A REVIEW OF THE MOLECULAR DIFFUSIVITIES OF H_2O, CO_2, CH_4, CO, O_3, SO_2, NH_3, N_2O, NO, AND NO_2 IN AIR, O_2 AND N_2 NEAR STP

W. J. MASSMAN

USDA/Forest Service, Rocky Mountain Station, 240 West Prospect, Fort Collins, CO 80526, U.S.A.

Abstract— Accurate knowledge of the coefficients of molecular diffusivity (D) of trace gases has important application to global change, atmospheric chemistry, combustion science, studies of indoor air pollution and atmosphere–biosphere interactions. This study reviews and re-analyzes the historical data and some modeling results for D for H_2O, CO_2, CH_4, CO, O_3, SO_2, NH_3, N_2O, NO, and NO_2 in air, N_2 and O_2. Because CO and N_2 are isosteric molecules the self-diffusion coefficient for N_2 and D for N_2 in O_2 are also evaluated as an independent check on the determination of D for CO. Also included is the coefficient of self-diffusion of O_2 (D_{O_2,O_2}) because an earlier model parameterized D for O_3 in O_2 in terms of D_{O_2,O_2}. Because D is a function of temperature and pressure, all modeling results and data are corrected to 1 atm pressure and then used with a one- and two-parameter regression model to determine optimal values for the temperature exponent and the value of D at 0°C. For most experimental data the loess regression technique is used to identify and eliminate outliers. To simplify comparisons and usage all results and recommendations are standardized to one regression curve. For some gases like H_2O and CO_2 present results are similar to some (but not all) values cited in current sources. However, the coefficient of diffusivity in air for some very important gases, such as O_3, NO and NO_2, have never been measured and therefore, remain relatively uncertain. Based on present recommendations it is suggested that the ratio of the diffusivities of water vapor and ozone should be 1.51 rather than the often cited 1.65. © 1998 Elsevier Science Ltd. All rights reserved.

Key word index: Gaseous coefficients of diffusivity, gaseous binary diffusion.

INTRODUCTION

Molecular diffusion occurs as different species of a mixture (of gases or liquids, etc.) move under the influence of concentration gradients and it plays a key role in a variety of atmospheric and biospheric sciences. For example, because gases must diffuse through the boundary layer and stomata of plant leaves diffusion is thought to be the dominant exchange process during plant transpiration, photosynthesis, and uptake of ozone and other pollutants. Diffusion also affects the rate of movement of gases in soils and is central to much of atmospheric chemistry. In general the rate of diffusion (or flux) is determined by the product of a concentration gradient (a property of an individual species) and a coefficient of diffusivity (a property of the mixture). In turn, the coefficient of diffusivity, $D(T, p)$, is known to be a function of temperature (T) and pressure (p), (e.g. Reid *et al.*, 1987). The purpose of this study is twofold. The first is to review the experimental data and some of the models used for predicting the coefficients of diffusivity for 10 specific gases (H_2O, CO_2, CH_4, CO, O_3, SO_2, NH_3, N_2O, NO and NO_2) in air, N_2 and O_2 at temperatures and pressures typically encountered near the

earth's surface (i.e. temperatures approximately between $-50°C$ and $100°C$ and pressure near 1 atm or less). The second purpose is to derive and recommend estimates for $D(T, p)$ for use in applications at conditions near STP (standard temperature and pressure). (For convenience $D(T, p)$ at STP will be denoted by $D(0, 1)$, because STP is defined as $T = 0°C$ and $p = 1$ atmosphere or 101.325 kPa.)

Although coefficients of diffusivity have been experimentally determined for over a century (e.g. Loschmidt, 1870a, b; Winklemann, 1884a, b) and a comprehensive review of $D(T, p)$ for many gases is available (i.e. Marrero and Mason, 1972), there is still considerable variation in the values quoted by different researchers and references. The coefficient of diffusivity of water vapor in air (D_w) can serve as an example for this, although the coefficient of diffusivity of carbon dioxide in air would also serve nearly as well. Marrero and Mason (1972) suggest that the most precise determination for $D_w(0, 1)$ is 0.209 $cm^2 s^{-1}$. Monteith and Unsworth (1990) suggest that $D_w(0, 1)$ is 0.212 $cm^2 s^{-1}$. Laisk *et al.* (1989), using the model of Chen and Othmer (1962), estimated $D_w(0, 1)$ to be 0.195 $cm^2 s^{-1}$. Extrapolating the value given by Hicks *et al.* (1985) to STP yields approximately

$D_w(0, 1) = 0.194 \text{ cm}^2 \text{s}^{-1}$. Tabulations by Andrussow (1969) suggest that $0.161 \leqslant D_w(0, 1) \leqslant 0.219 \text{ cm}^2 \text{s}^{-1}$ and finally List (1949), in The Smithsonian Meteorological Tables, quotes a value of $0.226 \text{ cm}^2 \text{s}^{-1}$ from Schirmer (1938) for $D_w(0, 1)$. In other words there is an approximate $\pm 15\%$ uncertainty in $D_w(0, 1)$ that results solely from which source is being quoted. Consequently, this study is motivated by a desire to reduce this uncertainty in $D(T, 1)$ for the gases examined herein. As will be shown later, there is an appropriate statistical technique and enough historical data for many gases to estimate $D(T, 1)$ more accurately than $\pm 10\%$.

A further source of uncertainty in $D(T, p)$ results from a misunderstanding of Graham's law. This occurs when estimating the diffusivity of a particular gas (D_u) in air (or other gas) by scaling a known diffusivity of another gas (D_k) by the square root of the ratio of molecular masses; i.e. $D_u = D_k\sqrt{M_k/M_u}$ where M_k and M_u are the appropriately corresponding molecular masses. Graham's law applies to the ratio of the fluxes of the interdiffusing gases, not to their respective diffusivities in another gas (e.g. Mason and Evans (1969) or Mason (1971)).

The present study is not the first attempt to estimate coefficients of diffusivity by assembling and analyzing the historical data set. Marrero and Mason (1972) (henceforth denoted as MM72) provide a comprehensive review and critical evaluation of binary diffusivity coefficients. Yet, in spite of the detailed analysis provided by MM72, there remains a definite need to update the state of knowledge of diffusivity coefficients. Consequently, the present study differs from MM72 in several ways. First, the present analysis includes (a) results from more recent theoretical studies (viz., Bzowski *et al.*, 1990a, b) and (b) several experimental determinations of $D(T, p)$ subsequent to MM72 (e.g. Cowie and Watts, 1971; Barr and Watts, 1972; Prichard and Currie, 1982). Second, the present study emphasizes $D(T, p)$ for O_3, SO_2, NH_3, N_2O, NO, NO_2 in air, N_2 and O_2 more than do MM72. Third, the present study focuses only on temperatures between about $-20°$ and $100°C$; whereas, MM72 included diffusivity data at much higher temperatures. The temperature range is restricted because the results of MM72's analysis clearly indicate a possible bias and/or considerably more variability in the measured values of $D_w(T, p)$ above $100°C$ than below $100°C$. Therefore, to avoid this potential bias this study limits the diffusivity data to temperatures below $100°C$. (Fortunately, this restriction has virtually no effect on any other data sets associated with the other gases examined herein.) Fourth, to facilitate comparisons between gases, the present analysis uses the same exponent to describe the temperature dependency. Fifth and lastly, the present study differs from MM72 in the method used to eliminate outliers from the data set. This study uses a local regression model technique known as loess (Cleveland *et al.*, 1992; Cleveland, 1993) to separate outliers from the more congruous

data; whereas, MM72 used their knowledge of theory and experimental procedures to evaluate the data quality.

More recent than MM72, Yaws (1995) also provides an analysis and compilation of binary diffusion coefficients in air. Like MM72, Yaws (1995) also uses a broad temperature range (200–1000 K). However, unlike MM72 and the present study, Yaws (1995) focuses on organic compounds. Consequently, the only overlap between the present study and Yaws (1995) are CO_2, CH_4 and CO.

The next section of this study describes the data sources, the loess technique and general methods of analysis. In a following section results are tabulated and compared and where applicable, comparisons between Yaws (1995), MM72's results and loess results are also made.

DATA SOURCES, MODELS AND METHODS OF ANALYSIS

Near STP the binary diffusivity as a function of temperature and pressure can be expressed as

$$D(T, p) = D(0, 1)(p_0/p)(T/T_0)^\alpha \qquad (1)$$

where $T_0 = 273.15$ K ($= 0°C$), T is temperature expressed in K, and the exponent α is limited by theory to a value between 1.5 and 2.0 (e.g. Dunlop and Bignell, 1997). This formulation is valid providing that the pressure (p) is not too near the critical pressure for the gas mixture. (All critical pressures for gases examined herein exceed 30 atmosphere's pressure.) If the critical pressure is exceeded then the simple inverse relationship between D and p is not valid (Reid *et al.*, 1987). Aside from this exception, equation (1), in general, is an extremely good approximation to the more exact formulation based on the kinetic theory of gases and the Chapman–Enskog theory (e.g. Reid *et al.*, 1987). For this reason, equation (1) is also the basis for this study. However, this study focuses on the variation of $D(T, p)$ with temperature, not with pressure. Consequently, all data used herein for analysis, but not originally obtained at $p = p_0$, are adjusted to p_0 and all modeling results will assume $p = p_0$. Furthermore, all data used in this study are limited to pressures less than 25 atm which is well below the critical pressure for any gas discussed herein. In essence, equation (1), is used in this study as a regression model for $D(T, 1)$ for the experimental data sets. Furthermore, it is used in both a two-parameter mode (when both $D(0, 1)$ and α are "fitted" parameters) and a one-parameter mode (when only $D(0, 1)$ is "fit" to the data and α is fixed at a value of 1.81). (The justification for this particular choice of α is discussed below.) In addition to fitting the experimentally derived data, equation (1) is also used in both one- and two-parameter modes for some of the model-predicted temperature curves. Comparing the one- and two-parameter regressions is one method of assessing the impact that constraining α to 1.81 has on

the quality of the model fit. For now, suffice it to say that constraining α to 1.81 causes no serious loss of information nor compromises the results in any significant way.

Using a fixed value of α has the advantage of simplifying the comparisons between different gases and different models. Furthermore, the value of 1.81 represents a reasonable compromise for both observational and modeling purposes. For example, $\alpha = 1.81$ is the basis of the model of Chen and Othmer (1962) and $\alpha = 1.81$ (± 0.01) results from two independent previous analyses for $D_w(T, 1)$ (Schrimer (1938) as cited by List (1949) and Vasilevskaya (1961)) and one previous study of $D(T, 1)$ for NH_3 in air (Wintergerst, 1930). Nevertheless, α could have been fixed at other values as indicated by other models. For example, Fuller *et al.* (1966) developed a model that indicates $\alpha = 1.75$ is valid for a large number of binary diffusivity coefficients. The present study focuses on the model of Chen and Othmer (1962) and the concomitant value of 1.81 for α, rather than the model of Fuller *et al.* (1966) because the Chen and Othmer (1962) model was developed in terms of critical temperatures and critical volumes, which are physical quantities, rather than in terms of elemental diffusion volumes which are determined from measured diffusion coefficients using least squares regression techniques. Consequently, for the present purposes the model of Chen and Othmer (1962) has greater predictive capabilities than does the model of Fuller *et al.* (1966).

Data sources

As much as possible only original sources were used for reconstructing the historical data set or for obtaining model parameters for use with model estimations of the diffusion coefficients. Furthermore, all data sources were checked for multiple references to the same diffusivity values to ensure that no data from any single experiment were duplicated during the analysis. However, experimental determinations of $D(T, 1)$ were averaged if, for any given experiment, $D(T, 1)$ was evaluated at several temperatures that were within $\pm 0.5°C$ of the mean temperature of the measurements. For convenience, all diffusivity values used throughout this study are expressed in $cm^2 s^{-1}$.

The major source for references to data is the bibliographic list of gaseous diffusion coefficients for binary mixtures given by MM72 and Gordon (1977) with secondary sources supplied by Bzowski *et al.* (1990a), Reid *et al.* (1987), Andrussow (1969), Liley (1962) and the author's continuing search of the literature.

Absolute uncertainty

Absolute uncertainty plays an important role in this study when evaluating the quality of data and the goodness of the model regression. After any regression has been performed, the maximum percentage difference between the values predicted with the regression curve and the data values is then determined. Herein this maximum difference is termed the absolute uncertainty and it is used to assess the inherent variability of any given data set.

