SUGAR CRYSTALLIZATION

Equilibrium Moisture Content and Crystallization of Amorphous Sucrose and Glucose

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Amorphous (metastable) sucrose and glucose powders were exposed to relative humidities ranging from 4.6 to 33.6% at 25° C. At humidities lower than about 12% for sucrose and 5% for glucose, moisture equilibrium was attained and practically no crystallization occurred in nearly 3 years. A vapor pressure isotherm was evaluated for sucrose-water solutions from 0 to 100% sucrose at 25° C. At higher humidities the absorbed water initiated crystallization of the sugars with subsequent release of moisture to yield essentially anhydrous materials. The rate of crystallization of amorphous sucrose, evaluated from changes in the moisture content, followed an exponential law with respect to time, after an initial induction period. This period was interpreted to be the time for a build-up of sufficient nuclei to initiate an appreciable rate of crystallization.

THE PREPARATION OF FREE-FLOWING POWDERS from fruit juices and fruit purees is being studied at this laboratory. Rapid dehydration of these materials—for example, by vacuum or spray drying—yields solids containing as much as 50% or more of sugars, which are generally present in an amorphous state. Such sugars are very hygroscopic and this property has an important bearing on the drying characteristics of the fruit powders (15) and their tendency to become sticky and to form a hard cake.

The caking tendency is further aggravated under some conditions by a transformation of the sugar from the amorphous to a crystalline state in the presence of small amounts of absorbed moisture. Although this type of transformation has been reported for lactose in spray-dried milk powders (19), for pure glucose (13), and for sucrose in "graining" of hard candies (2, 4), there is no published information on the behavior of the pure sugars under controlled conditions.

Prevention of caking and stickiness rests upon the knowledge of the moisture-absorption characteristics of the amorphous sugars in relation to the humidity of the surrounding atmosphere, and knowledge of the conditions that govern the transformation from the amorphous to the crystalline state. The purpose of the present study was to obtain such data for two of the important sugars, sucrose and glucose. The measurements were made by following the changes in weight of the sugars held in chambers at various controlled relative humidities (RH) varying from about 5 to 34% and at a constant temperature of 25° C. Both visual and microscopic observations were also made to determine changes in state during the experiment.

A companion paper (17) presents the results of measurements with an x-ray diffractometer of the rate of crystallization of amorphous sucrose held at 30 and 32.5% relative humidity.

Experimental

Preparation of Amorphous Sugars Sucrose powder was prepared by spray-drying a 20% aqueous solution in an experimental spray dryer. The product contained approximately 2% water and consisted mainly of hollow spheres which passed a 325-mesh screen and showed no evidence of crystallinity when examined under a polarizing microscope. The particles ranged from about 0.25 to 5 microns in diameter, the average being about 2 microns. A stock sample of essentially anhydrous powder was pre-prepared by further drying at room temperature, in vacuum, over phosphorus pentoxide for about 2 months.

Dextrose in amorphous form was not prepared by spray drying because the humidity in the dryer could not be lowered sufficiently to prevent stickiness and crystallization. A procedure which involved melting followed by rapid cooling was used instead. About 15-gram samples of anhydrous dextrose (Merck & Co., Inc.) were melted in borosilicate glass test tubes 25 mm. in diameter in an atmosphere of nitrogen by immersion in a 170° C. oil bath for approximately 8 minutes. After melting, the tubes were chilled rapidly in a dry ice–alcohol bath. The "glassy" plugs were dislodged from the tubes by rapid heating of the glass. A powdered preparation passing a 20-mesh screen was prepared by crushing and grinding the plugs in a cold room at −25° C. At this temperature the glassy sugar is very brittle and can be ground without gumming the mill. All subsequent transfers of this powder (as well as of the anhydrous sucrose) to sample bottles used in moisture absorption experiments were conducted in this room of low absolute humidity to ensure essentially anhydrous starting material. The dextrose powder was kept in a desiccator over phosphorus pentoxide for several months before use. Other investigators (13) who used a similar method for the preparation of amorphous dextrose have shown that negligible decomposition occurs in the process. This is further supported by observations that the glassy material was colorless and showed no fluorescence in aqueous solution. The latter test proved to be a sensitive indication of the chemical changes which give rise to brown products in overheated melts.

