

## Studies on Glass XII. Some New Heat Capacity Data for Organic Glasses. The Entropy and Free Energy of dLactic Acid

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percent, corresponds roughly to the three-percent change in packing volume over 2000 atmospheres. The stability of ice II at very low temperatures would thus seem to be due to a thermal contraction of the oxygen ion of the same order of magnitude as the volume change under 2000 atmospheres pressure. Accordingly, the density obtained from the x-ray measurements is not necessarily the same as that under pressure in the press. As both the phase diagram of Bridgman<sup>2</sup> and the low temperature ice I measurements of

Barnes<sup>3</sup> show, the thermal contraction is not in itself sufficient to cause the formation of ice II. The expenditure of external work is necessary to change the OH bond angles of ice I. This is in agreement with the giving off of latent heat during the course of the ice I-ice II reaction.

Further information regarding the effect of pressure on the water molecule can be obtained from the crystal structure of ice III. The results of the analysis of the ice III photographs already obtained will appear in the near future.

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## Studies on Glass

### XII. Some New Heat Capacity Data for Organic Glasses. The Entropy and Free Energy of *dl*-Lactic Acid

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(Received October 14, 1935)

Heat capacity measurements by the Nernst method have been made upon samples of secondary butyl alcohol and 3-methylhexane in the glassy and liquid condition and upon a sample of *dl*-lactic acid (1) in an incompletely crystallized state, (2) in the form of an *acid* glass and liquid, and (3) in the form of a *mixed* glass and liquid. From these results the specific heats and heat of fusion of pure crystalline *dl*-lactic acid also have been derived. The data for the

several glasses and undercooled liquids show a rapid rise from the heat capacity characteristic of a crystalline solid to that for the liquid state within a transition region of about 10° and the nature of this transition region has been discussed. A calculation of the molal entropy and free energy of formation of liquid *dl*-lactic acid at 298.1°K yields 45.9 ( $\pm 1.0$ ) e.u. and  $-124,300 \pm (2300)$  cal., respectively.

IN previous studies<sup>1</sup> dealing with organic glasses heat capacity data have been presented for ethyl alcohol, *n*-propyl alcohol, propylene glycol, and glucose, and for two mixed glasses or solutions containing glycerol and glucose and propylene glycol, glycerol and glucose, respectively. The data showed in every case a marked increase in heat capacity within a comparatively small temperature interval or *transition region*, the rate of increase being somewhat less rapid in the mixed glasses than with the pure substances. The materials represented in these earlier studies, however, were all primary alcohols or polyhydroxy compounds; and accordingly it seemed desirable to extend the measurements to other

types of substances. In the present study specific heat determinations have been made upon secondary butyl alcohol, *dl*-lactic acid, and 3-methylhexane—i.e., upon a typical secondary alcohol, a hydroxy acid, and a paraffin hydrocarbon. These substances all form stable glasses on cooling from the liquid state, although the lactic acid may also be obtained in the crystalline condition. It is interesting to note that in each case the molecule contains an asymmetric carbon atom and that the materials involved in the present study were in reality mixtures of equal amounts of the dextro and laevo forms.

#### MATERIALS

A very pure sample of secondary butyl alcohol was kindly prepared for us by H. E. Buc of the Standard Oil Development Company. Its boiling range was 99.52–99.55°C.

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<sup>1</sup> (a) Parks and Huffman, *J. Phys. Chem.* **31**, 1842 (1927); (b) Parks, Huffman and Cattoir, *J. Phys. Chem.* **32**, 1366 (1928); (c) Parks, Thomas and Gilkey, *J. Phys. Chem.* **34**, 2028 (1930).

