

# A New Gas Chromatographic Methodology for the Estimation of the Composition of Binary Gas Mixtures

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## Abstract

The relatively new technique of reversed-flow gas chromatography (RFGC) is used to determine the diffusion coefficients of pure gases into gas mixtures ( $D_{\text{mix}}^{\text{exp}}$ ). The pure gases are CO and CO<sub>2</sub>, and the mixtures consist of H<sub>2</sub> and He in various volume percentage compositions. A linear regression analysis of  $D_{\text{mix}}^{\text{exp}}$  of CO and CO<sub>2</sub> in various mixtures of H<sub>2</sub> and He against the percentage composition ( $X_{\text{H}_2}$  or  $X_{\text{He}}$ ) of the mixtures at different temperatures results in an empirical equation relating  $D_{\text{mix}}^{\text{exp}}$  to the corresponding theoretical values of the diffusion coefficients of CO and CO<sub>2</sub> in the pure gases H<sub>2</sub> and He, as they are calculated from the Fuller–Schettler–Giddings equation. The empirical equation shows that the diffusion coefficient of an analyte gas in a gas mixture is the partial sum of its diffusion coefficients in the component gases, therefore making possible the determination of the mole fractions of the components of the mixture. The found percentage volume compositions are very close to those determined independently by routine gas chromatography, indicating that the proposed RFGC methodology could be successfully applied to the accurate determination of the volume composition of binary gas mixtures.

## Introduction

The measurement of gaseous diffusion coefficients by non-gas chromatographic (GC) and GC methods is of both theoretical and practical importance. The gaseous diffusion coefficient is related to the intermolecular potential between molecules and can be used to derive intermolecular properties, which can be compared with values obtained from thermodynamic properties such as second virial coefficients. From a practical aspect, diffusion is important in a wide variety of chemical engineering problems. Although the diffusivities in binary gases at low density are almost composition-independent, the diffusion in multicomponent gases strongly depends on the gas mixture composition, thus making possible the estimation of the volume composition of the gas mixture from the measured gas diffusion coefficients. The dif-

fusion coefficients of pure gases and of binary and ternary gas mixtures into pure gases at various temperatures have been determined previously (1–5) by reversed-flow GC (RFGC). As is evident from the name, RFGC is a GC technique based on GC instrumentation and theory. In comparison with conventional GC, in which quantitative analysis of a solute is under investigation, in RFGC the main goal is the measurement of various physicochemical parameters.

Conventional GC involves the flow of a gaseous mobile phase in a defined direction over a stationary phase or packing that results in the selective retention of solute components. In RFGC the system is modified, having placed perpendicularly in the center of the chromatographic column (sampling column) the diffusion column. The carrier gas flows continuously through the sampling column, and it is stagnant in the diffusion column. A small part or all of the diffusion column can be filled with a solid or liquid substance. In contrast with conventional GC, in which the mobile phase is the center of interest, in RFGC the solid or liquid substance placed into the diffusion column is under investigation. Thus, RFGC can be assumed to be an inverse GC method.

The injection of the solute is done on the upper end of the diffusion column. Thus, the displacement of the injected solute into the diffusion column is only affected by its interaction with the stationary phase and its diffusion into the stagnant carrier gas. It is obvious that with the absence of any solid or liquid stationary phase, the displacement of the solute is a result of its diffusion into the carrier gas, which is quantitatively characterized by the diffusion coefficient. The previously described peculiarity makes RFGC ideal for the measurement of gas diffusion coefficients (2–5).

Another peculiarity of RFGC is the sampling procedure of the physicochemical phenomenon, which happens in the diffusion column. The sampling procedure is carried out using a four-part valve making reversals of the flow of the carrier gas for a short time and then restoring its flow in its original direction. The previously mentioned flow reversals result in a short enrichment of the solute quantity into the carrier gas, and extra chromatographic peaks are created on the continuous concentration–time curve (chromatogram). The extra peaks are symmetrical and their height (or area) is proportionate to the concentration

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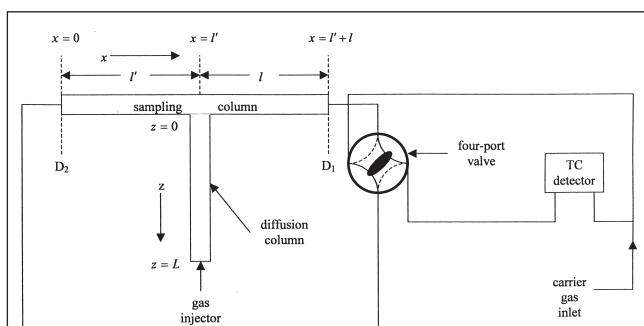


Figure 1. Schematic representation of the RFGC technique for the measurement of the diffusion coefficient of gas into gas mixtures.

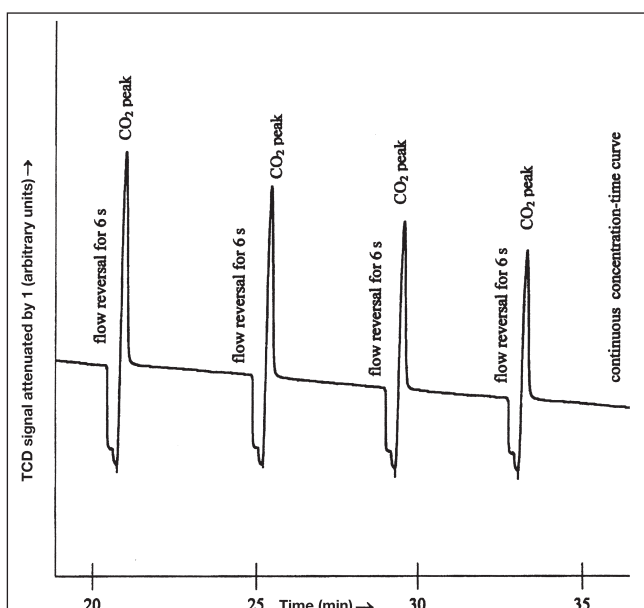


Figure 2. Reversed-flow chromatogram for the simultaneous determination of the diffusion coefficients of  $\text{CO}_2$  into the mixture of 75.05%  $\text{H}_2$  + 24.95% He at 324.7 K and 1 atm.