Measurement of Moisture Absorption Water uptake by the initially dry sugars was determined periodically from changes in weight of samples kept at 25 °C. in air-free desiccators with sulfuric acid solutions of different concentrations to maintain constant relative humidities ranging from 4.6 to 33.6%. Approximately 2-gram samples of the stock sugar preparations were accurately weighed into 25 × 20 mm. weighing bottles with outside ground stoppers and were used in triplicate at each humidity. Other details of the procedure have been described (9).

One of the triplicate samples was used during the course of the equilibration for examination of the degree of caking and for microscopic study with polarized light to detect the formation of any crystalline phases.
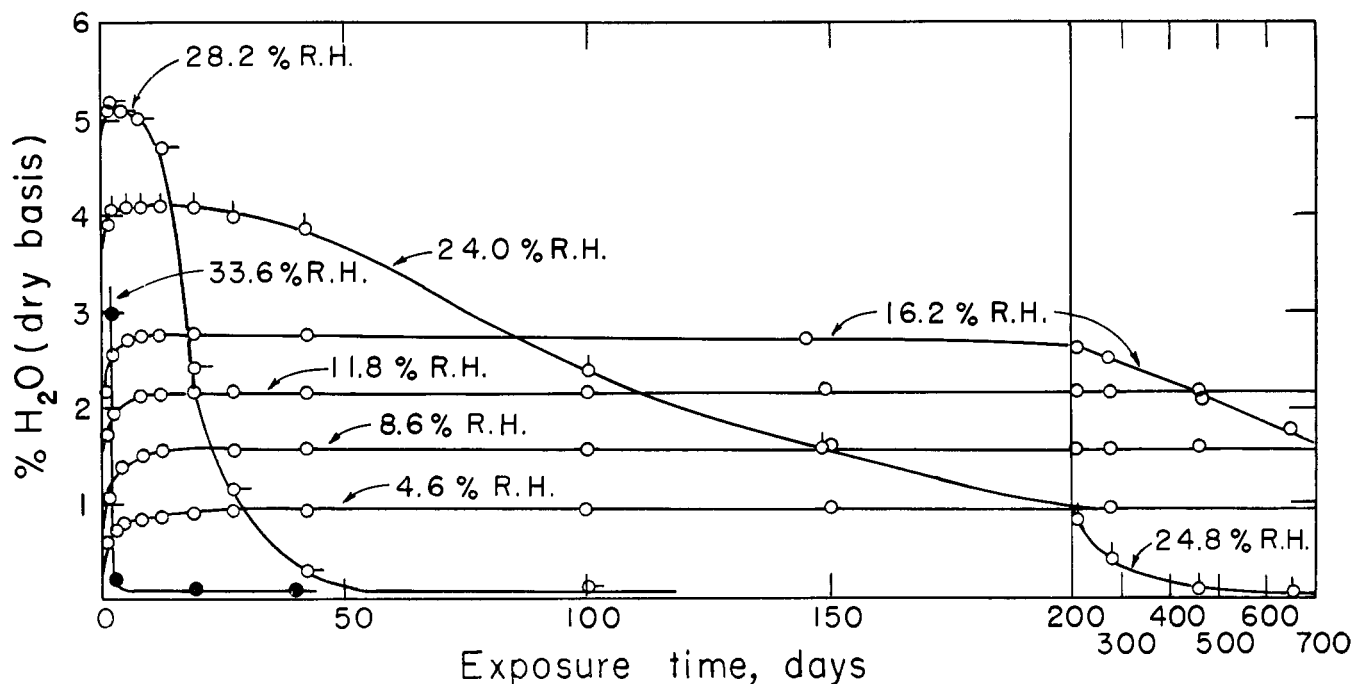
Figure 1. Absorption of water vapor by amorphous sucrose at various relative humidities (RH)

Results and Discussion

The course of the moisture uptake with time is given for sucrose in Table I and Figure 1. Similar data for glucose are shown graphically in Figure 2. An equilibrium moisture level was reached with sucrose at all relative humidities up to 24.0%; with glucose only at the lowest measured humidity of 4.6%. These powders maintained their free flowing character during the equilibration period and showed practically no evidence of crystallinity when examined microscopically under polarized light.

