Correlation and Prediction of Gaseous Diffusion Coefficients

A new correlation method for binary gaseous diffusion coefficients from very low temperatures to 10,000 K is proposed based on an extended principle of corresponding states, and having greater range and accuracy than previous correlations. There are two correlation parameters that are related to other physical quantities and that are predictable in the absence of diffusion measurements. Quantum effects and composition dependence are included, but high-pressure effects are not. The results are directly applicable to multicomponent mixtures.

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SCOPE

Quantitative knowledge of gas-phase diffusion coefficients is of importance for the understanding of many chemical and physical processes, and many schemes have been proposed for their correlation and prediction. The purpose of this work is to present a new scheme of improved range and accuracy, based on an extended principle of corresponding states involving only two parameters. This new correlation is based on a recent comprehensive critical survey of gaseous diffusion coefficients (Mason and Marrero, 1970; Marrero and Mason, 1972). The two correlation parameters can themselves be correlated with other physical quantities, and so are predictable in the face of meager or nonexistent experimental diffusion data.

The correlation covers a wide temperature range, from very low temperatures to 10,000 K, by incorporation of information on intermolecular forces from independent sources. The pressure range, however, is limited to the dilute gas regime, in which the diffusion coefficient is inversely proportional to the total gas pressure. The correlation includes corrections for quantum effects and for composition dependence. The present results can be applied to mixtures containing any number of components, since diffusion in multicomponent mixtures is described, apart from a small composition correction, by the same diffusion coefficients that describe binary mixtures.

Many previous correlations of gaseous diffusion coefficients have been published; references to these are given by Fuller et al. (1966) and by Marrero and Mason (1972). The most notable recent correlations are those of Fuller et al. (1966) and of Kestin et al. (1972). The latter is highly accurate but restricted to the noble gases and does not incorporate the correct asymptotic behavior at very low and very high temperatures. The procedure of Fuller et al. is less accurate but is applicable to a wide variety of substances through the use of special atomic diffusion volumes. Its main disadvantage is an oversimplification of the predicted temperature dependence for the diffusion coefficient.

CONCLUSIONS AND SIGNIFICANCE

The two-parameter corresponding-states equation for the temperature dependence of the diffusion coefficient $\mathcal{D}_{12}$ is, for low concentrations of the heavier component 1,

$$\mathcal{D}_{12}(x_1 \approx 0) = \left(\frac{M_1 + M_2}{2M_1M_2}\right)^{1/2} \frac{T^{3/2}}{p} \frac{1}{\omega\Omega_0}$$

where

$$\Omega_0 = 17.54 \left[\ln\left(\frac{T/\theta}{4.10 \times 10^7}\right)\right]^2 \exp [16.61(\theta/\mathrm{T}) + 35.87(\theta/\mathrm{T})^2] \quad \text{for } T/\theta \geqq 36.6$$

$$\Omega_0 = 1.83 \times 10^4\ (\theta/T)^{1/3} \quad \text{for } T/\theta < 36.6$$

in which θ and ω are the adjustable parameters. This equation holds from 10,000 K down to temperatures at which quantum effects become large. These quantum effects are evident in measurements of $\mathcal{D}_{12}$ only for light gases at very low temperatures; if the effects are less than about 10%, they can be represented by addition of the following increment to Ω_0:

$$\Delta\Omega_0 = 2415 - 10^3 \left[4892 \left(\frac{\theta}{T\omega\mu_0}\right)^2 + 5.832 \right]^{1/2}$$

where μ_0 denotes a relative reduced mass. The small composition dependence of $\mathcal{D}_{12}$ is adequately described by Equation (10) of the text. These equations appear to serve better than any other known method for the correlation and prediction of diffusion coefficients over very wide temperature ranges.

The two parameters θ and ω are predictable by several methods, the reliability depending on the information available for a given system. Since the tabulated atomic diffusion volumes of Fuller et al. (1966) can be used in the prediction scheme for the parameters, many of the advantages of the Fuller et al. correlation can be incorporated into the present correlation. The three main uses of the present correlation are expected to be as follows: (1) for mixtures with reliable diffusion data, the applicable temperature range can be extended to higher or lower temperatures with considerable reliability; (2) for mixtures with meager diffusion data, similar extrapolations can be made, but with less reliability; (3) for mixtures with no diffusion measurements, values of $\mathcal{D}_{12}$ can be predicted over several decades of temperature with fair reliability.

