[CONTRIBUTION FROM THE COLLOID LABORATORY, UNIVERSITY OF WISCONSIN]

DIFFUSION OF NON-ELECTROLYTES IN GELATIN GELS[1]

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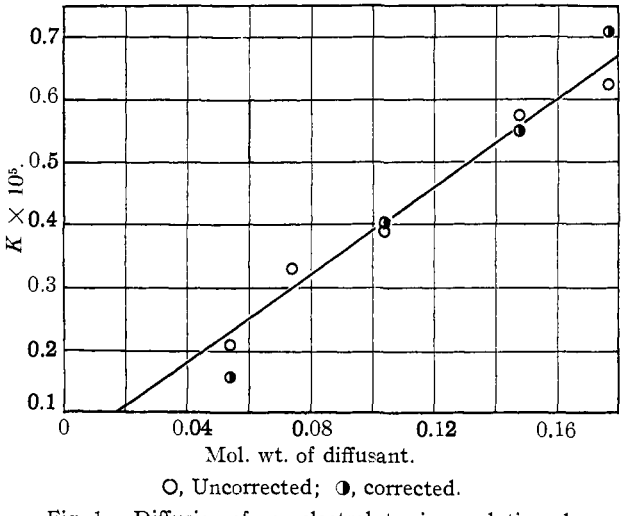
It was desired to investigate the diffusion in gels of materials with various molecular weights in order to determine whether the process followed the laws of diffusion or if it was specific for each diffusion substance regardless of the size of the molecule. If the former is true, then the product of the molecular weight and the square of the coefficient of diffusion should be a constant and the relation between the coefficient and the inverse of the square root of the molecular weight should be a straight line. The method of diffusion analysis described in a previous paper by Friedman and Kraemer was used.[1a]



O, Uncorrected; ◑, corrected.

Fig. 1.—Diffusion of non-electrolytes in a gelatin gel.

Experiments with several non-electrolytes showed that there was considerable variation from the relation mentioned above. An investigation of the effect of these non-electrolytes upon the diffusion process in gels was then carried out in an attempt to determine whether and to what extent the substance in question increased or decreased the rate of diffusion. These corrections have been applied to the coefficients for the non-electrolytes and curves are shown for both the uncorrected and corrected values.

Figure 1 shows the rates of diffusion for five substances in a 3.8% gelatin gel, Fig. 2 for nine substances in a 5% gel, the molecular weight range of the diffusate in each case being from 32 to 342.

[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin.

[1a] Friedman and Kraemer, THIS JOURNAL, **52**, 1295 (1930).

TABLE I

DIFFUSION OF VARIOUS NON-ELECTROLYTES IN A 3.8% GELATIN GEL

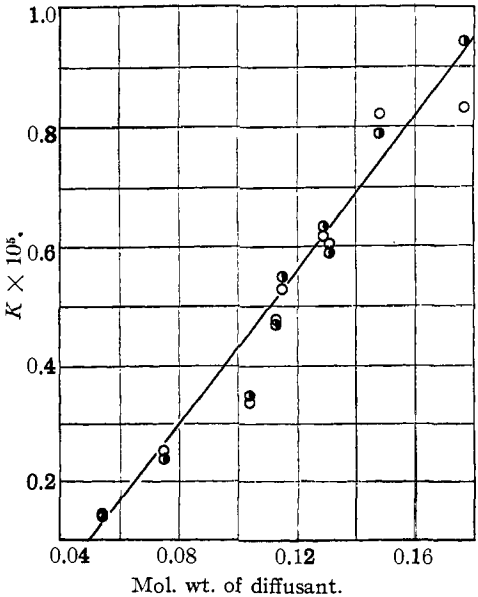
Diffusing substance	$\frac{1}{\sqrt{\text{Mol. wt.}}}$	Total time, hrs.	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean	Corrected
Methanol	0.177	216	8	0.866	0.442	0.626	0.710
Ethanol	.148	71	6	.660	.437	.576	.551
Glycerol	.104	71	6	.415	.363	.390	.405
Mannitol	.074	214	8	.379	.296	.331	.331
Sucrose	.054	216	8	.264	.144	.209	.158

