled carbon dioxide with hydrogen, and with propane, varies with concentration in the manner predicted by Wilke (*9*) and by Curtiss and Hirschfelder (*10*). The nonideality of carbon dioxide is again demonstrated by failure of the dense-gas approximation to predict diffusion coefficients at densities above about 0.6 lb.mole/cu.ft.

The relative scarcity of high-pressure diffusion data and the advantage of further evaluating the applicability of the dense-gas approximation suggest a need for additional measurements. This paper describes apparatus which has been constructed for such high-pressure diffusion studies. The results of some experimental measurements on the hydrogen-nitrogen, methane-ethane, nitrogen-ethane, and nitrogen-methane mixtures are presented together with an evaluation of several methods for predicting diffusion coefficients at elevated pressure in these binary gaseous systems.

THEORY

A lucid discussion of the various theoretical approaches to predicting diffusion coefficients in gases is given by Bird (*11*); a few pertinent results of the theoretical studies are summarized here.

Consideration of the kinetics of gaseous molecules by the Chapman-Enskog method leads to several different theoretical expressions for the diffusion coefficient in a binary mixture of gases 1 and 2, depending upon the particular molecular model chosen. If it is assumed that molecules act as rigid elastic spheres, then the expression derived is

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$$\mathcal{D}^{S}_{12} = \frac{3}{8n\sigma^2_{12}} \left\{ \frac{\kappa T(M_1 + M_2)}{2\pi M_1 M_2} \right\}^{1/2} \quad (1)$$

Values of $\mathcal{D}^{S}_{12}$ computed from Equation (1) by the use of collision diameters $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ from viscosity data are generally about 10 to 15% greater than experimental values of $\mathcal{D}_{12}$ at moderate temperatures. This disagreement is probably due to the assumption of rigid elastic spheres.

A more realistic description of molecular interactions is given by the Lennard-Jones (6-12) model. In the Lennard-Jones (6-12) model it is assumed that molecules attract one another with a force which is proportional to the −6 power of their separation and repel one another with a force proportional to the −12 power of separation. In addition to collision diameters, a force constant parameter is needed to describe a molecule in terms of the Lennard-Jones model. On the basis of this model the expression for $\mathcal{D}^{L}_{12}$ is given as (*11*)

$$\mathcal{D}^{L}_{12} = \frac{3}{16n\pi\sigma^2_{12}\Omega^{(1,1)*}} \left\{ \frac{2\pi RT(M_1 + M_2)}{M_1 M_2} \right\}^{1/2} \quad (2)$$

Bird, Curtiss, and Hirschfelder (*12*) have tabulated values of σ and ϵ for a large number of pure compounds and also values of $\Omega^{(1,1)*}$ as a function of $T^* = \kappa T/\epsilon_{12}$, where $\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2}$. The parameters σ and ϵ are best determined from pure-component viscosity data but may be empirically estimated from critical data. Slattery and Bird (*13*) show that for twenty-eight different binary gas mixtures the experimental diffusion coefficients are predicted to within an average deviation of 8.5% by the use of the Lennard-Jones model with parameters from viscosity data.

Both Equations (1) and (2) give first approximations to $\mathcal{D}_{12}$ which are independent of the relative proportions of the two molecular species. In such a situation it follows that $\mathcal{D}_{12} = \mathcal{D}_{21}$. Also these equations are known to be applicable only to gases at moderate pressures, since they are based upon only a first approximation of the probability of a binary molecular collision.

A dense-gas theory based on the solid-elastic-sphere model has been given by Enskog (*14*), but his results are not applicable to gas mixtures. Thorne (*1*) has extended Enskog's dense-gas theory to obtain a first-degree approximation for binary mixtures which can be applied to Equation (1) or (2) to determine diffusion coefficients at elevated pressures. Thorne's correction factor is simply applied as

$$\mathcal{D}^{LT}_{12} = \frac{\mathcal{D}^{L}_{12}}{\chi_{12}} \quad (3)$$

where

$$\chi_{12} = 1 + \frac{\pi}{12} n_1 \sigma_1^3 \left(8 - \frac{3\sigma_1}{\sigma_{12}} \right) + \frac{\pi}{12} n_2 \sigma_2^3 \left(8 - \frac{3\sigma_2}{\sigma_{12}} \right) + \cdots \quad (4)$$

Thus from (1) or (2) and (3) it follows that

$$\mathcal{D}^{LT}_{12} = \frac{(\mathcal{D}^{L}_{12})_o}{\chi_{12}} \cdot \frac{n_o}{n_p} \quad (5)$$

For an ideal gas, Equation (1) predicts that $\mathcal{D}_{12}$ should vary as $T^{3/2}$ at constant pressure. The dependence of $\mathcal{D}_{12}$ on temperature indicated by Equation (2) is masked by the variation of $\Omega^{(1,1)*}$ with temperature. Over a wide range of temperature for a given pair of molecules $\Omega^{(1,1)*}$ varies approximately as $e^{-b_1 T}$. Nevertheless both Equations (1) and (2) predict that the dependence of $\mathcal{D}_{12}$ on T should be independent of pressure. On the other hand, at elevated pressure where the dense-gas correction applies, it can be seen from Equation (4) that the effect of temperature on $\mathcal{D}_{12}$ depends upon the pressure level, because χ_{12} is a function of density.

