

SOME FACTORS AFFECTING THE TIME OF SOLUTION
OF DEXTROSE

by

Benjamin Franklin Buchanan

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Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

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SOME FACTORS AFFECTING THE TIME OF SOLUTION OF DEXTROSE

INTRODUCTION

Dextrose has gained rapidly in popularity as an ingredient in food preparations since the passage of legislation in 1931 permitting its use in such products without statement of the fact on the label (15). Increased use of dextrose is due largely to its desirable properties as a sweetening agent and its lower cost range with reference to sucrose.

In nearly all cases where a sugar is used in the preparation of food products a solution of the sugar is first prepared and this syrup used in the ensuing steps of the processing. This is true not only in the food industries, but also in many of the other industries that use a sugar in their operations.

With the increase in demand for dextrose to replace or supplement sucrose and to supply the required properties in new preparations many problems have arisen with respect to its use. The most serious disadvantage and the one which has greatly retarded the commercial utilization of dextrose is the long time required to

prepare reasonable concentrations of the sugar in cold water. The present investigation was undertaken to study some of the factors that affect the time of solution of dextrose in an effort to shorten the time required to prepare dextrose syrups. Also, it was hoped that information might be secured from the data obtained and from other available data which would assist in formulating a theory for the solution rate of dextrose.

HISTORICAL

Although little work has been done directly on the time of solution of dextrose, many investigations have been carried out on closely related problems. Most of the work on solution time or solution velocity of sugars has been confined to sucrose, the properties of which are somewhat different from those of dextrose; however, the close relationship between these two compounds requires a consideration of the investigations that have been made using sucrose. A determination of the rate of solution of sucrose in nearly saturated solutions of this sugar was attempted by Kucharenko and Nachmanovich (32) by measuring the decrease in size of crystals as the sugar dissolved. Because of etching during irregular dissolution of the sugar crystals, this method was considered

too inaccurate to be of value in determining rates. Sandera (53) made a comparison of the time required to dissolve sucrose crystals of various sizes and shapes. He reported that the larger the surface exposed, either by using a fine grain sugar or one having irregular surfaces, the greater would be the amount of sugar dissolved in a given quantity of water during the same time interval. In an attempt to obtain a more reliable method, Netuka (47) prepared sucrose pellets by dropping molten sucrose of about two to three per cent moisture content into cooled mercury. Using these pellets he found that the rate of solution at 40° C. was about fourteen times that at 20° C., and that at 70° C. the rate was about thirteen times that at 20° C., showing about the same rate of solution at the higher temperatures. At 20° C. he found that the pellets dissolved twice as fast in pure water as in an eighteen per cent sucrose solution and about ten times as fast as in a fifty per cent sucrose solution. The rate of solution in lime water, one per cent potassium sulfate, one per cent oxalic acid or five per cent sodium carbonate was slightly less than that in pure water.

Because of inconsistencies in methods previously employed, Cofman (10) developed a new method for the determination of the rates of solution of solid substances.

His solvometer consisted of a small, light weight, porous cage suspended from a special hydrometer made for liquids lighter than water. The hydrometer was calibrated so that when the cage was empty the zero mark of the hydrometer rested at the level of the liquid. The operation consisted in placing a weighed sample of the solid to be tested in the cage, suspending the solvometer in a tall cylinder of water and determining the time required for the zero mark on the spindle to reach the water level. This method was first adapted to the determination of the rates of solution of sugars by Borghi (7,8) who used rate of solution as a criterion of purity in sugar samples. He altered the method slightly in order to diminish the error prevalent as the last part of the sample dissolved. His procedure was to remove the cage when the hydrometer spindle reached an arbitrarily set reading before all the sample had dissolved, dry and weigh the residual sugar to determine how much dissolved during the time interval. In this way the large errors incurred by determining the exact time at which the spindle reading reached zero were reduced to a minimum, since the rise of the hydrometer becomes very slow near the end of the process.

A method giving better relative values was worked out later by Sandera and Mircev (55) in which they deter-

mined the time required for the complete solution of a five gram sample of sucrose held by a fine screen over the bell-end of a funnel through which water at a constant temperature was passed at a constant rate. In a later review these same investigators (56) compared the "buoy" method of Borghi with the flowing water method just described and also with another method employed by them consisting of the complete disintegration of a lump of sugar held in a double sieve and suspended in still water. The standard deviation in the time of solution for the "buoy" method and for the double sieve method was about twice as great as for the flowing water method. They concluded, therefore, that the flowing water method represented the most dependable means of determining time of solution. After checking these methods more thoroughly Sandera (54) attributed the previous excellent checks by the flowing water method to chance and, furthermore, found that checks within two per cent could be obtained by the "buoy" method, whereas checks of ten per cent were the best obtainable for the double sieve method. During the checking of these methods Sandera (57) found that varying the conditions under which sucrose was dried influenced to a considerable extent the time of solution. For example, drying the sugar cubes at 20° C. under atmospheric pressure or in a

vacuum did not change the time of solution to a measurable extent, but hot drying in any manner decreased materially the time of solution. In short, the more rapid the drying at 100° C. the shorter was the solution time.

In his investigations on solubility, heats of solution and velocity of solution, Gapon (24) points out that there is a direct relationship between solubility and velocity of solution. This inference bears out a fact familiar to sugar chemists: that, in general, under the same conditions the more soluble sugars dissolve more rapidly than do the less soluble.

According to Ganguly and Banerji (23), crystals partially immersed in a solvent dissolved more rapidly at the surface than within the solvent. This action was believed to result from the surface tension of the solution in supplying fresh solvent as rapidly as the more dense solution was carried down. Their explanation was supported by data showing a marked decrease in surface action upon the addition of substances that decrease the surface tension.

Perhaps the most significant work with respect to the rate of solution of the sugars was begun by Hudson (25) in his studies on milk sugar and his interpretation of the rate of solution of lactose as being actually a

measure of the rate of hydration of the anhydrous form or dehydration of the hydrated form in obtaining the final solubility. An expression was derived showing the mathematical relationship between solubility and rate of solution. In the case of the hydrated lactose the equation was given as:

$$1/t \log \frac{S_{\infty}^H - S_0^H}{S_{\infty}^H - S_H} = k_2$$

Where t = time

S_{∞}^H = final solubility

S_0^H = initial solubility

S_H = solubility at the time "t"

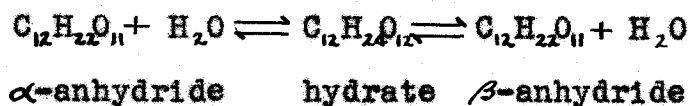
k_2 = maximum rate of solubility of lactose hydrate.

A similar expression was given for the relationship between solubility and rate of solution of anhydrous lactose:

$$1/t \log \frac{S_{\infty}^A - S_0^A}{S_{\infty}^A - S_A} = k_1$$

in which " k_1 ," represents the maximum rate of solution of anhydrous lactose. Later work by Hudson (27) supported the belief that a solution of lactose existed as an equi-

librium between three forms as shown by the reversible equation



in which the equilibrium between the α -anhydride and the hydrate was instantaneous as compared with that between the hydrate and the β -anhydride. In this case, then, the rate of solution was dependent not upon hydration or dehydration but rather upon the isomeric change from the α - to the β -form. This viewpoint was substantiated by data correlating the rate of mutarotation with the rate of solution.

Hudson's investigation on rates of mutarotation were extended to other sugars, notably dextrose (26). By combining data previously reported by Osaka (48) with data obtained by himself, Hudson derived the equation

$$k = 0.0096 + 0.258 [\text{H}] + 9750 [\text{OH}]$$

showing the effect of hydrogen ion concentration upon the rate of mutarotation of dextrose at 24.7° C. In this equation "k" represents the rate of mutarotation, [H] the molar concentration of hydrogen ions and [OH] the molar concentration of hydroxyl ions.

The effect of concentration and temperature upon the rate of mutarotation of dextrose as determined by Hudson and Dale (29) showed a constant rate for concentrations up to ten per cent, a maximum rate between fifteen and twenty-five per cent and a gradual lowering of the rate above thirty per cent dextrose; while an increase in temperature gave a decided increase in rate throughout the temperature range of 0° C. to 40° C. These results were correlated directly with the work of Hudson and Yanovsky (30) at the same time in a study of the rotatory behavior of dextrose by means of solubility experiments in eighty per cent alcohol. They found that the rate of mutarotation was the same as the rate of solution in the alcohol solvent and could be calculated by solubility measurements. Aqueous alcohol was used as the solvent because of the fact that dextrose is relatively less soluble in the alcoholic solution than in water.

The fact that the rate of solution was shown to be identical with the rate of mutarotation in aqueous alcohol suggested the possibility of a corresponding analogy between these two rates in pure water and in water solutions of mutarotative catalysts* such as an excess of

* Any substance which increases the rate of mutarotation of aqueous dextrose solutions is considered, in this paper, a mutarotative catalyst.

hydrogen or hydroxyl ions. A survey of the literature revealed that the first investigator to notice the phenomenon of mutarotation of glucose was Dubrunfaut (16) as early as 1846, although little was understood concerning this peculiar property until Fischer (20), in 1890, suggested that the change in rotatory power of glucose might be due to conversion of the sugar by combination with water into heptahydric alcohol of lower rotatory power. Fischer's suggestion stimulated a number of investigations into the chemical nature of the mutarotation of dextrose.

Tanret (60) was the first to isolate a new form of glucose which he named $\sqrt{\text{glucose}}$. Lowry (36) then advanced the view that the mutarotation of glucose in solution was caused by a balanced reaction between two forms to which he assigned the terms alpha- and beta-glucose. Later (37,38) he published data proving the assumption that a high rotating glucose (α -glucose) was converted into a low rotating glucose (β -glucose) until an equilibrium mixture was reached containing both forms in solution. This proof was confirmed by Armstrong (2) and by Behrend and Roth (4) in their mutarotatory studies of glucose. Summarizing the discoveries on the mutarotation of sugars, Hudson (28) proposed this scheme for the mutarotation:



A number of investigators have determined the effect of various reagents upon the mutarotation of dextrose. Since the rate of mutarotation is so closely related to rate of solution, a brief review of the more pertinent facts of these mutarotatory investigations is essential. Probably the first intensive study was that of Osaka (48) which has already been mentioned in a discussion of Hudson's report of the effect of hydrogen ion concentration on rate of mutarotation of dextrose.

Urech (63) and Trey (61) noticed a decided increase in the rate of mutarotation of lactose upon the addition of small amounts of alkali to the solution. Similarly Murchhauser (44), Colin and Chaudun (11) and Lowry and Wilson (40) found that small amounts of alkali materially catalyze the mutarotation rate of dextrose.

Concentrated solutions of alkalies have a somewhat more drastic action upon dextrose. For example, Effront (17) found a decided decrease in the specific rotatory power of dextrose in a one-half normal sodium hydroxide solution. Profilo (51) reported a diminution of rotatory power so far that the solution became l-rotatory then, finally, after a long interval, optically neutral. This action was discussed more fully in a review by Evans (19) in which he proposed an equilibrium

between d-glucose, d-mannose and d-fructose in strong alkaline solutions with the consequent fragmentation of the hexoses into smaller molecules including acids such as lactic, acetic and formic. The d-fructose formation may reach such proportions as to give an l-rotatory solution, after which decomposition finally neutralizes all optical activity.

Quite contrary to the theory of a shift in the equilibrium between the α - and β -forms during the decrease in rotation of dextrose solutions upon standing, Euler and Nilsson (18) suggested the formation of glucosate ions. This suggestion bears out the work of other investigators who have shown that dextrose forms compounds with various alkaline reagents. The possible formation of compounds of the alkali hydroxides with dextrose was first suggested by Powell (50). Aten, Ginneken and Verwey (3) reported a diminished activity of the metal ions of lithium, potassium and barium in dextrose solutions indicating possible compound formation. Definite evidence was reported by Darmon (12) to prove the existence of a stable compound having the formula $\text{MoO}_3 \cdot 2\text{C}_6\text{H}_{12}\text{O}_6$ in an alkaline dextrose solution of MoO_3 . By electrometric measurements Urban and Shaffer (62) found a definite reaction between dextrose and sodium hydroxide indicating a dextrose-sodium hydroxide compound formation.

Certain characteristic lines in the spectrum of sodium hydroxide solutions of dextrose were believed by Gabryelski and Marchlewski (21,22) to be due to a compound formation between the dextrose and sodium hydroxide. Percival (49) gave evidence of the dextrose compound formation with potassium hydroxide, sodium ethoxide and sodium methoxide. A compound having the formula $(C_6H_{12}O_6)_2 \cdot NaCl \cdot H_2O$ was shown to exist in sodium chloride solutions of dextrose by Matsuura (41). The addition of an excess of sodium chloride precipitated the compound which was in turn decomposed by the addition of water. In similar solutions of potassium chloride the analogous potassium chloride-dextrose compound formation did not occur, according to Matsuura (42). Such dextrose compound formations will be considered later in a discussion of their influence upon the solution time of dextrose.

