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

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

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

$$\log \Delta t = a + b c + \gamma c^2 + \delta c^3,$$

in which $\Delta t$ represents the boiling-point elevation in degrees Celsius at a given pressure, $c$ is the concentration in weight percentage of dextrose, and $a$, $b$, $\gamma$, and $\delta$ 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

$$t_s = a + b t_w + c t_w^2,$$

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] 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 $\Delta t$, the boiling point elevation given by the difference between $t_s$ and $t_w$, with respect to the concentration (or $\Delta t$/concentration versus concentration). From the resultant series of curves, one for each of the standard reference pressures, the values of $\Delta t$ 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]

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

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

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

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

$$\log \Delta t = a + b c + \gamma c^2 + \delta c^3,$$

in which the constants $a$, $b$, $\gamma$, and $\delta$ 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.

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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 0.005 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

<table>
<thead>
<tr>
<th>Charge</th>
<th>Original concentration of NaCl</th>
<th>Boiling rate</th>
<th>Boiling temperature</th>
<th>Hold-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.006</td>
<td>11.760</td>
<td>32</td>
<td>11.872</td>
<td>0.52</td>
</tr>
<tr>
<td>68.110</td>
<td>11.760</td>
<td>20</td>
<td>11.866</td>
<td>0.71</td>
</tr>
<tr>
<td>70.087</td>
<td>22.135</td>
<td>12</td>
<td>22.301</td>
<td>0.48</td>
</tr>
<tr>
<td>65.565</td>
<td>22.135</td>
<td>20</td>
<td>22.410</td>
<td>0.68</td>
</tr>
<tr>
<td>69.963</td>
<td>22.135</td>
<td>20</td>
<td>22.440</td>
<td>0.75</td>
</tr>
</tbody>
</table>

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
in vapor hold-up with variation of the pressure is small but can be significant, particularly for the pressure range.

By means of eq 1 the boiling points of the dextrose solutions and water, given in the last two columns, are given in table 2. The boiling temperatures of the solutions at the reference pressures were calculated using the formula

\[
\text{Boiling Temperature} = \sum_{i=1}^{n} \text{Boiling Temperature of Component } i \times \text{Percentage of Component } i
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Values of $\Delta t$ 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 expressed by eq 2 is ±0.04 mm. The larger maximum deviations shown in the last column of Table 5 were at the highest pressure, 1480.14 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 $\Delta t$ and concentration at a given pressure the constants $a$, $b$, $c$, and $d$ 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 $\Delta t$. They

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

<table>
<thead>
<tr>
<th>Concentration of dextrose</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>Average deviation</th>
<th>Maximum deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Percent</td>
<td>0.3876</td>
<td>0.00793</td>
<td>0.00413</td>
<td>±0.002</td>
<td>±0.002</td>
</tr>
<tr>
<td>20 Percent</td>
<td>0.3876</td>
<td>0.00793</td>
<td>0.00413</td>
<td>±0.002</td>
<td>±0.002</td>
</tr>
<tr>
<td>30 Percent</td>
<td>0.3876</td>
<td>0.00793</td>
<td>0.00413</td>
<td>±0.002</td>
<td>±0.002</td>
</tr>
<tr>
<td>40 Percent</td>
<td>0.3876</td>
<td>0.00793</td>
<td>0.00413</td>
<td>±0.002</td>
<td>±0.002</td>
</tr>
<tr>
<td>50 Percent</td>
<td>0.3876</td>
<td>0.00793</td>
<td>0.00413</td>
<td>±0.002</td>
<td>±0.002</td>
</tr>
<tr>
<td>60 Percent</td>
<td>0.3876</td>
<td>0.00793</td>
<td>0.00413</td>
<td>±0.002</td>
<td>±0.002</td>
</tr>
</tbody>
</table>

### Table 4. Boiling points of dextrose solutions at standard reference pressures

<table>
<thead>
<tr>
<th>Pressure (mm Hg)</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
<th>40%</th>
<th>50%</th>
<th>60%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dp/dt (mm Hg/°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 5. Vapor-pressure-temperature relationships of dextrose solutions

<table>
<thead>
<tr>
<th>Concentration of dextrose</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>Average deviation</th>
<th>Maximum deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Percent</td>
<td>7.91207</td>
<td>1036.390</td>
<td>224.575</td>
<td>±0.03</td>
<td>±0.03</td>
</tr>
<tr>
<td>20 Percent</td>
<td>7.92007</td>
<td>1037.390</td>
<td>224.575</td>
<td>±0.03</td>
<td>±0.03</td>
</tr>
<tr>
<td>30 Percent</td>
<td>7.92010</td>
<td>1037.390</td>
<td>224.575</td>
<td>±0.03</td>
<td>±0.03</td>
</tr>
<tr>
<td>40 Percent</td>
<td>7.92005</td>
<td>1037.390</td>
<td>224.575</td>
<td>±0.03</td>
<td>±0.03</td>
</tr>
<tr>
<td>50 Percent</td>
<td>7.92006</td>
<td>1037.390</td>
<td>224.575</td>
<td>±0.03</td>
<td>±0.03</td>
</tr>
<tr>
<td>60 Percent</td>
<td>7.92008</td>
<td>1037.390</td>
<td>224.575</td>
<td>±0.03</td>
<td>±0.03</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Pressure (mm Hg)</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
<th>40%</th>
<th>50%</th>
<th>60%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dp/dt (mm Hg/°C)</td>
<td></td>
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</tr>
</tbody>
</table>

* Extrapolated values.
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 comparison 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


WASHINGTON, July 17, 1950.

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### Wavelengths for Calibration of Prism Spectrometers

By Earle K. Plyer and C. Wilbur Peters

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 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) AlI-4 mercury lamp in the region visible to 24 μ; (3) toluene at 21.5 μ;