

FRUIT JELLIES

IV. THE RÔLE OF SALTS

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INTRODUCTION

A few years ago the Chemical Department of this Station undertook a systematic study of the factors influencing the jellation of fruit juices and pectin solutions. At that time it was planned to study separately the rôle of acid, sugar and pectin in jelly formation, as these three compounds, together with water were apparently essential to a good jelly. However, as the work progressed, it was found advisable to diverge somewhat from this plan, as indicated by the researches herein described, and by Tarr's bulletin.¹

Tarr first attacked the problem of jelly formation from the stand-point of acidity.² It is well that he did so since the important discovery was made that jelly formation is dependent upon the active acidity, or hydrogen ion concentration, rather than upon the total acidity. Any other line of attack would undoubtedly have been undertaken with the idea that total acidity was the controlling factor in jelly formation and without any regard whatsoever for the hydrogen ion concentration. This method of procedure would have necessitated a repetition of some of the work. As a result of Tarr's foresight his next work, that on "The Rôle of Sugar in Jelly Formation,"³ as well as all later and future work on fruit jellies at this Station was, and will be undertaken with a full realization of the importance of hydrogen ion concentration in connection with fruit jellies.

Tarr¹ described a jelly strength tester, devised in this laboratory, which will undoubtedly stimulate researches in the fruit jelly field in the future. Heretofore, the data presented in the literature relative to the strength of pectin jellies have been very vague. No

attempt has been made to assign any definite values to the jellies, consequently the personal equation is very much in evidence. By means of the jelly strength tester, it is possible to accumulate data on the strength of jellies that are more or less of a quantitative nature, and are comparable.

This bulletin marks the fourth of the series on fruit jellies. The data herein presented were accumulated by using the salient features of the earlier work as a guide and by utilizing the apparatus previously designed in this laboratory for the determination of jelly strength. This apparatus can now be obtained from the Arthur H. Thomas Company of Philadelphia.

Salts of the fruit acids are present in all natural fruit juices. It is impossible to obtain an ash-free pectin by a repeated precipitation with alcohol; however, the ash may be lowered appreciably by this method. It is, therefore, probable that salts are present in both the free and combined states. In order to decrease further the ash of the pectin, it must be given a special treatment. The addition of an acid to the pectin previous to the precipitation with alcohol is the method usually employed. That the acid treatment, however, changes the properties of the pectin was observed by Tarr.³ Wilson⁴ has observed that at a certain stage in his process of manufacturing a commercial pectin, a low grade product is obtained, having an ash content of 10-12%. Treating this product with an acid resulted in a much better product of lower ash content which would support from 140-220 times its own weight of sugar. He now states that he has prepared a special pectin which will support 310 times its weight of sugar.⁵

Other investigators in this field of research have also noted that salts have a bearing on the jellation of pectin solutions. In general, however, it may be stated that this phase of the problem has, up to this time, received very little attention.

PLAN OF PROCEDURE

Tarr's² conception of the importance of hydrogen ion concentration in jelly formation is the foundation upon which the researches of this Station, on Fruit Jellies, have been built. Briefly he found that the optimum and minimum points of jelly formation (meaning that point where the strongest jelly is formed and that point where a jelly will just form) occurred at definite hydrogen ion concentrations, regardless of total acidity, thereby explaining, in no small degree, the discrepancies in the literature regarding the acidity factor. Consequently hydrogen ion concentration is very carefully considered in these researches.

Salts influence, more or less, the hydrogen ion concentration of an acid solution, the extent of their influence being dependent somewhat upon the nature and concentration of the ions of the salt and acid in the solution. Therefore the procedure followed was to determine first the effect of the various salts on the hydrogen ion concentration of the acid-pectin solutions. Salts tend to exert a buffer action on acid solutions and consequently, at a definite hydrogen ion concentration, the total acidity will vary, to a certain extent, with the salt concentration. In these researches therefore, the total acidity within the limits of jelly formation was varied to a much greater extent than was done by Tarr, so that incidentally his conception of the relation of hydrogen ion concentration to jelly formation received the "acid test."

The hydrogen ion is a positive ion and Tarr¹ found that jelly strength increased with the concentration of the hydrogen ion up to a certain point. A further increase in the hydrogen ion concentration resulted in a corresponding decrease in jelly strength and subsequently syneresis occurred in the jelly. It is entirely possible that other positive ions may have a similar effect on the strength of pectin jellies.

Von Fellenberg⁶ stated that he was able to form jellies by the addition of certain salts to pectin solutions that did not contain acids. Halliday and Bailey⁷ have

shown that calcium chloride has a favorable effect on jelly formation. Should the positive ion of a salt be able to replace to any extent the hydrogen ion of the acid in the rôle it plays in jelly formation, it should be in evidence at the optimum and minimum points of jelly formation, which will be determined under the various conditions of salt concentration.

The complete study may be outlined as follows:—

1. Selection of Materials (Pectin, acids and salts).
2. The Effect on Jelly Formation of Variations in Hydrogen Ion Concentration.
3. The Effect on Jelly Formation of Variations in Salt Concentration (Total Acidity Maintained Constant).
4. The Effect on Jelly Formation of Variations in Salt Concentration (Hydrogen Ion Concentration maintained Constant).

SELECTION OF MATERIALS (PECTIN, ACIDS AND SALTS)

All materials used in these researches were selected and prepared under as nearly similar conditions as possible to those described by Tarr.¹ This was done with the idea of obtaining data under approximately the same conditions reported by him so that results obtained would be comparable with his.

Pectin:

The source of pectin was a commercial grade of apple pectin in the form of approximately a 4% solution. This pectin was purified by the usual alcoholic precipitation method and dried at 80° C. Four or five hundred grams of the dried purified pectin was prepared and well mixed so that uniform portions could be taken for experimental purposes. However this quantity of pectin was not sufficient to complete the work, so it became necessary to prepare an additional amount of pectin for the last phase of the problem.

It should be particularly noted that as no means of preparing an ash-free pectin was at hand and as the known methods for lowering the ash content result in a pectin of different properties, no attempt was made to purify the pectin beyond that obtained by precipitating it three times with alcohol. This resulted in a pectin having an ash content of 3.61%, but as the ash was constant throughout the work, it figured uniformly in the results obtained. However, the effect of even this small amount of salt was noticeable in the jelly strength curves as will be shown later.

Acids:

Three of the acids used by Tarr were selected for the work, namely, sulphuric, tartaric and citric. These acids were selected with the idea of testing out the stoichiometric relationship, which Tarr² found to exist between the acids and the pectin, under the various conditions of these experiments. With these acids it was also possible to determine the effect of the salts on strong and weak acids and their subsequent effect on jelly formation.

Salts:

Sodium salts of the three acids, sulphuric, tartaric, citric in the form of sodium sulphate, sodium hydrogen tartrate and di-sodium hydrogen citrate were the salts used in these researches. These salts had a hydrogen ion concentration of pH 7, 3.50 and 5.20 respectively. A salt having an alkaline reaction in solution was prohibitive due to its hydrolytic action on the pectin. The cation (sodium) of the salt was chosen because it was practically the only one of the alkali or alkaline earth metals that would form salts with these acids which would remain completely dissolved under the various conditions of these experiments. The choice was limited to the alkali and alkaline earth metals simply because the salts of natural fruit juices come mostly under this classification.

The first two salts were easily obtained in the pure state, but it was impossible to purchase pure di-sodium hydrogen citrate. This difficulty was obviated by using standard solutions of pure citric acid and sodium carbonate and mixing them in theoretical amounts to form the desired amount of salt.

THE EFFECT ON JELLY FORMATION OF VARIATION IN HYDROGEN ION CONCENTRATION

As the results of these experiments depended almost entirely upon the strength of the jelly that was produced under various conditions, it is apparent that jelly making and jelly strength measurements were of the utmost importance.

