

Boiling Points of Aqueous Solutions of Dextrose Within the Pressure Range of 200 to 1,500 Millimeters

By John L. Torgesen,¹ Vincent E. Bower, and Edgar R. Smith

By using twin ebulliometers of the Swietoslawski type, with water as the reference standard, data were obtained on the vapor-pressure-temperature relationship for aqueous solutions of dextrose. The pressures ranged from 200 to 1,500 millimeters and the concentrations of the solutions from 10 to 60 percent of dextrose by weight. The vapor-pressure-temperature relationship is expressed by equations of the form

$$\log_{10} p = A - \frac{B}{C+t}$$

in which p is the vapor pressure in standard millimeters of mercury exerted by a solution of a given concentration at the temperature, t , in degrees Celsius. A , B , and C are constants. The boiling-point elevations of aqueous dextrose solutions at a given pressure are expressed by equations of the form

$$\log_{10} \Delta t = \alpha + \beta c + \gamma c^2 + \delta c^3$$

in which Δt represents the boiling-point elevation in degrees Celsius at a given pressure, c is the concentration in weight percentage of dextrose, and α , β , γ , and δ are constants.

I. Introduction

The boiling points and boiling-point elevations of aqueous solutions of dextrose within the pressure range of 200 to 1,500 mm and the concentration range of 10 to 60 percent of dextrose by weight are reported in this paper. This work is part of a program sponsored by the Corn Industries Research Foundation to obtain physical data for materials of importance in the manufacture of various corn products.

The method used was a comparative dynamic one for measuring successively, with the same thermometer, the boiling point of a given solution and that of water in twin ebulliometers connected to a manostat. A series of corresponding boiling points of the solutions and of water at various pressures was thus obtained. The values of t_s , the boiling point of a solution of dextrose, and t_w , the corresponding boiling point of water at the various pressures were related by equations of the form

$$t_s = a + b t_w + c t_w^2 \quad (1)$$

in which the constants a , b , and c for each concentration of dextrose were evaluated by the method of least squares. The values of t_w and the corresponding pressures taken as reference standards were selected from the compilation of Osborne, Stimson and Ginnings [1]² and have previously been tabulated in convenient form [2].

No equation was found to relate the boiling points of the solutions to their concentrations, at a given pressure, with the precision of the experimental data. For this reason the boiling points of solutions

of even values of concentration were obtained graphically by plotting Δt , the boiling point elevation given by the difference between t_s and t_w , with respect to the concentration (or Δt /concentration versus concentration). From the resultant series of curves, one for each of the standard reference pressures, the values of Δt for even concentrations of dextrose were obtained, and the boiling points of the solutions were evaluated by adding the corresponding boiling point of water. These boiling points of the solutions were tabulated with their corresponding pressures and the constants A , B , and C in the Antoine equation [3]

$$\log p = A - \frac{B}{C+t} \quad (2)$$

were evaluated to obtain the relationship between vapor pressure and temperature for each of the several even concentrations. (The symbol "log" is used in this paper to denote the logarithm to the base 10.) Equation 2 is explicit in temperature when written in the form $t = B/(A - \log p) - C$. Also

$$\frac{dp}{dt} = \frac{p(A - \log p)^2}{B \log e} \quad (3)$$

The best equation that was found to represent the relationship between the measured boiling point elevations and the concentrations is of the form [4]

$$\log \Delta t = \alpha + \beta c + \gamma c^2 + \delta c^3 \quad (4)$$

in which the constants α , β , γ , and δ were evaluated by the method of least squares. But a comparison of the computed with the observed values of the boiling point elevation at a given pressure shows deviations that are several times larger than the precision of the original data.

¹ Research Associate at the National Bureau of Standards, representing the Corn Industries Research Foundation.

² Figures in brackets indicate the literature references at the end of this paper.

II. Apparatus and Materials

Except for minor changes, the apparatus was the same as described in a previous paper [2]. Two simple barometric ebulliometers, of the type developed by Swietoslawski [5], were sealed to a manostat. In the case of the solution ebulliometer, a flask containing water was interposed to inhibit the loss of water vapor from the solution to the manostat. Pressures below atmospheric were obtained with a mechanical pump, and those above were obtained by the addition of nitrogen from a cylinder.

