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SOME PHYSICAL PROPERTIES OF MANNITE AND ITS AQUEOUS SOLUTIONS.[1]

BY JOSEPH M. BRAHAM.

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This study was made in connection with an investigation on the laws of aqueous solutions. The compound, which is also termed mannitol and hexanhexol, is of interest in the latter connection since it contains a comparatively large number of hydroxyl groups. The literature on the subject is not very complete and very little recent work has been done on it. This paper presents the results of the study and includes a brief statement of earlier work on the subject.

I. Purification of Mannite.

An investigation was first made to ascertain the number of recrystallizations of commercial mannite that are required to yield a pure product, the melting point being the criterion of purity. The material was dissolved in distilled water at a temperature near 80°, forming an almost saturated solution. This solution was filtered to remove the suspended impurities which were present in considerable quantity, then cooled to

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[1] This article is based on a thesis submitted by the writer in 1915 to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Master of Science.

about 40° and alcohol added to reduce the solubility. The crystals were freed from the liquid as completely as possible and then dried in an electric oven at 120–130° for several hours. The second crystallization was made by dissolving the crystals, from which the mother liquor had been removed, in pure, hot water, allowing the solution to cool and then adding alcohol; a similar procedure was followed in the third and fourth crystallizations. Another lot was purified in precisely the same manner except that no alcohol was used and contact of the crystals with the filter paper was avoided, but no difference in the purity of the two lots could be distinguished.

II. Melting Point of Pure Mannite.

The most extensive set of determinations described in the literature was made by Landolt.[1] He found the freezing point of a mass consisting of 620 g. of mannite to be 165.69°; with a much smaller quantity of material the melting point was 165.73° and the freezing point 165.64°. Using an apparatus designed to avoid stem correction, the values 166.97° and 167.04° were obtained; the latter values are undoubtedly too high. The results obtained by other investigators are: Favre,[2] 166° (freezing point 162°); Stohmann and Langhein,[3] 166°; and Kroft and Dyes,[4] 166°. Since the true value is thus uncertain, this property was investigated.

A nitrogen filled mercury thermometer which had been checked by the Bureau of Standards was employed. It was graduated in 0.1°, ruled directly on the stem; readings to 0.01° were made with the aid of a reading glass. Three auxiliary thermometers were employed to determine the temperature of the emergent stem at various heights. The equilibrium mixture of mannite crystals and liquid was contained in a small Dewar tube closed by a tin foiled cork and stirred with a small glass rod with a loop at one end. The mannite was heated to about 175° in an electric oven or very carefully over a gas flame and the liquid poured into the previously heated Dewar tube. It was found impossible to obtain a perfectly clear liquid by either method of heating, the slight brown color seeming to indicate that carbonization occurs to a very limited extent; the color was first ascribed to the presence of fine filter paper shreds, but it was later observed in fused material with which special precautions had been taken to avoid contamination from that source. When the temperature of the liquid in the Dewar had dropped to about 170°, pure crystals were added. A temperature which remained constant for several minutes was soon reached. The following results were obtained:

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[1] *Z. physik. Chem.*, 4, 366 (1889).

[2] *Ann. chim. phys.*, [3] 11, 71 (1844).

[3] *J. prakt. Chem.*, [2] 45, 305 (1892).

[4] *Ber.*, 28, 2583 (1895).

Mannite.	Melting point.
Original material	165.10°
First crystallization	165.84
Second crystallization	166.05
Third crystallization	166.05
Fourth crystallization	166.05

It is evident from these data that two crystallizations of commercial mannite are necessary as well as sufficient for the production of pure mannite.

III. Specific Rotation.

Of the 3 optical forms of mannite, the so-called dextro form, which is actually levorotatory, is the most common. Very few determinations of the specific rotation of pure mannite in aqueous solutions have been made, although the literature contains numerous references to measurements on solutions of mannite with some other constituent such as borax, boric acid or sodium hydroxide. In 1873, G. Bouchardat[1] found that the rotation was less than 0.2° which was the smallest value then measurable, but the fact that it really was optically active was shown the following year by L. Vignon[2] in his researches on mannite solutions containing borax or boric acid. Using a greatly improved apparatus, G. Bouchardat[3] later found the specific rotation to be $[\alpha]_j \doteq -0.25°$ (estimated to be —0.23° referred to the sodium D line), the temperature of the solution not being given. In 1875, L. Vignon[4] again studied this property of mannite in pure aqueous solutions and found the following values, each of which is the average of 10 readings: $[\alpha]_D = 0.204°$, 0.260°, and 0.232°. The temperature of the solution was not stated.

