DIFFUSION VELOCITY AS A MEANS OF DETERMINING MOLECULAR WEIGHTS

by

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A THESIS

submitted to the

OREGON STATE AGRICULTURAL COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1937

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ACKNOWLEDGEMENTS

The writer wishes to express his appreciation to Dr. Leo Friedman who suggested the problem for this thesis and who has been a never-failing source of inspiration and helpful suggestions. Also to Dr. R. J. Williams who has provided much helpful counsel and has rendered financial aid to this investigation.

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DIFFUSION VELOCITY AS A MEANS OF DETERMINING MOLECULAR WEIGHT

I. Introduction

The molecular weights of substances may be determined by a number of standard methods which are, however, of limited applicability.

Vapor density measurements are applicable only to substances which are easily volatile and in a pure state.

Those determinations which depend upon osmotic phenomena, such as osmotic pressure, lowering of freezing point, elevation of boiling point, and lowering of vapor pressure are applicable only to substances which have low molecular weights and are in a pure state with considerable quantity of the substance available.

This leaves unsolved the problem of determining the molecular weights of substances which have very high molecular weights, substances which are in solution in very small quantities, and substances which contain some impurity.

A recent advance in the determination of large molecular weights is the development of the supercentrifuge by Svedberg (22,23,24). This gives quite accurate results for very large molecules. The equipment required, however, is very expensive and necessitates a trained staff of mechanics for operation. This makes it out of the question for use at any place except where specialized

research on the subject is being developed.

Another means of determining molecular weight, which is applicable to substances whose molecular weights are large, to substances which are present in small concentrations, and which may be used on fairly impure substances, is the use of diffusion velocity. This has the advantage that the apparatus employed is inexpensive. The molecular weight is related to the diffusion coefficient by the Stokes-Einstein equation (8);

$$(1) \quad D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$$

D is the diffusion coefficient in cm^2 / sec.

R is the gas constant.

N is Avagadro's number.

η is the viscosity of the solvent.

r is the radius of the particle.

In the development of the above equation, Einstein assumed that the particles were spherical, uncharged, and very large in comparison to the molecules of the dispersion medium.

The molecular weight can be determined by solving for the radius of the particle in the above equation and substitution in the following expression;

$$(2) \quad M = 4/3\,\pi N d r$$

M is the molecular weight.

N is Avagadro's number.

d is the density of the substance.

r is the radius of the particle.

Combining equations (1) and (2) the following expresion for the molecular weight may be obtained;

$$(3) \quad M = \frac{4}{3} \frac{\pi}{N^2} \left(\frac{R}{6\pi}\right)^3 \left(\frac{T}{\eta}\right)^3 \frac{d}{D^3}$$

It has been common practice to calculate molecular weights from diffusion coefficients determined at some one finite concentration. The investigators (16) have neglected the well-known fact that the diffusion coefficient varies with the concentration. Since the Einstein equation makes no provision for a change in concentration and is derived on the assumption of free diffusion, it would appear that the diffusion coefficient which should be used is the value at zero concentration. The aim of this investigation was to attempt to show that the value at infinite dilution used in the Einstein equation gives better values for molecular weights than D at any finite concentration.

II. Methods of Studying Diffusion Velocity

The methods of studying diffusion velocity may be divided into two general classes;--those which involve free diffusion and those which involve diffusion through a membrane.

Methods which involve free diffusion (1, 3, 4, 5, 6, 7, 9, 10, 14, 21, 25, 26, 27, 28, 29, 30, 31) require no standardization of the apparatus employed but, on the other hand, many sources of error may appear. In the process of free diffusion the solution containing the diffusate is placed below the pure solvent and diffusion is allowed to take place upward. It is almost impossible to keep such a system free from all vibration, changes in temperature resulting in convection currents, and mixing when the solution is introduced. Another distinct disadvantage is the length of time necessary to obtain experimental data, since diffusion must take place upward without any sharp gradient being established.

Graham (10) introduced the first method of studying free diffusion. His diffusion cell consisted of a bottle, in which he placed the solution, and a large cylinder. The bottle was placed in the cylinder which was then filled with solvent. This method gave only qualitative results.

Semmler (21) modified Graham's type of apparatus by the substitution of a cylinder for the bottle used in the

original setup. This allowed him to use Fick's equation (9) to calculate the diffusion velocities.

J. J. Coleman (5, 6, 7) originated a method for the study of the free diffusion of substances which would affect indicators. This was applicable only to electrolytes. The substance to be studied was placed in the bottom of narrow tubes and the rate of diffusion followed by indicators in the solvent above the solution.

Free diffusion was studied by Griffiths (11, 12, 13) by means of a series of diffusion tubes much like those of Coleman.

Thovert (25, 26, 27, 28, 29, 30, 31) accumulated a great deal of experimental data on diffusion coefficients. He employed a series of glass prisms and used optical methods to analyze the solutions. His results were reasonably accurate.

Oholm (20) used an apparatus much like that of Graham and avoided much of the error introduced by this method by working underground to avoid temperature changes, light, and vibrational disturbance. He obtained the first really accurate diffusion data.

Herzog (14) employed the Oholm apparatus and method for the measurement of diffusion velocities of proteins, determining the concentration of the various layers by gravimetric analysis.

Clack (3) used a modification of the method used by Fick. He suspended the solution in a spherical vessel from the arm of a balance and determined the change in concentration with time by change in weight.

Cohen and Bruins (4) devised a cell which provided for more accurate separation of the diffusion layers. It was of the Oholm type and consisted of six cylindrical plates fastened together in the middle by a pin about which they could rotate freely. The four inner discs had holes drilled through them in a position so that they could be aligned and produce a cylindrical cell. The opening in the next to the bottom plate was filled with diffusate solution and cut off from the others. The holes in the other three were filled with pure solvent and the discs then rotated so that all four holes coincided. Diffusion was allowed to take place and, after a sufficient length of time the discs were rotated so that a part of the column was trapped in each hole. The solutions were removed one at a time and analyzed.

In 1931, Bruins (1) developed an improved type of diffusion apparatus which consisted of a narrow cell built into a small interferometer. The diffusate solution was placed in the cell and pure solvent was passed over the top at a constant rate in order to provide a constant and maximum diffusion gradient.