At higher humidities the samples gained moisture up to a maximum (not necessarily the equilibrium moisture content) and then lost it at a rate which increased with rising humidity. It can be seen in Figures 1 and 2 that several samples returned to their original anhydrous condition after an initial gain of several per cent of water. With sucrose at 33.6% RH, only the descending branch of the absorption curve could be observed (Figure 1), owing to rapid crystallization. Glucose samples at 24.0, 28.2, and 33.6% RH (not shown in Figure 2) were converted to essentially anhydrous and crystalline state in about 5, 4, and 3 days, respectively. Microscopic examination of the samples showed that the loss of moisture was accompanied by progressive crystallization. There was also a slight caking with sucrose at 24.0 and 28.2% RH and much caking with some shrinkage at 33.6% RH. All glucose samples above 4.6% RH caked badly and shrank very markedly.

The release of the absorbed moisture occurs in a transformation of the amorphous sugars to an anhydrous crystalline state. Similar behavior with lactose was noted over 60 years ago by Schmoeger (14) and was studied in greater detail by Herrington (6) but not under controlled relative humidities as in the present study. It follows therefore that the moisture contents listed in Table I, or Figures 1 and 2, for the samples which undergo crystallization, represent the moisture localized in an unknown amount of remaining (yet uncrystallized) amorphous material. The extent of crystallization in the sucrose samples at any time can be calculated under certain assumptions from the present data.

The observed increase in rate of crystallization with increasing moisture content (or humidity) is probably due to decrease in internal viscosity which affects rate of orientation of the molecules (8, 12).

A comparison of the behavior of the two sugars shows that glucose crystallizes much more rapidly than sucrose at any given relative humidity—for example, at 11.8% RH, sucrose remained amorphous over the entire exposure time of 800 days. That this difference is not

Table I. Absorption of Water Vapor by Amorphous Sucrose at 25° C.

Exposure Time, Days	Relative Humidity,[a]						
	4.6	8.6	11.8	16.2	24.0	28.2	33.6
	Water[b], %						
1.0	0.59	1.07	1.72	2.17	3.91	5.10	2.96[c]
2.3	0.72	1.31	1.93	2.55	4.06	5.15	0.13[d]
3.3	0.74	1.37	2.02	2.64	4.07	5.06	0.12
5.0	0.78	1.42	2.07	2.71	4.09	5.01	0.11
8.0	0.82	1.47	2.11	2.74	4.09	5.00	0.12
12.0	0.85	1.51	2.13	2.76	4.08	4.69	0.12
19.0	0.88	1.61	2.16	2.77	4.08	2.42	0.11
27.0	0.91	1.54	2.17	2.71	3.99	1.13	0.11
42	0.91	1.56	2.15	2.69	3.86	0.28	0.11
100	0.91	1.55	2.15	...	2.37[c]	0.11[c]	0.10
149	0.95	1.60	2.18	2.71	1.55	0.10	0.12
208	0.95	1.57	2.18	2.61	0.83	0.10	0.11
277	0.95	1.58	2.18	2.51	0.40	0.10	0.11
457	0.95	1.60	2.19	2.13	0.11	0.09	0.10
782	0.98	1.59	2.18	1.52	0.12	0.08	0.09
846[e]	0.98	1.56	2.14	1.39	0.12	0.09	0.10

[a] Relative vapor pressures of H_2SO_4 solutions used calculated from data of Stokes and Robinson (16) and Wilson (23).

[b] Average % H_2O (dry basis) for two samples; replicate samples agreed to within 0.05% moisture content.

[c] Slight caking observed.

[d] Much caking.