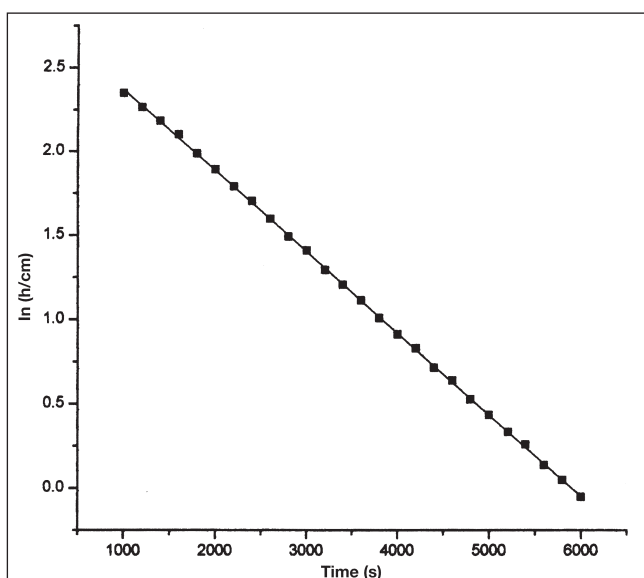


Figure 3. Plot of equation 1 for the diffusion of  $\text{CO}_2$  into the mixture 49.95%  $\text{H}_2$  + 50.05% He at 324.7 K and 1 atm.

of the solute in the junction of the diffusion and sampling columns, resulting in a higher sensitivity and accuracy for RFGC (2–5). The estimation of the various parameters (e.g., diffusion coefficients) is done by plotting the heights (or the areas) of the extra chromatographic peaks versus the time from the solute's injection and geometrical characteristics of the diffusion column (as will be discussed further in the Results and Discussion section).

RFGC has been applied with success for the determination of the diffusion coefficients of pure gases and ternary gas mixtures into gases (2–5); molecular diameters, critical volumes, and Lennard–Jones parameters of gases (6,7); the adsorption equilibrium constants (8); activity coefficients (9); mass transfer coefficients on solids and liquids (10–15); rate constants, activation parameters, and conversion of the reactants into products for var-

Table I. Experimental ( $D_{\text{mix}}^{\text{exp}}$ ) and Theoretical ( $D_{\text{mix}}^{\text{cal}}$ ) as Calculated from Equation 6 and Diffusion Coefficients of CO into Mixtures of  $\text{H}_2$  and He of Various Volume Compositions of Hydrogen at Various Temperatures\*

Temperature (K)	$X_{\text{H}_2}$ (%)	$D_{\text{mix}}^{\text{exp}}$ ( $\text{cm}^2/\text{s}$ )	$D_{\text{mix}}^{\text{cal}}$ ( $\text{cm}^2/\text{s}$ )	%Accuracy <sup>†</sup>
315.2	0	0.754	0.754	0.00
	25.05	0.771	0.770	0.13
	49.95	0.788	0.787	0.13
	75.05	0.804	0.803	0.12
	100	0.820	0.819	0.12
320.0	0	0.775	0.775	0.00
	25.05	0.789	0.791	0.25
	49.95	0.806	0.808	0.25
	75.05	0.826	0.824	0.24
	100	0.842	0.840	0.24
324.7	0	0.796	0.795	0.13
	25.05	0.813	0.812	0.12
	49.95	0.829	0.829	0.00
	75.05	0.847	0.845	0.24
	100	0.863	0.862	0.12
329.4	0	0.818	0.815	0.37
	25.05	0.834	0.832	0.24
	49.95	0.851	0.850	0.12
	75.05	0.868	0.867	0.12
	100	0.883	0.884	0.11
334.2	0	0.836	0.836	0.00
	25.05	0.851	0.854	0.35
	49.95	0.869	0.872	0.35
	75.05	0.891	0.889	0.22
	100	0.903	0.907	0.44
339.0	0	0.859	0.857	0.23
	25.05	0.876	0.875	0.11
	49.95	0.895	0.894	0.11
	75.05	0.913	0.912	0.11
	100	0.931	0.930	0.11
343.9	0	0.882	0.879	0.34
	25.05	0.899	0.897	0.22
	49.95	0.918	0.916	0.22
	75.05	0.937	0.934	0.32
	100	0.954	0.953	0.10

\*  $P = 1$  atm.

<sup>†</sup> Defined by equation 7.

ious important surface catalyzed reactions (16–19); rate constants for the sorption processes of various gases on bimetallic catalysts (20,21); Flory–Huggins interaction and solubility parameters in polymer-solvent systems (22); rate coefficients for the evaporation of liquids (23); rates for the drying of catalysts (24); and finally adsorption energies, local monolayer capacities, and local adsorption isotherms (25,26).

The aim of this study is to present a new methodology of the RFGC technique for the measurement of the diffusion coefficients of pure gases in gas mixtures. Based on the linear regression analysis of the experimental diffusion coefficients versus the volume composition of the gas mixtures, an empirical equation able to estimate the percentage volume composition of the gas mixtures will be derived.

**Table II. Experimental ( $D_{\text{mix}}^{\text{exp}}$ ) and Theoretical ( $D_{\text{mix}}^{\text{cal}}$ ) as Calculated from Equation 6 and Diffusion Coefficients of  $\text{CO}_2$  into Mixtures of  $\text{H}_2$  and He of Various Volume Compositions of Hydrogen at Various Temperatures\***

Temperature (K)	$X_{\text{H}_2}$ (%)	$D_{\text{mix}}^{\text{exp}}$ ( $\text{cm}^2/\text{s}$ )	$D_{\text{mix}}^{\text{cal}}$ ( $\text{cm}^2/\text{s}$ )	%Accuracy <sup>†</sup>
315.2	0	0.511	0.509	0.39
	25.05	0.555	0.558	0.54
	49.95	0.608	0.606	0.33
	75.05	0.656	0.655	0.15
	100	0.700	0.703	0.43
320.0	0	0.526	0.523	0.57
	25.05	0.570	0.573	0.52
	49.95	0.624	0.622	0.32
	75.05	0.670	0.672	0.30
	100	0.724	0.722	0.28
324.7	0	0.534	0.537	0.56
	25.05	0.589	0.588	0.17
	49.95	0.636	0.638	0.31
	75.05	0.691	0.689	0.29
	100	0.738	0.740	0.27
329.4	0	0.552	0.550	0.36
	25.05	0.599	0.603	0.66
	49.95	0.657	0.655	0.31
	75.05	0.704	0.708	0.56
	100	0.761	0.760	0.13
334.2	0	0.566	0.564	0.35
	25.05	0.615	0.618	0.49
	49.95	0.673	0.672	0.15
	75.05	0.727	0.725	0.28
	100	0.782	0.779	0.39
339.0	0	0.580	0.579	0.17
	25.05	0.635	0.634	0.16
	49.95	0.690	0.688	0.29
	75.05	0.745	0.743	0.27
	100	0.796	0.798	0.25
343.9	0	0.596	0.593	0.51
	25.05	0.647	0.650	0.46
	49.95	0.709	0.706	0.42
	75.05	0.759	0.763	0.52
	100	0.820	0.819	0.12

\*  $P = 1$  atm.  
<sup>†</sup> Defined by equation 7.