Membrane diffusion has its disadvantages as well as has free diffusion. The main difficulty is the fact that the apparatus must be standardized against something with a known diffusion coefficient. However, it does not possess the disadvantages of free diffusion in that it is not affected by convection currents due to vibration, temperature fluctuations, or light. There is no error introduced by mixing of solutions upon introduction of diffusate solution or when the solutions are removed for analysis. The diffusion gradient is confined to a definite distance and can be maintained at a constant maximum throughout the experiment.

Graham (10) in his first method of studying diffusion made use of a thin sheet of sponge to separate his solutions. He found that the presence of the sponge had no appreciable effect on the diffusion velocity.

Fick (9) used animal membranes to test the accuracy of his diffusion law and found them to be unsatisfactory.

The first practical method for the study of diffusion by the use of membranes was introduced by Northrop and Anson (19). Their cell consisted of a sintered glass membrane through which the substance to be studied could diffuse. This membrane effectively prevented mixing of the solutions used and confined the diffusion gradient between the solutions to a definite measurable distance. The nature of the membrane was such that one standard-

ization would serve to establish the constant of the cell as it was durable enough not to change in permeability through use. McBain and his coworkers applied this method to the measurement of the diffusion of electrolytes, non-electrolytes, and colloidal electrolytes (16); to mixtures of electrolytes and colloidal particles (17); and to the study of accelerated and retarded diffusion in solution (15).

Butkevich (2) used colloidion membranes to study diffusion but such a membrane must be standardized each time it is used thus increasing the experimental difficulty.

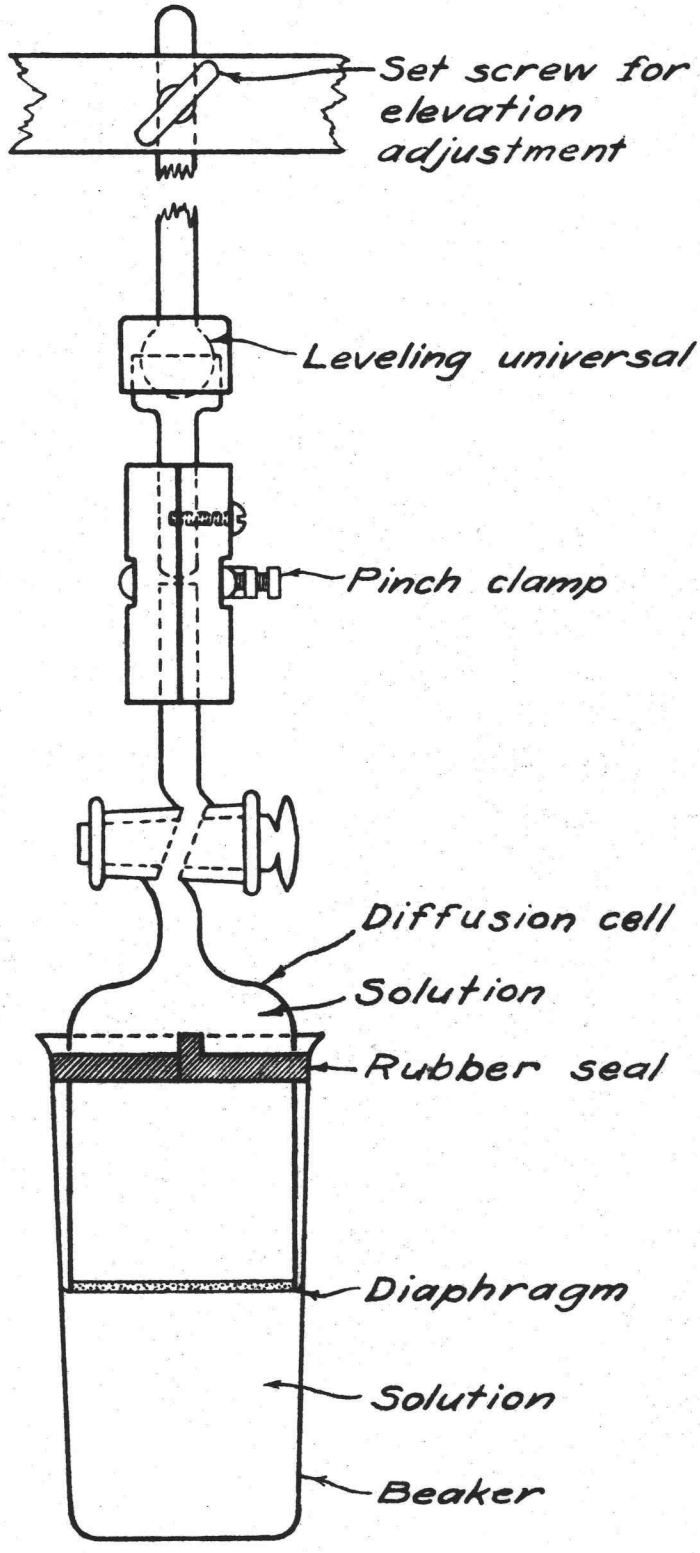
The diffusion apparatus developed by Northrop and Anson (19) affords the best method of determining diffusion coefficients quickly and accurately and for these reasons was used in the experimental work of this investigation.

III. Experimental

(1) Determination of Diffusion Velocity

The apparatus used to determine diffusion coefficients consisted of glass cells of the type employed by Northrop and Anson (19) which are closed at one end with a sintered glass diaphragm and at the other end with a stopcock to facilitate filling and emptying the cells. (See Fig. 1). The diffusate was placed in these cells and allowed to diffuse into beakers of water placed below them. The beakers were immersed in a constant temperature bath and kept at a temperature of 25° 0.2°. An essential precaution in the use of these cells is the elimination of all air from inside the diaphragm and from all solutions used. This was accomplished by drawing a liter of degassed water through the cells. The water was degassed by boiling under atmospheric pressure for thirty minutes and then cooling under reduced pressure. Solutions were made up using this degassed water and care was taken not to introduce any more air than could be avoided.

The cells have a volume of approximately 100 cc. and, to insure the fact that no dilution would take place, at least 400 cc. of the solution was drawn through them before the stopcock was closed. The cells were held in place by clamps equipped with universal joints which allowed adjustment of the cells so that the diaphragm was


Set screw for elevation adjustment
Leveling universal
Pinch clamp
Diffusion cell
Solution
Rubber seal
Diaphragm
Solution
Beaker

level. (See Fig. 1). The cells were then lowered into beakers of water and preliminary diffusion allowed to take place until a uniform gradient had been established. This usually took from two to three hours depending upon the rate of diffusion of the substance employed. These beakers were then replaced with beakers containing exactly the same volume of solvent as was contained in the cells. In order to prevent evaporation, the space between the sides of the cells and the beakers was sealed with a soft rubber strip. (See Fig. 1).

