

Computing Supersaturation for Sucrose Solutions

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In this paper the equation for "The Solubility at High Temperatures of Pure Sucrose in Water," by Taylor (1) is plotted against the "Boiling Point Elevation Equation for Pure Sucrose," by Spengler (2). The resulting data are used to construct tables and charts which we have found to be valuable in the study of the supersaturation of sucrose solutions. This discussion will be confined to the study of sucrose solutions of 100 percent purity. However, the problems encountered in correcting for purities less than 100 percent will be discussed briefly at the end of the paper.

At this point, mention should be made of the authors whose literature has been studied during my investigation of this interesting subject. Herzfeld's (3) table of the solubility of sucrose has been the standard in the industry for more than fifty years. Other early investigators (4) have been ambitious in their attempts to challenge the validity of Herzfeld's table, but have not been wholly successful in this attempt. Holven (5) in 1936 pointed out the differences between Herzfeld's values and that data which he and his co-workers at C & H had compiled. Taylor (1) in 1917 published a paper which successfully established a new and more accurate set of values for the solubility of pure sucrose in water solutions. Taylor's data and Holven's data are in very close agreement, especially in the temperature ranges in which most commercial sugar boiling is performed.

Taylor's results should be acceptable by reason of the high degree of accuracy of the experimental work and because of the sound analysis of the results. While Herzfeld's solubility data and Taylor's solubility data do not disagree by a very large amount, the difference is significant.

Claasen's (6) boiling point elevation tables for aqueous solutions of sucrose likewise have served the industry as a standard since 1904. Again, Holven (5) challenged these data on the grounds that the variation in boiling point elevation due to vapor pressure changes was not considered in Claasen's works and this constituted a serious error in the approach to the problem. Therefore, at the insistence of Claasen, Holven and others Spengler (2) (7) and his associates, in 1938 performed new experiments and determined with acceptable accuracy the boiling point elevation of pure and impure sucrose solutions at various concentrations under numerous conditions of vapor pressure. Spengler's (7) boiling point elevation data for pure sucrose solutions are, therefore, accepted as being more correct than any other data.

Kukhareenko (8) (4) in 1935 calculated a table of supersaturation and crystallization velocities for pure sucrose in water solutions. These calculations were based on Herzfeld's data for the solubility of pure sucrose in water.

Holven (9) in 1942 presented a paper in which he offered for the first time a method for determining the supersaturation of pure sucrose

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² Numbers in parentheses refer to literature cited.

solutions. This method consisted of measuring the boiling point elevation of the sucrose solution above the temperature of the vapor phase. By resorting to the use of special Dühring line charts and formulae, he was, thus, able to determine the supersaturation of sucrose solutions.

Using this concept, Holven (10) had designed and patented in 1938 an instrument for the continuous measurement and indication of supersaturation. At that time, 1938, he found it necessary to assume, for practical purposes all Dühring lines for sucrose solutions were straight lines. This was necessary in order to construct a workable instrument. The error as a result of the above simplification in assuming straight Dühring lines as compared to the actual curved lines is not great. Gillett (11) in his book on "Low Grade Sugar Crystallization" adheres to the original concept as established by Holven. Webre (12) in his many writings uses Gillett's book as a basis for his work.

In 1954 Miller (13) presented a paper describing his company's (Minneapolis-Honeywell Regulator Company) adaptation of the Holven patents to their design of Supersaturation Meter. By 1954 instrument design techniques were such that it was possible for the designers to permit the concept of curved Dühring lines to enter their thinking. Also, in order to bring their basic data up to date this group also used Taylor's solubility data and Spengler's boiling point elevation data. It may be interesting to note that Holven's instrument and the Minneapolis-Honeywell instrument both have facilities for making a purity adjustment during the boiling of the strike.

With the preceding brief discussions and history of the subject of solubility, and supersaturation of pure sucrose solutions as a background, I would like to proceed at once to the main topic of my paper.

First, we shall take Taylor's (1) equation for "The Solubility at High Temperatures of Pure Sucrose in Water" and calculate the sucrose concentrations at saturation 1.00 for solution temperatures from 30° C. to 100° C. Taylor's work was done in the temperature range from 64° C. to 82° C. However, as pointed out in Taylor's paper others have confirmed the validity of the equation at the low temperature of 25° C. and with but few misgivings I have also proceeded to calculate concentrations at saturations for temperatures of 90° C. and 100° C.