## Experimental

### Materials

The carrier gases, pure hydrogen and helium (99.999% purity), as well as mixtures of  $\text{H}_2$  and He (with the following percentage volume compositions: 25.05%  $\text{H}_2$  + 74.95% He, 49.95%  $\text{H}_2$  + 50.05% He, and 75.05%  $\text{H}_2$  + 24.95% He) were purchased from BOC Gases GmbH (Stuttgart, Germany). The actual gas mixture concentrations were measured by a GC (PerkinElmer XL Autosystem, Shelton, CT) with a TC detector using a column with a length of 3 m filled with molecular sieve 5A. The working temperature was 60°C, and the flow rate of the carrier gas Ar was 20 mL/min.

The analyte gases used were CO from Linde A.G. (Athens, Greece) (99.997% pure) and  $\text{CO}_2$  from Matheson Gas Products (Krefeld, Germany) (99.999% pure).

### Instruments

A Shimadzu (Kyoto, Japan) GC-8A GC with a thermal conductivity detector was modified for the RFGC technique (as shown in Figure 1).

Further details of the experimental setup have been described in the Introduction section and elsewhere (14), except for the diffusion column (L), which was placed inside the chromatographic oven (610- × 5.3-mm i.d.) with its closed end at the injector position of the GC. The diffusion column was empty of any material. The sampling column lengths ( $l$  and  $l'$ ) that were empty of any chromatographic material (505- × 5.3-mm i.d.) were also inside the oven as before. The lengths  $l$  and  $l'$  were almost equal. Both of

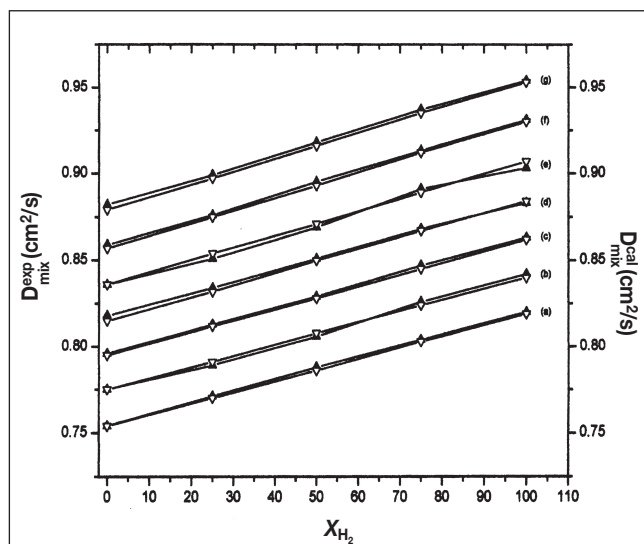
**Table III. Linear Regression of  $D_{\text{min}}^{\text{exp}}$  for CO Versus the Percentage Volume Composition of Hydrogen ( $X_{\text{H}_2}$ ) in the Mixtures of  $\text{H}_2$  and He at Various Temperatures**

Temperature (K)	$D_{\text{mix}}^{\text{exp}} = D_{\text{mix}}^{\text{exp}}(X_{\text{H}_2})$
315.2	= 0.754 + 0.066
320.0	= 0.773 + 0.068
324.7	= 0.796 + 0.067
329.4	= 0.818 + 0.066
334.2	= 0.835 + 0.070
339.0	= 0.859 + 0.072
343.9	= 0.882 + 0.073

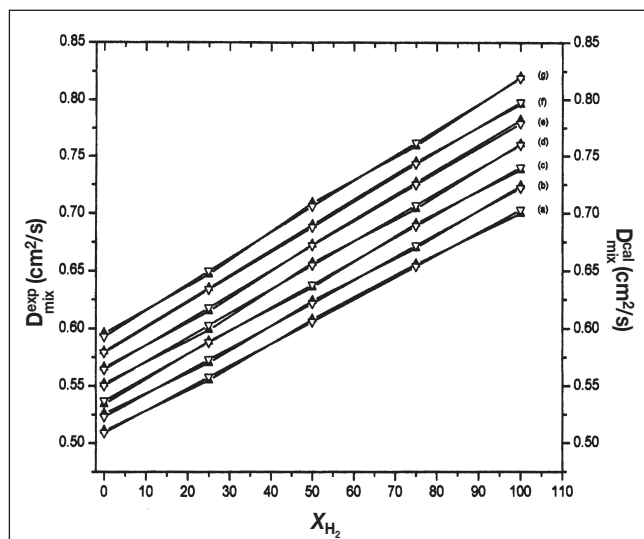
**Table IV. Linear Regression of  $D_{\text{min}}^{\text{exp}}$   $\text{CO}_2$  Versus the Percentage Volume Composition of Hydrogen ( $X_{\text{H}_2}$ ) in the Mixtures of  $\text{H}_2$  and He at Various Temperatures**

Temperature (K)	$D_{\text{mix}}^{\text{exp}} = D_{\text{mix}}^{\text{exp}}(X_{\text{H}_2})$
315.2	= 0.510 + 0.019
320.0	= 0.524 + 0.020
324.7	= 0.536 + 0.020
329.4	= 0.550 + 0.021
334.2	= 0.564 + 0.022
339.0	= 0.581 + 0.022
343.9	= 0.594 + 0.022

them were connected with the diffusion column through a  $\frac{1}{4}$ -inch ET-Union tee. Its length was 1 cm. The exact lengths of  $l$  and  $l'$  were not necessary for the estimation of the diffusion coefficient. Only the length of the diffusion column was necessary. This was easily and accurately measured by the lengths of the stainless steel diffusion column and ET-Union tee, which was equal to 1 cm. The exact value of the diameter of the diffusion column was not necessary for the estimation of diffusion coefficient. The used injector did not contribute to the length of the diffusion column.



**Figure 4.** Plot of experimental [ $D_{\text{mix}}^{\text{exp}}$  (▲)] and theoretical [ $D_{\text{mix}}^{\text{cal}}$  (▽)] diffusion coefficients of CO into mixtures consisting of  $\text{H}_2$  and He against the hydrogen percentage volume composition ( $X_{\text{H}_2}$ ) of the mixtures at various temperatures: (A) 315.2 K, (B) 320.0 K, (C) 324.7 K, (D) 329.4 K, (E) 334.2 K, (F) 339.0 K, and (G) 343.9 K.



**Figure 5.** Plot of experimental [ $D_{\text{mix}}^{\text{exp}}$  (▲)] and theoretical [ $D_{\text{mix}}^{\text{cal}}$  (▽)] diffusion coefficients of  $\text{CO}_2$  into mixtures consisting of  $\text{H}_2$  and He against the hydrogen percentage volume composition ( $X_{\text{H}_2}$ ) of the mixtures at various temperatures: (A) 315.2 K, (B) 320.0 K, (C) 324.7 K, (D) 329.4 K, (E) 334.2 K, (F) 339.0 K, and (G) 343.9 K.

