

AN ABSTRACT OF THE THESIS OF

William Norman Shearer for the Ph. D. in Chemistry

Date Thesis presented May 14, 1948

Title The Effect of Small Quantities of Non-electrolytes and Electrolytes upon Structure and Setting Time of Gelatin Gels

Abstract Approved

In an earlier investigation it was observed that the presence of a non-electrolyte in a gelatin gel into which urea was diffusing would affect the diffusion velocity of the urea quite markedly. No correlation between non-electrolyte used and effect of diffusion velocity was apparent so the present investigation was undertaken to determine the reasons for the changes in diffusion velocity of urea brought about by the presence of non-electrolytes in the gels.

The experiments were carried out at 5° by a method developed by Friedman and Kraemer, which had proven very reliable. The effect of glycerol, sucrose, urea, methanol, and glucose upon the diffusion of urea into 3% gelatin gels was studied. It was found that in every case the presence of a small amount of non-electrolyte caused an increase in the diffusion velocity of urea. With continued increase in the concentration of the non-electrolyte there was further increase in the diffusion velocity of urea until a maximum was reached which varied in the five non-electrolytes studied between 0.006 and 0.07 molar. With higher concentrations of non-electrolytes the diffusion velocity was lowered from this maximum value and beyond concentrations ranging from 0.08 to 0.18 molar the diffusion velocity was less than the normal diffusion velocity of urea into a pure gel.

To determine if this effect of non-electrolytes on the diffusion velocity of urea had a parallel effect on setting time, an experiment on the effect of sucrose, urea, and levulose on the setting time of 4.5% gels was performed using a penetrometer to test gel setting. This penetrometer tested the resistance of the gel to puncture and when this resistance reached an arbitrarily determined point the gel was considered set. When plotting percentage increase of setting time against concentration of non-electrolyte, curves very similar to the ones obtained in the previous

experiment on diffusion were obtained.

The effect of the electrolytes  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{HCl}$  and  $\text{NaOH}$  on the setting time of gelatin gels was studied next. In all cases except  $\text{AlCl}_3$  and  $\text{FeCl}_3$ , an S shaped curve was obtained when percentage increase of setting was plotted against molar concentration. In the lower concentrations the electrolytes gave a similar curve to non-electrolytes going through a maximum setting time from 0.002 to 0.008 molar but at higher concentrations the setting time instead of continuously decreasing with increase of concentration went through a minimum and from then on again increased in setting time with increase of concentration.

De Jong's theory of the setting of gelatin gels postulates the existence of hydrophobic spots on the gelatin particles than can join together making a gel framework. The experimental curves obtained can be explained by three factors one of which does not exist in non-electrolyte solution. The first effect is the adsorption of the substance added on these hydrophobic spots thus hindering the setting and making a more open pore structure. The second effect is the dehydration of the gelatin particles by further addition of electrolyte or non-electrolyte to form more hydrophobic spots which although not as efficient gel formers as those on the pure gel are nevertheless sufficiently greater in number to decrease the setting time and pore size. The last effect which occurs only with the electrolytes is due to the charge on the gelatin particles from adsorbed ions which causes the particles to repel each other thus increasing setting time.

THE EFFECT OF SMALL QUANTITIES  
OF NON-ELECTROLYTES AND ELECTROLYTES  
UPON STRUCTURE AND SETTING TIME  
OF GELATIN GELS

by

WILLIAM NORMAN SHEARER

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of  
the requirements for the  
degree of

DOCTOR OF PHILOSOPHY

June 1948

APPROVED:

---

Professor of Chemistry

In Charge of Major

---

*in given*  
Head of Department of Chemistry

---

Chairman of School Graduate Committee

---

Dean of Graduate School

#### ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. Leo Friedman, who suggested the problem and rendered valuable assistance and encouragement, without which this thesis would never have been completed.

## TABLE OF CONTENTS

I.	INTRODUCTION . . . . .	1
II.	MATERIALS AND EXPERIMENTAL PROCEDURE . . . . .	5
	Materials . . . . .	5
	Equipment . . . . .	5
	Diffusion Experiments . . . . .	6
	Setting Time Experiments with Non-	
	Electrolytes . . . . .	7
	Setting Time Experiments with Elec-	
	trolytes . . . . .	7
III.	RESULTS AND CONCLUSIONS. . . . .	.10
IV.	DISCUSSION OF RESULTS. . . . .	.15
V.	DATA AND SAMPLE CALCULATIONS . . . . .	.20
VI.	BIBLIOGRAPHY . . . . .	.44

## LIST OF TABLES

1.	The Effect of Non-Electrolytes upon Diffusion of Urea from a 3% Solution into 3% Gelatin Gels.	20
2.	The Effect of Non-Electrolytes upon Setting Time of 4.5% Gelatin Gels at 25°.	23
3.	The Effect of Sucrose on the Setting Time of 4.5 and 6.0% Gelatin Gels at 25°.	23
4.	The Effect of Levulose on the Setting Time of 4.5% Gelatin Gels at 25° and 17°.	25
5.	The Effect of Sodium Chloride on the Setting Time of 4.5% Gelatin Gels at 25°.	25
6.	The Effect of Sodium Nitrate on the Setting Time of Gelatin Gels at 25°.	28
7.	The Effect of Sodium Sulfate on the Setting Time of 6% Gelatin Gels at 25°.	29
8.	The Effect of Sodium Oxalate on the Setting Time of 6% Gelatin Gels at 25° - Run No. 14.	29
9.	The Effect of Trisodium Phosphate on the Setting Time of 6% Gelatin Gels at 25° - Run No. 15.	30
10.	The Effect of Trisodium Citrate on the Setting Time of 3% Gelatin Gels at 25° - Run No. 16.	30
11.	The Effect of Potassium Chloride on the Setting Time of 4.5% Gelatin Gels at 25°.	32
12.	The Effect of Calcium Chloride on the Setting Time of 4.5% Gelatin Gels at 25°.	32
13.	The Effect of Barium Chloride on the Setting Time of 4.5% Gelatin Gels at 25°.	33
14.	The Effect of Aluminum Chloride on the Setting Time of 4.5% Gelatin Gels at 25°.	33
15.	The Effect of Ferric Chloride on the Setting Time of 4.5% Gelatin Gels at 25°.	34

LIST OF TABLES (Cont.)

16. The Effect of Sodium Hydroxide on the Setting Time of 6.0% Gelatin Gels at 25° - Setting Time for pure gel 99 minutes. 34
17. The Effect of Hydrochloric Acid on the Setting Time of 6.0% Gelatin Gels at 25° 36
18. A Sample of Experimental Data and Calculations Used to Determine the Diffusion Constant and Percentage Increase in Diffusion Constant 40
19. A Sample of Experimental Data and Calculations Used to Determine the Setting Time and Percentage Increase in Setting Time. 42

## LIST OF FIGURES

1.	The Penetrometer	8
2.	The Effect of Non-Electrolytes on the Diffusion of Urea into 3% Gelatin Gels at 5°	22
3.	The Effect of Non-Electrolytes on the Setting Time of 4.5% Gelatin Gels at 25°	24
4.	The Effect of Sucrose on the Setting Time of 4.5% and 6% Gelatin Gels at 25°	26
5.	The Effect of Levulose on the Setting Time of 4.5% Gelatin Gels at 25° and 17°	27
6.	The Effect of Sodium Salts on the Setting Time of Gelatin Gels at 25°	31
7.	The Effect of Various Chlorides on the Setting Time of Gelatin Gels at 25°	35
8.	The Effect of NaOH and HCl on the Setting Time of Gelatin Gels at 25°	37
9.	The Effect of pH on Setting Time of Gelatin Gels at 25°	38
10.	Theoretical Curves	39
11.	Theoretical Curves	39

THE EFFECT OF SMALL QUANTITIES OF NON-ELECTROLYTES AND  
ELECTROLYTES UPON STRUCTURE AND SETTING TIME  
OF GELATIN GELS

I. INTRODUCTION

In an earlier investigation (3), it was observed that the presence of a non-electrolyte in a gelatin gel in which urea was diffusing would affect the diffusion velocity of the urea. The gels had been prepared to contain 1.5% of the non-electrolyte and urea was permitted to diffuse from a solution containing a like concentration of the same non-electrolyte into the gel. Of the ten non-electrolytes used, four caused a decrease in the diffusion velocity of urea and six caused an increase. The greatest decrease was 11.9% produced by methanol, and the greatest increase was 32.7% by sucrose. No correlation between chemical structure and the effect on diffusion velocity was apparent from this investigation. For example; while methanol slowed down the diffusion rate, as stated above, ethanol increased diffusion by 4.3%.

The present investigation had its beginning in an attempt to determine the reason for the changes in diffusion velocity of urea brought about by the presence of the non-electrolytes in the gels. It was soon discovered that varying the amounts of these non-electrolytes had a very unique effect on diffusion.

The question that logically followed this discovery was: Is this effect found only in diffusion or is it also

found in other properties of the gels? At the time the rate of setting of the gels seemed to be a good field for investigation. It was discovered that varying amounts of non-electrolytes had an effect on the setting time of gelatin gels that paralleled the effect on diffusion.

The question then arose whether or not electrolytes also had a similar effect on gelatin gels. Setting time experiments could be carried out in a few hours while the diffusion investigation would take a similar number of days. Although it was impossible to study the effect of electrolytes upon diffusion, due to the swelling of the gel caused by the electrolytes, the setting experiments could be carried out with electrolytes, because swelling is impossible in the absence of a liquid phase above the gel.

The total investigation is thus divided into three parts, each a consequence of the previous investigation, first the effect of small amounts of non-electrolytes on the diffusion of urea into gelatin gels, next the effect of non-electrolytes upon the rate of setting of gelatin gels, and last the effect of electrolytes upon the rate of setting of gelatin gels.

The method of studying diffusion employed in this work was that developed by Friedman and Kraemer (5) who made use of an equation developed by March and Weaver (8) to calculate the diffusion coefficient. The validity of

this method is well established not only in gelatin gels where it was shown by Friedman (3) to follow the laws of diffusion when diffusants with different molecular weights are used, but also it will work in such diversified systems as agar gels in water (4) and cellulose acetate gels in benzyl alcohol (6).

The method of impregnating the gel with the non-electrolyte was the same as described by Friedman (3) except varying amounts of each non-electrolyte were used instead of just 1.5%.