Diffusion was allowed to take place for from seventeen to twenty-four hours. The solutions were then removed from both the cell and the beaker and analyzed.

(2) Analysis of Solutions.

A modification of the iodate oxidation method of Williams, Rohrman, and Christensen (32) was employed in the analysis. Since the values obtained were based on comparisons, no effort was made to accurately standardize the solutions used, other than to weigh out roughly the amount needed. The inside solutions were diluted until they approximated the concentration of the outside solutions and aliquots of the solutions analyzed.

Five cc. of a potassium iodate solution, with a concentration great enough to provide a 25% excess over that which was needed for complete oxidation, were introduced

into a test tube. Ten cc. of the solution to be analyzed were next introduced and finally 2 cc. of concentrated sulfuric acid. This mixture was allowed to evaporate in an oven at about 110° Centigrade until it had a volume of approximately 3 cc. The temperature was then increased to 175° and allowed to remain there for one hour. The solutions were removed and the excess iodate decomposed by the addition of potassium iodide. The iodine thus liberated was titrated with sodium thiosulphate using starch as an indicator. Blanks were prepared as above, the only difference being that 10 cc. of distilled water took the place of the solution being analyzed. The concentration values were obtained by subtracting the titration values for oxidation of the samples from those of the blank.

(3) Calculation of Diffusion Coefficient.

To obtain diffusion coefficients from the concentration values the following relationship which was derived by McBain and Liu (16) was employed;

$$D = \frac{\log C_o - \log (C_o - 2C)}{K t_E}$$

D is the diffusion coefficient (calculated in cm^2/day)

C_o is the concentration of the solution at t_E equal to zero

C is the concentration of the solution outside the cell

after the elapse of the time t_E

K is the cell constant.

(4) Calculation of Cell Constants.

The cell constants were determined by diffusion of KCl in the cells, substituting the known D in the equation above, and solving for the cell constant. The experimental data and results are given in Table I. The cells were standardized against .1 N KCl whose diffusion coefficient at 25° C is 1.618 as determined by Oholm (20) and taken from the International Critical Tables.

Diffusion of Glucose at 25° C.

Measurements of the diffusion velocity of glucose have been made at 25° C at concentrations varying from 0.10 M to 0.60 M. The experimental results obtained are given in Table II and a summary of the calculated diffusion coefficients is given in Table III.

It will be noted that the diffusion coefficients show a gradual increase from the highest concentration to the lowest concentration.

Table I

DETERMINATION OF CELL CONSTANTS WITH .1 N KCl

Cell #	t hours	C_0	C	K
1	17.48	489.30	34.30	0.002319
1	18.10	482.13	34.63	0.002300
1	18.35	488.64	36.89	0.002394
1	17.08	488.43	32.68	0.002261
1	19.60	453.40	37.52	0.002350
1	15.48	464.00	29.45	0.002320
1	21.50	195.70	16.30	0.002279
	Mean cell constant			0.002317
2	17.48	495.49	26.74	0.001754
2	27.34	489.09	27.34	0.001752
2	18.42	491.38	28.13	0.001772
2	17.00	493.31	25.56	0.001717
2	19.62	467.00	29.57	0.001796
2	15.53	453.00	22.90	0.001811
2	21.50	499.90	32.90	0.001762
	Mean cell constant			0.001768
3	17.43	482.88	46.38	0.003285
3	18.23	488.70	48.70	0.003274
3	18.45	486.58	49.33	0.003297
	Mean cell constant			0.003285

Table I (Continued)

DETERMINATION OF CELL CONSTANTS WITH .1 N KCl

Cell #	t	C_o	C	K
3A	17.00	495.20	22.70	0.001517
3A	19.67	473.60	25.70	0.001543
3A	15.57	465.00	19.90	0.001537
3A	21.50	496.10	28.60	0.001529
	Mean cell constant			0.001538
4	17.40	489.44	36.69	0.002506
4	18.22	488.85	38.10	0.002496
4	18.55	489.98	38.73	0.002490
4	16.75	494.32	34.82	0.002434
4	19.67	455.60	41.07	0.002570
4	15.57	451.00	31.05	0.002482
	Mean cell constant			0.002493
4A	21.50	499.30	41.50	0.002288
	Mean cell constant			0.002288

Table II

DIFFUSION OF GLUCOSE AT 25° C

Conc.	Cell #	t hours	C_0	C	D (cm^2/day)
0.10	3A	17.15	246.00	4.38	0.5971
0.10	1	17.18	246.00	5.91	0.5373
0.10	3A	20.00	236.63	4.83	0.5884
0.10	4A	20.00	237.23	6.73	0.5417
		Average D	0.5661		
0.20	1	16.05	495.20	11.20	0.5520
0.20	4A	16.00	489.30	11.30	0.5610
		Average D	0.556		
0.25	2	17.17	618.75	11.15	0.5251
0.25	3A	17.13	612.38	14.78	0.5480
0.25	1	20.00	582.13	17.13	0.5684
0.25	2	20.00	579.35	13.20	0.5669
		Average D	0.552		
0.30	2	15.33	762.07	12.90	0.5515
0.30	4A	15.33	746.20	16.20	0.5495
		Average D	0.550		
0.355	1	21.00	875.62	25.27	0.5539
0.355	4A	21.00	883.90	25.60	0.5392
		Average D	0.5465		

Table II (Continued)

DIFFUSION OF GLUCOSE AT 25° C.