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THEORY

The basis for the correlation is the Chapman-Enskog kinetic theory of gases, which yields the following expression for the diffusion coefficient (Hirschfelder et al., 1964; Chapman and Cowling, 1970):

$$\mathcal{D}_{12} = \frac{3}{16}\left(\frac{2kT}{\pi\mu_{12}}\right)^{1/2}\frac{(1 + \Delta_{12} + \ldots)}{n\sigma_{12}^2\Omega_{12}^{(1,1)*}} \qquad (1)$$

where $\mu_{12} = m_1m_2/(m_1 + m_2)$ is the reduced mass of a pair of molecules. The correction term Δ_{12}, which is less than 5% for most gas pairs, contains the entire composition dependence of $\mathcal{D}_{12}$. For our purposes Δ_{12} can be considered negligibly small when the heavier component (always chosen as component 1) is in low concentration, and we postpone discussion of Δ_{12} to the end of this section. The critical portion of the expression is the group $\sigma_{12}^2\Omega_{12}^{(1,1)*}$, which contains the contribution of the intermolecular forces, and through them, part of the temperature dependence of $\mathcal{D}_{12}$. The parameter σ_{12} has the units of length and is some measure of molecular size or range of intermolecular force; its choice is arbitrary and can be made on any convenient basis.

If the intermolecular potentials for all the gas pairs of interest have the same shape, differing only through scale factors for range (σ_{12}) and for energy (ϵ_{12}), then the classical principle of corresponding states requires that the dimensionless collision integral $\Omega_{12}^{(1,1)*}$ depends on temperature only through the dimensionless ratio (Hirschfelder et al. 1964):

$$T^* = kT/\epsilon_{12} \qquad (2)$$

Of course, $\Omega_{12}^{(1,1)*}$ may also depend on other parameters of the potential, but these extra parameters are the same for all the gas pairs according to the assumption of similar potential shape. This assumption can be only approximately correct at best, but correlations based on it often prove to be surprisingly accurate. We may therefore select a parameter ω proportional to σ_{12}^2 and a parameter θ proportional to ϵ_{12}/k, and rewrite Equation (1) in the practical form

$$\mathcal{D}_{12}(x_1 \approx 0) = \left(\frac{M_1 + M_2}{2M_1M_2}\right)^{1/2}\frac{T^{3/2}}{p}\frac{1}{\omega\Omega_0(T/\theta)} \qquad (3)$$

where the numerical constants and the units have been absorbed into ω and Ω_0. The collision integral $\Omega_0(T/\theta)$ depends on temperature only through the ratio T/θ; the problem now is to discover what is the temperature dependence of Ω_0.

The safest way to determine the behavior of Ω_0 as a function of T/θ is probably to adopt a strictly empirical approach and use the most reliable experimental data on $\mathcal{D}_{12}$ directly. That is, one obtains experimental values of $\omega\Omega_0$ from measured $\mathcal{D}_{12}$ by Equation (3), and then tests whether such values for different gas pairs can be made to fall on one universal curve by suitable choices of ω and θ values. That this can be done will be demonstrated in the next section; the question then arises as to the best way to represent such an empirical curve of Ω_0 versus T/θ. At this point the inclusion of some theoretical information on the expected behavior of Ω_0, especially its asymptotic behavior at high and low temperatures, can greatly enhance the ability to extrapolate and predict. The theoretical information needed comes from knowledge of intermolecular forces and how they affect the behavior of $\Omega_{12}^{(1,1)*}$. This has been discussed by Marrero and Mason (1972), and we merely summarize the gist of the arguments here. At low temperatures the molecular collisions are dominated by the long-range part of the intermolecular potential, which for most molecules is the attractive London dispersion potential

$$\phi(r) = -C/r^6 \qquad (4)$$

According to classical mechanics the collision integral for this potential has the form

$$\sigma_{12}^2\Omega_{12}^{(1,1)*} \propto (C/kT)^{1/3} \qquad (5)$$

The constant of proportionality must be found by numerical integration and is known. At high temperatures the collisions are dominated by the repulsive short-range part of the potential, which for most molecules can be represented over a wide range by an exponential function,

$$\phi(r) = \phi_0\exp(-r/\rho) \qquad (6)$$

For this potential the temperature dependence of the collision integral can be represented as

$$\Omega_{12}^{(1,1)*} \propto [\ln(\phi_0/kT)]^2 \qquad (7)$$

At somewhat lower temperatures the attractive forces modify this behavior, and a good representation is

$$\Omega_{12}^{(1,1)*} \propto [\ln(\phi_0/kT)]^2\exp(S/T) \qquad (8)$$

The constant S is sometimes called the Sutherland-Reinganum constant. Thus the behavior of the collision integral is given by Equation (5) at low temperatures, and by Equation (8) at intermediate and high temperatures.

