

the theory and experiment shown in this figure is surprisingly close, particularly in view of the simplifying assumptions that were found necessary. This agreement would appear to confirm completely the postulated mechanism, *i. e.*, that the boundary is the result of the interaction of diffusion and of ionic migration, and gives us still further confidence in the moving boundary method.

Since the maximum in the total gradient curve does not occur at  $h = 0$ , it is essential to locate this maximum accurately in order to have a reference point on the abscissa scale from which to plot the experimental data. For this purpose the expression for  $d^2n/dh^2$  was obtained, set equal to zero, and the roots determined from a plot of the function. The position of the maximum depends, of course, on the relative values of the equivalent refraction increments and occurs at  $\ln y = 0.419$  for the lithium chloride:potassium chloride boundary and at  $\ln y = 0.037$  for the potassium iodate:potassium chloride boundary. In the latter case the theory also predicts a slight minimum in the gradient curve at  $\ln y = 2.8$ . It is of considerable interest that close inspection of the patterns reveals this minimum (see *d* of Fig. 2,

for example) and that both its position and magnitude are in agreement with the theory. Owing to the relatively great density of potassium iodate solutions the minimum in the refractive index gradient curve is not accompanied by a corresponding minimum in the density gradient and the boundary remains, therefore, gravitationally stable.

The author is indebted to Dr. D. A. MacInnes of these Laboratories for his continued interest and helpful discussion.

### Summary

Salt boundaries of the type used for the direct determination of transference numbers have been studied with the aid of the schlieren scanning camera. Several features of the direct moving boundary method that were assumed in previous work have now been confirmed experimentally. Under the influence of a constant current the concentration distribution through a moving boundary does not change with the time and is given accurately by Weber's theory. Moreover, the adjusted concentration of the indicator solution, and hence its transference number, may be determined from the electrophoretic patterns.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY]

## The System Ammonium Nitrate-Sodium Nitrate

BY EDWARD O. HOLMES, JR., AND DAVID REVINSON

In connection with the volunteer research program conducted by the Committee on Eutectics of the National Research Council, the senior author found that he was unable to confirm the accepted data on the system ammonium nitrate-sodium nitrate that he used to standardize his technique. The discrepancies in the determination of the points on the solubility curves were so large as to suggest that the work of Early and Lowry<sup>1</sup> on this system might be in error.

As a result, this investigation was begun to re-determine all parts of the system and to study the various factors that might lead to error such as (1) the method of purification of materials, (2) the length of drying of the purified materials and (3) the technique of determining points on the curve.

**Purification of Materials.**—The pure ammonium nitrate was supplied by the Committee on Eutectics.<sup>2</sup> It was of highest purity and the dry material was found by analysis to contain 100.01% ammonium nitrate. It was ground frequently and kept in a desiccator over Anhydrone for the entire period of the research. This material was used in all determinations.

The sodium nitrate (Merck Reagent) was further purified by two methods: (A) thrice recrystallized from

water, ground frequently and kept over Anhydrone; (B) precipitated by concentrated nitric acid, washed with water, twice recrystallized, ground and kept over Anhydrone.

**Thermometers.**—Two thermometers used were of the twenty-four inch 0.1° type. Both were calibrated against the melting points of pure organic compounds and one by the Bureau of Standards, in addition.

### The Melting Point Measurements

(a) **Standard Microtechnique.**—This technique consisted in weighing out a sample of a tenth of a gram into a three-inch test-tube, fusing the mixture and stirring until clear, cooling and removing the solid melt, grinding it to a powder, introducing a portion of the ground material into a 2-mm. capillary tube and then determining the point at which the last crystals disappeared on very slow heating.

