

# Determination of Binary Gas-Phase Diffusion Coefficients Using Chromatography<sup>†</sup>

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Binary diffusion coefficients of 15 organic vapors in nitrogen carrier gas were measured by using the peak arrest technique on a Hewlett-Packard 5840A gas chromatograph with a flame ionization detector. The experiments were conducted at atmospheric pressure, above the normal boiling point of the organic vapors. The experimentally obtained values were compared with those predicted by using various correlations and reported in literature. In general, the observed values were in excellent agreement with the values predicted by Fuller's correlation.

## Introduction

The binary diffusion coefficients of gases are important parameters needed in the design of reactors where gas-phase reactions are involved. Several techniques have been reported for the measurement of diffusion coefficients; however, evaluation of quantitative results is excessively time consuming in most of these techniques. Recent developments in the chromatographic theory have made it possible for rapid and accurate measurements of binary diffusion coefficients. Several of these techniques have been reviewed by Choudhary (1). Among these, the peak arrest method of Knox and McLaren (2) bypasses most of the experimental and theoretical difficulties encountered in the continuous elution methods. Several studies have been reported (3-8) recently using this technique for the measurement of binary diffusion coefficients of gases and organic vapors.

In the present work, the peak arrest technique is employed to measure the diffusion coefficients of 15 organic vapors with nitrogen as the carrier gas. The experimentally obtained values are compared with the predicted values by using the correlations of Fuller et al. (9), Chapman-Enskog (10), Slattery-Bird (11), Chen-Othmer (12), and Gilliland et al. (13).

## Experimental Procedure

Studies were conducted using a microprocessor-controlled gas chromatograph (HP 5840A) with a flame ionization detector. Nitrogen was used as a carrier gas and as a component of gas-vapor binary system. Nitrogen was predried by passing it through a sulfuric acid trap and a molecular sieve trap before its entry into the column. A stainless steel unpacked helical column of length 308 cm and internal diameter of 2.16 mm was employed. The carrier gas connection was made to the column through a three-way stopcock, and the volumetric flow rate ( $F$ ) was measured by means of a soap bubble flow meter with an accuracy of 1 s. The minimum time measured was around 300 s, whereas the maximum measured was 600 s. The output signal from the flame ionization detector was displayed by

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Table I. Physical Constants of Purified Components

component	refractive index		density	
	exptl	lit.	exptl	lit.
1-propanol	1.3860	1.3854 (14)	0.7955	0.7960 (17)
1-butanol	1.4000	1.3993 (15)	0.8023	0.8020 (17)
1-pentanol	1.4100	1.4099 (15)	0.8075	0.8076 (17)
1-hexanol	1.4130	1.4133 (14)	0.8186	0.8191 (15)
1-heptanol	1.4236	1.4233 (14)	0.8223	0.8219 (15)
1-octanol	1.4302	1.4304 (14)	0.8236	0.8239 (15)
nitrobenzene	1.5525	1.5524 (14)	1.1932	1.1936 (16)
chlorobenzene	1.5250	1.5251 (14)	1.0956	1.0948 (16)
bromobenzene	1.5602	1.5604 (14)	1.4814	1.4815 (17)
<i>o</i> -nitrotoluene	1.5475	1.5474 (14)	1.1628	1.1629 (17)
tetrachloroethane	1.4930	1.4921 (14)	1.5950	1.5953 (17)
methyl isobutyl ketone	1.3960	1.3959 (14)	0.8021	0.8025 (17)

Table II. Diffusion Coefficients of Organic Vapors in Nitrogen<sup>a</sup>

system	temp, K	$D_{AB}$ , cm <sup>2</sup> /s		lit. values <sup>b</sup>
		exptl	pred by Fuller's correln	
N <sub>2</sub> -1-propanol	373	0.153	0.159	
N <sub>2</sub> -1-butanol	393	0.161	0.155	
N <sub>2</sub> -1-pentanol	418	0.159	0.152	
N <sub>2</sub> -1-hexanol	433	0.141	0.147	
N <sub>2</sub> -1-heptanol	453	0.145	0.146	
N <sub>2</sub> -1-octanol	473	0.148	0.149	
N <sub>2</sub> -acetone	373	0.168	0.164	0.161 (20)
N <sub>2</sub> -methyl isobutyl ketone	423	0.141	0.144	
N <sub>2</sub> -chloroform	373	0.140	0.141	0.139 (20)
N <sub>2</sub> -carbon tetrachloride	373	0.120	0.127	0.118 (20)
N <sub>2</sub> -nitrobenzene	523	0.225	0.222	0.223 (7)
N <sub>2</sub> -chlorobenzene	423	0.165	0.164	
N <sub>2</sub> -bromobenzene	473	0.173	0.171	
N <sub>2</sub> - <i>o</i> -nitrotoluene	498	0.170	0.175	
N <sub>2</sub> -tetrachloroethane	423	0.143	0.145	