## Procedure

At a given time after injecting 1 mL of the analyte gas ( $\text{CO}$  or  $\text{CO}_2$ ) into the diffusion column, during which no signal was noted, an asymmetrical concentration–time curve for the gas was recorded (rising slowly and decaying more slowly). During the whole experimental period, flow reversals for a time period of 6 s, which was smaller than both the gas hold times in columns  $l$  and  $l'$ , were carried out by the four-port valve shown in Figure 1. This gave rise to a series of peaks (shown in Figure 2) corresponding with various times from the solute injection.

In whole series of experiments, the velocity of the carrier gas ( $\text{H}_2$ , He, and mixtures of  $\text{H}_2$  and He) was kept constant (1 mL/s) while the pressure drop along the column  $l + l'$  was negligible. The variations of temperature in the oven were less

**Table V. Theoretical Diffusion Coefficients of CO into Mixtures of  $\text{H}_2$  and He of Various Volume Compositions of Hydrogen ( $X_{\text{H}_2}$ ) at Various Temperatures\* Based on Equations 6 ( $D_{\text{mix}}^{\text{Eq.6}}$ ) and 8 ( $D_{\text{mix}}^{\text{Eq.8}}$ )**

Temperature (K)	$X_{\text{H}_2}$ (%)	$D_{\text{mix}}^{\text{Eq.6}}$ ( $\text{cm}^2/\text{s}$ )	$D_{\text{mix}}^{\text{Eq.8}}$ ( $\text{cm}^2/\text{s}$ )	%Deviation <sup>†</sup>
315.2	0	0.754	0.754	0.00
	25.05	0.770	0.770	0.00
	49.95	0.787	0.785	0.25
	75.05	0.803	0.802	0.12
	100	0.819	0.819	0.00
320.0	0	0.775	0.775	0.00
	25.05	0.791	0.790	0.13
	49.95	0.808	0.806	0.25
	75.05	0.824	0.823	0.12
	100	0.840	0.840	0.00
324.7	0	0.795	0.795	0.00
	25.05	0.812	0.811	0.12
	49.95	0.829	0.827	0.24
	75.05	0.845	0.844	0.12
	100	0.862	0.862	0.00
329.4	0	0.815	0.815	0.00
	25.05	0.832	0.831	0.12
	49.95	0.850	0.848	0.24
	75.05	0.867	0.866	0.12
	100	0.884	0.884	0.00
334.2	0	0.836	0.836	0.00
	25.05	0.854	0.853	0.12
	49.95	0.872	0.870	0.23
	75.05	0.889	0.888	0.11
	100	0.907	0.907	0.00
339.0	0	0.857	0.857	0.00
	25.05	0.875	0.874	0.11
	49.95	0.894	0.892	0.22
	75.05	0.912	0.911	0.11
	100	0.930	0.930	0.00
343.9	0	0.879	0.879	0.00
	25.05	0.897	0.896	0.00
	49.95	0.916	0.914	0.25
	75.05	0.934	0.934	0.12
	100	0.953	0.953	0.00

\*  $P = 1 \text{ atm}$ .

<sup>†</sup> %Deviation =  $|D_{\text{mix}}^{\text{Eq.6}} - D_{\text{mix}}^{\text{Eq.8}}| / D_{\text{mix}}^{\text{Eq.6}} \times 100$ .

than  $\pm 0.1^\circ\text{C}$ , and the working temperature range was  $315.20 < T < 343.90 \text{ K}$ .

## Results and Discussion

It has been shown previously (2,27) that the height of the sample peak ( $h$ ) in RFGC is given by the relation:

$$h = 2c(l',t) = \frac{6mD}{\sqrt{L^2}} \exp\left(-\frac{3D}{L^2}t\right) \quad \text{Eq. 1}$$

where  $c(l',t)$  is the concentration of the solute gas (CO or  $\text{CO}_2$ ) at  $x = l'$  (Figure 1), the time  $t$  (in seconds) is measured from the

moment of injecting the solute gas into the diffusion column,  $m$  is the amount of CO or  $\text{CO}_2$  injected (in mol),  $D$  is the diffusion coefficient of CO or  $\text{CO}_2$  into the carrier gas mixture of  $\text{H}_2$  and He (in  $\text{cm}^2/\text{s}$ ),  $\dot{V}$  is the volumetric flow rate of the carrier gas mixture (in mL/s), and  $L$  is the length of the diffusion column (in millimeters). The plot of  $\ln h$  versus  $t$  (after maximum) was linear during the whole experiment (Figure 3), thus making possible the determination of the diffusion coefficient of the pure gases CO and  $\text{CO}_2$  into the mixtures of  $\text{H}_2$  and He from the slope of the linear part of Figure 3 (Tables I and II).

The linear regression analysis of  $D_{\text{mix}}^{\text{exp}}$  for CO and  $\text{CO}_2$  into various mixtures of  $\text{H}_2$  and He against the hydrogen percentage volume composition ( $X_{\text{H}_2}$ ) at all temperatures referred to in

Temperature (K)	$X_{\text{H}_2}$ (%)	$D_{\text{mix}}^{\text{Eq.6}}$ ( $\text{cm}^2/\text{s}$ )	$D_{\text{mix}}^{\text{Eq.8}}$ ( $\text{cm}^2/\text{s}$ )	%Deviation <sup>†</sup>
315.2	0	0.509	0.509	0.00
	25.05	0.558	0.547	1.97
	49.95	0.606	0.590	2.64
	75.05	0.655	0.642	1.98
	100	0.703	0.703	0.00
320.0	0	0.523	0.523	0.00
	25.05	0.573	0.562	1.92
	49.95	0.622	0.606	2.57
	75.05	0.672	0.659	1.93
324.7	0	0.537	0.537	0.00
	25.05	0.588	0.577	1.87
	49.95	0.638	0.622	2.51
	75.05	0.689	0.676	1.89
	100	0.740	0.740	0.00
329.4	0	0.550	0.550	0.00
	25.05	0.603	0.591	1.99
	49.95	0.655	0.638	2.60
	75.05	0.708	0.694	1.98
	100	0.760	0.760	0.00
334.2	0	0.564	0.564	0.00
	25.05	0.618	0.606	1.94
	49.95	0.672	0.654	2.68
	75.05	0.725	0.711	1.93
	100	0.779	0.779	0.00
339.0	0	0.579	0.579	0.00
	25.05	0.634	0.622	1.89
	49.95	0.688	0.671	2.47
	75.05	0.743	0.729	1.88
	100	0.798	0.798	0.00
343.9	0	0.593	0.593	0.00
	25.05	0.650	0.637	1.97
	49.95	0.706	0.688	2.64
	75.05	0.763	0.748	1.98
	100	0.819	0.819	0.00

\*  $P = 1 \text{ atm}$ .  
<sup>†</sup> % Deviation =  $\left| \frac{D_{\text{mix}}^{\text{Eq.6}} - D_{\text{mix}}^{\text{Eq.8}}}{D_{\text{mix}}^{\text{Eq.6}}} \right| \times 100$ .