It was found that the Thiele-Dennis melting point apparatus did not give satisfactory results, so a melting point apparatus had to be devised that would permit better heat control and give more uniform results. This was accomplished by building a special gas control valve for the conventional apparatus which consists of a beaker full of oil over a microburner, and surrounding the bulb of the thermometer by a glass basket into which the capillary melting point tube was placed. A description of this apparatus can be found in the *Journal of Chemical Education*.<sup>3</sup>

This method worked quite satisfactorily for the left-hand side of the system, the solubility curve of ammonium nitrate, but difficulty was experienced on the right-hand side, the solubility curve of sodium nitrate. The trouble was caused by a rapid settling out of solid sodium nitrate

(1) R. G. Early and T. M. Lowry, *J. Chem. Soc.*, **121**, 963 (1922).

(2) Courtesy of Professor Edward Mack, Jr., Chairman.

(3) Edward O. Holmes, Jr., *J. Chem. Ed.*, **20**, 239-240 (1943).

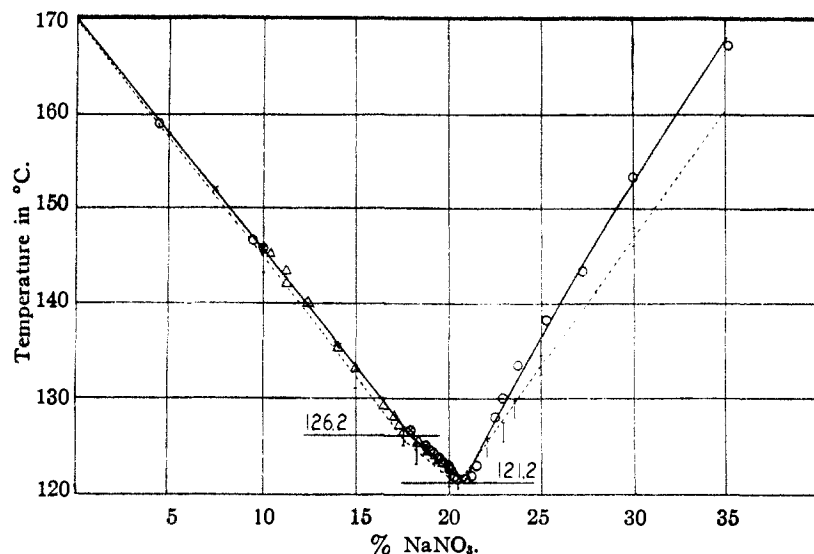


Fig. 1.—Phase diagram of the system ammonium nitrate-sodium nitrate (the dotted lines are Early and Lowry's curves).

crystals on cooling the original melt so that unless the melt was ground and mixed for a long time, a uniform sample could not be obtained. This process was undesirable as ammonium nitrate is very hygroscopic and every effort was made to keep the sample as dry as possible. On account of the steepness of solubility curves, it was absolutely necessary to use samples of accurately known composition, as a 0.1% error in composition makes a 0.3° error in the melting point of the mixture.

No such difficulty was encountered on the ammonium nitrate solubility curves as the crystals were of about the same density as the liquid melt and tended to float or rise slowly, and made a thick mesh long before the eutectic point was reached.

(b) **Improved Microtechnique.**—Our improved microtechnique consisted in eliminating a lack of uniformity of the sample by weighing tenth-gram samples of ammonium nitrate and sodium nitrate directly into a flared 12 mm. tube that had been drawn down into a thin-walled capillary and using the sample as a whole in the melting point determination.

As the rate of heating naturally makes a great difference in the temperature at which the last crystal disappears, observations were usually made at several rates of heating and the melting point at zero rate was obtained by graphical extrapolation.

Vigorous stirring of the oil-bath was necessary regardless of the rate of heating. Once in a while, we succeeded in stopping the oil-bath at the exact temperature at which the last crystal disappeared, which represents a zero-rate of heating. Temperatures so obtained corresponded with those from the zero-rate extrapolation method, as would be expected.

Both samples of sodium nitrate (A) and (B) were used here but no difference was found in the results. Points determined by this technique are considered to be the most reliable and those in which we have the most confidence.