Since no more recent determinations had been made, it seemed desirable to determine this constant with greater accuracy. A sample of purified mannite was fused to eliminate completely all traces of moisture and then finely powdered; but solutions from this material possessed a slight brown color which made satisfactory illumination of the solution impossible. Samples which had been thoroughly dried but not fused were therefore used. The solutions were prepared by dissolving 17.6067 g. of mannite in distilled water and making up to 100 cc. at 25°.

A triple field Schmidt and Haensch polarimeter fitted with a 100 cm. jacketed tube was used, and the solution under examination kept at 25°. A quartz mercury vapor lamp furnished the light, which was further purified by passing it through a spectroscope, the green E-line of mercury being employed. The specific rotation was found to be $[\alpha]^{25}_E = -0.244° \pm 0.002$. The values of —0.244° and —0.245 ± 0.002 were

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[1] *Compt. rend.*, **76**, 1550 (1873).

[2] *Ibid.*, **77**, 1191 (1874).

[3] *Ibid.*, **80**, 122 (1875).

[4] *Ann. chim. phys.*, [5] **2**, 440 (1875).

obtained at the same time by Mr. C. Scholl in this laboratory. Assuming that the same factor (0.8509)[1] may be used in converting the value referred to the mercury E line to the sodium D line as found for quartz, the rotation becomes $[\alpha]_D^{25} = -0.208 \pm 0.002$.

IV. Solubility—Freezing-Point Measurements.

At the time this investigation was begun, the data on the solubility of mannite in water and on the freezing points of relatively concentrated solutions were very meager. The solubility data contained in the literature are summarized in the following table:

Solvent.	Temp. Degrees.	G. mannite per 100 g. of solvent.	Investigator.
Water	14	12.8	H. D. Krusemann[2]
Water	16	16.0	Wanklyn-Erlenmeyer[3]
Water	18	15.6	M. Berthelot[4]
Water	23	18.5	M. Berthelot
Water	24.5	20.96	A. Findlay[5]
Water	35.8	29.93	A. Findlay
Water	50.8	46.69	A. Findlay
Ethyl alcohol (*d.* = 0.8985)	15.0	1.2	M. Berthelot[4]
Ethyl alcohol (absolute)	14	0.07	M. Berthelot

It was planned to obtain the complete freezing-point solubility diagram for the system mannite–water but difficulties, later referred to, limited the study to the temperature range between the eutectic point and 103°.

1. **Apparatus.**—The freezing point-solubility apparatus employed for measurements near and below zero is shown in Fig. 1. The metal container was completely surrounded by a mixture of water and cracked ice. For solubility determinations at higher temperatures, the Dewar vessel was surrounded by an electrically heated oil bath maintained at the proper temperature. A mechanical stirrer was used in the solutions. A standardized Beckmann thermometer was used near and below zero, a standard Baudin thermometer for temperatures near 25°, and a standardized thermometer graduated between 50° and 110° in 0.05° division for temperatures of 50° and higher. The Beckmann was checked against a standard Baudin thermometer over the range employed, readings being made to 0.001° with the aid of a telescope equipped with a vernier.

2. **Method of Sampling.**—The method of removing samples from the system for analysis and the types of filter are shown in Fig. 1. A filter consisting of a short alundum tip sealed into a hard glass tube proved

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[1] Bur. Standards, *Bull.* **2,** No. 2.

[2] *Ber.*, **9,** 1467 (1876).

[3] *J. prakt. Chem.*, **88,** 297 (1863).

[4] *Ann. chim. phys.*, [3] **47,** 301 (1856).