The rate of mutarotation of dextrose has been determined in varying concentrations of a number of different acids under various conditions. Bronsted and Guggenheim (9) found that the catalytic effect is dependent upon the strength of the acid. The rates of mutarotation of both α - and β -dextrose were found by Andrews and Worley (1) to be identical, but later (66) they altered their statements with regard to the initial stages of the muta-

rotation. The mutarotation of β -dextrose was initially accelerated by the presence of hydrochloric acid, whereas that of α -dextrose was somewhat retarded. A two-stage reaction in which the α -lactone structure was converted to the β -lactone structure through an intermediate compound, probably the aldehyde form, was used in the interpretation of the results. This theory was supported by Wolf from and Morgan (65) in their study of the optical behavior of sugars during the formation of their hemiacetals. In the higher acid concentrations the mutarotation is instantaneous, according to Schenk (58). The effect of a number of acidic, neutral and basic salts upon the rate of mutarotation was investigated by Naumann (46) with the conclusion that only a few produced any marked effect. Strong acids and salts that hydrolyze to give strong acids have been shown by Levin (33) to shorten materially the time of solution of dextrose.

Because of the peculiar effect of borates and boric acid upon the sugars there have been a number of studies with regard to the catalytic effect of these compounds upon the mutarotation of dextrose. The first report of the effect of borax upon the rotation of dextrose solutions was made by Rimbach and Weber (52) in 1905. They explained the lower rotatory power of the dextrose

in a borax solution as due to compound formation. This view was later challenged by Michaelis and Rona (43) and again by Murchhauser (45) when they showed that even though the rotatory power was lower it was still higher than for extremely dilute alkalies that were shown to form dextrose-alkali compounds.

Boric acid, on the other hand, was shown to form a definite compound with dextrose. Boeseken (5) and Boeseken and Couvert (6) found a decided increase in the conductivity upon the addition of dextrose to boric acid solutions. In addition to a marked increase in electrical conductance, Verschuur (64) found, also, a change in the specific rotation of dextrose solutions when boric acid was added. This evidence along with freezing point data led Levy (34) to the conclusion that a compound was formed between one molecule of dextrose and one molecule of sodium borate, (NaBO_2). By blocking the aldehyde group or the hydroxyl on the second carbon atom, thus preventing the complex formation, Levy showed that the sodium borate must involve these two groups in the complex formation. Furthermore, Levy, in his investigations with Doisy (35), revived the theory of compound formation of dextrose with sodium tetraborate, borax, by showing that a normal value for the specific rotation could be

obtained by acidifying the alkaline borax dextrose solution with an acid. Darmon and Peyroux (13) have also shown the existence of a dextrose-sodium tetraborate compound formation in solution. All the studies on boric acid and the alkali borates showed that the rate of mutarotation was increased.

Summarizing the investigations on the acidic and basic catalysis of mutarotation, Lowry (39) proposed an electrolytic theory of catalysis. Accordingly a proton was given up by the mutarotating compound to an acceptor which in turn returned the proton to the isomeric form of the mutarotatory compound. It was shown by this theory that the metallic ion could not act as a catalyst since it could neither accept nor donate protons.

During the discussion of the experimental data of this investigation an attempt will be made to correlate previous data on mutarotatory studies with the time of solution of dextrose.

EXPERIMENTAL

A. Definition of Terms

Before proceeding with an explanation of the method employed during this investigation it will be necessary to distinguish between the terms "rate of solution" and "time of solution". Ordinarily, "rate of solution" is used to express the weight of solute dissolved in a unit weight of solvent during a unit time interval. This expression is not a true measure of the rate at which the solute is dissolved by the solvent since immediately after dissolution has begun the solute is being dissolved by increasing concentrations of its solution and not by the pure solvent. All attempts to correct for this error have resulted in failure because of the experimental difficulties involved. The flowing water method of Sandera, which was discussed in the preceding historical sketch, presents the best method for measuring the true rate of solution of sucrose. However, because of the many difficulties involved and because of its impracticability a measure of the rate of solution is inadequate to accomplish the purpose of this study.

On the other hand, "time of solution" refers either to the time required to completely dissolve a unit weight of solute in a given weight of solvent or to

the time interval during which a unit weight of solute is dissolved by a given weight of solvent. It is obvious that a measure of the solution time has a much greater practical applicability than the solution rate since the preparation of syrups for use in the processing of a product requires complete solution of the sugar. In this investigation the time of solution is taken as the time required for complete solution of a given weight of dextrose in a definite weight of water at constant temperature.

The term solvent refers to pure water or to an aqueous solution of some mutarotatory catalyst, the latter term having been defined in the historical discussion.

B. Apparatus and Method

The apparatus used consisted of a series of ten flasks, each with a stirring unit, arranged in a black lined constant temperature bath controlled by a rheostat sensitive to 0.05° C. The solvent being tested was placed in one of the flasks and allowed to come to the temperature of the bath, after which the desired weight of dextrose was added. Except where otherwise stated 33.0 grams of anhydrous dextrose were added to the volume of solvent containing 50.0 grams of water. Constant stirring was continued until the dextrose sample had completely dissolved. By means of a strong light source directed into

the flask against the black background it was possible to determine within a few minutes the exact time at which the last few crystals of sugar disappeared. A set of preliminary determinations showed that duplicate runs could be checked within two per cent by this method even when the procedure was adapted to trials using one hundred pounds of sugar. This method is more nearly a duplication of the commercial syrup preparation practices than any method reported in the literature.

All solutions were prepared from conductivity water made by the alkaline permanganate distillation of previously distilled water. The dextrose was weighed on a balance sensitive to 0.05 gram, and the solvent used was measured from a calibrated burette using a calculated constant amount of water in the case of aqueous solutions.

C. Agents Affecting Solution Time

1. The effect of rate of stirring and shape of container.

Square glass paddles with a slight twist were used as stirrers and were just small enough to pass the neck of an ordinary 125 c.c. Erlenmeyer flask. Trial runs were made to determine the speed at which to rotate the stirrers so that all the sugar crystals were suspended throughout the time of solution. This stirring rate will,

therefore, be referred to as the "maximum stirring rate". Other stirring speeds will be referred to on the basis of this maximum rate. Table I shows the time of solution in minutes of a 36 per cent dextrose solution at 60° F. in different types of flasks and at different stirring rates.

Table I
Effect of stirring rate and shape of container
on solution time.

| (33.0 gms. dextrose hydrate added to 50.0 gms. water) | | | | | |
|---|-----------------------------|--------------------------|--------------------------|--------------------------|--|
| Container (type of flask) | Solution Time In Minutes | | | | |
| | Maximum Stirring Rate | .8 of Maximum Rate | .6 of Maximum Rate | .4 of Maximum Rate | |
| 125 c.c. Erlenmeyer Flask | 165 | 180 | 360 | >720 | |
| 150 c.c. Soxhlet Extraction Flask | 165 | 165 | 190 | >720 | |

Discussion of Data

From the data presented in Table I it is obvious that as the rate of stirring was decreased below that required to keep the sugar crystals suspended the time of solution increased. The fact that there was a progressive increase in the solution time as the stirring rate was decreased may readily be explained by observing that as the dextrose dissolved at the slower stirring rates the dextrose crystals tended to be more easily suspended by the solution of increasing specific gravity.

Because of the more spherical shape of the Soxhlet extraction flask a more thorough stirring of the solution resulted than in the case of the Erlenmeyer flask, thus the less pronounced increase in solution time with a corresponding decrease in stirring rate. In the trials where the stirring rate was only .8 of the maximum rate the sugar crystals remained suspended in the Soxhlet extraction flask, whereas a small amount settled out in the Erlenmeyer flask during the first one-half of the run.

In all the ensuing determinations of solution time the maximum stirring rate was maintained and Soxhlet extraction flasks were used in order to avoid errors resulting from a settling out of dextrose crystals.

2. The effect of rate of addition of dextrose.

By using the conditions set up in the preceding discussions it was possible to determine whether or not the rate of adding the dextrose to the water had any influence upon the time of solution. Two series of runs were made: one with hydrated dextrose and the other with anhydrous dextrose*. In each series a 36 per cent dextrose solution** was prepared and the sugar was added at three different rates, namely: instantaneously, uniformly during a ten second interval and uniformly during a thirty second interval.

No difference in the time of solution was observed in the hydrated dextrose series. Neither was there a difference in solution time in the anhydrous dextrose series when complete suspension of crystals was obtained. Invariably, however, when the anhydrous dextrose was added instantaneously lumps of dextrose formed due to

*Dextrose may be purchased commercially in many grades, the two of highest purity being: 1. Hydrated Dextrose in which each molecule of dextrose has one molecule of water of crystallization and 2. Anhydrous Cerelese, of about 99.8 per cent purity, supplied only by Corn Products Refining Company. All dextrose sold commercially at the present time is of the alpha-form.

**Where hydrated dextrose was used in this investigation an additional amount of the sugar and a correspondingly less amount of water was used to account for the molecule of water of crystallization.

intercrystal hydration before suspension of the anhydrous crystals could be accomplished. Such lumps were quite impervious to water and dissolved with extreme slowness only from the surface, consequently no attempt was made to correlate results from any run in which lumps were formed. This condition occurred rarely when ten seconds or more were taken for the addition of the sugar.

3. The effect of crystal size on solution time.

The observation in the last discussion of slowly dissolving lumps suggested the probable influence of crystal size on solution time. This influence is clearly illustrated in Table II.

Table II

The effect of crystal size on solution time.

(Weight of sugar used gave a 41.6% dextrose solution.)

| Sugar | Size of Crystal | Original Temp. °F. | Final Temp. °F. | Time of Solution |
|----------|-----------------------|--------------------------|-----------------------|------------------------|
| | 1-20 Mesh | 140 | 100 | 10 Min. |
| Dextrose | 20-40 Mesh | 140 | 99 | 7 Min. |
| Hydrate | 40-60 Mesh | 140 | 99 | 3 Min. |
| | 60+ Mesh | 140 | 99 | 2 Min. |
| | 1-20 Mesh | 140 | 115 | 5 Min. |
| Dextrose | 20-40 Mesh | 140 | 112 | 2 Min. |
| Anhyd. | 40-60 Mesh | 140 | 112 | 1 Min. |
| | 60+ Mesh | 140 | 112 | 1 Min. |

Because of the considerable variation in solution time of the different crystal sizes even at the high temperatures given in Table II it was necessary to determine the average crystal size in a number of different purchases of anhydrous and hydrated dextrose. Results of analyses on four different 100 pound bags of each sugar are given in Table III.

Table III

Average crystal size of commercial dextrose.

| Sugar | 1-20 Mesh | 20-40 Mesh | 40-60 Mesh | 60 + Mesh |
|------------------|--------------|---------------|---------------|--------------|
| Dextrose Hydrate | 0.4-1.2% | 18.2-21.6% | 24.2-27.0% | 50.2-53.6% |
| Dextrose Anhyd. | 0.3-0.5% | 5.1- 6.1% | 51.6-54.4% | 39.2-42.6% |

It will be noticed in Table III that not only was there a lower proportion of large crystals in the anhydrous dextrose, but also a larger proportion of crystals of uniform size than in the dextrose hydrate. Analyses on the two crystalline forms of dextrose showed a high purity for anhydrous dextrose in all cases, whereas the water content in different samples of dextrose hydrate varied considerably. For these reasons anhydrous dextrose was used in testing the effect of added reagents to be reported later in this paper. Another advantage in the

use of anhydrous dextrose was the noticeably less cooling effect on the solution during the initial dissolving period.

4. The effect of temperature and concentration.

It is a well known fact that at higher temperatures all sugars dissolve much more readily than at lower temperatures. Less time is required, also, in the preparation of the more dilute syrups than the more concentrated. Since no quantitative data were available, the following experiments were undertaken to determine values for the time of solution at varying temperatures and concentrations. The relationship between temperature, concentration and time of solution is shown in Table IV. Because of the heat of solution of dextrose there was an initial cooling effect the extent of which depends upon the kind of dextrose crystals, the concentration and the initial temperature. In order to obtain comparable results, preliminary trials were made in each case to determine the proper initial temperature to use so that when the dextrose was added the temperature dropped to that at which the run was to be made. This temperature was then maintained in a constant temperature bath until solution was complete. In each case 50 grams of water were used and the weight of dextrose calculated to give

the proper concentration. The dextrose used was screened to pass a 40 mesh sieve.

A common practice among syrup manufacturers is to replace varying amounts of the sucrose by dextrose. In order to make this study as representative as possible of plant operations, solution times were run on 50, 40 and 25 per cent replacements of 32°, 28° and 24° Baumé syrups. In terms of percentage concentration these solutions are as follows:

| | | | | | | | | | |
|---|---|---|---|-----|---|---|---|-------|---|
| 50% replacement of a 32° Bé syrup gives a 41.6% solution. | | | | | | | | | |
| 40% | " | " | " | " | " | " | " | 36.3% | " |
| 25% | " | " | " | " | " | " | " | 26.3% | " |
| 50% | " | " | " | 28° | " | " | " | 34.3% | " |
| 40% | " | " | " | " | " | " | " | 29.5% | " |
| 25% | " | " | " | " | " | " | " | 20.8% | " |
| 50% | " | " | " | 24° | " | " | " | 28.5% | " |
| 40% | " | " | " | " | " | " | " | 23.6% | " |
| 25% | " | " | " | " | " | " | " | 16.2% | " |

The solution times of these concentrations of the two types of dextrose crystals at varying temperatures are given in Table IV. These data are also summarized in Figures 1 and 2.