Taylor's equation for the solubility curve of sucrose is, $C = 63.608 + 0.1322t + 0.000722t^2$, where C is the concentration in grams per 100 grams of solution, or degrees Brix, and t is the saturation temperature, degrees Centigrade. Concentration can also be expressed as S,

where $S = \frac{s}{w} = \frac{C}{100-C}$, where $\frac{s}{w}$ is the ratio of sucrose to water and C is the concentration of sucrose in solution as derived from Taylor's formula. Table I shows C the concentration, and S the ratio of sucrose to water. These data are also displayed on Chart A in the form of S vs. t. S is plotted to a logarithmic scale and t, solution temperature, is plotted to a linear scale. An auxiliary scale is plotted along the right margin of the chart and is in equivalent values of C, or degrees Brix.

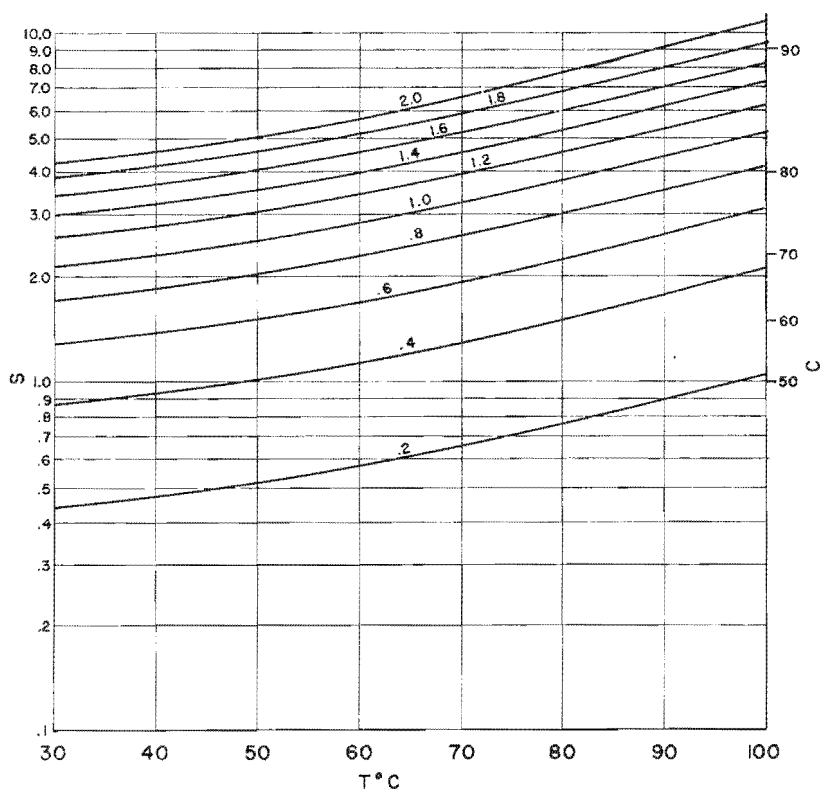


Chart A.—Saturation curves for pure sucrose.

Table I.—Saturation Concentrations vs. Temperature at 100 Purity.

T° C.	C	S
	$C = 63.608 - 0.13221t + 0.000722t^2$	
	$S = \frac{s}{w} = \frac{C}{100-C}$	
100	84.018	5.269
90	81.354	4.363
80	78.805	3.718
70	76.400	3.237
60	74.147	2.868
50	72.023	2.571
40	70.051	2.339
30	68.224	2.147

In addition to the saturation 1.00 line as plotted on Chart A, from Table I, there are also lines for several supersaturation values and for several undersaturation values. These can be calculated from S for saturation 1.00 as follows: For example, at a given temperature t , S' for supersaturation 1.60 would be $1.60 \times S$; likewise S' for undersaturation 0.60 would be

0.60 x S. Similarly, any other values of S' for supersaturations other than 1.00 can be found by multiplying S at saturation 1.00 by the desired degree of supersaturation. When these other supersaturation lines are plotted on Chart A, they form a family of curves parallel to the saturation 1.00 line. The value of using semi-logarithmic coordinates becomes immediately apparent when one studies the complete family of curves on Chart A.

Next we shall take the "Boiling Point Elevation Equation for Pure Sucrose," by Spengler (2) and calculate the Boiling Point Elevation for various concentrations C at a vapor temperature of 100° C. Log_{10} B.P.E. = $2.6157 \times 10^{-6}C^3 - 4.0185 \times 10^{-4}C^2 + 4.2567 \times 10^{-2}C - 1.1979$. These data are presented in Table 2.

Table 2.—B.P.E. vs. Concentration at 100 Purity.