There have been a number of methods described in the literature for the investigation of setting of gels. This phenomenon can be studied in three different ways. One way is to set the gels and in a certain length of time measure their strength. This is the standard method (2) now employed in testing the gel strength of glues. It is a good method, but requires a Bloom gelometer which is a rather expensive piece of equipment and was not available.

Another method as described by Pedersen (9) is to determine what concentration of gel reaches a standard strength in a certain length of time. This method was discarded in this investigation because it introduced another variable, that of varying concentrations of gelatin. Results obtained later indicated that the effects found were, within the limits of error, independent of the

gel concentration, so this method might have given good results if it had been used.

The third possible method, and the one that was chosen for these experiments, is to determine the length of time necessary for the gel to reach a certain strength. A number of methods have been used in the past to determine this strength. Prosod and Hattiangodi (10) measured the intensity of scattered light and assumed that a certain light scattering stood for a certain strength of gel. Cox (1) placed a rod upright in the gel and the gel was considered set when the rod would remain upright for a certain length of time. The disadvantage of this method is that a large surface area of the gel is destroyed at each trial. In the method finally chosen, use is made of an instrument called a "penetrometer," which was easy to make, quite accurate, and did not destroy much gel surface at each trial.

## II. MATERIALS AND EXPERIMENTAL PROCEDURE

**MATERIALS:** The gelatin used in the diffusion experiments was a good grade of calf-skin gelatin that was electrolyzed by the method of Friedman and Kraemer (5). Eastman Purified Calf Skin Gelatin was used in the setting experiments.

Other chemicals used were C. P. grade either Baker's Analyzed or Baker and Adamson.

**EQUIPMENT:** The 5° thermostat used in the diffusion experiments consisted of a metal vat wound with cooling coils and covered with insulation set in a wooden box about 4 feet by 4 feet by 3 feet. The cooling coils were connected to a standard home type Frigidaire compressor. The temperature was held at  $5^{\circ} \pm 0.1^{\circ}\text{C}$ .

The 25° thermostat used in the setting time experiments was equipped with immersion heaters and Fenwal Immersion Thermo-Switch sensitive to 0.06° centigrade.

The apparatus used for determining diffusion coefficients was similar to that described by Friedman and Kraemer (5).

The penetrometer (Fig. 1), used to determine when the gels had set, consisted of a glass tube about 45 cm. long and 8 mm. in diameter; sealed and rounded on the end of the tube 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. 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 breaking the surface of the gel it was considered to have completely set. This empirical method and homemade penetrometer were found to be convenient and accurate to one minute in an elapsed time of two hundred minutes.

**DIFFUSION EXPERIMENTS:** Three per cent gels by weight were used in the diffusion experiments and were made by weighing enough of the electrodyalized gelatin, to equal  $4\frac{1}{2}$  g. dry weight, into standard 500 ml. wide mouth bottles, whose cross sectional area had been accurately measured. The required amount of non-electrolyte and enough water to make the solution total 150 g. were then added. The gels were dissolved in a 55° bath. When the gels had set enough so that the surface would stay intact, usually about four hours, they were covered with 150 ml. of solution of non-electrolyte of concentration equal to that in the gel. After about 36 hours, the refractive index of the solution was read; 4.5 g. of urea

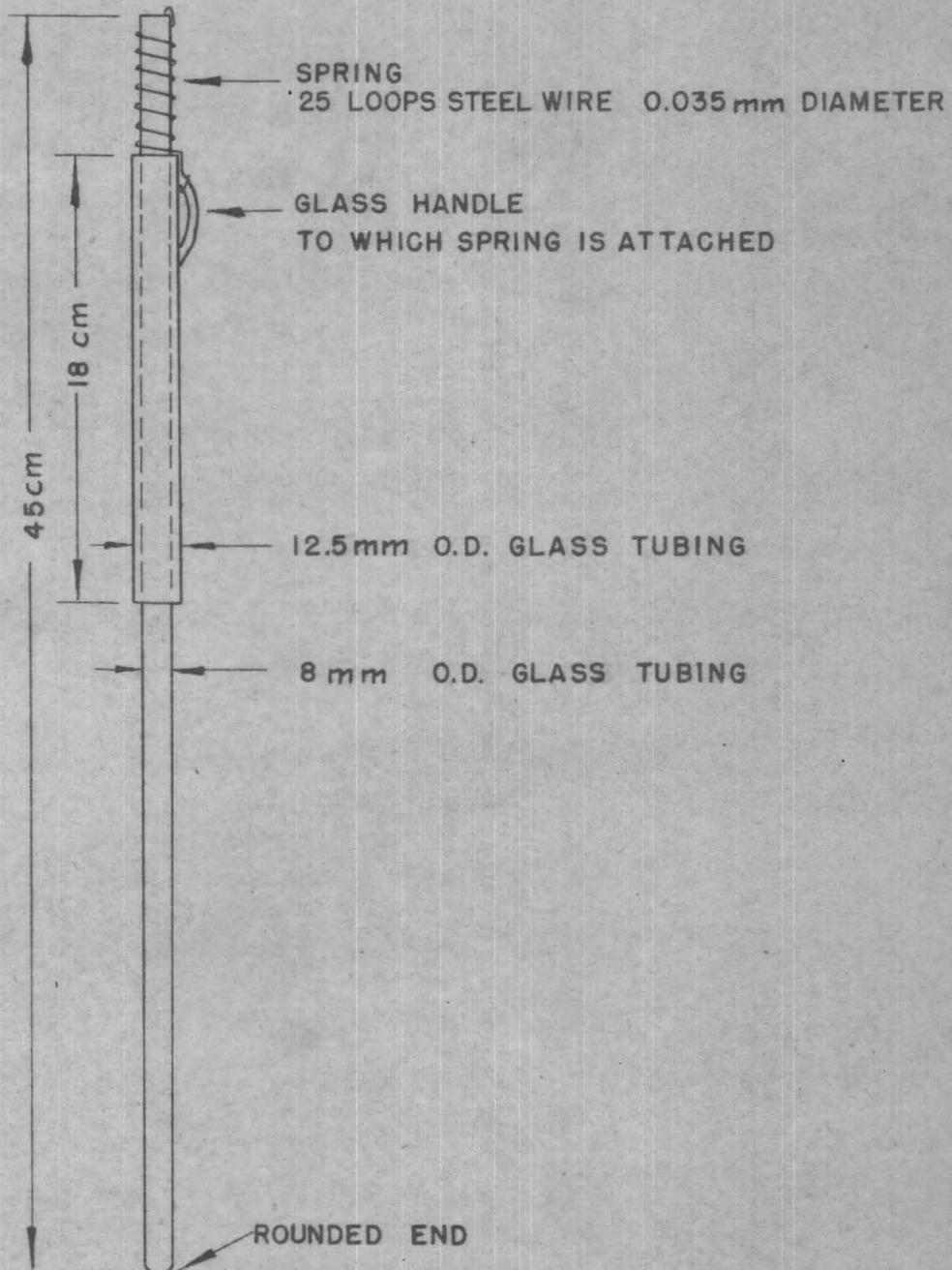
was added to the solution and stirring started. Refractometer readings taken from time to time show the change in concentration during diffusion and make possible calculation of the diffusion coefficients.

**SETTING TIME EXPERIMENTS WITH NON-ELECTROLYTES:** In the investigation of the effect of non-electrolytes on setting time 4½% gels were prepared as follows: 25 g. of gelatin was permitted to stand in a one-liter flask for twenty-four 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 non-electrolyte to be used were dissolved in enough water to make up 10 g. of solution. These non-electrolyte solutions were 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. Time required for the gels to set was determined through use of the penetrometer.

**SETTING TIME EXPERIMENTS WITH ELECTROLYTES:** In the investigation of the effect of electrolytes on the setting time 3, 4.5 and 6% gels were used. The variation in the concentration of the gelatin was made necessary by the variation of gel strength in the three shipments of Eastman gelatin used. Concentrations were chosen to place the time

Fig 1

## PENETROMETER



of set somewhere between two and six hours. Times shorter than two hours caused the gels to be setting so close to the same time that one could not accurately test and record the results fast enough to keep up. If the elapsed time was over six hours the problem of fitting the testing into the daily schedule became a factor.

Other variations in this investigation from that on the effect of non-electrolytes were as follows: 1,000 g. of total gel was dissolved each time instead of 500 g., thus allowing the setting of eleven gels at a time instead of five, and the warm solution immediately after dissolving was added to the bottles with the electrolyte dissolved in 10 ml. of water after which the bottles were set in the 25° thermostat. This later change was necessary to allow the testing to fit the investigator's daily program.

The penetrometer was used to determine when the gels had set. The pH measurements were made with a Beckman pH meter.

### III. RESULTS AND CONCLUSIONS

The results obtained in the diffusion experiments are shown in Table 1 and Fig. 2 where the percentage change in the diffusion coefficient of urea has been plotted against the molar concentration of the non-electrolyte present in the gel. It is to be noted that in every case the presence of a small amount of non-electrolyte caused an increase in the diffusion velocity of urea. With continued increase in concentration of the non-electrolyte there was further increase in the diffusion velocity of urea until a maximum value was reached. In the case of the five non-electrolytes studied this maximum value was at concentrations between 0.006 and 0.04 molar. With higher concentrations of the non-electrolytes the diffusion velocity was lowered from this maximum value and beyond concentrations ranging from 0.08 to 0.18 molar the diffusion velocity was less than the normal diffusion velocity of urea.

Table 2 and Fig. 3 give 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 the results obtained parallel the results from the diffusion experiments, for up to a concentration of 0.02 to 0.03 molar, setting time was increased, but this effect became less marked at higher concentrations and finally beyond 0.05 to 0.07 molar the setting time was decreased until

at 0.2 molar the decrease was greater than 20%.

Table 3 and Fig. 4 give the effect of sucrose on the setting time of both 4.5 and 6% gels. Although the actual times of setting are quite different the percentage increases in the setting time over that of the pure gel of the same concentration fall so close in each case as to be within the limits of error of the experiment. As further evidence that this behavior of gelatin gels is independent of concentration, at least within a limited range, it is to be noted that in Fig. 2, the 0.163 molar glycerol, 0.0438 molar sucrose, 0.25 molar urea, and 0.468 molar methanol points were not obtained in this experiment but were copied from the experiment by Friedman (3) which was done at the University of Wisconsin with gelatin from a different source and in 4.7 per cent gels instead of the 3 per cent gels which were used in this experiment. In spite of this, the points from Friedman's data fall right on the curves.

