Diffusion of Some Organic and Inorganic Compounds in Air

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Diffusion coefficients in air at 298.2°K and 1 atm have been determined for carbon dioxide, nitrous oxide, propane, isobutane, *n*-pentane, dichlorodifluoromethane, vinyl chloride, and vinylidene chloride. The experimental method observed, by infrared spectrophotometry, concentration changes of a gas diffusing from a cell into the atmosphere.

Data on the diffusion in air of compounds of commercial importance were, until recently, scant. Fuller et al. (*3*) have tabulated much older data, while Lugg (*9*) has published the results of measurements made on 147 different conpounds. Some data have also been obtained in this laboratory (*2*, *15*). Such data can be of value in toxicological studies. This paper presents the results of measurements on the diffusion coefficients in air of a number of compounds, most of which are commonly used as propellants in aerosol sprays.

EXPERIMENTAL

The compounds studied were pure grade (99 mol % or better), except where stated otherwise, and obtained in cylinders from the following sources: nitrous oxide and vinyl chloride, Matheson; propane and isobutane, Phillips Petroleum Co.; dichlorodifluoromethane (Freon 12), Du Pont; vinylidene chloride (contained polymerization inhibitor), The Dow Chemical Co. The *n*-pentane was supplied by the Ashland Refining Co., purity 98.5%, the residue being isopentane and cyclopentane. The carbon dioxide was obtained by evaporation of solid carbon dioxide.

Since the experimental method has been described in detail elsewhere (*2*), only a brief description is required here. The diffusion cell was an infrared absorption cell fitted with a side arm of precision bore capillary open to the atmosphere. This capillary was the defined path along which gas diffused from the cell to the atmosphere. The cell, filled with air containing a suitable concentration of the diffusing species, was placed in the beam of an infrared spectrophotometer. Changes in the gas concentration in the cell were followed by periodic determination of the infrared absorbance of a suitable absorption band. The solution of Fick's law for the conditions of this experiment are

$$\ln \alpha = -\mathfrak{D}(A/lv)t + B$$

where $\mathfrak{D}$ is the binary gaseous diffusion coefficient for equimolar counterdiffusion, α is the infrared absorbance at time t, v is the cell volume, A and l are the cross-sectional area and length, respectively, of the capillary, and B is a constant of integration. The diffusion coefficient was calculated from the slope of the best straight line on a plot of ln α against t as calculated by the method of least squares (*14*).

Several experiments were conducted for each compound at ambient temperature; consequently there is a variation of a few tenths of a degree during a single run, and of up to four degrees between different runs for the same compound due to day-to-day fluctuations in laboratory temperature. The temperature was averaged for each run. The runs in a single set were corrected to 298.2°K using the relationship

$$\mathfrak{D} = D_0 T^{1.75}$$

The temperature exponent of 1.75 appears to be the best average value for gaseous diffusion coefficients (*3*). Any error introduced by this procedure will be small and well within the experimental error because of the small adjustment in the value of the diffusion coefficient. The barometric pressure was recorded during each experiment, and all results are corrected to 1 atm pressure.

RESULTS AND DISCUSSION

The mean diffusion coefficient for each system, together with its standard deviation calculated in the usual way (*14*), is given in Table I. The infrared frequency used to follow concentration changes in the diffusion cell and the number of data obtained are also recorded.

The standard deviation of the majority of the data is in the range 1.3–4.3%. Vinyl chloride has the lowest precision of this group, perhaps because the frequency of the infrared peak used to follow the diffusion of vinyl chloride is in the water region of the spectrum. The relative humidity in the laboratory showed a day-to-day variation in the range 43–56%, so atmo-

Table I. Results of Diffusion Coefficient Measurements. Corrected to 298.2°K

Compound	Ir frequency, cm^{-1}	No. of data	$\text{Cm}^2\ \text{sec}^{-1}$ Exptl	Calcd	
CO_2	2360	10	0.1660 ± 0.0028	0.1530,	0.1521
N_2O	2240	6	0.1410 ± 0.0020	0.1530,	0.1535
Propane	2972	6	0.1144 ± 0.0015	0.1147	
Isobutane	2969	6	0.0964 ± 0.0016	0.1000	
n-Pentane	2970	6	0.0856 ± 0.0035	0.0881	
Dichlorodifluoromethane	1160 and 1100	6	0.0944 ± 0.0037		
Vinyl chloride	1620 (H_2O region)	6	0.1225 ± 0.0053		
Vinylidene chloride	1024 and 940	6	0.1144 ± 0.0087		