The solutions of dextrose were prepared from NBS Standard Sample dextrose previously dried in a vacuum oven at 60° to 70° C for 6 hours and weighed into known weights of water. All concentrations, expressed in weight percentage on a vacuum basis, are corrected for the vapor and liquid hold-up that prevailed in the ebulliometer during the boiling procedure. Crystalline α -dextrose undergoes mutarotation in aqueous solution to form an equilibrium mixture of α - and β -dextrose [6]. The rate of the conversion is dependent on the temperature and pH of the solution, and the equilibrium amounts of α - and β -dextrose present depend on the temperature and concentration of the solution. Hence the solutions studied contained a mixture of α - and β -dextrose. However, since both forms possess identical molecular weights, no effect on the boiling point or the vapor pressure of a solution is to be expected as a result of different ratios of the two isomeric forms at different temperatures and concentrations.

The solution ebulliometer was charged with a known weight and volume of solution, the water ebulliometer with the proper volume of distilled water and the filling tubes sealed off. Boiling temperatures were measured at as near the same boiling rate as could conveniently be achieved, the rate being controlled to return approximately 20 drops of condensate per minute to the boiler as observed in the drop-counter placed in the return tube. This boiling rate approximates the midpoint of the flat constant-temperature portion of the curve obtained by plotting boiling temperature with respect to boiling rate [5] and was determined by initial experiments. The comparative measurements of temperature were made with a platinum resistance thermometer (coiled filament type) and a Mueller thermometer bridge by the method described in another paper from this laboratory [7]. The temperatures were measured to 0.001 deg C, with an average reproducibility of 0.002 to 0.003 deg C and an estimated accuracy of 0.005 deg C on the International Temperature Scale. It was not necessary to hold the bridge at constant temperature, as the temperature corrections to the resistances were practically identical for the temperatures of the reference and measured substances in these comparative measurements.

The ratios of the boiling points of the solutions to those of water at normal atmospheric pressure taken at the beginning and end of a series of measurements did not differ by more than 0.008 percent in

the extreme case of the most concentrated solution. The average difference for the several concentrations studied was 0.003 percent. Refractive index measurements on the original and boiled solutions were practically identical. It is believed that no significant change in concentration occurred during the boiling procedure, although the solutions of higher concentration assumed a slight yellowish tint, particularly after boiling at the higher pressures. Specific rotations were not measured.

III. Experimental Results

The correction for the water vapor and liquid hold-up in the ebulliometer, to be applied to the concentrations of the solutions as originally prepared, was determined experimentally by using solutions of sodium chloride. For this purpose, a stopcock was sealed temporarily at the bottom of the solution ebulliometer for rapid withdrawal of samples while boiling. Solutions of sodium chloride of different known concentrations were placed in the solution ebulliometer and boiled in the usual fashion at normal atmospheric pressure. When boiling equilibrium had become established, as evidenced by steady boiling temperatures, a 25-ml sample was quickly withdrawn into a flask that was surrounded by ice water to minimize the loss of water vapor.

TABLE 1. Determination of ebulliometer hold-up

Charge	Original concentration of NaCl	Boiling rate	Boiling concentration of NaCl	Hold-up
<i>g</i>	<i>Percent</i>	<i>Drops/min</i>	<i>Percent</i>	<i>g</i>
65.086	11.760	12	11.873	0.62
65.110	11.760	20	11.891	.71
65.135	11.760	30	11.898	.75
70.008	22.195	12	22.391	.61
69.963	22.195	20	22.413	.68
70.087	22.195	30	22.440	.76

The samples were analyzed for sodium chloride by evaporation to dryness in platinum dishes on a steam bath, followed by heating to incipient fusion and weighing the sodium-chloride residue. The difference in concentration between the original and the boiling solution, together with the knowledge of the amount of original charge in the ebulliometer, provided data for the calculation of the hold-up of liquid and vapor while boiling was taking place at normal atmospheric pressure. It was assumed that the liquid hold-up remains essentially constant at all pressures involved. The vapor hold-up, which depends on the pressure and temperature, could be closely estimated from the knowledge of the free volume of the ebulliometer. Since this method of determining the hold-up may be of interest, the results are given in table 1. From these results, the amount of liquid and vapor hold-up at 20 drops a minute, which was the boiling rate employed in this work, was taken as 0.68 g, of which 0.61 g is attributed to liquid hold-up on the walls of the apparatus, and 0.07 g is a calculated value for the