Conc.	Cell #	t hours	C_0	C	D (cm^2/day)
0.40	2	16.03	961.55	16.55	0.5370
0.40	3A	16.02	966.85	14.85	0.5490
		Average D	0.5430		
0.50	2	17.23	1244.90	22.70	0.5298
0.50	4A	17.32	1262.48	29.83	0.5310
0.50	2	21.00	1247.37	28.12	0.5398
		Average D	0.5332		
0.60	1	15.33	760.40	12.90	0.5268
0.60	3A	15.33	746.20	16.20	0.5370
		Average D	0.5321		

Table III

DIFFUSION OF GLUCOSE AT 25° C

Summary of results

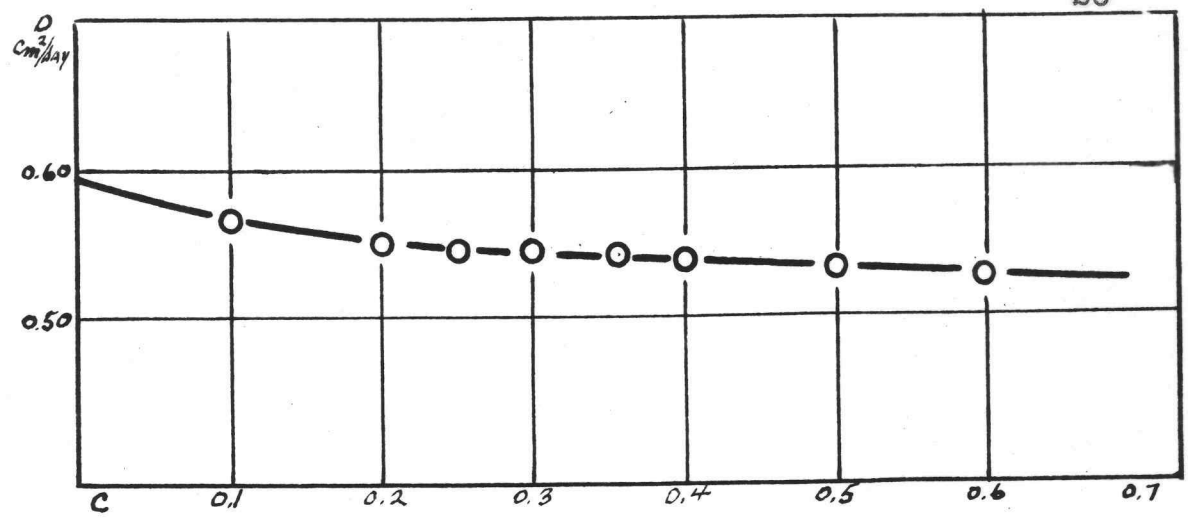
Concentration	D in cm^2/day	Calc. M. W.
0.60	0.532	240
0.50	0.533	238
0.40	0.543	225
0.355	0.5465	223
0.30	0.550	216
0.25	0.552	213
0.20	0.556	210
0.10	0.566	194
0.00 (extrapolate)	0.586	180

IV Discussion

The values of diffusion coefficients for glucose (Table III) if used at finite concentrations in the Stokes-Einstein equation give molecular weights varying from 240 to 194. If, however, the diffusion coefficients are plotted against the square root of the concentration and extrapolated to zero concentration a molecular weight is obtained which is within 2% of the theoretical.

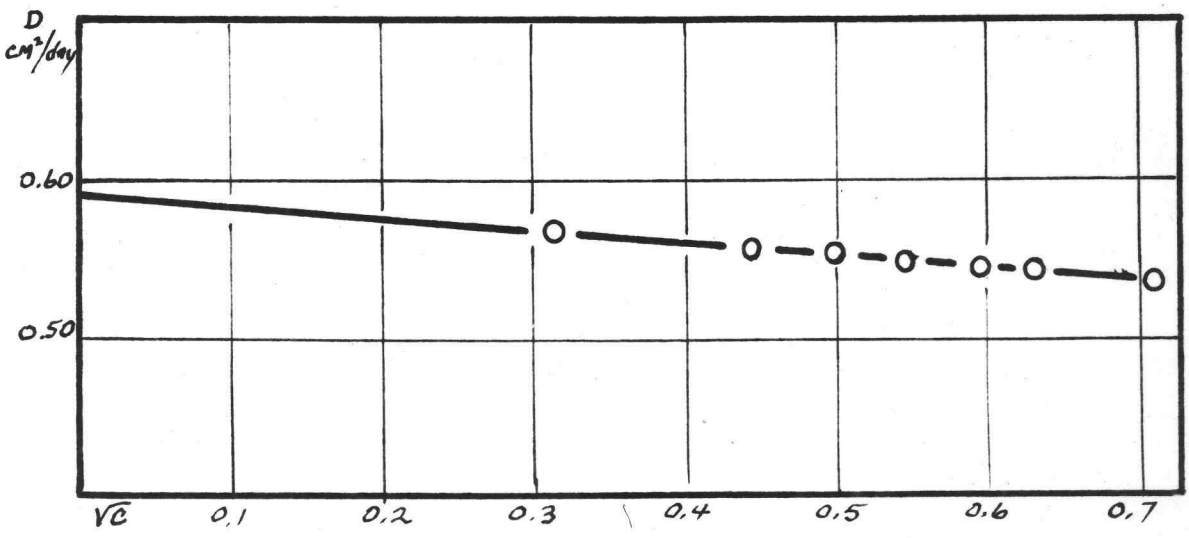
If the diffusion coefficient is plotted against the concentration a curve is obtained which is difficult to extrapolate to the zero concentration. On the other hand, the diffusion coefficient plotted against the square root of the concentration gives a straight line which is extrapolated with ease. Figure 2 shows the diffusion coefficient of glucose plotted against the concentration while Figure 3 shows the same values plotted against the square root of the concentration.

Substances with as low a molecular weight as that of glucose have been considered by some investigators not to conform to the Stokes-Einstein equation. They have, however, neglected the fact that the diffusion coefficient varies with the concentration, and have attempted to apply the diffusion coefficients at any finite concentration. As a result they have obtained values for the molecular weight which were as much as 100% in error.



Diffusion of Glucose at 25° C.