Quantum mechanics modifies the classical principle of corresponding states, and systematic deviations can be seen in Ω_0 for light gases at low T/θ. The new physical quantity introduced by quantum mechanics is the de Broglie wavelength, $\lambda = h/(2\pi\mu_{12}kT)^{1/2}$, with the result that $\Omega_{12}^{(1,1)*}$ is a function not only of T^* but also of the dimensionless ratio λ/σ_{12}. It can be shown that, if the intermolecular potential is an analytic function, without discontinuities in any of its derivatives, then the quantum deviations from classical behavior are functions of $(\lambda/\sigma_{12})^2$ (DeBoer and Bird, 1954). In terms of quantities already used, the deviations should thus have the form

$$\Delta\Omega_{12}^{(1,1)*} = f(h/\sigma_{12}^2\mu_{12}kT). \qquad (9)$$

It remains only to consider the small composition dependence embodied in Δ_{12}. Marrero and Mason (1972) have shown that Δ_{12} can be predicted with acceptable accuracy by the formula

$$\Delta_{12} = \zeta(6C_{12}^* - 5)\frac{ax_1}{1 + bx_1} \qquad (10)$$

where ζ is a numerical constant between 1 and 2, C_{12}^* is a dimensionless ratio of collision integrals, and

$$a = \frac{3[1 + (M_2/M_1)]^{1/2}}{20[1 + 1.8(M_2/M_1)]^2}\frac{\eta_2RT}{p\mathcal{D}_{12}M_2} \qquad (11)$$

$$b = 10a\,[1 + 1.8(M_2/M_1) + 3(M_2/M_1)^2] - 1 \qquad (12)$$

in which η_2 is the viscosity of the light component. The quantities a and b can usually be taken as constant over a very wide temperature range. Tables from which Δ_{12} can be calculated according to Equation (10) are available (Mason and Marrero, 1970; Marrero and Mason, 1972).

It should be emphasized that the use of the Chapman-Enskog theory limits the results to gas densities for which diffusion is controlled by binary molecular collisions, that is, to the regime in which $\mathcal{D}_{12}$ is inversely proportional to p. Additional density or pressure effects are beyond the scope of this theory. However, the theory predicts that, if all composition corrections like Δ_{12} are ignored, then the diffusion coefficients for multicomponent mixtures are the same as those for the corresponding binary mixtures (Hirschfelder et al., 1964; Chapman and Cowling, 1970). The present correlation can therefore be applied with confidence to mixtures containing more than two components. It should also be mentioned that the low-temperature asymptote of Equation (5) does not apply to pairs of polar or valence unsaturated molecules.

CALCULATION METHODS AND RESULTS

The experimental information necessary for the calculation of Ω_0 as a function of T/θ is contained in the critical survey of Marrero and Mason (1972). The most reliable values of $\mathcal{D}_{12}$ are those for the ten noble gas pairs, whose molecular characteristics are also the most consistent with the fundamental assumptions of the Chapman-Enskog theory, and it was therefore decided to base the determination of Ω_0 on these data alone. The key results selected for the determination were the measurements of $\mathcal{D}_{12}$ by van Heijningen et al. (1968) in the range between 65 and 400 K, and the values of $\mathcal{D}_{12}$ calculated from molecular-beam potentials at 1000 and 10000 K by Marrero and Mason (1972). All data were corrected to the mixture composition $x_1 \approx 0$ by means of Equation (10). Since the London constants C of Equation (4) are accurately known for the noble gases (Dalgarno, 1967; Starkschall and Gordon, 1971), it was decided to take full advantage of the asymptotic behavior given by Equation (5) in determining Ω_0. If the London constant is given in atomic units, then the classical asymptotic behavior is given by (Mason, 1954)