It might be expected that the temperature dependence of the diffusion coefficient in highly compressed gases would be similar to that in liquids at moderate pressures. Although the theory of diffusion in the liquid state is not well developed, simple considerations (*15*) indicate that the diffusion coefficient can be expressed as follows at constant pressures:

$$D_L = b_2 e^{-E/RT} \quad (6)$$

It has been found experimentally by Timmerhaus and Drickamer (*4*) that diffusion in compressed gases does depend upon temperature, approximately as indicated in Equation (6).

Slattery and Bird (*13*) have utilized a modified form of the Enskog dense-gas theory with generalized gas-viscosity and compressibility correlations to prepare a correlation chart. This chart can be used for predicting a reduced diffusion coefficient as a function of reduced temperature and reduced pressure. It was prepared from pure-component data, but it is anticipated that it might be used, with pseudocritical constants to predict diffusion coefficients in dense-gas mixtures.

PROCEDURE

Apparatus

For the determination of diffusion coefficients in gases under pressure the technique originally used by Loschmidt (*16*) appears to be the most satisfactory. Apparatus used for determinations by this technique must provide for the separate filling of two diffusion cavities at a specified temperature and pressure. In addition the two cavities must be brought together at the initiation of an experiment in such a manner that the system undergoes no change in total volume. If the latter requirement is not met, it is found that turbulent mixing occurs as a result of the sudden volume change, obscuring the effects of simple diffusional transfer. The measurements reported here were made with a cell which meets these requirements.

Figure 1 is a sectional drawing of the working section. The cell is composed of two stainless steel pistons (*A*) and (*B*), enclosed within an outer stainless steel casing (*C*). The function of the shell (*C*) is to align properly and to support the pistons (*A*) and (*B*) and to provide a mass of high heat capacity to aid in stabilizing the temperature of the diffusing gases.

Diffusion occurs in the cylindrical cavities shown in the pistons. These cavities, each ¼ in. in diameter and 4 in. in length, are capable of confining fluids at pressures up to 15,000 lb./sq. in. abs. Figure 1 shows the configuration of the pistons when in the diffusing position. Rotating the piston (*A*) one quarter of a revolution about the axis of the cell brings the system to the fill or sampling position. The small lines for filling and sampling do not show in the sectional drawing. The line for filling the lower piston (*B*) is located in the upper piston (*A*), and the line for filling the upper piston (*A*) is located in the lower piston (*B*). The lower piston (*B*) receives an axial thrust from the end plug (*D*) and is pinned into the cell body (*C*) to prevent rotation about the cell axis. No pressure seal is necessary at the lower end of the cell body, since the region (*E*) is maintained at atmospheric pressure.

A disk of carbon-impregnated Bakelite (*F*) about ⅛-in. thick is pinned to the upper face of the lower piston. This disk provides a low-friction bearing surface for the rotating face of the upper piston and serves as a packing material to prevent leakage to the region (*E*) and to prevent communication between the diffusion chambers when these chambers are not in the diffusing position. Over a 16-hr. period there was no appreciable leakage between the two chambers with hydrogen at 10,000 lb./sq. in. abs. pressure in one chamber and a static vacuum of 0.1 mm. Hg in the other chamber.

The pressure on the Bakelite packing (*F*) is provided by a downward thrust from the upper piston. This thrust is generated by hydraulic action of oil within the annulus (*G*), the oil being confined by means of two O-ring seals (*H*). To eliminate the friction that would otherwise be generated at the O-ring–steel surface, bands of Teflon are inserted between the O rings and the body of the outer cell. The top of the upper piston is machined to receive a socket wrench and can be turned manually with ease, even when the oil pressure at (*G*) is 15,000 lb./sq. in. abs.

The small, unsupported area-seal plug (*I*) may be removed if desired to check

alignment of the diffusion cavities. Under normal operating conditions the limits of rotation of piston (A) are fixed by a spring-loaded pin mounted externally on the cell body (C). This pin is not shown in Figure 1.

Figure 2 shows a flow diagram of the entire apparatus. Pressure was transmitted to the gas phase through floating pistons in two 450-ml. stainless steel pressure-transmitting cylinders. Pressure was generated within the oil phase by means of a conventional hydraulic pump and was measured by 0 to 3,750 and 0 to 15,000 lb./sq. in. Heise Bourdon-tube gauges connected directly to the oil line. These gauges were calibrated periodically in place against a dead-weight tester which was attached to the gas-phase side of the pressure transmitters.

The diffusion cell was mounted vertically in a cylindrical air bath. A slight positive temperature gradient (usually 0.1 to 0.2°F.) was maintained in the vertical direction as a safeguard against thermal disturbances which might give rise to natural convection. It was not found necessary to use a porous packing material in the cell to eliminate convection. The experiments reported by Boyd *et al* (*17*) in which the diffusion process was observed interferometrically indicate that with careful experimental procedures it is possible to eliminate initial convection even in a cell of moderately large cross-sectional area.