(c) **Macrotechnique.**—The macrotechnique consisted in using a 20-g. sample (to reduce weighing error) in a test-tube, usually six-inch, then heating the sample over a microburner with the same apparatus as in the micro-determination except that the thermometer was placed directly in the melt, and the glass basket omitted. The melt was stirred by a glass stirrer shaped like a ring, which could be moved up and down around the thermometer. With a heating rate of about 0.3–5° per minute, the temperature at which the last crystal disappeared was noted.

The reason for taking such large samples was that

Early and Lowry<sup>1</sup> used samples of this size and we wanted to see whether or not the size of the sample had any effect on the temperature at which the last crystal disappeared.

(d) **Cooling Curves.**—In order to compare points obtained by an entirely different method, we ran cooling curves on mixtures weighing 20 g. representing compositions in the various sections of the phase diagram, three on the ammonium nitrate solubility curve, one close to the eutectic and two on the sodium nitrate solubility curve.

The method consisted in weighing the 20-g. samples directly into a test-tube, usually six-inch, fitted with a stirrer. The sample was melted in an oil-bath and then the test-tube with its molten contents was placed in a larger test-tube having glass wool in the bottom and a cork ring to keep the smaller inner tube containing the melt properly centered. The larger tube was placed in an oil-bath over

a microburner and the oil stirred with a large ring stirrer during all determinations.

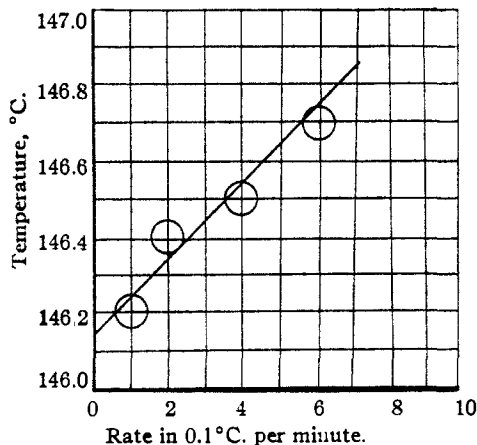


Fig. 2.—Temperatures at which last crystals dissolved, extrapolated to zero rate.

The temperature of the oil-bath was raised until it was several degrees above that at which the crystals were expected to appear on cooling and the melt was perfectly clear. Now the burner valve was set in such a position that the oil-bath would cool slowly to about 115°. The melt and the oil-bath were constantly stirred and the temperature of both read at regular intervals. The temperature at which the first crystals appeared was carefully

TABLE I

% NaNO <sub>3</sub> in sample	Temperatures, °C.			
	First crystals appeared at	Break in curve, if any, at	Transition point	Eutectic halt
7.500	151.7	151.7	126.2	117.2
14.000	135.3	135.0	126.2	120.6
19.00	124.0	124.0	...	121.2
20.90	121.6	...	...	121.2
25.00	137.7	134.5	...	121.2
30.00	153.1	...	...	120.9

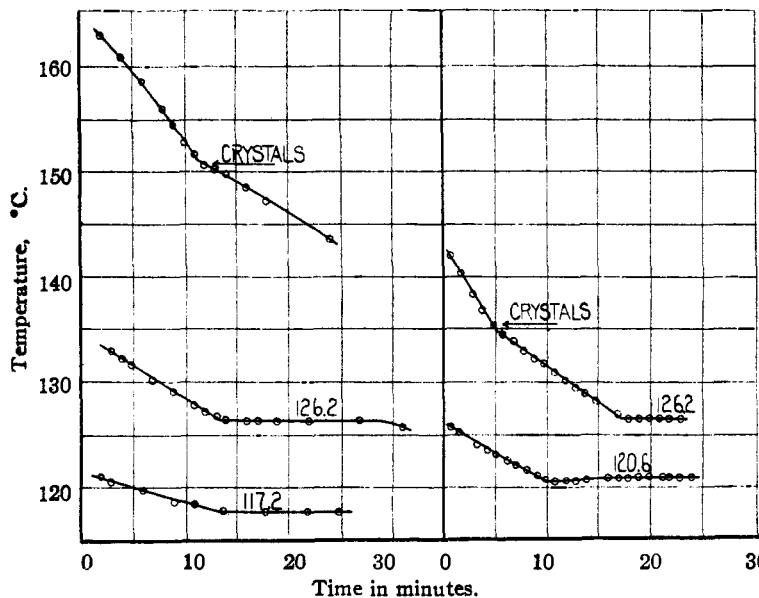


Fig. 3A.—Cooling curve for mixture containing 7.5% NaNO<sub>3</sub>.