**Table VII. Percentage Volume Compositions of  $\text{H}_2$  ( $X_{\text{H}_2}^{\text{found}}$ ) in Mixtures of  $\text{H}_2$  and He Found by RFGC from Experiments of Diffusion of CO at Various Temperatures Versus the Determined by Independent GC Analysis Compositions of the Mixtures ( $X_{\text{H}_2}^{\text{given}}$ )**

Temperature (K)	$X_{\text{H}_2}^{\text{given}}$ (%)	$X_{\text{H}_2}^{\text{found}}$ (%)	%Accuracy*
315.2	0	-0.74	0.74 <sup>†</sup>
	25.05	25.77	2.87
	49.95	52.28	4.66
	75.05	77.23	2.90
	100	102.18	2.18
320.0	0	0.47	0.47 <sup>†</sup>
	25.05	21.73	13.25
	49.95	47.54	4.82
	75.05	77.92	3.82
	100	102.21	2.21
324.7	0	1.90	1.90 <sup>†</sup>
	25.05	27.07	8.06
	49.95	50.76	1.62
	75.05	77.40	3.13
	100	101.09	1.09
329.4	0	4.39	4.39 <sup>†</sup>
	25.05	27.49	9.74
	49.95	52,034.16	
	75.05	76.57	2.03
	100	98.23	1.77
334.2	0	0.21	0.21 <sup>†</sup>
	25.05	18.51	26.11
	49.95	46.66	6.59
	75.05	77.62	3.42
	100	94.51	5.49
339.0	0	2.78	2.78 <sup>†</sup>
	25.05	26.12	4.27
	49.95	52.20	4.50
	75.05	76.92	2.49
	100	101.63	1.63
343.9	0	4.33	4.33 <sup>†</sup>
	25.05	27.09	8.14
	49.95	52.52	5.15
	75.05	77.96	3.88
	100	100.72	0.72

\* Defined by equation 9.  
<sup>†</sup> These calculations were based on  $X_{\text{He}}^{\text{given}}$  and  $X_{\text{He}}^{\text{found}}$  values.

Tables I and II resulted in an empirical equation relating  $D_{\text{mix}}^{\text{exp}}$  to the individual diffusion coefficients of CO and CO<sub>2</sub> into the pure H<sub>2</sub> ( $D_{\text{H}_2}$ ) and He ( $D_{\text{He}}$ ), as they were calculated by the Fuller–Schettler–Giddings (F.S.G.) equation (28), as well as with the given percentage volume composition of the gas mixture. All of these equations are compiled in Tables III and IV. In order to investigate whether all of these relations obeyed a general empirical equation, we started from a particular equation (for instance, from one valid for CO at 315.2 K):

$$D_{\text{mix}}^{\text{exp}} = 0.754 + 0.066 X_{\text{H}_2} \quad \text{Eq. 2}$$

where 0.754 is the experimental diffusion coefficient of CO into

pure He in cm<sup>2</sup>/s and  $0.754 + 0.066 \times 1 = 0.820$  cm<sup>2</sup>/s is the diffusion coefficient of CO into pure H<sub>2</sub>. The same held for all of the studied temperatures and both solutes (CO and CO<sub>2</sub>). The general empirical equation for CO and CO<sub>2</sub> in all of the carrier gas mixtures and at all temperatures was derived from equation 2:

$$D_{\text{mix}}^{\text{exp}} = 0.754 + (0.820 - 0.754) X_{\text{H}_2} \quad \text{Eq. 3}$$

or

$$D_{\text{mix}}^{\text{exp}} = D_{\text{He}} + (D_{\text{H}_2} - D_{\text{He}}) X_{\text{H}_2} \quad \text{Eq. 4}$$

or

$$D_{\text{mix}}^{\text{exp}} = D_{\text{H}_2} X_{\text{H}_2} + D_{\text{He}} (1 - X_{\text{H}_2}) \quad \text{Eq. 5}$$

Thus, the empirical equation takes the simple form:

$$D_{\text{mix}} = X_{\text{H}_2} D_{\text{H}_2} + X_{\text{He}} D_{\text{He}} \quad \text{Eq. 6}$$

In order to test the validity of equation 6 (because the diffusion coefficient is not generally an additive parameter), we calculated the diffusion coefficients of CO and CO<sub>2</sub> into the various gas mixtures with the known volume composition at all of the working temperatures  $D_{\text{mix}}^{\text{cal}}$ , using the values calculated from the F.S.G. equation (Tables I and II). The accuracy given in the last column of Tables I and II was a measure of the deviation of the experimental values in this study from the calculated ones  $D_{\text{mix}}^{\text{cal}}$ , which was defined as:

$$\text{Accuracy (\%)} = \frac{|D_{\text{mix}}^{\text{exp}} - D_{\text{mix}}^{\text{cal}}|}{D_{\text{mix}}^{\text{exp}}} \times 100 \quad \text{Eq. 7}$$

In all cases the accuracy was very good because the percentage deviation was lower than 0.66, indicating that the proposed empirical equation 6 was valid at least for the systems used and the gas volume compositions applied.

The linear variation of  $D_{\text{mix}}^{\text{exp}}$  with  $X_{\text{H}_2}$  was also verified by Figures 4 and 5, in which, for comparison purposes, the variation of  $D_{\text{mix}}^{\text{cal}}$

<b>Table VIII. Percentage Volume Compositions of H<sub>2</sub> (<math>X_{\text{H}_2}^{\text{found}}</math>) in Mixtures of H<sub>2</sub> and He Found by RFGC from Experiments of the Diffusion of CO<sub>2</sub> at Various Temperatures Versus the Determined by Independent GC Analysis Compositions of the Mixtures (<math>X_{\text{H}_2}^{\text{given}}</math>)</b>			
Temperature (K)	$X_{\text{H}_2}^{\text{given}}$ (%)	$X_{\text{H}_2}^{\text{found}}$ (%)	%Accuracy*
315.2	0	0.81	0.81 <sup>†</sup>
	25	23.56	5.95
	50	50.63	1.36
	75	75.78	0.98
	100	98.53	1.47
320.0	0	1.47	1.47 <sup>†</sup>
	25	23.62	5.71
	50	50.81	1.72
	75	73.98	1.43
	100	101.17	1.17
324.7	0	1.28	1.28 <sup>†</sup>
	25	25.72	2.67
	50	48.79	2.32
	75	75.79	0.99
	100	98.86	1.14
329.4	0	0.83	0.83 <sup>†</sup>
	25	23.32	6.91
	50	51.09	2.28
	75	73.58	1.96
	100	100.87	0.87
334.2	0	0.76	0.76 <sup>†</sup>
	25	23.62	5.71
	50	50.69	1.48
	75	75.89	1.12
	100	101.56	1.56
339.0	0	0.62	0.62 <sup>†</sup>
	25	25.65	2.40
	50	50.69	1.48
	75	75.73	0.91
	100	98.94	1.06
343.9	0	1.17	1.17 <sup>†</sup>
	25	23.81	4.95
	50	51.33	2.76
	75	73.53	2.03
	100	100.61	0.61

\* Defined by equation 9.  
<sup>†</sup> These calculations were based on  $X_{\text{He}}^{\text{given}}$  and  $X_{\text{He}}^{\text{found}}$  values.