[5] *J. Chem. Soc.*, **81,** 1219 (1902).

to be very satisfactory for solutions up to 50°. With solutions of greater viscosity, however, it was necessary to use a filter of less resistance since the suction necessary to draw the solution through the alundum tip caused vaporization to occur within the sampling tube, and a cotton plug placed in the constricted end of a glass tube was therefore used to filter these solutions. It was evident that crystals did not pass through the cotton since the solution rising in the withdrawal tube did not quickly crystallize when exposed to the lower temperature in the upper part of the tube, as would have been the case if crystals had been present. At the higher temperatures the solution became so viscous that its passage even through the cotton was extremely slow, requiring a careful adjustment of the suction to avoid evaporation as the liquid emerged from the cotton. To prevent crystallization in the tube during this rather slow

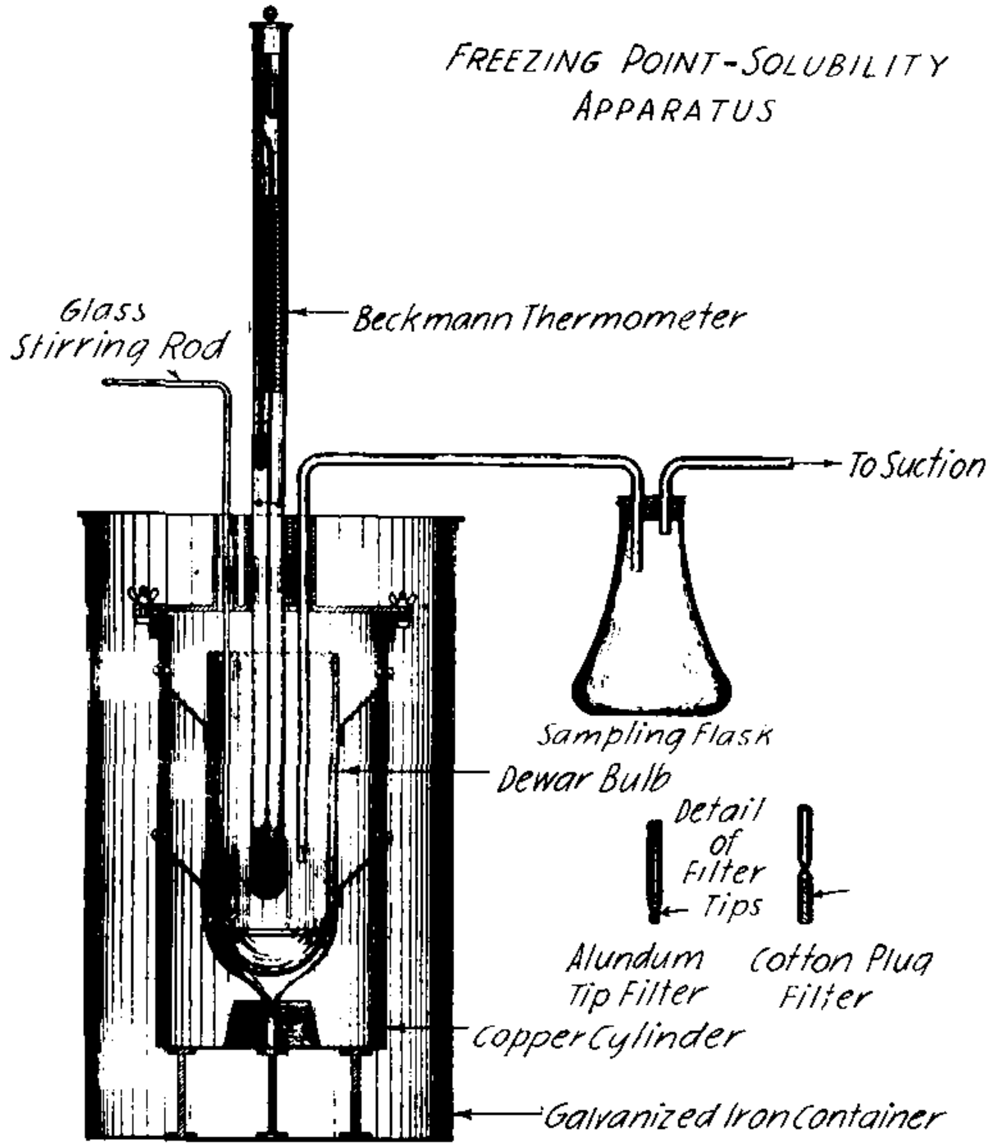

FIG 1
Scale 1:6

process the upper part of the withdrawal tube was therefore heated electrically, but even with this precaution, solidification occurred in several instances. The first portion of the solution withdrawn was discarded, the sample taken for analyses being collected in a weighed flask.