To obtain the *dl*-lactic acid for this investigation a C. P. commercial syrup was subjected to two successive vacuum distillations at 115° and 2 to 3 mm pressure. The middle fraction of the final distillate was kept frozen in an ice bath until used in the calorimeter. As shown by Thurmond and Edgar<sup>2</sup> and by others, lactic acid samples ordinarily contain some lactide ( $C_6H_8O_4$ ), lactic anhydride ( $C_6H_{10}O_5$ ) and water, formed from the acid. These are inevitable concomitants of the distillation process; although in an investigation, carried out subsequently to this one, Borsook, Huffman and Liu<sup>3</sup> have discovered that such anhydro compounds can be practically eliminated by fractional crystallization of the lactic acid from a mixture of ethyl and isopropyl ethers. In the present case the free acid was determined by titration with standard sodium hydroxide solution, with phenolphthalein as an indicator. Excess sodium hydroxide was next added; the solution was boiled to complete the hydrolysis of the anhydro forms; and then a back titration with standard hydrochloric acid sufficed to give the percentage of these anhydro forms, calculated as lactide, in the original sample of acid. The amount of water was determined by difference. Our final product, freshly prepared, gave in duplicate analyses (by weight): 98.4 percent lactic acid; 1.4 percent lactide; and 0.2 percent water. A portion of this product, subsequently kept for thirty days around -5°C, changed to 97.2 percent lactic acid and 2.2 percent lactide. At higher temperatures alterations were much more rapid. Thus a portion kept for ten days at 22°C analyzed 94.7 percent lactic acid and 4.4 percent lactide, and a sample heated at 82°C for forty-six hours changed to 68.3 percent lactic acid and 26.4 percent lactide.

The 3-methylhexane was prepared in very pure form by Edgar, Calingaert and Marker<sup>4</sup> and has been fully described by them in other places. A sample of this material was loaned to us for the present investigation by the Ethyl Gasoline Corporation.

These three substances showed practically no optical rotation when tested with a polariscope.

<sup>2</sup> Thurmond and Edgar, *Ind. Eng. Chem.* **16**, 823 (1924).

<sup>3</sup> Borsook, Huffman and Liu, *J. Biol. Chem.* **102**, 449 (1933).

<sup>4</sup> Edgar, Calingaert and Marker, *J. Am. Chem. Soc.* **51**, 1483, 1540 (1929).

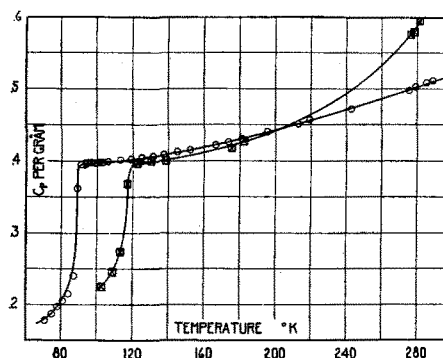


FIG. 1. The specific heats in cal. per degree of glassy and liquid secondary butyl alcohol (squares) and 3-methylhexane (circles) plotted against the absolute temperature.

### METHOD AND EXPERIMENTAL RESULTS

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats. The apparatus and details of experimental procedure have been fully described in other places.<sup>5</sup> In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is probably less than 1 percent; the fortuitous errors, which are naturally of greater importance in a comparative study of heat capacities over a range of temperatures, were usually under 0.3 percent. The results have been expressed in terms of the 15° calorie (=4.185 joules) per gram, with all weights reduced to a vacuum basis.

The specific heat data for secondary butyl alcohol and 3-methylhexane are given in Tables I and III. They are also represented graphically in Fig. 1. Neither of these substances showed any tendency to crystallize; with progressive cooling they simply became more viscous and finally hardened to glasses at the lower temperatures. The individual heat capacity determinations

TABLE I. *Specific heats in cal. per degree for sec.-butyl alcohol, glass and liquid.*

<i>T</i> (°K)	<i>C<sub>p</sub></i>	<i>T</i> (°K)	<i>C<sub>p</sub></i>	<i>T</i> (°K)	<i>C<sub>p</sub></i>
102.8	0.225	123.0	0.397	182.3	0.427
109.3	.246	130.2	.399	276.5	.576
113.5	.274	138.5	.401	278.3	.580
116.7	.368	175.5	.418	281.7	.596

<sup>5</sup> Parks, *J. Am. Chem. Soc.* **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.* **30**, 47 (1926).