$$\pi\sigma_{12}^2\Omega^{(1,1)*} = 71.1(C/T)^{1/3} \qquad (13)$$

for σ_{12} in angstroms and T in kelvin. Values of $\mathcal{D}_{12}$ calculated from Equation (13) were included with the other selected values of $\mathcal{D}_{12}$, and values of $\omega\Omega_0$ then calculated from Equation (3). These values were plotted against T on accurate double logarithmic scales, one separate plot for each system, and then the plots were shifted relative to one another until the plotted points fell along one smooth curve with minimum scatter. The classical asymptotes were forced to agree exactly. The horizontal displacement along the log T axis then gave log θ, and the vertical displacement gave log ω. Since the numerical values of both θ and ω are arbitrary within a multiplicative constant that can be chosen for convenience, the system He-Ar was taken as a reference system and assigned values of $\theta = 1$ and $\omega = 1$. The values of θ and ω are given in Table 1, together with the values of C used.

TABLE 1. OPTIMUM SCALING PARAMETERS FOR THE CORRELATION OF $\mathcal{D}_{12}$ ACCORDING TO EQUATION (3)

System	θ	$\omega^{1/2}$	C(a.u.)†
He-Ne	0.78	0.86	3.0
Ar	1.00*	1.00*	9.6
Kr	0.89	1.07	13.0
Ke	0.71	1.19	19.0
Ne-Ar	1.51	1.05	20.0
Kr	1.35	1.13	27.0
Xe	1.29	1.21	38.0
Ar-Kr	3.02	1.21	91.0
Xe	3.72	1.24	130.0
Kr-Xe	4.27	1.29	190.0

* Arbitrary reference value.

† 1 a.u. = $(1e^2/a_0)\,(1a_0{}^6) = 0.957 \times 10^{-60}$ erg-cm^6. These values are from Dalgarno (1967).

The data for the noble gases clearly indicated that log Ω_0 was a rather complicated nonlinear functon of log (T/θ). We did not obtain a single mathematical expression for Ω_0 applicable over the entire temperature range because of the difficulty of devising a suitable expression to connect the form of Equation (13) at low temperatures with the form given by Equation (8) for higher temperatures. Instead we simply switched from one expression to the other at their intersection point; this produces a kink in the curve, which is of no importance for most purposes. The procedure was as follows. An additonal Sutherland-Reinganum constant was added to Equation (8), the constants determined by least-squares fit to a smooth curve drawn through the points, and the value of the intersection point with the classical asymptote found. The results are

$$\Omega_0 = 17.54\left[\ln\left(\frac{T/\theta}{4.10 \times 10^7}\right)\right]^2 \exp[16.61(\theta/T) + 35.87\,(\theta/T)^2] \text{ for } T/\theta \geqq 36.6 \qquad (14)$$

$$\Omega_0 = 1.83 \times 10^4\,(\theta/T)^{1/3} \text{ for } T/\theta < 36.6 \qquad (15)$$

These equations are to be used in conjunction with Equation (3) for $\mathcal{D}_{12}$, which will be given in cm^2/s when M_1 and M_2 are in g/mole, T is in kelvin, and p is in atm. The key $\mathcal{D}_{12}$ values for the noble gas systems, 61 in all, had deviations from these equations of less than 12% in all cases, and the average absolute deviations for each gas pair ranged from about 1 to 3%. The overall average absolute deviation of all 61 values was 2.3%. These deviations include corrections for quantum effects, which were determined as described below.

Systematic deviations from a general smooth curve were noticeable for several systems at low temperatures. The theoretical relation of Equation (9) suggests that such deviations should be a universal function of a dimensionless group of variables proportional to $(\lambda/\sigma_{12})^2$; an appropriate plot of the deviations could be fitted satisfactorily by the expression

$$\Delta\Omega_0 = 2415 - 10^3\,[4892(\theta/T\omega\mu_0)^2 + 5.832]^{1/2} \qquad (16)$$

where μ_0 is the ratio of the reduced mass of the system to that of the He-Ar reference system. The correction $\Delta\Omega_0$ is to be added to the value of Ω_0, which is thereby reduced because $\Delta\Omega_0$ is negative. However, the correction as given by Equation (16) is not reliable when its magnitude becomes larger than about 10% of Ω_0, because of the oscillatory behavior of large quantum effects (Imam-Rahojoe et al., 1965; Munn et al., 1965).

The results are illustrated in Figure 1, where Equations (14) and (15) are compared with the key experimental values, with the omission of those showing appreciable quantum effects. The quantum effects are illustrated in Figure 2 on a larger scale, where it can be seen that Equation (16) gives a satisfactory estimate.