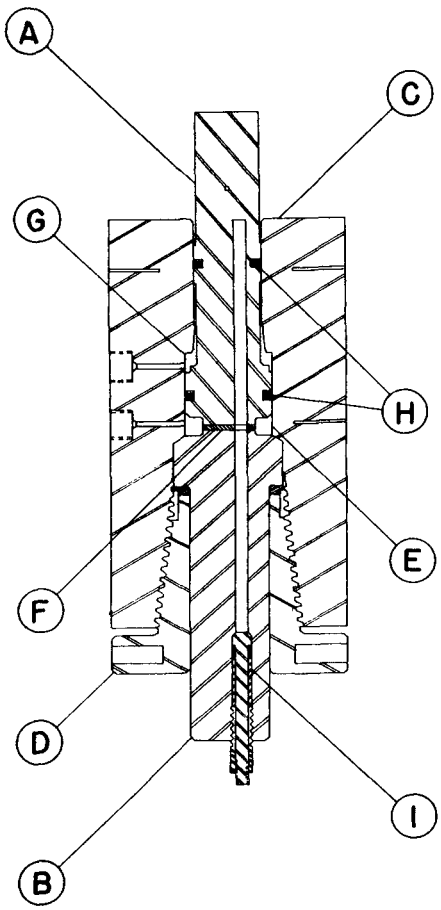

Fig. 1. Cross section of diffusion cell.

Experimental Procedure

Gases were introduced into the two chambers of the diffusion cell through separate manifolds. The more dense gas was placed in the lower chamber, since otherwise natural convective transfer, resulting from the gravitational instability, would completely overshadow that due to diffusion. After the gases had come to temperature equilibrium, the pressures on the two sides of the cell were balanced as nearly as possible by interconnecting the oil sides of the two pressure transmitters. The transmitters were then closed off completely, and the two gas chambers of the cell were directly interconnected through a long, auxiliary line of small diameter, permitting complete equalization of gas pressure. The length of line from the valve to each side of the cell was sufficiently great to prevent any diffusion or flow of gas through the line from one of the diffusion chambers into the other. It was found necessary to locate this valve at a point level with the center of the working section.

When the gas pressures were equalized, the upper piston was rotated 90 deg. to the diffusing position. It is estimated that the total time required to open the chambers to one another did not exceed 1 sec. Since the diffusion times generally exceeded 1,000 sec., this uncertainty in the starting time is considered negligible. The diffusion coefficient is known to depend at least weakly upon concentration. To achieve reproducibility all run times were chosen so that the diffusion process would proceed approximately half way to equilibrium.

Following the diffusion process, the diffusion chambers were again separated by rotation of the upper piston, and samples from each half of the cell were obtained by expansion of the gas into either 500- or 3,000-ml. glass vessels which had been evacuated to a pressure of less than 0.1 mm. Hg. Gas analyses were adjusted slightly to account for the fact that some of the gas, differing from the average sample composition, still remained in the cell and in the connecting lines.

Gas analyses were made on a mass spectrometer with an error of as much as ±0.2 % by composition, resulting in an uncertainty of approximately ±2% in the calculated diffusion coefficients. The length of the diffusion path was known to within several thousandths of an inch over a total length of approximately 8 in. The area of the diffusion cavity did not vary more than ±0.5%. Pressures were measured on Heise Bourdon-tube gauges calibrated throughout their entire ranges. Accuracy is estimated to be ±5 lb./sq. in. over the range of conditions investigated. For cell-temperature measurements, thermocouples were calibrated in place against a conventional, strain-free platinum resistance thermometer. Temperatures at the point of measurement were known to about ±0.02°F; the temperature difference between successive runs did not exceed 0.05°F.

During the process of initiating a diffusion run some pressure mixing of the gases must occur, first because of a shearing action which takes place as the open end

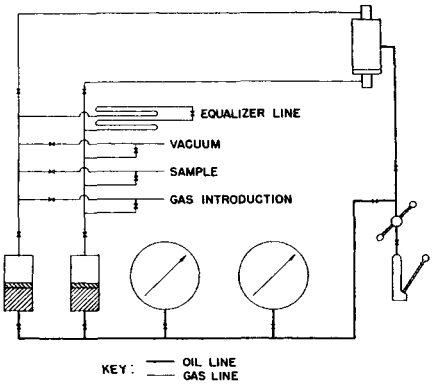

Fig. 2. Flow diagram of diffusion apparatus.

of one gas chamber passes over the open end of the other and second because of inertial forces which act to maintain the motion of the gas in the rotating chamber after the motion of the cell has ceased. Several experiments were made at a pressure of about 220 lb./sq. in. abs. to determine the magnitude of the effect of initial convection. This was done by comparing coefficients calculated for runs of different time duration.

Diffusion coefficients were measured at 3 temperatures at pressures up to about 10,000 lb./sq. in. abs. for the hydrogen-nitrogen and the methane-ethane systems. Measurements were made at one temperature at pressures up to about 2,500 lb./sq. in. abs. with the nitrogen-methane and nitrogen-ethane systems. Most of the methane-ethane measurements were made with one cell containing methane and the other containing a mixture having about 40 to 50 mole % ethane. Some of the low-pressure methane-ethane measurements were made with pure components in each of the two cells. This latter starting condition was used for all measurements with the other binary mixtures.

All gases used were commercial-grade cylinder gases, analyses of which were determined on a mass spectrometer.