[e] Observations after 846 days: material powdery at 4 lowest humidities, at 28.2% RH, slightly caked; at 33.6% RH, badly caked and somewhat shrunken.
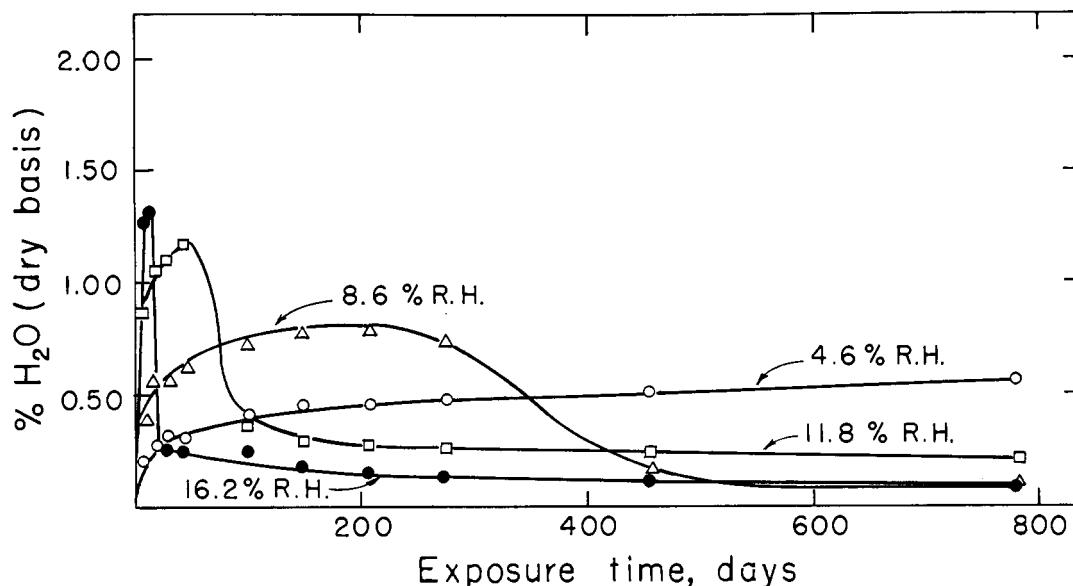
Figure 2. Absorption of water vapor by amorphous glucose

directly related to the amount of moisture present is suggested by the results at 4.6% RH, which show that the moisture content at equilibrium is actually higher for sucrose (1.0% water) than for glucose (0.6% water). Though the present data do not permit a similar comparison at higher humidities, it may be assumed that the difference lies in the larger molecular weight and the more viscous character of the sucrose and the sucrose-water systems at this temperature.

This conclusion is further supported by the observation that the shrinkage accompanying crystallization was very marked with glucose but occurred in sucrose only at 28.2 and 33.6% RH. The shrinkage must involve a coalescence or deformation of the particles through a flow mechanism which takes place more readily with glucose. Another factor which may contribute to the shrinkage is the possibility that the water liberated during crystallization cannot diffuse out as rapidly as it is produced and may give rise to local high concentrations of moisture (above the equilibrium value) in the adjacent, still amorphous, material. This liberated water lowers the viscosity of the amorphous sugar, promotes cementation of the particles, and increases the rate of crystallization. It is clear that if the crystallization process were occurring not in a constant humidity chamber but in a closed vessel without a humectant, the liberated moisture would all be absorbed by the yet uncrystallized part of the sample. Thus the percentage of moisture in the amorphous portion of the sugar would increase with time, and the rate of crystallization would increase in an autocatalytic manner and would result in caking of the sample. This kind of process was previously observed with amorphous lactose in sealed packages of milk powders (5).

Equilibrium Moisture Content The maximum values for the absorbed water in sucrose samples that did not crystallize represent the equilibrium moisture content for the corresponding relative humidities (up to 11.8% RH). The data are shown in Table II. Two additional equilibrium values were estimated for sucrose from the maxima in the absorption curves (Figure 1) for 16.2 and 24.0% RH. Although crystallization eventually occurred under these conditions, the rate was so slow and the maxima so broad as to justify this step. This is further borne out in a plot of the absorption isotherm in Figure 3, which is based both on data from this investigation and on previously published results for sucrose solutions of different concentrations. The two sets of results are concordant and cover the whole range of concentrations from pure sugar to pure water. In the metastable region (*OPS* of Figure 3) portion *PS* can be realized experimentally only for a very short time, if at all, because of the rapidity of crystallization which tends to occur at this temperature. At lower temperatures it should be possible, however, to arrest the crystallization over a wider range of moisture content than over region *OP* found in the present study.

It is interesting to evaluate from the interpolated portion of the curve in Figure 3 the equilibrium moisture content for 28.2% RH. This amounts to 48.7 mole % (or 5.0% water), which is in good agreement with the maximum moisture, 5.15%, attained by this sample (Figure 1). Thus it would seem that even in this experiment, where the subsequent crystallization was very rapid, the entire sample had at first attained complete equilibrium with the surrounding water vapor.