Table IV

The effect of temperature and concentration on solution time.

| Sugar | Temp. °F. | Time of Solution in Minutes | | | | | | | | | |
|---------------------|--------------|-----------------------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--|
| | | 41.6% conc. | 36.3% conc. | 34.3% conc. | 29.5% conc. | 28.5% conc. | 26.3% conc. | 23.6% conc. | 20.8% conc. | 16.2% conc. | |
| Dextrose Hydrate | 110 | 2 | 1 | $\frac{3}{4}$ | $\frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | |
| | 100 | 5 | $1\frac{1}{2}$ | $1\frac{1}{4}$ | 1 | < 1 | $\frac{3}{4}$ | $< \frac{3}{4}$ | $\frac{1}{2}$ | $< \frac{1}{2}$ | |
| | 90 | 20 | $4\frac{1}{2}$ | 2 | $1\frac{1}{4}$ | 1 | 1 | < 1 | < 1 | $\frac{3}{4}$ | |
| | 80 | 65 | 23 | 12 | 3 | 2 | 2 | $1\frac{3}{4}$ | 1 | < 1 | |
| | 70 | 150 | 70 | 48 | 15 | $5\frac{1}{2}$ | 4 | $2\frac{1}{2}$ | $1\frac{3}{4}$ | $1\frac{1}{4}$ | |
| | 60 | 330 | 165 | 120 | 47 | 32 | 22 | 7 | 4 | $1\frac{1}{2}$ | |
| Dextrose anhyd. | 110 | 1 | $\frac{3}{4}$ | $\frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | |
| | 100 | 2 | 1 | < 1 | $\frac{3}{4}$ | $< \frac{3}{4}$ | $\frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | |
| | 90 | 10 | $2\frac{1}{2}$ | $1\frac{3}{4}$ | 1 | $\frac{3}{4}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $< \frac{1}{2}$ | $< \frac{1}{2}$ | |
| | 80 | 68 | 12 | 9 | $1\frac{3}{4}$ | 1 | < 1 | $\frac{3}{4}$ | $\frac{3}{4}$ | $\frac{1}{2}$ | |
| | 70 | 160 | 80 | 15 | 4 | $2\frac{3}{4}$ | $1\frac{3}{4}$ | 1 | < 1 | $\frac{3}{4}$ | |
| | 60 | 330 | 165 | 105 | 14 | 5 | 3 | 3 | 2 | 1 | |

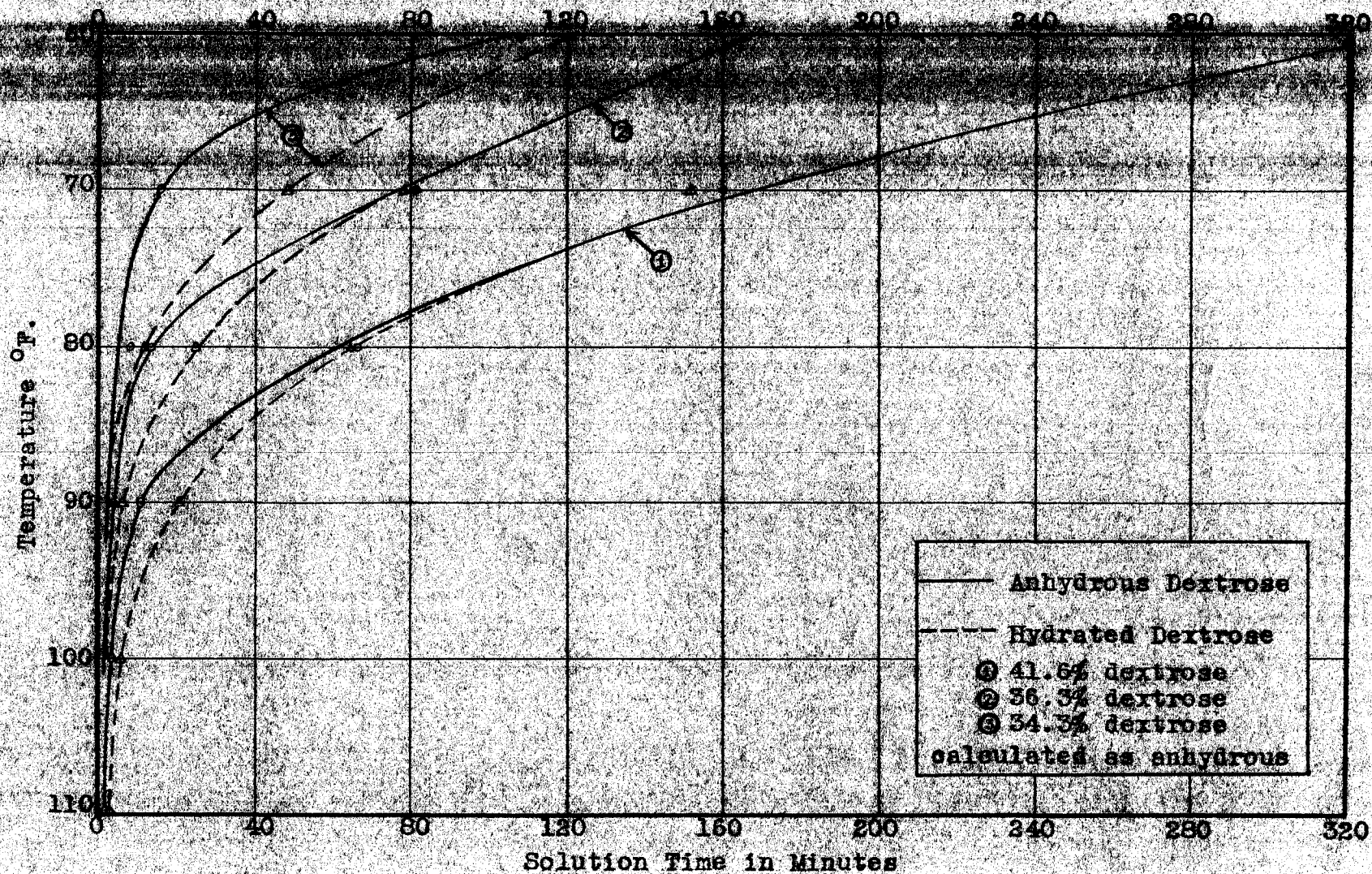


Figure 1. Effect of temperature on solution time of dextrose.

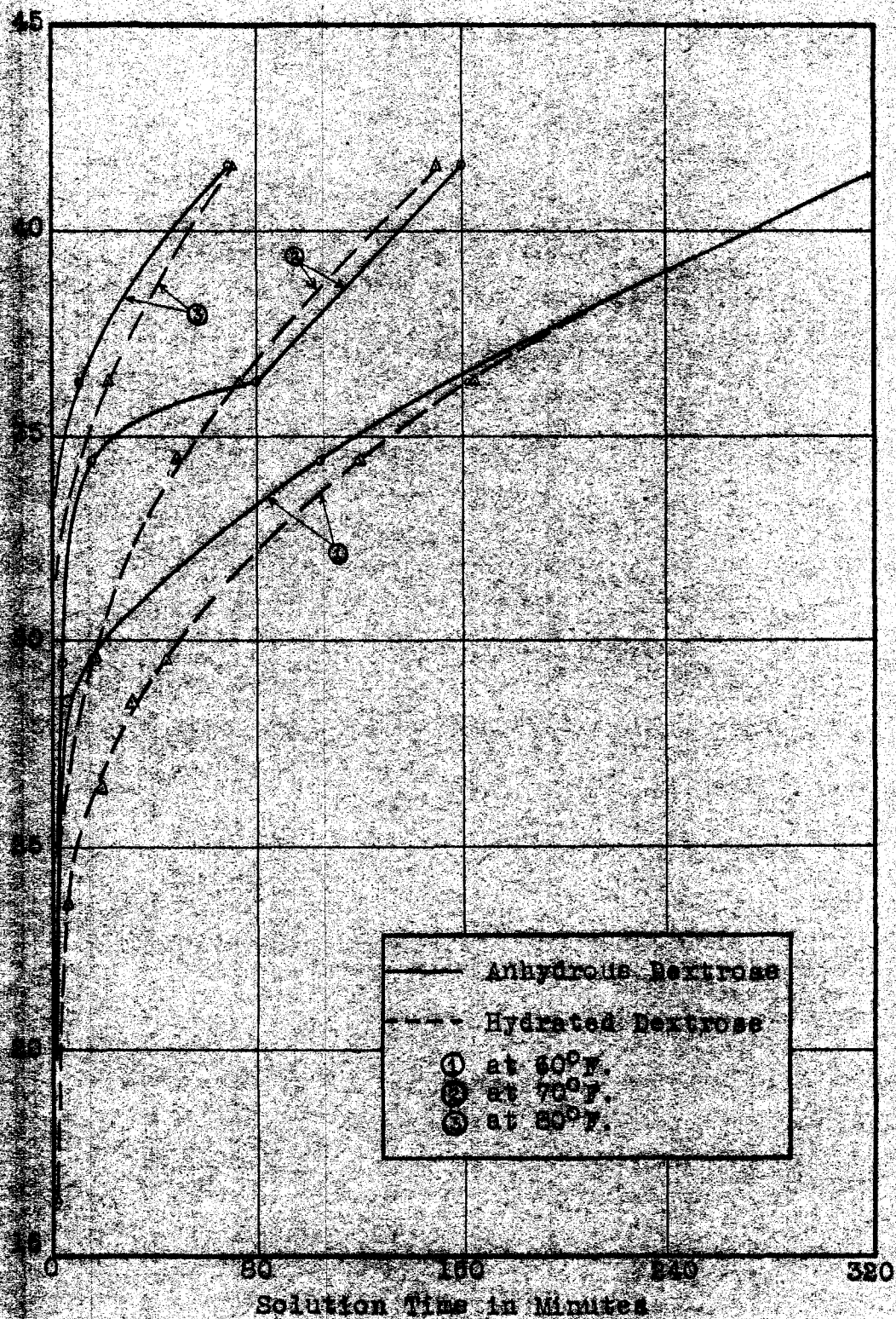


Figure 2. Effect of concentration on solution time of dextrose.

Discussion of Data

At the higher temperatures used here, namely, 110° and 100° F., both dextrose samples dissolved almost instantaneously even in the highest concentration. For that reason correlations will be made on the results at the lower temperatures.

It will be noted from the data in Table IV and Figures 1 and 2 that the time of solution for dextrose hydrate increased regularly with either a decrease in temperature or an increase in concentration. On the other hand, the time of solution for anhydrous dextrose showed a decided increase at definite temperatures and concentrations. For example, in the 41.6 per cent concentrations of anhydrous dextrose, the time of solution at 80° F. was approximately seven times that at 90° F.; in the 36.3 per cent concentrations the time of solution at 70° F. was approximately seven times that at 80° F.; and in the 34.3 per cent concentrations the time of solution at 60° F. was seven times that at 70° F. In terms of ten degree temperature intervals the critical point on the curve for any one concentration may be represented by the expression

$$\Delta F_{10} = 7M$$

in which " ΔF_{10} " denotes a temperature decrease of ten de-

degrees Fahrenheit and "M" represents time of solution in minutes. Ordinarily, however, it will be noticed that a decrease of ten degrees in temperature resulted in an increase in the time of solution of only two to three times that at the higher temperature.

A check of the variation in time of solution with a change in concentration at any one temperature reveals a critical concentration at which the time factor was tremendously increased by a slight increase in the concentration. At this critical concentration in each case an increase of five per cent anhydrous dextrose increased the time of solution by nearly seven times, whereas at other concentrations an increase of five per cent sugar increased the time of solution only two to three times. Denoting the five per cent increase in concentration by ΔC_5 we may represent the critical concentration relationship with solution time as

$$\Delta C_5 = 7M$$

The correlation between time of solution, critical temperature and critical concentration becomes

$$\Delta F_{10} = \Delta C_5 = 7M$$

Furthermore, the relationship between temperature and concentration at the critical point on the curve may be

represented as

$$F/C = k$$

in which "F" denotes temperature on the Fahrenheit scale and "C" the concentration in percentage. The constant "k" is very close to two over the temperature and concentration range used in these experiments, therefore, the expression becomes

$$F/C = 2$$

By means of this equation it is possible to calculate the maximum concentration of anhydrous dextrose that can be dissolved quite readily in water at a given temperature.

Because of the apparent partial recrystallization in all the trials made at the critical temperature and concentration for anhydrous dextrose a more thorough study was made of this phenomenon. Tests were made to determine how much dextrose was dissolved during varying time intervals from a sample which would give a definite concentration if completely dissolved. This was done by starting a series of duplicate runs that would give the desired concentration of dextrose if completely dissolved, filtering the first sample after one-half minute, the second sample after two minutes, the

third sample after five minutes and so on at increasing time intervals until the last sample was completely dissolved. An analysis of each filtrate was then made to determine how much dextrose had dissolved in the given time interval. Both anhydrous and hydrated dextrose were used for each concentration in order to make a comparison between the two types of crystals.

The determination of the concentration of dextrose in each filtrate of the first series was made by the method of Shaffer and Hartman (59) and also by polarization in a saccharimeter. Since the results of the determination checked well within the experimental error at these high concentrations and since the polarization method was both more rapid and less expensive it was used in all subsequent analyses.

Tabulation of the results obtained at 60° F. and 77° F. will be found in Tables V and VI, respectively. Figure 3 presents a comparison of concentrations in the "45" series at 60° F. illustrating the general phenomenon at the higher concentrations and lower temperatures.