Calculation of Observed Diffusion Coefficients

The definition of the diffusion coefficient is chosen as

$$\dot{N}_1 = -\mathcal{D}_{12} A \frac{\partial n_1}{\partial z} \qquad (7)$$

Application of this equation, together with a material balance on an element of volume, yields the following expression which must be satisfied throughout the system:

$$\frac{\partial}{\partial z}\left(\mathcal{D}_{12}\frac{\partial n_1}{\partial z}\right) = \frac{\partial n_1}{\partial t} \qquad (8)$$

The boundary conditions for the procedure used are equivalent to

$$\frac{\partial n_1}{\partial z} = 0 \qquad z = \pm L, t > 0$$

$$n_1 = n_{10} \qquad 0 < z < L, t = 0$$

$$n_1 = 0 \qquad -L < z < 0, \ t = 0$$

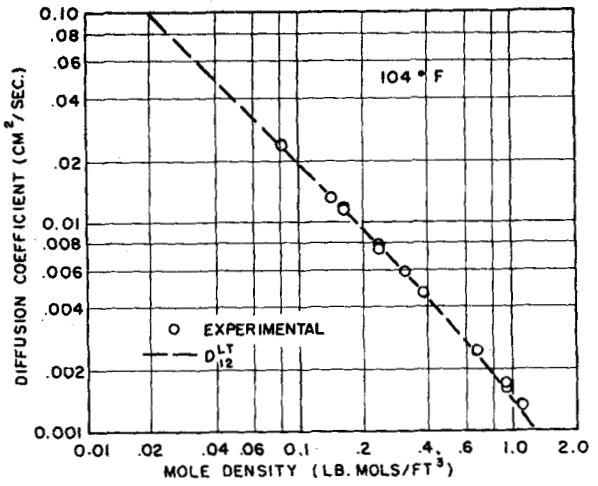

Fig. 3. Diffusion coefficients for the hydrogen-nitrogen system at 104°F.

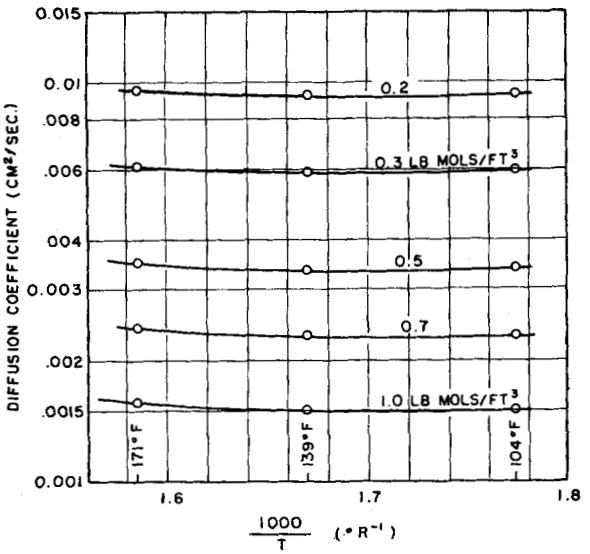

Fig. 4. Smoothed values of the diffusion coefficient for the hydrogen-nitrogen system.

If $\mathcal{D}_{12}$ is assumed to be independent of concentration, Equation (8) may be integrated to yield

$$\frac{n_1}{n_{10}} = \frac{1}{2} + \frac{2}{\pi}\sum_{m=0}^{\infty}\frac{1}{(2m+1)}\, e^{\frac{-(2m+1)^2\pi^2\mathcal{D}_{12}t}{4L^2}} \sin\frac{(2m+1)\pi z}{2L} \qquad (9)$$

The average number density of component 1 in the upper chamber is then obtained by integrating Equation (9) over $0 \leq z \leq L$:

$$\frac{\overline{n_1}}{n_{10}} = \frac{1}{2} + \frac{4}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\, e^{\frac{-(2m+1)^2\pi^2\mathcal{D}_{12}t}{4L^2}} \qquad (10)$$

This relationship assumes that no volume change occurs on mixing. Although small volume change does occur in many situations, it is so slight that it may usually be ignored. Experimentally determined values of $\overline{n_1}$, n_{10}, t, and L were used to establish average values of the diffusion coefficient according to Equation (10). Values of the series in Equation (10) have been tabulated as a function of the argument $(\mathcal{D}_{12}t/L^2)$ (*18*).

Table 1. Effect of Length of Test on Observed Diffusion Coefficient

Hydrogen-Nitrogen System at 104°F.

Pressure, lb./sq. in. abs.	Length of test, sec.	Diffusion coefficient, sq. cm./sec. $\mathcal{D}^{OBS.}_{12}$	$\mathcal{D}^{LT}_{12}$
220	80	0.0552	
220	158	0.0559	
			0.0542
215	309	0.0560	
219	630	0.0567	

Calculation of Theoretical Diffusion Coefficients

Diffusion coefficients were predicted by the use of the Lennard-Jones model with Thorne's correction, Equations (2), (4), and (5). Predictions for the methane-ethane, nitrogen-methane, and nitrogen-ethane systems were also made by means of the reduced-state correlation of Slattery and Bird (*13*).