Fig. 3B.—Cooling curve for mixture containing 14.0% NaNO<sub>3</sub>.

Discussion of Results

Both theory and practice indicate that the values of the eutectic temperature from the cooling curve method (Fig. 3) are more reliable than those obtained by any melting point method. It was impossible, no matter how hard we tried nor what technique was used to cause mixtures to melt sharply at or close to the eutectic point: stirring is impossible and heat conduction is the poorest just when the largest amount of heat must be transferred. The melting point methods, whether micro or macro, are at their worst at the eutectic point but improve rapidly at higher temperatures where good stirring is possible and less heat must be transferred through the glass walls of the capillary.

Construction of the Phase Diagram (Fig. 1).—Much careful consideration was given to the construction of the phase diagram.

noted in each run. These temperatures appear in Fig. 1 as points marked (X) on the ammonium nitrate solubility curves. Several runs were made on each mixture. In at least one run, each of the mixtures was allowed to cool to the eutectic point. A characteristic cooling curve for each mixture is plotted in Fig. 3 and the results are tabulated in Table I.

When these values, which are averaged values derived from our cooling curves, are considered in relation to the values obtained from our improved microtechnique, it is seen that the temperature of the appearance of crystals and the breaks in the cooling curves correspond closely on the ammonium nitrate side of the diagram. However, on the sodium nitrate side the temperature at which the first crystals appeared on cooling falls above the curve but the break in the cooling curve falls much below in the case of the 25.00% mixture and does not appear at all in the case of the 30.00% mixture. The arrows in Fig. 3 indicate the temperature at which the crystals appeared.

We found the transition temperature for the change of ammonium nitrate I into ammonium nitrate II to be  $126.2 \pm 0.2^\circ$  which is a degree higher than the value obtained by Early and Lowry.<sup>1</sup>

We also found that the temperature of the eutectic halt varied with the composition of the melt as Early and Lowry<sup>1</sup> had previously noticed, those values nearer to the eutectic point being constant and in good agreement, while those further away, in either direction, were lower as Table I shows. It seemed reasonable to these authors and also to us to take the average of these constant values near the eutectic point as the true value of the eutectic point, namely,  $121.2 \pm 0.2^\circ$ . This value is  $0.4^\circ$  higher than that of Early and Lowry.<sup>1</sup>

The eutectic temperature and the transition temperature were assumed to be correct, as we obtained repeated check values ( $\pm 0.2^\circ$ ) for these. We assumed the solubility curve for ammonium

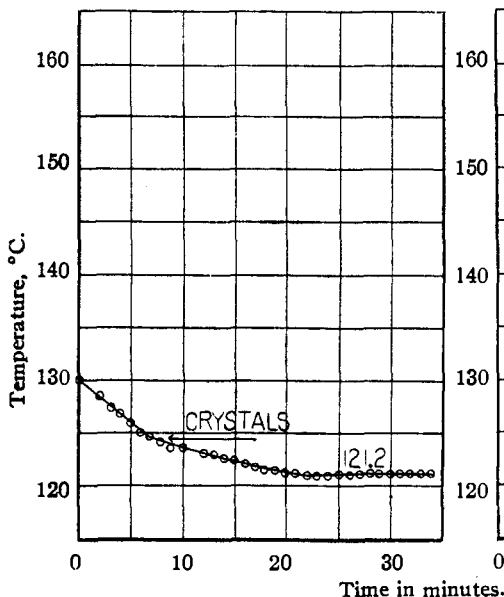


Fig. 3C.—Cooling curve for mixture containing 19.00% sodium nitrate.