Figure 2



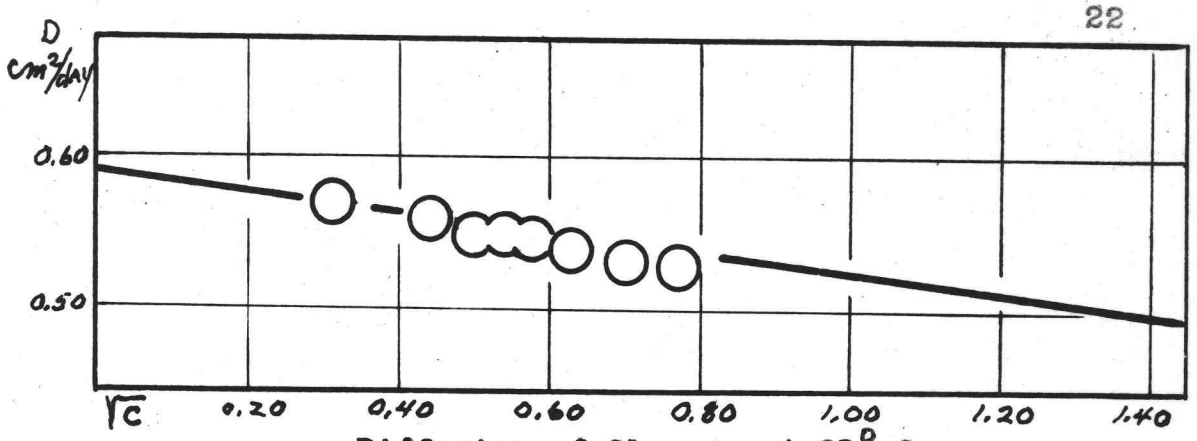
Diffusion of Glucose at 25° C.

Figure 3

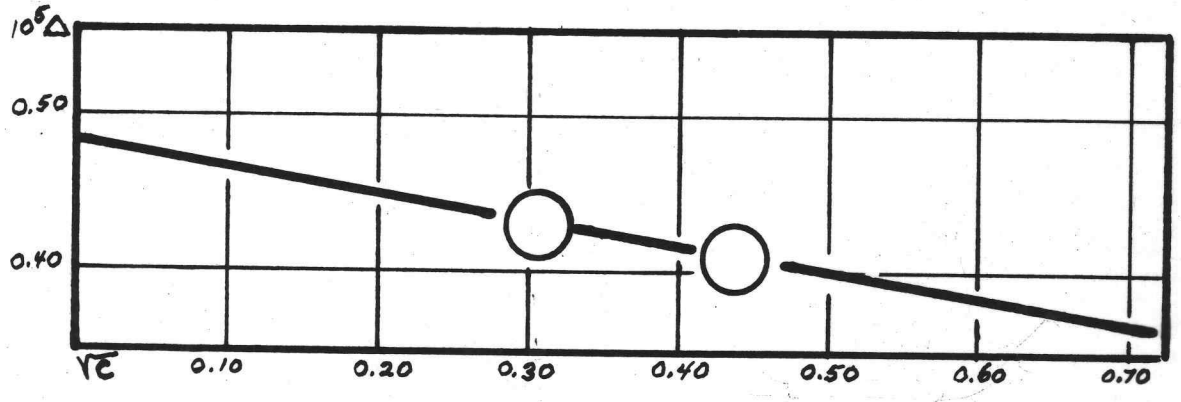
This not only holds for glucose but also holds for a number of other non-electrolytes whose diffusion coefficients were taken from the International Critical Tables (18). Figures (4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15) show these diffusion coefficients plotted against the square root of the concentration and extrapolated to zero concentration. The circles representing the experimental values have been drawn to indicate the magnitude of the experimental error. In all cases these lines have been purposely made to hit the zero axis at the value of diffusion coefficient which gives the correct molecular weight. It will be seen that in no case does the line drawn through the values lie outside the limits of experimental error and in many cases it is the best line which can be drawn through the points.

Table IV shows the results obtained by calculating molecular weights at any finite concentration. It will be seen that the values for molecular weights approach the theoretical the more nearly the concentration approaches zero.

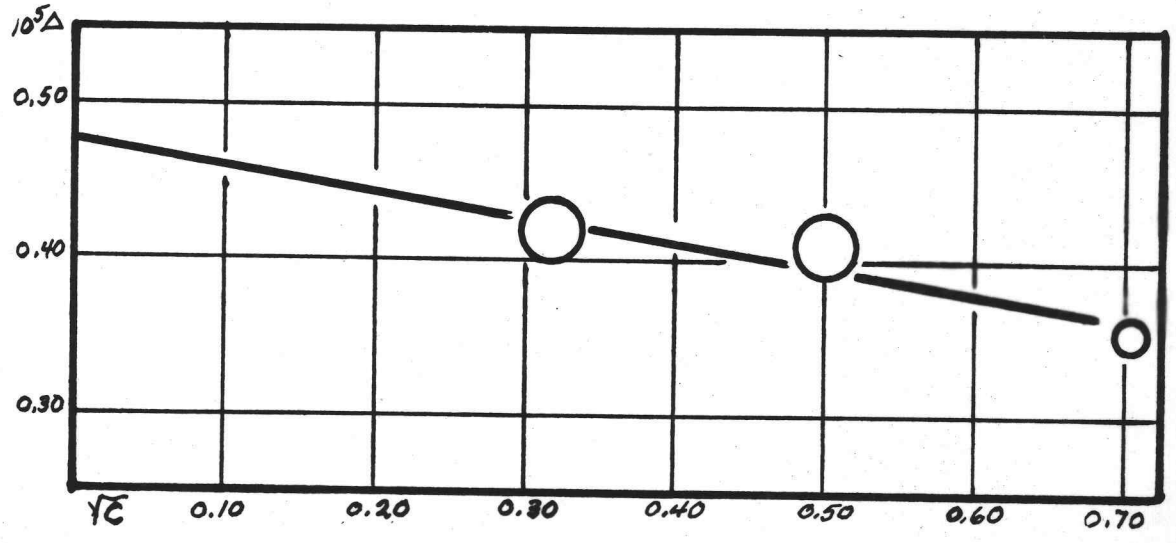
The use of the diffusion coefficient at zero concentration seems justified after a careful study of the Stokes-Einstein equation. The equation was derived on the assumption of free diffusion with no inter-attraction between molecules. This ideal condition could be reached only at the point of infinite dilution.