Jelly Making:

In making jellies, three factors were maintained constant throughout the work, namely, pectin, added sugar, and percentage sugar in the resulting jelly. The variables in these researches were the total acidity, hydrogen ion concentration and added salt. The procedure was as follows—

An agate pan and electric hot plate were first balanced on a solution balance; 100 cc. of a 1% pectin solution was then pipetted into the pan, and the variables, acid and salt, were added together with enough water to make the total volume 135 cc. When more than 35cc. of 0.1N acid was required, stronger acid was used. The larger amounts of tartaric and citric acids were added in the solid form. The pan and its contents were then placed on the hot plate which had, by this time, reached its maximum temperature. At the expiration of exactly four minutes, 100 g. of sugar was introduced into the solution and stirred with a silver spoon until dissolved. The spoon was removed and boiling continued until the contents of the pan weighed 144 g. Figuring the percent sugar in the final product from the weight of the finished jelly and the weight of sugar added, all jellies

contained approximately 69.4% sugar. The contents of the pan were then quickly transferred to a standard jelly glass and sealed with a tight fitting lid. After standing about 24 hours the strength of the jelly was measured. Jelly strength measurements were taken on the top of the jelly before removal from the glass and on the bottom after removal from the glass. However, only the top measurements are given in these researches as the bottom measurements are very similar, differing only in magnitude.¹

Jelly Strength Measurements:

All jelly strength measurements were made with the jelly strength tester.¹ The tester is very simple in construction and easy to operate. The parts necessary for its construction consists of a Woulff bottle, Lüer syringe, manometer, three way stopcock and connections. These pieces of apparatus are connected so that the air pressure, created in the Woulff bottle by the water run into it drop-wise from a tap, forces the plunger of the syringe into the jelly. This pressure is indicated on the manometer in cm. of water.

The apparatus is standardized before each measurement by placing the plunger of the syringe on an unyielding object and regulating the height of water in the Woulff bottle by means of a siphon attached thereto, rather than by the rate of flow of water from the tap, so that the water in the manometer rises to a definite height in a definite interval of time. The pressure in the system is then released by means of a three way stopcock, the jelly carefully placed under the plunger of the syringe, the water in the Woulff bottle run out to the desired level, previously determined during standardization, and the stopcock closed. As the air pressure increases the plunger of the syringe is actuated and eventually breaks through the surface of the jelly. At this point the column of water in the manometer remains stationary and then suddenly drops. The point of maximum pressure is recorded as the jelly strength.

It is desirable that all jelly strength measurements be uniform so that any set of data in researches of this nature may be compared with any other set. In order to insure this uniformity, a certain amount of pectin was put aside and used only for the preparation of standard jellies. These standards were made by boiling 100 cc. of a 1% pectin solution, 100 g. sugar and 5 cc. 0.1N sulphuric acid to a weight of 144 g. Two of these jellies were made up with the unknowns and were measured with them. In this manner a factor was obtained from time to time by means of which all jellies were corrected to the same basis.

Jelly strength testers of the type described will give uniform strength measurements. The results of one laboratory could not be exactly duplicated in other laboratories, however, as differences in the diameter and weight of the plunger cause variations in the measurements. A standard jelly, that would be more uniform than a pectin jelly, perhaps could be used for the standardization of all jelly strength testers. A uniform gelatine, for example, might be used for this purpose.

In determining the effect on jelly formation, of the addition of salts to the solution from which the jellies were made, the salts were maintained constant and the acidity of the solutions was varied. Three series of jellies were made, one for each of the acids. Each series was divided into four parts, namely, pectin alone, pectin with 1 g. sodium sulphate, pectin with 0.5 g. sodium hydrogen tartrate, pectin with 0.5 g. di-sodium hydrogen citrate. Acids in varying amounts were added to these pectin-salt solutions and the strengths of the resulting jellies recorded.

The hydrogen ion concentrations of the various solutions under the varying conditions of acidity were determined electrometrically using the Leeds and Northrup type K potentiometer. It should be particularly noted that all hydrogen ion measurements were made on the solutions before boiling and before adding sugar. This procedure is in accord with the methods used by Tarr²

who pointed out that jelly formation could be controlled by regulating the hydrogen ion concentration of the solution used for jelly making. In no case was the hydrogen ion concentration of the resulting jelly considered.

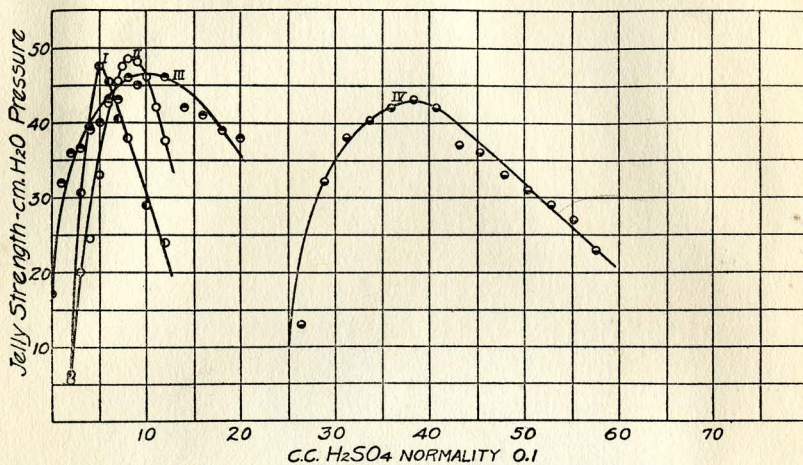
The data accumulated by following the procedure outlined above, made it possible to plot hydrogen ion concentration, as well as total acidity, against jelly strength. The data obtained are given in Tables I-IV and the curves in Figures I-VII inclusive.

TABLE I

The Effect of Sulphuric Acid on Jelly Formation with and without the Addition of Salts.

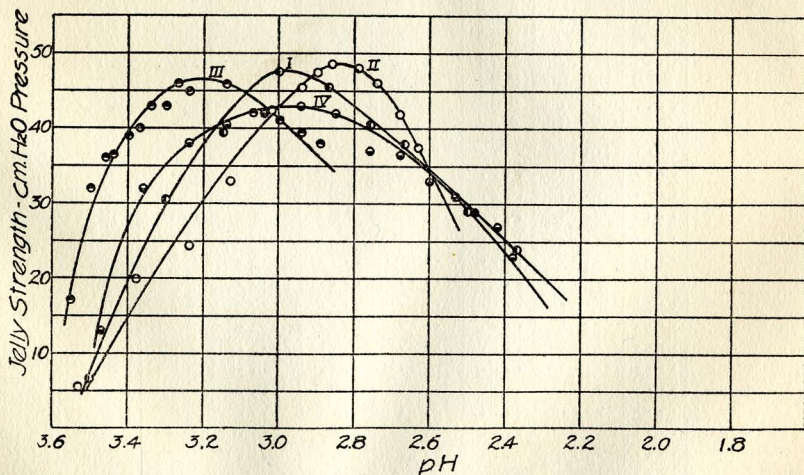
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Fig. I. Curves Showing the Effect of Total Acidity on Jelly Formation with and without Added Salts.



- I. Without Added Salt.
- II. With 1 g. Sodium Sulphate.
- III. With 0.5 g. Sodium Hydrogen Tartrate.
- IV. With 0.5 g. Di-Sodium Hydrogen Citrate.

Fig. II. Curves Showing the Effect of Hydrogen Ion Concentration on Jelly Formation using Sulphuric Acid with and without Added Salts.



- I. Without Added Salt.
- II. With 1 g. Sodium Sulphate.
- III. With 0.5 g. Sodium Hydrogen Tartrate.
- IV. With 0.5 g. Di-Sodium Hydrogen Citrate.

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Fig. III. Curves Showing the Effect of Total Acidity on Jelly Formation with and without Added Salts.

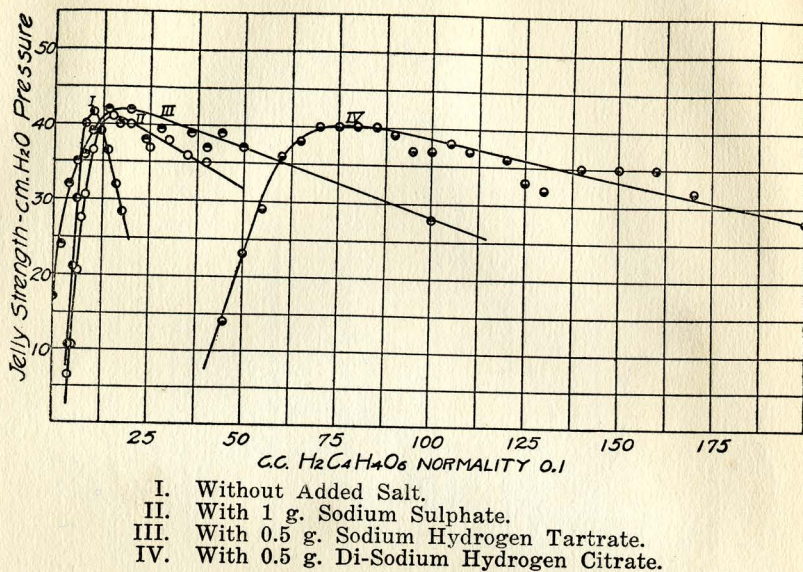


Fig. IV. Curves Showing the Effect of Hydrogen Ion Concentration on Jelly Formation using Tartaric Acid with and without Added Salts.