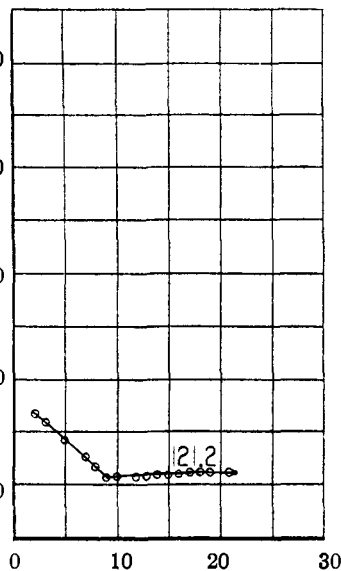


Fig. 3D.—Cooling curve for mixture containing 20.90% sodium nitrate.

nitrate II to be a straight line and its equation was found<sup>4</sup> by the method of least squares, using all points as the consistency of the data is good over

(4) The authors wish to acknowledge their indebtedness to Professor Royal M. Frye of the Physics Department for his laborious and painstaking work in applying least square methods to our data.

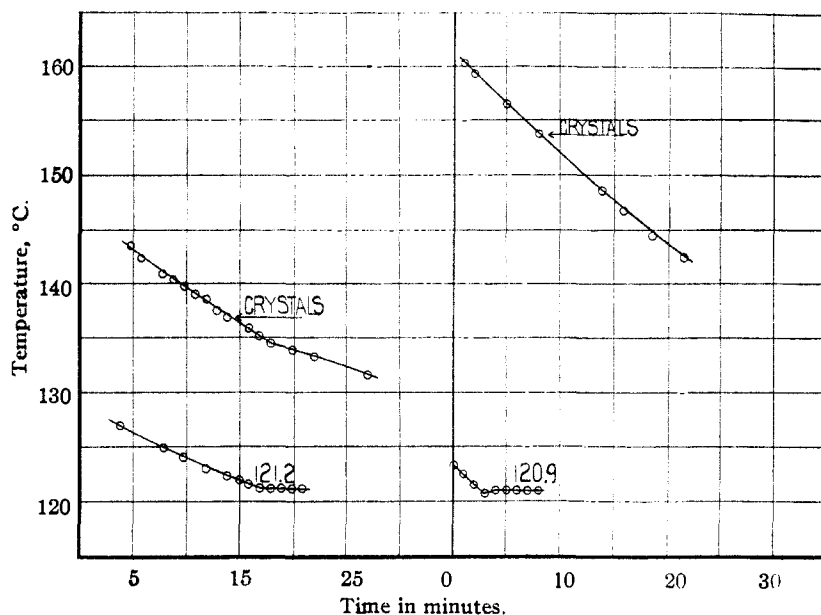


Fig. 3E.—Cooling curve for mixture containing 25.0%  $\text{NaNO}_3$ .

Fig. 3F.—Cooling curve for mixture containing 30.0%  $\text{NaNO}_3$ .

this range. By substituting the eutectic temperature ( $121.2^\circ$ ) in this equation we found the eutectic composition to be  $21.0 \pm 0.1\%$ . Similarly, we found the composition at which this line comes to an end at the transition temperature to be  $18.0 \pm 0.1\%$ .

The equation for the solubility curve of ammonium nitrate II plotted in the region above  $120^\circ$  is

$$\% \text{NH}_4\text{NO}_3 = -0.586(T^\circ\text{C.} - 120) + 21.6563$$

For the solubility curve of ammonium nitrate I, we drew a straight line from its melting point to the end of the solubility curve for ammonium nitrate II, as there appeared to be no curvature.

The solubility curve for sodium nitrate presented a problem. Considerable deviation was noticed in the data obtained by the various methods. Moreover, the data suggested that it might consist of two parts but in absence of any other substantiating information we assumed it to be a smooth parabolic curve.

