

TABLE I
THE VAPOR PRESSURE OF NORMAL DEUTERIUM

Run no.	Temp., °K.	Press. obsd., atm.	Press., atm.	Equation (1)		
				obsd. - calcd.	$\frac{\Delta P}{\Delta T}$ obsd. - calcd.	
Triple point ^a						
	18.72	0.1691	0.1692	-0.0001	0.00	
"	21.00	.4239	.4320	-.0081	.04	
"	22.00	.6033	.6128	-.0095	.04	
"	23.00	.8371	.8398	-.0027	.01	
Boiling point ^a						
1	23.57	1.0000	1.0004	-.0004	.00	
2	29.00	3.6988	3.6864	.0124	-.02	
3	29.85	4.3644	4.3490	.0154	-.02	
4	30.90	5.2747	5.2777	-.0030	.00	
5	31.95	6.3265	6.3386	-.0121	.01	
6	32.89	7.3895	7.4100	-.0205	.02	
7	33.91	8.7122	8.7136	-.0014	.00	
8	35.00	10.2530	10.283	-.030	.02	
9	35.79	11.526	11.544	-.018	.01	
10	36.65	13.062	13.045	.017	-.01	
11	37.49	14.636	14.648	-.012	.00	
12	37.81	15.357	15.297	.060	-.02	
13	37.93	15.575	15.546	.029	-.01	
14	37.97	15.639	15.630	.009	.00	
15	37.99	15.701	15.672	.029	-.01	
16	38.02	15.754	15.735	.019	.00	
17	38.06	15.829	15.819	.010	.00	
18	38.19	16.071	16.097	-.026	.01	
18	Critical point	38.34	16.4215	16.420	.001	.00

^a Cf. ref. 7.

with the results of our four-constant equation obtained by the method of least squares.

Equation 1

$$\log p(\text{atmospheres}) = 3.57979 - 74.2894/T - 0.029345T + 0.00047507T^2 \quad (1)$$

represents the data to within 0.02°K., which is the absolute uncertainty in the temperature scale. This equation fits values computed from the Bureau of Standards vapor pressure equation⁷ fairly well down to the triple point.

The isotopic effect on hydrogen vapor pressures above the boiling point is illustrated in Fig. 1 which compares our curve for hydrogen⁸ with that for deuterium. Critical and boiling points are shown on the same diagram.

(2) **Critical Constants.**—The critical temperature and critical pressure were found to be 38.34°K. and 16.421 atmospheres, respectively. Correction for the 0.3 atomic per cent. of H would raise the critical temperature of pure deuterium to 38.35°K. if it be assumed that the critical constants change linearly with this composition, and would raise the critical pressure to 16.432 atmospheres.

It is interesting to note that the critical temperature of pure normal deuterium exceeds that of normal hydrogen by 5.11° and that its critical pressure exceeds that of hydrogen by 3.635 atmospheres.

(7) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *Natl. Bur. Standards J. Res.*, **41**, 379 (1948).

COLUMBUS 10, OHIO

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[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Determination of Diffusion Coefficients by Measurements of Surface Tension

BY E. ROGER WASHBURN AND H. NEAL DUNNING¹

A new experimental method for the determination of diffusion coefficients has been developed. The process of diffusion of a surface active solute through a liquid in a calibrated capillary is followed by measurements of surface tension. The diffusion coefficient may be calculated by either an application of Fick's second law or an application of a heat conduction equation of Ingersoll and Zobel. The value of the diffusion coefficient for normal butyl alcohol in water as determined by this method is of the same order of magnitude as the values recorded in the literature.

The possibility of using the results of capillarimetric measurements of surface tension in the calculation of diffusion coefficients of surface-active solutes was suggested by Bigelow and Washburn.² The ordinary type of capillarimeter is not applicable to the making of pertinent measurements since the length of the liquid column through which diffusion occurs changes as the surface tension changes. This feature would lead to calculations of great complexity.