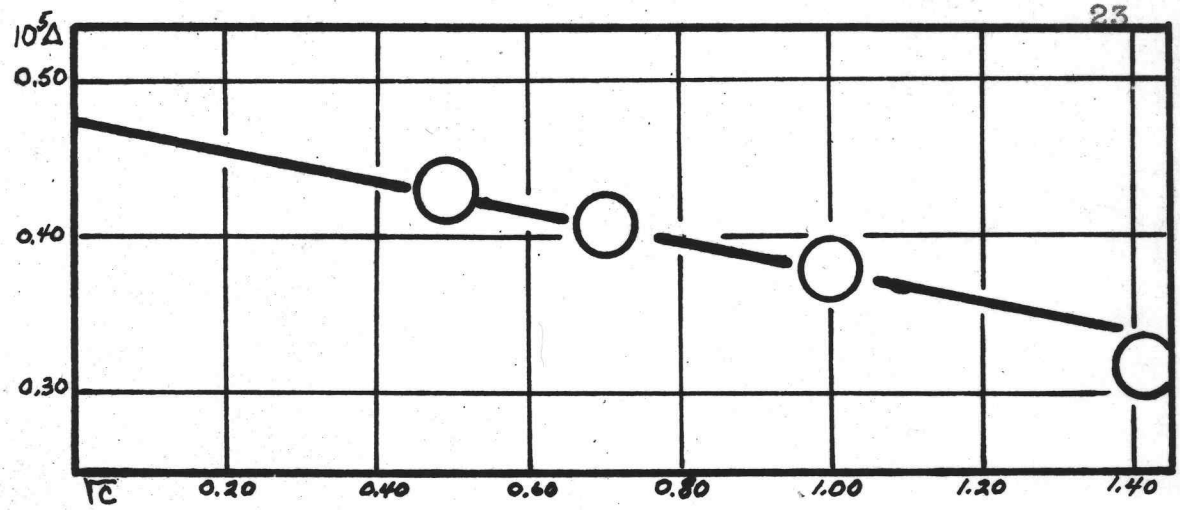
Diffusion of Glucose at 25° C.
Figure 4



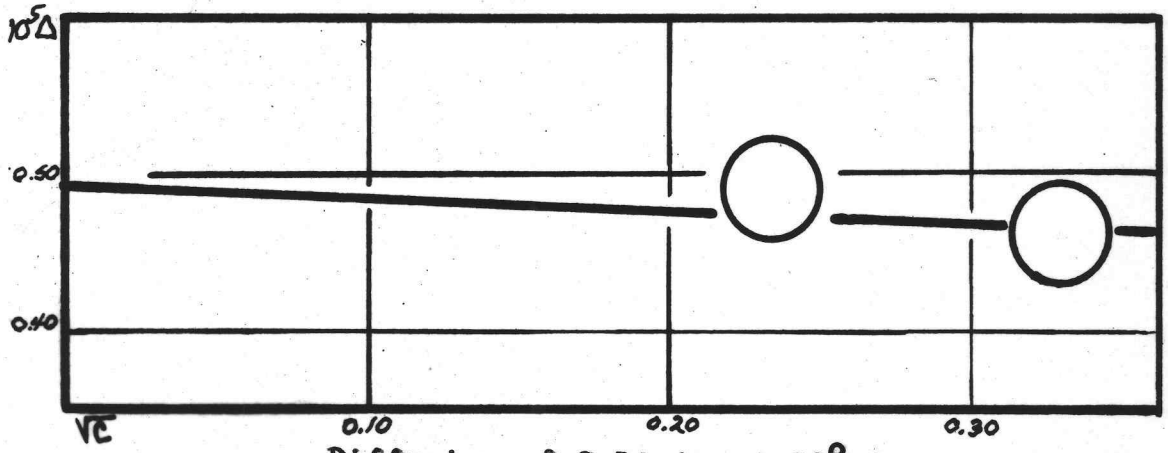
Diffusion of Lactose at 20° C.
Figure 5



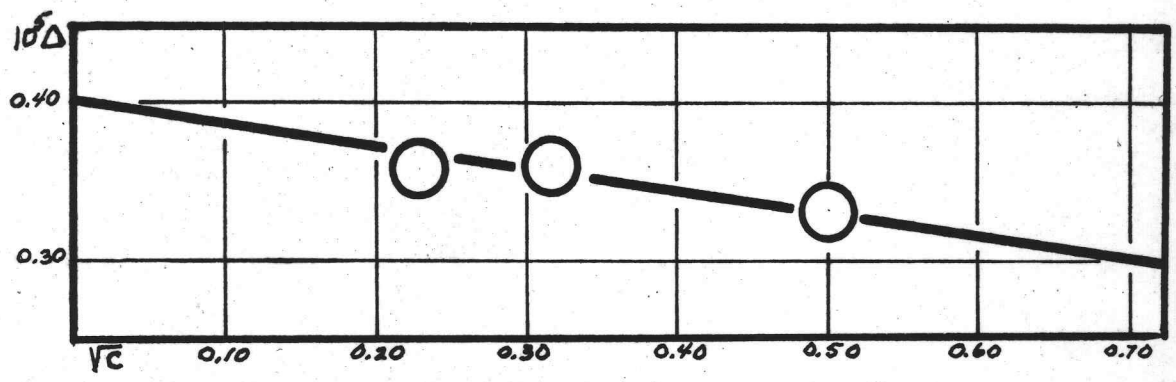
Diffusion of Maltose at 20° C.
Figure 6



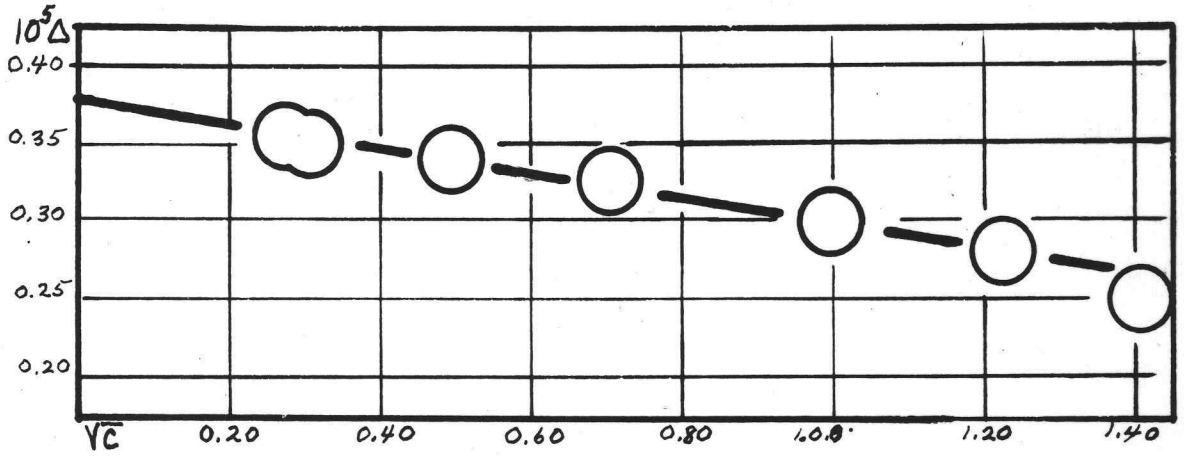
Diffusion of Sucrose at 20° C.
Figure 7