Log_{10} B.P.E. = $2.6157 \times 10^{-6}C^3 - 4.0185 \times 10^{-4}C^2 + 4.2567 \times 10^{-2}C - 1.1979$									
$F_t = \frac{(T_t)^2}{(T_{100})^2} \frac{L_{100}}{L_t}$									
Vap.	T°C	100	90	80	70	60	50	40	30
	Ft	1.000	.9363	.8755	.8180	.7630	.7108	.6607	.6135
	S				B.P.E.				
10.00	20.70	19.38	18.16	16.93	15.79	14.71	13.68	12.70	11.82
9.00	19.27	18.04	16.91	15.76	14.70	13.70	12.73	11.82	10.85
8.00	17.69	16.56	15.52	14.47	13.50	12.57	11.69	10.85	10.02
7.00	15.93	14.92	13.98	13.03	12.15	11.32	10.53	9.77	9.02
6.00	13.98	13.09	12.27	11.44	10.67	9.94	9.24	8.58	7.94
5.00	11.81	11.06	10.36	9.66	9.01	8.39	7.80	7.24	6.70
4.00	9.44	8.84	8.31	7.72	7.20	6.71	6.24	5.79	5.35
3.00	6.88	6.44	6.04	5.63	5.25	4.89	4.55	4.22	3.90
2.00	4.25	3.98	3.73	3.48	3.24	3.02	2.81	2.61	2.41
1.00	1.79	1.68	1.57	1.46	1.37	1.27	1.18	1.10	1.02
0.50	0.74	0.69	0.65	0.61	0.56	0.53	0.49	0.45	0.41

In order to calculate the Boiling Point Elevation for Pure Sucrose solutions at a given vapor temperature less than 100° C. we must calculate a correction factor in the following manner:

$F_t = \frac{(T_t)^2}{(T_{100})^2} \frac{L_{100}}{L_t}$ where F_t is the correction factor at the given vapor temperature, T_t is the absolute vapor temperature °Kelvin for the given vapor temperature, T_{100} is the absolute vapor temperature °Kelvin equivalent to 100° C., L_{100} is the latent heat of the vapor 100° C., and L_t is the latent heat of the vapor at the given vapor temperature t. $\text{B.P.E.}_t = F_t \times \text{B.P.E.}_{100}$.

The correction factor F_t , and the B.P.E. data for vapor temperatures less than 100° C. are also presented in Table 2.

Chart B is a repetition of Chart A but with the addition of the B.P.E. data plotted from Table 2. A close study of Chart B will reveal that it is now possible for one to determine the B.P.E. and/or the solution temperature when one is given the vapor temperature and the degree of supersaturation of the solution. Conversely, given the vapor temperature and the solution temperature one can determine the degree of supersaturation of pure sucrose solutions.

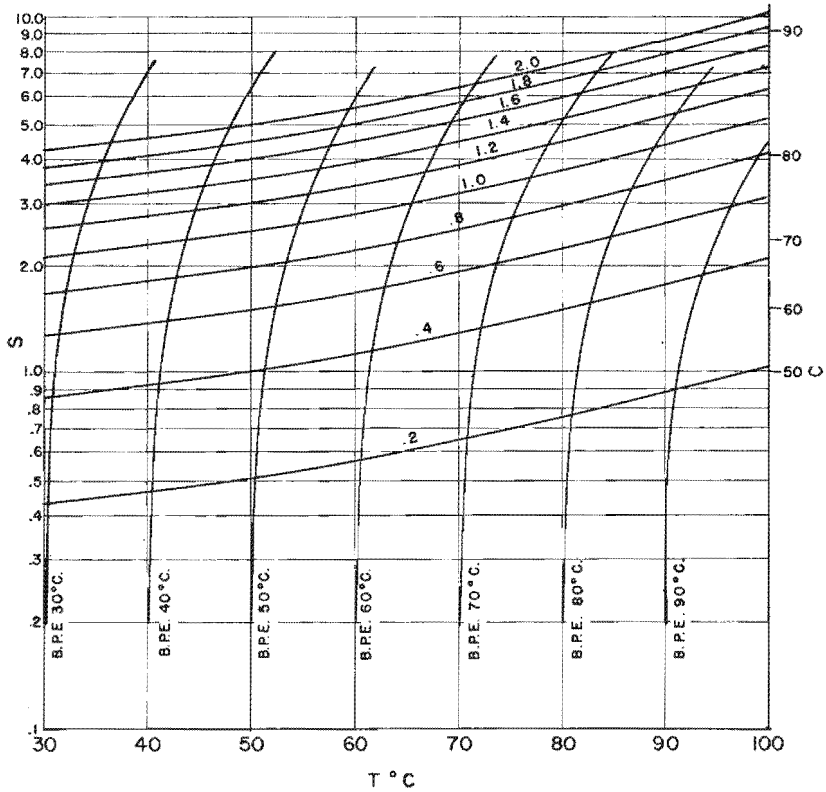


Chart B.—B.P.E. vs. saturation at 100 purity.