For this study it is possible a priori to estimate a lower bound on the absolute uncertainty. MM72 note that $D(T, 1)$ is a relatively weak function of composition; that is $D(T, 1)$ is weakly influenced by the mole fraction of the two interdiffusing gases. In most cases this effect is usually less than about 4% (MM72). Unlike MM72, the present study does not attempt to correct the data for composition dependence; rather it is assumed that the lower bound on the absolute uncertainty is $\pm 4\%$. Because in general any data set is likely to possess more than one source of variability, it is probably unreasonable to assume that this level of absolute uncertainty can be achieved in the present study.

The loess technique for analysis of experimentally determined data

Because Cleveland *et al.* (1992) and Cleveland (1993) provide a detailed account of the loess technique, it is sufficient for the present purposes to provide only a brief summary of how it was employed for evaluating $D(0, 1)$. Loess, as implemented in this study, is a relatively simple iterative technique that provides a method for fitting regression functions to data and for detecting potential outliers in the data set that may need to be eliminated because they can skew the parameter values and bias the results. Except to weight the outliers with a value of 0, this study does not include a local weighting function for fitting the data.

As implemented in this study the loess technique consists of two iterated steps. First, all experimentally determined diffusivity values ($N =$ total number of values) are adjusted for $p = p_0$ and then fit to equation (1) with a least squares minimization technique to determine the optimal values of $D(0, 1)$ and α. Second the residuals (e_i: $i = 1, N$) are calculated and the median value (e_{med}) of the $e_i's$ is determined. Then all diffusivity values with a residual (e) at least three times the median value ($e \geqslant 3e_{med}$) are removed from the data set and the process is repeated until one of two conditions is met: either (1) there are no remaining data points with residuals greater than 3 times the median value or (2) the absolute uncertainty of the data relative to the regression curve is not changed significantly by the removal of any more data points. (Note that e_{med} can change with each iteration.) Once the most consistent (congruous) data set has been identified (i.e. all probable outliers have been removed), then a one-parameter fit is performed for $D(0, 1)$ (with $\alpha = 1.81$). Finally, an estimate of the absolute uncertainty is determined for the one-parameter regression. Both $D(0, 1)$ and the absolute uncertainty for the one-parameter regressions are tabulated in this study. As employed herein the absolute uncertainty does not include the outliers, but pertains only to the congruous data set.

As will be shown later this method works well for diffusivities of H_2O and CO_2 in air and N_2 because these are relatively large data sets with many easily identified outliers. Nevertheless, results at each iteration are examined for all gases before the next iteration is performed. In general the loess technique is quite amenable to computer implementation and therefore is relatively objective, but it should not be used as a substitute for careful examination of any data set. In some cases the diffusivity data sets inherently possess large variability or they consist of only a few experimental determinations. In these and other cases it becomes difficult to determine which data points are useful for further analysis and which are outliers. Consequently, the analysis for each diffusivity data set includes a brief discussion of its unique features and whatever adaptations were necessary for implementing the loess technique.

Models

The models of Bzowski *et al.* (1990a, b), Chen and Othmer (1962) and the Chapman–Enskog theory with the Lennard–Jones 6–12 potential (e.g. Reid *et al.*, 1987) are included and compared with the data analyses and with each other in this study. (Henceforth, Bzowski *et al.* (1990a, b) will be denoted as Bea90, Chen and Othmer (1962) as CO62 and the Chapman–Enskog/Lennard–Jones model as LJ.)

Bea90 provides calculated values of $D(T, 1)$ for CO_2, CH_4, CO, N_2O and NO in N_2 and O_2 which are used for one- and two-parameter fits with equation (1). However, the fitting procedures are done only once and the loess procedure is not required, because the model is (by necessity) already quite similar to equation (1).

The model of CO62 is as follows:

$D(T, 1) =$

$$\frac{2.616\sqrt{1/M_i + 1/M_j}(T/T_0)^{1.81}}{(Tc_i Tc_j/10,000)^{0.1405}[(Vc^i/100)^{0.4} + (Vc_j/100)^{0.4}]^2} \quad (2)$$

where, henceforth the subscripts "i" and "j" refer to the specific gases under consideration, M_i and M_j are their respective molecular masses (gm mol^{-1}), Tc_i and Tc_j are their respective critical temperatures (K), and Vc_i and Vc_j are their respective critical volumes ($cm^3 mol^{-1}$). The CO62 model is basically an empirical approximation to the more rigorous Chapman–Enskog theory, given next.

$$D(T, 1) = \frac{8.380\sqrt{1/M_i + 1/M_j}(T/T_0)^{3/2}}{\sigma_{ij}^2 \Omega_{ij}} \quad (3)$$

where σ_{ij} is a typical length scale characterizing the molecular size or range-of-force between molecules of the two gases during the diffusive process (Å) and Ω_{ij} is the (dimensionless) reduced collision integral for diffusion which, in general, is a weak function of temperature. For binary diffusion, σ_{ij} is usually evaluated as the arithmetic average of the appropriate

σ-values for each gas (i.e. $\sigma_{ij} = (\sigma_i + \sigma_j)/2$) (e.g. Reid *et al.*, 1987) and Ω_{ij} is determined from a model of the potential function describing the potential field between molecules of the two gases during the diffusive process (e.g. Reid *et al.*, 1987; MM72). For convenience, this study assumes the Lennard–Jones 6–12 potential (e.g. Reid *et al.*, 1987; MM72) which yields the following form for the temperature dependence for Ω_{ij}

$$\Omega_{ij} = \Omega_{ij}(kT/\varepsilon_{ij}) \quad (4)$$

where k is Boltzmann's constant and ε_{ij} is the maximum energy of attraction between the two molecules.

In general ε_{ij} is approximated by the geometric mean of the individual ε's, i.e. $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$, and the ε's, like the σ's above and the critical constants Tc and Vc earlier, have often been previously determined for many gas species and are often available from tabulations (e.g. Reid *et al.*, 1987; Svehla, 1962; Yaws, 1972; Ambrose, 1992; Kee *et al.*, 1986; Dandy, 1997). For this study Table 1 summarizes all values of M, Tc, Vc, σ and ε/k used with the CO62 and LJ models. Except for σ and ε/k for O_3 and Tc and Vc for NO_2 all values presented in Table 1 are well documented. The discussion of these four exceptions is deferred until later.

For this study $\Omega_{ij}(kT/\varepsilon_{ij})$ is approximated by the (highly accurate) analytical expression of Neufeld *et al.* (1972). For comparison with other models and data results the LJ model is treated the same way as Bea90. That is, the LJ model is used to predict $D(T, 1)$ at several different temperatures and then these model-generated diffusivities are used as input data for one-parameter and two-parameter regressions with equation (1).

Blanc's law

For all model calculations and some of the data-based results it is necessary to estimate the coefficients of diffusivity for diffusion in air from the diffusivities appropriate to N_2 and O_2. This study uses Blanc's law for combining coefficients of binary diffusion to estimate $D(T, p)$ of a gas diffusing into a mixture of gases. Blanc's law (e.g. Reid *et al.*, 1987; MM72) applied to the conditions of the present study yields:

$$D_{i,air}(T, p) = [\chi_{N_2}/D_{i,N_2}(T, p) + \chi_{O_2}/D_{i,O_2}(T, p)]^{-1} \quad (5)$$

where $D_{i,air}$ is the diffusivity of gas "i" in air, D_{i,N_2} and D_{i,O_2} are the respective diffusivities of the same gas in N_2 and O_2, χ_{N_2} ($=0.79$) and χ_{O_2} ($=0.21$) are the approximate respective mole fractions of N_2 and O_2 in the atmosphere.

Blanc's law was used in a few cases to estimate the diffusivity of water vapor and CO_2 in air from experimental determinations of $D(T, 1)$ in N_2 and O_2, but only if the temperatures of the respective $D(T, 1)$ values were within about 0.5°C. Furthermore, any diffusivity data appropriate to N_2 and O_2 combined using Blanc's law were not used again in any later

Table 1. Parameter values used for CO62 and LJ models

Gas	M (gm mol^{-1})	T_c (K)	V_c (cm^3 mol^{-1})	$\overset{\circ}{\sigma}$ (Å)	ε/k (K)
N_2	28.01	126.2	89.49	3.798	71.4
O_2	32.00	154.6	73.39	3.467	106.7
H_2O	18.02	647.1	55.96	2.641	809.1
CO_2	44.01	304.1	94.04	3.941	195.2
CH_4	16.04	190.5	99.01	3.758	148.6
CO	28.01	132.9	93.06	3.690	91.7
SO_2	64.06	430.8	122.20	4.026[a]	363.0[a]
O_3	48.00	261.1	88.89	3.875[b]	208.4[b]
NH_3	17.03	405.5	72.50	2.900	558.3
N_2O	44.01	309.6	97.37	3.828	232.4
NO	30.01	180.0	57.71	3.492	116.7
NO_2	46.01	431.0[b]	83.64[b]	3.765[c]	210.0[c]

Note. Critical temperature (T_c) and critical volume (V_c) used with CO62. Molecular size (σ) and energy of attraction (ε/k) used with LJ model. Molecular mass (M) used with both models. Unless noted otherwise M and T_c are taken from Ambrose (1992) and V_c is computed from critical density, ρ_c, which is also taken from Ambrose (1992); i.e. $V_c = M/\rho_c$. Unless noted otherwise σ and ε/k are taken from Reid *et al.* (1987).
[a] From Monchick and Mason (1961).
[b] See discussion in text.
[c] From Svehla and Brokaw (1966).

Table 2. Coefficients of diffusivity (cm^2 s^{-1}) of selected gases in air

Gas	This study	CO62[a]	Bea90[a]	LJ[a]	Other
H_2O	0.2178	0.1934	NA	0.1837	$0.2090(T/T_0)^{2.072}$[b]
CO_2	0.1381	0.1404	0.1391	0.1314	$0.2020\exp(-\frac{0.3738}{T/T_0})(T/T_0)^{1.590}$[b]
CH_4	0.1952	0.1909	0.1951	0.1862	$0.1859(T/T_0)^{1.747}$[b]
CO	0.1807[a]	0.1755	0.1794	0.1716	$0.1838(T/T_0)^{1.730}$[b]
SO_2	0.1089[c]	0.1122	NA	0.1087	NI
O_3	NM	0.1444	NA	0.1301	NI
NH_3	0.1978[d]	0.1908	NA	0.1866	NI
N_2O	0.1436	0.1382	0.1401	0.1318	NI
NO	NM	0.1988	0.1802	0.1729	NI
NO_2	IM	0.1361	NA	0.1349	0.1222[e]

Note: Unless otherwise noted only $D(0, 1)$ is given and $D(T, 1) = D(0,1)(T/T_0)^{1.81}$ is assumed. NA = not available. NM = never measured. IM = impossible to measure. NI = not included herein.
[a] From Blanc's law and $D(0, 1)$ for gas in N_2 and in O_2.
[b] Marrero and Mason (1972).
[c] Based on combining two data points: one for air and one for N_2.
[d] Wintergerst (1930).
[e] Blanc's law and results from Fan and Mason (1962) for NO_2 and O_2 and (indirectly) from Sherwood and Chambers (1937) for NO_2 and N_2.

analysis of $D(T, 1)$ in N_2 and O_2. This is done to avoid introducing any unnecessary biases into the separate analyses for air, N_2 and O_2.

RESULTS

All results are summarized in Tables 2–7. Tables 2–4 list the results of the loess and regression analysis for the diffusivities of the 10 selected gases in air (Table 2), N_2 (Table 3) and O_2 (Table 4). Also listed in these three tables are the respective diffusivi-

ties predicted by the Bea90 model, the CO62 model, the LJ model, the regression results of MM72 and a few miscellaneous data/modeling results. Tables 5–7 present the absolute uncertainties associated with the data and loess regression, as well as the percent difference between the data-based estimates of diffusivity and the (Bea90, CO62 and LJ) model predictions for air (Table 5), N_2 (Table 6) and O_2 (Table 7). The rest of this section includes a brief description and explanation of the entries in these tables and brief discussions of the data sets and figures.