When converted to engineering units, Equations (2), (4), and (5) become

$$\mathcal{D}^{L}_{12} = \frac{0.01600}{p\,\sigma^2_{12}\,\Omega^{(1,1)*}}\left\{\frac{T^3(M_1+M_2)}{2M_1M_2}\right\}^{1/2} \qquad (11)$$

$$\chi_{12} = 1 + 2.3557\times10^{20}\frac{p}{Z_{12}T}\left[x_1\sigma_1^3\left(8-\frac{3\sigma_1}{\sigma_{12}}\right) + x_2\sigma_2^3\left(8-\frac{3\sigma_2}{\sigma_{12}}\right)\right] \qquad (12)$$

$$\mathcal{D}^{LT}_{12} = \frac{(\mathcal{D}^{L}_{12})_0}{\chi_{12}}\cdot\left(\frac{Z_{12}}{p}\right)p_0 \qquad (13)$$

with p in pounds per square inch absolute, T in degrees Rankine, and σ_{12} in centimeters.

Values of the collision diameters and force constants were taken from the tabulation of Bird, Curtiss, and Hirschfelder (*12*) as follows:

	σ, cm	ϵ/κ, °K.
H_2	2.968	33.3
N_2	3.681	91.5
C_1	3.882	137
C_2	4.418	230

Tables of $\Omega^{(1,1)*}$ vs. T^* given in the same reference were also used.

Compressibility data were taken from references *19* to *22*. Data available for the methane-ethane system to only 3,000 lb./sq. in. abs. were extrapolated to 10,000 lb./sq. in. abs. through the use of a reduced-state correlation for the compressibility of natural gas (*23*). At 3,000 lb./sq. in. abs. this correlation agreed with the Sage-Lacey (*20*) experimental data to within better than 0.5%.

In all cases the diffusion coefficients were predicted for a mixture having a composition equal to the average composition in the test cell.

RESULTS AND DISCUSSION

Effect of Length of Test on Results

Results of four different diffusion experiments with the hydrogen-nitrogen system at 220 lb./sq. in. abs. and

Table 2. Smoothed Values of Diffusion Coefficients in the Hydrogen-Nitrogen System (sq. cm./sec.)

	104°F.			139°F.			171°F.	
lb./sq. in. abs.	lb.-mole/ cu. ft.	$\mathcal{D}^{OBS.}_{12}$	$\mathcal{D}^{LT}_{12}$	lb.-mole/ cu. ft.	$\mathcal{D}^{OBS.}_{12}$	$\mathcal{D}^{LT}_{12}$	lb.-mole/ cu. ft.	$\mathcal{D}^{OBS.}_{12}$	$\mathcal{D}^{LT}_{12}$
1000	.1606	.0115	.0116	.1512	.0125	.0130	.1436	.0135	.0141
2500	.3796	.00462	.00448	.3574	.00498	.00504	.3393	.00540	.00552
5000	.6810	.00240	.00223	.6443	.00259	.00251	.6132	.00283	.00275
7500	.9176	.00166	.00153	.8746	.00176	.00170	.8362	.00195	.00186
10000	1.1097	.00132	.00119	1.0609	.00140	.00132	1.0199	.00154	.00144
Average absolute error			5.73%			3.48%			4.12%

TABLE 3.-SMOOTHED VALUES OF DIFFUSION COEFFICIENTS IN THE METHANE-ETHANE SYSTEM

(D_{12}, SQ. CM./SEC.)
(80% methane)

lb./sq. in. abs.	lb.-mole/ cu. ft.	104°F. $D^{OBS.}_{12}$	D^{LT}_{12}	D^{R}_{12}
1000	.1945	.00210	.00164	.00179
2000	.4469	.00084	.000605	.000848
4000	.7855	.00043	.000286	.000431
8000	1.0465	.00030	.000190	—
10000	1.1172	.00027	.000173	—
Average absolute error			31.2%	5.3%

lb./sq. in. abs.	lb.-mole/ cu. ft.	140°F. $D^{OBS.}_{12}$	D^{LT}_{12}	lb.-mole/ cu. ft.	171°F. $D^{OBS.}_{12}$	D^{LT}_{12}
1000	.1764	.00233	.00193	.1630	.00249	.00221
2000	.3895	.00099	.000757	.3499	.00113	.000904
4000	.7121	.00050	.000345	.6569	.00058	.000403
8000	.9931	.00034	.000216	.9482	.00039	.000241
10000	1.0667	.00031	.000194	1.0252	.00036	.000216
Average absolute error			29.1%			28.0%

104°F. are shown in Table 1.* The time of duration of the tests ranged from 80 to 630 sec. The calculated diffusion coefficients are seen to vary by only about 3%, the largest value of the coefficients being calculated for the longest runs. If initial convection were present to any appreciable extent, apparent diffusion coefficients would be largest for the shortest runs. This is due to the fact that the total transfer would greatly exceed that attributable to diffusion. Furthermore the relative independence of the results on the length of the test suggests that gross convection is not appreciable. Table 1 also includes the value of the diffusion coefficient calculated from Equation (13). The calculated result is 2 to 4% less than the experimental value; however the coefficient calculated from Equation (13) at atmospheric pressure and 32°F. is also 2½% less than the experimental value reported for those conditions (*24*). Therefore on the basis of the information in Table 1 it is concluded that the apparatus and experimental technique are suitable for the determination of average diffusion coefficients in compressed binary gaseous mixtures which do not undergo large changes in volume on mixing.

