

acid to the resulting solution of the quaternary hydroxide, clusters of yellow needles from ethanol, m. p. 125.4°.

Anal. Calcd. for $C_{15}H_{22}N_4O_7$: C, 48.64; H, 5.99; N, 15.13. Found: C, 48.92; H, 5.98; N, 15.04.

Mixing an aqueous solution of this salt with another of sodium picrate gave the mixed salt, m. p. 188°.

Allyltrimethylammonium bromide (IV), obtained by the method used to prepare I, formed a picrate, long yellow needles from ethanol-water, m. p. 220.3–220.5° dec.

Anal. Calcd. for $C_{12}H_{16}N_4O_7$: C, 43.90; H, 4.91. Found: C, 43.92; H, 4.71.

The action of sodium styphnate on IV in aqueous solution gave a styphnate, long slender yellow bars from water, m. p. ca. 155° dec.

(2,3-Dibromo-*n*-propyl)-trimethylammonium bromide (V) was prepared from IV as described above in the preparation of II, colorless flossy sheaves from ethanol, m. p. 178° dec. (Partheil (see ref. 2) gives m. p. 173°). The picrate was recrystallized from ethanol, brilliant yellow needles, m. p. 127.5–128.5°.

Anal. Calcd. for $C_{12}H_{16}Br_2N_4O_7$: C, 29.53; H, 3.30. Found: C, 29.56; H, 3.31.

Hydrogenation of V (0.68 g.) was carried out as with II. After one hour, the hydrogen-uptake was negligible and 109.6 ml. had been absorbed (theory 103.5 ml.). The light brown crystalline residue obtained by evaporation of the catalyst-freed solution weighed 0.36 g. (calcd. 0.36 g.). The picrate prepared from this crude product was identical with an authentic sample of *n*-propyltrimethylammonium picrate (m. p. and mixed m. p., see below).

Authentic *n*-propyltrimethylammonium bromide was prepared from *n*-propyl bromide by the action of trimethylamine in benzene; the crude product was dissolved in a small amount of warm ethanol and diluted with acetone, irregular etched colorless bars or parallelepiped plates, m. p. 242.5–243.0° dec.

Anal. Calcd. for $C_6H_{10}BrN$: C, 39.57; H, 8.86; N, 7.69. Found: C, 39.42; H, 8.73; N, 7.77.

The corresponding picrate formed opaque yellow striated bars from water, m. p. 200–201°.¹¹

(11) Hanhart and Ingold, *J. Chem. Soc.*, 1014 (1927), give m. p. 195–196°; Ries, *Z. Kryst. und Min.*, **55**, 485 (1915–1920), m. p. 207°.

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Diffusion Coefficients and Molecular Radii of Hydrogen Cyanide, Cyanogen Chloride, Phosgene and Chloropicrin¹

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In studies of the mechanism of removal of gases by porous adsorbents such as charcoal, it is necessary to have information on the diffusion coefficients of these molecules in air.² While approximate methods are available for estimating these coefficients³ it was considered desirable to obtain accurate information for a number of substances of historical interest as toxic agents. Since classical kinetic theory correlates the molecular radius with the diffusion coefficient of a gas, it is also possible to use the data obtained to calculate radii for the substances investigated. These radii may be of particular interest in connection with the

(1) This work was performed under OSRD contract OEMsr-282 between Northwestern University and the Office of Scientific Research and Development, Washington, D. C.

(2) I. M. Klotz, *Chem. Rev.*, **39**, 241 (1946).

(3) E. R. Gilliland, *Ind. Eng. Chem.*, **26**, 681 (1934).

determination of surface areas from adsorption methods.

Experimental

The rate of evaporation of the substance in the liquid state was measured with an apparatus which is essentially the Winkelmann modification of Stefan's method.⁴ In brief the diffusion coefficient is determined by following the rate of fall of the meniscus of a column of the liquid in a small glass tube across the top of which a current of fresh air is blown. Experiments were carried out at a number of different rates of flow in order to be certain that zero concentration of toxic gas was maintained at the open end of the small glass tube. All experiments were carried out in duplicate. Temperatures were constant within $\pm 0.05^\circ$.

Results and Calculations

The diffusion coefficient, D , was calculated from the equation

$$D = \frac{x \Delta p RT}{M \rho \bar{p} \ln \left[\frac{\bar{p}}{\bar{p} - p_s} \right]} \quad (1)$$

where

- x = average distance, in cm., from the level of the meniscus to the top of the tube during the experiment
- Δx = change in the level of the meniscus in the time t
- ρ = density of the liquid
- R = gas constant
- T = absolute temperature
- M = molecular weight of the vapor
- \bar{p} = total pressure
- p_s = saturation pressure of the vapor at the temperature T

The results obtained are summarized in Table I.

TABLE I

Vapor	Temperature, °C.	D (sq. cm./sec.)
CCl_3NO_2	25	0.088
$COCl_2$	0	.095
$CNCl$	0	.111
HCN	0	.173

From Table I, it is evident that the diffusion coefficient rises with decreasing molecular weight, as would be expected from the kinetic theory of gases. It is also of interest to note that the values obtained fall quite close to the approximate curve used previously for general calculations.²

Estimates of the radii of these vapor molecules have been made from the measured diffusion coefficients with the aid of the equation^{5,6}

$$(r + 1.54 \times 10^{-8})^2 = \frac{\sqrt{\bar{C}_1^2 + \bar{C}_2^2}}{3\pi D n (1 + \alpha)} \quad (2)$$

where

- r = the radius of the vapor molecule
- \bar{C}_1 = the mean velocity of the vapor molecule
- \bar{C}_2 = the mean velocity of an air molecule
- $\bar{C} = 0.921 \sqrt{3RT/M}$
- n = the number of molecules in one cc. of air at 760 mm. and the temperature T
- α = a correction factor depending on the relative masses of the vapor and air molecules^{5,6}

(4) K. Jellinek, "Lehrbuch der physikalischen Chemie," Vol. II, 2nd ed., F. Enke, Stuttgart, 1928, pp. 615–618.