<sup>a</sup> Pressure = 1 atm. <sup>b</sup> Corrected to the experimental temperature.

means of variable-speed chart recorder; in order to get a broader peak the chart speed through out the investigation was maintained at 1 cm/min.

Among the chemicals used, acetone, carbon tetrachloride, and chloroform were of spectroscopic grade. The others were purified by doubly distilling in a packed column; the first and last portions of the distillate were discarded and the rest was used in the measurements. Physical properties such as density and refractive index were measured at the temperature of referred literature value and compared in the chart given in Table I.

A typical experimental run was started by maintaining a constant flow rate of the carrier gas for over an hour. Meanwhile the chromatograph was turned on and stabilized. A sharp band of organic liquid (1  $\mu$ L) was injected during the shortest possible time and eluted from the column at a known linear velocity,  $V$  (cm/s). The retention time was noted. In the subsequent runs, when the band moved about half-way down the column, the flow was stopped by diverting the carrier gas outside the column using the three-way stopcock. The flow of the carrier gas was stopped for an arrest time,  $t$  (s), during which band spreading occurred as a result of diffusion only. The band was eluted after the arrest time and its spreading recorded. Runs were repeated with different arrest times for the

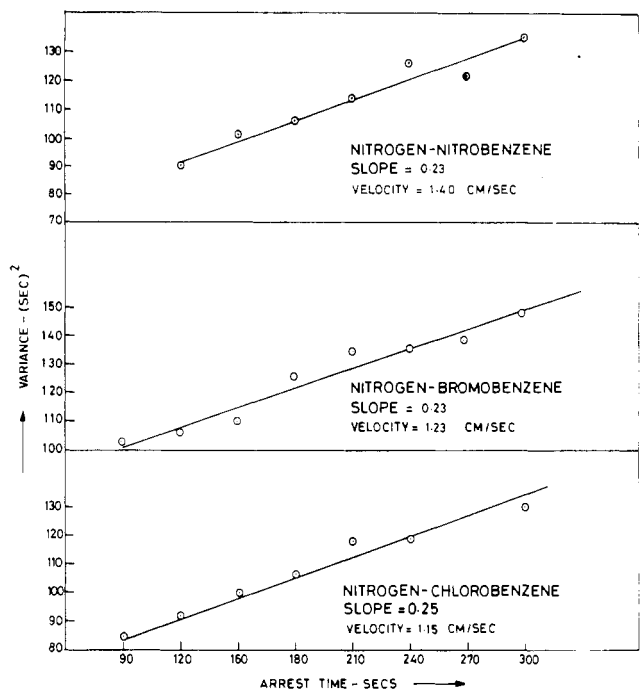


Figure 1. Rectangular plots of variance square vs. arrest time.

same gas velocity. Thus at a particular gas velocity, different values of standard deviation ( $\sigma_t$ ) were obtained for the corresponding arrest time by measuring the peak width. These were measured to an accuracy of 0.5 mm. This accuracy corresponds to a maximum error of 2.5% in the peak width measurement. This complete operation constituted one run. Runs were repeated with the same and different flow velocities for checking reproducibility.

### Results and Discussions

Table II shows the comparison of experimental and theoretical values predicted by Fuller's correlation of different binary pairs. The percentage deviation from Fuller's value (9) is minimum (0.7–5.8). The experimental values are also compared with the values of Slattery–Bird (11), Chen–Othmer (12), Gilliland (13), and the theoretically formulated Chapman–Enskog (10) method. The percentage deviations from these correlations are (0.7–15.3), (0.8–11.2), (5.2–25.8), and (0.6–22.8), respectively. The experimental values also compare well with the literature values available for the four binary pairs shown in the Table II.