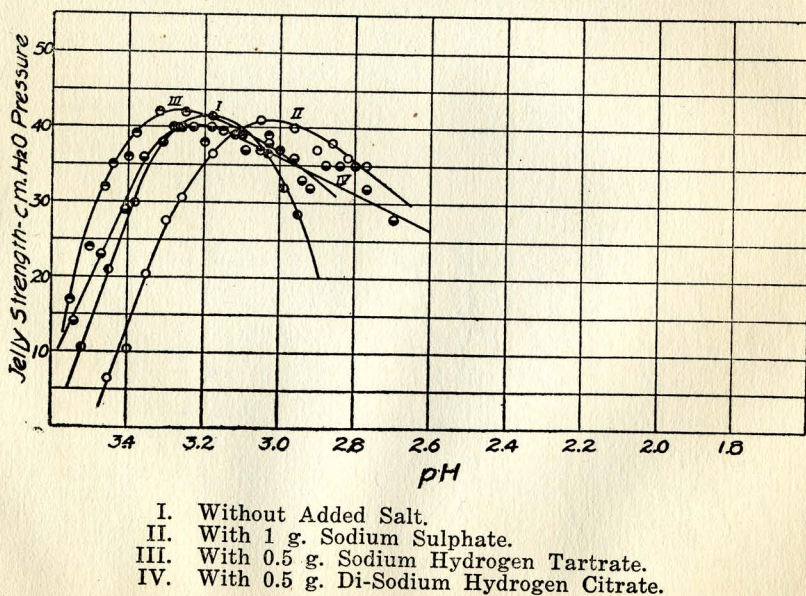
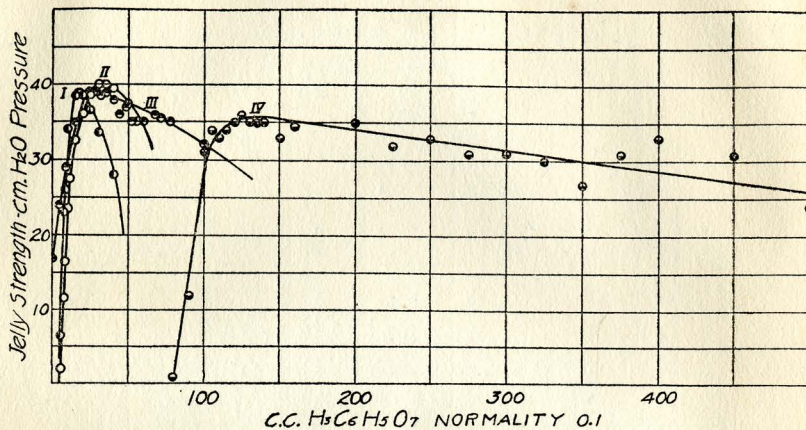


TABLE III

Effect of Citric Acid on Jelly Formation with and without the Addition of Salts.

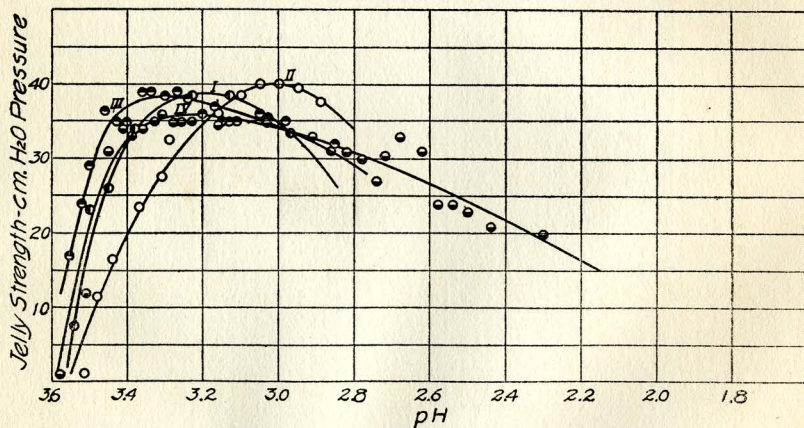
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Fig. V. Curves Showing the Effect of Total Acidity on Jelly Formation with and without Added Salts.



- I. Without Added Salt.
- II. With 1 g. Sodium Sulphate.
- III. With 0.5 g. Sodium Hydrogen Tartrate.
- IV. With 0.5 g. Di-Sodium Hydrogen Citrate.

Fig. VI. Curves Showing the Effect of Hydrogen Ion Concentration on Jelly Formation using Citric Acid with and without Added Salts.

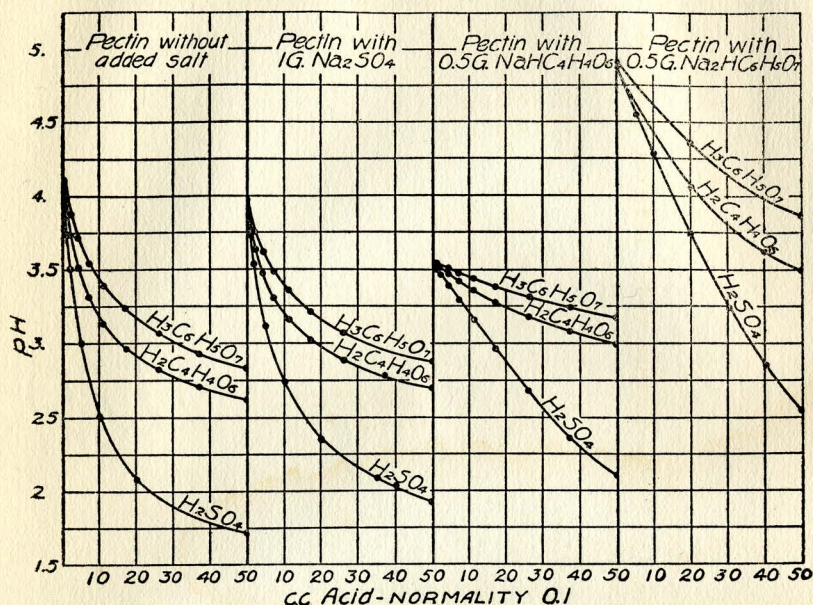


- I. Without Added Salt.
- II. With 1 g. Sodium Sulphate.
- III. With 0.5 g. Sodium Hydrogen Tartrate.
- IV. With 0.5 g. Di-Sodium Hydrogen Citrate.

TABLE IV
The Effect of the Three 0.1N Acids on 100 cc. of a 1% Pectin Solution under Different Conditions of Salt Concentration

ACID cc.	SULPHURIC				TARTARIC				CITRIC			
	No Ad- ded Salt	1 G. Na ₂ SO ₄	0.5 G. NaHC ₄ H ₄ O ₆	0.5 G. Na ₂ HC ₆ H ₃ O ₇	No Ad- ded Salt	1 G. Na ₂ SO ₄	0.5 G. NaHC ₄ H ₄ O ₆	0.5 G. Na ₂ HC ₆ H ₃ O ₇	No Ad- ded Salt	1 G. Na ₂ SO ₄	0.5 G. NaHC ₄ H ₄ O ₆	0.5 G. Na ₂ HC ₆ H ₃ O ₇
	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
0	4.12	3.99	3.54	4.88	4.12	3.99	3.55	4.88	4.13	3.98	3.55	4.91
0.5	3.88	3.85	3.52	3.99	3.85	3.53	4.05	3.91	3.55
1.0	3.74	3.73	3.50	3.89	3.76	3.52	3.99	3.85	3.54
1.5	3.62	3.62
2.0	3.51	3.53	3.47	3.73	3.63	3.50	3.88	3.75	3.52
2.5	3.41	3.45
3.0	3.48
4.0	3.39	3.52	3.47	3.47	3.72	3.62	3.51
5.0	3.00	3.12	4.54	3.42
7.0	3.29	3.32	3.30	3.55	3.48
10.0	2.50	2.74	4.28
11.0	3.16	3.13	3.16	3.36	3.39	3.35	3.44
17.0	2.96	2.96	3.01	3.28	3.23	3.22	3.39
20.0	2.08	2.35	3.74	4.06	4.36
26.0	2.68	2.82	2.88	3.18	3.06	3.08	3.32
30.0	3.24
35.0	1.83	2.08
37.0	2.36	2.70	2.79	3.09	2.93	2.98	3.25
40.0	2.04	2.85	3.62
50.0	1.71	1.92	2.10	2.55	2.62	2.70	2.99	2.83	2.88	3.17	3.87
60.0	2.35	3.36	3.57
80.0	3.19

Fig. VII. Electro Titration Curves of Pectin and Acid with and without Added Salts.