The data for glucose do not lend them-

selves to a similar analysis, because crystallization could not be arrested except at 4.6% RH, which yields an equilibrium moisture content of about 0.6% (Figure 2). If the absorption could be measured over a wider humidity range (perhaps at lower temperatures) it would be similar to sucrose. The absorption isotherms of both amorphous sugars more closely resemble those of high polymers, such as cellulose or starch, than the stepwise isotherms of crystalline hydrates. Previously published conclusions (1, 3) to the effect that noncrystalline glucose or sucrose, or certain mixtures of these with other sugars, do not absorb any water below 22.5% relative humidity cannot be considered correct in the light of the present data.

Table II. Equilibrium Moisture Content for Amorphous Sucrose at 25° C.

| Relative Humidity, % | Moisture Content | |
	Weight %[a]	Mole, %
4.6	0.9	14.9
8.6	1.6	23.3
11.8	2.2	29.5
16.2	2.8	34.7
24.0	4.1	43.7
85.3[b]	47.7	90.0
87.8[c]	58.4	91.8
90.6[c]	73.1	93.3
93.3[c]	98.7	94.9
95.8[c]	146.5	96.6

[a] Dry basis.
[b] Saturated sucrose solution (22).
[c] Sucrose solutions (7).

Extent and Rate of Crystallization in Amorphous Sucrose When the rate of crystallization is slow, it can be assumed that the moisture content of the remaining amorphous sugar is always very close to the equilibrium value for the ambient humidity. With this assumption and the fact that crystalline sucrose is anhydrous, it is possible to calculate the fraction of sucrose not crystallized (in such samples) at any time by dividing the amount of moisture present by the amount that would be present if the entire sample were amorphous. Thus, for the sample at 16.2% RH, the fraction not crystallized after 700 days is 1.6/2.8 = 0.6 (Figure 1). This assumption

has been substantiated by x-ray diffraction analysis (11).

The rate of crystallization, in accordance with the views of Tammann (18), probably involves two steps—the rate of formation of nuclei and the rate of growth of crystals from the nuclei. Experimental data show that the course of the crystallization is characterized by a lag or induction period followed by an increasing rate (see experiments at 16.2, 24.0, and 28.2% RH in Figure 1). The induction period, which varies from several days at 28.2% RH to about 150 days at 16.2% RH, is evidently the period of slow appearance of the nuclei. After the induction period, the amount of uncrystallized material decreases exponentially with time, suggesting first-order kinetics. This is shown by the linear plots in Figure 4, where the logarithm of the moisture content (which is proportional to the amount of residual amorphous sucrose) is plotted against time. The existence of the induction period is clearly seen in these plots.

On the basis of these observations an attempt has been made to derive an expression which will quantitatively describe the course of the crystallization.

It is assumed first that the crystallization within a given sucrose particle does not affect the neighboring particles, as if all particles were isolated from each other. This assumption is supported by the observed excellent reproducibility of

Table III. Crystallization Constants for Amorphous Sucrose

Relative Humidity, %	Moisture Content[a], %	k, (Days)$^{-1}$ × 10^4	τ, Days	Nucleation Half-Time, H, days[b]	τ/H
16.2	2.8	9.8	350	704	0.5
24.0	4.1	89	58	77	0.8
28.2	5.1	945	17	7.3	2.3

[a] Of uncrystallized amorphous sucrose (dry basis).
[b] $H = 0.69/k$.

crystallization rate as shown by the moisture content of replicate samples (except at 33.6% RH, where the viscosity of the amorphous sugar is relatively low) and by microscopic observations. The existence of partially or completely crystallized individual particles among the amorphous ones was commonly noted. Turnbull (20) pointed out that the mentioned reproducibility in rate is not likely to occur except under conditions where the above assumption holds.

It is assumed further that the nucleation frequency follows a first-order law—namely, that the frequency, dN_t/dt, is proportional to the number of particles, N_0-N_t, that have no nuclei at time t. N_0 is the initial number of unnucleated particles and N_t is the number that has been nucleated between time $t = 0$ and time t. (In subsequent analysis of experimental data, N_0 was assumed to be the total number of particles, because

microscopic observations showed no evidence of crystallinity at $t = 0$.)

Thus

$$dN_t/dt = k(N_0 - N_t) \qquad (1)$$

and

$$N_t = N_0(1 - e^{-kt}) \qquad (2)$$

where k is the specific rate of nucleation.