**Table IX. Experimental [ $D^{\text{exp}}(T^{\text{exp}})$ ] and Literature [ $D^{\text{lit}}(T^{\text{lit}})$ ] Diffusion Coefficients of CO and CO<sub>2</sub> into Pure H<sub>2</sub> and He at One Atmosphere**

Binary mixture	Temperature (K)	$D^{\text{exp}}(T^{\text{exp}})$ (cm <sup>2</sup> /s)	$D^{\text{lit}}(T^{\text{lit}})$ (cm <sup>2</sup> /s)	$D^{\text{exp}}(T^{\text{lit}})$ (cm <sup>2</sup> /s)	Deviation* (%)
CO→H <sub>2</sub>	295.6	0.820	0.743 (28) <sup>†</sup>	0.733	1.35
	315.2				
CO <sub>2</sub> →H <sub>2</sub>	298.0	0.700	0.646 (28) <sup>†</sup>	0.635	1.86
	315.2				
CO→He	295.6	0.754	0.702 (28) <sup>†</sup>	0.674	3.99
	315.2				
CO <sub>2</sub> →He	317.2	0.511	0.531 (28) <sup>†</sup>	0.517	2.64
	315.2				

\* % Deviation =  $\frac{|D^{\text{lit}}(T^{\text{lit}}) - D^{\text{exp}}(T^{\text{lit}})|}{D^{\text{lit}}(T^{\text{lit}})} \times 100$ .  
<sup>†</sup> Reference number.

was also involved. The assumption of the linear variation of  $D_{\text{mix}}^{\text{exp}}$  with gas volume composition (shown in Figures 4 and 5) has also been proven useful previously (29), as it is predicted from the Stefan–Maxwell (S.M.) equation for small mole fractions of the analyte gases (CO and CO<sub>2</sub>) into the mixtures of H<sub>2</sub> and He.

A similar equation results from the general form of the S.M. equation for the diffusion of an analyte gas (CO or CO<sub>2</sub>) in a multicomponent gas mixture (29), considering that the components of the mixture (H<sub>2</sub> and He) are stationary in the diffusion column (in which the diffusion process under study took place).

$$D_{\text{mix}} = \frac{D_{\text{H}_2} \times D_{\text{He}}}{X_{\text{H}_2} D_{\text{He}} + X_{\text{He}} D_{\text{H}_2}} \quad \text{Eq. 8}$$

A comparison of the  $D_{\text{mix}}$  values [as they were calculated from equation 8 ( $D_{\text{mix}}^{\text{Eq.8}}$ ) with those found from equation 6 ( $D_{\text{mix}}^{\text{Eq.6}}$ ) (Tables V and VI)] showed an excellent agreement in all cases, indicating that for the systems under study and the working composition and temperature ranges, the simple empirical equation 6 is valid with a high accuracy for the estimation of the diffusion coefficient of a pure gas into a gas mixture.

Equations 5 and 6 show that if the diffusion coefficient of a pure gas into a gas mixture with known components but with unknown volume composition is measured with a simple experi-

**Table X. Experimental ( $D_{\text{mix}}^{\text{exp}}$ ) and Theoretical ( $D_{\text{mix}}^{\text{cal}}$ ) as Calculated from Equation 6. Diffusion Coefficients of CO into Mixtures of H<sub>2</sub> and He of Various Volume Composition of H<sub>2</sub> ( $X_{\text{H}_2}$ ) at Various Temperatures\* Using Various Empirical Equations for the Estimation of the Diffusion Coefficient of CO into Pure H<sub>2</sub> and He**

Temperature (K)	$X_{\text{H}_2}$ (%)	$D_{\text{mix}}^{\text{exp}}$ (cm <sup>2</sup> /s)	F.S.G. (cm <sup>2</sup> /s)	S.M. (cm <sup>2</sup> /s)	H.B.S. (cm <sup>2</sup> /s)	C.O. (cm <sup>2</sup> /s)	F.S.G.	S.M. (%)	Deviation <sup>†</sup>	
									H.B.S.	C.O.
315.2	0	0.754	0.754	0.578	0.718	0.847	0.00	23.34	4.77	12.33
	25.05	0.771	0.770	0.611	0.715	0.848	0.13	20.75	7.26	9.99
	49.95	0.788	0.787	0.644	0.712	0.850	0.13	18.27	9.64	7.87
	75.05	0.804	0.803	0.676	0.709	0.852	0.12	15.92	11.82	5.97
	100	0.820	0.819	0.709	0.706	0.854	0.12	13.54	13.90	4.15
320.0	0	0.775	0.775	0.592	0.739	0.870	0.00	23.61	4.65	12.26
	25.05	0.789	0.791	0.625	0.736	0.872	0.25	20.79	6.72	10.52
	49.95	0.806	0.808	0.659	0.732	0.874	0.25	18.24	9.18	8.44
	75.05	0.826	0.824	0.692	0.729	0.876	0.24	16.22	11.74	6.05
	100	0.842	0.840	0.725	0.726	0.878	0.24	13.90	13.78	4.28
324.7	0	0.796	0.795	0.605	0.760	0.893	0.13	23.99	4.52	12.19
	25.05	0.813	0.812	0.639	0.756	0.895	0.12	21.40	7.01	10.09
	49.95	0.829	0.829	0.673	0.752	0.897	0.00	18.82	9.29	8.20
	75.05	0.847	0.845	0.707	0.748	0.899	0.24	16.53	11.69	6.14
	100	0.863	0.862	0.741	0.745	0.901	0.12	14.14	13.67	4.40
329.4	0	0.818	0.815	0.618	0.781	0.917	0.37	24.45	4.52	12.10
	25.05	0.834	0.832	0.653	0.776	0.919	0.24	21.70	6.95	10.19
	49.95	0.851	0.850	0.688	0.772	0.921	0.12	19.15	9.28	8.23
	75.05	0.868	0.867	0.723	0.768	0.923	0.12	16.71	11.52	6.34
	100	0.883	0.884	0.758	0.764	0.925	0.11	14.16	13.48	4.76
334.2	0	0.836	0.836	0.631	0.802	0.941	0.00	24.52	4.07	12.56
	25.05	0.851	0.854	0.667	0.798	0.943	0.35	21.62	6.23	10.81
	49.95	0.869	0.872	0.703	0.793	0.945	0.35	19.10	8.75	8.75
	75.05	0.891	0.889	0.739	0.789	0.947	0.22	17.06	11.45	6.29
	100	0.903	0.907	0.774	0.784	0.949	0.44	14.29	13.18	5.09
339.0	0	0.859	0.857	0.645	0.824	0.966	0.23	24.91	4.07	12.46
	25.05	0.876	0.875	0.682	0.819	0.968	0.11	22.15	6.51	10.50
	49.95	0.895	0.894	0.718	0.815	0.970	0.11	19.78	8.94	8.38
	75.05	0.913	0.912	0.755	0.810	0.972	0.11	17.31	11.28	6.46
	100	0.931	0.930	0.791	0.805	0.974	0.11	15.04	13.53	4.62
343.9	0	0.882	0.879	0.659	0.847	0.991	0.34	25.28	3.97	12.36
	25.05	0.899	0.897	0.694	0.842	0.993	0.22	22.80	6.34	10.46
	49.95	0.918	0.916	0.734	0.836	0.996	0.22	20.04	8.93	8.50
	75.05	0.937	0.934	0.771	0.831	0.998	0.32	17.72	11.31	6.51
	100	0.954	0.953	0.808	0.826	1.000	0.10	15.30	13.42	4.82
<b>Mean value of %deviation</b>							0.18	19.22	9.07	8.37