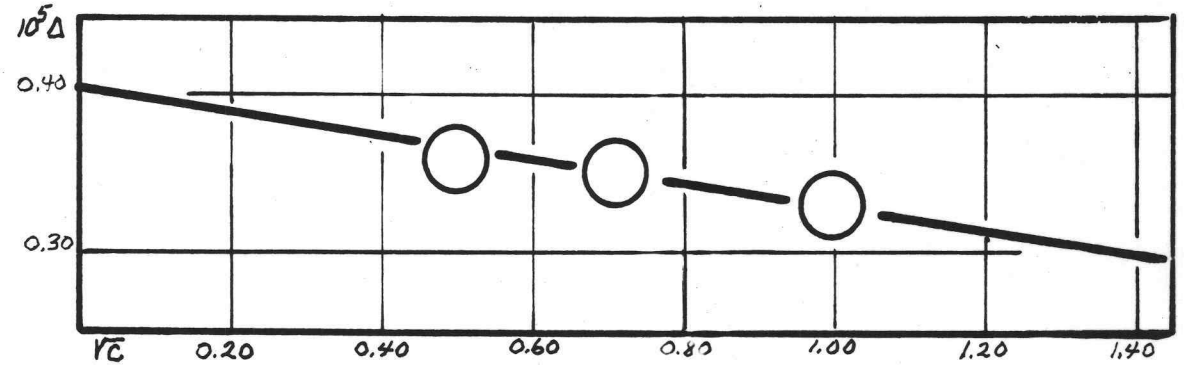
Diffusion of Salicin at 20° C.
Figure 8



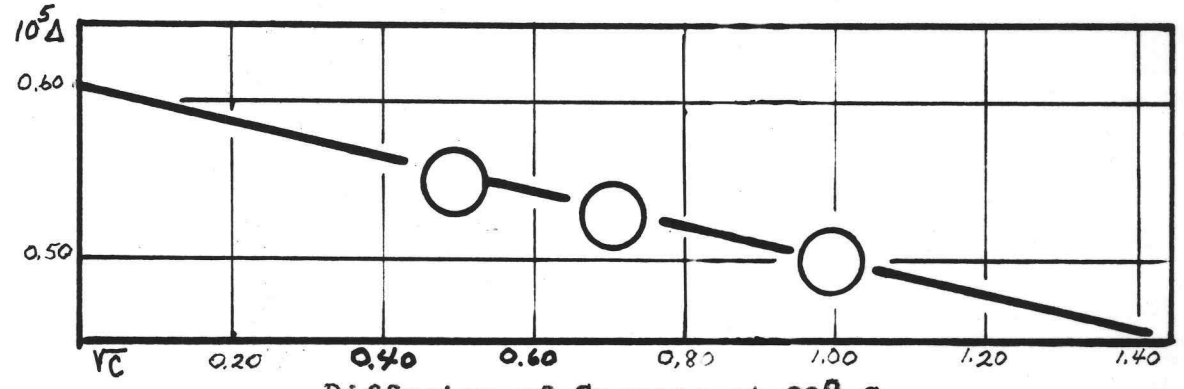
Diffusion of Raffinose at 20° C.
Figure 9



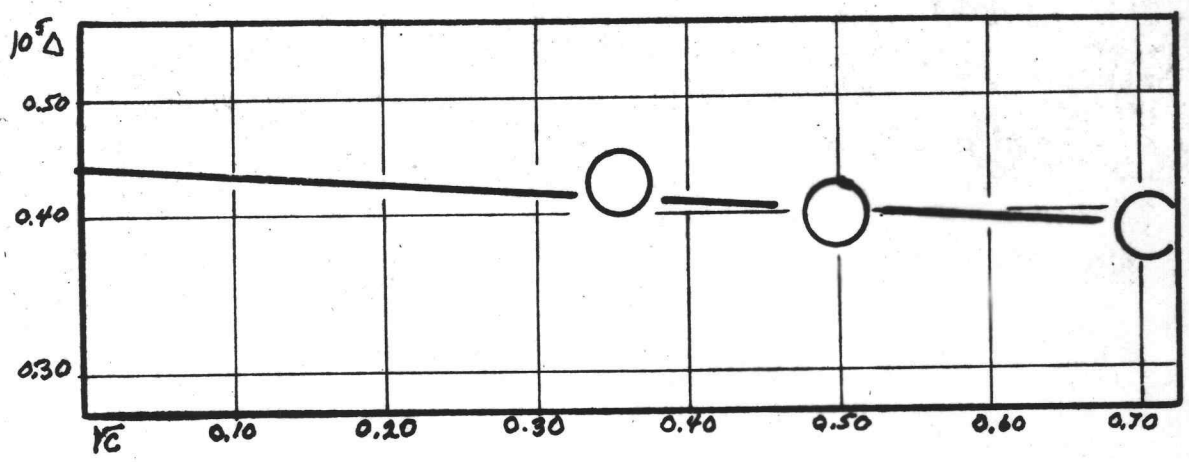
Diffusion of Sucrose at 12° C.
Figure 10



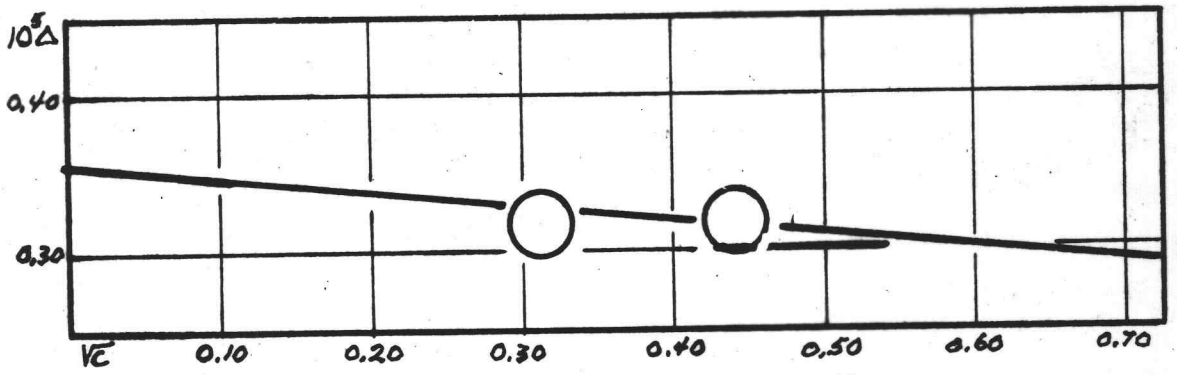
Diffusion of Sucrose at 14° C.
Figure 11