Table 3. Coefficients of diffusivity ($cm^2 s^{-1}$) of selected gases in N_2

Gas	This study	CO62	Bea90	LJ	Other
H_2O	0.2190	0.1922	NA	0.1841	$0.2100(T/T_0)^{2.072}$[a]
CO_2	0.1429	0.1401	0.1392	0.1326	$0.21072\exp(-\frac{0.1458}{T/T_0})(T/T_0)^{1.570}$[a]
CH_4	0.1892	0.1899	0.1943	0.1858	$0.1836(T/T_0)^{1.750}$[a]
CO	0.1804	0.1749	0.1789	0.1713	$30.433(e1/e2)(T/T_0)^{1.576}$[a,b]
SO_2	0.1089[c]	0.1122	NA	0.1094	NI
O_3	NM	0.1441	NA	0.1306	NI
NH_3	0.1978	0.1896	NA	0.1869	NI
N_2O	NM	0.1379	0.1402	0.1322	NI
NO	0.1809	0.1979	0.1798	0.1727	NI
NO_2	IM	0.1359	NA	0.1352	0.1210[d]
					0.1460[e]

Note: Unless otherwise noted only $D(0, 1)$ is given and $D(T, 1) = D(0, 1)(T/T_0)^{1.81}$ is assumed. NA = not available. NM = never measured. IM = impossible to measure. NI = not included herein.
[a] Marrero and Mason (1972).
[b] $e1 = \exp(\frac{0.135}{T/T_0} - \frac{0.051247}{(T/T_0)^2})$, $e2 = (-13.2616 + \ln(T/T_0))^2$
[c] Based on combining two data points: one for air and one for N_2.
[d] Adapted from Sherwood and Chambers (1937).
[e] Adapted from Sviridenko *et al.* (1973). See Text.

Table 4. Coefficients of diffusivity ($cm^2 s^{-1}$) of selected gases in O_2

Gas	This study	CO62	Bea90	LJ	Other
H_2O	0.2457[a]	0.1984	NA	0.1821	$0.2110(T/T_0)^{2.072}$[b]
CO_2	0.1402	0.1414	0.1386	0.1300	$0.17383\exp(-\frac{0.2244}{T/T_0})(T/T_0)^{1.661}$[b]
CH_4	0.1942	0.1946	0.1978	0.1877	$0.2265\exp(-\frac{0.1618}{T/T_0})(T/T_0)^{1.695}$[b]
CO	0.1817	0.1777	0.1813	0.1729	$0.1793(T/T_0)^{1.724}$[b]
SO_2	NM	0.1121	NA	0.1059	NI
O_3	NM	0.1454	NA	0.1285	$\frac{5}{6}D_{O_2,O_2}(T, 1)$[d]
					$\frac{0.2072(T/T_0)^{3/2}}{1+0.622(T/T_0)}$[e]
NH_3	0.1992	0.1951	NA	0.1857	NI
N_2O	NM	0.1391	0.1396	0.1301	NI
NO	NM	0.2024	0.1815	0.1739	0.1749[c]
NO_2	IM	0.1369	NA	0.1334	0.1271[c]

Note: Unless otherwise noted only $D(0, 1)$ is given and $D(T, 1) = D(0, 1)(T/T_0)^{1.81}$ is assumed. NA = not available. NM = never measured. IM = impossible to measure. NI = not included herein.
[a] From a single determination given by Walker and Westenberg (1960).
[b] Marrero and Mason (1972).
[c] From Fan and Mason (1962).
[d] From Hirschfelder *et al.* (1953).
[e] From Campbell (1965).

Table 5. Absolute error associated with $D(T, 1)$ from data analysis and difference between model predictions of $D(T, 1)$ and data-derived estimates

Gas pair	Absolute error (N)	CO62	Bea90	LJ
H_2O/air	$\pm 7\%$ ($N = 41$)	-11.2%	NA	-15.6%
CO_2/air	$\pm 5\%$ ($N = 56$)	$+1.7\%$	$+0.7\%$	-4.9%
CH_4/air	$\pm 5\%$ ($N = 11$)	-2.2%	-0.1%	-4.6%
CO/air	$\pm 5\%$ ($N = 0$)[a]	-2.9%	-0.7%	-5.0%
SO_2/air	I ($N = 2$)	$+3.0\%$	NA	-0.2%
O_3/air	I ($N = 0$)	I	NA	I
NH_3/air	$\pm 9\%$ ($N = I$)	-3.5%	NA	-5.7%
N_2O/air	I ($N = 4$)[b]	-3.8%	-2.4%	-8.2%
NO/air	I ($N = 0$)	I	I	I
NO_2/air	I ($N = 0$)	I	NA	I

Note: N = number of data points. NA = not applicable. I = indeterminate.
[a] From Blanc's law. Absolute uncertainty assumed to be the same as that determined for diffusivity in N_2 and O_2.
[b] Data from only one experiment showed very little variability; therefore, absolute uncertainty could not be evaluated.

Table 6. Absolute error associated with $D(T, 1)$ from data analysis and difference between model predictions of $D(T, 1)$ and data-derived estimates

Gas pair	Absolute error (N)	CO62	Bea90	LJ
H_2O/N_2	$\pm 6\% (N = 10)$	-2.2%	NA	-15.9%
CO_2/N_2	$\pm 6\% (N = 33)$	-2.0%	-2.6%	-7.2%
CH_4/N_2	$\pm 5\% (N = 9)$	$+0.4\%$	$+2.7\%$	-1.8%
CO/N_2	$\pm 5\% (N = 12)$	-3.0%	-0.8%	-5.0%
SO_2/N_2	$I (N = 2)$	$+4.4\%$	NA	$+0.5\%$
O_3/N_2	$I (N = 0)$	I	NA	I
NH_3/N_2	$\pm 5\% (N = 5)$	-4.1%	NA	-5.5%
N_2O/N_2	$I (N = 0)$	I	I	I
NO/N_2	$I (N = 2)$	$+9.4\%$	-0.6%	-4.5%
NO_2/N_2	$I (N = 0)$	I	NA	I

Note: $N =$ number of data points. NA $=$ not applicable. I $=$ indeterminate.

Table 7. Absolute error associated with $D(T, 1)$ from data analysis and difference between model predictions of $D(T, 1)$ and data-derived estimates

Gas pair	Absolute error (N)	CO62	Bea90	LJ
H_2O/O_2	$I (N = 1)$	-19.3%	NA	-25.9%
CO_2/O_2	$\pm 5\% (N = 12)$	$+0.9\%$	-1.1%	-7.3%
CH_4/O_2	$I (N = 1)$	$+0.2\%$	$+1.9\%$	-3.3%
CO/O_2	$\pm 5\% (N = 6)$	-2.2%	-0.2%	-4.8%
SO_2/O_2	$I (N = 0)$	I	NA	I
O_3/O_2	$I (N = 0)$	I	NA	I
NH_3/O_2	$I (N = 2)$	-2.1%	NA	-6.8%
N_2O/O_2	$I (N = 0)$	I	I	I
NO/O_2	$I (N = 0)$	I	I	I
NO_2/O_2	$I (N = 0)$	I	NA	I

Note: $N =$ number of data points. NA $=$ not applicable. I $=$ indeterminate.

H_2O

Figure 1 summarizes the results of this study for the diffusivity of water vapor in air. The final recommended value for $D_w(T, 1)$ shown in this figure is $0.2178(T/T_0)^{1.81}$ with an absolute uncertainty of $\pm 7\%$ and a regression $R^2 = 0.972$. ($R^2 = 1 -$ [Sum of squared regression residuals]/[Variance of data relative to the mean of the data].) Before applying the loess technique to $D_w(T, 1)$, the two-parameter regression yielded $D(T, 1) = 0.2043(T/T_0)^{2.2172}$ with an $R^2 = 0.75$ and an absolute uncertainty of about $\pm 25\%$. After the first application of the loess technique the two-parameter fit yielded $D(T, 1) = 0.2191(T/T_0)^{1.8464}$ with an $R^2 = 0.91$ and an absolute uncertainty of about $\pm 12\%$. The second application of the loess technique yielded some improvements over the first and the third and final application resulted in $D(T, 1) = 0.2188(T/T_0)^{1.7768}$ with an $R^2 = 0.972$. The subsequent one-parameter regression yielded $D(T, 1) = 0.2178(T/T_0)^{1.81}$ with an $R^2 = 0.972$ and an absolute uncertainty of about $\pm 7\%$. The standard error of the estimate for $D_w(0, 1)$ with the one-parameter regression is ± 0.001.

In all 17 data points of a total of 58 determinations from 28 experiments were eliminated on the basis of the loess technique. But, the data identified as outliers were not randomly distributed throughout the full data set. Rather the outliers encompassed 7 of the 27 different experiments for $D_w(T, 1)$. The fact that these data points are associated with specific experiments suggests (at least to the author) that there were problems with the experimental techniques or their implementation as employed by the researchers. All data from Summerhays (1930), Houghton (1933), Ackermann (1934), Klibanova *et al.* (1942), Bose and Chakraborty (1955–56), Richardson (1959) and Petit (1965) were eliminated for the final regression as indicated by the loess technique.

Figure 2 summarizes the results of this study for the diffusivity of water vapor in N_2. For comparison, Fig. 2 also includes some of the measured diffusivities for water vapor in O_2 (which were not used in the analysis). Although these diffusivities have been measured far fewer times than $D_w(T, p)$ (Fig. 1), the results of the loess analysis and the subsequent one- and two-parameter regressions are very similar to $D_w(T, 1)$. The one independent determination of water vapor in O_2 (Walker and Westenberg, 1960), when used to estimate $D(0, 1)$ for water vapor in O_2 (equation (1) with $\alpha = 1.81$), yielded $D(0, 1) = 0.2457$ cm^2 s^{-1}. This value is sufficiently different from theoretical predictions (Table 4) that it is
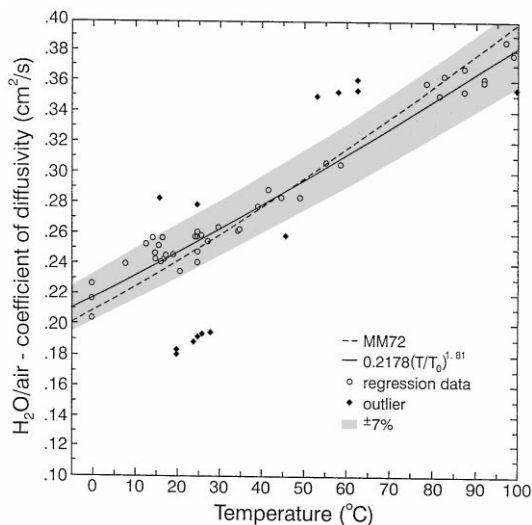
Fig. 1. Observed and modeled diffusivities for water vapor in air. Data sources are: Guglielmo (1881, 1882) as tabulated in Andrussow (1969); Winkelmann (1884a, b, 1888, 1889) including corrections as discussed in Trautz and Müller (1935a) and Mason and Monchick (1962); Houdaille (1897); Brown and Escombe (1900); Mache (1910); LeBlanc and Wupperman (1916); Summerhays (1930); Houghton (1933); Ackermann (1934), data not shown because values exceed $0.4 \ cm^2 \ s^{-1}$; Gilliland (1934); Schirmer (1938) as discussed in List (1949); Klibanova et al. (1942); Brookfield et al. (1947); Schwertz and Brow (1951) with Blanc's law; Kimpton and Wall (1952); Rossié (1953); Lee and Wilke (1954); Bose and Chakraborty (1955–56) including some estimates from Blanc's law; Narsimhan (1955–1956); Nelson (1956); Richardson (1959); Petit (1965); Andrussow (1969) quoting an unidentified source no. 156; Wilhelm and Battino (1972).
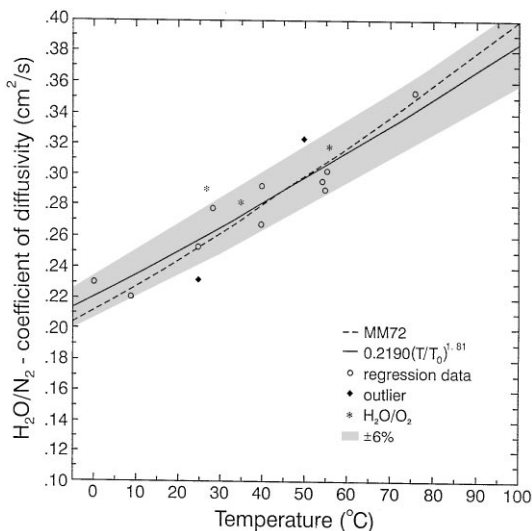
Fig. 2. Observed and modeled diffusivities for water vapor in N_2. Data are from Hippenmeyer (1949), Crider (1956), Nelson (1956), and O'Connell et al. (1969). Included but not used in the analysis are some observed diffusivities of water vapor in O_2 for which the data sources are Schwertz and Brow (1951) and Walker and Westenberg (1960). Not shown here are the O_2 data from Bose and Chakraborty (1955–1956) because they were used with Blanc's law to estimate $D(T, 1)$ for water vapor in air and subsequently eliminated by the loess analysis.
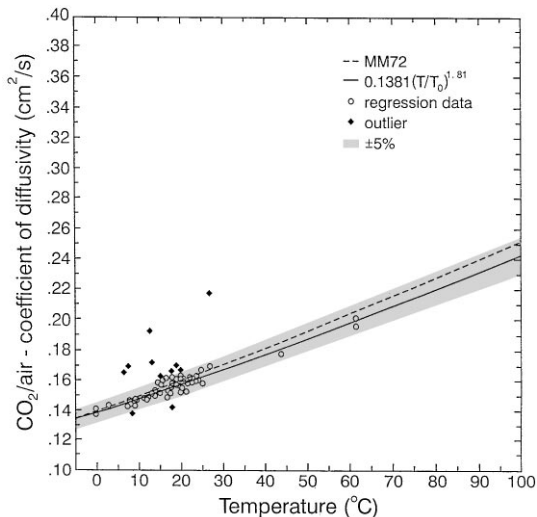
Fig. 3. Observed and modeled diffusivities for CO_2 in air. Data sources are: Loschmidt (1870a, b); von Obermayer (1880, 1882a, b, 1883, 1887), including corrections to earlier results discussed by von Obermayer (1887); Waitz (1882a, b); Brown and Escombe (1900); Buckingham (1904); Coward and Georgeson (1937); Klibanova et al. (1942); Waldmann (1944, 1947) with Blanc's law; Andrew (1955); Gwertsiteli et al. (1961); Suemin and Ivakin (1961); Holsen and Strunk (1964); Barr and Watts (1972); Pritchard and Currie (1982); Robjohns and Dunlop (1982) with Blanc's law.