The likely error in the experimental results may be attributed to the factors like dispersion, dead volume, nonconstant flow, detection, and measuring peak width. Every attempt was made to minimize these effects through a careful choice of column size and material, sample injection, and detection. Trial runs were conducted by varying the sample size from 1–5  $\mu\text{L}$ . The peak width remains unchanged, confirming that the sample size has no detectable effect on the dispersion of the peak. Evans and Kenny (18) demonstrated that the injected sample should not be more than 1% of the volume of the dispersion tube, and 1  $\mu\text{L}$  of the sample used during these runs is well within this limitation and it developed an excellent chromatograph.

According to Wakeham and Slater (19), the Reynolds number employed should be as low as possible. In the present investigation the carrier gas flow rate was 1–2 cm/s. In order to maintain constant gas flow rates sensitive flow regulators were deployed. For each experimental point the gas flow rate was checked 3–4 times.

The flow rate measured by the soap bubble flow meter was

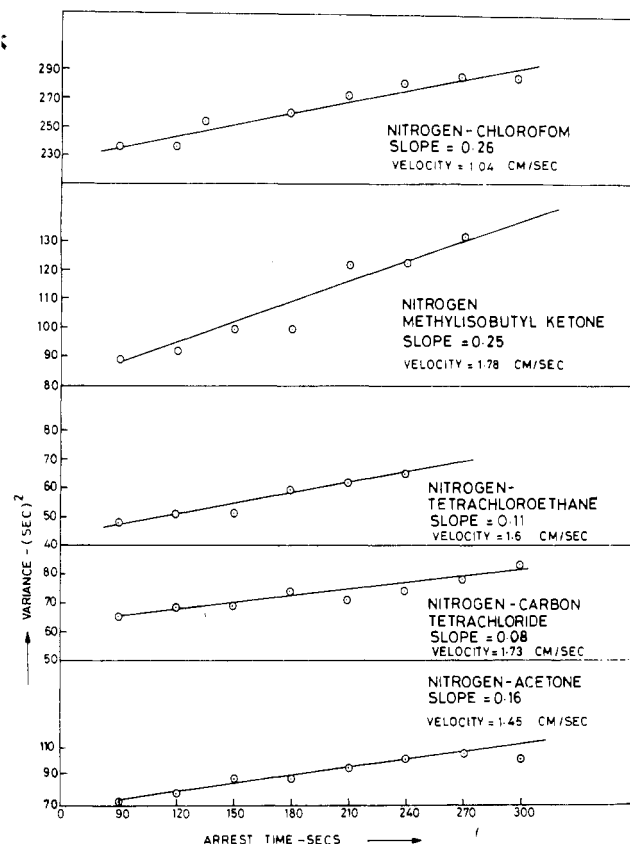


Figure 2. Rectangular plots of variance square vs. arrest time.

corrected to the conditions prevailing in the column by using the equation (5)

$$F_c = F \frac{T}{T_{fm}} \frac{(P_{fm} - P_w)}{P_{fm}} \quad (1)$$

In eq 1,  $T$  and  $T_{fm}$  are the column and flow meter temperatures and  $P_{fm}$  and  $P_w$  are the flowmeter and water-vapor pressures at  $T_{fm}$ , respectively. The corrected flow rate ( $F_c$ ) thus obtained was corrected for compressibility. The compressibility factors were calculated from the values of inlet and outlet pressure ( $P_i$  and  $P_o$ ), using the procedure given by Conder and Young (6). The linear velocity,  $V$ , was obtained from this corrected flow rate by the relation  $V = F_c/A$ . The average reading of 3–4 measurements of the diameter was taken to calculate the cross-sectional area ( $A$ ) of the tube.

The other sources of error, namely, timing and geometrical measurements, contribute to an uncertainty of only  $\pm 0.2\%$  (18). This was reduced by taking the average of 3–4 measurements. The error in peak width measurement was further reduced by keeping the chart speed at 1 cm/min in order to get a broader peak. For each experimental point three runs were conducted and the average peak width was determined from them. The standard deviation of the eluted peak was obtained from the peak width,  $W$ , by using the equation  $\sigma_t = W/4$ . Triangulation method was used for smoothing the peak width at the base.