Table V

Progressive concentrations of dextrose at 60° F.

| Time : in : Min. : | Anhydrous Dextrose (% dissolved) | | | | | : | Dextrose Hydrate (% dissolved) | | | | |
|--------------------------|----------------------------------|------|------|------|------|---|--------------------------------|------|------|------|------|
| | 45* | 40* | 36* | 33* | 30* | : | 45* | 40* | 36* | 33* | 30* |
| $\frac{1}{2}$ | 40.2 | 38.4 | 35.8 | 32.9 | 30.1 | : | 25.0 | 24.4 | 23.7 | 23.9 | 22.9 |
| 2 | 36.7 | 36.8 | 35.8 | 32.2 | | : | 25.2 | 25.0 | 24.3 | 24.0 | 23.8 |
| 5 | 31.6 | 31.1 | 34.4 | 32.6 | | : | 25.8 | 26.1 | 26.4 | 26.2 | 26.0 |
| 10 | 29.5 | 29.6 | 31.5 | 32.7 | | : | 26.2 | 26.6 | 26.6 | 27.1 | 27.9 |
| 20 | 29.6 | 29.4 | 30.5 | 32.6 | | : | 27.8 | 28.2 | 28.0 | 27.8 | 30.1 |
| 60 | 30.6 | 31.9 | 31.2 | 32.9 | | : | 30.5 | 31.1 | 30.9 | 29.9 | |
| 90 | 34.1 | | 32.4 | | | : | 32.2 | | | | |
| 120 | 35.1 | 35.0 | 34.0 | | | : | 33.8 | 34.2 | 33.9 | | |
| 180 | 37.1 | 37.0 | | | | : | 36.3 | | | | |
| 300 | 39.5 | 39.0 | | | | : | 40.0 | 39.0 | | | |
| 480 | 41.7 | | | | | : | 42.2 | | | | |
| 960 | 43.6 | | | | | : | 43.8 | | | | |

* These figures represent the possible percentage concentration if the total amount of sugar were dissolved. (All percentages are calculated on the anhydrous basis).

Table VI

Progressive concentrations of dextrose at 74° F.

| Time in Min. | Anhydrous Dextrose (% dissolved) | | | Dextrose Hydrate (% dissolved) | | |
|--------------------|-------------------------------------|------|------|-----------------------------------|------|------|
| | 45* | 40* | 36* | 45* | 40* | 36* |
| $\frac{1}{2}$ | 43.4 | 39.6 | 36.0 | 28.4 | 27.7 | 27.5 |
| 2 | 39.7 | 39.3 | 36.1 | 28.6 | 28.3 | 27.8 |
| 10 | 38.6 | 38.8 | 36.0 | 34.2 | 33.7 | 33.3 |
| 20 | 37.1 | 37.3 | 36.1 | 35.4 | 35.7 | 35.3 |
| 60 | 43.5 | | | 41.8 | | |

* These figures represent the possible percentage concentration if the total amount of sugar were dissolved. (All percentages are calculated on the anhydrous basis).

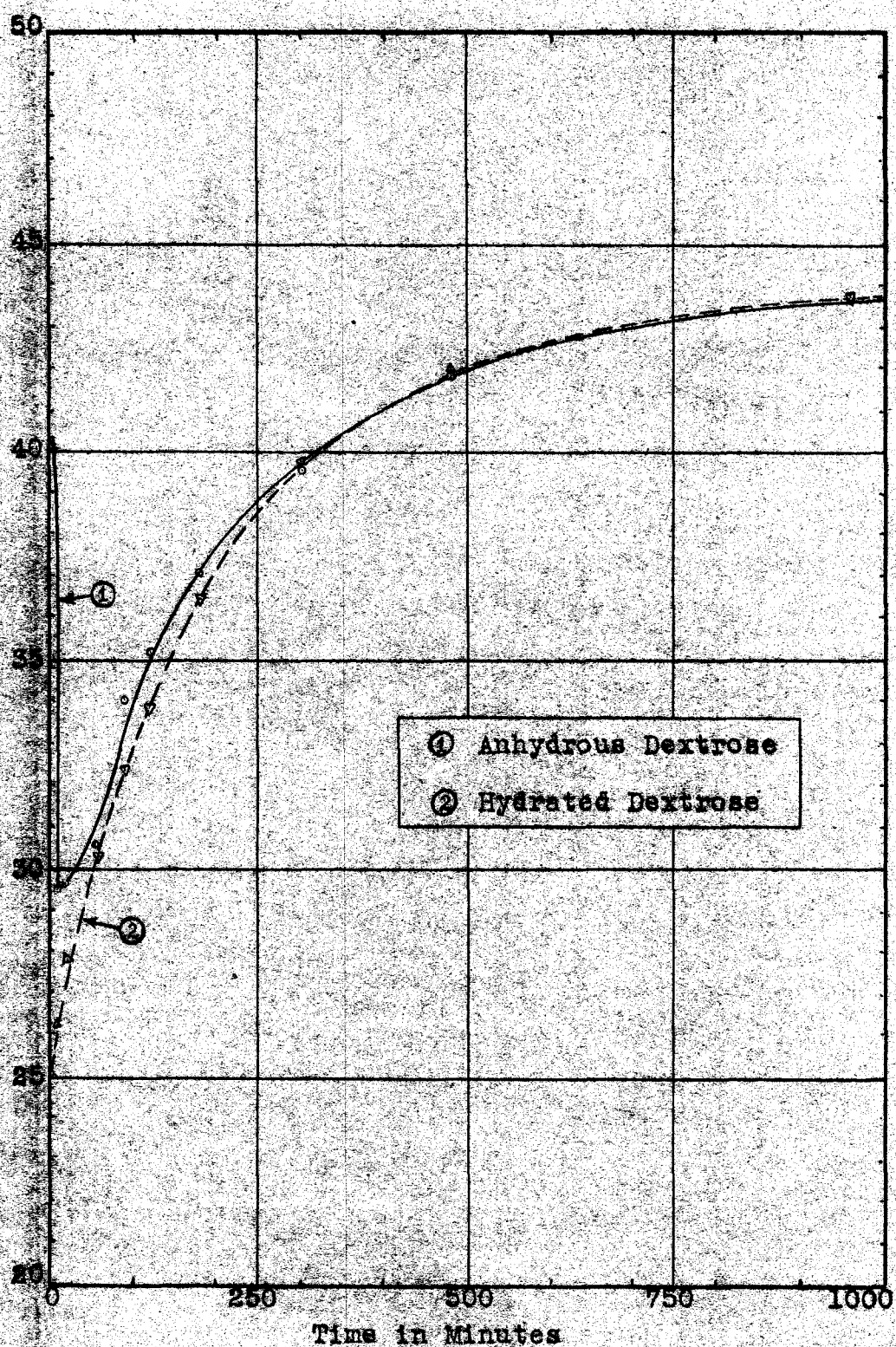


Figure 3. Progressive concentrations of dextrose dissolved at 60°F.

It is evident from the data in Table V that the time of solution for anhydrous dextrose was dependent upon the concentration. For example, dissolution was practically instantaneous in concentrations below 33 per cent. Furthermore, the initial concentration (that after one-half minute of stirring) for either the anhydrous or hydrated dextrose was dependent upon the amount of the solid sugar added, although after twenty minutes of stirring the concentrations of dissolved dextrose were practically the same for both anhydrous and hydrated dextrose regardless of the amount of solid sugar originally added. These data show clearly the difficulty involved in a calculation of the "rate of solution", according to the equation derived by Hudson (25) and discussed in the historical sketch of this paper. In his equation " S_0 " would be different not only for every temperature, but also for every concentration; whereas " S_H " or " S_A " would remain a constant after the initial twenty minute period. Direct substitution into the equation given would result in a variation of the constant " k " with concentration.

An examination of the curves plotted in Figure 3 shows that the initial concentration for hydrated dextrose was very close to that calculated by Jackson and Silsbee (31) from the equilibrium mixture of the alpha-

and beta-forms. On the other hand, the initial concentration for anhydrous dextrose was nearly twice as great, but there was a marked decrease in the amount of dissolved sugar after the first ten minutes. Analysis of this crystallized mass showed that it was practically all hydrated dextrose. Therefore, the anhydrous form of the sugar rapidly converted to the hydrated form in solution until an equilibrium was set up between the two forms.

Extrapolation of the curve representing concentrations of anhydrous dextrose after ten minutes back to the initial time would give a concentration of about 29.4 per cent. Since the initial concentration of hydrated dextrose was approximately 25.0 per cent, the increased concentration to the extrapolated curve must represent the amount of anhydrous dextrose in the anhydrous-hydrate equilibrium mixture at the extrapolated initial concentration. Hence,

$$29.4 - 25.0 = 4.4 ,$$

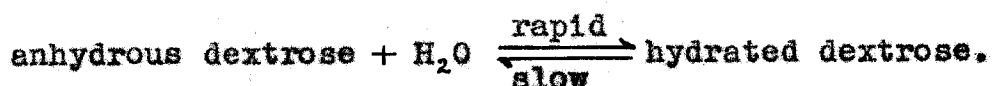
which was the percentage of the anhydrous form present. This anhydrous-hydrate equilibrium mixture must contain then

$$\frac{4.4}{29.4} \times 100 = 15\% \text{ anhydrous dextrose}$$

and $\frac{25.0}{29.4} \times 100 = 85\% \text{ hydrated dextrose.}$

Although previous investigators have pointed out that the conversion of hydrated to anhydrous dextrose is a reversible reaction, the individual rates of which are identical under the same conditions, the evidence presented in the curves of Figure 3 contradict this view. Because of the rapid crystallization of hydrated dextrose from the original anhydrous dextrose solution the conversion of anhydrous to hydrated dextrose must be very rapid. This conversion and crystallization takes place until the equilibrium mixture results and then dissolution of the solid sugar again begins. The subsequent lag period occurs as a result of the remaining anhydrous dextrose being dissolved and converted to the hydrate, thus retarding immediate dissolution of the crystallized hydrated dextrose.

If the conversion of hydrated dextrose to the anhydrous took place as rapidly as the reverse reaction, the initially dissolved hydrated dextrose would immediately partially convert to the anhydrous, thus permitting a much more rapid solution of the hydrate form. This reversible change may be indicated as follows:



The fact that the two curves in Figure 3 coincide after the first sixty minutes is further evidence that the same form of dextrose was being dissolved in each case.

With these facts as supporting evidence, the following assumptions may be made:

1. The molecular structure of dextrose during dissolution is unaltered until after the molecule becomes a part of the liquid phase, thereafter, at any instant, the molecule may be changed depending upon the prevailing conditions.
2. Any factor which tends to alter the structure of the dextrose, immediately after solution, into a more soluble form or condition will decrease the time factor in dissolving dextrose.

Data given in Table VI show the effect of heat upon the hydrate crystallization phenomenon. Instead of a minimum of 29.4 per cent, as was true at 60° F., the lowest percentage sugar at 77° F. was 37.1, showing that dehydration was more rapid at the higher temperature, thus resulting in a more rapid solution time.

D. Reagents Affecting Solution Time

In accord with the assumptions set forth in the preceding discussion, a study was made of the effect on solution time of various added reagents which have been shown by previous investigators to react with dextrose or to have some apparent action upon dextrose solutions. Since the influence of acids, acid salts and neutral salts has been reported from previous investigations in this laboratory (33), this thesis will deal chiefly with substances that give a basic reaction when dissolved in water with special reference to the pH values of the resulting solutions. All pH measurements were made by means of a Coleman electrometer having a glass electrode. In the tables to follow the column headed "pH - Before" refers to the pH of the solvent while that headed "pH - After" gives the pH values after dissolving the dextrose.

A temperature of 60° F. was chosen for all determinations in order to reproduce as nearly as possible the average temperature of tap water used in commercial practices. At this temperature, then, concentrations of above thirty per cent anhydrous dextrose would be necessary in order to require a length of time useful for comparisons. Because of the common practice of replacing forty per cent of the sucrose in a 32° Baume syrup by dextrose this con-

centration was used. As was shown previously, this would give a 36.3 per cent solution. By cooling the solution to 60° F. before the dextrose was added and stirring at this temperature until solution was complete the temperature factor was held constant. It was necessary to determine the specific gravity and concentration of each reagent solution in order to calculate the volume required to give a constant amount of water for each trial.

1. The effect of alkaline hydroxides.

It has been shown definitely, as was pointed out in the historical sketch, that sodium and potassium hydroxides react with dextrose. A study of the effect of varying concentrations of these and other alkaline hydroxides was, therefore, made. These results are summarized in Table VII and Figure 4.