COMPARISON WITH OTHER METHODS

The most significant previous correlations of gaseous diffusion coefficients are probably those of Fuller et al. (1966) and of Kestin et al. (1972). The former write

$$\mathfrak{D}_{12} = 1.00 \times 10^{-3} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2} \frac{T^{1.75}}{p} \frac{1}{(v_1^{1/3} + v_2^{1/3})^2} \quad (17)$$

where v_1 and v_2 are empirical diffusion volumes. With He-Ar as a reference system, this expression is equivalent to

$$\Omega_0 = 1.10 \times 10^4 / T^{0.25} \quad (18)$$

which is shown in Figure 1 as a long dashed line. The average absolute deviation of Equation (17) for all 61 key noble gas values is 5.6%, which is somewhat poorer than the present correlation, but Equation (17) clearly furnishes an excellent simple method for estimates of $\mathfrak{D}_{12}$. The major fault of Equation (17) is its low-temperature behavior, as can be seen from Figure 1.

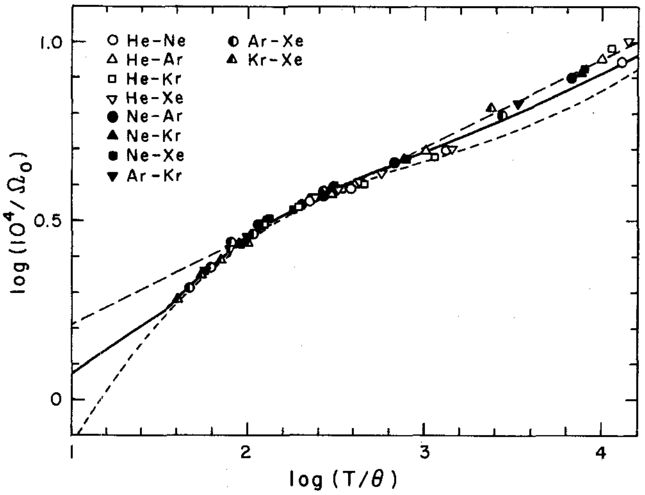

Fig. 1. Corresponding-states correlation for gaseous diffusion coefficients. The solid curve is the present correlation according to Equations (14) and (15), the long dashed line is the correlation of Fuller et al. according to Equation (18), and the short dashed curve is the correlation of Kestin et al. according to Equation (20).

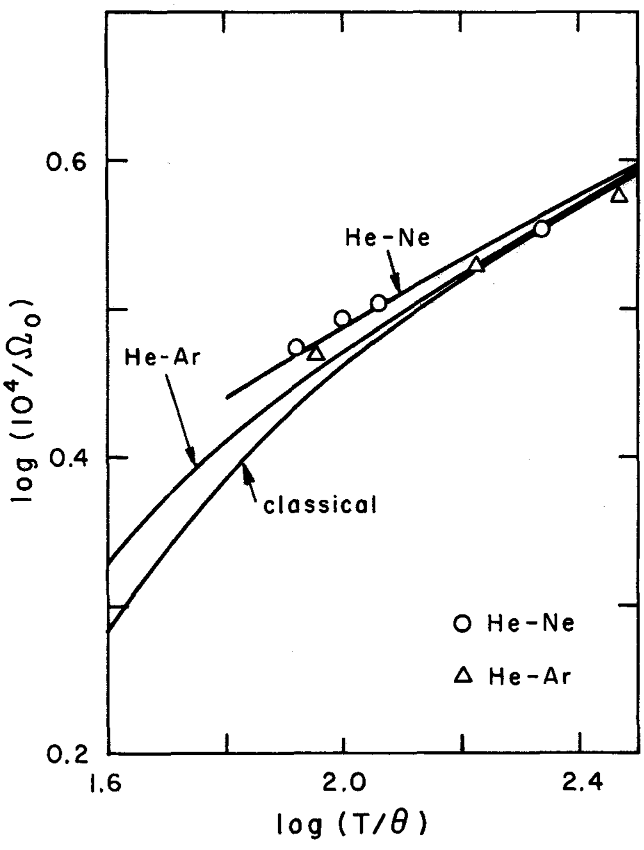

Fig. 2. Corresponding-states correlation for mixtures with quantum effects, according to Equation (16).