3. **Analysis of Solutions.**—The quantity of mannite in a given sample was determined by an interferometer, the use of which has been described in detail by L. H. Adams.[1] The instrument was calibrated by determining the readings at 25° on mannite solutions of known composition as follows:

G. mannite (weights *in vacuo*) per 1000 g. of water. C.	Reading of interferometer at 25°. r.	C/r.
11.806	7.77	1.5194
15.881	10.46	1.5183
23.336	15.48	1.5075
26.090	17.37	1.5020
26.594	17.72	1.5008
31.001	20.84	1.4876
37.808	25.79	1.4660

A curve was constructed from these data in which the ratio C/r was plotted against r. It was necessary to use the shortest solution chamber (5 mm.) to bring the solutions within the concentration range of the instrument; even with this chamber it was necessary to dilute greatly the samples taken at the higher temperatures, since the maximum concentration directly measurable was 0.25 molal. In general, the samples were diluted to approximately the same concentration and calibration values were redetermined from time to time for this region to insure as accurate results as possible with the method employed.

4. **Freezing-Point Lowering and Eutectic Temperature.**—Exceedingly accurate determinations of the freezing-point lowering of aqueous solutions of mannite have been made by L. H. Adams[2] and also by R. E. Hall and W. D. Harkins.[3] The former found that the difference between the observed and calculated freezing-point depression is not greater than 0.0001° for concentrations of 4.02 to 62.59 millimols per 1000 g. of water. E. H. Loomis[4] made freezing-point measurements over a wider range of concentrations, using the Beckmann method; the difference between the observed and calculated[5] depression for a solution containing 206.1 millimols per 1000 g. of water is —0.0013°, the observed value being less than that calculated, contrary to the usual experience.

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[1] This Journal, **37**, 1181 (1915).

[2] *Ibid.*, **37**, 481 (1915).

[3] *Ibid.*, **38**, 2668 (1916).

[4] *Z. physik. Chem.*, **32**, 599 (1900).

[5] Calculated from the equation $\Delta t_F = 103.20\ (x_1 + 0.428\ x_1^2)$, Washburn's "Principles of Physical Chemistry," **1915**, p. 173, McGraw-Hill Co., New York.

In the present investigation the determination of the eutectic temperature and a freezing point between the eutectic and 0° was made. To determine the latter, the zero reading of the Beckmann thermometer was first determined by placing it in a mush of pure water and ice contained in a Dewar tube in the apparatus already described. A portion of the water was replaced by a solution of mannite previously cooled to 0°, and having approximately the concentration required for the desired depression. When the temperature became constant, a sample was withdrawn through the alundum filter, properly diluted and then analyzed. To determine the eutectic temperature most of the mannite solution was removed from the Dewar and replaced by a cooled saturated solution together with a large excess of mannite crystals. The mixture was well stirred but did not attain constant temperature for several hours, when a sample of the equilibrium mixture was withdrawn and its composition determined. The data are given in the following table:

Concentration moles per 1000 g. of water.	Freezing-point depression observed.	Freezing-point depression calculated.[1]	Difference observed-calculated.
0.2709	0.505°	0.501°	0.004°
0.5460	1.019° (eutectic)	1.009°	0.010°

The figures in the fourth column show that the deviation from the calculated value is significant with solutions of high concentration and that the deviation is a function of the concentration.

5. Solubility Measurements.—In determining the solubility at and near 25°, 4 different procedures were tried: (1) water contained in a Dewar tube was saturated with mannite at 35–40° and cooled with stirring to the final temperature; (2) water at 25° was added to a large excess of crystals and frequently stirred for several hours; (3) water was added to a large quantity of crystals in a bottle and shaken in a thermostat at 25° for 24 hours; (4) same conditions as in (3) except that the solution was initially saturated at 40°. The results of these experiments are:

Procedure.	Temperature Degrees.	G. solubility of mannite per 100 g. of water.
(1)	24.9	21.48
	25.0 (interpolated)	21.57
(2)	25.2	18.66
(3)	25.0	21.54
(4)	25.0	21.63

It is quite evident that procedure 2 cannot be employed. Methods 3 and 4 are known to give the best results but require a long time. Procedure 1 may be employed since it yields results similar to those of the standard methods and, moreover, it possesses the advantage of requiring but a short time.