probably an outlier. This notion is further supported by the comparisons in Fig. 2 and the results of MM72 who suggest that the diffusivity of water vapor in N_2 and O_2 are nearly identical to $D_w(T, 1)$. Consequently, present results suggest that the diffusivity of water vapor in O_2 is relatively uncertain and further experimental determinations are needed.

Also shown in Figs 1 and 2 are the respective regression models of MM72. As can be seen, the results from MM72 and the present study are in good agreement. In fact, it may be said that the two models agree to within the absolute uncertainty of the (congruous) data. The present results for $D_w(T, 1)$ are also in good agreement with Vasilevskaya (1973), who found, for temperatures exceeding 100°C, that $D_w(T, 1) = 0.2106(T/T_0)^{1.82}$.

CO_2

Figure 3 shows the results of the analysis for CO_2 and air. Unlike the $D_w(T, 1)$ data, the CO_2 shows very little inherent variability, so that the loess iterations were terminated after two applications and from a total of 67 data points only 11 were excluded from the final regression. But, as with $D_w(T, 1)$ the excluded data points were not randomly distributed; rather they basically comprised the data of Brown and Escombe (1900), Buckingham (1904), Andrew (1955) and Kosov (1957). The final two-parameter regression yielded $D(T, 1) = 0.1369(T/T_0)^{1.9206}$ with an $R^2 = 0.958$ and the one-parameter regression yielded

$D(0, 1) = 0.1381 (\pm 0.0005)$ with an $R^2 = 0.952$. (Note that the standard error of the estimate is enclosed in parentheses in the last sentence.) Figure 3 also indicates good agreement between the present analysis and the results of MM72. Although not shown, the model of Yaws (1995) is in agreement with the present result to within the absolute uncertainty of the loess analysis.

The analysis of the data for CO_2 and N_2 did not follow the pattern outlined above for the three previous gas combinations. The first regression produced only one data point that might be considered an outlier by the loess technique. In other words the data set which is comprised of 46 data points from 23 experiments, was extremely consistent. The two-parameter regression gave the following result: $D(T, 1) = 0.1347(T/T_0)^{2.2240}$ with an $R^2 = 0.912$. However, the exponent (α) is somewhat too high since kinetic theory and virtually all model and data analyses suggest that $1.5 \leqslant \alpha \leqslant 2$. This suggests that the regression may be slightly skewed. A careful examination of the data did suggest that at relatively low temperatures the data of Schäfer et al. (1951) and Ivakin and Suetin (1964a) slightly underestimated the actual value for $D(T, 1)$ while at relatively high temperatures the data of Nagata and Hasegawa (1970) overestimated the actual value of $D(T, 1)$. This combination of biases is not random and tends to bias the results toward a higher

value of α than would otherwise be expected. After removing these (12) potentially biased data points, the regression was performed again and one data point from Giddings and Seager (1967) was identified as an outlier. The final regression result is shown in Fig. 4. The two-parameter regression yielded $D(T, 1) = 0.1405(T/T_0)^{1.9212}$ with an $R^2 = 0.972$ and the one-parameter regression produced $D(0, 1) = 0.1429(\pm 0.0008)$ with an $R^2 = 0.969$. This one-parameter regression curve is virtually identical with the regression curve of MM72 (Fig. 4).

The results and comparisons for CO_2 and O_2 are presented in Tables 4 and 7; they are not presented graphically. The data, taken from Loschmidt (1870b), Wrestchko (1870), von Obermayer (1882a), Kosov and Zhalgasov (1959), Walker and Westenberg (1960) and Suetin and Ivakin (1961), were all within $\pm 5\%$ of $0.1402(T/T_0)^{1.81}$ and displayed no obvious outliers. The agreement between the present one-parameter regression curve and the curve given by MM72 is even closer than shown in Fig. 4 for CO_2 and N_2.

CH_4

Figure 5 shows the results of the present analysis for CH_4 in air and compares them with MM72's curve. No loess iteration was performed on the data because the absolute uncertainty was already relatively small ($\pm 5\%$). The present results differ nearly uniformly from the results of MM72 by about 5.5%. However MM72's result is based on Blanc's law, not on a regression determination. Yaws' (1995) result (not shown) differs from the present result by approximately -3.3%. The results and comparisons for CH_4 and N_2 and O_2 are presented in Tables 3, 4, 6 and 7; they are not presented graphically. The data for
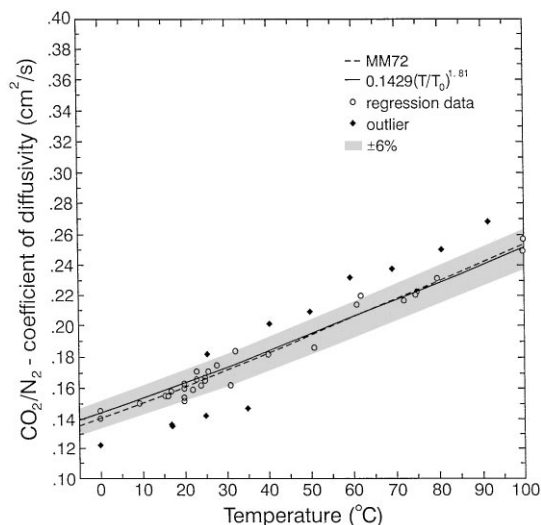

Fig. 4. Observed and modeled diffusivities for CO_2 in N_2. Data sources are: Boardman and Wild (1937); Wicke and Kallenbach (1941); Boyd et al. (1951); Schäfer et al. (1951); Westenberg and Walker (1957); Walker and Westenberg (1958); Walker (1958); Walker et al. (1960); Bohemen and Purnell (1961); Giddings and Seager (1962); Ivakin and Suetin (1964b); Weissmann (1964); Vyshenskaya and Kosov (1965); Kestin et al. (1966); Pakurar and Ferron (1966); Coates and Mian (1967); Mian (1967); Ellis and Holsen (1969); Schneider and Schäfer (1969); Lannus (1970); Nagata and Hasegawa (1970).
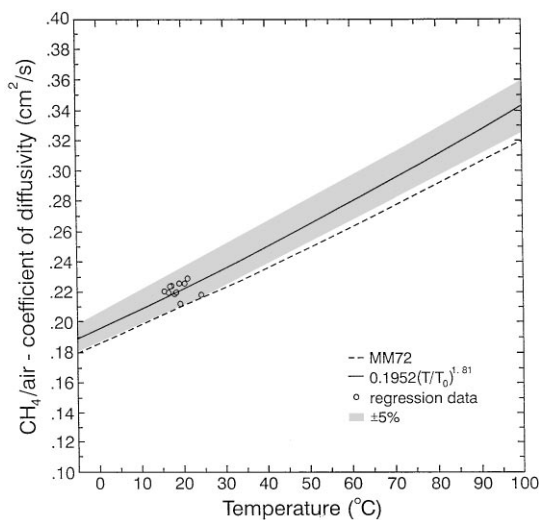

Fig. 5. Observed and modeled diffusivities for CH_4 in air. Data are from Coward and Georgeson (1937), Gwertsiteli et al. (1961) and Cowie and Watts (1971).
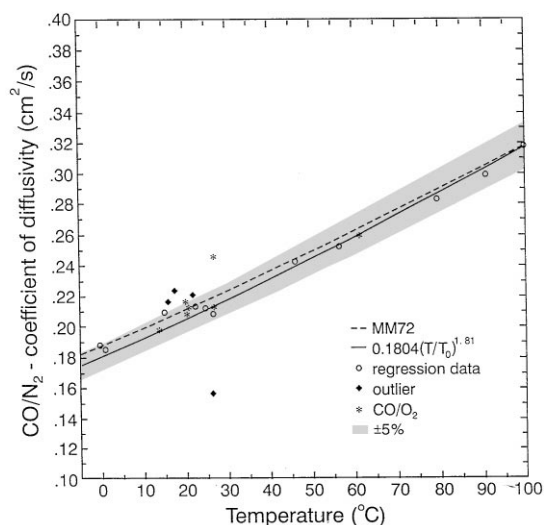
Fig. 6. Observed and modeled diffusivities for CO in N_2. Data sources are: Trautz and Müller (1935b); Boardman and Wild (1937); Wicke and Hugo (1961); Weismann and Mason (1962); Amdur and Schuler (1963); Ivakin and Suetin (1964a); Vugts *et al.* (1970).

Fig. 7. Observed and modeled diffusivities for SO_2. The diffusivity datum for SO_2 in air is from Andrew (1955) ($T = 20°C$) and the diffusivity of SO_2 in N_2 is from Schäfer (1959) ($T = -10°C$). These diffusivity values are used in a combined data set for the model regression.

CH_4/N_2 were taken from Berry and Koeller (1960), Mueller and Cahill (1964), Arai *et al.* (1967), Jacobs *et al.* (1970), Engel and Knapp (1973) and Wakeham and Slater (1973). Only one data point from Wakeham and Slater (1973) was identified as an outlier. For CH_4/O_2 the author is aware of only one observation and it is given by Walker and Westenberg (1960). The comparisons between MM72 and the present analysis is much better for CH_4/N_2 and CH_4/O_2 than for CH_4/air.