TABLE II

DIFFUSION OF VARIOUS NON-ELECTROLYTES INTO A 5% GELATIN GEL

Diffusing substance	$\frac{1}{\sqrt{\text{Mol. wt.}}}$	Total time, hrs.	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean	Corrected
Methanol	0.177	23	2	0.933	0.737	0.835	0.945
Ethanol	.148	70	2	.830	.817	.824	.790
Acetone	.131	121	3	.855	.427	.605	.589
Urea	.129	96	4	.668	.573	.618	.634
Trimethyleneglycol	.115	121	3	.765	.402	.528	.550
Pyridine	.113	121	3	.581	.410	.479	.470
Glycerol	.104	97	4	.351	.324	.338	.351
Glucose	.075	96	4	.336	.188	.255	.240
Lactose	.054	67	2	.150	.138	.144	.141

It is to be noted that the points fall quite close to a straight line when the coefficient of diffusion is plotted against the inverse of the square root of the molecular weight, close enough to show that the size of the molecule does, to a large extent, determine the rate of diffusion, but each substance used does have its own specific influence upon the gelatin, altering its structure to change the rate of diffusion in the gel. The correction values determined in the next part of this paper do not place all of the values of the coefficients on the straight line, but do, in most cases, bring them much nearer to this relation. Even in studies of diffusion in water this relation does not hold much better, as shown by values given by Thovert[2] for the diffusion of



O, Uncorrected; ◑, corrected.

Fig. 2.—Diffusion of non-electrolytes in a gelatin gel.

[2] Thovert, "Tabelles Annuelles Internationalles de Constantes," Vol. 4, p. 746.

about twenty non-electrolytes where his calculated values of $K\sqrt{M} \times 10^5$ varied from 5.9 to 8. This was, however, considered a satisfactory constant, and so it is felt that the relations shown for the diffusion in gels can be considered good indication that the diffusion laws hold in the gels.

TABLE III

EFFECT OF NON-ELECTROLYTES UPON DIFFUSION OF UREA INTO A 4.7% GELATIN GEL FROM A 3% SOLUTION

Substances present in the gel	Total time, hrs.	Diffusion constants ($K \times 10^5$) Expts.	Max.	Min.	Mean	Increase in rate for urea, %
.....	95	5	0.555	0.443	0.510	..
Urea	95	5	.546	.455	.497	−2.5
Glycerol	97	5	.525	.432	.491	−3.7
Glucose	99	5	.602	.512	.564	10.6
Ethanol	99	5	.615	.484	.532	4.3
.....	47	7	.626	.567	.596	..
Sucrose	47	8	.932	.705	.791	32.7
Acetone	47	8	.731	.476	.608	2.8
Methanol	47	8	.555	.470	.525	−11.9
.....	53	7	.638	.592	.618	..
Lactose	52	9	.674	.576	.630	1.9
Pyridine	51	8	.712	.510	.630	1.9
Trimethyleneglycol	52	9	.653	.557	.593	−4.0

In order to determine the effect of various non-electrolytes on the diffusion process in gelatin gels, the gels were prepared to contain 1.5% of the non-electrolyte material and were then covered with a solution containing the same amount of the non-electrolyte (to avoid its diffusion) and in addition 3% of urea. The results are shown in Table III, where it is readily seen that most of the non-electrolytes have some effect upon the structure of the gels, the sucrose and glucose surprisingly large effects.

Effect of Temperature of Setting and Age of Gel upon Rate of Diffusion.—Because of the difficulty of reproducing results with gelatin gels with different previous heat treatment and the numerous references to the fact that the rate of setting determines to a large extent the physical structure of the gel, several investigations were made of the effect of temperature of setting and age upon the rate of diffusion in the gel. Gelatin gels cooled slowly are usually stronger physically, showing a more rigid solid structure. Hardy[3] has found that the more rapid the cooling the finer the structure will be. The results of the investigation are shown in Table IV.

