

electric point or the solutions must contain a sufficient amount of salt, if the results are to be used for the calculation of particle size.

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Summary

The effect of pH upon diffusion velocity of gela-

tin solutions has been measured over the pH range 0.05 to 6.4.

The effect of added potassium chloride at the various pH 's upon the diffusion coefficient has been measured.

Results obtained indicate that between pH 's 2 and 6.4 only a small change in particle size takes place in 3% gelatin solution at 35°, but below pH 2, there is a rapid decrease in particle size.

CORVALLIS, OREGON

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

The Effect of Non-electrolytes upon the Time of Setting of Gelatin Gels

BY LEO FRIEDMAN AND W. N. SHEARER¹

In an earlier investigation² a study was made of the effect of non-electrolytes upon diffusion velocity in gelatin gels. Interpretations of the results obtained involved the hypothesis that non-electrolytes present in gelatin gels actually influenced gel structure. With the view to further investigate this possible influence the following study of the setting of gelatin gels was undertaken.

Experimental.—Gelatin solutions containing 25 g. of electrolyzed calfskin gelatin in 475 ml. of water were made up. The gelatin was first placed in 200 ml. of water in a one-liter flask and permitted to stand for twenty-two hours in a thermostat at 25°, after which 275 ml. of water was added and the solution heated to 55° until the gelatin was dissolved completely. This solution was then cooled to 25° in the thermostat.

Varying amounts of the non-electrolytes to be used were dissolved in enough water to make up 10 g. of solution. These non-electrolyte solutions were then placed in wide-mouthed bottles, approximately 6.3 cm. in diameter, and 90 ml. of the gelatin solution was poured into each bottle. The bottles were placed immediately in the thermostat and tightly stoppered.

In order to determine when the gels had set a penetrometer was used. The penetrometer consisted of a glass tube about 45 cm. long and 8 mm. in diameter sealed and rounded on the end which was used to test the gel. At the other end of the glass tube was fastened a larger glass tube 18 cm. long and 12.5 mm. in diameter. Around

the first tube was a coil consisting of 25 loops of steel wire 0.035 mm. in diameter so fastened that the spring resisted the movement of the smaller glass tube into the larger. As an indication that a gel had set the following criterion was followed.

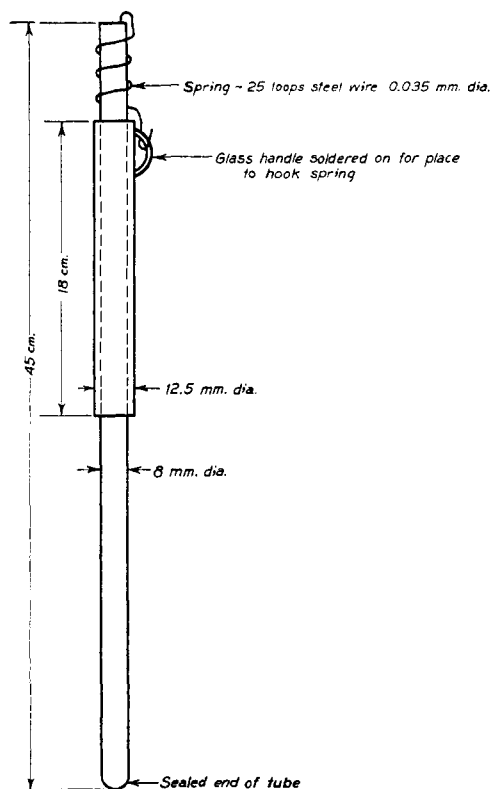


Fig. 1.—Penetrometer.

When a gel had set enough so that the tube would go into the gel far enough to stretch the spring to the 2.6 cm. mark from the starting point without

(1) Present address: Western Waxed Paper Co., North Portland, Oregon.

(2) Leo Friedman and W. N. Shearer, *THIS JOURNAL*, **56**, 1323 (1934).