Table VII

Effect of alkaline hydroxides on dextrose solution time

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | | |
|--|--------------------------------|--------|-------|--|
| | | Before | After | |
| LiOH solutions | | | | |
| 0.1 | 2 | 12.38 | 9.85 | |
| 0.05 | 3 | 12.23 | 9.58 | |
| 0.025 | 6 | 11.96 | 9.27 | |
| 0.010 | 20 | 11.62 | 8.87 | |
| 0.005 | 35 | 11.28 | 8.48 | |
| NaOH solutions | | | | |
| 0.5 | 2 | >12.00 | 10.23 | |
| 0.1 | 7 | >12.00 | 9.59 | |
| 0.05 | 10 | 11.95 | 9.25 | |
| 0.01 | 35 | 11.28 | 8.50 | |
| 0.005 | 75 | 10.82 | 7.96 | |
| KOH solutions | | | | |
| 0.5 | 2 | 12.67 | 10.10 | |
| 0.1 | 8 | 12.14 | 9.40 | |
| 0.05 | 12 | 11.88 | 9.11 | |
| 0.01 | 45 | 11.04 | 8.24 | |
| 0.005 | 90 | 10.60 | 7.75 | |
| Blank | 168 | 6.90 | 5.93 | |

Table VII (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | | |
|--|--------------------------------|--------|-------|--|
| | | Before | After | |
| Ca(OH) ₂ solutions | | | | |
| 0.1 | 1 | 12.28 | 9.60 | |
| 0.05 | 2 | 12.12 | 9.02 | |
| 0.01 | 30 | 11.41 | 8.58 | |
| 0.005 | 58 | 10.98 | 8.11 | |
| 0.001 | 145 | 10.01 | 7.48 | |
| Sr(OH) ₂ solutions | | | | |
| 0.3 | 1 | 12.00 | 9.30 | |
| 0.1 | 8 | 11.63 | 8.89 | |
| 0.05 | 70 | 11.18 | 8.42 | |
| 0.01 | 135 | 10.20 | 7.44 | |
| 0.005 | 165 | 9.62 | 7.02 | |
| Ba(OH) ₂ solutions | | | | |
| 1.0 | 1 | 12.68 | 10.02 | |
| 0.5 | 3 | 12.36 | 9.68 | |
| 0.1 | 15 | 11.82 | 9.01 | |
| 0.05 | 35 | 11.56 | 8.80 | |
| 0.01 | 140 | 10.82 | 7.94 | |

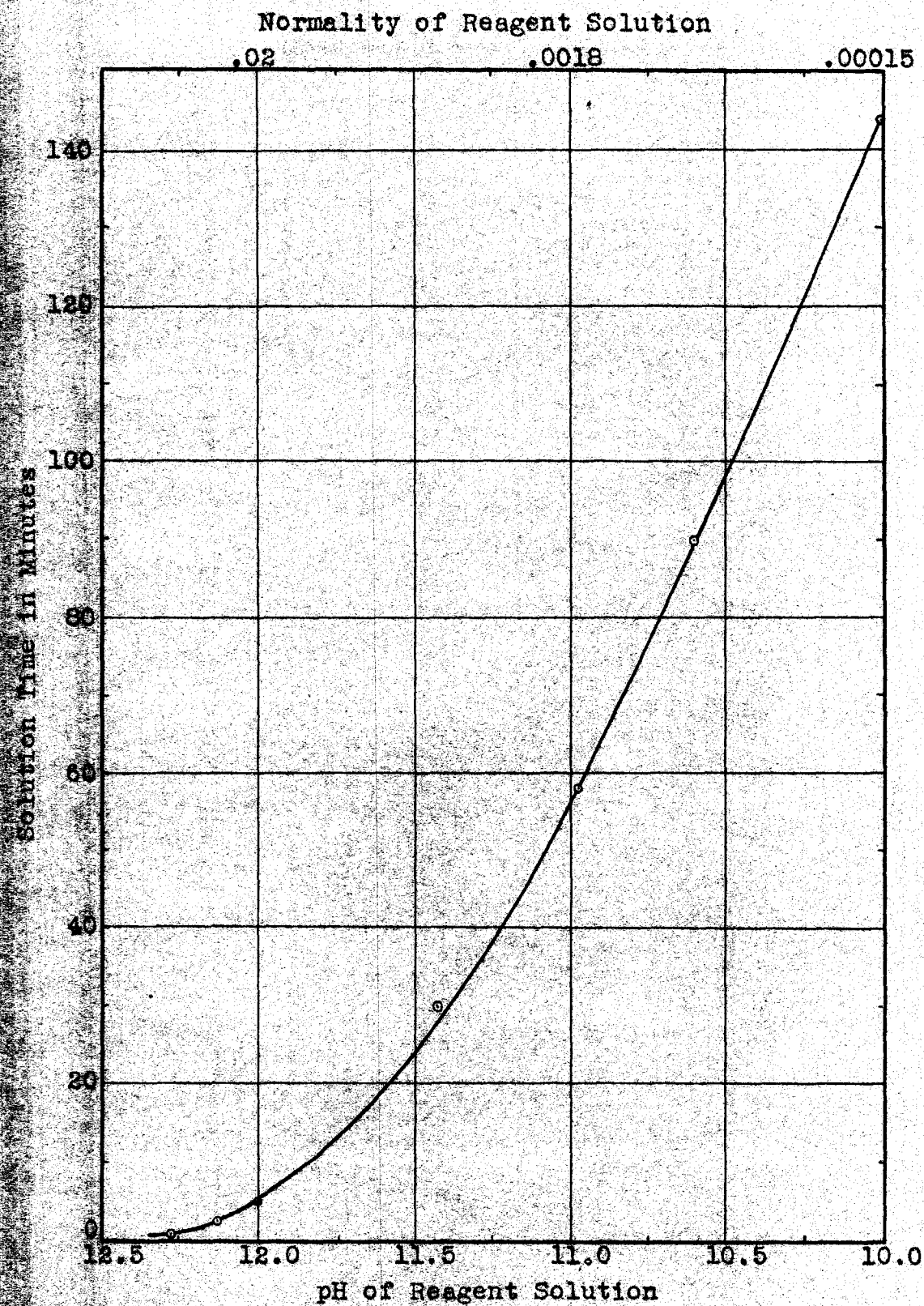


Figure 4. Effect of pH in alkaline hydroxide reagents on dextrose solution time at 60°F.

Discussion of Data

Examination of the data in Table VII shows the decided influence of the alkaline hydroxides upon the time factor in dissolving dextrose. Even the very dilute alkaline solutions decrease to a large extent the time factor.

Since it is assumed that in the more dilute alkaline solutions ionization is practically complete, a comparison of the effect of the metallic ions of these hydroxides may be made. The time of solution at corresponding hydroxyl ion concentrations, either calculated or measured, is practically a constant. For example, in a 0.0025 N hydroxide solution as calculated from the data in Table VII the time of solution is in the neighborhood of thirty-five minutes for each base. This concentration of base corresponds to an observed pH of about 11.3 as compared with a calculated pH of 11.4 from the relationship

$$\text{pH} = \log \frac{1}{[\text{H}]} \quad .$$

Representative values of pH in the alkaline hydroxide solutions plotted against solution time as shown in Figure 4 give a relatively smooth curve over this highly alkaline range.

Since these facts show that the time of solution depends upon hydroxyl ion concentration, regardless of the base used, the metallic ion of the alkaline hydroxide has little influence upon the time factor. Consequently, lower concentrations of calcium hydroxide than of sodium hydroxide produce the same acceleration in solution time.

The acidic nature of dextrose in solution is clearly revealed in the decided decrease in pH of these alkaline solutions. This evidence, therefore, points to the possible neutralization effect of the alkaline hydroxides in acting as positive catalysts in dissolving dextrose.

2. The effect of basic salts.

Because of the many salts that hydrolyze to give basic solutions a study of the effects of various ions of these salts on the solution time of dextrose was made. In Table VIII are listed data showing the effect of a number of basic salts in representative concentrations.

Table VIII

Effect of basic salts on dextrose solution time

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | | |
|--|--------------------------------|--------|-------|--|
| | | Before | After | |
| Li ₂ CO ₃ solutions | | | | |
| 0.5 | 1½ | 11.20 | 9.66 | |
| 0.05 | 10 | 10.91 | 9.11 | |
| 0.005 | 90 | 10.00 | 8.00 | |
| Na ₂ CO ₃ solutions | | | | |
| 0.5 | 2 | 11.11 | 9.59 | |
| 0.05 | 18 | 10.80 | 8.86 | |
| 0.005 | 100 | 10.09 | 7.74 | |
| K ₂ CO ₃ solutions | | | | |
| 0.5 | 2 | 11.01 | 9.60 | |
| 0.05 | 23 | 10.67 | 8.70 | |
| 0.005 | 120 | 9.81 | 7.30 | |
| NaHCO ₃ solutions | | | | |
| 5.0 | 5 | 9.20 | 8.61 | |
| 0.1 | 30 | 9.58 | 8.40 | |
| 0.01 | 130 | 9.30 | 7.40 | |
| KHCO ₃ solutions | | | | |
| 5.0 | 15 | 8.39 | 8.21 | |
| 0.1 | 60 | 8.71 | 7.82 | |
| 0.01 | 140 | 8.25 | 7.30 | |

Table VIII (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | | |
|---|--------------------------------|--------|-------|--|
| | | Before | After | |
| Na ₃ PO ₄ solutions | | | | |
| 0.5 | 2 | 11.72 | 9.63 | |
| 0.05 | 35 | 10.87 | 7.90 | |
| 0.005 | 140 | 8.10 | 6.94 | |
| Na ₂ B ₄ O ₇ solutions | | | | |
| 5.0 | 50 | 9.38 | 5.68 | |
| 0.5 | 120 | 9.19 | 5.49 | |
| 0.05 | 140 | 9.24 | 5.50 | |
| NaBO ₂ solutions | | | | |
| 2.0 | 3 | 10.11 | 6.98 | |
| 0.5 | 115 | 10.20 | 6.88 | |
| 0.05 | 150 | 10.12 | 6.40 | |
| Na ₂ S solutions | | | | |
| 0.1 | 1 | 11.78 | 9.30 | |
| 0.01 | 30 | 11.00 | 8.51 | |
| 0.005 | 55 | 10.77 | 7.57 | |
| K ₂ S solutions | | | | |
| 0.1 | 3 | 10.26 | 7.60 | |
| 0.01 | 100 | 8.50 | 7.56 | |
| 0.005 | 150 | 7.90 | 7.60 | |

Table VIII (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | | |
|---|--------------------------------|--------|-------|--|
| | | Before | After | |
| (NH ₄) ₂ CO ₃ solutions | | | | |
| 1.0 | 5 | 8.63 | 8.33 | |
| 0.1 | 25 | 8.62 | 8.24 | |
| 0.01 | 70 | 8.55 | 7.79 | |
| Na ₂ SnO ₃ solutions | | | | |
| 5.0 | 5 | 11.32 | 9.11 | |
| 1.0 | 10 | 11.19 | 8.58 | |
| 0.1 | 75 | 10.70 | 8.30 | |
| KCNS solutions | | | | |
| 5.0 | 140 | 7.12 | 6.80 | |
| 0.5 | 170 | 6.98 | 5.60 | |
| Mg Acetate solutions | | | | |
| 5.0 | 60 | 7.18 | 6.99 | |
| 0.5 | 135 | 7.15 | 6.94 | |
| Zn Acetate solutions | | | | |
| 5.0 | 50 | 6.48 | 6.14 | |
| 0.5 | 125 | 6.61 | 6.23 | |
| Cd Acetate solutions | | | | |
| 5.0 | 70 | 7.28 | 6.58 | |
| 0.5 | 140 | 7.00 | 6.48 | |

Table VIII (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | | |
|--|--------------------------------|--------|-------|--|
| | | Before | After | |
| Ca Acetate solutions | | | | |
| 5.0 | 45 | 7.87 | 7.42 | |
| 0.5 | 135 | 7.78 | 7.09 | |
| Sr Acetate solutions | | | | |
| 5.0 | 70 | 7.73 | 7.30 | |
| 0.5 | 140 | 7.40 | 6.96 | |
| Ba Acetate solutions | | | | |
| 5.0 | 55 | 8.00 | 7.37 | |
| 0.5 | 145 | 7.14 | 6.91 | |
| Cu Acetate solutions | | | | |
| 5.0 | 45 | 5.34 | 4.67 | |
| 0.5 | 60 | 5.89 | 5.33 | |
| Al Acetate solutions | | | | |
| 0.25 | 165 | 4.69 | 4.58 | |
| AlOH Acetate solutions | | | | |
| Sat. | 165 | 5.00 | 4.88 | |
| Pb Acetate solutions | | | | |
| 5.0 | 50 | 6.10 | 5.48 | |
| 0.5 | 125 | 6.10 | 5.56 | |

Discussion of Data

Inspection of the results assembled in Table VIII shows that the solution time of dextrose is not a direct function of pH in basic salt solutions, but depends upon the kind of salt present and its concentration. As the salts become more and more basic in reaction, however, the solution time of dextrose parallels more nearly that in the alkaline hydroxide solutions discussed previously, and thus becomes more nearly a function of pH. This is particularly true in the carbonate and phosphate solutions which all hydrolyze to give highly basic solutions.

A striking anomaly to this condition occurs in the case of borate solutions which give relatively high pH values yet are less effective than other solutions of lower pH in shortening the solution time of dextrose. This condition might best be explained by the reaction between dextrose and the borates. It will be noted that the pH after solution of the dextrose is approximately 3.5 points lower than before addition of the dextrose, whereas this difference is 1.5 to 2.0 points in other reagents of a corresponding initial pH. Furthermore, the final pH values are nearly constant for varying concentrations of the same borate solution. These facts indi-

oate that the borate molecules responsible through hydrolysis for the high alkalinity are combined with dextrose almost completely as soon as the dextrose begins to dissolve and are, therefore, ineffective as a solution aid.

A further check of the data shows that the metallic ions of the acetates have little effect upon dextrose solution time. This fact helps to support the assumption made in discussing the alkaline hydroxide series that the metallic ion itself is not an accelerator to solution time of dextrose.

In general, salts aid in dissolving dextrose although in some cases the action may be only slight as was true of potassium thiocyanate and basic aluminum acetate.