* Tabular material has been deposited as document No. 6261 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

Hydrogen-Nitrogen Diffusion Coefficients

Experiments were made at pressures up to 10,000 lb./sq. in. abs. for three temperatures: 104°, 139°, and 171°F. Diffusion coefficients determined at 104°F. are shown plotted as a function of density in Figure 3. Data of similar quality were obtained at the two higher temperatures. The repeated measurements shown for the 104°F. isotherm indicate the degree to which the data for this system are reproducible. The maximum variation in coefficients from reproduced tests was ±2.5% from the mean value at 1500 lb./sq. in. abs. and 104°F. The dashed curve shown in Figure 3 was calculated from Equations (11) and (13). It is seen that the predicted data diverge from the experimental data beyond densities of about 0.2 lb.-mole/cu. ft. The predicted coefficients are low, indicating that Thorne's method results in an overcorrection. Without the dense-gas correction the theory predicts a simple inverse relationship between density and diffusivity.

Smoothed values of the observed coefficients at 104°, 139°, and 171°F. are compared in Table 2 with values calculated on the basis of the Lennard-Jones model with Thorne's correction. At equal values of density the error between observed and predicted coefficients is about the same at each of the three temperatures investigated. At a pressure of 10,000 lb./sq. in. abs. the error is —9.85% at 104°F., —5.72% at 139°F., and —6.49% at 171°F. It was not possible to obtain coefficients for the hydrogen-nitrogen system from the Slattery-Bird correlation because the reduced temperature is outside the range of the correlation chart.

Smoothed values of the observed data are plotted vs. $1/T$ in Figure 4 with density as a parameter. The nearly linear relationship shown between log $\mathcal{D}_{12}$ and $1/T$ indicates agreement with the form of Equation (6). This

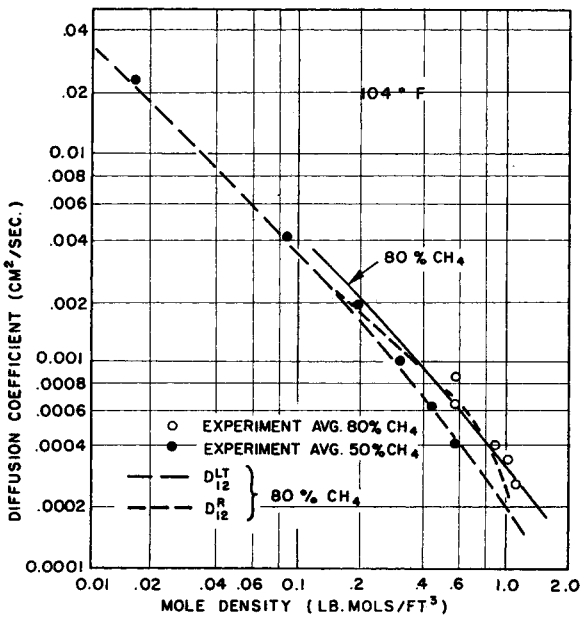

Fig. 5. Diffusion coefficients for the methane-ethane system at 104°F.

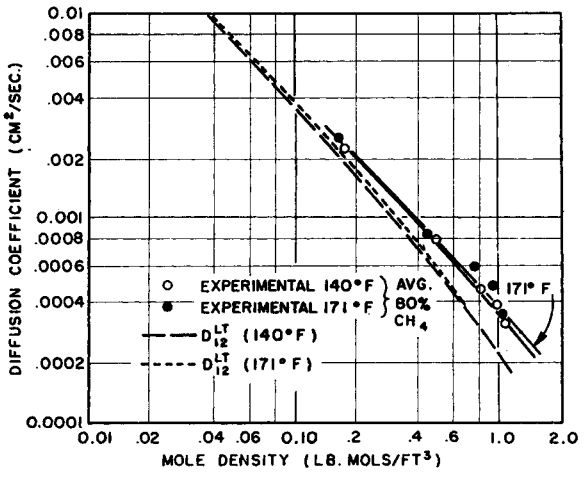

Fig. 6. Diffusion coefficients for the methane-ethane system at 140° and 171°F.

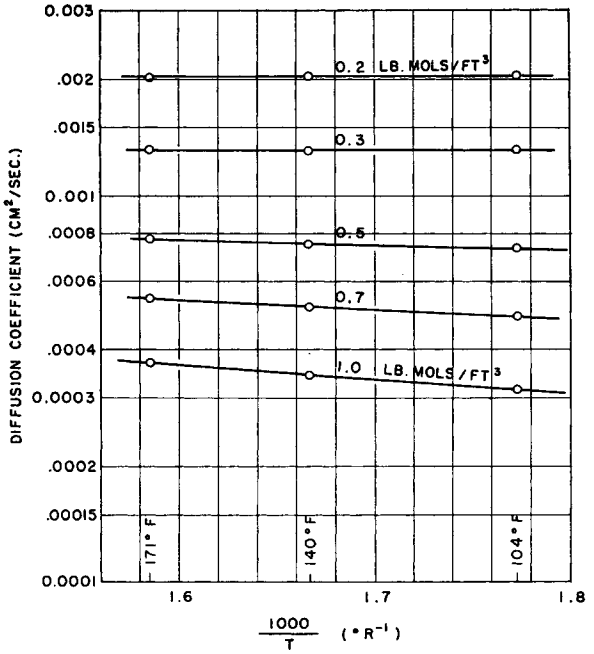

Fig. 7. Smoothed values of the diffusion coefficient for the methane-ethane system.