Using the points obtained from our improved microtechnique only, which we considered most reliable because our sample had dried the longest time and our technique had been perfected, we<sup>4</sup> applied the method of least squares to our data and obtained the best parabola that would intersect the solubility curve of ammonium nitrate II at  $121.2^\circ$ . The equation for this parabola plotted in the area above  $120^\circ$  is

$$\% \text{NaNO}_3 = 20.645 + 0.2556(T^\circ\text{C.} - 120) + 0.0009737(T^\circ\text{C.} - 120)^2$$

While this is not the best one for the points chosen, the sums of the squares of the deviations are very little greater than those of the best

possible parabola that could be drawn through the points. It was felt that the physical chemistry of the problem required that the parabola chosen must meet the solubility curve of ammonium nitrate II at  $121.2^\circ$  and  $21.0 \pm 0.1\%$  sodium nitrate, the eutectic point.

### Remarks and Conclusions

From a consideration of our final curve in Fig. 1, we could not discover that the method of purification nor the time of drying of the sodium nitrate nor the size of the sample used in the determination made any difference. All techniques gave good results for the solubility curves of the two forms of ammonium nitrate. On the other hand the only one that

TABLE II  
COMPARISON OF OUR RESULTS WITH THOSE OF EARLY AND LOWRY<sup>1</sup>

	Holmes and Revinson	Early and Lowry
Eutectic point, $^\circ\text{C.}$	121.2	120.8
Eutectic composition, %	21.0 $\text{NaNO}_3$	20.5 $\text{NaNO}_3$
Transition temp., $^\circ\text{C.}$	126.2	125.2
Transition compn., %	18.0	....

TABLE III

Techniques: S, standard microtechnique, symbol  $\Delta$  in Fig. 1; I, improved microtechnique, symbol  $\circ$  in Fig. 1; M, macrotechnique, symbol  $\otimes$  in Fig. 1; C, cooling curve, symbol X in Fig. 1. When two letters are given, it means that two points coincided.

$\% \text{NaNO}_3$	Temp. of disappearance of last crystal, $^\circ\text{C.}$	Technique used	$\% \text{NaNO}_3$	Temp. of disappearance of last crystal, $^\circ\text{C.}$	Technique used
4.5	158.6	I	19.2	124.2	S
7.5	151.7	C	19.4	123.9	I
9.5	146.3	I	19.4	123.7	S
10.0	145.6	M	19.6	123.3	S
10.0	145.7	M	19.8	123.4	I
10.0	145.8	M	20.0	122.8	M
10.5	145.0	S	20.0	123.0	M
11.2	143.2	S	20.0	122.7	I
11.3	142.0	S	20.3	122.4	S
12.5	139.9	S	20.5	121.7	I
14.0	135.5	C	20.7	121.8	S. & M.
14.1	135.3	S	20.9	123.0	C
15.0	133.0	S	20.9	121.7	I
16.5	129.4	S	21.2	121.9	I
17.0	128.2	S	21.6	123.1	I
17.2	127.2	S	22.1	125.0	I
17.5	126.1	S	22.6	128.1	I
18.0	126.7	M. & M.	22.9	130.0	I
18.3	125.5	S	23.7	132.3	I
18.8	125.1	M	25.4	138.3	I
18.9	124.6	S	27.2	143.5	I
19.0	124.4	M	30.0	153.2	I
19.0	124.0	C	35.2	167.2	I

gave consistent and reliable results on the sodium nitrate solubility curve was our improved microtechnique. Hence points obtained by this technique only were used in the plotting of this curve. For the sake of comparison, Early and Lowry's solubility curves for this system are included as dotted lines.