Assume also that the nucleation immediately initiates the crystallization process, which proceeds at an average mass rate c, so that a particle of an average mass m crystallizes completely in a time

$$m/c = \tau \qquad (3)$$

The rate of disappearance of an amorphous mass, M_t, at time t is therefore represented by the rate of crystallization of those particles which have become nucleated during time $t - \tau$. (All the particles nucleated previously are inactive because they have already completely crystallized.) Mass rate of crystallization is thus

$$dM_t/dt = -c(N_t - N_{t-\tau}) \qquad (4)$$

where N_t and $N_{t-\tau}$ are numbers of nucleated particles at times t and $t - \tau$, respectively, and the term $(N_t - N_{t-\tau})$ is the number of particles undergoing active crystallization.

Combining Equations 2 and 4, integrating, and making use of the identity derived from Equation 3 that $N_0m = N_0c\tau = M_0$, where M_0 is the initial mass of amorphous material, yields:

$$M_t = M_0[1 - (e^{-kt} + kt - 1)/k\tau] \qquad (5)$$
$$\text{for } t \leqslant \tau$$

and

$$\log M_t = \log [M_0(e^{k\tau} - 1)/k\tau] - kt/2.3 \qquad (6)$$
$$\text{for } t \geqslant \tau$$

These two equations give an M_t which is continuous, with continuous first derivative.

From Equation 6 it is possible to obtain the constants, k and τ, by plotting log M_t [or the proportional value, log (% water)] against t. The specific nucleation rate, k, is evaluated from the slope of the straight line, and the average crystallization time, τ, per particle, is calculated by successive approximations from the intercept on the log M_t [or log (% water)] axis, which is defined by the second term in Equation 6.

Figure 3. Water vapor absorption isotherm for amorphous sucrose at 25° C.