Table 4 and Fig. 5 give the results obtained on the effect of levulose on the setting time of gelatin gels at 25° and 17°. The temperature 17° was chosen because it was the lowest temperature that could be maintained in the thermostat on the day of the experiment. At 17° the gels set so rapidly that the measurements do not have the same degree of accuracy as the rest of the experiments but it is to be noted that the maximum increase in setting time falls at the same concentration and the curves are rather

close together when one considers that at 17° the actual setting time is less than one fourth at 25°. It is also to be noted that, in general, levulose effects the setting time less at 17° than at 25°.

Tables 5 to 10 and Fig. 6 give the results obtained on the effect of the sodium salts of two mono-, two di-, and two tribasic acids on the setting time of gelatin gels. These curves are more complicated than in the case of non-electrolytes, which is not surprising because the system is more complicated due to the charges on the particles added. In every case addition of sodium salts increased the setting time. Also in every case an "S" shaped curve is obtained. On the addition of a small amount of salt, a marked increase in setting time is obtained until a maximum is reached between 0.002 and 0.008 molar. In this respect the behavior is identical with that of non-electrolytes except the maximum is reached at a lower molarity. On further increase of salt a minimum is reached varying between 0.003 molar for  $\text{Na}_3\text{PO}_4$  to 0.018 for Na Cl. Nothing like this minimum was found with non-electrolytes. Further increase of salt causes a constant increase of setting time. It is to be noted that the tables give in some cases a much higher range of molar concentration of salt than is shown in Fig. 6 but in all cases at this higher concentration the setting time is increased. These higher concentrations are omitted from Fig. 6 to allow a wider spacing of the

lower concentrations to better show the maximum and minimum points.

In general more runs were necessary to obtain these curves than in the previous determinations due to the difficulty of hitting the maximum and minimum points at the first choice of concentrations. At time different lots of gelatin were used for one electrolyte necessitating gels with different concentrations so duplicate points were tested for the different lots. In no case did the duplicate points fall very far apart as can be seen on Fig. 6. This is added proof that the phenomenon studied here is independent of gel concentration.

Tables 5, 11, 12, 13, 14, and 15 and Fig. 7 give the results obtained from studying the effect of the chlorides of two mono-, two di-, and two triacid bases on the setting time. Here the system is still more complicated, because although the chlorides of the mono- and di-valent cations give curves similar to the electrolytes already studied, the trivalent cations  $Al^{+++}$  and  $Fe^{+++}$  give a decrease of setting time with small concentrations and  $Fe^{+++}$  gives a curve that is a mirror image of the curves of the other electrolytes if the zero concentration line is used as the axis.  $Al^{+++}$  on the other hand after reaching a minimum at 0.001 molar keeps increasing the setting time till it crosses the zero axis about 0.008 molar and keeps on increasing without reaching a maximum.

Tables 16 and 17 and Fig. 8 give the effect of HCl and Na OH on the setting time. Both give the "S" shaped curves found with most electrolytes but the deflections are so small with HCl that only a change in slope is found and no maximum and minimum. On the other hand Na OH has a big deflection giving a quite pronounced maximum and minimum.

Fig. 9 is also taken from Tables 16 and 17 and shows a plot of per cent increase in setting time against pH. No correlation is apparent between this and other gel properties, such as swelling, that vary with pH (12).

## IV. DISCUSSION OF RESULTS

Fig. 10 shows that curve N, which is typical of the effect of non-electrolytes on the gelling properties studied, can be the sum of two curves A and B both of which are typical adsorption isotherms (11) while Fig. 11 shows that curve E, which is typical of the effect of most electrolytes studied on the setting properties, can be the sum of three curves, two of which are similar to the A and B of Fig. 10.

These figures show that the effect of non-electrolytes could be due to two opposing effects one of which is the stronger at low concentrations but soon levels off while the opposite effect keeps on increasing until it becomes predominant. The effect of electrolytes can be represented by these two plus a third which acts in a similar direction to the first but does not level off so quickly.

De Jong (7) had advanced the theory that the gelling of gelatin is due to hydrophobic spots that form as the temperature is lowered. These spots allow the gelatin particles to join together at these points thus setting up a framework for the gel. The time factor involved in the setting of a gel is the time required for these spots to find each other in large enough quantities to make the gel. If some foreign substance could be added that would adsorb on these spots to make the joining more difficult, the forming of the framework would be slower and the spots

that join would be farther apart thus making a more open structure allowing a more rapid rate of diffusion in the gel.

The adsorption on these spots can explain the initial effect of all substances studied in both setting and diffusion except aluminum and ferric chlorides. These two special cases will be discussed later.

The second effect that causes a decrease in gelling time and a slowing of diffusion can be explained by the dehydration of the gelatin by increasing amounts of the foreign material after the spots are well covered. This dehydration is due to the foreign material taking the place of part of the adsorbed water thus causing many more spots to be formed where joining could take place. These individual spots thus formed are likely not nearly as effective as the spots on the pure gelatin but the fact that there are so many more of them causes a more rapid rate of setting and a finer gel structure thus causing slower diffusion. The oxonium ion would not be expected to be very strong at this dehydration which explains the lack of a minimum in the HCl curve.

The third effect which is the extra effect exhibited by most of the electrolytes can be explained by the charge on the adsorbed particle. That gelatin sols will pick up a charge due to adsorption of ions of an electrolyte is well

known (7). As like charges repel each other these charges will inhibit particles from coming together. This will cause slower setting. Whether this last effect causes a more open structure is not known but does not necessarily follow from the theory advanced here.

The unique effects of aluminum and ferric chlorides can be attributed to the well known fact (12) that both the aluminum and the ferric ions tan proteins. That is, they form an insoluble compound with gelatin that does not have the same properties as gelatin. Consequently, it is to be expected that these two would not give curves that would follow the theory advanced here.

This theory does not give pH any particularly unique place which is in accord with the fact that nothing definite could be found in the experiments on the effect of pH on setting time.

Many studies have been made of electrolytes on various properties of gelatin, but the effects of such small quantities as have been used here have not been carefully studied before. Very little work has been done prior to this time on the effect of non-electrolytes on gel properties of gelatin. The effects that have been discovered here have not been recognized before. This effect is of course, as is all such data, of theoretical importance, but it is also likely of practical importance because if anything so widely used as gelatin can be affected so markedly by so

small an amount of foreign material a control of the foreign material would aid in the commercial value of the gelatin products.

The author was connected for some time with the production of gummed tape which used a gelatin adhesive. It was found that small amounts of material in the range of the molar concentrations used in this experiment had very marked effects on the quality of the adhesive. During war years it would have been impossible to have maintained quality of product with the material available if it had not been for previous knowledge of these effects. In conversation with representatives of large animal glue manufacturing concerns the author has heard the statement made several times that the standard glue tests now used do not tell the whole story of adhesiveness.

Two lots of glue can be made as nearly as possible the same way and give the same tests yet behave very differently in adhesive properties. It would be worth-while for the glue manufacturers to study the effect of small amounts of impurities to see if the variations arise from that source.

There are several problems that arise from this investigation. One is the testing of a larger number of electrolytes to correlate the effects found with the lyotropic series and possibly advance a theory that will quantitatively predict the effects. Another is testing the effects of molecules with such widely varying molecular weights as

methyl alcohol and the carbowaxes. Another is a more complete study of varying temperatures. Still another is the testing of other gelling substances both elastic and non-elastic to see if similar results are found or whether this is just a property of gelatin gels. Also no work was done here on adding two substances at once to see if they worked together or independently in their effect.

## V. DATA AND SAMPLE CALCULATIONS

Table I

The Effect of Non-Electrolytes upon Diffusion of Urea from a 3% Solution into 3% Gelatin Gels.

Sub- stance present in gel	Molarity	Run no.	D x 10 <sup>5</sup> for pure gel	D x 10 <sup>5</sup> for impreg- nated gel	Per Cent Increase of D
Glycerol	0.0067	1	0.586	0.671	14.5
	.03	4	.532	.597	12.2
	.06	4	.532	.575	7.9
	.1	4	.532	.564	6.0
	.14	10	.622	.630	1.0
	.163	*	.515	.491	-3.7
	0.167	9	.591	.578	-2.2
	2.222	4	.532	.426	-19.9
Sucrose	0.001	3	0.678	0.692	2.1
	.0067	1	.586	.664	13.3
	.04	10	.622	.842	35.4
	.0438	*	.596	.791	32.7
	.088	2	.582	.619	6.4
	.1	3	.678	.597	-11.9
	.117	10	.622	.515	-18.8
	.175	2	.582	.425	-26.9
.8	3	.678	.258	-62.0	
Urea	0.003	8	0.604	0.693	14.7
	.0067	1	.586	.695	18.6
	.025	8	.604	.678	12.2
	.05	5	.597	.650	8.9
	.1	5	.597	.625	4.5
	.15	5	.597	.599	0.3
	.25	*	.510	.497	-2.5
	0.5	2	.582	.510	-12.4
2.0	5	.597	.391	-34.5	
Methanol	0.005	8	0.604	0.676	11.9
	.01	7	.617	.758	22.8
	.02	8	.604	.673	11.4
	.05	7	.617	.636	3.1
	.1	7	.617	.605	-1.9
	.468	*	.596	.525	-11.9

Table 1 cont.

Sub- stance present in gel	Molarity	Run no.	D x 10 <sup>5</sup> for pure gel	D x 10 <sup>5</sup> for im- pregnated gel	Per Cent Increase of D
Glucose	0.0067	1	0.586	0.701	19.6
	.02	9	.591	.788	33.3
	.04	6	.587	.653	11.2
	.07	6	.587	.616	4.9
	.167	9	.591	.600	1.5
	.2	6	.587	.550	-6.3
	.7	6	.587	.446	-24.0

\* These values are from the experiments of Friedman (3).