TABLE I
EFFECT OF NON-ELECTROLYTES UPON TIME OF SETTING OF GELATIN GELS

Molar concn.	Sucrose at 25°		Urea at 25°		Levulose at 25°		Levulose at 17°	
	S. T. Min.	Incr. % S. T., %	S. T. Min.	Incr. % S. T., %	S. T. Min.	Incr. % S. T., %	S. T. Min.	Incr. % S. T., %
0.00	212	305	185	45
.01	219	3.3	331	8.5	200	8.1
.02	243	14.6	351	15.1	204	10.3	49	8.9
.03	232	9.4	359	17.7	201	8.7
.04	221	4.2	355	16.4	195	5.4
.05	215	1.4	175	- 5.4	47	4.4
.06	318	4.3
.10	201	- 5.2	141	-23.8	42	- 6.7
.20	166	-21.7	235	-22.9	136	-25.5	34	-24.4

breaking the surface of the gel, it was considered to have completely set. This empirical method and home-made penetrometer were found to be very accurate and convenient in testing gels.

Table I gives the results obtained in the study of the time of setting of gelatin gels in the presence of sucrose, urea, and levulose. It is to be noted that up to a concentration of 0.02 to 0.03 molar non-electrolyte setting time was increased, but this effect became less marked at higher concentrations and finally at concentrations of 0.2 molar, setting times had been decreased by more than 20%.

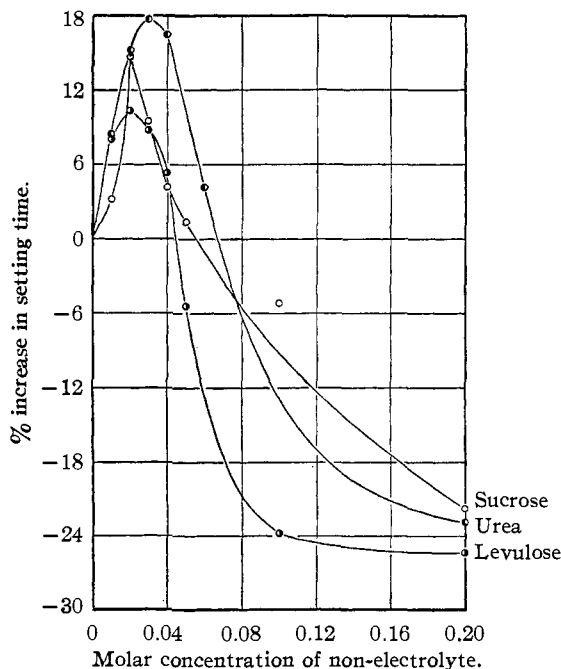


Fig. 2.—Effect of non-electrolytes on setting of gelatin gels.

Discussion

In the investigation of the effect of non-electro-

lytes upon diffusion velocity in gelatin gels,² it was found that low concentrations of non-electrolyte brought about an increase in diffusion velocity, this effect reaching a maximum at concentrations below 0.04 molar. At higher concentrations of non-electrolyte the diffusion velocity was increased less and at concentrations above 0.08 to 0.18 molar for the various non-electrolytes used the diffusion velocity was slower than in the absence of any non-electrolyte. These results were explained by assuming that non-electrolytes influence diffusion in gels in two ways: (1) by increasing the radii of the pores within the gel due to a decrease in the hydration of the solid phase, and (2) by increasing the viscosity of the medium through which diffusion takes place.

As early as 1900, Hardy³ observed that the rate of setting influenced the structure of gels, and that gels which had been cooled rapidly had a "finer structure." In an earlier investigation by one of the authors⁴ on diffusion of non-electrolytes in gelatin gels, it was observed that when gels were set at low temperatures, which results in rapid setting, gels were formed through which diffusion was more rapid than through gels set at higher temperatures.

On the other hand those concentrations of non-electrolytes which through their presence slow down gel formation yield gels through which diffusion is more rapid than through those gels that have set more rapidly due to the presence of higher concentrations of non-electrolytes. When rate of setting is influenced by foreign substances, it appears that slow setting yields gels with a more open structure, since diffusion velocity in gels² varied directly with time of setting.

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(3) Hardy, *J. Physiol.*, **24**, 288 (1899); *Proc. Roy. Soc. (London)*, **66**, 95 (1900).

(4) Leo Friedman, *THIS JOURNAL*, **52**, 1305 (1930).

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Summary

A study of the effect of non-electrolytes upon the rate of setting of gelatin gels has been carried out.

Small concentrations of non-electrolytes in-

crease setting time, this effect becoming a maximum at 0.02-0.03 molar.