TABLE 2. SCALING PARAMETERS FOR THE CORRELATIONS OF FULLER ET AL. AND KESTIN ET AL., FOR COMPARISON WITH THE RESULTS IN TABLE 1

	Fuller et al.		Kestin et al.			
System	$v_1^{1/3} + v_2^{1/3}$	$\omega^{1/2}$	ϵ/k	σ	θ	$\omega^{1/2}$
He-Ne	3.20	0.81	21.12	2.644	0.382	0.910
Ar	3.95	1.00*	55.24	2.904	1.000*	1.000*
Kr	4.26	1.08	32.13	3.230	0.582	1.112
Xe	4.78	1.21	22.87	3.595	0.414	1.238
Ne-Ar	4.30	1.09	63.70	3.085	1.153	1.062
Kr	4.61	1.17	77.43	3.158	1.402	1.087
Xe	5.13	1.30	80.98	3.360	1.466	1.157
Ar-Kr	5.36	1.36	180.61	3.391	3.270	1.168
Xe	5.88	1.49	234.03	3.455	4.237	1.190
Kr-Xe	6.19	1.57	277.12	3.595	5.017	1.238

* Arbitrary reference value.

Kestin et al. (1972) present a correlation in the form of Equation (1), with the collision integral given by the empirical expression

$$\ln \Omega_{12}^{(1,1)*} = 0.347 - 0.444 (\ln T^*) + 0.093 (\ln T^*)^2 - 0.010 (\ln T^*)^3 \quad (19)$$

The values of σ_{12} and ϵ_{12} were chosen empirically to produce an optimum fit in the reduced temperature range of $T^* = 0.5$ to 8, and Equation (19) is claimed to be extendable to about $T^* = 30$. With He-Ar as a reference system, this expression is equivalent to

$$\log \Omega_0 = 5.360 - 1.672 [\log (T/\theta)] + 0.491 [\log (T/\theta)]^2 - 0.053 [\log T/\theta)]^3 \quad (20)$$

which is shown in Figure 1 as a short dashed curve. The average absolute deviation of the Kestin et al. correlation for all 61 key noble gas values is 3.7%, which is somewhat poorer than the present correlation, but Figure 1 shows that this is caused by a poor fit at the highest temperatures. If the values at 10000 K are omitted from the comparison, the average absolute deviation drops to 1.5%, which is excellent agreement. The major fault of Equation (19) or (20) is thus the high-temperature behavior. It also behaves poorly at low temperatures, as seen in Figure 1, but there are no diffusion measurements presently available in this low temperature range. In any case, the low-temperature behavior could easily be fixed by switching to the correct classical asymptote at a suitable reduced temperature, as is done in our correlation scheme.

It is apparent from the foregoing equations that there should be at least a rough correspondence among the size parameters $(v_1^{1/3} + v_2^{1/3})$, σ_{12}, and $\omega^{1/2}$ and between the energy parameters ϵ_{12} and θ. The empirical parameters used by Fuller et al. and by Kestin et al. are shown in Table 2, where they are also adjusted to He-Ar as a reference system for comparison with our values given in Table 1. The concordance is fairly good for the size parameters. It is apparently poorer for the energy parameters, especially for those systems involving helium, but the results are less sensitive to the energy parameter than to the size parameter. Furthermore, when an energy parameter appears to be small, the corresponding size parameter is large, and vice versa, and the effects tend to compensate.

PREDICTION OF PARAMETERS

Two parameters are required for the application of the present correlation, and a variety of methods can be used for their prediction. In this section we suggest several methods that have been tested by spot calculations. Extensive testing of these and other methods that may be suggested against extensive and accurate experimental data is a formidable undertaking that remains for the future.

If the London constant is known, then only one parameter must be predicted since θ and ω are related to the London constant by the expression

$$\theta\omega^3 = 0.104\, C \tag{21}$$

where C is in atomic units and θ and ω are chosen for He-Ar as the reference system. Many values of C are available (Dalgarno, 1967; Starkschall and Gordon, 1971); if C is not available directly, approximate values may be calculated by the Slater-Kirkwood (1931) formula

$$C = \frac{\frac{3}{2}\alpha_1\alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}} \tag{22}$$

where α_i is the polarizability of the atom or molecule in atomic units and N_i is the number of valence electrons. This formula can also be used as the basis of an accurate combination rule for the calculation of an unknown value of C from known values for other systems (Wilson, 1965; Kramer and Herschbach, 1970).