Fig. 2  
 EFFECT OF NON-ELECTROLYTES  
 UPON DIFFUSION OF UREA  
 INTO 3% GELATIN GELS AT 25 °C

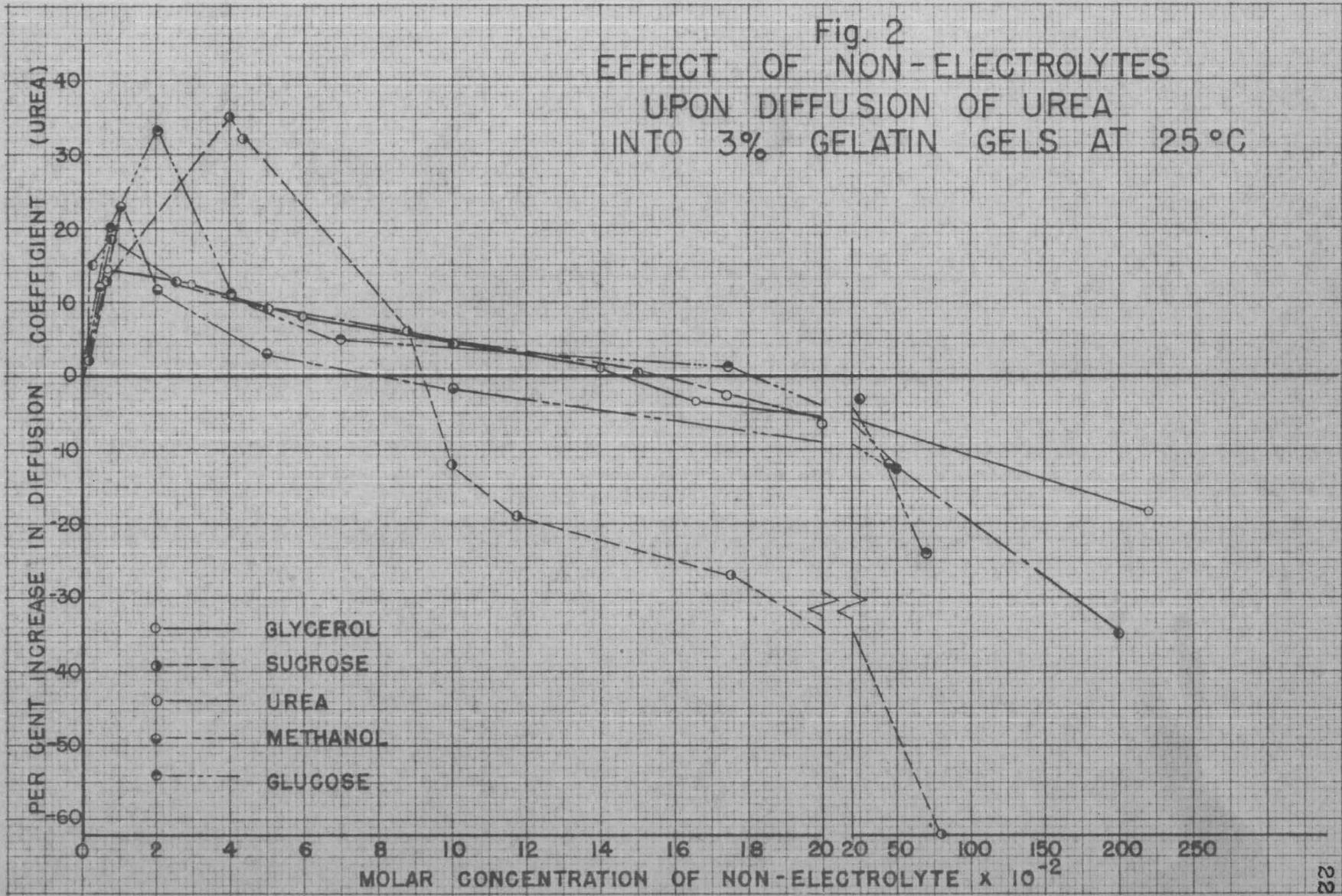


Table 2

The Effect of Non-Electrolytes upon Setting Time of 4.5% Gelatin Gels at 25°

Molarity	<u>Sucrose</u>		<u>Urea</u>		<u>Levulose</u>	
	A *	B*	A	B	A	B
0.00	212	...	305	...	185	...
.01	219	3.3	331	8.5	200	8.1
.02	243	14.6	351	15.1	204	10.3
.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
.06	...	...	318	4.3	...	...
.10	201	-5.2	...	...	141	-23.8
.20	166	-21.7	235	-22.9	136	-25.5

\*A - Setting time in minutes

\*B - Per cent increase in setting time

Table 3

The Effect of Sucrose on the Setting Time of 4.5 and 6.0% Gelatin Gels at 25°

Molarity	Setting time in minutes		Per Cent increase in setting time	
	4.5%	6.0%	4.5%	6.0%
	0.00	212	155	...
.01	219	161	3.3	3.2
.02	243	178	14.6	14.1
.05	215	159	1.4	1.9
.10	201	148.5	-5.2	-4.8
.20	166	122	-21.7	-21.8

Fig. 3

EFFECT OF NON-ELECTROLYTES  
ON SETTING TIME OF  
4.5% GELATIN GELS AT 25°C

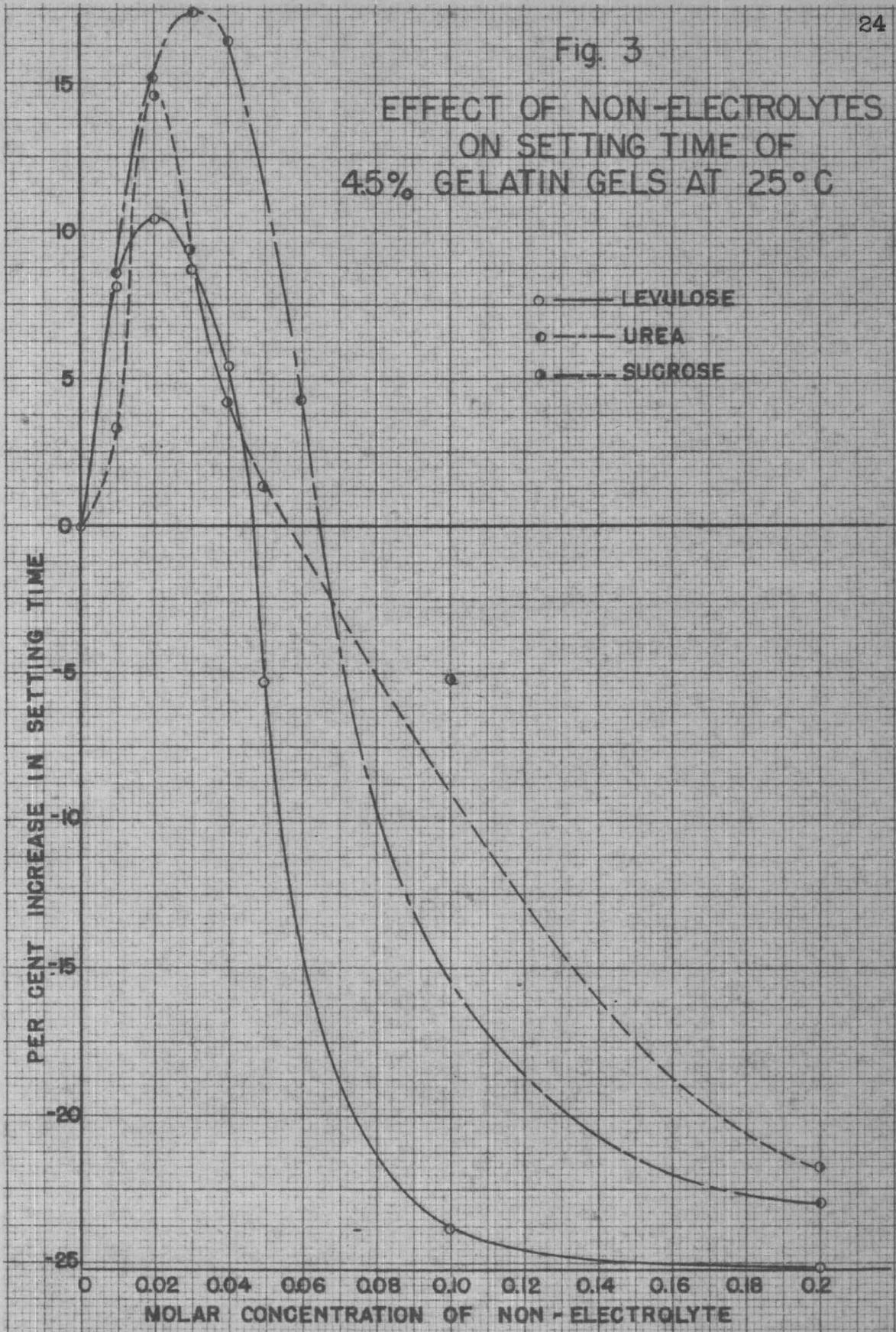


Table 4

The Effect of Levulose on the Setting Time of 4.5% Gelatin Gels at 25° and 17°

Molarity	Setting time in minutes		Per cent increase in setting time	
	25°	17°	25°	17°
0.00	185	45	...	...
.02	204	49	-10.3	8.9
.05	175	47	-5.4	4.4
.10	141	42	-23.8	-6.7
.20	136	34	-25.5	-24.4

Table 5

The Effect of Sodium Chloride on the Setting Time of 4.5% Gelatin Gels at 25°

Molarity of salt	Run no.	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.004	6	352	370	5.1
.005	1	300	325	8.3
.006	6	352	391	11.1
.007	7	285	345	21.0
.008	6	352	450	27.8
.008	7	285	359	25.9
.009	7	285	358	25.6
.01	1	300	372	24.
.014	6	352	430	22.1
.016	6	352	429	21.9
.018	5	271	325	19.9
.02	1	300	365	21.8
.024	5	271	339	25.1
.03	1	300	385	28.3
.04	1	300	420	40.0
.1	1	300	306	102.0