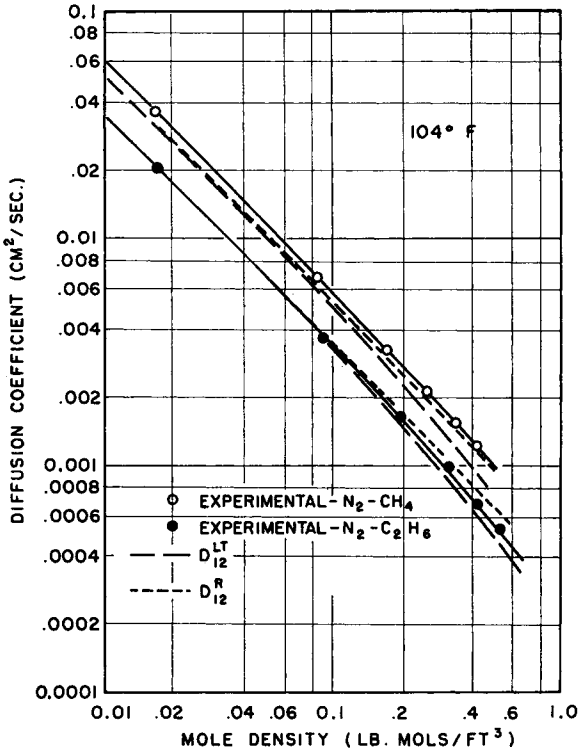

Fig. 8. Diffusion coefficients for the nitrogen-methane and nitrogen-ethane systems at 104°F.

further substantiates the conclusion that the actual temperature dependence of diffusion in dense gases is similar to that of liquids (*4*).

Methane-Ethane Diffusion Coefficients

Measurements were made with the methane-ethane systems at temperatures of 104, 140, and 171°F. and pressures to 10,000 lb./sq. in. abs. Experimental diffusion coefficients are shown plotted as a function of density at 104°F. in Figure 5 and at 140 and 171°F. in Figure 6. Data calculated with Equations (11) and (13) and those obtained from the Slattery-Bird reduced state correlation are also shown in Figure 5. The smoothed experimental and calculated and correlated diffusion coefficients are compared at 104°F. and various densities in Table 3.

From a comparison between Figures 3 and 5 it is seen that there is considerably more scatter in the experimental data for the methane-ethane system than for the hydrogen-nitrogen system. A plausible explanation for this difference might be found in the nonideal mixing in the methane-ethane system. Compressibility data indicate a 7.5% decrease in pressure when equal volumes of methane and ethane are mixed at 100°F. and 3,000 lb./sq. in. abs. The same experiment with hydrogen and nitrogen would show a 1.2% increase in pressure on mixing. The relatively large pressure defect in the methane-ethane system could give rise to a nonreproducible mass flux in the test cell which would have a pronounced effect on the precision and accuracy of observed diffusion coefficients.

The data points shown in Figure 5 as filled circles were determined from experiments in which each half of the cell initially contained a pure gas. The open circles pertain to experiments in which the upper half of the cell initially contained pure methane, and the lower half contained a mixture of methane and ethane such that the total cell content averaged about 80% methane. No effect of concentration is apparent in the data; this is surprising in view of the fact that the self-diffusion coefficient in methane is about five times as great as that in ethane.

Equation (13) does not predict a large effect of concentration on diffusion coefficients in binary systems, and this is apparently consistent with the experimental data. Thorne's dense-gas correction however does reflect a small effect of concentration through the weighting of terms in Equation (12) and through the mixture compressibility factor. The dense-gas correction used for $\mathcal{D}^{LT}_{12}$ in Figure 5 was calculated for a mixture containing 80 mole % methane.

In spite of the large divergence between experimental and calculated coefficients it is significant that both show about the same change in slope in the high-density region in Figure 5. This suggests that the dense-gas correction for density is satisfactory. It is surprising that this should be the case for a nonspherical molecule such as ethane in view of the fact that the dense-gas theory was derived for spherically symmetrical molecules.

Coefficients obtained from the reduced state correlation of Slattery and Bird fit the experimental data better than do the data calculated from kinetic theory. The Slattery-Bird correlation is based on extrapolated data beyond $p_r = 4.0$. This probably accounts for the anomalous shape of the curve of $\mathcal{D}^{R}_{12}$ in the high-density region. Over the range $0.3 < p_r < 4.0$ and $T_r = 1.262$ the average deviation of correlated factors from observed ones is about 10%. The average deviation of the calculated factors over this same range of conditions is about 25%. On the basis of these data, then, it is recommended that the reduced state correlation of Slattery and Bird be used to

Table 4. Smoothed Values of Diffusion Coefficients in the Methane-Nitrogen and Ethane-Nitrogen Systems