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[1] Washburn, $\Delta t_F = 103.20 (x_1 + 0.428 x_1^2)$, "Principles of Physical Chemistry," 1915, p. 173, McGraw-Hill Co., New York.

The procedure in all solubility determinations between 50° and 90° was essentially the same. The solution was saturated at a temperature about 10° higher than that at which the determinations were to be made, cooled to approximately 3° above the desired temperature, and then poured into a Dewar tube which was surrounded by an oil bath electrically heated and the contents mechanically stirred. In the determinations between 90 and 103° it was usually found impossible to draw the samples for analysis into the flask in spite of all precautions, since the solutions were very concentrated and consequently highly sensitive to temperature change. A column of liquid about 14 cm. in length was usually obtained in the withdrawal tube before solidification occurred; the tube was then removed and cooled to completely solidify the contents. The middle portion of the tube was cut off, the contents dissolved in warm water, and the final solution analyzed in the usual manner. The weight of the sample was determined from the difference in weight of the glass tubing before and after removing the contents.

It was the original intention to determine the solubility at 125 and 150° but it was found impossible to obtain a mixture at those temperatures which could be sampled. In attempting to obtain the solubility at 125°, mannite was added to a boiling solution but the highest temperature reached at which the solution possessed even a medium degree of fluidity was about 110°. At this temperature water vapor was given off rapidly, resulting in the solidification of the solution. In an endeavor to obtain a solution at 150°, mannite crystals were melted and boiling water grad-

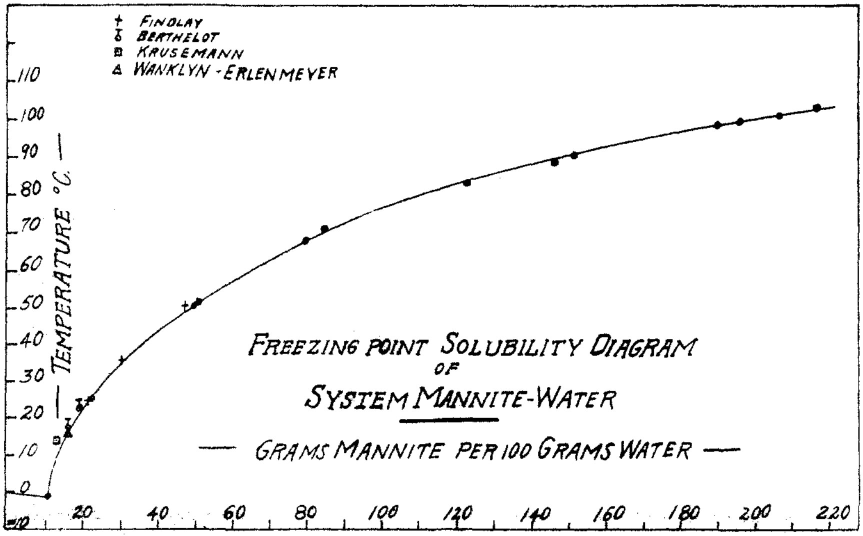

Fig. 2.

ually added. Most of the water immediately vaporized. The addition of water caused a cooling of the liquid mannite and solidification of the entire mass resulted. To investigate the composition of solutions at these temperatures, therefore, pressure apparatus would be necessary.

The results of the solubility determination are given in Table I.

TABLE I.

Temperature. Degrees.	G. of mannite in 100 g. of water (weights *in vacuo*).
—1.019	9.942
25.00	21.63
25.00	21.57
50.70	49.0
51.50	49.9
67.4	78.6
70.5	83.9
82.9	121.9
88.1	145.5
90.1	150.6
98.0	189.0
99.3	195.0
100.8	200.0
101.8	206.0
103.6	216.0

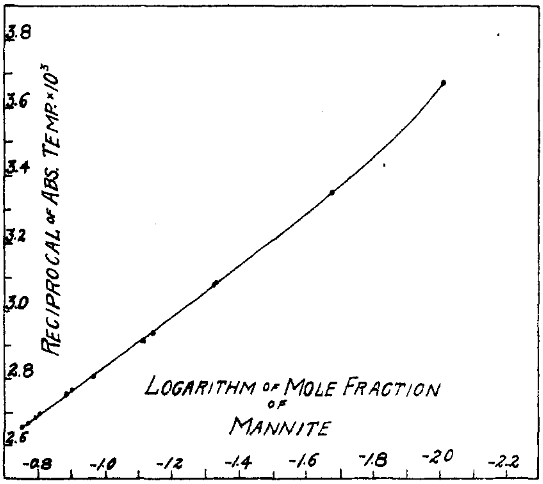

Fig. 3.