CO

The diffusivity coefficient for CO in air has never been measured. Figure 6 shows the results of the present analysis and MM72's result for CO/N_2. Of the 16 data points 4 were removed with two iterations of the loess technique. These outliers came from the data of Trautz and Müller (1935b), Boardman and Wild (1937) and Wicke and Hugo (1961). The results for CO/O_2 are not shown graphically, but are included in Tables 4 and 7. Data for CO/O_2 are taken from Loschmidt (1870b), von Obermayer (1883), Trautz and Müller (1935b), Walker and Westenberg (1960) and Weissman and Mason (1962) and the analysis suggested that the datum of Trautz and Müller (1935b) is an outlier. The agreement between MM72 and the present result for CO/O_2 is similar to that shown in Fig. 6 for CO/N_2. The results for CO/N_2 and CO/O_2 were combined using Blanc's law to provide an estimate of $D(0, 1)$ for CO/air. Although not shown a comparison of the present determination of $D(T, 1)$ for CO/air with MM72 and Yaws (1995) indicates that the present analysis and MM72 are nearly identical, whereas for the temperature range con-
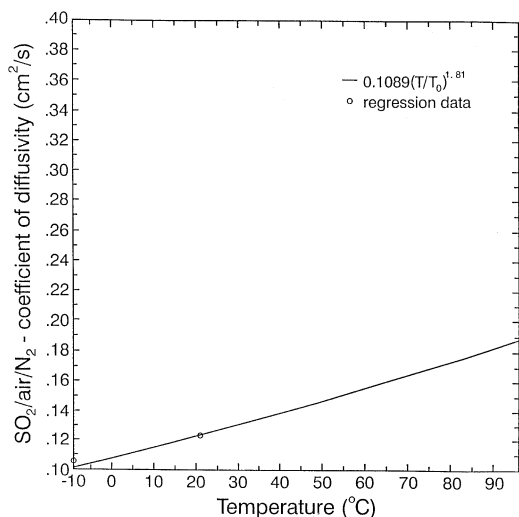
sidered herein Yaws (1995) is approximately 10% less than the present results.

SO_2

Because the diffusivity of SO_2 has only been measured twice (once for SO_2/air and once for SO_2/N_2), these two experimental determinations have been combined for the purposes of analysis (Fig. 7). Consequently, the resulting value of $D(0, 1)$ is used for both SO_2/air and SO_2/N_2. This combined approach yielded results that more closely approximated the modeling predictions than did treating the determinations of diffusivity separately. Finally, $D(0, 1)$ for SO_2/O_2 is assigned the same value in accordance with Blanc's law. Nevertheless, the paucity of diffusivity data for SO_2 suggests that more experimental determinations need to be made for this gas.

O_3

Apparently, the diffusivity of ozone in any gas has never been measured. However, the critical constants have been measured (Ambrose (1992), who ultimately cites Mathews (1972)). Consequently, CO62 can easily be used for estimating the diffusivity of O_3 in air (Table 2), N_2 (Table 3) and O_2 (Table 4). For the LJ model σ and ε/k were estimated from the following relations discussed by Reid *et al.* (1987): $\sigma = 1.18V_b^{1/3}$ and $\varepsilon/k = 1.15T_b$; where V_b is the liquid molar volume ($cm^3 mol^{-1}$) and T_b is the boiling point at 1 atm pressure (K). For ozone Reid *et al.* (1987) give $T_b = 181.2$ K and $V_b = (48.0 \text{ gm mol}^{-1})/(1.356 \text{ gm cm}^{-3}) = 35.4$ $cm^3 mol^{-1}$. The resulting estimates for σ and ε/k are given in Table 1 and the corresponding CO62 and LJ model estimates for $D(0, 1)$ are given in Tables 2–4.
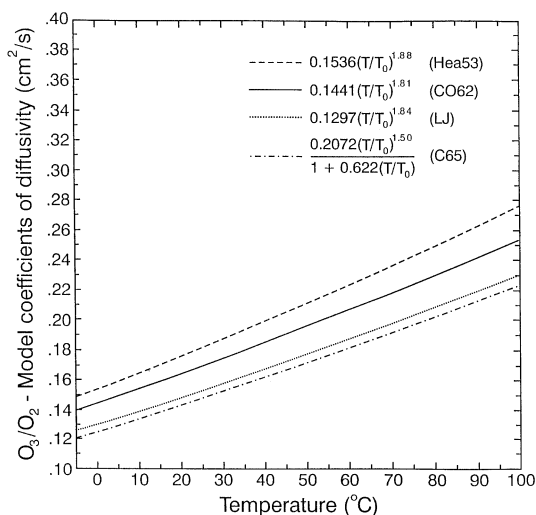
Fig. 8. Model predictions of the coefficient of diffusivity for O_3 in O_2. The LJ and CO62 results are from this study with the LJ model being the two parameter fit. Hea53 is adapted from the model of Hirschfelder *et al.* (1953) and C65 is the model of Campbell (1965). See the text for a discussion of the Hea53 and C65 models.

Fig. 9. Observed and modeled diffusivities for NH_3 in air. The model is the regression model of Wintergerst (1930). Otherwise the data are from Andrew (1955) and Ivakin and Suetin (1964a).

In addition to the LJ and CO62 models of $D_{O_3,O_2}(T, 1)$ discussed in the present study, there are two other models that are included in Table 4. These are the models of Herschfelder *et al.* (1953) (Hea53) and Campbell (1965) (C65). The assumptions made by Hea53 lead to the following relation: $D_{O_3,O_2}(T, 1) = 5D_{O_2,O_2}(T, 1)/6$. For use with Hea53 $D_{O_2,O_2}(T, 1)$ was estimated from the data of Winn (1950) and Winter (1951) using the loess technique. The results of the two parameter fit is $0.1843(T/T_0)^{1.88}$ with $N = 5$ and $R^2 = 0.956$. The one parameter fit yielded $D(0, 1) = 0.1862 \, \text{cm s}^{-1}$ with $N = 5$, $R^2 = 0.955$ and an absolute uncertainty of $\pm 7\%$. The LJ and CO62 models of $D_{O_3,O_2}(T, 1)$ are compared in Fig. 8 with the models of Hea53 and C65. Hea53 predict the highest values for $D_{O_3,O_2}(T, 1)$ and C65 predicts the lowest values. The variability between the four models is about $\pm 10\%$ about the mean of the two extremum models and because the CO62 model is very close to this mean, this $\pm 10\%$ variability is likely to represent the uncertainty of the CO62 model predictions for the diffusivity of ozone.

NH_3

The results of the analysis for NH_3/air are shown in Fig. 9. However, no regression was done on these data for this study. Rather Fig. 9 combines Wintergerst's (1930) estimate of $D(0, 1)$ and $\alpha = 1.81$ with more recent determinations of $D(T, 1)$. Wintergerst (1930) published only the regression analysis for his experimental determinations of $D(T, 1)$. He did not tabulate any of the data on which the regression was based. Nevertheless, Wintergerst (1930) found that $\alpha = 1.80$ from a
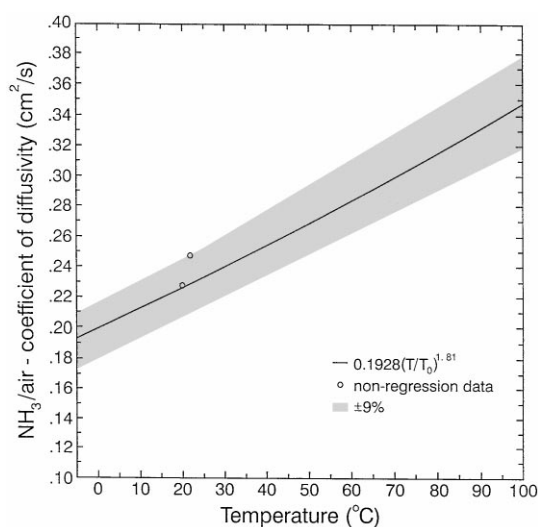
regression of his observations. Consequently, the value of 1.81 used in Fig. 9 is a very good approximation to his findings. The absolute uncertainty of $\pm 9\%$ shown in Fig. 9 was determined from the more recent data of Andrew (1955) and Ivakin and Suetin (1964a) as compared with the curve presented in Fig. 9. Since no information is available from the Wintergerst (1930) concerning the variability of his original data, no data were eliminated as outliers.

Results for NH_3/N_2 and NH_3/O_2 are not presented graphically, but are summarized in Tables 3, 4, 6 and 7. The data for this analysis are taken from Trautz and Müller (1935b), Bunde (1955) [data also reported by Mason and Monchick (1962)], Ivakin and Suetin (1964a) and Weissman (1964). For NH_3/O_2 the data of Trautz and Müller (1935b) exceed the data of Weissman (1964) and the LJ and CO62 models by 15 to 25%, therefore the data of Trautz and Müller (1935b) are assumed to be outliers. For NH_3/N_2 one datum from Ivakin and Suetin (1964a) and one datum from Trautz and Müller (1935b) were eliminated by the loess technique as outliers. Although the other datum from Trautz and Müller (1935b) was not eliminated as an outlier by the loess technique, for the present study it is also eliminated as untrustworthy because all other data from Trautz and Müller (1935b) have either been identified as outliers by the loess technique or have significantly disagreed with other data or the model predictions (also see discussions of CO and NO).

N_2O

The results of the present analysis for the diffusivity of N_2O in air are presented in Fig. 10. For this pair of gases there are a total of five experimental determinations of $D(T, 1)$ from two experiments and these two
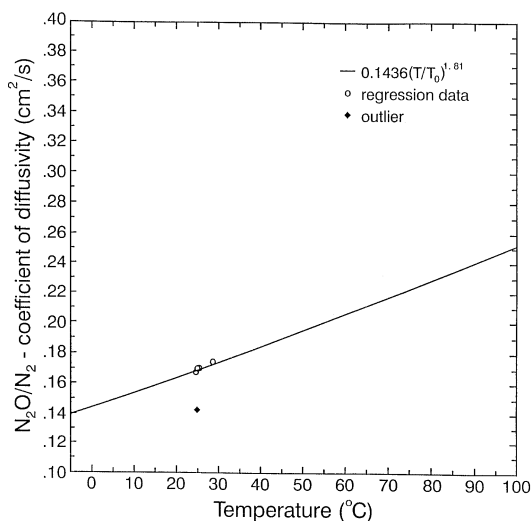
Fig. 10. Observed and modeled diffusivities for N_2O in air. Data are from Barr and Watts (1972) and Pritchard and Currie (1982).

Fig. 11. Observed and modeled diffusivities for NO in N_2. Data are from Trautz and Müller (1935b) and Weissman (1964).

experiments seem to give somewhat differing results. The single data point of Barr and Watts (1972) was eliminated as an outlier, but only because the other four points were in much better agreement with one another. However, these four "acceptable" data points are from the same experiment (Pritchard and Currie, 1982) and could conceivably be outliers relative to the data of Barr and Watts (1972). But, the data of Pritchard and Currie (1982) agree more closely with modeling results than does the datum of Barr and Watts (1972), so they are assumed to be more accurate. Nevertheless, given the paucity of data for the diffusivity of N_2O in air and the apparent conflicts, more diffusion experiments for N_2O/air need to be made. The same thing can be said for the diffusivity of N_2O in N_2 and O_2 because no data are available for these gas pairs.

NO

Neither the diffusivity of NO/air nor of NO/O_2 has been measured. However, there are four data for NO/N_2, which are shown in Fig. 11. But, the two sources of these data do not appear to be in reasonable agreement, as the data of Trautz and Müller (1935b) are systematically about 12% higher that the data of Weissman (1964). To further complicate matters, the data of Weissman (1964) are in very good agreement with the results of Bea90 (Tables 3 and 6), whereas the data of Trautz and Müller (1935b) are in equally good agreement with the model of CO62 (not shown). Considering that in general the Bea90 model performs slightly better than CO62 (Tables 5–7, excluding the NO comparisons) and that other datum of Trautz and Müller (1935b) have been previously identified as outliers by the present method of analysis (see discussions concerning CO and NH_3 above), it is assumed that the
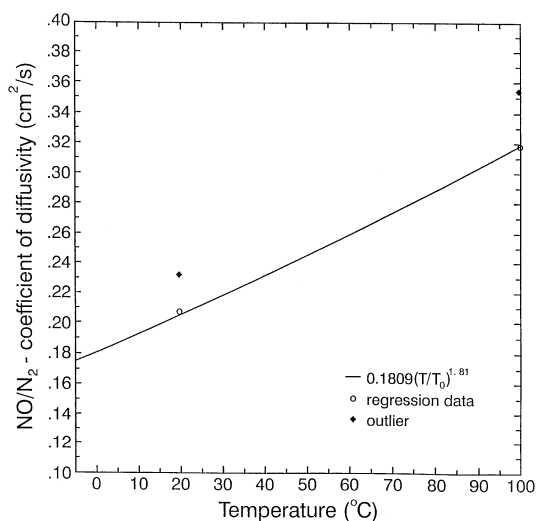
data of Weissman (1964) is the more reliable of the two data sources. Figure 11 shows the results of the one-parameter regression using only the Weissman (1964) data.