Figure 1 shows the solubility curves of ammonium nitrate to be slightly higher than Early and Lowry's<sup>1</sup> curves for the corresponding parts. The solubility curve of sodium nitrate is most interesting as it runs considerably above that of these authors. Although the curve was obtained by the method of least squares using only the data from our improved microtechnique, actually we determined seventeen other points by the other methods previously mentioned in this paper which, although scattered, support the data actually used rather well. Adding the distances above the curve and parallel to the temperature axis together and subtracting the sum of the distances below the curve from these and then dividing by the number of points, we find that the average deviation per point is  $0.05^\circ$  under the curve.

### Summary

The system ammonium nitrate-sodium nitrate has been redetermined over the range 0-35% sodium nitrate. The solubility curves for the two forms of ammonium nitrate are linear while that for sodium nitrate is distinctly parabolic. An improved microtechnique has been developed that gives good results except near the eutectic point where all melting point methods are at their worst.

The eutectic temperature was found to be  $121.2 \pm 0.2^\circ$  and the transition temperature to be  $126.2 \pm 0.2^\circ$  by the cooling curve method which is most reliable for these temperatures. Using these points and applying the method of least squares to the curves, the eutectic composition was found to be  $21.0 \pm 0.1\%$  sodium nitrate and the transition composition to be  $18.0 \pm 0.1\%$ .

The method of purification of the sodium nitrate, the length of time of drying the materials and the size of the sample appear to have no effect on the temperature of disappearance of the last crystal on heating the melt.

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[CONTRIBUTION NO. 495 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH]

## The Heat of Acetylation of $\alpha$ - and $\beta$ -D-Glucose from the Heats of Combustion of the Pentaacetates<sup>1</sup>

BY THEODORE H. CLARKE AND G. STEGEMAN

In the investigation of the thermal properties of sugars which is being carried out in this Laboratory, some interest developed in the determination of the heats of combustion of  $\alpha$ - and  $\beta$ -D-glucose pentaacetate, wherein the isomeric structural differences involve a much heavier radical than is present in the case of  $\alpha$ - and  $\beta$ -D-glucose.

In this paper are presented the results of the combustion measurements, the specific heats of the compounds at  $25^\circ$ , and an approximate value of the density (used to correct the weight to the vacuum basis). From these and other data the heats of formation and the heats of acetylation were calculated.

A general description of the calorimetric equipment used in these determinations has been reported.<sup>2</sup> The energy equivalent of the calorimeter was determined by the use of benzoic acid obtained from the National Bureau of Standards. Sample No. 39e having a certified heat of combustion of 26428.4 international joules<sup>3</sup> or 6317.60 conventional cal. per gram mass *in vacuo*, was employed under the following conditions which are recommended.

The reaction is referred to  $25^\circ$ ; the oxygen pressure should be 30 atmospheres; the weight of the sample should be 3 g. per liter of bomb volume; the bomb is to contain 3 g. of water per liter of bomb volume.

These conditions were adhered to with sufficient exactness so that no additional corrections were necessary.

The results of six determinations produced a value:  $C_{\text{sys}} = 2772.95 \pm 0.2$  cal./ $^\circ\text{C}$ . (precision error,  $\pm 0.009\%$ ). The value was redetermined upon the completion of the measurements and no change was detected. The bomb has a volume of 0.516 liter and contained 1.5 ml. of water and oxygen at an initial pressure of 30 atmospheres. The initial temperature of the calorimeter was adjusted to  $22.6$  to  $22.7^\circ$  and the average temperature rise was  $3.15^\circ$ . The temperature rise in degrees was determined from the resistance *vs.* time readings as outlined by Dickinson.<sup>4</sup> Calculations of the heats of combustion were made following the method outlined by Dickinson which gives the heat of combustion at the final temperature reached in the combustion process. The necessary specific heats were employed to correct the values to  $25^\circ$ .

(1) This investigation was made possible by a grant from the Buhl Foundation, Pittsburgh, Pa.

(2) Clarke and Stegeman, *THIS JOURNAL*, **61**, 1726 (1939).

(3) Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(4) Dickinson, *Bur. Standards Bull.*, **11**, 189-257 (1915).