\*  $P = 1$  atm.

$$\dagger \% \text{ Deviation} = \frac{|D_{\text{mix}}^{\text{exp}} - D_{\text{mix}}^{\text{cal}}|}{D_{\text{mix}}^{\text{exp}}} \times 100.$$

ment in RFGC ( $D_{\text{mix}}^{\text{exp}}$ ) and the values calculated by the F.S.G. equation are used as diffusion coefficients of the analyte gas into the pure components of the mixture, we can determine the percentage volume compositions of the mixture  $X_{\text{H}_2}^{\text{found}}$  (Tables VII and VIII).

The precision of the values  $X_{\text{H}_2}^{\text{found}}$  (given in the last column of Tables VII and VIII) was the deviation of the experimental values ( $X_{\text{H}_2}^{\text{found}}$ ) from those determined by independent GC analysis ( $X_{\text{H}_2}^{\text{given}}$ ):

$$\text{Accuracy (\%)} = \frac{|X_{\text{H}_2}^{\text{found}} - X_{\text{H}_2}^{\text{given}}|}{X_{\text{H}_2}^{\text{found}}} \times 100 \quad \text{Eq. 9}$$

With the exception of the value  $X_{\text{H}_2}^{\text{found}} = 26.11\%$  (which can be

attributed to accidental errors), the average accuracy was 4.57% for the 34 values of  $X_{\text{H}_2}^{\text{found}}$  listed in Table VII for the diffusion of CO into various mixtures of H<sub>2</sub> and He at various temperatures, whereas it was 2.06% for the 35 values of  $X_{\text{H}_2}^{\text{found}}$  listed in Table VIII for the diffusion of CO<sub>2</sub> into the various mixtures and temperatures. The  $X_{\text{H}_2}^{\text{found}}$  values of Tables VII and VIII resulted in an average accuracy of 3.32%, which encourages us to further investigate the GC methodology for the estimation of the volume composition of gas mixtures (a project of great practical importance) using other substances and mixtures of gases to possibly modify the proposed empirical equation and increase its accuracy.

Apart from the comparison of the experimentally determined

**Table XI. Experimental ( $D_{\text{mix}}^{\text{exp}}$ ) and Theoretical ( $D_{\text{mix}}^{\text{cal}}$ ) as Calculated from Equation 6. Diffusion Coefficients of CO<sub>2</sub> into Mixtures of H<sub>2</sub> and He of Various Volume Compositions of H<sub>2</sub> ( $X_{\text{H}_2}$ ) at Various Temperatures\* Using Various Empirical Equations for the Estimation of the Diffusion Coefficient of CO<sub>2</sub> into Pure H<sub>2</sub> and He**

Temperature (K)	$X_{\text{H}_2}$ (%)	$D_{\text{mix}}^{\text{exp}}$ (cm <sup>2</sup> /s)	F.S.G. (cm <sup>2</sup> /s)	S.M. (cm <sup>2</sup> /s)	H.B.S. (cm <sup>2</sup> /s)	C.O. (cm <sup>2</sup> /s)	Deviation <sup>†</sup>			
							F.S.G.	S.M. (%)	H.B.S.	C.O.
315.2	0	0.511	0.509	0.503	0.559	0.733	0.39	1.57	9.39	43.44
	25.05	0.555	0.558	0.534	0.562	0.737	0.54	3.78	1.26	32.79
	49.95	0.608	0.606	0.565	0.566	0.741	0.33	7.07	6.91	21.88
	75.05	0.656	0.655	0.597	0.570	0.744	0.15	8.99	13.11	13.41
	100	0.700	0.703	0.628	0.573	0.748	0.43	10.29	18.14	6.86
320.0	0	0.526	0.523	0.515	0.575	0.754	0.57	2.09	9.32	43.35
	25.05	0.570	0.573	0.547	0.578	0.757	0.52	4.04	1.40	32.81
	49.95	0.624	0.622	0.578	0.582	0.761	0.32	7.37	6.73	21.96
	75.05	0.670	0.672	0.610	0.585	0.765	0.30	8.96	12.69	14.18
	100	0.724	0.722	0.642	0.588	0.768	0.28	11.33	18.78	6.08
324.7	0	0.534	0.537	0.526	0.590	0.774	0.56	1.50	10.49	44.94
	25.05	0.589	0.588	0.559	0.594	0.778	0.17	5.09	0.85	32.09
	49.95	0.636	0.638	0.591	0.597	0.781	0.31	7.08	6.13	22.80
	75.05	0.691	0.689	0.624	0.601	0.785	0.29	9.70	13.02	13.60
	100	0.738	0.740	0.656	0.604	0.789	0.27	11.11	18.16	6.91
329.4	0	0.552	0.550	0.538	0.606	0.794	0.36	2.54	9.78	43.84
	25.05	0.599	0.603	0.571	0.610	0.798	0.66	4.67	1.84	33.22
	49.95	0.657	0.655	0.604	0.613	0.802	0.31	8.07	6.70	22.07
	75.05	0.704	0.708	0.637	0.616	0.806	0.56	9.52	12.50	14.49
	100	0.761	0.760	0.671	0.620	0.810	0.13	11.83	18.53	6.44
334.2	0	0.566	0.564	0.549	0.623	0.815	0.35	3.00	10.07	43.99
	25.05	0.615	0.618	0.583	0.626	0.819	0.49	5.20	1.79	33.17
	49.95	0.673	0.672	0.617	0.629	0.823	0.15	8.32	6.54	22.29
	75.05	0.727	0.725	0.651	0.632	0.827	0.28	10.45	13.07	13.76
	100	0.782	0.779	0.685	0.636	0.831	0.39	12.40	18.67	6.27
339.0	0	0.580	0.579	0.561	0.639	0.837	0.17	3.28	10.17	44.31
	25.05	0.635	0.634	0.596	0.642	0.841	0.16	6.14	1.10	32.44
	49.95	0.690	0.688	0.631	0.646	0.845	0.29	8.55	6.38	22.46
	75.05	0.745	0.743	0.665	0.649	0.849	0.27	10.74	12.89	13.96
	100	0.796	0.798	0.700	0.652	0.853	0.25	12.06	18.09	7.16
343.9	0	0.596	0.593	0.573	0.657	0.859	0.51	3.86	10.23	44.13
	25.05	0.647	0.650	0.609	0.660	0.863	0.46	5.87	2.01	33.38
	49.95	0.709	0.706	0.644	0.663	0.867	0.42	9.17	6.49	22.28
	75.05	0.759	0.763	0.680	0.666	0.871	0.52	10.41	12.25	14.76
	100	0.820	0.819	0.715	0.669	0.876	0.12	12.80	18.41	6.83
<b>Mean value of % deviation</b>							0.35	7.40	9.83	23.95