Also included in Table 4 is a model based estimate of the diffusivity of NO/O_2 from Fan and Mason (1962). It is based on the LJ model but with slightly different values for σ and ε/k. It is included here for the sake of completeness and because very few results of any type are published for the diffusivity of NO.

NO_2

The diffusivity of NO_2 has never been directly measured with any other gas. In fact $D(T, 1)$ for NO_2 may be impossible to measure directly because at high concentrations NO_2 dimerizes to N_2O_4. Therefore, it may not be possible to obtain a pure sample of NO_2 for direct experimental determinations of $D(T, 1)$. However, Sherwood and Chambers (1937) made indirect estimations of $D(0, 1)$ and $D(10, 1)$ for N_2O_4 in N_2 from which it is possible to estimate $D(0, 1)$ for NO_2 in N_2. In their analysis Chambers and Sherwood (1937) assumed that the ratio $D_{NO_2, N_2}(T, 1) = 1.43 D_{N_2O_4, N_2}(T, 1)$, which from their tabulated values for $D_{N_2O_4, N_2}(T, 1)$ yields $D_{NO_2, N_2}(0, 1) = 0.1210 \text{ cm}^2 \text{ s}^{-1}$. Although Sviridenko et al. (1973) do not discuss the dimerization of NO_2 with N_2O_4 with their data for $D_{N_2O_4, N_2}(T, 1)$, their results will also be used to estimate $D_{NO_2, N_2}(T, 1)$. Using a factor of 1.46 from CO62 for the ratio of the diffusivities of these two dimers, the results from Sviridenko et al. (1973) yield $D_{NO_2, N_2}(T, 1) = 0.1460(T/T_0)^2$. These two estimates of $D_{NO_2, N_2}(0, 1)$ are included in Table 3 of this study.

The critical temperature and critical volume for NO_2 used in this study (Table 1) for the model of

CO62 are derived from the critical constants for N_2O_4 given by Ambrose (1992). It is assumed that the critical temperature is the same for both gases; but that the critical volume for NO_2 is half the critical volume for N_2O_4. This last assumption is made because the molecular mass of NO_2 is half that of N_2O_4. Also included in Table 4 is the model-derived estimate of $D(0, 1)$ for NO_2 in O_2 from Fan and Mason (1962). Comparing the various estimates for NO_2 (Tables 2–4) indicate that the estimate derived from Sviridenko et al. (1973) is about 7% greater than CO62, that the CO62 and LJ models are in close agreement, that Sherwood and Chambers (1937) and Fan and Mason (1962) are in close agreement and that these last two pairs of estimates differ from one another by approximately 11%. As with O_3 the CO62 model appears to be a reasonable median value with an approximately $\pm 10\%$ uncertainty. However, present results also suggest that the diffusivity for NO_2 is relatively uncertain and that experiments like those of Sherwood and Chambers (1937) and Sviridenko (1973) should be repeated.

Isosteric molecules — CO and N_2

Because CO and N_2 have identical molecular mass, molecular shape and size and electronic configuration they are isosteric molecules. According to kinetic theory therefore, CO and N_2 should have virtually identical coefficients of self-diffusion, $D(T, 1)$. For example, in a companion study to Bea90, Boushehri et al. (1987) suggest that $D_{N_2,N_2}(T, 1) = D_{CO,CO}(T, 1)$ is accurate to greater than 99.99%. Likewise the diffusion coefficients for N_2 and CO interdiffusing with nonpolar gases like N_2 and O_2 can also be expected to be very similar. For example, the modeling results of Boushehri et al. (1987) and Bea90 suggest that $D_{N_2,N_2}(T, 1) = D_{CO,N_2}(T, 1)$ is accurate to within $\pm 0.5\%$ and that $D_{N_2,O_2}(T, 1) = D_{CO,O_2}(T, 1)$ is accurate to within 0.1%. As an independent check of $D(T, 1)$ for CO, this study uses the loess regression technique to evaluate the coefficient of self-diffusion for N_2 in N_2 and the coefficient of diffusivity of N_2 in O_2.

The data for the coefficient of self-diffusion for N_2 are taken from Winn (1948, 1951), Winter (1951), DeLuca (1954) and Vugts et al. (1970). No data were eliminated as outliers and only one regression was necessary with $N = 13$. The results for the two parameter fit are $D(T, 1) = 0.1803(T/T_0)^{1.7288}$ with an $R^2 = 0.989$. The results for the one parameter fit are $D(0, 1) = 0.1783(\pm 0.001)$ with and $R^2 = 0.987$ and an absolute uncertainty of $\pm 5\%$. The value of $D(0, 1)$ for CO in N_2 found earlier is 0.1804 cm² s⁻¹ (Table 4) or 1.2% greater than the present value for the self-diffusion coefficient of N_2. This confirms the expectations that these isosteric molecules should have very similar values of $D(0, 1)$ and provides greater confidence in the present methods and results.

The data for evaluating $D_{N_2,O_2}(T, 1)$ are taken from von Obermayer (1880, 1882b), Lonnius (1909),

Waldmann (1944, 1947), Bohemen and Purnell (1961), Giddings and Seager (1962), Weissman and Mason (1962), Arnikar et al. (1967a, b), Saxena and Gupta (1970), Hellemans et al. (1973) and Shankland and Dunlop (1980). The data point of Giddings and Seager (1962) was identified as the only outlier. The final regression results are for $N = 21$: $D(T, 1) = 0.1847$ $(T/T_0)^{1.6522}$ with an $R^2 = 0.927$ for the two parameter fit and for the one parameter fit $D(0, 1) = 0.1809$ (± 0.002) with an $R^2 = 0.913$ and an absolute uncertainty of $\pm 9\%$. The value for $D_{CO,O_2}(0, 1)$ discussed earlier is 0.4% greater than the present value of $D_{N_2,O_2}(0, 1)$, thereby again confirming expectations.

Synthesis and recommended values for $D(0, 1)$

The recommended values for $D(0, 1)$ are listed in Table 8. The recommended values of $D(0, 1)$ for water vapor in air, N_2 and O_2 are the same ($= 0.2178$ cm² s⁻¹) primarily because the difference between $D_{H_2O,air}(0, 1)$ and $D_{H_2O,N_2}(0, 1)$ is so small and because $D_{H_2O,O_2}(0, 1)$ is imprecisely known. Likewise the recommended value for D_{SO_2,O_2} is taken to be the same as $D(0, 1)$ for SO_2 in air and N_2. Otherwise the recommended values for $D(0, 1)$ are taken from the corresponding tables (i.e. Tables 5–7). As much as possible the recommended values are derived from data. But in some cases the recommended values result from model calculations. These model-based recommendations were made only after the models were compared and evaluated relative to the data analysis. The model comparisons shown in Tables 5–7 suggest that the model of Bea90 tends to be slightly more accurate than the model of CO62, and both of these models tend to be more accurate than LJ. Therefore, the order of preference for model-based recommendations is Bea90 first, and then CO62 over LJ. However, recommending one model over another is not intended to suggest that one model is necessarily significantly better than another. With the exception of water vapor, no model results differ from the data analysis by more

Table 8. Recommended coefficients of diffusivity (cm² s⁻¹) of selected gases in air, N_2 and O_2

Gas	Air	N_2	O_2
H_2O	0.2178	0.2178	0.2178
CO_2	0.1381	0.1429	0.1402
CH_4	0.1952	0.1892	0.1942
CO[a]	0.1807[b]	0.1804	0.1817
SO_2	0.1089	0.1089	0.1089
O_3	0.1444	0.1441	0.1454
NH_3	0.1978	0.1978	0.1992
N_2O	0.1436	0.1402	0.1396
NO	0.1802	0.1809	0.1815
NO_2	0.1361	0.1359	0.1369
N_2[a]	0.1788[b]	0.1783	0.1809
O_2	0.1820[b]	0.1809	0.1862

Note: Only $D(0, 1)$ is given, $D(T, p) = D(0, 1)$ (p_0/p) $(T/T_0)^{1.81}$ is assumed.
[a] Isosteric molecules.
[b] From Blanc's law and $D(0, 1)$ for gas in N_2 and in O_2.

than about $\pm 10\%$ and usually the difference is much less. Therefore, in these cases the data and modeling results support one another because where data are available all modeling and data results are about equally uncertain.

The situation is unfortunately somewhat different for the cases with no data. Given the performances of the models for water vapor and NO/N_2, it seems possible that the model estimates of $D(0, 1)$ for O_3, NO, and NO_2 could be in error by as much as $\pm 25\%$, and indeed such large discrepancies between observed and modeled values for $D(T, 1)$ have been previously noted for other gases (Reid *et al.*, 1987). Consequently, all recommendations for $D(0, 1)$ for NO, NO_2 and O_3 must be viewed as quite uncertain and need to be verified experimentally if at all possible.

CONCLUSIONS

The loess regression technique is very effective for identifying outliers in the diffusivity data sets and worked especially well for the coefficients of diffusivity of H_2O and CO_2 which had relatively large data sets. For smaller data sets, the loess method is not necessarily as useful because the inherent variability of the data is sometimes too great. Under these circumstances it is impossible to evaluate the data in a completely objective manner, because the disparities within the data set are often so great as to suggest that the data are contradictory. Nevertheless, for H_2O, CO_2, CH_4 and CO the final regression curve developed with the loess technique gave results that were extremely close to the regression curves developed by Marrero and Mason (1972). Because Marrero and Mason (1972) used an understanding of theory and experimental techniques to evaluate data quality, the close agreement between their results and the present results suggests that those specific experiments identified as outliers by the loess technique should be considered the least trustworthy of the experimental determinations of $D(T, p)$.

The recommended values for the diffusivity are in many cases relatively precise and are valid to within an absolute uncertainty of $\pm 5\%$ to $\pm 9\%$. Furthermore, when the model predictions and data analysis are in close agreement they tend to mutually support one another. However, in spite of over a century of diffusivity measurements for a variety of gases, the diffusivities of O_3, NO and NO_2 in air remain relatively uncertain. Given the importance of these gases to atmospheric chemistry and atmosphere–biosphere interaction studies, there is an obvious need to verify the recommended values presented in Table 8 of this study. For example, the recommended ratio of the diffusivity of water vapor in air to the diffusivity of ozone in air is 1.51 which is about 10% less that the often quoted value of 1.65.

Finally the present results demonstrate that the misuse of Graham's law to estimate $D(T, p)$ can lead to significant errors. For example, using $D_w(0, 1)$ as the known diffusivity, the tabulations in Table 8 suggest that this approach can lead to errors of as much as 23%. Such inaccuracies should not be unexpected because the misapplication of Graham's law is in opposition to all theoretical results (e.g. equations (2) and (3), Reid *et al.*, 1987) which demonstrate that $D(0, 1) \propto \sqrt{1/M_i + 1/M_j}$, not to $\sqrt{M_i/M_j}$.

REFERENCES

Ackermann, G. (1934) Theorie der verdunstungskühlung. *Ingenieur-Archiv* **5**, 124–146.

Ambrose, D. (1992) Critical constants, boiling points, and melting points of selected compounds. In *CRC Handbook of Chemistry and Physics*, 73rd Edn, ed. D. R. Lide. CRC Press, Boca Raton, Florida.

Amdur, I. and Shuler, L. M. (1963) Diffusion coefficients of the systems CO–CO and CO–N_2. *Journal of Chemical Physics* **38**, 188–192.

Andrew, S. P. S. (1955) A simple method of measuring gaseous diffusion coefficients. *Chemical Engineering Science* **4**, 269–272.

Andrussow, L. (1969) Diffusion. In *Landholt-Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophyik und Technik; Transportphänomene I*, pp. 513–725. Springer, Berlin.

Arai, K. Saito, S. and Maeda, S. (1967) On the dispersion mechanism in laminar flow through tubes. *Kagaku Kogaku* **31**, 25–31.

Arnikar, H. J., Rao, T. S. and Karmarkar, K. H. (1967a) The use of an electrodeless discharge as a detector in gas chromatography. *Journal of Chromatography* **26**, 30–34.

Arnikar, H. J., Rao, T. S. and Karmarkar, K. H. (1967b) Electrodeless discharge as detector in gas chromatography III. Study of inter-diffusion of gases. *International Journal of Electronics* **22**, 381–385.