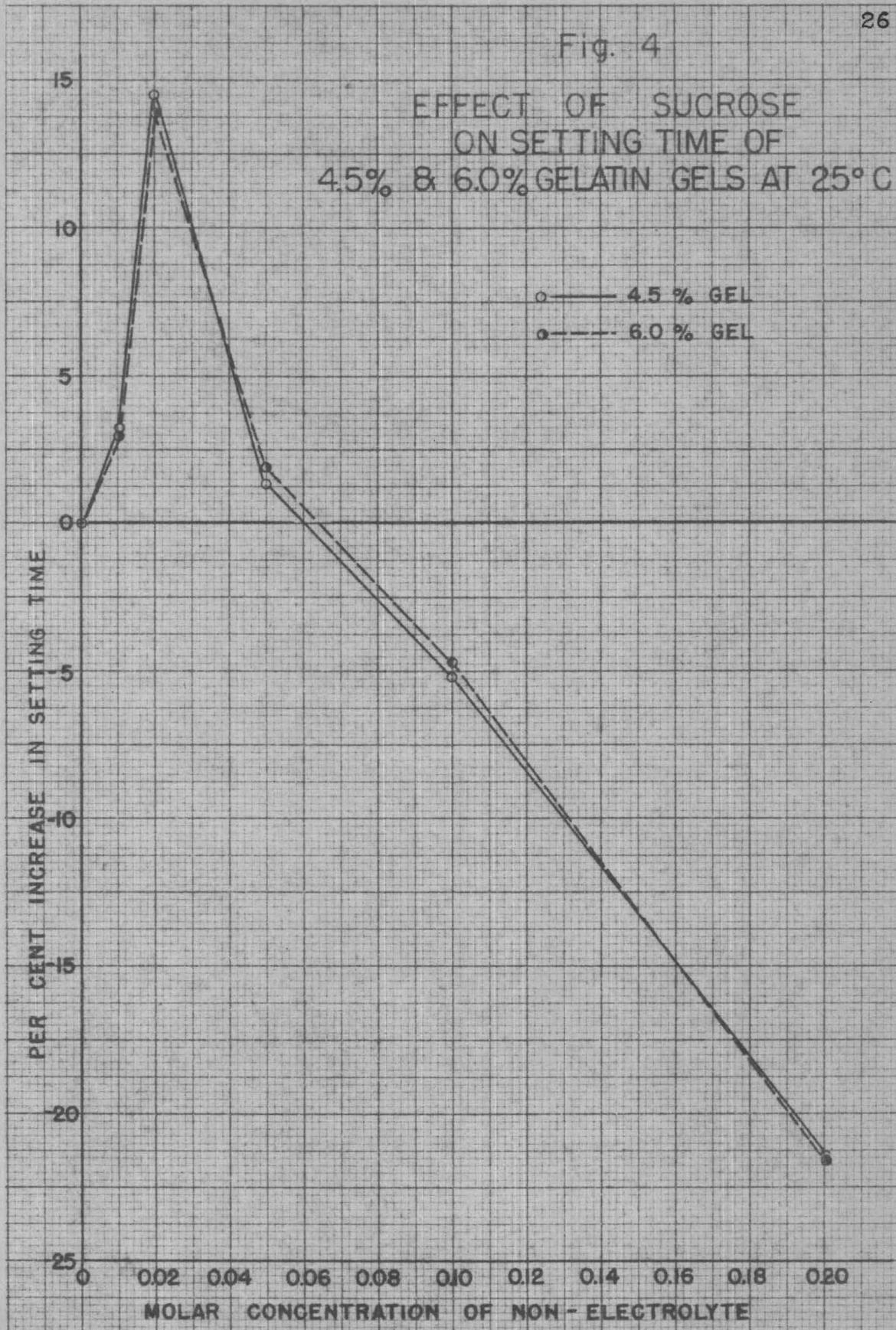
Fig. 4

EFFECT OF SUCROSE  
ON SETTING TIME OF  
4.5% & 6.0% GELATIN GELS AT 25°C

○ — 4.5% GEL  
● — 6.0% GEL

PER CENT INCREASE IN SETTING TIME

MOLAR CONCENTRATION OF NON-ELECTROLYTE



EFFECT OF LEVULOSE  
ON SETTING TIME OF  
4.5% GELATIN GELS AT 25°C & 17°C

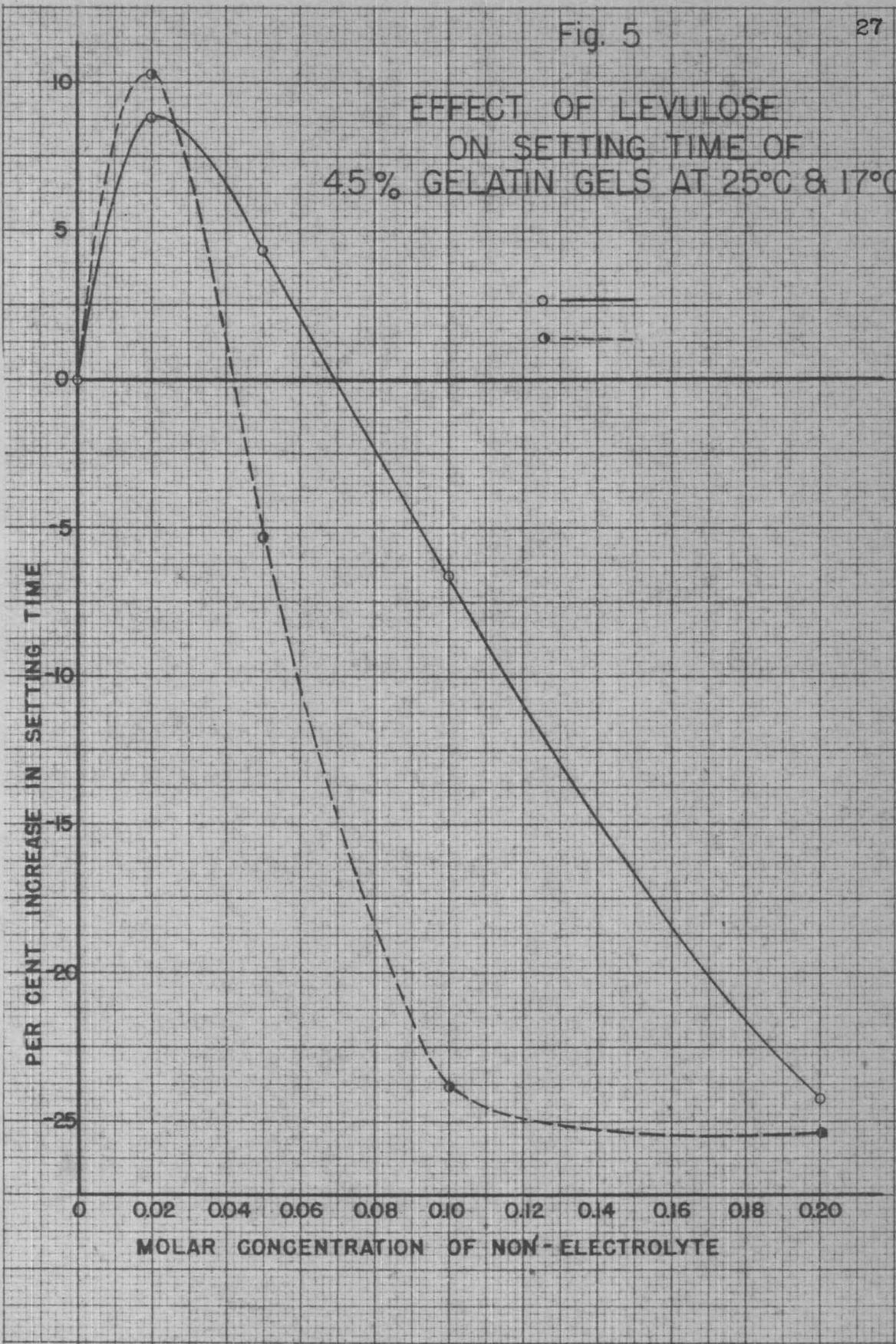


Table 6

The Effect of Sodium Nitrate on the Setting Time of Gelatin Gels at 25°

Gel concentration per cent	Molarity of salt	Run no.	Pure gel minutes	Impregnated gel - minutes	Increase per cent
6.0	0.001	10	126	133	5.6
6.0	.001	12	190	202	6.3
6.0	.002	10	126	146	15.9
6.0	.002	12	190	225	18.4
6.0	.003	10	126	149	18.3
6.0	.004	12	190	237	24.7
6.0	.005	12	190	224	17.9
6.0	.006	12	190	217	14.2
6.0	.007	12	190	213	12.1
4.5	.008	9	565	622	10.1
6.0	.008	11	234	258	10.3
4.5	.010	9	565	633	17.3
6.0	.010	11	234	268	14.5
4.5	.012	9	565	695	23.0
6.0	.012	12	190	236	24.2
4.5	.016	9	565	759	32.6
4.5	.020	9	565	802	42.0

Table 7

The Effect of Sodium Sulfate on the Setting Time of 6% Gelatin Gels at 25°

Molar- ity of salt	Run no.	Pure gel minutes	Impreg- nated gel - minutes	Increase per cent
0.001	11	234	268	6.0
.002	13	130	140	7.7
.004	10	126	133	5.6
.004	13	130	138	6.2
.005	13	130	136	4.6
.006	13	130	135	3.8
.007	13	130	137	5.4
.008	13	130	139	6.9
.010	13	130	140	7.7
.012	13	130	141	8.5
.014	13	130	142	9.2

Table 8

The Effect of Sodium Oxalate on the Setting Time of 6% Gelatin Gels at 25° - Run No. 14

Molarity of salt	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.001	160	166	3.8
.002	160	183	14.4
.003	160	220	37.5
.004	160	199	24.4
.005	160	183	14.4
.006	160	209	30.6
.003	160	227	41.8
.01	160	232	45.0
.012	160	234	46.2
.014	160	236	47.5

Table 9

The Effect of Trisodium Phosphate on the Setting Time of  
6% Gelatin Gels at 25° - Run No. 15

Molarity of Salt	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.0005	134	138	3.0
.001	134	142	6.0
.0015	134	147	9.7
.002	134	146	9.0
.0025	134	145	8.2
.003	134	144	7.5
.004	134	147	9.7
.005	134	149	11.2
.007	134	154	14.9
.010	134	199	47.5

Table 10

The Effect of Trisodium Citrate on the Setting Time of  
3% Gelatin Gels at 25° - Run No. 16

Molarity of Salt	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.001	298	342	14.8
.002	298	365	22.5
.004	298	383	28.5
.006	298	382	28.1
.008	298	392	31.5
.010	298	424	42.3
.020	298	464	55.7