3. The effect of silicates.

The sodium silicates present a wide variability of sodium oxide-silicon oxide ratios and, thus are a good source of alkaline solutions for studying solution time acceleration of dextrose. A series of the representative soluble sodium silicates was obtained from the Philadelphia Quartz Company with their assay as follows:

| Grade | $\text{Na}_2\text{O}:\text{SiO}_2$ Ratio | % Na_2O | % SiO_2 | % H_2O |
|---------------------|---|-------------------------|------------------|------------------------|
| "Metso 99" | 1:0.646 | 36.89 | 23.83 | 39.27 |
| "Metso Crystals" | 1:0.968 | 29.23 | 28.33 | 42.43 |
| "BW" | 1:1.58 | 19.4 | 30.6 | 49.7 |
| "C" | 1:2.00 | 18.0 | 36.0 | 45.0 |
| "U" | 1:2.44 | 13.8 | 33.7 | 52.2 |
| "K" | 1:2.84 | 11.0 | 31.2 | 57.5 |
| "N" | 1:3.22 | 8.85 | 28.5 | 62.2 |
| "S" | 1:3.86 | 6.4 | 24.7 | 68.6 |

In this series the first two were solid compounds to which the formulas $3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$ and $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$, respectively, have been assigned. The other members of the series were heavy solutions of the soluble mixtures. In order to have a basis for comparison of the oxide ratios the concentrations used were calculated on the moisture free basis.

Table IX

Effect of silicates on dextrose solution time

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | |
|--|--------------------------------|--------|-------|
| | | Before | After |
| "Metso 99" solutions | | | |
| 0.25 | 3 | 12.02 | 9.58 |
| 0.05 | 8 | 11.68 | 8.79 |
| 0.01 | 35 | 10.67 | 8.08 |
| 0.005 | 100 | 10.00 | 8.00 |
| "Metso Crystals" solutions | | | |
| 0.25 | 3 | 11.94 | 9.77 |
| 0.05 | 8 | 11.48 | 9.10 |
| 0.01 | 40 | 10.40 | 8.28 |
| 0.005 | 105 | 9.95 | 7.99 |
| Grade "BW" solutions | | | |
| 0.25 | 3 | 11.51 | 9.68 |
| 0.05 | 15 | 11.00 | 8.93 |
| 0.01 | 47 | 10.38 | 8.12 |
| 0.005 | 110 | 9.84 | 7.80 |
| Grade "C" solutions | | | |
| 0.25 | 3 | 11.09 | 9.59 |
| 0.05 | 17 | 10.68 | 8.87 |
| 0.01 | 50 | 10.28 | 8.13 |
| 0.005 | 110 | 9.68 | 7.60 |

Table IX (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | |
|--|--------------------------------|--------|-------|
| | | Before | After |
| Grade "U" solutions | | | |
| 0.25 | 3 | 10.68 | 9.51 |
| 0.05 | 17 | 10.33 | 8.78 |
| 0.01 | 60 | 10.01 | 8.06 |
| 0.005 | 115 | 9.72 | 7.61 |
| Grade "K" solutions | | | |
| 0.25 | 3 | 10.51 | 9.46 |
| 0.05 | 20 | 10.13 | 8.67 |
| 0.01 | 65 | 9.75 | 7.76 |
| 0.005 | 120 | 9.18 | 7.16 |
| Grade "N" solutions | | | |
| 0.25 | 3 | 10.54 | 9.38 |
| 0.05 | 20 | 9.91 | 8.63 |
| 0.01 | 135 | 9.20 | 7.55 |
| 0.005 | 150 | 8.60 | 7.30 |
| Grade "S" solutions | | | |
| 0.25 | 5 | 10.32 | 9.18 |
| 0.05 | 40 | 9.76 | 8.40 |
| 0.01 | 145 | 8.38 | 7.22 |
| 0.005 | 160 | 8.20 | 7.05 |

Discussion of Data

Although the solution time of dextrose is about the same for the higher concentrations of the silicates, as shown in Table IX, there is a noticeable decrease in the accelerating effect in the dilute solutions as the sodium oxide-silicon oxide ratio decreases. Using the concentration of 0.01 grams of reagent per 100 c.c. of water as an example, it was found that the time for dissolving dextrose increases from 35 minutes to 145 minutes as the sodium oxide-silicon oxide ratio decreases from 1:0.646 to 1:3.86. In other words, as the oxide ratio becomes smaller, either by an increase in the percentage of silicon oxide or a decrease in the percentage of sodium oxide, there results a corresponding increase in the time of solution of dextrose. A check of the pH values of this series of solutions indicates that the probable cause of the catalytic effect was the high alkalinity of the silicate solutions. The high sodium oxide content of the higher oxide ratios hydrolyzed to give the more caustic solutions, thus exhibiting the more pronounced acceleration upon the solution time of dextrose.

4. The effect of ammonium hydroxide and
ammonium hydroxide derivatives.

Ammonium hydroxide is considered a weak base, however, because of the nature of the compound, this base is often quite effective in isomeric shifts of organic compounds. This is particularly true in accelerating the transformation of one form of a mutarotatory sugar to the other. A study was made of the methyl and ethyl substitution products of ammonium hydroxide in order to determine what effect this molecular change had upon the solution time of dextrose. The results of this series of runs are summarized in Table X.

Table X

Effect of ammonium hydroxide and its
derivatives on solution time of dextrose

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | |
|--|--------------------------------|--------|-------|
| | | Before | After |
| NH ₄ OH solutions | | | |
| 0.1 | 1 | 10.80 | 9.34 |
| 0.05 | 3 | 10.66 | 9.14 |
| 0.01 | 25 | 10.09 | 8.61 |
| 0.005 | 35 | 10.00 | 8.38 |
| 0.001 | 80 | 9.59 | 8.01 |
| NH ₃ (CH ₃)OH solutions | | | |
| 0.1 | 2 | 11.52 | 9.50 |
| 0.025 | 12 | 11.19 | 9.03 |
| 0.005 | 50 | 10.40 | 8.38 |
| NH ₂ (CH ₃) ₂ OH solutions | | | |
| 0.1 | 3 | 11.39 | 9.35 |
| 0.025 | 35 | 10.90 | 8.74 |
| 0.005 | 80 | 10.00 | 7.80 |
| NH(CH ₃) ₃ OH solutions | | | |
| 0.1 | 3 | 10.98 | 9.11 |
| 0.025 | 40 | 10.63 | 8.76 |
| 0.005 | 155 | 8.44 | 7.28 |
| Blank | 170 | 6.80 | 5.90 |

Table X (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | | |
|--|--------------------------------|--------|-------|--|
| | | Before | After | |
| N(CH ₃) ₄ OH solutions | | | | |
| 0.1 | 3 | 11.88 | 9.22 | |
| 0.025 | 30 | 11.26 | 8.70 | |
| 0.005 | 140 | 9.90 | 7.74 | |
| NH ₃ (C ₂ H ₅)OH solutions | | | | |
| 0.1 | 3 | 11.21 | 9.22 | |
| 0.025 | 25 | 10.57 | 8.74 | |
| 0.005 | 165 | 8.63 | 7.34 | |
| NH ₂ (C ₂ H ₅) ₂ OH solutions | | | | |
| 0.1 | 3 | 11.38 | 9.37 | |
| 0.025 | 25 | 10.97 | 8.68 | |
| 0.005 | 165 | 9.76 | 7.65 | |
| NH(C ₂ H ₅) ₃ OH solutions | | | | |
| 0.1 | 3 | 11.20 | 9.13 | |
| 0.025 | 55 | 10.43 | 8.22 | |
| 0.005 | 165 | 8.42 | 7.20 | |
| N(C ₂ H ₅) ₄ OH solutions | | | | |
| 0.1 | 3 | 11.58 | 9.18 | |
| 0.025 | 35 | 10.70 | 8.33 | |
| 0.005 | 150 | 9.86 | 7.99 | |

Discussion of Data

The data presented in Table X show some interesting facts concerning the action of strongly basic solutions upon the time of solution of dextrose.

Ammonium hydroxide is a very effective catalyst for dissolving dextrose. On the basis of concentration and especially for comparable pH values it is much more effective than any of the strong alkaline hydroxides listed in Table VII.

An increase in the weight of the ammonium radical by introduction of methyl radicals tends to increase the basicity of the solution, however, the solution time of dextrose is increased to a considerable extent in these solutions. Introduction of ethyl radicals likewise produces a more basic solution than ammonium hydroxide with an even greater increase in the solution time of dextrose.

Solutions of the tetra-methyl and tetra-ethyl substituted products are considerably more basic than the other solutions, yet little effect was noticed in the solution time of dextrose.

5. The effect of alkaline salts of homologous organic acids and of basic organic compounds.

Because of the apparent effect of organic radicals on the solution time of dextrose, a study was made of the sodium and potassium salts of a number of organic acids in a homologous series. Table XI includes the effect of a few basic organic compounds.

Table XI

Effect of organic basic substances on dextrose solution time

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | |
|--|--------------------------------|--------|-------|
| | | Before | After |
| 5 Na Formate | 50 | 7.90 | 7.28 |
| 1 " " | 120 | 7.23 | 7.05 |
| 5 K " | 55 | 7.60 | 7.00 |
| 1 " " | 130 | 7.12 | 6.94 |
| 5 Na Acetate | 55 | 8.13 | 7.59 |
| 1 " " | 135 | 7.73 | 7.25 |
| 5 K " | 60 | 8.35 | 7.80 |
| 1 " " | 135 | 7.89 | 7.37 |
| 5 Na Propionate | 60 | 8.12 | 7.62 |
| 1 " " | 125 | 7.68 | 7.21 |
| 5 K " | 60 | 8.22 | 7.78 |
| 1 " " | 120 | 7.75 | 7.23 |
| 5 Na Butyrate | 65 | 8.11 | 7.57 |
| 1 " " | 105 | 7.95 | 7.11 |
| 5 K " | 60 | 8.10 | 7.58 |
| 1 " " | 110 | 7.96 | 7.08 |
| 5 Na iso-butyrate | 70 | 8.22 | 7.61 |
| 1 " " " | 110 | 8.08 | 7.10 |
| 5 K " " | 70 | 8.12 | 7.57 |
| 1 " " " | 115 | 7.90 | 7.12 |

Table XI (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | |
|--|--------------------------------|--------|-------|
| | | Before | After |
| 5 Na Valerate | 60 | 8.10 | 7.54 |
| 1 " " | 120 | 7.96 | 7.16 |
| 5 K " | 62 | 8.10 | 7.58 |
| 1 " " | 125 | 7.90 | 7.20 |
| 5 Na iso-valerate | 60 | 8.30 | 7.58 |
| 1 " " " | 105 | 8.07 | 7.11 |
| 5 K " " | 65 | 8.27 | 7.62 |
| 1 " " " | 110 | 7.94 | 7.20 |
| 5 Na Caprylate | 65 | 8.40 | 7.90 |
| 1 " " | 110 | 7.90 | 7.00 |
| 5 K " | 65 | 8.43 | 7.88 |
| 1 " " | 100 | 8.04 | 7.28 |
| 5 Na Caproate | 70 | 8.30 | 7.70 |
| 1 " " | 115 | 7.88 | 7.28 |
| 5 K " | 70 | 8.18 | 7.67 |
| 1 " " | 110 | 7.78 | 7.28 |
| 5 Na ₂ Oxalate | 83 | 7.50 | 7.14 |
| 1 " " | 145 | 7.00 | 7.00 |
| 5 K ₂ " | 73 | 7.76 | 7.16 |
| 1 " " | 140 | 7.04 | 6.77 |

Table XI (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | |
|--|--------------------------------|--------|-------|
| | | Before | After |
| 5 Na ₂ Malonate | 45 | 8.32 | 7.74 |
| 1 " " | 85 | 8.28 | 7.56 |
| 5 K ₂ " | 45 | 8.37 | 7.78 |
| 1 " " | 80 | 8.24 | 7.58 |
| 5 Na ₂ Succinate | 50 | 7.10 | 7.01 |
| 1 " " | 60 | 7.12 | 7.00 |
| 5 K ₂ " | 50 | 7.20 | 7.00 |
| 1 " " | 65 | 7.18 | 7.14 |
| 5 Na Glycolate | 70 | 8.08 | 7.30 |
| 1 " " | 130 | 8.04 | 6.76 |
| 5 K " | 65 | 8.08 | 7.28 |
| 1 " " | 130 | 8.06 | 6.79 |
| 5 Na ₂ Tartrate | 10 | 9.64 | 8.68 |
| 1 " " | 35 | 9.81 | 8.18 |
| 5 K ₂ " | 60 | 8.04 | 7.56 |
| 1 " " | 100 | 8.50 | 7.56 |
| 5 Na ₃ Citrate | 55 | 7.84 | 7.63 |
| 1 " " | 90 | 8.08 | 7.72 |
| 5 K ₃ " | 60 | 6.90 | 6.71 |
| 1 " " | 120 | 7.02 | 7.01 |