Once C is known, the remaining parameters can be estimated by several alternate methods. Probably the best way is from a few reliable measurements of $\mathcal{D}_{12}$ (a single measurement is sufficient in principle). The parameter θ can be obtained by simple graphical analysis similar to that used to obtain the original values of θ and ω. Applying this procedure to Ar-Kr by pretending that the only known value of $\mathcal{D}_{12}$ was a measurement at 295.0 K (van Heijningen et al., 1968), we calculated values of $\mathcal{D}_{12}$ over the range 169 to 10000 K that differed from the key values by an average absolute deviation of less than 0.5%, an accuracy virtually the same as that obtained with the correlation parameters of Table 1. By comparison, the correlation of Fuller et al. led to an average absolute deviation of about 6%, due largely to its low-temperature failure, and the correlation of Kestin et al. led to about 3% average absolute deviation, due largely to its high-temperature failure. As a further test, we applied the same procedure to the system H_2-N_2, which was not used in the original correlation; the key values were the measurements of van Heijningen et al. (1966) between 65 and 295 K, and the values at 1000 and 10000 K obtained by Marrero and Mason (1972) from molecular-beam potentials. The average absolute deviations were 4 to 5%, depending on the value of C used. The correlation of Fuller et al. also gave about 5% average absolute deviation; for this system the low-temperature failure is fortuitously compensated by quantum effects.

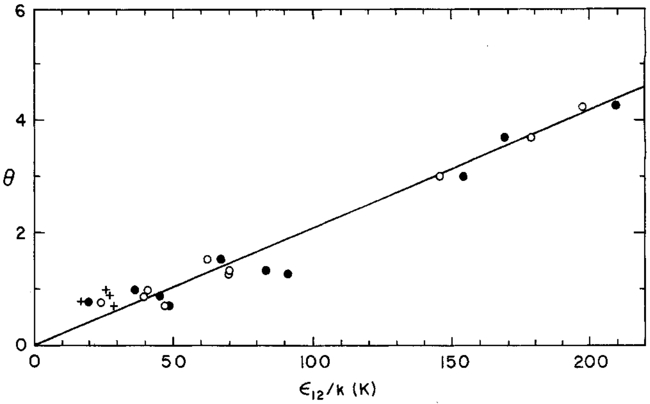

Fig. 3. Proportionality between the correlation parameter θ and the potential well depth ϵ_{12}. The straight line represents Equation (23), and the points are from the following sources: ○ van Heijningen et al. (1968), ● Hirschfelder et al. (1964), + Berstein and Muckerman (1967).

If no reliable experimental values of $\mathcal{D}_{12}$ are known, θ can still be predicted. One obvious way is through the presumed proportionality between θ and the depth of the intermolecular potential energy well, which we can denote as ϵ_{12}. The trouble with this method is that the true value of ϵ_{12} is seldom known accurately. Figure 3 shows a plot of θ against ϵ_{12}/k for the ten noble gas pairs, with three sources of ϵ_{12} values; from diffusion coefficients (van Heijningen et al., 1968), from viscosity data and combination rules (Hirschfelder et al., 1964), and from measurements of the scattering of thermal-energy molecular beams (Bernstein and Muckerman, 1967). The results can be simply approximated by

$$\theta = 0.021\,(\epsilon_{12}/k) \tag{23}$$

but a detailed analysis is unwarranted because of the large uncertainties in ϵ_{12}. A better prediction scheme relates θ to the polarizability and the London constant. Since polarizabilities are, in a sense, atomic or molecular volumes, we expect a rough proportionality between α and σ^3 or $\omega^{3/2}$. Using an arithmetic mean combination rule for σ or $\omega^{1/2}$, and assuming from Equation (21) that $\theta\omega^3 \propto C^n$, we find that the values of θ for the noble gas pairs can be correlated by the equation

$$\theta(\alpha_1^{1/3} + \alpha_2^{1/3})^6 = 40.3\, C^{1.516} \tag{24}$$

for α_i and C in atomic units. This result is illustrated in Figure 4. Using it we calculated values of $\mathcal{D}_{12}$ for Ar-Kr and H_2-N_2 that differ from the key values by average absolute deviations of 1% and 5%, respectively.