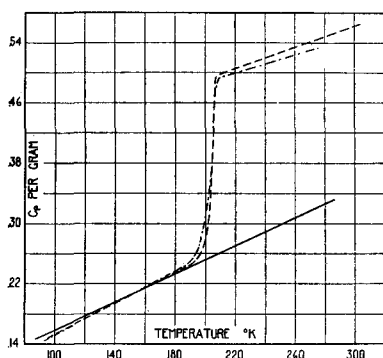


FIG. 2. The specific heat curves for lactic acid in the pure crystalline form (solid line), in the form of the acid glass and liquid (broken line), and in the form of the mixed glass and liquid (dot-and-dash line). Specific heats are in cal. per degree.

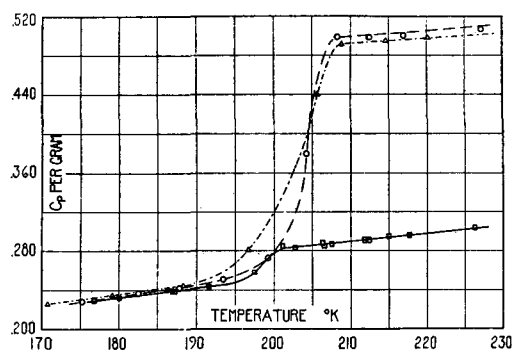


FIG. 3. The specific heat curves for lactic acid in the immediate neighborhood of the transition region. The squares refer to the 87.8 percent crystallized system; the circles to the acid glass and liquid; and the triangles to the mixed glass and liquid. Specific heats are in cal. per degree.

were made consecutively, with intervals of at least one hour, proceeding up the temperature scale.

The *dl*-lactic acid sample was transferred to the calorimeter as a liquid, promptly frozen therein by maintenance around 0°C, and then the calorimeter was installed in the specific heat apparatus. During this installation, which took about a day, the sample undoubtedly melted and underwent some alteration. To determine the approximate extent of this alteration, a portion of our purified lactic acid was given similar treatment; subsequent analysis yielded 97.0 percent lactic acid, 2.4 percent lactide and

0.6 percent water. The lactic acid sample in the calorimeter was first carefully crystallized again and a series of heat capacity measurements and a heat of fusion determination were made. Some of the specific heat values thus obtained are represented by the squares and solid line in Fig. 3. They disclose an appreciable sudden rise around 200°K, indicative of the presence of considerable amorphous or glassy material. Subsequent quantitative comparison of this curve with the two curves representing lactic acid in a completely uncrystallized state showed that this amorphous phase in contact with the crystals represented about 12.2 percent of the material.

The lactic acid sample, now a liquid, was next cooled very quickly in liquid air to produce what we have designated as the *acid glass*, and a series of heat capacity measurements was made on this material in the glassy and liquid condition. The specific heat values thereby obtained are given columns 1 and 2 of Table II and are represented graphically by broken lines in Figs. 2 and 3.

Following the completion of these measurements the calorimeter and contents were heated to a temperature of 70°C for forty-eight hours to promote the partial conversion of the acid to water and anhydro forms. The calorimeter was next cooled to liquid-air temperatures, whereupon the material formed a noncrystallizing glass which will be subsequently designated as the *mixed glass*, in view of the fact that it contained such appreciable quantities of the anhydro

TABLE II. Specific heats in cal. per degree for *dl*-lactic acid.