A large scale graph of these data was constructed in the form shown by Fig. 3. The data given in Table II were derived from this curve and present the results in a more convenient form.

TABLE II.

Temperature. Degrees.	Solubility g. of mannite in 100 g. of water.	Mole fraction of mannite in solution.
—1.019 (eutectic)	9.942	0.0097
0.00	10.36	0.0101
5.00	11.9	0.0117
10.00	13.7	0.0134
15.00	16.0	0.0156
20.00	18.6	0.0181
25.00	21.6	0.0209
30.00	25.2	0.0243
40.00	34.6	0.0331
50.00	47.6	0.0450
60.00	64.4	0.0598
70.00	86.2	0.0785
80.00	115.0	0.1019
90.00	150.0	0.1294
100.00	197.0	0.1633

Although the curve in Fig. 3 is not a perfectly straight line, the deviation does not indicate the presence of hydrates. Fig. 2 shows the freezing point-solubility diagram of the system mannite–water. The experimental difficulties in obtaining accurate measurements of the solubility near 100° were quite great and, consequently, the results in this region are somewhat uncertain. To complete the solubility curve for normal pressure a determination of the composition of the boiling saturated solution would be necessary.

V. Other Physical Properties.

In connection with this investigation the literature was carefully searched for data on physical properties other than those already mentioned. These data have been briefly summarized in the following sections:

1. **Density.**—All of the references to the density of mannite are old and do not contain sufficient information as to the conditions under which the measurements were made. Kruseman[1] obtained the values 1.4589 and 1.3938 at 0° and 50°, respectively, for purified crystalline mannite. Prunier[2] found the density to be 1.51 at 13°. He used a specific gravity flask with ether as the contact liquid but did not state what form the mannite was in. Several determinations were made by Schröder[3] on mannite in the form of coarse crystals and also of finely powdered material, using the displacement method with benzene as the contact liquid. His results are: 1.489 on a powdered sample of purified mannite, "Karlsruher Sammlung;" and 1.486 on Kahlbaum's crystals. The density is referred to water at 4° but the temperature was not stated. His values are undoubtedly the most dependable of the three.

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[1] *Ber.*, **9**, 1468 (1876).

[2] *Bull. soc. chim.*, Paris, **28**, 556 (1877).

[3] *Ber.*, **12**, 562 (1879).

2. **Specific Heat.**—Three investigators have determined the specific heat of mannite, using two somewhat different methods. Hermann Kopp[1] employed the method of observing the heat effect produced when a known quantity of mannite, covered by a liquid in which it was not soluble, was heated to a definite temperature and then immersed in a calorimeter. He obtained the value of 0.324 calorie per degree for a temperature range of 0–100°. Using essentially the same procedure, M. W. Longuinine[2] obtained as the average of 5 determinations the value 0.3277 calorie per degree for the temperature range 28–100°. W. F. Magie[3] determined the specific heat over a relatively short temperature range, using an apparatus primarily designed for very accurate measurements of the specific heats of solutions. He obtained the value 0.315 calorie per degree over the range 14–26°, with a possible error of 2 or 3%.

3. **Heat of Combustion.**—The heat of combustion of mannite was determined by Berthelot and Vieille,[4] using an oxygen bomb calorimeter. It was also determined by Stohmann and Langbein[5] who made two series of measurements, the last being on mannite recrystallized from alcohol several times, using a bomb calorimeter designed for very accurate work. The several results follow:

Berthelot and Vieille.	Stohmann and Langbein.	
(1887).	(1885).	(1892).
3.9997 Cal./gram	3.949 Cal./gram	3.9959
	3.922	4.0046
3.9928	3.946	3.9944
	3.947	3.9982
4.0110	3.940	3.9961
Av., 4.0012	3.941	3.9978

4. **Heat of Dilution.**—Measurements of the heat of dilution[6] of aqueous mannite solutions have shown, as would be expected, that only a slight evolution of heat occurs on dilution and that it is practically independent of the temperature.