Barr, R. F. and Watts, H. (1972) Diffusion of some organic and inorganic compounds in air. *Journal of Chemical and Engineering Data* **17**, 45–46.

Berry, V. J., Jr. and Koeller, R. C. (1960) Diffusion in compressed binary gaseous systems. *Americal Institute of Chemical Engineering Journal* **6**, 274–280.

Boardman, L. E. and Wild, N. E. (1937) The diffusion of pairs of gases with molecules of equal mass. *Proceeding of Royal Society London* **A 162**, 511–520.

Bohemen, J. and Purnell, J. H. (1961) Diffusional band spreading in gas-chromatographic columns. Part I. The elution of unsorbed gases. *Journal of the Chemical Society* 360–367.

Bose, N. K. and Chakraborty, B. N. (1955–56) Diffusion coefficients of vapours into pure gases and their mixtures. *Transaction of the Indian Institute of Chemical Engineers* **8**, 67–72.

Boushehri, A., Bzowski, J., Kestin, J. and Mason, E.A., (1987) Equilibrium and transport properties of eleven polyatomic gases at low density. *Journal of Physics and Chemistry Reference Data* **16**, 445–466.

Boyd, C. A., Stein, N., Steingrimsson and Rumpel, W. F. (1951) An interferometric method of determining diffusion coefficients in gaseous systems. *Journal of Chemical Physics* **19**, 548–553.

Brookfield, K. J., Fitzpatrick, H. D. N., Jackson, J. F., Matthews, J. B. and Moelwyn-Hughes, E. A. (1947) The escape of molecules from a plane surface into a still atmosphere. *Proceedings of th Royal Society London* **A 190**, 59–67.

Brown, H. T. and Escombe, F. (1900) Static diffusion of gases and liquids in relation to the assimilation of carbon and translocation in plants. *Philosophical Transactions of the Royal Society London* **B 190**, 223–291.

Buckingham, E. (1904) Contributions to our knowledge of aeration of soils. U.S. Department of Agriculture, Bureau of Soils, Bulletin no. 25, Washington, D.C.

Bunde, R. E. (1955) Studies of the diffusion coefficients of binary gas mixtures. Ph.D. thesis, University of Wisconsin, Madison, Wisconsin.

Bzowski, J., Kestin, J., Mason, E. A. and Uribe, F. J. (1990a) Equilibrium and transport properties of gas mixtures at low density: eleven polyatomic gases and five noble gases. *Journal of Physics and Chemistry Reference Data* **19**, 1179–1232.

Bzowski, J., Kestin, J., Mason, E. A. and Uribe, F. J. (1990b) TABLES IV, V, VI, VII, VIII + TABLES 1–108 (pp. 20–127). (Supplement to Bzowski *et al.* 1990a)., American Institute of Physics, Physics Auxiliary Publication Service, New York, New York. PAPS JPCRD-19-1179-98.

Campbell, E. S. (1965) A theoretical analysis of chemical and physical processes in an ozone flame. *Chemical Engineering Science* **20**, 311–329.

Chambers, F. S., Jr. and Sherwood, T. K. (1937) Absorption of nitrogen dioxide by aqueous solutions. *Industrial and Engineering Chemistry* **29**, 1415–1422.

Chen, N. H. and Othmer, D. F. (1962) New generalized equation for gas diffusion coefficient. *Journal of Chemical and Engineering Data* **7**, 37–41.

Cleveland, W. S. (1993) *Visualizing Data*. Hobart Press, Summit, New Jersey, U.S.A.

Cleveland, W. S., Grosse, E. and Shyu, W. M. (1992) Local regression moels. In *Statistical Models in S*, eds J. M. Chambers and T. J. Hastie, pp. 309–376. Wadsworth & Brooks/Cole Advanced Books & Software, Pacific Grove, California.

Coates, J. and Mian A. A., (1967) Measurement and prediction of binary gaseous diffusion coefficients. *Industrie Chimique Belge* **32 (Spec. No.) (Pt. 1)**, 285–292.

Coward, H. F. and Georgeson, E. H. M. (1937) The diffusion coefficient of methane and air. *Journal of the Chemical Society* 1085–1087.

Cowie, M. and Watts H. (1971) Diffusion of methane and chloromethanes in air. *Canadian Journal of Chemistry* **49**, 74–77.

Crider, W. L. (1956) The use of diffusion coefficients in the measurement of vapor pressure. *Journal of American Chemical Society* **78**, 924–925.

Dandy, D. (1997) personal communication.

DeLuca, L. B. (1954) Self-diffusion coefficient of nitrogen. *Physical Review* **95**, 306.

Dunlop, P. J. and Bignell, C. M. (1997) Prediction of the temperature dependence of binary diffusion coefficients of gaseous systems from thermal diffusion factors and diffusion coefficients. *International Journal of Thermophysics* **18**, 939–945.

Ellis, C. S. and Holsen, J. N. (1969) Diffusion coefficients for the helium–nitrogen and nitrogen–carbon dioxide at elevated temperatures. *Industrial and Engineering Chemistry Fundamentals* **8**, 787–791.

Engel, J. and Knapp, H. (1973) Experimentelle bestimmung von diffusionkoeffizienten in den gasförmigen systemen He–CH_4, He–N_2 und CH_4–N_2. *Wärme- und Stoffübertragung* **6**, 146–152.

Fan, S. S. T. and Mason, D. M. (1962) Properties of the system $N_2O_4 \leftrightarrow 2NO_2 \leftrightarrow 2NO + O_2$. *Journal of Chemical and Engineering Data* **7**, 183–186.

Fuller, E. N, Schettler, P. D. and Giddings, J. C. (1966) A new method for prediction of binary gas phase diffusion coefficients. *Industrial and Engineering Chemistry* **53**, 19–27.

Giddings, J. C. and Seager, S. L. (1962) Method for rapid determination of diffusion coefficients. *Industrial and Engineering Chemistry Fundamentals* **1**, 277–283.

Gilliland, E. R. (1934) Diffusion coefficients in gaseous systems. *Industrial and Engineering Chemistry* **26**, 681–685.

Gordon, M. (1977) References to experimental data on diffusion coefficients of binary gas mixtures. National Engineering Laboratory, Glasgow, Scotland. NEL Report No. 647.

Guglielmo, G. (1881) Sulla evaporazione dell'acqua e sull'assorbimento del vapore acqueo per effetto delle soluzioni saline. *Atti della Accademia delle Scienze di Torino* **17**, 54–72.

Guglielmo, G. (1882) Sulla determinazione del coefficiente di diffusione del vapor acqueo per nell'aria, nell'idrogeno e nell'acido carbonico. *Atti della Accademia delle Scienze di Torino* **18**, 93–107.

Gwertsiteli, I. G., Kapamyan, A. T. and Menabde, N. E. (1961) Variation of the coefficient of diffusion of binary gas mixtures. *Soobshcheniia Akademii Nauk Gruzinskoi SSR* **26**, 409–413.

Hellemans, J. M., Kestin, J. and Ro, S. T. (1973) The viscosity of oxygen and some of its mixtures with other gases. *Physica* **65**, 362–375.

Hicks, B. B., Baldocchi, D. D., Hosker, Jr. R. P., Hutchinson, B. A., Matt, D. R., McMillen, R. T. and Satterfield, L. C. (1985) On the use of monitored air concentrations to infer dry deposition (1985). NOAA Air Resources Laboratory, Silver Spring, Maryland NOAA Technical Memorandum ERL ARL-141.

Hippenmeyer, B. (1949) Die diffusion von wasserdampf in wasserstoff, stickstoff und deren gemischen. *Zeitschrift fur Angewandte Physik* **1**, 549–557.

Hirschfelder, J. O., Curtiss, C. F. and Campbell, D. E. (1953) Theory of flame propagation IV. *Journal of Physical Chemistry* **57**, 403–414.

Holsen, J. N. and Strunk, M. R. (1964) Binary diffusion coefficients in nonpolar gases. *Industrial and Engineering Chemistry Fundamentals* **3**, 143–146.

Houdaille, F. (1897) Measure du coefficient de diffusion de al vapeur d'eau dans l'atmosphere et du coefficient de frottement de la vapeur d'eau. *Fortschritte der Physik* **52**, 442–443.

Houghton, H. G. (1933) A study of the evaporation of small water drops. *Journal of Applied Physics* **4**, 419–424.

Ivakin, B. A. and Suetin, P. E. (1964a) Diffusion coefficient of some gases measured by the optical method. *Soviet Physics Technical Physics* **8**, 748–751.

Ivakin, B. A. and Suetin, P. E. (1964b) An investigation of the temperature dependence of the diffusion coefficient of gases. *Soviet Physics Technical Physics* **9**, 866–872.

Jacobs, T., Peeters, L. and Vermant, J. (1970) Binary diffusion coefficients of lower alkanes in nitrogen and argon. *Bulletin des Sociétés Chimiques Belges* **79**, 337–342.

Kee, R. J., Dixon-Lewis, G., Warnatz, J., Coltrin, M. E. and Miller, J. E. (1986) A fortran computer code package for the evaluation of gas-phase, multicomponent transport properties. Sandia National Laboratory, Report SAND86-8246, Albuquerque, New Mexico. Available from Reaction Design, 11436 Sorrento Valley Road, San Diego, CA 92121.

Kestin, J., Kobayashi, Y. and Wood, R. T. (1966) The viscosity of four binary, gaseous mixtures at 20° and 30°C. *Physica* **32**, 1065–1089.

Kimpton, D. D. and Wall, F. T. (1952) Determination of diffusion coefficients from rates of evaporation. *Journal of Physical Chemistry* **56**, 715–717.

Klibanova, T. M., Pomerantsev, V. V. and Frank-Kamenet-skiĭ, D. A. (1942) Diffusion coefficients of gases at high temperatures. *Journal of Technical Physics USSR* **12**, 14–30.

Kosov, N. D. (1957) Some methods for determining the diffusion coefficient of gases. In *Issledovanie Fizicheskikh Osnov Rabochego Protesessa Topok i Pechei*, ed. L. A. Vulis, pp. 285–290. Alma-Ata, Izd-vo Akademie nauk Kazakhskoi SSR, Sbornik.

Kosov, N. D. and Zhalgasov, A. (1970) Coefficients of mutual diffusion of H_2 and O_2 in CO_2 measured from room temperature to $-77°C$. *Zhurnal tekhnicheskoi fiziki* **40**, 1325–1327.

Laisk, A., Kull, O. and Moldau, H. (1989) Ozone concentration in leaf intercellular air spaces is close to zero. *Plant Physiology* **90**, 1163–1167.

Lannus, A. (1970) An approximate calculation of diffusion and other transport coefficients of dilute gases. Ph.D. thesis, Drexel University, Philadelphia.

Le Blanc, M. and Wupperman, G. (1916) Über die verdampfungsgeschwindigkeit von flüssigkeiten. *Zeitschrift für Physikalische Chemie, Stöchiometric und Verwandtschaftslehre* **91**, 143–154.

Lee, C. Y. and Wilke, C. R. (1954) Measurement of vapor diffusion coefficient. *Industrial and Engineering Chemistry* **46**, 2381–2387.

Liley, P. E. (1962) Survey of recent work on the viscosity, thermal conductivity, and diffusion of gases and liquefied gases below 500 K. In *Progress in International Research on Thermodynamic and Transport Properties.*, eds J. F. Masi and D. H. Tsai, pp. 313–339, Second Symposium on Thermophysical Properties, The American Society of Mechanical Engineers, New York and Academic Press, New York.

List, R. J. (1949) *Smithsonian Meteorological Tables*, 6th revised edition. Smithsonian Institution Press, Washington, D.C.

Lonius, A. (1909) Die abhängigkeit des gasdiffusionskoeffizienten vom mischungsverhältnis. *Annalen der Physik* **29**, 664–678.

Loschmidt, J. (1870a) Experimental-Untersuchungen über die diffusion von gasen obne poröse scheidewände. I. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **61**, 367–380.

Loschmidt, J. (1870b) Experimental-Untersuchungen über die diffusion von gasen obne poröse scheidewände. II. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **62**, 468–478.

Mache H. (1910) Über die verdunstungsgeschwindigkeit des wassers in wasserstoff und luft. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **119**, 1399–1423.

Marrero, T. R. and Mason E. A. (1972) Gaseous diffusion coefficients. *Journal of Physics and Chemistry Reference Data* **1**, 3–118.