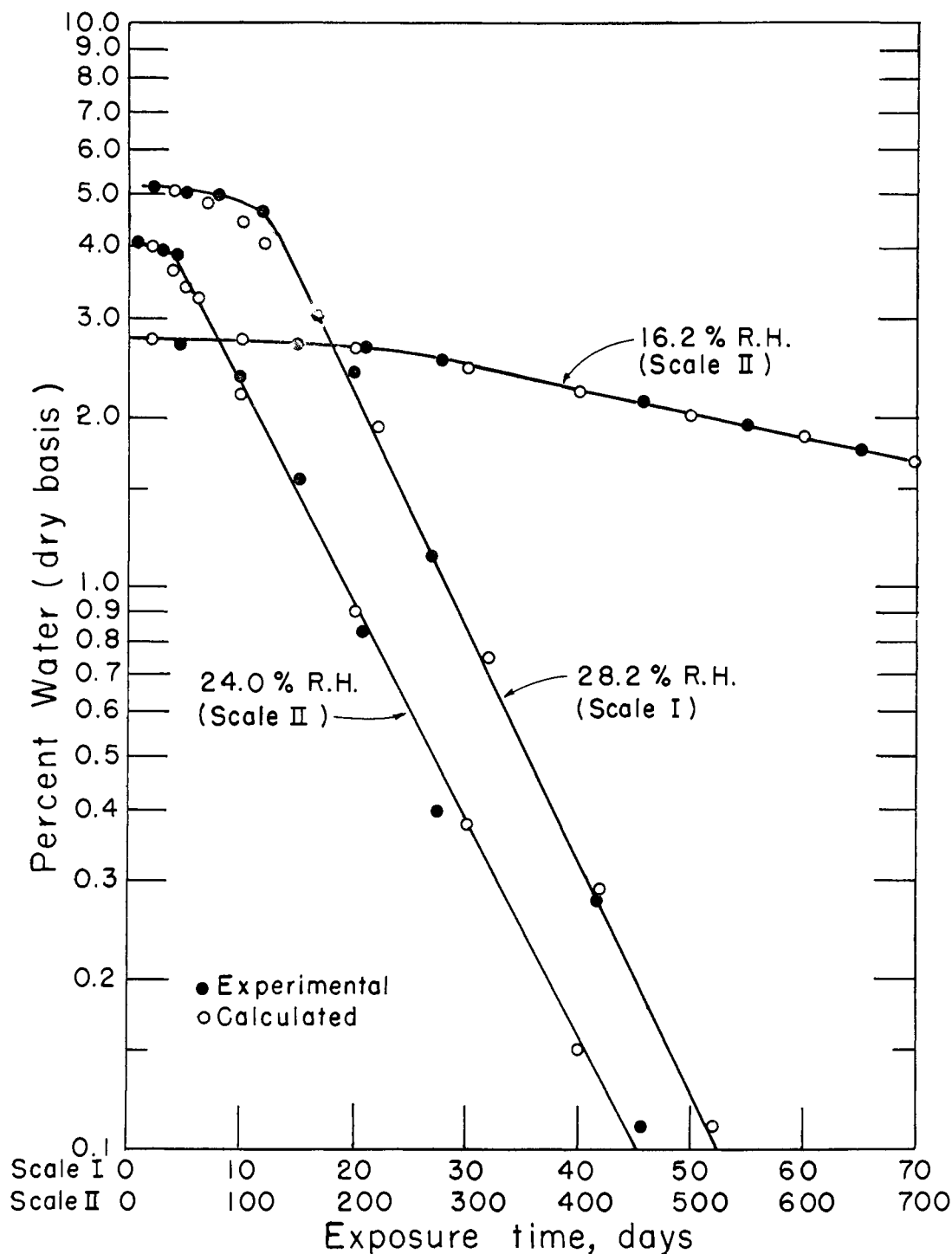Plot includes aqueous solutions under and above saturation
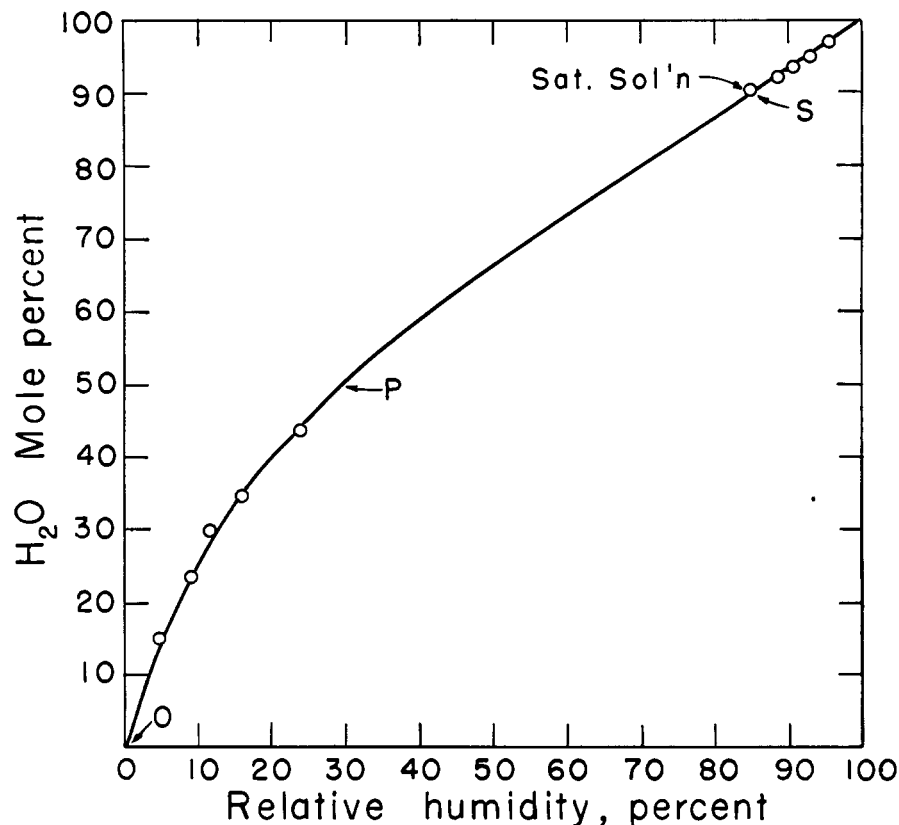
Figure 4. Log (% H₂O) vs. time for amorphous sucrose at three relative humidities at 25° C.