A perusal of the above tables and figures points to the fact that there is absolutely no correlation between jelly formation and total acidity, but that hydrogen ion concentration may be correlated with jelly formation as Tarr² pointed out. He worked with purified pectin and pure acid and sugar, while the conditions of the experiments reported here more nearly approximate those of fruit juices, in that the solutions are more highly buffered than his. Consequently, it was possible to vary the total acidity at definite hydrogen ion concentrations between very wide limits, yet the minimum and optimum points of jelly formation remained fairly constant, approximately at the same pH values as those reported by Tarr.¹

Considering the pH-jelly strength curves in Figures II, IV, VI, it may be seen that the curves for the various salts are in the same relative positions in respect to the straight acid curves. The points on the curves in-

dicating optimum jelly strengths are on the right of the optimum points for the straight acids in the case of sodium sulphate, while those of tartrate and citrate are on the left in all cases. This relation is an indication of the effect of salts on the hydrogen ion concentration at the optimum point of jelly formation and is exactly what was expected, since Tarr¹ pointed out that the hydrogen ion concentration at the optimum point of jelly formation varied slightly with the nature of the acid. These optimum points were reported by him as occurring at a pH of 3.10 with sulphuric acid, 3.20 with tartaric acid and 3.30 with citric acid. The data herein reported indicate the corresponding points to be at pH's of 2.97, 3.18 and 3.18 respectively, checking with Tarr's results as closely as could reasonably be expected. The optimum points of jelly formation, when salts are added, vary in the same order as the acids occurring at the highest hydrogen ion concentration with the sulphate, but at lower and practically equal hydrogen ion concentrations with the tartrate and citrate.

An explanation for the cause of this variation in hydrogen ion concentration at the optimum point of jelly formation is drawn from some of the ensuing data, and will be presented later.

It should be particularly observed that the hydrogen ion concentration at the optimum point of jelly formation is not exactly the same with added salt as without added salt. Thus it varies slightly with salt concentration which in some measure explains the slight difference between Tarr's optimum points and those reported here, as the pectins used in the two cases did not have the same ash content. The data presented in Table IV and Figure VII show that all the curves including those with pectin alone, are more or less buffered. The curves for the acids and distilled water are omitted in order to conserve space, but each jelly strength curve is represented in this figure.

Comparing the jelly strength curves with the electrometric titration curves some similarity is observed.

Generally speaking, the more buffered the titration curves the more buffered the jelly strength curves. For instance in Figure I the curve for sulphuric acid and no salt rises and falls abruptly from the optimum point with cc. 0.1N acid added. Near the optimum point a difference of a few drops of 0.1N acid makes considerable difference in jelly strength. With citric acid and di-sodium hydrogen citrate (Figure V) the curve rises less abruptly to the optimum point and decreases gradually from that point on, with cc. of 0.1N acid added. Referring again to the electro-metric titration curves in Figure VII, it may be seen that the curve for sulphuric acid and pectin is the least buffered of all, while the curve for citric acid, pectin and the citrate is very highly buffered. Jellies made from highly buffered solutions are apparently less sensitive to changes in total acidity than jellies made from slightly buffered solutions.

Turning now to the pH-jelly strength curves in Figures II, IV, VI, it is observed that the curves are more nearly alike than the cc. 0.1N acid-jelly strength curves, and that jelly strength varies with the hydrogen ion concentration regardless of the buffering power of the solutions from which the jellies are made. This relation indicates of course that total acidity cannot be correlated with jelly formation and that hydrogen ion concentration can be so correlated. However, there is a tendency for the jelly strength-pH curves to flatten out when working with the more buffered solutions. For instance, comparing the jelly strength curve for citric acid and di-sodium hydrogen citrate in Figure VI with the sulphuric acid and no salt curve in Figure II, it may be seen that in the case of the former the jelly strength is less sensitive to a change in hydrogen ion concentration than in the case of the latter. The salt in this case apparently acts as a stabilizer. This stabilizing effect is noticeable in the character of the jellies made under the conditions cited above. When sulphuric acid alone was used syneresis occurred at about pH 2.90, very soon after the optimum point was reached, while with citric acid

and the di-sodium hydrogen citrate syneresis was not in evidence until a pH of approximately 2.50 was reached. Of course these results were obtained at a definite concentration of salt and do not necessarily apply to other concentrations, yet the salt effect is noticeable. Fruit juices contain salts of the fruit acids and these salts tend to repress the ionization of the acids so that good jellies may be obtained over a wide range of total acidity. In the absence of salts the range is very narrow and the total acidity must be carefully regulated. Thus it is seen why the housewife can make jellies from fruit juices and why their manufacture is not limited to the technical man. The salt content of the juice insures, to a certain extent, the production of a good jelly.

Another interesting point in connection with the above data is the effect of added salt on the hydrogen ion concentration of 100 cc. of a 1% pectin solution. The initial hydrogen ion concentration of the 1% pectin solution was at a pH value of 4.12. The pH values of the salts, sodium sulphate, sodium hydrogen tartrate and di-sodium hydrogen citrate, were 7, 3.50 and 5.20 respectively. After the addition of the indicated amounts of these salts to the pectin solution the resultant pH values of the solution were 3.97, 3.54 and 4.88 respectively. The last two results are quite natural as they are between the pH values of the pectin and the salt. The figure 3.97 for the sodium sulphate, however, is lower than either the salt or the pectin. The most probable explanation of this is given by Bancroft,⁸ who finds that when a solution of a neutral salt is shaken with a colloid the hydrogen ion concentration of that solution is either increased or decreased, depending upon the ability of that colloid to adsorb the base or acid (formed by hydrolysis) of that salt. With sodium sulphate the colloidal pectin evidently adsorbs the sodium hydroxide, causing more of the salt to hydrolyze and the acid to build up. This observation might be of importance in determining the isoelectric point of pectin as it is known that colloids will adsorb bases above the isoelectric point and acids

below that point. Thus if a series of pectin solutions were adjusted to various hydrogen ion concentrations and equal quantities of neutral sodium sulphate added to them the pH values of the resultant solutions should be lowered in those solutions of hydrogen ion concentration above the isoelectric point of pectin and increased in those below this point. At the isoelectric point there would of course be no change in hydrogen ion concentration after the addition of the salt.

This observation also probably explains in some measure why it is so difficult to prepare pure pectin. The inorganic content of the pectin, which is so difficult of separation, is probably held very tenaciously by the colloidal pectin and cannot be removed until the hydrogen ion concentration of the colloidal solution is properly adjusted. This point will be taken up in our researches on "The Rôle of Pectin."

THE EFFECT ON JELLY FORMATION OF VARIATIONS IN SALTS CONCENTRATION (TOTAL ACIDITY MAINTAINED CONSTANT)

Viewing the data so far presented from a more practical side, the conclusion is reached that it should be possible to add a salt to a fruit juice too high in acidity but with sufficient pectin to form a jelly and thus buffer off the acid to a hydrogen ion concentration favorable to the production of a good jelly. This idea was tested out in the following experiment.

Three series of jellies were made up in the usual manner, one series for each of the acids, sulphuric, tartaric and citric. In each series the total acidity was maintained constant and the concentration of di-sodium hydrogen citrate was varied from zero to a point where no jelly was obtained. The object of this experiment was to add enough acid to the pectin solution to give it a hydrogen ion concentration greater than that at the optimum point of jelly formation and by successive increases in salt concentration to buffer off the hydrogen ion concentration of the solution, through the optimum and

down to the minimum point, eventually reaching a concentration where no jelly would form.