\*  $P = 1$  atm.

$$\dagger \% \text{ Deviation} = \frac{D_{\text{mix}}^{\text{exp}} - D_{\text{mix}}^{\text{cal}}}{D_{\text{mix}}^{\text{exp}}} \times 100.$$



diffusion coefficients with those calculated from equation 8, in order to test the accuracy of the RFGC method in measuring gas diffusion coefficients, literature data concerning the diffusion coefficients of the analyte gases (CO and CO<sub>2</sub>) into the pure components of the mixtures (H<sub>2</sub> and He) were compiled in Table IX (28). Although the literature values referred to different temperatures, the experimental diffusion coefficients [ $D^{\text{exp}}(T^{\text{exp}})$ ] were reduced to the temperature  $T^{\text{lit}}$  [ $D^{\text{exp}}(T^{\text{lit}})$ ], in which the literature values [ $D^{\text{lit}}(T^{\text{lit}})$ ] are given, taking into account the 1.75 power temperature dependence of the diffusion coefficient proposed by the F.S.G. equation. The percentage deviation shown in the last column of this table indicates a relatively good accuracy. It must be pointed out that we did not find in the literature any diffusion coefficient values of CO and CO<sub>2</sub> in mixtures of H<sub>2</sub> and He for the purpose of comparison with our experimental data.

The choice of the F.S.G. equation to calculate the  $D_{\text{H}_2}$  and  $D_{\text{He}}$  that was to be used in equation 6 for the estimation of the diffusion coefficients of the analyte gases (CO and CO<sub>2</sub>) in the mixtures of H<sub>2</sub> and He was based on the fact that  $D_{\text{mix}}^{\text{exp}}$  was closer to  $D_{\text{mix}}^{\text{cal}}$  based on the F.S.G. equation. For comparison purposes, except for the F.S.G. equation, the S.M., Hirschfelder–Bird–Spotz (H.B.S.), and Chen–Othmer (C.O.) equations (28,30) were also used (Tables X and XI). The average percentage deviation calculated from equation 6 using as  $D_{\text{He}}$  the values estimated from the F.S.G., S.M., H.B.S., and C.O. equations were 0.18%, 19.22%, 9.07%, and 8.37%, respectively, for CO and 0.35%, 7.40%, 9.83%, and 23.95%, respectively, for CO<sub>2</sub>. These results indicate that the F.S.G. equation has the higher accuracy of all of the tested empirical equations because this relationship is the result of the fitting of more than 340 experimental diffusion coefficients owing to 153 different binary mixtures (28,30).

## Conclusion

From the results obtained in this study, the following conclusions can be drawn: (a) the experimental diffusion coefficients of CO and CO<sub>2</sub> into the pure gases H<sub>2</sub> and He were in excellent agreement with those calculated using the F.S.G. equation (28); (b) the experimentally determined RFGC diffusion coefficients of CO and CO<sub>2</sub> into H<sub>2</sub> and He were in good agreement with those found in the literature (28) using different techniques; (c) the found diffusion coefficients of CO and CO<sub>2</sub> in various mixtures of H<sub>2</sub> and He were in excellent agreement with those calculated using an empirical equation proposed for the first time in this study, which correlates the diffusion coefficient of the analyte gas (CO or CO<sub>2</sub>) in the gas mixture with the volume composition of the mixture and the diffusion coefficients of the analyte in the pure components of the mixture; (d) the experimental diffusion coefficients of CO and CO<sub>2</sub> in the mixtures of H<sub>2</sub> and He were in excellent agreement with those calculated using the known empirical S.M. equation (29); (e) the proposed empirical equation allowed for the estimation of the volume composition of the binary gas mixtures from the experimentally determined diffusion coefficients; and (f) the estimated compositions of the binary gas mixtures were in good agreement with those found independently by a routine GC analysis, indicating that the RFGC tech-

nique, in combination with the proposed empirical equation 6, can be successfully applied to the accurate determination of the volume composition of the gas mixtures. Possible sources of errors in the estimation of this composition were the following: (a) the experimental error of the RFGC method in measuring gas diffusion coefficients; (b) the error of the F.S.G. equation in estimating the diffusion coefficients of the analyte gases into the pure components of the mixture, which are necessary in the proposed empirical equation for the determination of the mixture's volume composition; and (c) the "gas imperfection correction", which takes into account the gas-phase interactions. It requires a knowledge of the second virial coefficients of the pure solute and the mixed second virial coefficients of a solute + carrier gas mixture. The size of the combined gas imperfection term increases through the carrier sequence N<sub>2</sub>→H<sub>2</sub>→He (31). This is supported by the fact that the percentage deviation of the found values ( $X_{\text{H}_2}^{\text{found}}$ ) from those determined by an independent routine GC analysis ( $X_{\text{H}_2}^{\text{given}}$ ) is higher in mixtures rich in He (25.05% H<sub>2</sub> + 74.95% He).

As a general conclusion, one could say that the RFGC technique can be successfully used for the estimation of the volume composition of binary gas mixtures. The proposed empirical equation relates satisfactorily the experimental values of diffusion coefficients of the gas solute into the gas mixture with the volume composition of the mixture and the diffusion coefficients of the solute gas into the pure components of the mixture as they are determined by the F.S.G. equation. The relatively high accuracies, taking into consideration the various errors of the method and the F.S.G. equation used, encourage us to further investigate the possible sources of errors in the proposed methodology so as to increase its accuracy.

## Acknowledgments

The authors thank Mrs. M. Barkoula for her assistance. Mr. Khan Rashid Atta is grateful to the Greek State Scholarships Foundation for the scholarship.

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Manuscript accepted January 28, 2003.