Concentrations of non-electrolyte exceeding 0.1 molar cause gels to set more rapidly than in the absence of non-electrolytes.

Comparison with results of diffusion experiments leads to the conclusion that the slower setting gels have a more open structure.

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Catalytic Dehydration of C₆-C₈ Aliphatic Alcohols

BY SEYMORE GOLDWASSER AND HUGH S. TAYLOR

An apparatus for the study of vaporized hydrocarbons and its application to the dehydrogenation of cycloöctene were described in a previous paper.¹ In seeking a good source of aliphatic hydrocarbons, it was found that certain alcohols were available in comparatively large quantities. Catalytic dehydration of these alcohols in this same apparatus proved to be an excellent source of alkenes and provided certain information concerning the mechanisms of dehydration and isomerization.

The separation of the pure isomers resulting from the dehydration of an alcohol was accomplished by the use of a modification of the Podbielniak column together with a special head which permits controlled reflux ratio.

Apparatus.—The column proper is shown in Fig. 1. It consists simply of a Pyrex tube, A, 1.5 meters long and 4.5 mm. i.d., flared at both ends to fit in a 1.8-meter long 16-mm. tube, B, which has a 16-mm. ground joint at one end and is ring-sealed at 1 and 2 at both ends. The space between the two tubes is evacuated through a side tube with the column at about 150°, the necessary heat being provided electrically with 12.2 meters of no. 20 chromel wire wound externally. About 6.1 meters of no. 20 chromel are wound spirally on a rod of such size that, when the spiral is stretched to six or seven turns per inch (2.5 cm.), it fits snugly inside the center tube of the column. This is the Podbielniak type packing. It does not allow reflux liquid to run down the column but causes it to travel down in a spiral path. More time is thus afforded for equilibrium to be set up and separation is excellent. The hold-up is small and the amount of liquid reaching the head without flooding is much larger than can be secured with the helical glass packing. A 200° thermometer, C, graduated in tenths of one degree is tied with asbestos directly to the column so that the

bulb of the thermometer touches the evacuated jacket about one-third from the bottom. Just above the ground joint and also 1.5 meters up the column are wound asbestos strips so that the column is tightly supported inside a 1.5-meter 35-mm. Pyrex tube.

The head, D, which is described by J. H. Simons,² is sealed on just above the outermost insulating jacket and fitted with a thermometer, E, which is calibrated at 0, 56.7 and 100°. This head is a total condensing variable take-off type and has the advantage that it will accurately control reflux ratio, that it allows accurate and direct temperature measurement, and that hot hydrocarbon vapors can in no way come in contact with any contaminating surfaces. It can be adjusted for total return so that, in adjusting the column for operation, there is no loss.

Heating of the liquid is supplied by a small electrical heater, F. Either a 100-cc. or 200-cc. flask, G, with interchangeable ground joints may be used. The receivers are 30 cm. long 12-mm. tubes immersed in an ice-bath so that the outlet tube, H, from the head is at a lower level than the

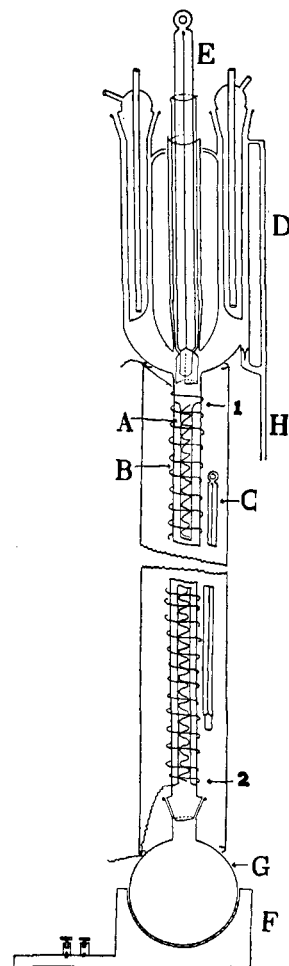


Fig. 1.—Fractionation apparatus.

(1) S. Goldwasser and H. S. Taylor, *THIS JOURNAL*, **61**, 1260 (1939).

(2) J. H. Simons, *Ind. Eng. Chem., Anal. Ed.*, **10**, 29 (1938).