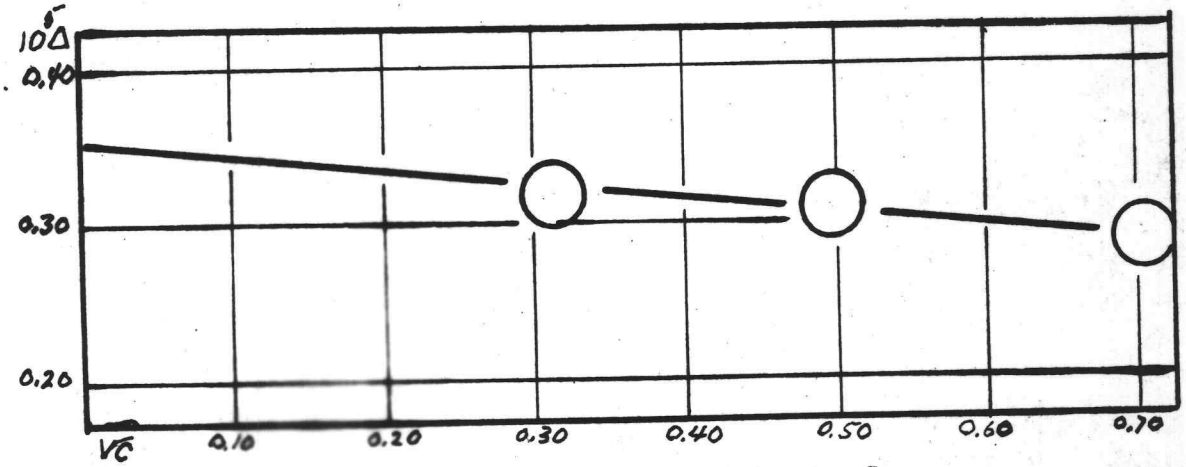
Diffusion of Sucrose at 29° C.
Figure 12



Diffusion of Mannitol at 10° C
Figure 13



Diffusion of Lactose at 10° C.
Figure 14



Diffusion of Maltose at 10° C.
Figure 15

Table IV

Molecular Weight Calculations from Diffusion Coefficients

Mannitol at 10° C

C_0	$10^5\Delta$	Calc. M.W.
0.5	0.39 ± .02	242
0.25	0.40 ± .02	224
0.125	0.42 ± .02	194
0*	0.432	182

Lactose at 10° C

C_0	$10^5\Delta$	Calc. M.W.
0.2	0.32 ± .02	459
0.1	0.32 ± .02	459
0*	0.353	342

Lactose at 20° C

C_0	$10^5\Delta$	Calc. M.W.
0.2	0.41 ± .02	531
0.1	0.43 ± .02	460
0*	0.475	342

Maltose at 10° C

C_0	$10^5\Delta$	Calc. M.W.
0.5	0.29 ± .01	623
0.25	0.31 ± .02	510
0.1	0.32 ± .02	463
0*	0.354	342

Maltose at 20° C

C_0	$10^5\Delta$	Calc. M.W.
0.5	0.38 ± .01	862
0.25	0.41 ± .02	536
0.1	0.42 ± .02	499
0*	0.476	342

Sucrose at 12° C

C_0	$10^5\Delta$	Calc. M.W.
2.0	0.25 ± .02	1183
1.5	0.28 ± .02	842
1.0	0.30 ± .02	685
0.5	0.325 ± .02	539
0.25	0.34 ± .02	471
0.1	0.35 ± .02	431
0.075	0.355 ± .02	413
0*	0.381	342

Sucrose at 14° C

C_0	$10^5\Delta$	Calc. M.W.
1.0	0.33 ± .02	838
0.5	0.35 ± .02	702
0.25	0.36 ± .02	645
0*	0.381	342

Sucrose at 20° C

C_0	$10^5\Delta$	Calc. M.W.
2.0	0.32 ± .02	903
1.0	0.38 ± .02	679
0.5	0.41 ± .02	540
0.25	0.43 ± .02	468
0*	0.481	342

Table IV (Continued)

Sucrose at 29° C			Salicin at 20° C		
C_0	$10^5 \Delta$	Calc. M.W.	C_0	$10^5 \Delta$	Calc. M.W.
1.0	0.50 ± .02	607	0.12	0.46 ± .03	300
0.5	0.53 ± .02	510	0.06	0.49 ± .03	248
0.25	0.55 ± .02	448	0*	0.494	286
0*	0.611	342			

*For 0 concentration the value of $10^5\Delta$ has been calculated from the molecular weight.

Results obtained in this study appear to make necessary further diffusion studies on several colloids where molecular weight values have been reported from diffusion coefficients at only a single concentration. It is possible that in some cases concentrations used were low enough so that the error introduced has been small. However, it would appear that correct molecular weights can be obtained only from the diffusion coefficient at zero concentration.

Further careful study of diffusion velocities of substances which have a molecular weight of less than 180 may yield data which will allow calculation of molecular weight through the use of an empirical correction factor depending upon the size of the diffusion coefficient obtained. This method of determining molecular weight has the advantage that it can be used on very dilute solutions where some sensitive means of determining concentrations is available and can be used in the case of fairly impure preparations.

Summary

A survey of the different methods of studying diffusion velocity has been made and the advantages and disadvantages of each pointed out. Diffusion coefficients of glucose at 25° C have been determined at concentrations varying from 0.1 M to 0.6 M and values varying from 0.566 to 0.532 have been obtained. These values have been plotted against the square root of the concentration and the value at zero concentration used to calculate the molecular weight with an accuracy of 2%. Literature values of diffusion coefficients of non-electrolytes have been similarly treated and found to give values for the molecular weight corresponding in accuracy with the accuracy of determination of diffusion coefficients. The value of using diffusion velocity as a means of calculating molecular weight is pointed out and the need for using diffusion coefficients at zero concentration is explained.

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