

Summary

1-Benzoylacenaphthene, obtained conveniently from the available 1-aceto compound by a phenyl Grignard reaction on the corresponding amide, gives 1',9-methylene-1,2-benzanthracene on pyrolysis in 13% yield.

Further data are given on the preparation of 1-acetoacenaphthene by the hydrogen fluoride procedure and on the characterization and oxidation of the ketone.

A study of the pyrolysis of *vic.-o*-xylyl α - and β -naphthyl ketones shows that methyl groups in the α -positions 5 and 8 of the 1,2-benzanthracene molecule withstand to some extent the conditions of the Elbs reaction but that with the α -naphthyl isomer there appears to be both migration of the aroyl group and partial elimination of the methyl substituent.

CONVERSE MEMORIAL LABORATORY

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 3, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Diffusion Velocity and Molecular Weight. I. The Limits of Validity of the Stokes-Einstein Diffusion Equation

BY LEO FRIEDMAN AND PAUL G. CARPENTER¹

Considerable interest has been evidenced in recent years in the use of diffusion velocity studies as a means of determining molecular weights.²⁻⁴ Some results have been obtained that are in excellent agreement with results yielded by other methods.³ On the other hand, the results of Northrop and Anson on hemoglobin^{2,5} have been discouraging, as were the results of one of the authors on gelatin (to be reported in a later paper of this series).

In the use of diffusion velocity as a means of determining molecular weights, too little attention has been paid to the concentration of the diffusate. Since the Stokes-Einstein diffusion equation makes no provision for change in concentration and is derived on the assumption of free diffusion, it would appear that the diffusion coefficient to be used for the calculation of molecular weight should be determined at infinite dilution.

In a classical paper on this subject Sutherland⁶ made an effort to apply the Stokes-Sutherland-Einstein equation to the evaluation from diffusion data of the molecular weights of a number of non-electrolytes ranging in molecular weight from methyl alcohol to raffinose. Undoubtedly his failure to obtain closer agreement between diffu-

sion data and molecular weight was due to inaccuracy of data available at that time. In this paper he also gives a general empirical equation for use as the molecular weight becomes small.

Attempt to Evaluate Molecular Weights of Non-Electrolytes from their Diffusion Coefficients.—Examination of the diffusion data for non-electrolytes to be found in the "International Critical Tables" shows that the diffusion coefficient varies considerably with the concentration of the diffusate. Calculations of the molecular weights of these non-electrolytes have been made by use of the Stokes-Einstein diffusion equation

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r}$$

combined with the relationship

$$M = \frac{4}{3}\pi r^3 d N$$

Results of several of these calculations are given in Table I. In the case of each non-electrolyte, the last value of the diffusion coefficient labeled 0 concentration has been calculated from the molecular weight of the substance. It is to be observed in each case that the value so obtained is not unreasonable when compared with the experimental values reported in the "International Critical Tables."

If the results of Table I are represented graphically by plotting the diffusion coefficient against the square root of the concentration of the diffusate, it is possible to draw a straight line from the theoretically calculated diffusion coefficient through the experimental points taken from the

(1) Present address: Willamette University, Salem, Oregon.

(2) J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

(3) J. W. McBain and T. S. Liu, *THIS JOURNAL*, **53**, 59 (1931).

(4) J. W. McBain, C. R. Dawson and H. A. Barker, *ibid.*, **56**, 1021 (1934).

(5) M. L. Anson and J. H. Northrop, *J. Gen. Physiol.*, **29**, 575 (1937).

(6) W. Sutherland, *Phil. Mag.*, [6] **9**, 781 (1905).

TABLE I
 MOLECULAR WEIGHT CALCULATIONS FROM DIFFUSION COEFFICIENTS

C_0	$10^5 D$ cm. ² /sec.	Calcd. mol. wt.	C_0	$10^5 D$ cm. ² /sec.	Calcd. mol. wt.
Mannitol at 10°			Sucrose at 12°		
0.5	0.39 ± 0.02	242	2.0	0.25 ± 0.02	1183
.25	.40 ± .02	224	1.5	.28 ± .02	842
.125	.42 ± .02	194	1.0	.30 ± .02	685
0 ^a	.432	182	0.5	.325 ± .02	539
Lactose at 10°			0.25	.34 ± .02	471
0.2	0.32 ± 0.02	459	0.1	.35 ± .02	431
0.1	.32 ± .02	459	0.075	.355 ± .02	413
0 ^a	.353	342	0 ^a	.381	342
Lactose at 20°			Sucrose at 14°		
0.2	0.41 ± 0.02	531	1.0	0.33 ± 0.02	838
0.1	.43 ± .02	460	0.5	.35 ± .02	702
0 ^a	.475	342	0.25	.36 ± .02	645
Maltose at 10°			0 ^a	.402	342
0.5	0.29 ± 0.01	623	Sucrose at 20°		
.25	.31 ± .02	510	2.0	0.32 ± 0.02	903
.01	.32 ± .02	463	1.0	.38 ± .02	679
0 ^a	.354	342	0.5	.41 ± .02	540
Maltose at 20°			0.25	.43 ± .02	468
0.5	0.38 ± 0.01	862	0 ^a	.481	342
.25	.41 ± .02	536	Sucrose at 29°		
.1	.42 ± .02	499	1.0	0.50 ± 0.02	607
0 ^a	.476	342	0.5	.53 ± .02	510
			0.25	.55 ± .02	448
			0 ^a	.611	342
			Salicin at 20°		
			0.12	0.46 ± 0.03	300
			0.06	.49 ± .03	248
			0 ^a	.494	286

^a For 0 concentration the value of $10^5 D$ has been calculated from the molecular weight.