TABLE 2. Corresponding boiling points of dextrose solutions and water

10.34- percent solution	Water	21.26- percent solution	Water	32.50- percent solution	Water	40.31- percent solution	Water	50.54- percent solution	Water	59.60- percent solution	Water	63.23- percent solution	Water
°C	°C												
100.054	99.724	100.567	99.788	101.286	99.869	101.686	99.686	103.237	100.083	104.806	100.059	105.386	99.867
100.063	99.732	100.563	99.783	101.293	99.878	101.685	99.684	103.246	100.072	104.813	100.066	101.183	99.745
94.182	93.883	94.267	93.514	95.533	94.163	95.288	93.330	99.271	96.170	98.302	93.711	96.579	91.272
94.200	93.881	94.273	93.520	95.520	94.490	95.725	95.879	103.323	100.140	99.890	96.462	91.387	96.222
86.414	86.109	86.927	86.207	81.624	80.358	80.303	78.523	99.134	96.044	80.696	76.489	84.844	79.809
86.433	86.128	86.940	86.220	92.864	91.513	90.033	91.122	94.684	91.673	69.077	65.082	76.696	71.771
75.946	75.652	76.675	75.992	101.389	99.965	101.483	99.472	99.448	86.522	90.314	86.488	105.293	99.742
75.977	75.684	76.704	76.021	101.653	100.229	101.701	99.686	82.844	80.011	104.634	99.882	110.639	104.931
100.261	99.929	64.876	64.232	101.653	100.233	101.698	99.688	75.432	72.705	111.295	106.362	115.148	109.315
100.261	99.928	64.940	64.292	106.877	105.417	106.970	104.898	103.161	99.985	117.229	112.147	119.269	113.303
105.559	105.218	78.142	77.455	111.307	109.798	111.431	109.306	103.162	99.990	122.262	117.038	122.863	116.788
105.562	105.220	87.363	86.638	115.220	113.683	115.416	113.248	108.270	105.011	125.670	120.369	126.482	120.304
109.860	109.507	94.560	93.793	118.782	117.212	119.115	116.895	112.778	109.442	116.143	111.123	105.324	99.795
109.882	109.511	100.616	99.632	122.419	120.805	122.526	120.264	116.880	113.457	104.542	99.828		
113.867	113.508	100.791	100.007	101.522	100.098	116.730	114.542	120.461	116.972				
113.873	113.512	105.994	105.186				110.091	107.987	123.864	120.324			
117.356	116.988	110.293	109.463				101.731	99.722	103.181	100.031			
117.364	116.994	114.495	113.649										
120.838	120.461	117.897	117.030										
120.844	120.462	121.007	120.118										
118.216	117.843												
118.224	117.850	117.891	117.023										
114.205	113.843	114.405	113.556										
114.214	113.851	110.298	109.469										
110.450	110.095	105.652	105.044										
110.458	110.104	100.689	99.907										
106.190	105.844												
106.200	105.855												
100.266	99.934												
100.230	99.896												
100.235	99.902												
94.021	93.699												
94.034	93.712												
86.212	85.905												
86.228	85.922												
76.098	75.799												
78.124	75.825												
62.585	62.297												
62.641	62.344												
77.031	76.732												
86.288	85.982												
94.084	93.783												
100.080	99.747												

vapor hold-up at 760-mm pressure and the boiling temperature. At 200- and 1,500-mm pressure the calculated vapor hold-up is 0.02 and 0.12 g, respectively, giving a total hold-up at these extreme pressures of 0.63 and 0.71 g, respectively, assuming that the liquid hold-up remains constant over this pressure range.