Mason, E. A. (1971) Diffusion in gases. In *Diffusion Processes*, eds J. N. Sherwood, A. V. Chadwick, W. M. Muir and F. L. Swinton, Vol. 1, pp. 3–27, Gordon and Breach, London.

Mason, E. A. and Evans, R. B. III (1969) Graham's laws: Simple demonstrations of gases in motion. Part I, Theory. *Journal of Chemical Education* **6**, 358–364.

Mason, E. A. and Monchick, L. (1962) Transport properties of polar-gas mixtures. *Journal of Chemical Physics* **36**, 2746–2757.

Mathews, J. F. (1972) The critical constants of inorganic substances. *Chemical Reviews* **72**, 71–100.

Mian, A. A. (1967) Measurement and prediction of binary gaseous diffusion coefficients. Ph.D. thesis, Louisiana State University, Baton Rouge, Louisiana.

Monchick, L. and Mason, E. A. (1961) Transport properties of polar gases. *Journal of Chemical Physics* **35**, 1676–1697.

Monteith, J. L. and Unsworth, M. H. (1990) *Principles of Environmental Physics*, 2nd Edn. Edward Arnold, London.

Mueller, C. R. and Cahill, R. W. (1964) Mass spectrometric measurement of diffusion coefficients. *Journal of Chemical Physics* **40**, 651–654.

Nagata, I. and Hasegawa, T. (1970) Gaseous interdiffusion coefficients. *Journal of Chemical Engineering of Japan* **3**, 143–145.

Narsimhan, G. (1955–56) Measurement of vapor diffusion coefficient. *Transactions of the Indian Institution of Chemical Engineers* **8**, 73–75.

Nelson, E. T. (1956) The measurement of vapour diffusivities in coal–gas and some common gases. *Journal of Applied Chemisty* **6**, 286–292.

Neufeld, P. D., Janzen, A. R. and Aziz, R. A. (1972) Empirical equations to calculate 16 of the transport collision integrals $\Omega^{(l,s)*}$ for the Lennard–Jones (6-12) potential. *Journal of Chemical Physics* **57**, 1100–1102.

O'Connell, J. P., Gillespie, M. D., Krostek, W. D. and Prausitz, J. M. (1969) Diffusivities of water in nonpolar gases. *Journal of Physical Chemistry* **73**, 2000–2004.

Pakurar, T. A. and Ferron, J. R. (1966) Diffusivities in the system: carbon dioxide–nitrogen–argon. *Industrial and Engineering Chemistry Fundamentals* **5**, 553–557.

Petit, M.-C. (1965) Ètude de la diffusion de la vapeur d'eau dans l'air. *Comptes Rendus Acad. Sc. Paris* **260**, 1368–1370.

Prichard, D. T. and Currie, J. A. (1982) Diffusion of coefficients of carbon dioxide, nitrous oxide, ethylene and ethane in air and their measurement. *Journal of Soil Science* **33**, 175–184.

Reid, R. C., Prausnitz, J. M. and Poling, B. E. (1987) *The Properties of Gases and Liquids*, 4th Edn. McGraw-Hill, New York.

Richardson, J. F. (1959) The evaporation of two-component liquid mixtures. *Chemical Engineering Science* **10**, 234–242.

Robjohns, H. L. and Dunlop, P. J. (1984) Diffusion and thermal diffusion in some binary mixture of the major components of air. *Bericht Deutsche Bunsengesellschaft für Physikalische Chemie*, **88**, 1239–1241.

Rossié, K. (1953) Die diffusion von wasserdampf in luft bei termperaturen bis 300°C. *Forschung auf dem Gebiete des Ingenieurwessens* **19A**, 49–58.

Saxena, S. C. and Gupta, G. P. (1970) Experimental data and procedures for predicting thermal conductivity of multicomponent mixtures of nonpolar gases. *Journal of Chemical and Engineering Data*, **15**, 98–107.

Schäfer, K., Corte, H. and Moesta, H. (1951) Über die messung der temperatur- und konzentrations-abhängigkeit der diffusionkoeffizienten von gasen. *Zeitschrift für Elektrochemie und Angewandte Physikalischechemie* **55**, 662–664.

Schäfer, K. (1959) Zwischenmolekulare kräfte, temperatur- und druckabhängigkeit der diffusion von gasen. *Zeitschrift für Elektrochemie* **63**, 111–117.

Schirmer, R. (1938) Die diffusionszahl von wasserdamf-luftgemischen und die verdampfungsgeschwindigkeit. *Zeitschrift des Vereines Deutsher Ingenieure, Beiheft Folge* **6**, 170–177.

Schneider, M. and Schäfer, K. (1969) Gasdiffusionsmessungen zwischen 273 und 1300°K. *Bericht Deutsche Bunsengesellschaft für Physikalische Chemie* **73**, 702–706.

Schwertz, F. A. and Brow, J. E. (1951) Diffusivity of water vapor in some gases. *Journal of Chemical Physics* **19**, 640–646.

Shankland, I. R. and Dunlop, P. J. (1980) Pressure dependence of the mutual diffusion coefficients of the binary systems $N_2 + Ar$, $N_2 + O_2$, $O_2 + Ar$ and $Ar + Kr$ at 300 and 323 K. *Physica* **100A**, 64–84.

Suetin, P. E. and Ivakin, B. A. (1961) Coefficients of mutual diffusion of some gases measured by optical method. *Soviet Physics Technical Physics* **6**, 359–361.

Summerhays, W. E. (1930) A determination of the coefficient of diffusion of water vapour. *Proceedings of the Physics Society London* **42**, 218–225.

Svehla, R. A. (1962) Estimated viscosities and thermal conductivities of gases at high temperature. NASA Lewis Research Center, Cleveland, Ohio. NASA Technical Report R-132.

Svehla. R. A. and Brokaw, R. S. (1966) Thermodynamic and transport properties for the $N_2O_4 \leftrightarrow 2NO_2 \leftrightarrow 2NO + O_2$ system. NASA Lewis Research Center, Cleveland, Ohio. NASA Technical Note, NASA TN D-3327.

Sviridenko, Y. F., Makhin, V. A. and Shandorov, G. S. (1973) Determining the diffusivity of nitrogen tetroxide. *Journal of Engineering Physics* **24**, 351–353.

Trautz, M. and Müller, W. (1935a) Die korrektion der bisher mit der verdampfungsmethode gemessenen diffusionskonstanten. *Annalen der Physik* **22**, 333–352.

Trautz, M. and Müller, W. (1935b) Neue messungen von diffusionskonstanten und abschließende zusammenfassung über gas-diffusionskonstanten. *Annalen der Physik* **22**, 353–374.

Vasilevskaya, Y. D. (1961) The diffusion coefficient for the T-5 fuel vapor-air system. *Trudy* **132**, 144–160.

von Obermayer, A. (1880) Über die abhänggigkeit des diffusionscoëfficienten der gase von der temperatur. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **81**, 1102–1127.

von Obermayer, A. (1882a) Versuche über diffusion von gasen. I. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **85**, 147–169.

von Obermayer, A. (1882b) Versuche über diffusion von gasen. II. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **85**, 748–761.

von Obermayer, A. (1883) Versuche über diffusion von gasen. III. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **87**, 188–263.

von Obermayer, A. (1887) Versuche über diffusion von gasen. IV. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **96**, 546–577.

Vugts, H. F. Boerboom, A. J. H. and Los, J. (1970) Diffusion coefficients of isotopic mixtures of CO and N_2. *Physica* **50**, 593–605.

Vyshenskaya, V. F. and Kosov, N. D. (1965) Temperature dependence of the diffusion coefficient of gases. Oak Ridge National Laboratory, Oak Ridge, Tennessee, Translation from Russian by A. L. Monks. ORNL-TR-506.

Waitz, K. (1882a) Ueber die diffusion der gase. *Annalen der Physik und Chemie* **17**, 201–236.

Waitz, K. (1882b) Nactrag zu der abhandlung: Ueber die diffusion der gase. *Annalen der Physik und Chemie* **17**, 351–352.

Wakeham, W. A. and Slater, D. H. (1973) Diffusion coefficients for *n*-alkanes in binary gaseous mixtures with nitrogen. *Journal of Physics B: Atomic Molecular Physics* **6**, 886–896.

Waldmann, L. (1944) Eine neue meßmethode für thermodiffusions- und diffusionkoeffizienten in gasen. *Naturwissenschaften* **32**, 223–224.

Waldmann, L. (1947) Die temperaturescheinungen bei der diffusion in ruhenden gases und hire meßtechnische anwendung. *Zeitschrift für Physik* **124**, 2–29.

Walker, R. E. (1958) Molecular diffusion studies in binary gas systems. Ph.D. thesis, University of Maryland, College Park, Maryland.

Walker, R. E. and Westenberg, A. A. (1958) Molecular diffusion studies in gases at high temperature. II. Interpretation of results on the He–N_2 and CO_2–N_2, systems. *Journal of Chemical Physics* **29**, 1147–1153.

Walker, R. E. and Westenberg, A. A. (1960) Molecular diffusion studies in gases at high temperature. IV. Results and interpretation of the CO_2–O_2, CH_4–O_2, CO–O_2, and H_2O–O_2 systems. *Journal of Chemical Physics* **32**, 436–442.

Walker, R. E., deHaas, N. and Westenberg, A. A. (1960) Measurements of multicomponent diffusion coefficients for the CO_2–He–N_2 system using the point source technique. *Journal of Chemical Physics* **32**, 1314–1316.

Weissman, S. and Mason, E. A. (1962) Determination of gaseous-diffusion coefficients from viscosity measurements. *Journal of Chemical Physics* **37**, 1289–1300.

Weissman, S. (1964) Estimation of diffusion coefficients from viscosity measurements: polar and polyatomic gases. *Journal of Chemical Physics* **40**, 3397–3406.

Westenberg, A. A. and Walker, R. E. (1957) New method of measuring diffusion coefficients of gases. *Journal of Chemical Physics* **26**, 1753–1754.

Wilhelm, E. and Battino, R. (1972) Binary gaseous diffusion coefficients I. Methane and carbon tetrafluoride with *n*-hexane, *n*-heptane, *n*-octane, and 2,2,4-trimethylpentane and one-atmosphere pressure at 10–70°C. *Journal of Chemical and Engineering Data* **17**, 187–189.

Wicke, E. and Kallenbach, R. (1941) Die oberflächendiffusion von kohlendioxyd in aktiven kohlen. *Kolloid Zeitschrift* **97**, 135–151.

Wicke, E. and Hugo, P. (1961) Gleitungserscheinungen bei der gasdiffusion. *Zeitschrift für Pysikalische Chemie* **28**, 410–421.

Winkelmann, A. (1884a) I. Ueber die diffusion von gasen und dämpfen. *Annalen der Physik und Chemie* **22**, 1–31.

Winkelmann, A. (1884b) II. Ueber die diffusion von gasen und dämpfen. *Annalen der Physik und Chemie* **22**, 152–161.

Winkelmann, A. (1888) Die verdampfung in ihrer abhänggigkeit vom äusseren druck, *Annalen der Physik und Chemie* **33**, 445–453.

Winkelmann, A. (1889) Ueber den einfluss der temperatur auf die verdampfung und auf die diffusion von dämpfen. *Annalen der Physik und Chemie* **36**, 93–114.

Winn, E. B. (1948) The self-diffusion coefficient of nitrogen. *Physical Review* **74**, 698–699.

Winn, E. B. (1950) The temperature dependence of the self-diffusion coefficients of argon, neon, nitrogen, oxygen, carbon dioxide, and methane. *Physical Review* **80**, 1024–1027.

Winter, E. R. S. (1951) Diffusion properties of gases. *Transactions of the Faraday Society* **47**, 342–347.

Wintergerst, E. (1930) Bestimmung der diffusionszahl von ammoniak gegen luft. *Annalen der Physik, Ser. 5* **4**, 323–351.

Wretschko, A. (1870) Experimental-untersuchungen über die diffusion von gasgemengen. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wein* **62**, 575–589.

Yaws, C. L. (1972) *Physical Properties — A Guide to the Physical, Thermodynamic and Transport Property Data of Industrially Important Chemical Compounds.* McGraw-Hill, New York.

Yaws, C. L. (1995) *Handbook of Transport Property Data.* Gulf, Houston.