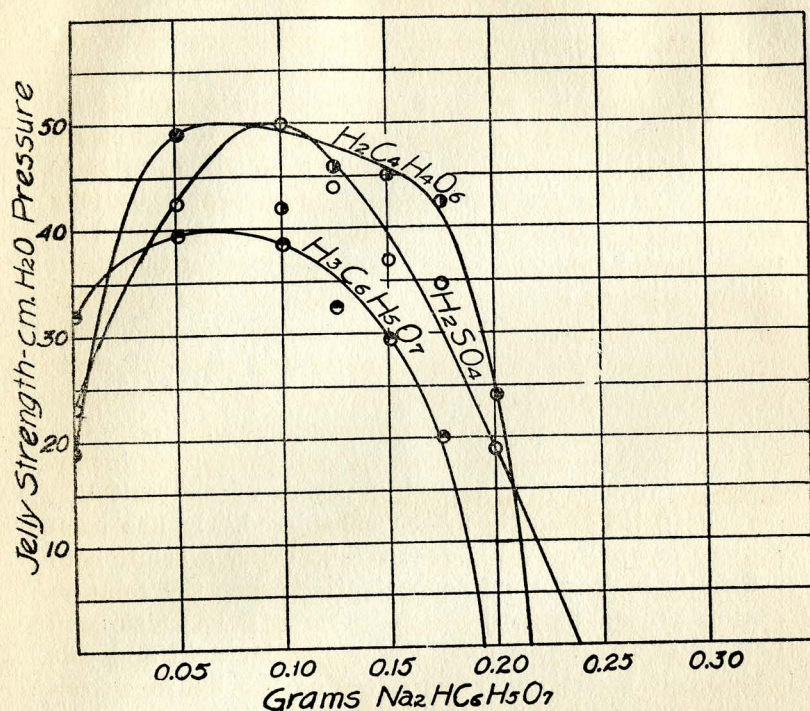
From the data previously reported using 0.5 g. di-sodium hydrogen citrate to 100 cc. of a 1% pectin solution, approximately 26 cc. of 0.1N sulphuric acid, 45 cc. 0.1N tartaric acid and 80cc. of 0.1N citric acid were required to just form a jelly. Using no salt these amounts of the several acids would probably prohibit the formation of a jelly. Consequently, smaller quantities of the acids were used, namely, 12 cc. of 0.1N sulphuric acid, 24 cc. of 0.1N tartaric and 34cc. of 0.1N citric acid for each 100 cc. of 1% pectin solution used. The hydrogen ion concentrations of the resulting solutions were at pH values of 2.36, 2.84 and 2.93 respectively, being well below the optimum points of jelly formation for the respective acids, yet permitting jellies to form. In Figure VII it will be observed that for 0.5 g. of di-sodium hydrogen citrate, 100 cc. of 1% pectin solution and 12 cc. of sulphuric acid the hydrogen ion concentration is at a pH of 4.22; with 24 cc. 0.1N tartaric it is at a pH of 3.96 and with 34 cc. of 0.1N citric acid it is at a pH of 4.10. All of these values are above the minimum point of jelly formation so that before a concentration of 0.5 g. of salt is reached, a point should be obtained where no jelly will form.

This was found to be the case as is shown in Table V and in Figure VIII.

TABLE V
The Effect on Jelly Formation of Variations in Salt Concentration
(Total Acidity Maintained Constant).

Salt Added G.	12 cc. Sulphuric Acid 0.1N	24 cc. Tartaric Acid 0.1N	34 cc. Citric Acid 0.1N
	Jelly Strength Cm. H ₂ O Pressure	Jelly Strength Cm. H ₂ O Pressure	Jelly Strength Cm. H ₂ O Pressure
0.00	23.0	19.0	32.0
0.05	42.5	49.0	39.5
0.10	50.0	42.0	38.5
0.125	44.0	46.0	32.5
0.150	37.0	45.0	29.5
0.175	34.0	42.5	20.0
0.200	19.0	24.0	No Jelly
0.250	No Jelly	No Jelly	

Fig. VIII. Curves Showing the Effect of a Salt on Jelly Formation when the Total Acidity is Maintained Constant.



At a concentration of 0.25 g. of salt no jelly was obtained with the sulphuric and tartaric acids, while with the citric acid, which has an ion in common with the salt and consequently was buffered to a greater extent, no jelly formed at 0.2 g. of salt.

These results offer further proof that hydrogen ion concentration is the controlling factor in jelly formation rather than total acidity. The total acidity was maintained constant, in fact was slightly increased due to the addition of the acid salt, yet when the hydrogen ion concentration fell below the minimum point of jelly formation no jelly formed.

One other point that has not so far been called to attention, is the fact that apparently salts have a greater effect on citric acid jellies than upon tartaric and sulphuric acid jellies, and that of the two fruit acids citric and tartaric, the latter produces the stronger and more

favorable jelly. This point has been observed by Tarr,² Goldthwaite⁹ and others, and is born out in all of the jelly strength curves so far presented. It is especially noticeable in Figure VIII.

Therefore, the addition of a salt to a fruit juice of a hydrogen ion concentration too high to produce a favorable jelly offers the possibility of adjusting it to a hydrogen ion concentration more favorable to jelly formation. However, no definite statement should be made in this regard without first considering the effect of the cation of the salt added.

THE EFFECT ON JELLY FORMATION OF VARIATIONS
IN SALT CONCENTRATION (HYDROGEN ION CON-
CENTRATION MAINTAINED CONSTANT)

So far only the buffering power of the salt due mainly to its anion has been considered. It has been shown that more acid is required to bring a solution to a definite hydrogen ion concentration when the solution contains a salt than when it does not. It has also been pointed out that this excess of molecular acid and this added salt has a negligible effect on the hydrogen ion concentration at the optimum and minimum points of jelly formation as determined by Tarr.² Everything has been in support of his theory of hydrogen ion concentration in relation to jelly formation. It is important, however, to investigate the effect of other positive ions as the hydrogen ion is not the only positive ion involved in fruit jelly formation. It has been shown that the hydrogen ion plays the important rôle but it has also been shown that the hydrogen ion concentration at the optimum and minimum points of jelly formation varies slightly under certain conditions, which is an indication that the cation of the salt might play a minor rôle in jelly formation as a supplement of the hydrogen ion.

The object of this experiment was therefore to determine the effect of the cation of the salt on jelly formation. This effect was determined by maintaining the

sugar, pectin, and hydrogen ion concentration constant while varying the salt concentration. This method necessitated a variation in total acidity, but as previously pointed out, total acidity has practically no effect on jelly formation. It has also been shown that the anion of the salt simply acts as a buffer so that any variations in jelly strength with salt concentration may be attributed to the cation of the salt.

Three series of jellies were made up using tartaric acid and sodium hydrogen tartrate in each series. In the first series jellies were made from solutions of hydrogen ion concentration of pH equals 3.49, the second series from solutions of pH equals 3.35 and the third series from solutions of pH equals 3.25. In each series the particular hydrogen ion concentration was maintained constant by adding enough 0.1N tartaric acid to offset the buffer effect of the added salt, and the concentration of sodium hydrogen tartrate was varied from zero to 3 g. The results of this experiment are given in Table VI and Figure IX.

TABLE VI

The Effect on Jelly Formation of Variations in Salt Concentration
(Hydrogen Ion Concentration Maintained Constant).

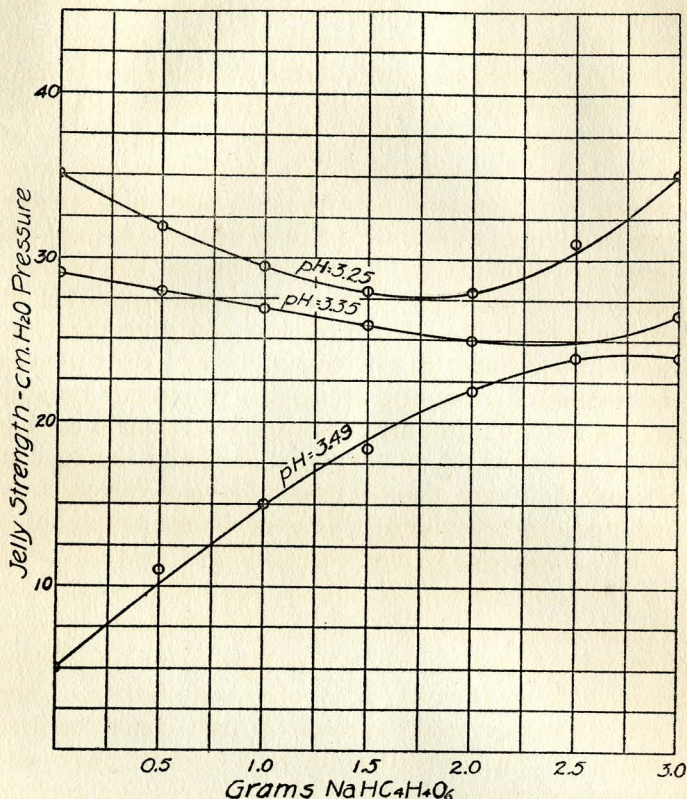
NaHC ₄ H ₄ O ₆ G.	pH = 3.49		pH = 3.35		pH = 3.25	
	0.1N H ₂ C ₄ H ₄ O ₆ cc.	Jelly Strength	0.1N H ₂ C ₄ H ₄ O ₆ cc.	Jelly Strength	0.1N H ₂ C ₄ H ₄ O ₆ cc.	Jelly Strength
0.00	5.50	5.0	8.00	29.0	10.50	35.0
0.50	4.25	11.0	14.20	28.0*	23.00	32.0*
1.00	5.00	15.0	22.70	27.0*	36.50	29.5†
1.50	3.50	18.5	27.00	26.0*	50.50	28.0†
2.00	8.00	22.0	51.00	25.0	81.50	28.0*
2.50	5.55	24.0*	50.00	24.0	90.00	31.0
3.00	0.00	24.0†	56.00	27.0	100.00	35.0

* Slight Syneresis.