Table 3.—B.P.R. vs. Supersaturation at 100 Purity

Vap. T °C	50	60	65	70	80
S.S.					
0.60	2.26	2.81	3.15	3.57	4.63
0.80	3.27	4.06	4.56	5.15	6.71
1.00	4.32	5.36	6.01	6.79	8.86
1.20	5.39	6.68	7.48	8.44	10.98
1.30	5.92	7.33	8.21	9.25	12.02
1.40	6.46	7.98	8.93	10.05	13.03
1.60	7.50	9.24	10.32	11.59	14.94
1.80	8.52	10.45	11.64	13.03	16.72
2.00	9.49	11.60	12.89	14.41	18.34

In order that the above data can be used readily in the sugar factory, I have calculated the exact intersections of the supersaturation lines and the B.P.E. lines for a range of vapor temperatures from 50° C. to 80° C. and for supersaturations from 0.60 to 2.00. Special emphasis is given to vapor temperature 65° C. and supersaturation 1.30. The B.P.E. values are accurate to plus or minus 0.01° C. These data are recorded in Table 3, and

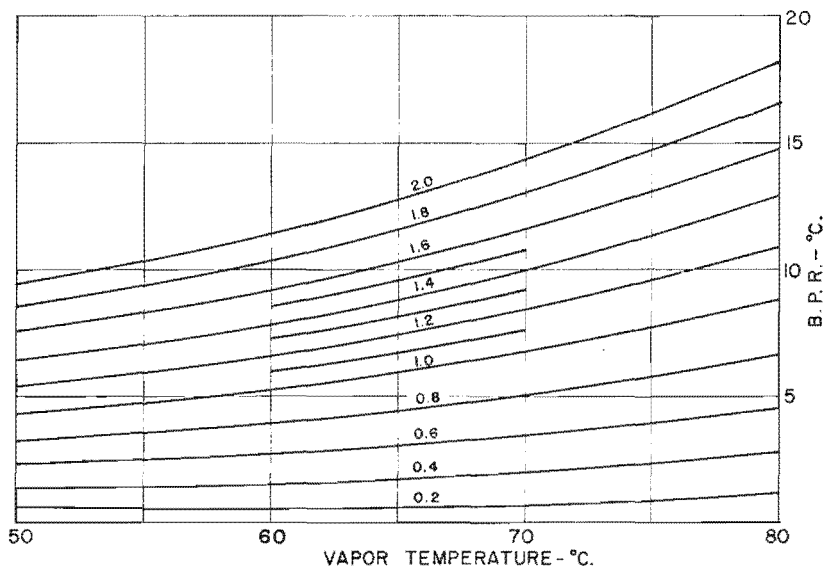


Chart C.—Saturation values at 100 purity for B.P.R. vs. vapor T.^o C.

are plotted on Chart C. Note that in Table 3 and on Chart C I have changed the nomenclature for Boiling Point Elevation to Boiling Point Rise, or simply B.P.R. It appears that the latter term is more widely used than the former.

During the earlier phases of this investigation, purity correction was overly simplified; i.e., for example, at a purity of 80 percent the saturation 1.00 curve for 80 percent purity was assumed to be identical with that of the supersaturation 1.25 curve for purity 100 percent, and Spengler's B.P.E. curve for purity 80 percent was used to determine the B.P.E. values at 80 percent purity. Similar data were developed for other purities and the data were interpolated for use with the lower purity liquors in the sugar factory. We found that these data were not accurate; in fact, they were so far from being accurate that we discarded this method of correcting for purity changes.

During this campaign, 1955-56, we discovered that the B.P.R. data for white sugar boiling has varied by as much as 3° C. from the beginning of campaign to the present. This, in spite of the fact that we have endeavored to maintain a standard liquor purity within plus or minus 0.5 points of the desired purity. The only conclusion we can draw is the nature and solubility of the non-sugars has varied so greatly during the campaign as to make our former concepts of B.P.R. at saturation versus purity inadequate in explaining the differences. This has given us considerable justification for embarking on a line of study which will aid in correlating saturation, boiling point rise, purity, and the nature of the non-

sugars into a more workable form. Therefore, at this time I have chosen to confine the discussion to the one case for 100 percent pure sucrose, and to point out that considerable work must be done before we can extend this study to include the lower purity liquors.

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