Table XI (continued)

| Gms. reagent per 100 c.c. water used | Time of solution minutes | pH | |
|--|--------------------------------|--------|-------|
| | | Before | After |
| 5.0 Na ₂ Maleate | 30 | 8.14 | 7.75 |
| 2.0 " " | 60 | 8.25 | 7.70 |
| 0.5 " " | 90 | 8.23 | 7.62 |
| 5.0 K ₂ " | 35 | 7.76 | 7.60 |
| 2.0 " " | 70 | 7.80 | 7.62 |
| 0.5 " " | 95 | 7.91 | 7.49 |
| 5.0 Na ₂ Fumarate | 80 | 7.40 | 7.04 |
| 2.0 " " | 105 | 7.40 | 6.82 |
| 0.5 " " | 145 | 7.20 | 6.56 |
| 5.0 K ₂ " | 85 | 7.80 | 7.53 |
| 2.0 " " | 105 | 7.78 | 7.40 |
| 0.5 " " | 150 | 7.54 | 7.01 |
| 5.0 Triethanol- amine | 5 | 10.48 | 9.25 |
| 1.0 " " | 12 | 10.23 | 8.91 |
| 0.1 " " | 25 | 10.68 | 8.40 |
| 0.05 " " | 50 | 9.50 | 7.12 |
| 0.5 Quinoline | 140 | 8.38 | 7.74 |
| 0.1 " " | 165 | 7.37 | 7.18 |
| 5.0 Pyridine | 15 | 9.24 | 8.62 |
| 1.0 " " | 60 | 8.82 | 8.40 |
| 0.1 " " | 140 | 8.03 | 7.81 |

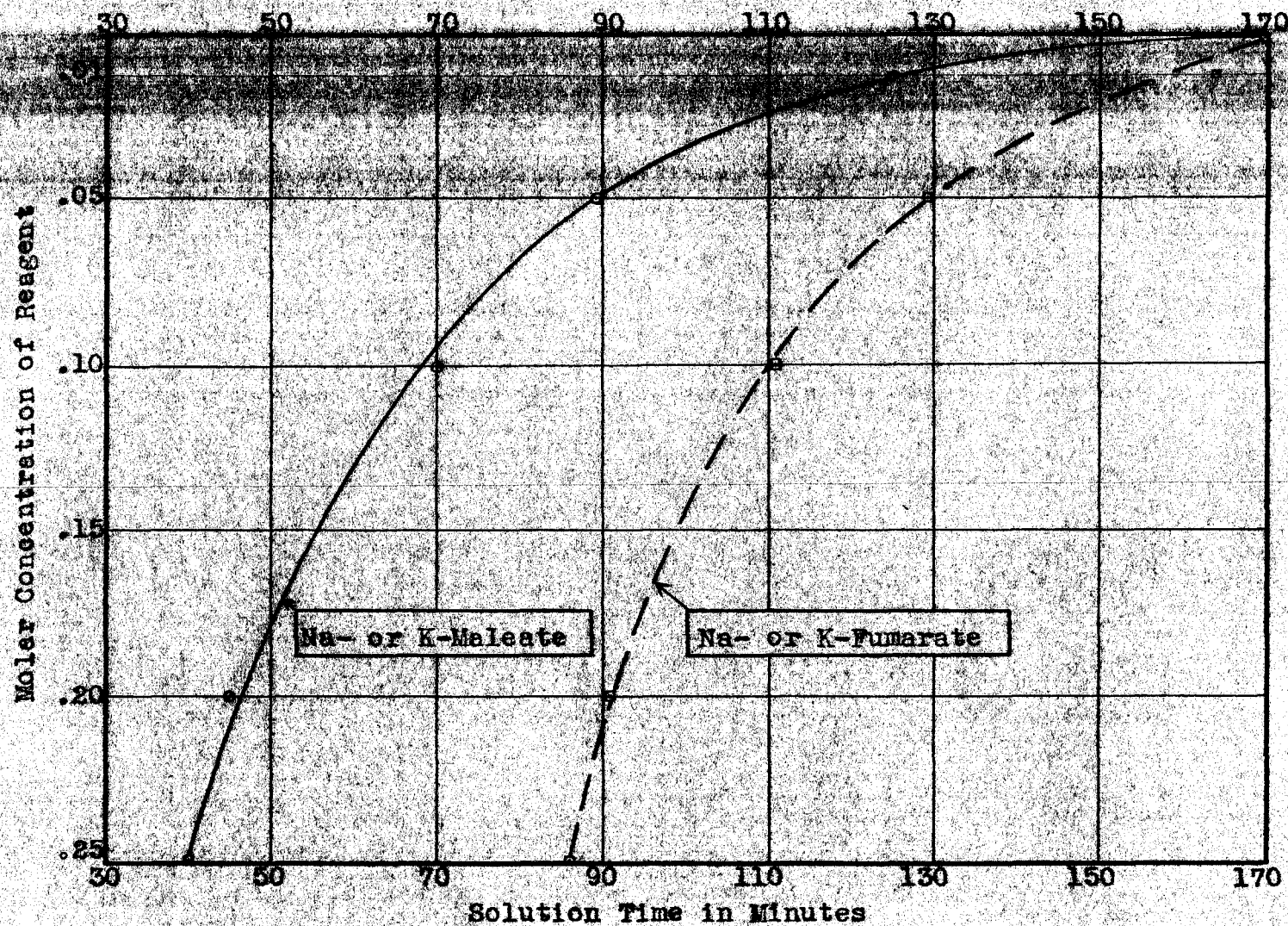


Figure 5. Effect of geometric isomers on solution of dextrose at 60°F.

Discussion of Data

The data presented in Table XI bear out the previous observation that the presence of basic salts shortens the solution time of dextrose. In the mono-basic acid series there is little difference in the times of solution for corresponding concentrations of the reagents. Likewise, little difference was exhibited between the sodium and potassium salts of the acids. However, in general, the branched chain compounds are slightly less effective in speeding up the solution of dextrose than are the straight chain isomers. Since the observed pH among these isomeric salts is approximately the same an explanation of their difference in catalytic action upon the solution time of dextrose lies in their possible reaction with dextrose. In accordance with the assumptions set forth in a preceding discussion, therefore, a condition is produced in the case of the branched chain compounds which is less conducive to the acceleration of the solution of dextrose.

A considerably greater effect on solution time is found in the case of the dibasic acid salts. Because of the fact that oxalic acid is a somewhat stronger acid than its higher homologues, less basic solutions are

produced by its alkaline salts than by those of malonic or succinic acid. For this reason the malonates and succinates shorten the solution time of dextrose more, by virtue of the greater alkalinity of their solutions, than do the oxalates.

The introduction of hydroxyl groups into the carbon chain has little effect except in the case of sodium tartrate. According to the data, there is evidence of a favorable reaction between dextrose and sodium tartrate which does not occur, or is much less noticeable, in the case of the other salts in this series. Even a third basic group, as in the citrates, does not change appreciably the effect of the compounds.

A striking illustration of the influence of the molecular structure of the reagent upon the solution time of dextrose is shown in the case of the alkali salts of maleic and fumaric acids. The time required in the case of the maleates is decidedly less than in the case of the fumarates, although the pH values are almost identical in corresponding concentrations. These facts point again to the possible reaction between dextrose and the alkali salts of organic acids with such a reaction being more favorable to dextrose solution in some

cases than in others. This difference in activity between the geometric isomers is well exemplified by the curves in Figure 5.

Organic compounds which provide highly basic solutions are quite effective as an aid to dextrose solution. This is well illustrated in the triethanolamine solutions; however, because of the bulkiness of the molecule, considerably higher concentrations of this compound are necessary to produce an effect comparable to that for the substituted ammonium compounds listed in Table X.

Since crystallization from pyridine is the classical method for preparing beta-dextrose, it was thought that solutions of this compound would shorten the time of solution of the alpha-form. Trial runs, however, show that this compound has about the same effect as the salts of organic acids. The fused ring base, quinoline, has practically no catalytic effect whatever, even in its saturated solution. Since, again, here, there is but a slight difference in the pH of these two bases in corresponding concentrations, the difference in catalytic effect must depend upon the nature of the reagent.

6. The effect of phosphate buffer solutions.

Buffered solutions present the best means of studying the pH effect over a wide range. Because of the convenience in preparing phosphate buffer mixtures a study of this series was made. Varying hydrogen ion concentrations were obtained by titrating phosphoric acid with the appropriate alkali. Volumes of standard phosphoric acid and alkali solutions were used so that exactly two grams of reagent resulted from the theoretical reaction. A calculated amount of water was added, considering also the water produced in the neutralization reaction, so that a constant weight of water was used in each trial. Results of these trials are listed in Table XII and Figure 6.

Table XII

Effect of phosphate buffers on dextrose solution time

| Gms. reagent per 100 c.c. water used | | Time of solution minutes | pH | |
|--|----------------------------------|--------------------------------|--------|-------|
| | | | Before | After |
| H ₃ PO ₄ | NaH ₂ PO ₄ | | | |
| 2.00 | ----- | 54 | 1.47 | 1.32 |
| 1.90 | 0.10 | 57 | 1.52 | 1.38 |
| 1.30 | 0.70 | 65 | 1.81 | 1.52 |
| 0.40 | 1.60 | 75 | 2.50 | 2.10 |
| 0.10 | 1.90 | 80 | 3.10 | 2.76 |
| ----- | 2.00 | 80 | 3.90 | 3.63 |
| Na ₂ HPO ₄ | | | | |
| 0.05 | 1.95 | 70 | 4.79 | 4.28 |
| 0.10 | 1.90 | 60 | 5.17 | 4.72 |
| 0.40 | 1.60 | 50 | 5.91 | 5.48 |
| 1.00 | 1.00 | 25 | 6.58 | 6.18 |
| 1.60 | 0.40 | 20 | 7.08 | 6.70 |
| 1.90 | 0.10 | 18 | 7.69 | 7.22 |
| 2.00 | ----- | 14 | 8.32 | 7.71 |
| | Na ₃ PO ₄ | | | |
| 1.95 | 0.05 | 9 | 9.82 | 8.94 |
| 1.75 | 0.25 | 7 | 10.13 | 9.00 |
| 1.00 | 1.00 | 3 | 10.85 | 9.69 |
| 0.10 | 1.90 | 1 | 11.20 | 9.97 |
| ----- | 2.00 | 1 | 11.22 | 10.00 |

Table XII (continued)

| Gms. reagent per 100 c.c. water used | | Time of solution minutes | pH | |
|--|---------------------------------|--------------------------------|--------|-------|
| | | | Before | After |
| H ₃ PO ₄ | KH ₂ PO ₄ | | | |
| 2.00 | ----- | 55 | 1.42 | 1.28 |
| 1.90 | 0.10 | 65 | 1.45 | 1.30 |
| 1.30 | 0.70 | 80 | 1.80 | 1.48 |
| 0.40 | 1.60 | 100 | 2.52 | 2.28 |
| 0.10 | 1.90 | 110 | 3.25 | 3.05 |
| ----- | 2.00 | 104 | 4.78 | 4.32 |
| K ₂ HPO ₄ | | | | |
| 0.05 | 1.95 | 90 | 5.26 | 4.76 |
| 0.10 | 1.90 | 80 | 5.48 | 4.97 |
| 0.40 | 1.60 | 50 | 6.07 | 5.59 |
| 1.00 | 1.00 | 34 | 6.69 | 6.17 |
| 1.60 | 0.40 | 29 | 7.26 | 6.73 |
| 1.90 | 0.10 | 25 | 7.99 | 7.48 |
| 2.00 | ----- | 21 | 9.28 | 8.16 |
| | K ₃ PO ₄ | | | |
| 1.95 | 0.05 | 18 | 9.63 | 8.32 |
| 1.75 | 0.25 | 12 | 10.55 | 8.95 |
| 1.00 | 1.00 | 5 | 11.35 | 9.61 |
| 0.10 | 1.90 | 1 | 11.99 | 10.00 |
| ----- | 2.00 | 1 | 12.03 | 10.00 |

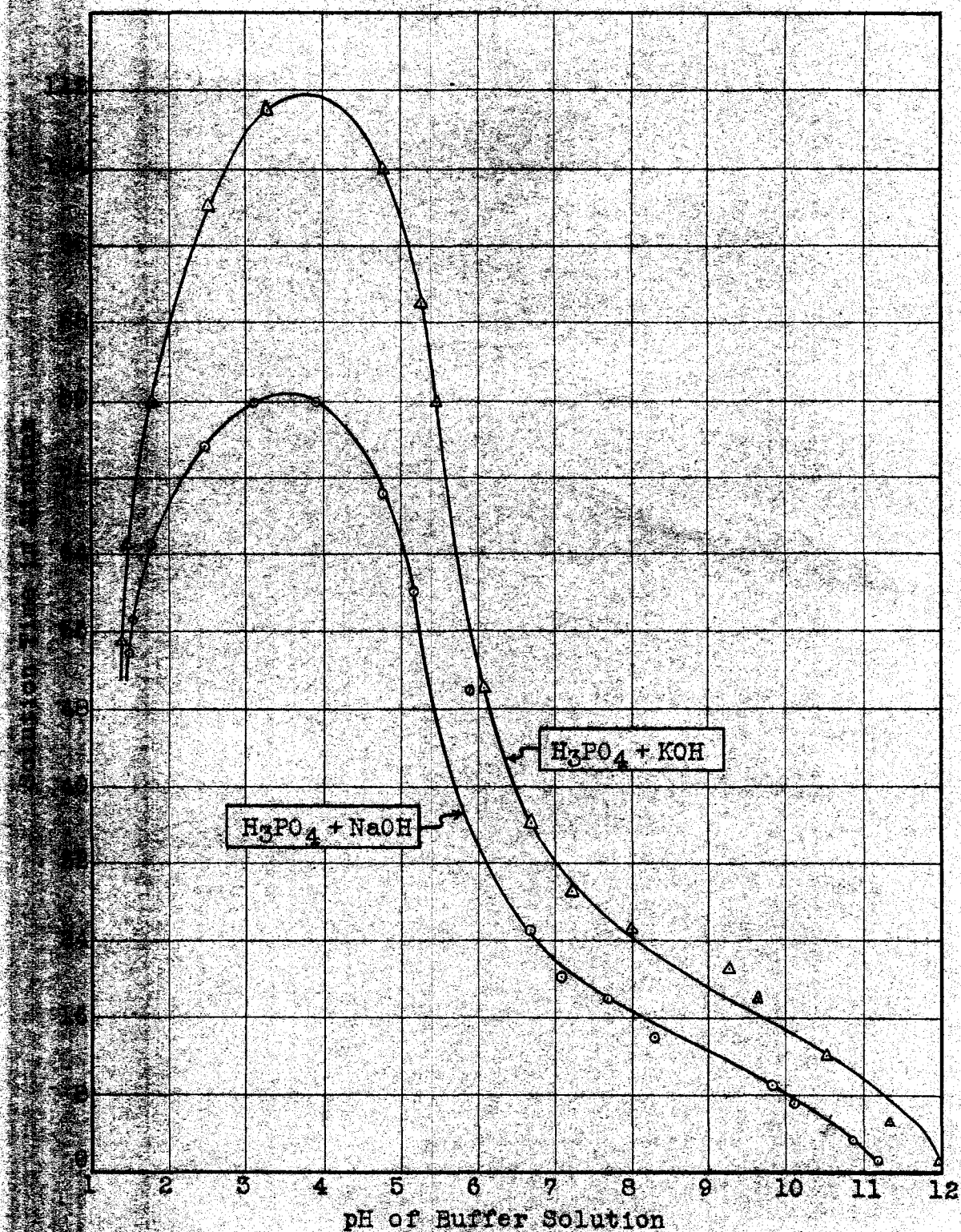


Figure 6. Effect of pH of phosphate buffers on solution time of dextrose at 60°F.