Finally, the correlation between the parameter ω and the diffusion volumes of Fuller et al. means that the advantages of their correlation scheme can be incorporated into the present correlation scheme with some improvement. That is, the present scheme can be used to remedy the low-temperature failure illustrated in Figure 1. For instance, the parameter ω could be obtained from the expression (based on He-Ar as the reference system)

$$\omega^{1/2} = 0.253\,(v_1^{1/3} + v_2^{1/3}) \tag{25}$$

Then θ could be obtained from either Equation (21) or Equation (24) if C were known or were calculated from Equation (22). More simply, the correlation of Fuller et al. could be used directly down to a temperature at which the low-temperature failure starts and the present correlation used below that temperature, if necessary. From Figure 1 we see that this temperature is approximately $T/\theta \approx 80$.

In short, a number of methods can be used to predict $\mathcal{D}_{12}$ over a wide temperature range, the reliability depending on the quality and extent of the starting information.

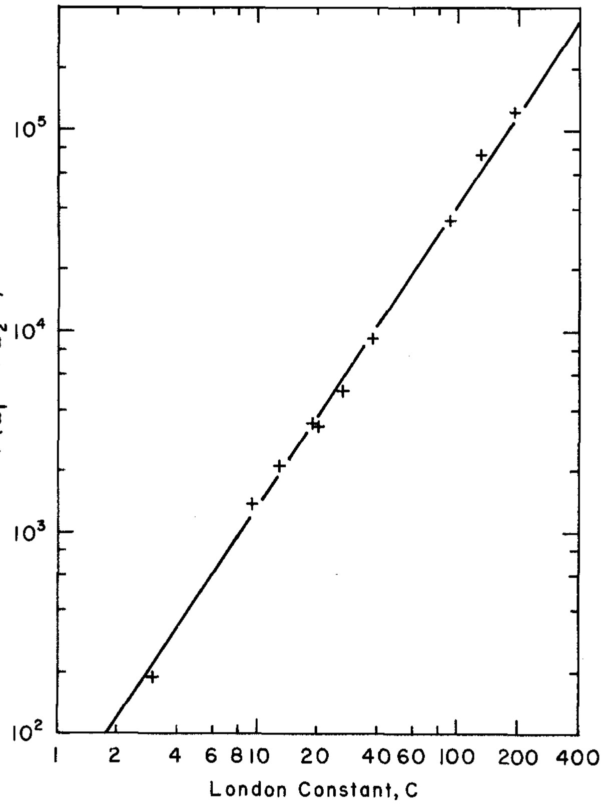

Fig. 4. Correlation of the parameter θ as a function of the London constant C. The straight line represents Equation (24); atomic units are used for C, α_1, and α_2.

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NOTATION

a, b = dimensionless quantities in Equations (10) to (12)
C = London dispersion constant
C_{12}^* = dimensionless ratio of collision integrals in Equation (10)
$\mathcal{D}_{12}$ = binary diffusion coefficient of species 1 and 2, cm^2/s
h = Planck constant
k = Boltzmann constant
m_i = molecular mass of species i
M_i = molar mass of species i, g/mole
n = molecular density, molecules/cm^3; $n = p/kT$
N_i = number of valence electrons
p = total gas pressure, atm.
r = intermolecular separation
R = gas constant
S = Sutherland-Reinganum constant in Equation (8)
T = absolute temp., K
T^* = reduced temperature defined in Equation (2)
v_i = diffusion volume of species i
x_i = mole fraction of species i

Greek Letters

α_i = molecular polarizability of species i in a.u. (1 a.u. = $1a_0^3 = 0.148 \times 10^{-24}$ cm^3)
Δ_{12} = composition-dependent part of $\mathcal{D}_{12}$ in Equations (1) and (10)
ϵ_{12} = scale factor for energy, usually the depth of the intermolecular potential energy well
ζ = dimensionless constant in Equation (10)
η_2 = viscosity of lighter component
θ = scale factor for temperature
λ = thermal de Broglie wave length; $\lambda = h/(2\pi\mu_{12}\,kT)^{1/2}$
μ_0 = ratio of reduced masses in Equation (16)
μ_{12} = reduced mass of species 1 and 2; $\mu_{12} = m_1m_2/(m_1 + m_2)$
ρ = potential parameter of exponential repulsion potential, Equation (6)
σ_{12} = scale factor for size or distance, usually the separation for which $\phi(r)$ is zero.
ϕ_0 = potential parameter of exponential repulsion potential, Equation (6)
$\phi(r)$ = intermolecular potential energy function
ω = scale factor for the collision integral
Ω_0 = empirical collision integral
$\Delta\Omega_0$ = quantum correction to Ω_0
$\Omega_{12}^{(1,1)*}$ = reduced collision integral

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