		104°F.						
		Methane nitrogen				Ethane nitrogen		
lb./sq. in. abs.	lb.-mole/ cu. ft.	$\mathcal{D}^{OBS.}_{12}$	$\mathcal{D}^{LT}_{12}$	$\mathcal{D}^{R}_{12}$	lb.-mole/ cu. ft.	$\mathcal{D}^{OBS.}_{12}$	$\mathcal{D}^{LT}_{12}$	$\mathcal{D}^{R}_{12}$
100	.0166	.0364	.0312	.0311	.0168	.0208	.0207	.0204
500	.0843	.00680	.00587	.00612	.0898	.00370	.00366	.00364
1000	.1710	.00327	.00274	.00299	.1951	.00166	.00156	.00167
1500	.2579	.00211	.00173	.00195	.3117	.000985	.000897	.00107
2000	.3429	.00155	.00124	.00145	.4278	.000669	.000607	.000797
2500	.4256	.00122	.00095	.00116	.5279	.000522	.000463	.00064
Average absolute error			17.4%	8.7%			6.9%	9.1%

predict diffusion coefficients in dense gases, at p_r less than 4.0, containing polyatomic asymmetric molecules.

Smoothed diffusion coefficients from the three methane-ethane isotherms are plotted vs. $1/T$ with density as a parameter in Figure 7. This graph confirms the observation from the hydrogen-nitrogen data that the dependence of diffusion on temperature in dense gases is of an exponential form. Since this relation was found for both a near-ideal system (hydrogen-nitrogen) and a relatively nonideal system (methane-ethane), it is thought safe to conclude that the diffusion coefficient in compressed binary gas mixtures varies with temperature approximately as $e^{-b_3/T}$

Nitrogen-Methane and Nitrogen-Ethane Diffusion Coefficients

Diffusion coefficients determined for the nitrogen-methane and nitrogen-ethane systems at 104°F. and to a pressure of 2,500 lb./sq. in. abs. are plotted as a function of density in Figure 8. Curves of theoretical coefficients calculated from Equations (11) and (13) and determined from the Slattery-Bird correlation are also shown. Numerical values of the data are compared in Table 4. In these systems too it is seen that the coefficients calculated from kinetic theory diverge below the experimental data in the high-density region. The calculated data provide a better fit for the nitrogen-ethane system than for the nitrogen-methane system. There is a constant percentage difference between the calculated and observed data in the methane-nitrogen system at low densities. This indicates that the value of $(\mathcal{D}^L_{12})_0$ from Equation (11) is in error.

Over the experimental pressure range coefficients from the reduced state correlation show an average deviation of 8.7% from the observed data in the nitrogen-methane system and 9.1% from observed data in the nitrogen-ethane system. It is clear in Figure 8 that the Slattery-Bird correlation gives better agreement with the experimental diffusion coefficients than do the data calculated from Equations (11) and (13). A similar observation was made from the methane-ethane data above. On the basis of these observations it is concluded that the Slattery-Bird reduced state correlation provides slightly better estimates of diffusion coefficients in dense-gas mixtures than do kinetic-theory calculations based on the Lennard-Jones model with Thorne's binary dense-gas correction.

CONCLUSIONS

1. Apparatus and experimental techniques have been developed which are suitable for the determination of average diffusion coefficients in compressed binary gaseous mixtures which do not undergo large changes in volume on mixing.

2. The diffusion coefficient in compressed binary gas mixtures varies with temperature approximately as $e^{-b_3/T}$.

3. The Slattery-Bird reduced state correlation provides slightly better estimates of diffusion coefficients in dense-gas mixtures than do kinetic-theory calculations based on the Lennard-Jones model with Thorne's binary dense-gas correction.

NOTATION

A = cross-section area of diffusion cell
b_1, b_2, b_3 = arbitrary constants
$\mathcal{D}_{12}$ = diffusion coefficient in binary gas mixture of components 1 and 2
D_L = diffusion coefficient in the liquid state at temperature T
E = activation energy
L = half length of diffusion cell
M = molecular weight
N = Avogadro's number
N_1 = number flux of component 1
n = number of molecules per unit volume = Np/ZRT
p = pressure, lb./sq. in. abs.
R = gas law constant
T = absolute temperature, °R.
t = time variable
V = volume per mole of gas at p and T
x = mole fraction
z = position along axis of diffusion cell
Z = compressibility factor = pV/RT

Greek Letters

ϵ = force parameter for Lennard-Jones potential
κ = Boltzmann constant
σ = molecular collision parameter
χ_{12} = Thorne's binary dense-gas correction factor
$\Omega^{(1,1)*}$ = collision integral given as a function of $\kappa T/\epsilon$

Superscripts

S = calculated from the solid elastic sphere model
L = calculated from the Lennard-Jones model
LT = calculated from the Lennard-Jones model with Thorne's dense-gas correction
R = obtained from Slattery-Bird reduced state correlation
$-$ = average value

Subscripts

1 or 2 = component 1 or 2
12 = mixture of components 1 and 2
0 = value at time = zero; value at p_o = 14.696 lb./sq. in. abs.
r = value of property divided by its critical or pseudocritical value

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Manuscript received June 8, 1959; revision received August 12, 1959; paper accepted August 13, 1959. Paper presented at A.I.Ch.E. Kansas City meeting.