Fig. 6

EFFECT OF VARIOUS SODIUM SALTS  
ON SETTING TIME OF  
GELATIN GELS AT 25°C

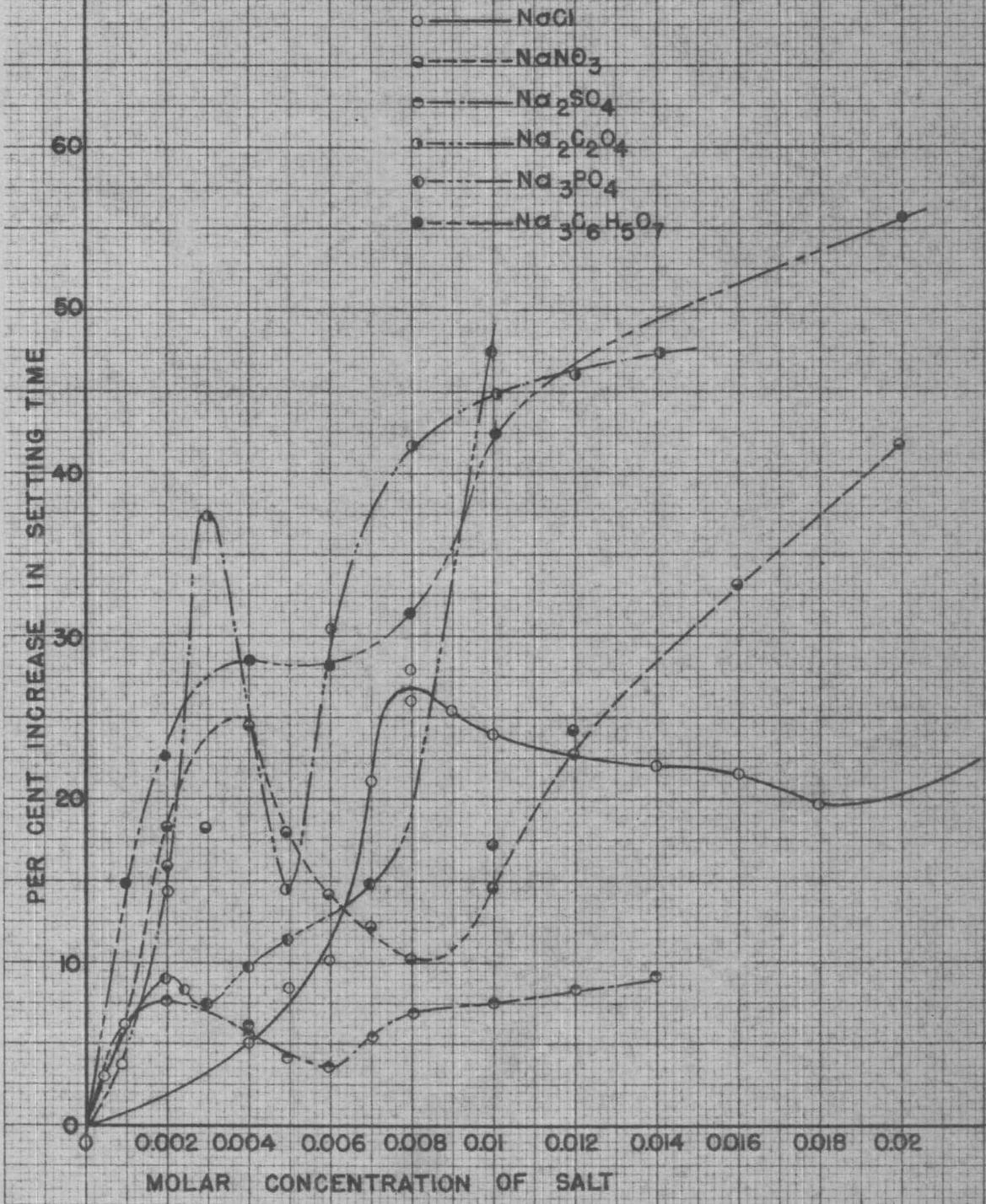


Table 11

The Effect of Potassium Chloride on the Setting Time of  
4.5% Gelatin Gels at 25°

Molarity of Salt	Run no.	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.004	6	352	370	5.1
.006	6	352	391	11.1
.006	8	370	409	10.5
.008	7	285	355	24.5
.009	7	285	348	22.1
.010	7	285	344	20.7
.012	8	370	344	20.0
.014	8	370	475	28.4
.016	8	370	495	33.8
.018	8	370	505	36.5
.04	8	370	535	44.6

Table 12

The Effect of Calcium Chloride on the Setting Time of  
4.5% Gelatin Gels at 25°

Molarity of Salt	Run no.	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.002	5	271	285	5.2
.003	5	271	288	6.3
.005	2	260	290	11.5
.006	6	352	449	27.5
.006	7	285	356	24.9
.007	5	271	326	20.3
.007	7	285	357	25.2
.0075	6	352	435	23.6
.009	5	271	288	6.3
.010	5	271	287	5.9
.011	7	285	312	9.5
.012	7	285	315	10.5
.020	2	260	314	20.8
.030	2	260	332	27.7
.050	2	260	357	37.3

Table 13

The Effect of Barium Chloride on the Setting Time of 4.5% Gelatin Gels at 25°

Molarity of Salt	Run no.	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.0005	9	565	592	4.5
.001	9	565	641	13.5
.002	9	565	720	27.4
.003	9	565	731	29.4
.004	8	370	425	14.9
.006	8	370	465	25.5
.008	8	370	506	36.8
.01	8	370	530	43.2

Table 14

The Effect of Aluminum Chloride on the Setting Time of 4.5% Gelatin Gels at 25°

Molarity of Salt	Run no.	Pure gel minutes	Impregnated gel - minutes	Increase per cent
0.005	4	270	193	-28.5
.001	4	270	177	-34.5
.0015	4	270	180	-33.3
.002	3	270	187	-30.7
.003	4	270	197	-27.0
.004	3	270	217	-19.7
.006	3	270	234	-13.3
.008	2	260	265	1.9
.010	2	260	312	20.0
.015	2	260	333	31.9

Table 15

The Effect of Ferric Chloride on the Setting Time of 4.5% Gelatin Gels at 25°

Molarity of Salt	Run no.	Pure gel minutes	Impregnated gel - minutes	Increase per cent
.001	4	270	224	-17.0
.002	3	270	221	-18.1
.003	4	270	217	-19.6
.004	3	270	208	-23.0
.005	3	270	189	-30.0
.006	4	270	200	-25.9
.007	4	270	210	-22.2
.008	3	270	220	-18.5
.010	3	270	210	-22.2
.015	4	270	205	-24.1
.040	3	270	180	-33.3

Table 16

The Effect of Sodium Hydroxide on the Setting Time of 6.0% Gelatin Gels at 25° - Setting time for pure gel 99 minutes.

Molarity of Salt	Run no.	pH	Impregnated gel - minutes	Increase per cent
0.0010	19	4.88	108	9.1
.0020	18	4.43	123	24.2
.0031	19	4.70	123	24.2
.0041	18	4.52	125	26.3
.0051	19	4.90	123	24.2
.0061	18	5.08	119	20.2
.0072	19	5.00	109	10.1
.0082	18	4.99	112	13.1
.0092	19	5.11	112	13.1
.0103	18	5.04	122	23.2
.0123	18	5.27	135	36.4
.0144	18	5.71	145	46.5
.0174	18	6.32	164	65.7
.0205	18	7.00	187	65.7
.0513	18	9.92	Not set in 60 hrs.	