In other methods for the determination of surface tension as the drop weight methods, maximum bubble pressure method and others, the length of the diffusion column is variable or reduced to so small a value that calculations based on these measurements are generally invalidated by barriers to diffusion that may occur in the surface phase.³

For these reasons the manometric capillarimeter suggested by Ferguson⁴ and used more recently by De Witt, Makens and Helz⁵ seems almost uniquely qualified for the determination of diffusion coefficients. With this instrument, modified by calibration of the capillary throughout its length, it is possible to establish a constant column through which diffusion to the surface occurs. Measurements of surface tension afford a record of the varying concentration at a hypothetical plane very near the meniscus. This hypothetical plane is located at the point nearest the surface at which concentration is still unaffected by the "surface excess" that accumulates at the surface of solutions of surface-active substances. The capillary protrudes into the container so the assumption may be made that the concentration at one end of the column is constant. Therefore, the instrument is readily used in studies of diffusion in solution.

(1) E. I. de Pont de Nemours and Co. Fellow, 1948-1949; Standard Oil Company Fellow, 1949-1950.

(2) Bigelow and Washburn, *J. Phys. Chem.*, **32**, 321 (1928).

(3) Ward and Tordai, *J. Chem. Phys.*, **14**, 453 (1946).

(4) Ferguson and Dowson, *Trans. Faraday Soc.*, **17**, 384 (1921).

(5) De Witt, Makens and Helz, *This Journal*, **57**, 796 (1936).

A determination involves the plotting of a surface tension-time curve in the diffusion experiment proper, and a surface tension-concentration curve for analytical purposes.

Initially a dilute solution of known concentration in the bulb of the capillarimeter surrounds the end of the calibrated capillary and is in contact with a column of pure solvent, of the desired length, in the capillary. Raising or lowering a bob in one arm of a U tube partially filled with water maintains the proper pressure above the capillary meniscus to maintain a column of liquid of constant length while the diffusion proceeds. This pressure is measured by observation with a cathetometer of the differences in height of the levels in a water-filled manometer. The manometer was constructed of constant bore tubing to eliminate surface tension effects.

Measurements of pressure permit a continuous record to be kept of the surface tension as the solute particles diffuse through the column of solvent to the capillary meniscus. After a certain time, dependent on conditions, a state is reached in which the surface tension decreases linearly with time. The slope of this line is a measure of the rate of diffusion of the solute molecules.

By conversion of observed values of surface tension to values of concentration it is possible to know the concentration at a given distance up the diffusion column as a function of time. This is the data required to calculate the diffusion coefficient of the solute molecules that are causing the observed decrease in surface tension.

It was experimentally observed that during a certain portion of the determination the surface tension-time curve was linear. As will be shown this indicates that the concentration-time curve is also linear. If, during this time it is assumed that there is a linear concentration gradient which may be represented by $dc/dx = k_1x$ and that $dk_1/dt = 0$, an expression involving Fick's second law may be integrated twice to give the expression

$$D = (m^2 dc/dt)/2(C_0 - C_h)$$

where

D = diffusion coefficient.

C_0 = concentration at end of capillary (g./cm.³)

C_h = concentration at the hypothetical plane (g./cm.³)

m = distance of the hypothetical plane from the end of the capillary in the direction of diffusion (cm.).

Though the assumption of a linear concentration gradient contradicts the exact equations of the problem, Barnes⁶ shows that the assumption does not ordinarily lead to appreciable errors.

The application of this expression, involving the stated approximations, to the calculation of a diffusion coefficient will be illustrated with results obtained in a typical study of *n*-butyl alcohol in water at 25.0°.

The diffusion coefficient may be calculated by a somewhat different method. The boundary conditions of this diffusion problem are essentially those of diffusion from a constant source into a finite bar, with an impervious plate at a distance m from the source. This is true since the bulk concentration is sensibly constant, and since the sur-

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DATA AND CALCULATION OF THE DIFFUSION COEFFICIENT OF *n*-BUTYL ALCOHOL

A. Measured values

Surface tension of water	72.1 dynes/cm.
Slope of surface tension-concentration curve, $dc/d\gamma$	3.42×10^{-4} g./cm. ² dyne
Length of water column in capillary, m	0.500 cm.
Concentration of bulk solution, C_0	0.01482 g./cm. ³
Surface tension after diffusion for 60 minutes	67.1 dynes/cm.
Slope of surface tension-time curve, $d\gamma/dt$	2.48×10^{-3} dyne/cm. sec.