† Strong Syneresis.

These results were obtained with a freshly prepared pectin having an ash content of 5.10%. The results on jelly strength are therefore not necessarily comparable to the other results obtained with a pectin with an ash content of 3.60%. However, the results show clearly the rôle of the cation of the salt in jelly formation.

Fig. IX. Curves Showing the Effect of a Salt on Jelly Formation when the Hydrogen Ion Concentration is Maintained Constant.



The curve for pH of 3.49 in Figure IX is first considered. This hydrogen ion concentration is very close to that at the minimum point of jelly formation since without the addition of salt the resulting jelly had a strength of 5, yet the jelly strength increased with the salt concentration up to a certain point reaching the optimum point at a little less than 2.5 g. of salt. Immediately after the optimum point was reached syneresis occurred in the jellies and the jelly strength decreased. A much more satisfactory basis of comparison would have been obtained in this case by plotting the sodium ion concentration against the jelly strength. By such means the effect of the hydrogen ion and sodium ion con-

centrations could have been compared. It is impossible to do so however, as the sodium ion concentration could not be determined. It is reasonable to assume nevertheless that the ionization of the sodium acid tartrate was considerably depressed by the tartaric acid as this acid has two ions in common with the salt, namely the hydrogen ion and the acid radical. From the same line of reasoning it may be assumed that the concentration of the sodium ion decreases with the increase in hydrogen ion concentration. Therefore the effect of the salt on the jelly strength at the higher hydrogen ion concentrations was brought about by a lower concentration of sodium ion than at the lower hydrogen ion concentration. It follows, therefore, that if these results were plotted against sodium ion concentrations the variations in jelly strength would be much more pronounced than is shown in Figure IX where jelly strength is plotted against g. of salt added. This line of reasoning is supported by the fact that a much sharper curve is obtained when jelly strength is plotted against hydrogen ion concentration than is the case when it is plotted against total acidity.

Considering the curve for pH 3.25 which is very close to that hydrogen ion concentration at which the optimum jelly is formed, it is observed that the jelly strength decreases with increase in salt concentration, or sodium ion concentration, up to a certain point and then increases considerably. This hydrogen ion concentration is very close to the hydrogen ion concentration which will cause syneresis in the jelly, so that if the cation of the salt supplements the hydrogen ion in this capacity it should weaken the jelly and eventually cause syneresis. This is exactly what happened. Syneresis occurred at the points indicated on the lower part of the curve.

It is interesting to note that after a definite amount of salt was added the jelly strength increased with the salt concentration and syneresis gradually disappeared. (Curve for pH 3.25). Tarr² noted that syneresis occurred soon after the hydrogen ion concentration at the

optimum point of jelly formation was reached and attributed this phenomena to the excess of hydrogen ion. These researches support his views; but also indicate that the positive ion of the salt may supplement the action of the hydrogen ion in this respect, as syneresis was obtained in jellies made from solutions at hydrogen ion concentrations near the minimum point of jelly formation. In this instance syneresis was caused by the cation of the salt, or by the total cation concentration, including the hydrogen ion.

Colloids in general may be coagulated by the addition of an electrolyte, an acid, an alkali or a salt. If the colloid has a negative charge the coagulation is affected by the cation of the electrolyte, if a positive charge, by the opposite ion. Syneresis, therefore, may be due to the coagulation of the colloidal pectin, breaking down the cellular structure of the jelly and allowing the liquid contents to seep out. The particular pectin used in these researches had a negative charge as determined by cataphoresis studies, hence the cation of the salt was responsible for the coagulation. As the concentration of the salt increased the concentration of the anion also increased and eventually stabilized or peptized the colloidal pectin. Syneresis subsequently disappeared and the strength of the jelly increased.

For some unknown reason it was impossible to measure the hydrogen ion concentration of a pectin solution containing more than 3 g. of sodium acid tartrate in 100 cc. of solution. It would have been interesting had it been possible to increase the salt concentration above 3 g. However, the result can be roughly predicted. It is obvious that the curve for pH 3.25 cannot rise indefinitely beyond the minimum point because the cation concentration will eventually reach a point where it will again coagulate the pectin and the jelly strength will then decrease. Therefore it is possible to have two regions on the curve where syneresis will occur. Considering the curve for pH 3.49 in this respect, this curve would have two optimum points, one point at approximately

2.8 g. of salt and the other point somewhere beyond this point.

The curve for pH 3.35 is intermediate between those for pH 3.25 and pH 3.49 as would be expected. It should be noticed that the minimum point of the curve is at a salt concentration beyond that of curve for pH 3.25. The minimum point on the curve for pH 3.49 would be at a still higher concentration of salt. It would be interesting to know the total cation concentration at these points on the curves as they apparently have a tendency to occur at the same concentration.

In the experiment immediately preceding this it was shown that a pectin solution too high in hydrogen ion concentration to be favorable to jelly formation could be corrected to the proper hydrogen ion concentration by the addition of a salt to the solution. A good jelly could then be made from the solution. In this experiment it has been shown that the total cation concentration is an important factor and may cause syneresis in the resulting jelly. On the other hand the concentration of the anion tends to oppose the action of the cation and may eventually peptize the pectin, thereby overcoming syneresis. Therefore a good jelly may or may not result from the addition of a salt to a fruit juice of high hydrogen ion concentration.

The data in Table VI were obtained by boiling the solutions to a constant weight of 144 g. so that calculating the per cent sugar in the finished jelly from the weight of sugar added (100 g.) all jellies contained approximately 69% sugar. The per cent of total solids, however, increased with the salt added. The results therefore might be criticized from the standpoint of decreased solubility of sugar with salt concentration which might tend to weaken the jelly. Tarr and Baker³ found that with other conditions remaining constant, the optimum jelly was obtained when the solution from which it was made was boiled down to a point where it became saturated with respect to sugar. Thus the resulting jelly contained approximately 69% sugar. Increasing or de-

creasing the percentage sugar from this point resulted in a decrease in jelly strength.

Throughout this experiment the percentage sugar in the jelly remained constant at 69%, but the salt concentration was varied. If the solution had become supersaturated with respect to sugar, due to decrease solubility with variation in salt concentration, then the jelly should have become weaker. In the curve for pH 3.49 (Figure IX) it is seen that jelly strength increased with salt concentration. At the higher hydrogen ion concentration the jelly contained more invert sugar than at the lower values, and since a water solution containing invert sugar can contain more sugar when it is saturated than one that contains only cane sugar, the jelly strength at the higher hydrogen ion concentrations should increase rather than decrease. But in the curve for pH 3.25 and 3.35 the jelly strength decreased with salt concentration. Therefore it is very unlikely that the salt, in concentrations used in this experiment, had a noticeable effect on the solubility of the sugar, so it is entirely probable that the variations in jelly strength as recorded were due mainly to variations in the ionic concentrations of the solutions from which the jellies were made.

One other point in connection with this experiment is quite interesting. Standard jellies were made up each day as described on page 8. The jellies in this experiment were quite clear and sparkling while the standard jellies, in contrast, were cloudy and dull. The former contained added salt while the latter were made from pectin, acid, sugar and water and contained no added salt.

DISCUSSION

It is generally conceded that the jelling properties of fruit juices are dependent, to a great extent, upon their acid and pectin content. This Station, as a result of its researches, is led to believe that with the pectin content of the juice sufficient to support jelly formation, the deciding factor is the hydrogen ion concentration of

the juice. Total acidity cannot be correlated with jelly formation. In working out this theory Tarr² used solutions containing the minimum amount of impurities. Consequently, these solutions were not buffered, from the standpoint of the hydrogen ion, to the extent that would be expected of fruit juices. It has been the purpose of these researches to test out the applicability of Tarr's conception of the importance of hydrogen ion concentration in jelly formation, under conditions more nearly approximating those existing in fruit juices.

Fruit juices naturally contain many substances that tend to buffer the acidity of the juice. The most important of these substances are the salts of the fruit acids. In addition to pectin there are also other colloids, such as the starches, gums, tannic acid or tannates, proteins, etc., which undoubtedly exhibit some buffer action. These researches have considered chiefly the effect of salts on the hydrogen ion concentration of pectin solutions and their subsequent effect on jelly formation. A discussion of the acidity factor is first presented.

All of the data, and the curves drawn therefrom, presented throughout this study, point to one conclusion, namely, that hydrogen ion concentration is of paramount importance in jelly formation. There is absolutely no correlation between total acidity and jelly formation. Nowhere do the results contradict this statement. The total acidity was varied from 2 cc. 0.1N sulphuric acid to an equivalent of 1000 cc. of 0.1N citric acid, yet the optimum and minimum points of jelly formation occurred at fairly definite hydrogen ion concentrations.