The comparative boiling points of dextrose solutions of several concentrations and water, in the order as actually measured, are given in table 2. The concentrations listed are those prevailing during the boiling procedure at 760-mm pressure. The change in concentration accompanying the change in vapor hold-up with variation of the pressure is small but can be significant, particularly for the more concentrated solutions. For example, a 10-percent solution changes in concentration by -0.01 percent at 200 mm and by +0.01 percent of dextrose at 1,500 mm. A 60-percent solution changes by -0.04 and +0.04 percent at these extreme pressures.

By means of eq 1 the boiling points of the dextrose solutions were expressed as functions of the boiling points of water over the pressure range involved. The constants *a*, *b*, and *c* for each of the solutions are given in table 3. The average and maximum devia-

tions of the experimental points from those calculated by eq 1 with the appropriate constants are given in the last two columns. The average deviations increase from ±0.002 deg C in the case of the more dilute solutions to ±0.013 deg C for the most concentrated solution. An explanation for the increasing experimental deviations at higher concentrations of dextrose is that the boiling equilibrium in the latter cases is established with less certainty. The pumping action in the ebulliometers is probably less efficient because of the increased viscosity of the solutions and, also, the concentration of the solution in the boiler may vary due to incomplete mixing of the condensate with the highly concentrated solution.

The boiling temperatures of the solutions at the standard reference pressures were calculated by means of eq 1 with the constants from table 3. The difference between the boiling temperatures of solution and water at a given pressure represents the boiling-point elevation, Δt , at that pressure. For each reference pressure, Δt was plotted with respect to the concentration on a scale that permitted the plotting and reading of temperatures to ±0.005 deg C and of concentrations to ±0.01 percent of dextrose.

Values of Δt at even concentrations were read from the curves and added to the corresponding boiling points of water to obtain the boiling temperatures of the solutions listed in table 4 at the reference pressures. A separate set of the constants A , B , and C in eq 2 was evaluated to fit the data for each solution given in table 4. Values of the constant C were determined by the method of averages, followed by an evaluation of constants A and B by the method of least squares. The values of the constants are given in table 5. The over-all average deviation of the vapor-pressure-temperature relationships ex-

TABLE 4. Boiling points of dextrose solutions at standard reference pressures

Pressure	Boiling point of water	Boiling point of solutions					
		10%	20%	30%	40%	50%	60%
mm Hg	°C	°C	°C	°C	°C	°C	°C
187.57	65	65.277	65.600	66.047	66.624	67.555	69.045
233.72	70	70.280	70.615	71.073	71.670	72.625	74.137
289.13	75	75.284	75.631	76.101	76.718	77.697	79.235
355.22	80	80.289	80.648	81.130	81.767	82.772	84.338
433.56	85	85.295	85.666	86.161	86.818	87.849	89.446
525.86	90	90.302	90.685	91.194	91.871	92.929	94.560
633.99	95	95.310	95.705	96.229	96.926	98.011	99.680
760.00	100	100.319	100.728	101.265	101.983	103.096	104.804
906.06	105	105.329	105.748	106.303	107.042	108.183	109.935
1,074.58	110	110.340	110.771	111.343	112.102	113.273	115.070
1,268.03	115	115.352	115.793	116.385	117.163	118.365	120.212
1,489.14	120	120.365	120.819	121.428	122.226	123.460	125.359

TABLE 3. Boiling points of dextrose solutions in terms of the boiling points of water

$t_s = a + bt_s + ct_s^2$					
Concentration of dextrose	a	b	c	Average deviation	Maximum deviation
Percent				°C	°C
10.34	0.3376	0.997929	0.2011×10^{-4}	± 0.002	± 0.003
21.26	.5516	.999929	.2377	$\pm .002$	$\pm .004$
32.50	.9815	1.000342	.4030	$\pm .003$	$\pm .005$
40.31	1.2027	1.004451	.3826	$\pm .004$	$\pm .007$
50.54	1.9000	1.007563	.5115	$\pm .007$	$\pm .012$
59.69	3.2872	1.008318	1.0854	$\pm .009$	$\pm .026$
63.23	4.7004	.988355	2.0042	$\pm .013$	$\pm .023$

pressed by eq 2 is ± 0.04 mm. The larger maximum deviations shown in the last column of table 5 were at the highest pressure, 1489.14 mm, in every case. Values of the temperature and rates of change of pressure with temperature at even values of the pressure are given in table 6.