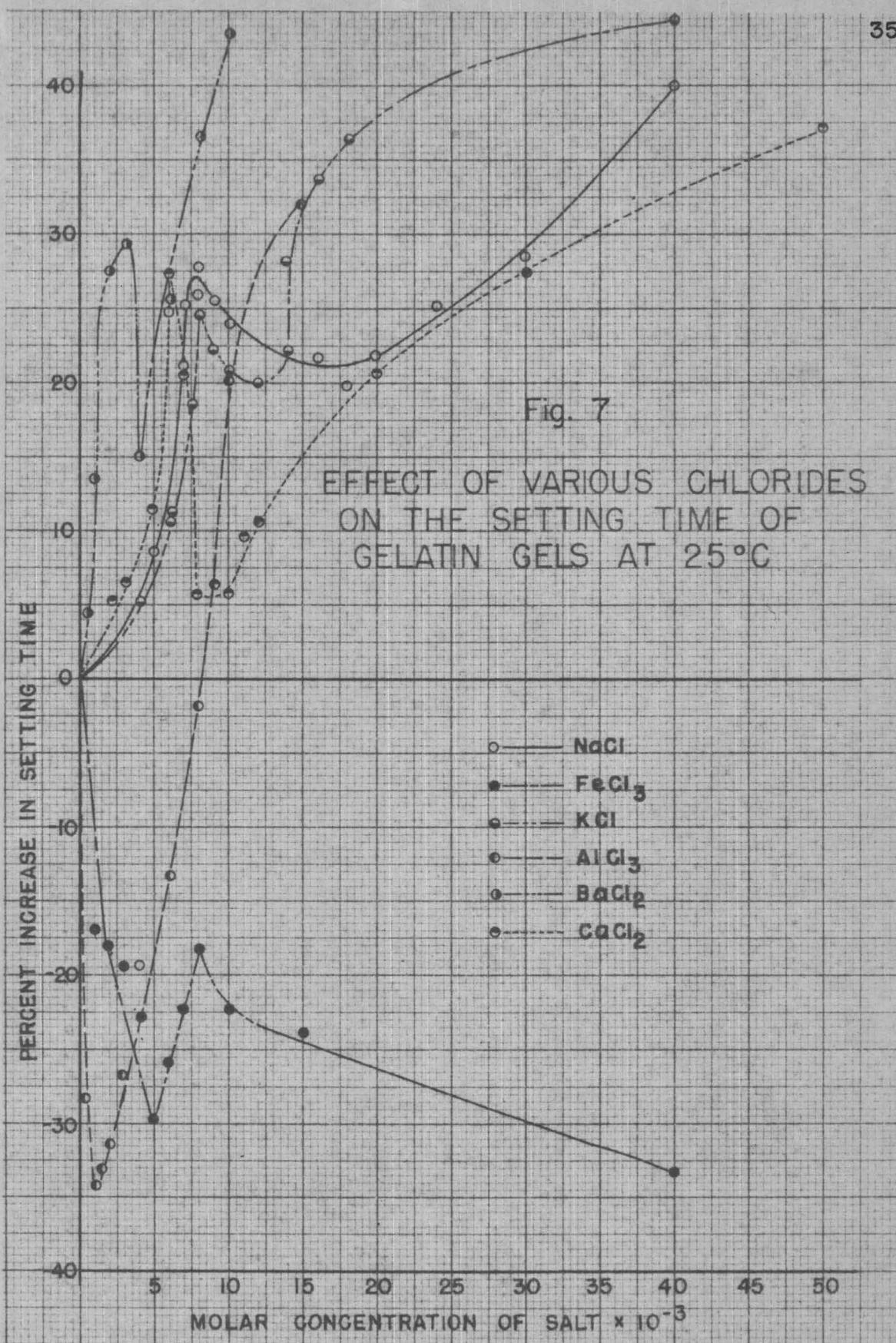
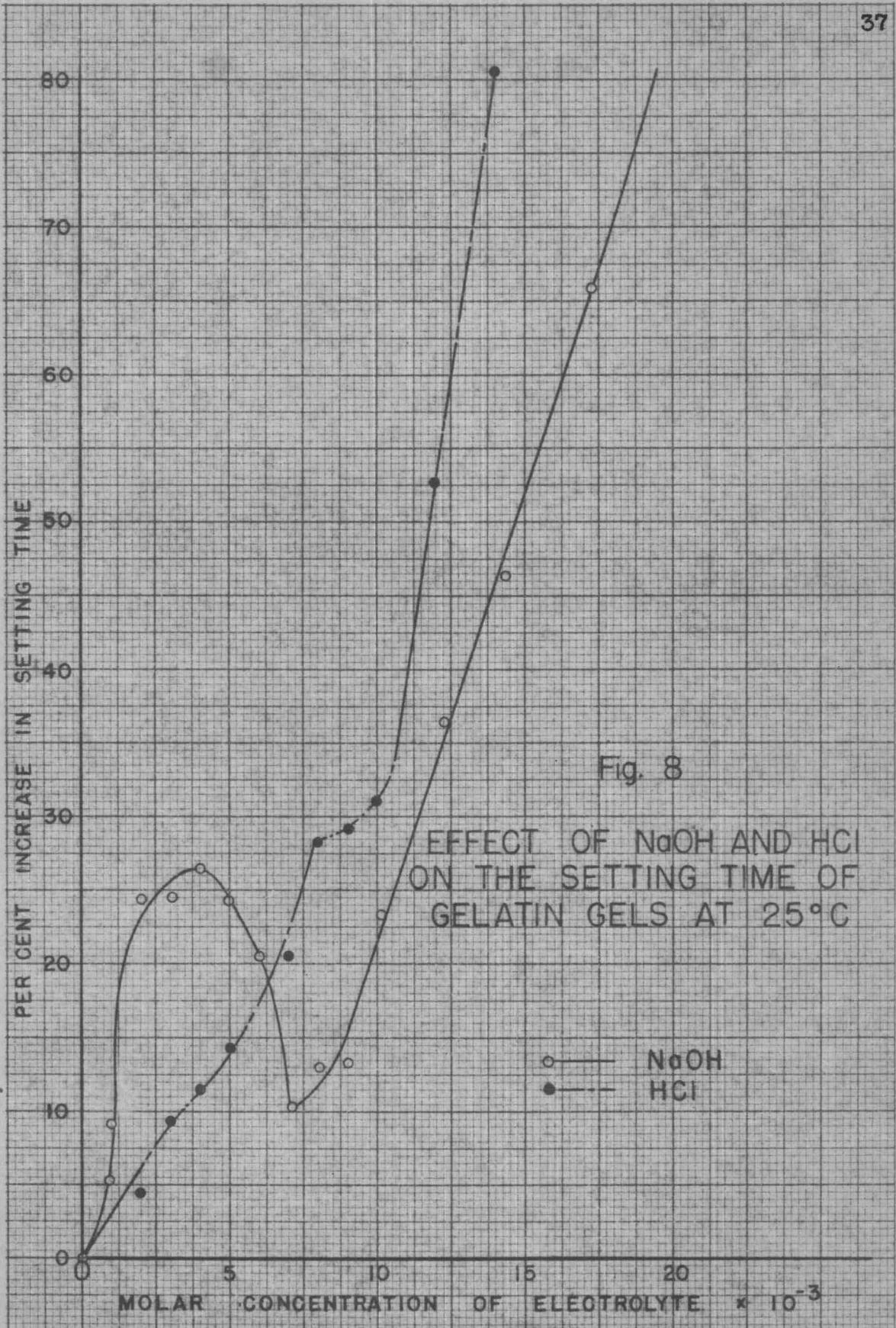


Table 17

The Effect of Hydrochloric Acid on the Setting Time of  
6.0% Gelatin Gels at 25°

Molarity of Salt	Run no.	pH	Pure gel minutes	Impregnated gel - minutes	In- crease per cent
0.001	19	4.55	99	104	5.0
.002	17	4.55	138	144	4.4
.003	19	4.50	99	108	9.1
.004	17	4.46	138	154	11.6
.005	19	4.41	99	113	14.1
.006	17	4.38	138	166	20.5
.007	19	4.35	99	119	20.2
.008	17	4.21	138	177	28.3
.009	19	4.32	99	128	29.2
.010	17	4.24	138	181	31.1
.012	17	4.18	138	211	52.8
.014	17	4.10	138	249	80.5
.017	17	4.00	138	354	156.6
.020	17	3.90	138	518	275.0
.049	17	2.57	138	Not set in 25 hrs.	