From the (a) part it can be seen that if a gel is allowed to stand at one temperature long enough (in this case 92 hours), it will, for the most part, take up the structure of a gel originally set at that temperature. However, the other determinations show quite a variation in the diffusion constant.

[3] Hardy, *J. Physiol.*, **24**, 288 (1899).

TABLE IV

EFFECT OF TEMPERATURE OF SETTING AND AGE OF GEL UPON DIFFUSION OF UREA FROM A 3% SOLUTION INTO A GELATIN GEL MEASURED AT 5°

Temp. of setting, °C.	Kept at this temp., hours	Kept at 5°, hours	Total time, hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean
			(a) 4% Gel				
5	116	116	149	11	0.831	0.389	0.605
5	3	3	146	9	.695	.518	.597
0	24	92	143	10	.705	.443	.598
10	24	92	144	9	.711	.498	.603
24	24	92	145	9	.782	.390	.616
			(b) 5.2% Gel				
5	49	49	123	9	0.665	0.498	0.578
5	2	2	122	9	.586	.434	.514
0	50	0	123	8	.582	.457	.512
23	49	0	123	9	.545	.400	.481
23	24	25	125	8	.591	.492	.541
			(c) 4.3% Gel				
5	2	2	51	2	0.635	0.600	0.618
0	24	0	53	4	.613	.562	.589
23	27	0	54	4	.640	.419	.504

Since the information obtained from these experiments was so meager, diffusion at 5, 10, 15 and 20° was measured, using the same supply of gelatin and varying the conditions of setting as previously. The results are given in Table V, but not enough regularity has been shown here to warrant any quantitative discussion of the change in structure under these conditions.

TABLE V

EFFECT OF TEMPERATURE OF SETTING UPON DIFFUSION INTO A 5.1% GELATIN GEL

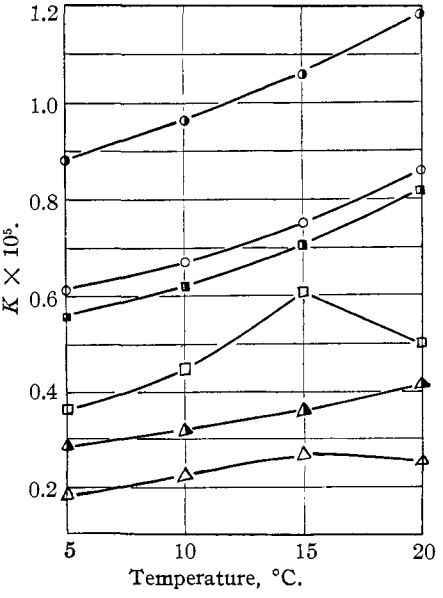
Temp. of set-ting, °C.	Kept at this temp., hours	Temp. of diff., °C.	Kept at this temp., hours	Total diff., hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean
				Urea from a 3% solution				
5	24	5	24	32	10	0.709	0.553	0.609
5	23	5	23	55	10	.609	.442	.535
25	24	5	1	31	9	.677	.541	.598
30	3	5	23	32	10	.846	.502	.593
0	24	5	2	33	9	.700	.545	.615
10	24	10	24	31	10	.751	.471	.667
24	24	10	1	32	11	.701	.477	.515
0	24	10	1	32	10	.757	.563	.693
15	24	15	24	29	10	.829	.605	.750
25	24	15	1	29	10	.820	.712	.772
0	24	15	1	29	10	.958	.710	.801
20	24	20	24	26	9	.990	.613	.859
25	24	20	1	25	9	.909	.644	.829
0	24	20	1	26	9	.855	.660	.767

TABLE V (*Concluded*)