(5) J. H. Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge, 1921, p. 316.

(6) E. Mack, Jr., *THIS JOURNAL*, **47**, 2468 (1925).

The average radius of an air molecule was taken as 1.54×10^{-8} cm.⁶ and is the second term in the parentheses on the left-hand side of the equation.

The radii so calculated are listed in Table II, together with molecular radii calculated from the densities of the corresponding liquids on the assumption that the molecule occupies a volume equal to that of a cube with a side whose length equals the diameter of the molecule. The agreement between the two methods is excellent.

TABLE II
MOLECULAR RADII

Vapor	From diffusion coefficient, in Å.	From liquid density, in Å.
CCl ₃ NO ₂	2.78	2.75
COCl ₂	2.42	2.45
CNCl	2.31	2.19
HCN	2.03	2.00

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Dielectric Studies. VIII. Dipole Moments of Solvents in Nonpolar Solvents of Unknown Molecular Weights¹

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In a recent paper Li and Chu³ reported the dipole moment of acetonitrile in three solvents of unknown and variable molecular weights, namely, gasoline, kerosene and petroleum ether. It was shown that in determining the molar polarization at infinite dilution, graphical extrapolation is not necessary and the molecular weight of the non-polar solvent used need not be known, if the dielectric constant and density of dilute solutions are linear functions of weight fractions of the solute. In this study we report dipole moment values of two polar solvents, namely, acetone and chloroform in two different samples of gasoline of different physical properties.

Acetone of tested purity was refluxed over potassium permanganate, placed over anhydrous calcium chloride and subsequently carefully fractionated. The fraction boiling between 56 and 56.5° was taken, its refractive index being n_{25}^D 1.3567. Chloroform of U.S.P. grade was purified from alcohol by one thorough extraction with 9 *M* sulfuric acid followed by six extractions with water. The product was dried over freshly-fused calcium chloride and distilled, b. p. 61–61.5°. Gasoline, colorless grade, was used without further purification. The samples came from different sources with different refractive indices: sample A, n_{25}^D 1.4242; sample B, n_{25}^D 1.4287.

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City Meeting, April, 1947.

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(3) Li and Chu, *THIS JOURNAL*, **69**, 558 (1947).

The apparatus for determinations of dielectric constant, density and refractive index have been described by Li and Chu.²

The results of the experimental work are presented in Tables I and II. The dielectric constant data are accurate to about 0.1%.

TABLE I

Acetone in gasoline (sample A) 25°			Chloroform in gasoline (sample B) 15°		
W_2	E	d	W_2	E	d
0.0000	2.032	0.7452	0.0000	2.051	0.7525
.0182	2.253	.7461	.0384	2.097	.7708
.0330	2.452	.7466	.0582	2.119	.7795
.0541	2.700	.7475	.0719	2.136	.7856
.0615	2.778	.7479	.0933	2.163	.7943
.0861	3.111	.7489			

In Table I the headings W_2 , E , d are the weight fraction of solute, dielectric constant and density, respectively.

TABLE II

CONSTANTS OF THE GASOLINE

	Sample A	Sample B
$C (= 3/d_1(E_1 + 2)^2)$	0.2476	0.2430
$p_1 = (E_1 - 1)/(E_1 + 2)d_1$.3435	.3447

Subscript 1 refers to solvent.

Data in Table I indicate that dielectric constant and density are linear functions of weight fractions W_2 , and therefore the method and formulas described by Li and Chu² can be used and a knowledge of the molecular weight of the non-polar solvent is not necessary. The formulas used are

$$P_{2(\infty)} = [p_1(1 - b) + CaE_1]M_2 \quad (1)$$

$$\mu = 0.01273 \times 10^{-18} \sqrt{(P_{2(\infty)} - P_{2D})T} \quad (2)$$

where $P_{2(\infty)}$ is the molar polarization of the solvents at infinite dilution, p_1 is the specific polarization of the solvent $\left(\frac{E_1 - 1}{E_1 + 2} \frac{1}{d_1}\right)$, a and b are the dielectric constant and density coefficients in the equations $E = E_1(1 + aW_2)$ and $d = d_1(1 + bW_2)$, respectively, $C = 3/d_1(E_1 + 2)^2$, M_2 is the molecular weight of the solute. The dipole moments for acetone and chloroform in gasoline are calculated to be 2.8 and 1.16×10^{-18} , respectively. These values are in good agreement with the values given in the literature, namely, 2.72 and 1.15×10^{-18} , respectively, when solvents of known and definite molecular weights were used.

For the past four years the senior author of this paper and his students have examined over ten different compounds dissolved in non-polar solvents of unknown molecular weights. In each case they have found that the dielectric constant and density of the mixture are linear functions of weight fractions for solutions whose concentrations are less than 8%, and that the values of the dipole moments thus obtained are correct. Many different samples of gasoline, kerosene and petroleum