The derived constants for experiments at the three humidities where the course of the crystallization could be readily followed are shown in Table III. Their validity was tested by using them in Equations 5 and 6 to calculate the course of the crystallization as shown in Figure 4. Experimental data represented by the curves and by shaded circles are compared with calculated values, open circles, derived from Equations 5 and 6. In the calculations, the onset of crystallization (zero time) at 28.2% RH was assumed to be at the beginning of the third day of exposure, when moisture

equilibrium was reached. In the other two experiments the equilibration time was negligibly small compared to the crystallization period and no correction was made. The calculated values (shown by open circles) agree well with the experimental data. This agreement lends credence to the assumptions offered to explain the induction period and the subsequent exponential character of the crystallization.

Included in Table III are also calculated values for nucleation half-time H, and the ratio, τ/H. It is seen that an increase of moisture from 2.8 to 5.1%

causes a very large corresponding decrease in the two constants, about 100-fold for H and about 20-fold for τ. Hence, a small decrease or increase in moisture outside of the range shown in Table III will result in a rate either immeasurably slow or fast, respectively. This is undoubtedly associated with changes of similar order of magnitude in the viscosity of the glasslike amorphous sugar, as shown by Tammann (17) and by Parks and Gilkey (12).

The ratio, τ/H, is not very far from unity and the rate of nucleation is of about the same order of magnitude as that of crystallization in the moisture region investigated. Inasmuch as the ratio decreases with decreasing moisture content, one would predict that at very low moistures the nucleation frequency would become the rate-determining step and the crystallization process would follow a simple exponential law, without any induction period, as shown theoretically and experimentally by Turnbull (21) for solidification of mercury droplets. At higher moistures, crystal growth will tend to become rate-determining. With increase in moisture, however, there is a decrease in viscosity which eventually leads to coalescence of the particles. Under those conditions the simplifying assumptions (especially Equation 3) and the mathematical formulation would no longer hold.

It is possible, however, that such a coalesced sugar mass might behave in a manner similar to that recently described

for amorphous bulk polymers by Mandelkern, Quinn, and Flory (10). In their interesting paper, these authors explained the observed induction period and crystallization kinetics in terms of the concept of concurrent nucleation and crystal growth, just as has been done in the present work.

The present measurements were all made at one temperature. It would be of considerable interest to obtain data at several temperatures in order to determine the temperature coefficients of k and τ and to evaluate the effect of temperature on the crystallization kinetics.

Acknowledgment

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SUGAR CRYSTALLIZATION

X-Ray Diffractometer and Microscopic Investigation of Crystallization of Amorphous Sucrose

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An x-ray diffractometer method has been developed for determining the crystalline-to-amorphous ratio in a spray-dried sample of sucrose. The results obtained by application of this method to samples stored at 30.0 and 32.5% R.H. are discussed. The effect on the rate of crystallization of adding 5% finely ground crystalline sucrose to a sample of amorphous sucrose before storage at 30% R.H. has been measured. Observations made on these same samples with a polarizing microscope are used in conjunction with other evidence to postulate a mechanism for the crystallization process in spray-dried amorphous sucrose under the conditions of this experiment.

RESULTS ON THE VARIATION OF MOISTURE CONTENT of amorphous sucrose with time when stored at relative humidities (R.H.) between 5.1 and 29.1% have been presented (6). This paper is concerned primarily with the development of an x-ray diffractometer procedure for measuring the extent of crystallization which occurs when amorphous sucrose is stored and determines whether or not the moisture content is a reliable index of crystallization. In addition, the x-ray procedure has been used to make a

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quantitative study of the rate of crystallization of amorphous sucrose stored at relative humidities of 30 and 32.5% at 24° C. These particular conditions were chosen because the results of Makower and Dye (6) indicated that under these conditions crystallization occurs at a convenient rate.

There does not appear to be a previous investigation of the crystallization of amorphous sucrose. On the other hand a great deal of work has been done on the crystallization of amorphous lactose, because of the importance of the crystallization behavior of this sugar on the storage stability of many milk products. Supplee (10) observed that dried milk powder

absorbed water when exposed to a moist atmosphere, but upon standing the water content decreased. Troy and Sharp (11) suggested that Supplee's observation was due to absorption of water by the hydrophilic components of dried milk including amorphous lactose followed by the formation of crystalline α-lactose monohydrate. Because lactose monohydrate bound less water than amorphous lactose absorbed under the experimental conditions used, the dried milk powder lost weight when lactose crystallized. Herrington (3) has also made a rather thorough study of the transformation of lactose from the glassy to crystalline state, and in particular used the