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spheric moisture may well have interfered with these measurements. The precision of the vinylidene chloride value is considerably lower than that of the other measurements. It is known that liquid vinylidene chloride dissolves oxygen and rapidly reacts with it to form a peroxide (*10, 11*). Thus, it seems likely that this reaction is taking place in the gas phase in the diffusion cell causing loss of precision in the measurements.

Of the systems studied, only carbon dioxide and *n*-pentane have been investigated previously. Andrew (*1*) obtained 0.165 ± 0.003 $cm^2\ sec^{-1}$ for the diffusion coefficient of carbon dioxide in air at 293°K while Holsen and Strunk (*6*) found 0.142 ± 0.0007 and 0.177 ± 0.0017 $cm^2\ sec^{-1}$ at 276.2 and 317.2°K, respectively. Agreement with the present result is within experimental error when allowance is made for the small temperature difference. Lugg (*9*) obtained 0.0842 ± 0.00182 $cm^2\ sec^{-1}$ for *n*-pentane in air at 298°K, in excellent agreement with the present result.

Values of the diffusion coefficients for several systems were calculated as described previously (*2, 15*) using a kinetic theory equation (*5*), together with values of the collision integral for a Lennard-Jones 6–12 potential function tabulated by Hirschfelder et al. (*5*). Molecular interaction parameters for like-like interactions calculated from viscosity measurements and tabulated (*5*) were combined using the Hudson-McCoubrey combining rules (*8*). The ionization potentials used in this calculation were Stevenson and Hipple's value for isobutane (*12*), Honig's value for propane and *n*-pentane (*7*), Tate and Baker's value for dichlorodifluoromethane (*13*) and values for other compounds given by Herzberg (*4*).

For carbon dioxide and nitrous oxide two sets of values of the intermolecular interaction parameters were used. Diffusion coefficients calculated with the two sets are, for all practical purposes, the same. The discrepancy between experimental and theoretical values is about 8%. For the three hydrocarbons, agreement between experimental and theoretical results is excellent.

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Electromotive Force Studies of Cell, $Cd_xHg_y\,|\,CdSO_4(m)\,|\,Hg_2SO_4$, Hg, in Dioxane–Water Media

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From the emf measurements of cell, $Cd_xHg_y|CdSO_4(m)|Hg_2SO_4$, Hg, at 25°, 30°, and 35°C, the $-\Delta G°$, $-\Delta H°$, and $-\Delta S°$ for the reaction, $Cd + H_2SO_4 \rightarrow CdSO_4 + 2Hg$, have been calculated. The dissociation constants of $CdSO_4$ in dioxane–water media are 8.5×10^{-4}, 4.0×10^{-5}, and 2.5×10^{-8}, respectively, in 20, 40, and 60% by wt of dioxane in dioxane–water media at 25°C. The effect of temperature appears to be small.

In this communication the electromotive force studies of cadmium sulfate in dioxane–water media have been reported. For the purpose the cell,

$$Cd_xHg_y|CdSO_4(m),\ \text{dioxane}(X)\ H_2O(Y)|Hg_2SO_4,\ Hg \qquad (1)$$

has been set up and the emf measured at different temperatures. From these the thermodynamic properties of the system have been evaluated.

EXPERIMENTAL

BDH, AR-grade cadmium sulfate was used in preparing the solution. The concentration of the stock solution was checked by estimating sulfate gravimetrically and cadmium by EDTA titration.

The purification of the solvents has been described earlier (*1*). Hg, Hg_2SO_4 electrode was set up in the manner reported in our earlier communication. The cadmium amalgam (11% Cd) was prepared and the cell filled following the method of Harned and Fitzgerald (*3*) in an atmosphere of nitrogen instead of under vacuum. Pure and presaturated nitrogen was bubbled through

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