B. Calculated values

Average over-all concentration in diffusion column at 60 minutes	0.00826 g./cm. ³
Concentration at hypothetical plane at 60 minutes, $C_h = (72.1 - 67.1) \times 3.42 \times 10^{-4}$	0.00171 g./cm. ³
$dc/dt = dc/d\gamma \times d\gamma/dt = 3.42 \times 10^{-4} \times 2.48 \times 10^{-3}$	8.48×10^{-7} g./cm. ³ sec.
Diffusion coefficient, $D = (0.5)^2 \times 8.48 \times 10^{-7}/2(0.01482 - 0.00171)$	0.81×10^{-5} cm. ² /sec.

face tension-concentration curve was established under equilibrium conditions when an equal amount of solute was passing the hypothetical plane in both directions. Ingersoll and Zobel⁷ arrive at the solution of the problem in heat conduction in a finite bar. The conditions assumed by these workers are that the front face of a wall is raised to the temperature T_s and remains constant while the rear face is impervious to heat. They show that this case can be treated as that of a slab of twice the thickness, the rear (impervious) face of the wall corresponding to the middle of the slab, ($m = L/2$), where L is the thickness of the slab. According to their solution, the expression giving the temperature of the rear face is: $T = T_s(1 - S_{(z)})$. Interpreted in terms of a diffusion problem, the solution is $C_h = C_0(1 - S_{(z)})$ where $z = Dt/L^2$ and $S_{(z)} = 4/\pi(e^{-\pi^2 z} - 1/3e^{-9\pi^2 z} + 1/5e^{-25\pi^2 z} - \dots)$ and the concentration terms have the meanings previously assigned to them. In this study the length of the diffusion column m was 0.500 cm. Since $L = 2m$, $z = Dt$. The series $S_{(z)}$ has fortunately been tabulated by Ingersoll and Zobel.

For a range of values of z , 0.030 to 0.060, the value of $dS_{(z)}/dz$ is equal to -7.1 within 4%.

We may then rewrite the diffusion equation as

$$C_h = C_0 + C_0 7.1 Dt/L^2 + C_0 t$$

This indicates that the diffusion coefficient is determined by this relation

$$D = \frac{dC_h/dt}{7.1 C_0/L^2}$$

Substituting values for dC_h/dt , C_0 and $L = 2m$ from Table I gives a value of 0.81×10^{-5} cm.²/sec. for D .

(7) Ingersoll and Zobel, "Heat Conduction," McGraw-Hill Book Co., Inc., New York, N. Y., 1948, p. 127.

(6) Barnes, *Physics*, 5, 4 (1934).

Though there is probably some adsorption of solute at the glass-liquid interface, calculations show that the amount of butyl alcohol necessary to form a monomolecular layer over the interior of the capillary is negligible compared to the amount of alcohol in the capillary at the beginning of the period of calculation. Since much of the glass-liquid interface would be covered with alcohol prior to the period of calculation, this error is largely eliminated by the methods of calculation.

Stearn, Irish and Eyring⁸ list a value of D for butyl alcohol of 0.88×10^{-6} cm.²/sec.

In a further study of diffusion by this method, a capillary length of 0.50 cm. was used while the bulk concentration at the lower end of the capillary was varied. Preliminary observations indicated that the rate of change in concentration at the hypothetical plane was nearly proportional to the bulk concentration. There was observed a slight tendency for the ratio (change in concn.)/(bulk concn.) to increase with bulk concentration. This seems indicative of a small increase in the diffusion coefficient as the over-all average concentration in the capillary increases. This tendency was also noted

(8) Stearn, Irish and Eyring, *J. Phys. Chem.*, **44**, 990 (1940).

in the original determinations of diffusion coefficient.

Another preliminary study was made using a bulk concentration of 0.01482 weight per cent. and varying the length of the diffusion column from one determination to another. It was observed that within experimental error the change in concentration at the hypothetical plane was inversely proportional to the square of the capillary length involved in the diffusion process.