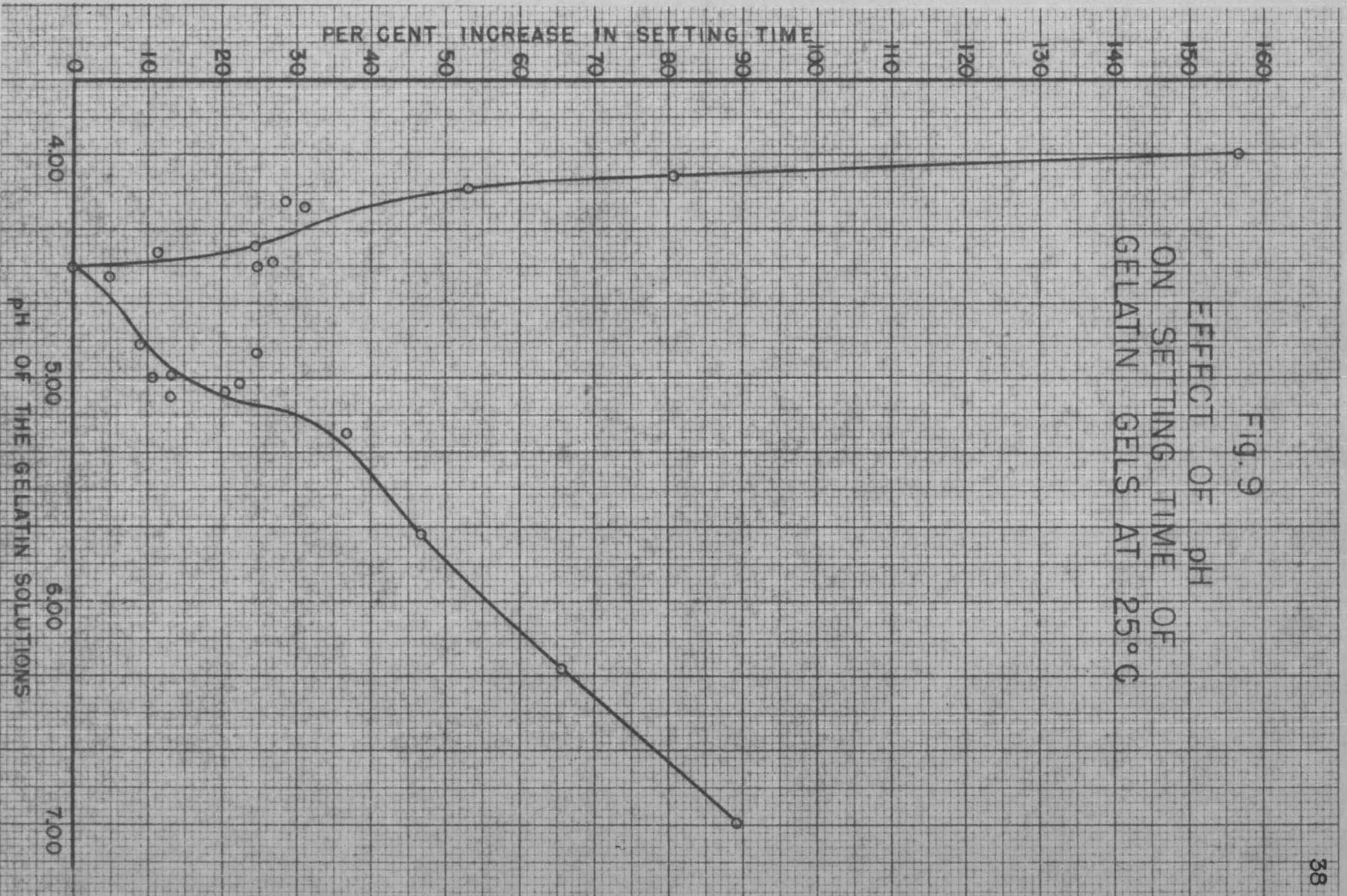


Fig. 9  
EFFECT OF pH  
ON SETTING TIME OF  
GELATIN GELS AT 25°C

THEORETICAL CURVES

Fig. 10

Fig. 11

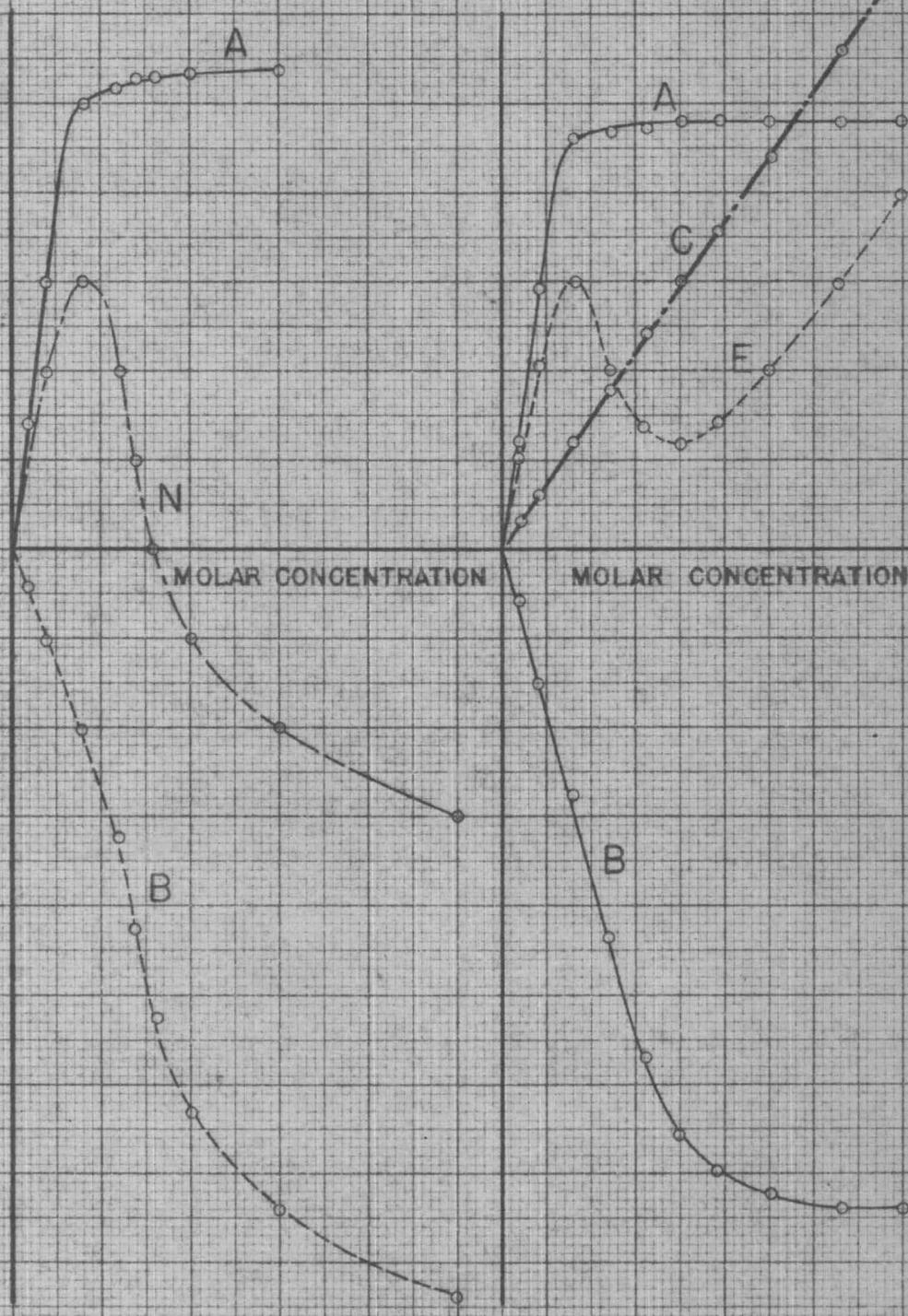


Table 18

A Sample of Experimental Data and Calculations Used to Determine the Diffusion Constant and Percentage Increase in Diffusion Constant

1	2	3	4	5	6	7
Time of reading	Refractometer reading	Elapsed time in hours	Refractometer shift	V	T	$D \times 10^5$
5:41 PM May 6	80.49					
3:21 PM May 7	78.70	21.67	1.79	0.164	0.0279	0.434
9:34 AM May 8	78.21	39.88	2.28	.209	.0995	.418
11:15	78.06	41.57	2.43	.223	.0580	.469
2:55 PM	78.00	45.23	2.49	.229	.0628	.468
4:24	78.00	46.72	2.49	.229	.0628	.453
1:18 PM May 9	77.61	67.62	2.88	.265	.0897	.446
2:43	77.58	69.03	2.91	.268	.0923	.450
3:53	77.61	70.20	2.88	.265	.0897	.430
						<u>8/3.568</u>
						.446

Table 18 was copied from the determinations of the diffusion constant for urea, diffusing from a 3% solution into a 3% gelatin gel, both in a 0.7 molar solution of glucose. Column 1 is a record of the time the readings were taken and column 2 the refractometer readings. Column 3 is the elapsed time in hours from the start of the diffusion and is calculated from column 1. Column 4 is the refractometer shift and is calculated from column 2. The initial reading of the 0.7 molar solution of glucose before the urea was added was 69.61, so, the shift in the refractive index due to the 3% urea is initial refractometer reading, 80.49, minus 69.61 which equals 10.88.

Column 5 is the fraction of the urea that has diffused into the gel and is calculated by dividing the refractometer shift of column 4 by the total shift due to 3% urea 10.88. The first four terms of the series of the equation of March and Weaver relating  $V$ , the fraction diffused to  $T$  have been previously calculated and plotted in a graph. The  $V$  values of column 5 are found on this graph and the corresponding  $T$  values of column 6 are read from them.

$T$  is connected with the diffusion constant  $D$  by the equation  $D = a^2 T/t$  where  $a$  is the height of the gel layer and also the liquid layer in cm. and  $t$  is the time in seconds. This diffusion had been carried out in bottle number VII which had a cross sectional area of 43.07 sq. cm. A constant has been calculated for each bottle by dividing the cross sectional area by 150 which gives the height of the gel  $a$ . This is then squared and divided by 3600, which converts the elapsed time in hours to  $t$  in seconds. This constant for bottle VII is 0.003369. Column 7 is the diffusion constant which has been calculated by dividing the  $T$ 's of column 6 by the corresponding elapsed time of column 3 and multiplying by the bottle constant 0.003369.

The average of these  $D$ 's is the diffusion constant,  $.446 \times 10^{-5}$ . In the pure gel of this same run the diffusion constant, by a similar calculation to the above, was

found to be  $0.587 \times 10^{-5}$ . The speeding of diffusion was found to be  $0.446 \times 10^{-5}$  minus  $0.587 \times 10^{-5}$  which equals a  $-0.141 \times 10^{-5}$ . This divided by the blank diffusion constant and multiplied by 100 gives the per cent of diffusion to be a  $-24.0\%$ .

Table 19 is a copy of run no. 7 in the determinations of setting time. Most of the columns are self-explanatory from the headings. Additional information on this run is: the time the gels were placed in the bath was 9:50 AM. Columns 4 and 5 add up to the 10 ml. of salt solution to which the 90 ml. of gel is added. Column 6, the molarity of salt in gel, is calculated by multiplying 3 by column 4 and dividing by 100. Column 8 is calculated from column 7, column 9 is the increase of the other gels of column 8 over that of the pure gel and column 10 is figured by dividing column 9 by 285, the time of set of the pure gel, and multiplying by 100.

Table 19

A Sample of Experimental Data and Calculations Used to Determine the Setting Time and Percentage Increase in Setting Time.

1*	2	3	4	5	6	7	8	9	10
1	Cal <sub>2</sub>	0.1	6	4	0.006	3:46 PM	356	71	24.9
2	" <sup>2</sup>	0.1	7	3	.007	3:47	357	72	25.2
3	"	.2	5.5	4.5	.011	3:02	312	27	9.5
4	"	.2	6	4	.012	3:05	315	30	10.5
5	---	.0	0	10	.000	2:35	285	---	---
6	NaCl	.2	3.5	6.5	.007	2:35	345	60	21.0
7	NaCl	.2	4	6	.008	3:49	359	74	25.9

Table 19 Cont.

1	2	3	4	5	6	7	8	9	10
8	NaCl	0.2	4.5	5.5	0.009	3:48 PM	358	73	25.6
9	KCl	.2	4	6	.008	3:45	355	70	24.5
10	"	.2	4.5	5.5	.009	3:38	348	63	22.1
11	"	.2	5	5	.010	3:34	344	59	20.7

- \*1 Bottle Number
- 2 Salt Used
- 3 Molarity of salt solution
- 4 Ml. of salt solution
- 5 Ml. of water
- 6 Molarity of salt in gel
- 7 Time set
- 8 Time of set in minutes
- 9 Increase of setting time
- 10 Per cent increase of setting time

## VI. BIBLIOGRAPHY

1. Cox, Ernest, A Study of Silica Gel. Thesis, Lewis and Clark Library, 1934.
2. DeBeaukelaer, Powell and Bahlmann, Standard Methods for Determining Viscosity and Jelly Strength of Glue. Analytical Edition of Industrial and Engineering Chemistry, Vol. 2, p. 348, 1930.
3. Friedman, Leo, Diffusion of Non-Electrolytes in Gelatin Gels. Journal of the American Chemical Society, 52:1305, 1930.
4. Friedman, Leo, Structure of Agar Gels from Studies of Diffusion. Journal of the American Chemical Society, 52:131, 1930.
5. Friedman, Leo, and Kraemer, E. O., The Structure of Gelatin Gels from Studies of Diffusion. Journal of the American Chemical Society, 52:1295, 1930.
6. Klemm, Karl, and Friedman, Leo, The Structure of Cellulose Acetate Gels from Studies of Diffusion. Journal of the American Chemical Society, 54:2637, 1932.
7. Kruyt, H. R., Colloids, 2nd ed. New York, John Wiley and Sons, 1930. pp 1:275.
8. March and Weaver, The Diffusion Problem for a Solid in Contact with a Stirred Liquid. Physical Review, 31:1072, 1928.
9. Pedersen, Determination of Gelatinization Power of Gelatin. Kem. Maanedstidende 23:1434, 1942. C.A., 36:7392, 1942.
10. Prasad and Hattiangodi, The Time of Setting of Silicic Acid Gels. The Journal of the Indian Chemical Society, 6:653-663, 1929.
11. Prutten, C. F., and Maron, S. H., Fundamental Principles of Physical Chemistry. New York, The MacMillan Co., 1944, pp. 1-762.
12. Wilson, J. A., The Chemistry of Leather Manufacture. 2nd ed., New York, The Chemical Catalog Co., Inc.

## VI. BIBLIOGRAPHY (Cont.)

12. (Cont.) 1928, pp. 1-682.