"International Critical Tables." When the circles used to represent the experimental values are so drawn that they represent the probable experimental error of each point, the straight line will pass through each circle, although it must be admitted that one could not determine where to draw this line from the experimental points alone. The data in the "International Critical Tables" are too limited to make this possible.

Experimental Studies on the Diffusion of Glucose.—Since the diffusion values found in the "International Critical Tables" are relatively few and are not so exact as can now be obtained with newer methods of studying diffusion, a study of the diffusion velocity of glucose has been made. The apparatus used consisted of glass cells of the type employed by Northrop and Anson,² and McBain and his co-workers.^{3,4} The experimental procedure used by McBain and co-workers was

followed. Because of the extremely low concentrations resulting in the outside solution, this method effectively measures diffusion against water. Cell constants were calculated from the diffusion coefficient of potassium chloride as listed in the "International Critical Tables" from the work of Öholm. The glucose concentrations were measured by determining the amount of potassium iodate needed for complete oxidation of a sample.⁷

All experiments on glucose were carried out at 25° and several determinations of diffusion velocities were made at each concentration. The results of this study are given in Table II, in the third column of which the apparent molecular weight of glucose has been calculated from the diffusion coefficient obtained at each concentration.

(7) R. J. Williams, E. Rohrman and B. E. Christensen, *THIS JOURNAL*, **59**, 291 (1937).

TABLE II
DIFFUSION OF GLUCOSE AT 25°

Concn.	D in cm. ² /day	Calcd. mol. wt.
0.60	0.535	237
.50	.539	232
.40	.543	227
.355	.546	223
.30	.550	218
.25	.552	216
.20	.556	211
.10	.566	200
.00 (extrap.)	.586	180

The experimental values are reported graphically in Figs. 1 and 2, in which it is evident that

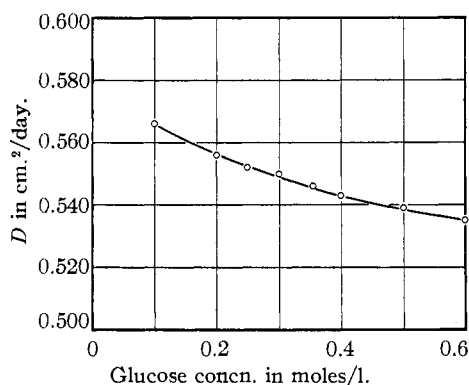


Fig. 1.—Diffusion of glucose at 25°.

when sufficiently accurate diffusion data are obtained, it is possible by plotting diffusion coefficient against square root of the concentration to extrapolate to infinite dilution and thus obtain the value of diffusion coefficient that will yield the

correct molecular weight when substituted in the Stokes-Einstein diffusion equation.

Even more striking is the fact that this relationship holds for a substance of molecular weight of 180 whereas most investigators have felt that the Einstein relationship could not be applied to substances of such low molecular weight.

Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 19, School of Science, Department of Chemistry.

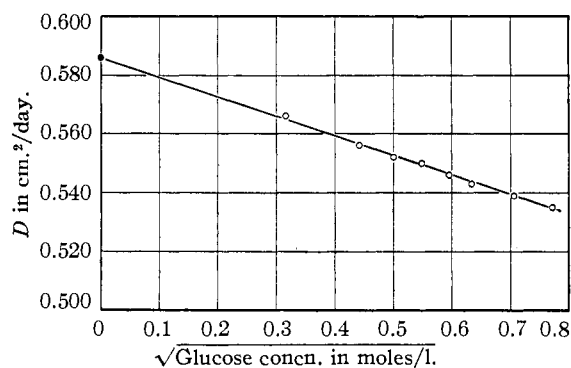


Fig. 2.—Diffusion of glucose at 25°.

Summary

It has been shown that molecular weights of simple non-electrolytes can be calculated from diffusion coefficients determined at infinite dilution, (1) by an examination of the values of diffusion coefficient to be found in the "International Critical Tables," and (2) by experimental study of the diffusion velocity of glucose.

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RECEIVED FEBRUARY 20, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Diffusion Velocity and Molecular Weight. II. The Effect of pH upon Particle Size in Gelatin Solutions

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Change of hydrogen ion concentration of a gelatin solution brings about marked changes in many of the properties of the solution. In seeking explanations of these changes, some investigators have attributed them to increased or decreased hydration with changing pH or to increased or decreased particle size with changing pH. Investigators of diffusion of colloidal materials have ob-

served marked changes in diffusion velocity with changing pH.²⁻⁴

Experimental

In order to investigate the effect of pH upon particle size in gelatin solutions, diffusion experiments have been carried out using 3% solutions of Eastman Kodak Co. electro dialyzed gelatin, adjusted to various pH's by the

(2) H. R. Bruins, *Kolloid Z.*, **54**, 265, 272 (1931); **57**, 152 (1931).

(3) J. Lazle and J. Groh, *Biochem. Z.*, **173**, 248 (1926).

(4) J. W. McBain, C. R. Dawson and H. A. Barker, *THIS JOURNAL*, **56**, 1021 (1934).

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