Discussion of Data

Inspection of the curves in Figure 6 shows that in the phosphate buffer mixtures the maximum time for solution occurs at a pH of 3.5 to 4.0. Strongly acid solutions shorten the solution time materially, but a considerably greater effect is apparent in the alkaline solutions. In both the sodium and potassium phosphate buffer mixtures the same general type of curve results. Dawson and Dean (14) introduced the term "catalytic catenary" to describe a similar curve for the effect of pH on the velocity of hydrolysis of an ester.

It will be noticed that the maximum time for solution occurs at approximately the pH obtained by the buffer mixture when one hydrogen of the phosphoric acid has been neutralized by either base, and furthermore, that there is a sharp reduction in solution time until approximately one-half the total amount of alkali has been added. Since phosphates are known to react with dextrose, these observations are, no doubt, a measure of the difference in reaction between dextrose and the various phosphate compounds that may exist in this buffer mixture. Therefore, at the pH of maximum solution time the reaction is least favorable for the formation of the more soluble dextrose compounds or a condition equivalent to the more soluble compounds.

E. The Effect of Crystal Structure on Solution Time

1. Mutarotation and solution time.

Pure alpha-dextrose was used in all preceding time of solution determinations, therefore, the observed time was in part a result of the establishment of an equilibrium between the alpha- and beta-forms through mutarotation. This phenomenon of mutarotation (multi-rotation, birotation) occurs in all freshly prepared dextrose solutions and continues until an equilibrium mixture of about 37 per cent alpha- and 63 per cent beta-dextrose results. At the temperature used in these determinations (60° F.) this conversion takes place rather slowly in pure water. However, as shown by Hudson and Dale (29), the rate of mutarotation is dependent upon hydrogen ion concentration and is very rapid in the case of high concentrations of either hydrogen or hydroxyl ions.

In view of the close relationship between rate of mutarotation and Hudson's rate of solution in 80 per cent alcohol, a study was made of the correlation between mutarotation and time of solution in pure water. In Table XIII the concentration of reagent is given in grams per 100 cubic centimeters of water used and solution time of dextrose in minutes. All rotations were made in a 100 millimeter tube on the saccharimetric scale.

The solutions tested for mutarotation were obtained by adding an excess of anhydrous alpha-dextrose to the reagent solution, stirring vigorously for fifteen to twenty seconds and filtering as rapidly as possible. The initial rotation, as indicated in the table, is that before one minute had elapsed after adding the dextrose to the reagent solution. Rotations were then made at increasing time intervals to approximately thirty-six hours. This last reading was taken as the constant rotation and was, therefore, labeled the rotation after an infinite time interval. According to the reports of Effront (17), Profilo (51), Evans (19) and others, this is not a constant rotation, nevertheless, the values given in Table XIII will serve as a comparison of mutarotation among solutions showing a wide variation in the time of solution of dextrose.

Table XIII

Mutarotation of dextrose in various reagents

| Reagent used | Conc. | Solution time of dextrose | R O T A T I O N | | | | | |
|---|-------|---------------------------------|-----------------|---------|---------|-------|--------|--------|
| | | | Initial | 10 Min. | 30 Min. | 1 Hr. | 2 Hrs. | 5 Hrs. |
| NaOH | 0.1 | 7 Min. | 75 | 64.5 | 64.4 | 64.4 | 64.4 | 64.4 |
| " | 0.01 | 35 Min. | 112 | 78.0 | 66.0 | 64.5 | 64.4 | 64.4 |
| Na ₂ CO ₃ | 0.1 | 10 Min. | 97 | 64.8 | 64.5 | 64.5 | 64.5 | 64.5 |
| " | 0.01 | 60 Min. | 114 | 100.0 | 72.6 | 64.5 | 64.3 | 64.3 |
| KOH | 0.1 | 8 Min. | 80 | 64.2 | 64.1 | 64.1 | 64.1 | 64.1 |
| " | 0.01 | 45 Min. | 114 | 91.5 | 70.6 | 64.8 | 64.4 | 64.4 |
| Na ₃ PO ₄ | 0.1 | 15 Min. | 102 | 64.6 | 64.4 | 64.4 | 64.4 | 64.4 |
| " | 0.05 | 35 Min. | 114 | 83.0 | 66.0 | 64.8 | 64.6 | 64.6 |
| " | 0.01 | 120 Min. | 116 | 106.0 | 86.5 | 77.8 | 68.0 | 64.4 |
| H ₂ SO ₄ | 5.0 | 15 Min. | 114 | 67.5 | 64.2 | 64.2 | 64.2 | 64.2 |
| " | 0.5 | 60 Min. | 115 | 105.0 | 78.3 | 65.8 | 63.6 | 63.2 |
| H ₂ C ₂ O ₄ | 2.0 | 45 Min. | 114 | 93.0 | 73.3 | 65.5 | 64.8 | 64.6 |
| Na ₂ C ₂ O ₄ | 1.0 | 145 Min. | 120 | 108.0 | 98.4 | 83.8 | 67.4 | 64.1 |
| Na ₃ Citrate | 1.0 | 90 Min. | 114 | 102.0 | 96.6 | 82.0 | 65.5 | 64.3 |
| Control | | 165 Min. | 117 | 115.0 | 96.0 | 83.5 | 68.6 | 62.6 |

Discussion of Data

A check of the data in Table XIII reveals that all reagents in which the time of solution of dextrose is fifteen minutes or less catalyze mutarotation to the extent that equilibrium is reached within approximately the same time required for complete solution. Furthermore, as the solution time of dextrose increases the rate of mutarotation decreases, approaching, in both cases, the values for pure water. In general, when more than one hour is required for solution time, the rate of mutarotation is but slightly greater than in pure water. This is particularly true in the less basic reagents. These facts, in addition to the observations already made on the slightly basic reagents, support the theory that dextrose is converted to a more soluble condition in these reagents. One explanation, as pointed out previously, is the formation of dextrose compounds with the reagents. A second possibility lies in the more rapid dehydration of the hydrated dextrose form which crystallizes out during the initial dissolution period. The presence of reagents evidently shifts the dextrose molecules into a condition which permits of more rapid dehydration.

The evidence in the case of strongly acidic and basic solutions, as reported in Table XIII, points

directly to the more rapid formation of the alpha-beta equilibrium mixture in shortening the time of solution. This is probably the most significant factor to be considered when only a minute concentration of the reagent is required for the rapid solution of dextrose.

2. The effect of other sugars on alpha-dextrose solution time.

Since the solution of alpha-dextrose has been shown to depend in part upon its conversion into the beta-form a check was made on the influence of pure beta-dextrose in dissolving the alpha-form. Varying amounts of pure beta-dextrose, prepared by the method of Hudson and Dale (29), were mixed with pure alpha-dextrose and the solution time of these mixtures determined. Similar mixtures were made with sucrose and alpha-dextrose. A third series was made in which the corresponding weight of alpha-dextrose was dissolved in varying concentrations of the equilibrium mixture and the alpha- and beta-forms in the required amount of water. As a check, the solution time of corresponding weights of alpha-dextrose was determined in pure water. These data are tabulated in Table XIV, the time of solution being given in minutes in all cases. All runs were made at 60° F. using fifty-three grams of water.

Table XIV
Effect of other sugars on α -dextrose solution time

| Per cent replacement by other sugar | gm. alpha- dextrose | gm. other sugar | Solution time of alpha-dextrose | | | |
|--|---------------------------|-----------------------|--------------------------------------|---|-------------------------------|---------------------|
| | | | Mixed with pure beta- dextrose | In solution of alpha-beta equilibrium | Mixed with pure sucrose | In pure water |
| --- | 30.2 | --- | 170 | 170 | 170 | 170 |
| 5 | 28.7 | 1.5 | 150 | 165 | 148 | 135 |
| 10 | 27.2 | 3.0 | 130 | 155 | 125 | 110 |
| 15 | 25.6 | 4.6 | 100 | 140 | 100 | 95 |
| 20 | 24.1 | 6.1 | 60 | 100 | 60 | 60 |
| 25 | 22.6 | 7.6 | 5 | 60 | 5 | 5 |
| 30 | 21.1 | 9.1 | 3 | 30 | 3 | 3 |
| 40 | 18.1 | 12.1 | 2 | 3 | 2 | 2 |
| 100 | ---- | 30.2 | < $\frac{1}{2}$ | --- | 2 | --- |

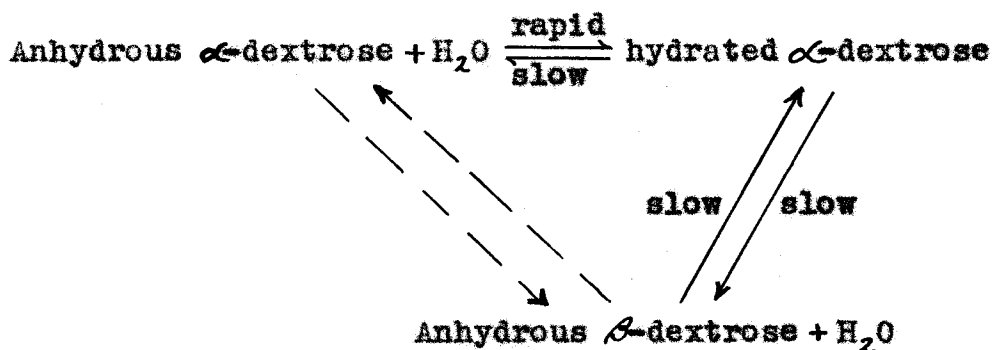
Discussion of Data

The data in Table XIV along with evidence in the preceding data give conclusive proof that any mutarotation accelerator will act also as a solution catalyst. Pure beta-dextrose dissolves almost instantaneously at 60° F. in this concentration, and furthermore, its presence as a part of the total weight of dextrose has little influence on the solution time of the alpha-form. Likewise, the presence of sucrose as a part of the total weight of sugar has little influence on the solution time of alpha-dextrose. However, the presence of the equilibrium mixture of the alpha- and beta-forms of dextrose has the same effect as would the calculated weight of the alpha-form of the equilibrium mixture.

The sharp break in time of solution observed in each series is to be expected in accordance with the discussion of the results in Table IV. In each case the weight of alpha-dextrose that dissolves readily (within five minutes) would give a concentration of approximately thirty per cent when completely dissolved.

SUMMARY AND CONCLUSIONS

1. The solution time of dextrose was found to depend upon rate of stirring, shape of container, rate of addition, size of crystals, temperature, concentration, crystalline form of the dextrose and the presence of foreign substances in the solution.
2. The percentage concentration of anhydrous alpha-dextrose which will dissolve completely in pure water within fifteen to twenty minutes may be taken as approximately one-half the numerical value of the Fahrenheit temperature at which the sugar is to be dissolved.
3. For a consideration of solution time the following equilibrium depicts the condition in a dextrose solution:



4. Any factor which tends to change the dextrose being dissolved into a more soluble condition accelerates the solution of dextrose.

5. Reagents that produce strongly basic solutions even in low concentrations accelerate the solution of dextrose by virtue of high concentrations of hydroxyl ions which are effective in a rapid conversion of alpha-dextrose into the more soluble beta-form.
6. Reagents that produce only feebly basic solutions accelerate the solution of dextrose by reaction with the sugar in such a way as to produce a more favorable condition for solution to take place.
7. The effectiveness of catalysts in dissolving dextrose depends to some extent upon their molecular structure. This is particularly true among the isomeric organic compounds.
8. The metallic ions of inorganic basic substances are not effective as solution catalysts in dissolving dextrose.

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