Without adding any salt to the pectin solution, the minimum jelly was formed with 2 cc. of 0.1N sulphuric acid, while the optimum jelly was obtained with 5.25 cc. of the same acid. A pectin solution containing 0.5 g. of di-sodium hydrogen citrate required 26.4 cc. 0.1N sulphuric acid and 80 cc. 0.1N citric acid to just form a jelly while the optimum jelly formed at 38 cc. of sulphuric and 135 cc. of citric acid. However, the

hydrogen ion concentrations at the optimum and minimum points were practically the same in every instance.

If 80 cc. of 0.1N sulphuric acid had been added to the pectin solution containing no salt the hydrogen ion concentration of the solution would have been too high to permit a jelly to form. On the other hand had 5.25 cc. of 0.1N sulphuric acid, the amount necessary to form the optimum jelly with no added salt, been added to the pectin solution containing 0.5 g. di-sodium hydrogen citrate, the hydrogen ion concentration would not have been sufficient to form a jelly.

The data in Table V and the curves in Figure VIII also indicate that total acidity is not a factor in jelly formation. In this instance the total acidity remained constant and the hydrogen ion concentration was decreased by the addition of a salt. It was possible to buffer off the hydrogen ion concentration in this manner to such an extent that a jelly failed to form.

The data in Table VI and the curves in Figure IX also show the importance of the hydrogen ion concentration. In this instance the hydrogen ion concentration was maintained constant at the indicated values and the salt was increased. As more salt was added it required more acid to bring the hydrogen ion concentration of the solution up to the desired value, so that the total acidity was varied between the limits of 5 cc. and 100 cc. of 0.1N tartaric acid. However, the strengths of the resulting jellies were in all cases greater at the higher hydrogen ion concentrations, regardless of total acidity. At pH's of 3.25 and 3.35 the jelly strength actually decreased with increase in total acidity while at pH 3.49 it increased showing again that there is no correlation between total acidity and jelly formation.

Tarr¹ has observed that the hydrogen ion concentration at the optimum point of jelly formation was not always the same for the different acids. With sulphuric acid the optimum point was at a pH of 3.10, with tartaric acid 3.20, and with citric acid 3.30. In these researches it has been pointed out that not only does the hydrogen

A resumé of some of the more important data taken from Tables I-IV inclusive and from the curves in Figures I-VII is given in Table VII.

TABLE VII

	Minimum Points of Jelly Formation										Optimum Points of Jelly Formation									
	No Salt Added		1 G. Na_2SO_4		0.5 G. $\text{NaHC}_4\text{H}_4\text{O}_6$		0.5 G. $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$		1 G. Na_2SO_4		0.5 G. $\text{NaHC}_4\text{H}_4\text{O}_6$		0.5 G. $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$		pH		pH		pH	
	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.	C.C.
	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N	0.1N
	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid	Acid
H_2SO_4	3.50	2.0	3.53	2	...	3.47	26.4	2.97	2.85	3.20	3.20	10	2.95	38						
$\text{H} \cdot \text{C}_4\text{H}_4\text{O}$	3.52	4.0	3.45	4	...	3.54	45	3.18	3.01	3.25	20	3.20	78							
$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	3.54	6.0	3.51	6	...	3.58	80	3.18	3.01	3.25	38.5	3.25	135							
C.C. 0.1N Acid Necessary to Give Solution pH Value 3.50																				
	No Salt Added		1 G. Na_2SO_4		0.5 G. $\text{NaHC}_4\text{H}_4\text{O}_6$		0.5 G. $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$		1 G. Na_2SO_4		0.5 G. $\text{NaHC}_4\text{H}_4\text{O}_6$		0.5 G. $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$		pH		pH		pH	
H_2SO_4	2.00		2.25		1.00		26		6.5		16		37							
$\text{H} \cdot \text{C}_4\text{H}_4\text{O}$	4.25		3.25		2.00		44		17.5		50		111							
$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.00		6.25		6.75		90		34.0		..		210							
C.C. 0.1N Acid Necessary to Give Solution pH Value of 3.00																				
	No Salt Added		1 G. Na_2SO_4		0.5 G. $\text{NaHC}_4\text{H}_4\text{O}_6$		0.5 G. $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$		1 G. Na_2SO_4		0.5 G. $\text{NaHC}_4\text{H}_4\text{O}_6$		0.5 G. $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$		pH		pH		pH	
H_2SO_4	2.00		2.25		1.00		26		6.5		16		37							
$\text{H} \cdot \text{C}_4\text{H}_4\text{O}$	4.25		3.25		2.00		44		17.5		50		111							
$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.00		6.25		6.75		90		34.0		..		210							

ion concentration vary slightly at the optimum and minimum points with the nature of the acids used, but also with the nature of the salt used. In Table VII these variations are readily apparent. The curves in Figures II, IV, VI also show that the hydrogen ion concentrations at the optimum and minimum points on the curves do not exactly coincide. All jellies were made up under as nearly the same conditions as possible. The only variables throughout the work were the total acidity, salt and hydrogen ion concentration, so that the explanation will probably be found in either the total acidity or salt concentration. The total acidity may be divided into active acidity and molecular acidity, the active acidity being that part of the total acidity which ionizes, and the molecular acidity that part of the acidity which does not ionize. The hydrogen ion concentration is a measure of the active acidity and there is no reason to believe that the molecular acidity would have any bearing on the variation in hydrogen ion concentration at the optimum and minimum points of jelly formation. The molecular acidity is inactive and, as such, is not a factor in jelly formation. The explanation then should center around the salt which, with its introduction into the pectin solution, increases the ionic concentration of that solution if the hydrogen ion concentration is maintained constant by the addition of more acid.

Considering the curves shown in Figures II, IV, VI it is seen that the optimum points of the curves occur at lower hydrogen ion concentrations when salt is added than when it is not, disregarding for the moment the sodium sulphate curve. It is also observed that at the lower hydrogen ion concentrations these same curves are above those representing the jelly strength of jellies made from solutions to which no salt has been added. At the higher hydrogen ion concentrations these curves are below them. Turning to Figure IX it is seen that at the lower hydrogen ion concentration, pH 3.49, the jelly strength increased with the salt concentration and at the higher hydrogen ion concentration, pH 3.25 and

3.35, it decreased with salt concentration. The explanation of this increase and decrease in jelly strength with salt concentration is given on page 27, and was attributed to the supplementary action of the cation of the salt to that of the hydrogen ion.

A general idea of the variation in hydrogen ion concentration at the optimum point of jelly formation may be obtained by a consideration of the curve pH 3.25 (Figure IX). With tartaric acid and no added salt the hydrogen ion concentration at the optimum point of jelly formation was very close to this value. As the salt concentration increased (with a consequent increase in cation) the jelly strength decreases up to a certain salt concentration and syneresis eventually occurred in the resulting jelly. This means that the optimum point of jelly formation has been passed and that the hydrogen ion concentration at the optimum point was no longer at a pH of 3.25. Decreasing the hydrogen ion or cation (of the salt) concentration will increase the strength of the jelly until the optimum point is reached. Consequently, hydrogen ion concentration at the optimum point of jelly formation will be at a lower value in the presence of salts than in their absence.

Similarly, it may be shown that the hydrogen ion concentration at the minimum point of jelly formation is at a lower value in the presence of a salt than when no salt is added. Such a relation is shown in the curve for pH 3.49.

These findings are in accord with the findings of Tartar and Gailey¹⁰ who have shown that mastic and gamboge sols are coagulated at definite hydrogen ion concentrations. The addition of salts, however, lowered the hydrogen ion concentration at the coagulation point.

Considering the sodium sulphate curves in Figures II, IV, VI, it is observed that instead of being above the acid curves they are all below at the lower hydrogen ion concentrations and above at the higher hydrogen ion concentrations. Sodium sulphate differs from the other salts used, in that it is a salt of a strong base and a

strong acid and hence will ionize to a much greater extent. It has been pointed out that the curve for pH 3.49 Figure IX is on the downward trend at a concentration of 3 g. of sodium hydrogen tartrate. In fact syneresis was obtained at this point which resulted subsequently in a decrease in jelly strength. As the sulphate ionizes to a greater extent than the tartrate and as 1 g. of this salt was used instead of 0.5 g. it is not impossible to conceive of the cation (of the salt) concentration as being sufficient to actually cause a decrease in jelly strength at the lower hydrogen ion concentrations. In other words the cation concentration at the optimum point of jelly formation, at the lower hydrogen ion concentrations, has been exceeded, thereby causing a decrease in jelly strength.