A rectangular plot of variance,  $\sigma_t^2$ , vs. arrest time,  $t$ , was prepared for each experimental run. The resulting plot was linear and a straight line was fitted by using a linear square program. The slope of the line was used to obtain the diffusion coefficient directly from the following equation (12)

$$\frac{d}{dt} \sigma_t^2 = \frac{2D_{AB}}{V^2} \quad (2)$$

where  $D_{AB}$  ( $\text{cm}^2/\text{s}$ ) is the binary diffusion coefficient. Typical

plots of  $\sigma_t^2$  vs. arrest time are shown in Figures 1 and 2. Taking into account all the precautions discussed above the maximum possible error in the experimental results can be of the order of error in the peak width measurements.

### Conclusion

Arrested flow technique has been used to measure binary gas diffusion coefficients of organic vapors in nitrogen. This technique is the quickest and reasonably accurate method available to the experimentalists today. The observed values of the diffusion coefficients are in excellent agreement with values predicted from Fuller's correlation, and for the four systems  $N_2$ -acetone,  $N_2$ -chloroform,  $N_2$ -carbon tetrachloride, and  $N_2$ -nitrobenzene, the experimental values match nicely with those reported in the literature. Experiments are in progress to extend the data base for other organic vapors with nitrogen and hydrogen as the carriers. It is also proposed to conduct experiments covering a wider range of temperatures.

### Glossary

$A$	cross-sectional area, $cm^2$
$D_{AB}$	binary diffusion coefficient, $cm^2/s$
$F, F_c$	volumetric flow rates, $cm^3/s$
$P_{fm}, P_w$	flow meter and water-vapor pressure at $T_{fm}$ , atm
$t$	arrest time, s
$T, T_{fm}$	temperatures of column and flow meter, K
$P_i, P_o$	column inlet and outlet pressures, atm
$V$	linear velocity, $cm/s$
$W$	peak width at base, cm

### Greek Letters

$\sigma_t$	standard deviation, $s^2$
$\mu$	micro

**Registry No.** 1-Propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; acetone, 67-64-1; methyl isobutyl ketone, 108-10-1; chloroform, 67-66-3; carbon tetrachloride, 58-23-5; nitrobenzene, 98-95-3; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; *o*-nitrotoluene, 88-72-2; tetrachloroethane, 79-34-5.

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## Activity Coefficients of Hexaamminecobalt(III) Iodate in Aqueous Solutions of Different Electrolytes

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The solubility of hexaamminecobalt(III) iodate in aqueous solutions of NaCl, KCl,  $NH_4Cl$ ,  $NaNO_3$ ,  $KNO_3$ ,  $NH_4NO_3$ , NaBr, KBr,  $NH_4Br$ ,  $(CH_3)_4NBr$ ,  $(C_2H_5)_4NBr$ ,  $(C_3H_7)_4NBr$ , and  $(C_4H_9)_4NBr$  has been determined over an ionic strength range of 0.032–0.20 mol  $kg^{-1}$  at 298.15 K by a spectrophotometric method. The solubility results were treated to yield the relative activity coefficients.

### Introduction

Investigations of the thermodynamic properties of aqueous solutions of mixed electrolytes are interesting because they serve to study ion-ion interactions. A detailed examination of activity coefficients, especially by means of solubility measurements, has shown (1–3) the activity of ions to depend

markedly on their individual natures and also to be influenced by the nature of the ions of the salt solutions serving as solvents.

The present investigation is designed to complement the previous study of the effect of different electrolytes on the solubility of  $(Co(NH_3)_6)_2(C_2O_4)_3$  and of  $Co(NH_3)_6Fe(CN)_6$ . The relative activity coefficients of hexaamminecobalt(III) iodate in the presence of different electrolytes were evaluated from solubility determinations and are reported in this work.

### Experimental Section

**Materials.** Hexaamminecobalt(III) iodate was prepared by precipitation of hexaamminecobalt(III) chloride with an aqueous solution of sodium iodate (Carlo-Erba RPE), as described in the literature (3, 4) and was recrystallized. Analysis gave the following mass percentages: Co, 8.4 and  $NH_3$ , 15.0. The calculated values for  $Co(NH_3)_6(IO_3)_3$  are Co, 8.6 and  $NH_3$ , 14.9. Hexaamminecobalt(III) chloride was the same as that used in previous work (1, 2). All the other salts were Merck, Riedel,

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