Temp. of setting, °C.	Kept at this temp., hours	Temp. of diff., °C.	Kept at this temp., hours	Total diff., hours	Diffusion constants ($K \times 10^5$) Expts.	Max.	Min.	Mean
Sucrose from a 3% solution								
10	24	10	24	33	11	0.274	0.187	0.220
15	24	15	24	29	10	.286	.228	.266
20	24	20	24	27	9	.297	.160	.252
Glycerin from a 3% solution								
10	24	10	24	32	11	0.505	0.318	0.444
15	24	15	24	29	10	.706	.501	.606
20	24	20	24	27	9	.630	.350	.500

In Table VI the results of the last four runs are summarized and it is to be noticed that in three cases out of the four the gel set at 25° gives a lower rate of diffusion while that set at 0° gives a higher rate than the gel set at the temperature of diffusion. Qualitatively, then, the lower the temperature of setting the higher the rate of diffusion.

Figure 3 shows the rates of diffusion of urea, glycerol and sucrose in a 5.1% gelatin gel and in water at 5, 10, 15 and 20°; the variation is due to the change in structure at higher temperature causing slower diffusion. From each curve it is to be noted that at 20° there is much slower diffusion than would be expected from the values at 5°. The curve for glycerin in the gel shows a peculiar behavior, but roughly the same effect is noticeable. These curves would tend to substantiate the statement that gels set at lower temperature offer less resistance to diffusion than gels set at higher temperatures.



◑, Diffusion of urea in water; ○, diffusion of urea in gel; ▲, diffusion of sucrose in water; △, diffusion of sucrose in gel; ◨, diffusion of glycerin in water; □, diffusion of glycerin in gel.

Fig. 3.—Diffusion in gels *vs.* temperature.

The values for the coefficients of diffusion in water at the various temperatures were obtained from the following values of $K \times 10^5$ given by Öholm:[4] sucrose, 0.380 at 22°; glycerin, 0.816 at 20°; and urea, 1.183 at 20°. To change to the various

[4] Öholm, *Medd. Vetenskapsakad. Nobelinst.*, 2, n23.

TABLE VI

EFFECT OF TEMPERATURE OF SETTING UPON DIFFUSION OF UREA IN 5.1% GELATIN

Temp. of setting, °C.	$K \times 10^5$ 5°C.	10°C.	15°C.	20°C.
25	0.598	0.565	0.772	0.829
0	.615	.693	.801	.767
Temp. of diff.	.609	.667	.750	.859

TABLE VII

DIFFUSION IN 5.1% GELATIN GELS AT DIFFERENT TEMPERATURES

Diffusing substance	$K \times 10^5$ 5°C.	10°C.	15°C.	20°C.
Urea	0.609	0.667	0.750	0.859
Glycerin	.363	.444	.606	.500
Sucrose	.182	.220	.266	.252

DIFFUSION IN WATER AT DIFFERENT TEMPERATURES CALCULATED FROM ÖHOLM

Diffusing substance	$K \times 10^5$ 5°C.	10°C.	15°C.	20°C.
Urea	0.880	0.962	1.061	1.183
Glycerin	.552	.618	0.704	0.816
Sucrose	.285	.318	.359	.413

temperatures, use was made of the empirical equation $K_{t_1} = K_{t_2}/1 + \alpha(t_2 - t_1)$, where $\alpha = 0.026 - 0.021 \log K$.[5]

Summary

1. Diffusion constants for several non-electrolytes in gelatin gels have been determined.

2. It has been shown that the diffusion laws hold for these compounds in gelatin gels.

3. It has been found that each non-electrolyte has a very specific action on the rate of diffusion in gelatin gels; those outstanding were the increase by sucrose of 32%, and the decrease by methanol of 12%.

4. Study of the effect of temperature of setting and age of the gel has shown that, in general, gels set at low temperature are more permeable to molecules than those set at higher temperature. This has been interpreted to indicate a more open structure.

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[5] Öholm, *Z. physik. Chem.*, **70**, 399 (1909).