The relationship between boiling point elevation and concentration was obtained by using the data in table 3 to calculate the boiling points of the solutions and boiling point elevations at the reference pressures. From the tabulations of Δt and concentration at a given pressure the constants α , β , γ , and δ in eq 4

were evaluated by the method of least squares. These constants are given in table 7 for several reference pressures over the range 200 to 1,500 mm. As the deviations given in the last two columns are considerably larger than the experimental precision, these equations were not used to evaluate Δt . They

TABLE 5. Vapor-pressure-temperature relationships of dextrose solutions

$\log p = A - \frac{B}{C+t}$					
Concentration of dextrose	A	B	C	Average deviation	Maximum deviation
Percent				mm Hg	mm Hg
10	7.912637	1636.365	224.883	± 0.03	± 0.08
20	7.902317	1633.713	224.618	$\pm .05$	$\pm .14$
30	7.900496	1637.294	224.907	$\pm .05$	$\pm .25$
40	7.888662	1638.304	224.764	$\pm .01$	$\pm .02$
50	7.853013	1622.430	223.205	$\pm .05$	$\pm .11$
60	7.779591	1587.450	219.244	$\pm .04$	$\pm .17$

TABLE 6. Values of pressure, temperature, and rates of change of pressure with temperature for dextrose solutions

Pressure	Concentration of dextrose solutions											
	10 Percent		20 Percent		30 Percent		40 Percent		50 Percent		60 Percent	
	Temperature	dp/dt	Temperature	dp/dt	Temperature	dp/dt	Temperature	dp/dt	Temperature	dp/dt	Temperature	dp/dt
mm Hg	°C	mm/°C	°C	mm/°C	°C	mm/°C	°C	mm/°C	°C	mm/°C	°C	mm/°C
*100	51.87	4.92	52.17	4.91	52.58	4.90	53.11	4.88	53.99	4.86	55.42	4.85
200	66.72	8.86	67.05	8.84	67.50	8.82	68.08	8.79	69.02	8.75	70.51	8.71
300	76.17	12.47	76.52	12.45	76.99	12.41	77.61	12.36	78.59	12.31	80.14	12.24
400	83.25	15.87	83.62	15.84	84.11	15.79	84.76	15.73	85.77	15.65	87.36	15.55
500	88.98	19.13	89.36	19.08	89.87	19.03	90.54	18.95	91.58	18.85	93.21	18.72
600	93.82	22.26	94.21	22.20	94.73	22.14	95.42	22.05	96.50	21.93	98.16	21.77
700	98.03	25.30	98.43	25.23	98.96	25.16	99.67	25.06	100.77	24.92	102.46	24.72
760	100.32	27.08	100.73	27.01	101.27	26.93	101.98	26.82	103.10	26.67	104.81	26.46
800	101.77	28.25	102.18	28.18	102.72	28.10	103.44	27.98	104.56	27.82	106.29	27.59
900	106.14	31.14	105.55	31.06	106.11	30.97	106.85	30.84	107.99	30.65	109.74	30.40
1,000	108.21	33.96	108.64	33.87	109.20	33.77	109.95	33.63	111.11	33.43	112.89	33.14
1,100	111.04	36.73	112.47	36.63	112.05	36.53	112.81	36.37	113.99	36.14	115.79	35.82
1,200	113.67	39.45	114.11	39.34	114.69	39.23	115.46	39.06	116.65	38.81	118.48	38.46
1,300	116.12	42.12	115.57	42.01	117.15	41.89	117.94	41.71	119.15	41.44	121.00	41.05
1,400	118.42	44.76	118.87	44.64	119.47	44.50	120.26	44.31	121.49	44.02	123.36	43.60
1,500	120.59	47.35	121.05	47.22	121.65	47.08	122.46	46.88	123.70	46.57	125.59	46.11
*1,600	122.65	49.91	123.11	49.78	123.72	49.63	124.54	49.41	125.79	49.08	127.70	48.59

* Extrapolated values.