The agreement of the experimental results of these preliminary studies with predicted results indicates that either or both the length of column, or the bulk concentration may be varied within limits dictated by experimental technique, without invalidating determinations of diffusion coefficients.

The practical and theoretical aspects of this method are being further explored. It would seem that it should be applicable to the many and varied types of molecules which show surface activity in water or in other solvents. A slight modification should permit the study of diffusion of vapors from the vapor side of the interface.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Reaction of Nitrous Acid with Diaminoguanidine in Acetic Acid Media. Isolation and Structure Proof of Reaction Products¹

BY EUGENE LIEBER AND DEWEY ROBERT LEVERING

The reaction of diaminoguanidine with one and two molar proportions of nitrous acid in acetic acid media has been studied. Tetrazolyl azide, in the form of its alkali salt is the only solid isolable product, the structure being established by degradation, synthesis and infrared absorption. The preparation and properties of pure tetrazolyl azide are described. With two molar proportions of nitrous acid the yield of tetrazolyl azide varies from 20 to 77%, the yield increasing with decrease in concentration of the reagents. A gaseous decomposition product, comprising equal quantities of nitrogen and nitrous oxide, accompanies the diazotization reaction, the amount of gas increasing with increase in concentration of reagents. The reaction of diaminoguanidine with one molar proportion of nitrous acid in acetic acid yields chiefly unreacted starting material, a small yield (0.5 to 6.0%) of tetrazolyl azide and gaseous decomposition products.

Introduction

Diaminoguanidine, $\text{HN}=\text{C}(\text{NHNH}_2)_2$, was first prepared almost fifty years ago by Stollé^{2,3} and the method improved by Pellizzari and Gaiter.⁴ Two other methods are mentioned in the literature.^{5,6} However, none of these methods of preparation is very satisfactory and a different one is referred to in this paper. These few communications on the preparation of diaminoguanidine, its salts and a few selected derivatives comprise the only studies carried out on this compound.

The reactions of nitrous acid with aminoguanidine, $\text{H}_2\text{NC}(=\text{NH})\text{NHNH}_2$, in strong acid media and in neutral and acetic acid media have been summarized in a review article on aminoguanidine and related substances by Lieber and Smith.⁷

The study of the reaction of nitrous acid with diaminoguanidine in strong acid, weak acid and neutral media is currently under investigation in this laboratory. The purpose of this work is the preparation and reactions of high nitrogen-containing compounds. This paper reports the results of the reaction in weak acid solution.

Reaction with Two Mole Proportion of Nitrous Acid.—When diaminoguanidine nitrate (I) is treated with two moles of nitrous acid in acetic acid solution, the only isolatable product is potassium or sodium tetrazolyl azide (II) depending upon whether potassium or sodium nitrite is the source of nitrous acid. The same compound (II) is obtained when buffered acetic acid is the reaction medium.

Pure potassium tetrazolyl azide precipitates in the form of lustrous white plates when ether is added to a solution of it in acetone. Potassium tetrazolyl azide is very soluble in water, alcohol and acetone but it is insoluble in benzene, carbon tetrachloride and ether. This azide salt (II) is *extremely sensitive* to pressure, friction or heat and must be handled with care and in small amounts. Very small amounts (less than 0.01 g.)

(1) Abstracted from a portion of the thesis submitted by Dewey Robert Levering to the Graduate School of the Illinois Institute of Technology in partial fulfillment for the Ph.D. degree.

(2) R. Stollé and K. Hofmann, *Ber.*, **37**, 4524 (1904).

(3) R. Stollé, *J. prakt. Chem.*, **75** [2] 423 (1907).

(4) G. Pellizzari and A. Gaiter, *Gazz. chim. ital.*, **44**, IIA, 72 (1914).

(5) R. Stollé and K. Krauch, *J. prakt. Chem.*, **88**, 306 (1913).

(6) R. Phillips and J. F. Williams, *This Journal*, **50**, 2465 (1928).

(7) E. Lieber and G. B. L. Smith, *Chem. Rev.*, **25**, 213 (1939).