At the higher hydrogen ion concentrations using sodium sulphate, the increase in jelly strength over that where no salt was used, may be explained from the curve pH 3.25. This curve declines to a minimum with added salt and then rises abruptly due, as previously explained, to the peptization of the colloidal pectin by the anion of the salt or acid. It may be assumed therefore, that at the higher hydrogen ion concentrations, using 1 g. of sodium sulphate, the ionic concentrations are similar to those existing on that portion of the curve (pH 3.25) from 2 g. to 3 or more g. At any point between these limits a decrease in hydrogen ion concentration would cause a decrease in the strength of the jelly, and an increase in hydrogen ion concentration would cause an increase in jelly strength. Thus at any salt concentration between the minimum and optimum points on the curve (the optimum point being, in this case, beyond a concentration of 3 g. salt) the optimum jelly would be at a higher hydrogen ion concentration than at any lower concentration of salt. Such a relation actually existed in the case of the sodium sulphate curves at the higher hydrogen ion concentrations. Therefore the variations in the curves for pH-jelly strength as indicated in Figures II, IV, VI are what might be expected if the

assumptions are correct. The entire data supports these assumptions. The ionic concentrations were not measured because no method for doing so was available.

The reader might be led to believe that jelly formation could occur in the presence of salts without the addition of any acid. Von Fellenberg⁶ has stated that he was able to form a jelly in this way by using salts of the fruity acids. He does not give the hydrogen ion concentration of the solutions from which the jellies were made, and it is possible that acid salts were used or that the adsorption of the base of the salt by the pectin was sufficient to give the solution the proper hydrogen ion concentration. It has been shown in these researches that the addition of 1 g. sodium sulphate of pH 7 to 100 cc. of a 1% pectin solution of pH 4.12 resulted in a pH of 3.97. It was also possible to form a jelly by the addition of 0.5 g. sodium hydrogen tartrate to this same pectin solution, but in this case the resultant hydrogen ion concentration was at a pH of 3.54, close to the hydrogen ion concentration existing at the minimum point of jelly formation.

Thinking that perhaps the hydrogen ion concentration of the pectin solution might be still further increased by the addition of larger amounts of the sodium sulphate, attempts were made to produce jellies from 100 cc. portions of 1% pectin solution in which the salt was varied between the limits of 0.5-15 g. No jelly was obtained. Perhaps the 1 g. pectin had adsorbed all the base it could from the 1 g. sodium sulphate and consequently the hydrogen ion concentration could not increase much beyond pH 3.97. Then again the larger amounts of sodium sulphate would tend to buffer off the acidity. Perhaps if the 1 g. sodium sulphate had been added to a solution containing more than 1 g. of pectin the hydrogen ion concentration might have been increased sufficiently to permit a jelly to form, but it is very unlikely that this would happen.

It has been impossible to prepare jellies in this laboratory from solutions with hydrogen ion concentra-

tions above pH of 3.60. Thus the positive ion of a salt is a factor in jelly formation only in the presence of certain concentrations of the hydrogen ion. The hydrogen ion alone can support jelly formation but, so far as is known, other positive ions cannot. The hydrogen ion, therefore, functions as do other positive ions, but to a greater extent, and in addition plays an important rôle in jelly formation that other positive ions are incapable of doing. This particular rôle of the hydrogen ion in jelly formation is at the present time purely theoretical.

It is generally conceded that acids must be present before jelly formation can occur. It is also well known that acids can hydrolyze pectin and split off methoxy groups. Von Fellenberg⁶ states that it is impossible to form a jelly with a fully methoxylated pectin containing eight methoxy groups. Therefore it is entirely possible that the function of the hydrogen ion is to split off methoxy groups from the pectin and that jelly formation cannot occur until a certain number are split off. The number of methoxy groups are then dependent upon the hydrogen ion concentration of the solution. When the pectin solution is adjusted to that hydrogen ion concentration corresponding to the optimum point of jelly formation, the most efficient pectin compound is formed. Increasing the hydrogen ion concentration above this point decreases the strength of the jelly, because too many methoxy groups are split off from the pectin, eventually forming pectic acid, a fully de-methoxylated pectin which has no jellying properties.

Another possible function of the hydrogen ion is the splitting off of the salts from the pectin molecule. If the pectin has an isoelectric point it will combine with alkalies above this point, and with acids below this point. Perhaps jelly formation occurs below the isoelectric point of the pectin. In such an event the hydrogen ion would have to be present in certain concentrations before jelly formation could occur.

These theories are being investigated in the studies on the rôle of Pectin in Jelly Formation now being conducted in this laboratory.

Tarr² has shown that a stoichiometric relationship exists between the pectin and the acids. He found that if it required 2 cc. of a 0.1N monobasic acid to give 100 cc. of a 1% pectin solution a definite hydrogen ion concentration, it required approximately 4 cc. of a 0.1N di-basic and approximately 6 cc. of a 0.1N tri-basic acid to produce the same hydrogen ion concentration. The divergence from 1, 2, 3 ratio was greatest in the case of the weaker acid citric due, as he pointed out, to the greater effect of the salt contained in the pectin.

The data in Table VII parts 3 and 4 supports Tarr in this contention. It is seen that the cc. 0.1N sulphuric, tartaric and citric acid required to give 100 cc. of a 1% pectin solution a hydrogen ion concentration of 3.50 are in the ratio of 1:2:3 and that the citric acid shows the greatest divergence from this ratio, especially when in the presence of a salt having an ion in common with it. At the higher hydrogen ion concentration (pH 3.00) the divergence is much greater, as pointed out by Tarr,² and is as would be expected.

Considering now parts 1 and 2 of this table, it is seen that at the minimum points of jelly formation this 1:2:3 relationship is almost exactly maintained regardless of the salt. This relationship is also surprisingly well maintained at the optimum points of jelly formation. There is then a tendency to maintain this relationship and for the hydrogen ion concentration at these points to vary accordingly. This is explained by the effect of the positive ion of the salt supplementing the effect of the hydrogen ion as previously explained.

This 1:2:3 relationship indicates that the acid is actually combining with something, either the pectin or with some compound split off from the pectin. Loeb¹¹ has shown this same relationship to exist between acids and proteins and has definitely proven the existence of

protein acid compounds such as gelatine sulphate, chloride, oxalate, phosphate, etc.

An effort is now being made in this laboratory, in the studies on the Rôle of Pectin in Jelly Formation, to determine with what the acid combines.

SUMMARY

- (1) The effect of salts on jelly formation was studied, the pectin, sugar and water factors being maintained as nearly constant as possible.
- (2) The presence of salts in fruit juices is largely responsible for the buffer action exerted by the juices.
- (3) Salts exert a greater buffer action on the weaker acids than on the stronger ones.
- (4) The quantity of acid that may be present in a juice of good jellying properties is dependent upon the buffer action exerted by the juice.
- (5) The jellying properties of a fruit juice are determined by its hydrogen ion concentration rather than by its acid content, other conditions being equal.
- (6) The hydrogen ion concentrations at the minimum and optimum points of jelly formation are at definite pH values regardless of total acidity.
- (7) Jelly strength is not as sensitive to a change in hydrogen ion concentration when the jelly is made from highly buffered solutions.
- (8) The anion of the salt functions mainly as a buffering agent and may also function as a peptizing agent if present in sufficient quantities, thereby increasing the strength of jellies and preventing syneresis.
- (9) The cation of the salt functions in a manner similar to that of the hydrogen ion of the acid, but only at definite hydrogen ion concentrations.
- (10) Syneresis in jellies may be caused by the hydrogen ion alone or by the hydrogen ion and cation of the salt together, but not by the action of the cation of the salt alone.
- (11) The strength of a jelly increases to an optimum with the cation of the salt, at the lower hydrogen ion concentrations. Further increase in cation concentration causes a decrease in jelly strength.
- (12) The strength of a jelly decreases to a minimum with an increase in cation concentration at the higher hydrogen ion concentrations. Further increase in cation concentration causes an increase in jelly strength.

- (13) It may or may not be possible to correct the acidity of a fruit juice by the addition of a salt. The character of the jelly will be dependent upon the total ionic concentration of the juice from which the jelly is made. If the ionic concentration is too high after the addition of a salt, syneresis will occur in the jelly the same as before addition of salt.
- (14) Jelly formation does not occur simply by the addition of neutral salts to pectin solutions. A certain concentration of hydrogen ion must be present.
- (15) Variations in the hydrogen ion concentrations at the minimum and optimum points of jelly formation are due mainly to differences in the ionic concentrations of the acids and salts present.
- (16) Clear, sparkling jellies were obtained from pectin solutions containing appreciable quantities of a salt, while cloudy and dull appearing jellies otherwise resulted.

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