TABLE 7. Boiling-point elevation of dextrose solutions

$\log \Delta t = \alpha + \beta C + \gamma C^2 + \delta C^3$						
Pressure	α	β	γ	δ	Average deviation	maximum deviation
mm Hg					°C	°C
233.72	-0.980843	5.118375×10 ⁻¹	-7.377463×10 ⁻¹	5.528603×10 ⁻⁴	±0.017	+0.032
355.22	-.982743	5.191070	-7.435453	5.463234	±.023	+.045
525.86	-.967871	5.238106	-7.477459	5.427242	±.028	+.055
760.00	-.944029	5.235447	-7.427223	5.345987	±.031	+.061
1,074.58	-.918243	5.251193	-7.490898	5.396036	±.033	+.067
1,469.14	-.885843	5.225459	-7.476027	5.404016	±.033	+.067

are useful, however, in calculating the boiling point elevations of dextrose solutions to within 0.05° to 0.1° C.

Molal boiling point elevations of aqueous solutions of dextrose have been measured by Juettner [8], but only at normal atmospheric pressure. A com-

parison of his values with those of this investigation is given in table 8. Apparently, there are no other published measurements of the vapor pressures of aqueous solutions of dextrose in the range reported in this paper.

IV. References

TABLE 8. Molal boiling-point elevation of dextrose solutions (760 mm Hg)

Molality	Juettner [8]	This paper
	°C/mole	°C/mole
1	0.53	0.520
2	.53	.525
3	.53	.531
4	-----	.537
5	-----	.544
6	-----	.552
7	-----	.561
8	-----	.570
9	-----	.580

- [1] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Research NBS* **23**, 261 (1939) RP1229.
- [2] E. R. Smith, *J. Research NBS* **24**, 229 (1940) RP1280.
- [3] G. W. Thomson, *Chem. Rev.* **38**, 1 (1946).
- [4] F. J. Bates and Associates, *Polarimetry, saccharimetry, and the sugars*, NBS Circular C440, p. 365 (1942).
- [5] W. Swietoslowski, *Ebulliometry* (Reinhold Publishing Corp., New York, N. Y., 1945).
- [6] H. S. Isbell and W. W. Pigman, *J. Research NBS* **18**, 178 (1937) RP969.
- [7] E. R. Smith and H. Matheson, *J. Research NBS* **20**, 641 (1938) RP1097.
- [8] F. Juettner, *Z. physik. Chem.* **38**, 76 (1901); *Int. Crit. Tables III*, 327 (1928).

WASHINGTON, July 17, 1950.

Wavelengths for Calibration of Prism Spectrometers

By Earle K. Plyer and C. Wilbur Peters¹

Several absorption bands of polystyrene, 1,2,4-trichlorobenzene, and other compounds have been measured in the infrared region from 1.5 to 24 μ on grating spectrometers. These bands have been determined with sufficient accuracy for use in calibration of prism instruments. A table is included that gives the cell thicknesses used in the measurements. The emission lines of mercury for the region from 0.5 to 2.4 μ are included. In order that the table may be of most value, a number of bands that have been determined by previous observers have also been included.

Many infrared absorption bands have been carefully measured, and their reported wavelengths [1]² are useful for calibrating spectrometers. Techniques of calibration utilizing vibrational bands with resolved rotational structures, including those of ammonia, carbon dioxide, and water vapor, have been described by Oetjen, Kao, and Randall [2]. When one undertakes to calibrate an infrared spectrometer he soon finds that additional reference lines or bands would be extremely helpful and that the information available has some serious disadvantages. In certain regions there are an insufficient number of

standards. In some cases where a band has a rotational fine structure that is not resolved by a prism, it is not possible to locate any individual band with sufficient precision to justify its use for calibration. Furthermore, some absorbing materials require impractically long absorption cells. To avoid these disadvantages and increase the number of calibration points, additional lines and bands in the region from the visible to 24 μ have been measured by using sources or absorbers convenient for the calibration of prism instruments. These include: (1) polystyrene films and trichlorobenzene, which provide standards between 15 and 24 μ ; (2) AH-4 mercury lamp in the region visible to 24 μ ; (3) toluene at 21.5 μ ;

¹ University of Michigan.

² Figures in brackets indicate the literature references at the end of this paper.