VI. Summary.

The following physical properties of mannite and its aqueous solutions have been studied: The melting point of pure mannite, the specific rotation in aqueous solution, the freezing point-solubility diagram up to 103°. A brief summary of previous work on the subject has been given.

Since certain physical constants of mannite given in handbooks are

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[1] *Trans. Roy. Soc. London*, **155**, I, 71 (1865).

[2] *Ann. chim. phys.*, **27**, 144 (1892).

[3] *Phys. Rev.*, **14**, 193 (1902); **17**, 105 (1903).

[4] *Ann. chim. phys.*, [6] **10**, 456 (1887).

[5] *J. prakt. Chem.*, [2] **31**, 291 (1885); **45**, 305 (1892).

[6] F. R. Pratt, *J. Frank. Inst.*, **185**, 663 (1918).

not in accord with the best data, the following values based on results of the present investigation and on the most dependable results given in the literature are suggested for adoption: melting point, 166.05°; specific rotation $[\alpha]_{\mathrm{E}}^{25°} = -0.244° \pm 0.002$ and $[\alpha]_{\mathrm{D}}^{25°} = -0.208 \pm 0.002$ (calculated); density 1.48_7 (room temperature), specific heat $C_{(28-100°)} = 0.327_7$ cal./deg. and $C_{(14-26°)} = 0.31_5$ cal./deg.; heat of combustion, 4.00° cal./gram.

The writer wishes to acknowledge his indebtedness to Dr. E. W. Washburn under whose direction this investigation was made.

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA.]

THE CALCULATION OF THE TEMPERATURE COEFFICIENT OF THE DISTRIBUTION RATIO.

BY F. H. MACDOUGALL.

Received July 10, 1919.

The present communication owes its origin to a recent paper[1] by Forbes and Coolidge dealing with the system water, ether and succinic acid and contains some new relations between various functions of the variables of ternary systems not contained in their article and, in particular, new additional relationships between the various partial derivatives to be defined later. The authors determined the composition of a large number of solutions both unsaturated and saturated with respect to various components. They use the following system of symbols:

s = mole fraction of succinic acid in water layer.
e = mole fraction of ether acid in water layer.
w = mole fraction of water acid in water layer.
σ = mole fraction of succinic acid in ether layer.
ω = mole fraction of water acid in ether layer.
ϵ = mole fraction of ether acid in ether layer.

The distribution ratio is $R = s/\sigma$ and the temperature coefficient is $\frac{dR}{dt} = \frac{1}{\sigma}\frac{ds}{dt} - \frac{s}{\sigma^2}\frac{d\sigma}{dt} = \frac{1}{\sigma}\left(\frac{ds}{dt} - R\frac{d\sigma}{dt}\right)$.

The authors put $\left(\frac{ds}{de}\right)_t = a$, $\left(\frac{ds}{dt}\right)_e = b$, $\left(\frac{de}{ds}\right)_t = m$, and $\left(\frac{de}{dt}\right)_s = n$. Then since $\frac{ds}{dt} = \left(\frac{ds}{dt}\right)_e + \left(\frac{ds}{de}\right)_t \frac{de}{dt} = b + a\frac{de}{dt}$ and $\frac{de}{dt} = \left(\frac{de}{dt}\right)_s + \left(\frac{de}{ds}\right)_t \frac{ds}{dt} = n + m\frac{ds}{dt}$ they obtain $\frac{ds}{dt} = \frac{b + an}{1 - am}$. Similarly they obtain $\frac{d\sigma}{dt} = \frac{\beta + \alpha\nu}{1 - \alpha\mu}$, where $\alpha = \left(\frac{d\sigma}{d\omega}\right)_t$, $\beta = \left(\frac{d\sigma}{dt}\right)_\omega$, $\mu = \left(\frac{d\omega}{d\sigma}\right)_t$ and $\nu = \left(\frac{d\omega}{dt}\right)_\sigma$.

[1] THIS JOURNAL, 41, 150 (1919).