ACID GLASS AND LIQUID T(°K)	C <sub>p</sub>	MIXED GLASS AND LIQUID T(°K)	C <sub>p</sub>	PURE CRYSTALS AND LIQUID T(°K)	C <sub>p</sub>
103.5	0.1572	95.8	0.1471	90	0.148
110.3	.1612	101.3	.1533	100	.158
122.6	.1753	108.1	.1611	120	.177
135.4	.1876	156.1	.2109	140	.196
141.0	.1940	170.7	.2263	160	.214
154.8	.2075	179.1	.2357	180	.233
169.4	.2207	188.3	.2444	200	.252
175.2	.2283	196.7	.2809	210	.261
182.5	.2364	205.7	.4409	230	.280
187.9	.2421	208.8	.4921	250	.298
193.5	.2512	214.6	.4946	280	.326
199.2	.2729	220.2	.4986	289.9	Fusion
204.2	.3700	262.7	.5254	290	.554
208.3	.4988	267.4	.5282	300	.563
212.5	.4982				
217.0	.5003				
227.2	.5070				
293.5	.5562				
297.5	.5585				
303.0	.5655				

TABLE III. *Specific heats in cal. per degree for 3-methylhexane, glass and liquid.*

$T(^{\circ}\text{K})$	$C_p$	$T(^{\circ}\text{K})$	$C_p$	$T(^{\circ}\text{K})$	$C_p$
71.1	0.178	96.7	0.398	151.8	0.415
74.7	.187	99.1	.398	166.2	.422
78.0	.197	101.1	.399	173.8	.426
81.1	.205	103.1	.399	181.0	.430
84.0	.215	106.3	.400	195.7	.440
86.9	.240	112.7	.402	212.9	.451
89.2	.362	118.9	.403	219.8	.457
91.0	.395	125.1	.405	243.1	.473
92.8	.397	131.4	.407	275.8	.502
93.0	.395	137.6	.409	285.4	.514
95.1	.397	144.8	.413	289.2	.517

forms. The series of specific heat values represented in the third and fourth columns of Table II and by the dot-and-dash lines in Figs. 2 and 3 was then obtained. The material taken out of the calorimeter immediately after these measurements analyzed: 69.6 percent lactic acid, 24.2 percent lactide and 6.2 percent water.

From the relations of the three curves in an enlargement of Fig. 3 it was possible to deduce easily, in two successive approximations, the percentage of the amorphous material in the first series of measurements on the two-phase, crystalline-amorphous system, the heat capacity of this amorphous fraction at various temperatures, and finally the specific heats of the pure crystalline and liquid lactic acid. These last are given for various even temperatures in Table II and the crystal values also are represented by the practically straight, solid line in Fig. 2. It is interesting that at the lowest temperatures these specific heats for the crystals are slightly higher than those for the glasses. This is a rather unusual situation, although White<sup>6</sup> has observed it previously in the case of certain silicates. The heat of fusion of the crystals, with allowance for 12.2 percent amorphous phase, was calculated as 30.1 cal./gram at 289.9°K.

## DISCUSSION

### The glasses

In general characteristics the heat capacity curves for these three substances in the glassy and liquid condition are strikingly similar to those found previously for various glass-forming organic materials of a predominantly alcoholic character. Of course, such behavior might be

expected for the secondary butyl alcohol and probably for the lactic acid, but the 3-methylhexane is a distinctly novel case.<sup>7</sup> Here we encounter a nonpolar hydrocarbon, while the other organic glasses have been formed from oxygen-containing compounds that yield highly associated liquids.

Three rather distinct regions appear in all these heat capacity curves. At the lower temperatures, where the material forms a hard glass, the specific heats are of the order of magnitude of those found for the same substances, or for closely related ones, in the crystalline state. At the higher temperatures the material is a more or less viscous liquid and the specific heats even below the melting point of the crystals, as in the case of lactic acid, lie on a portion of the curve which is clearly characteristic of the ordinary liquid state and considerably above that of the corresponding crystalline state. Intermediate between these two portions of the curve appears a *transition region*, 8° to 20° in magnitude depending on the nature of the glass-forming material and its thermal history, within which the specific heats increase very rapidly. Its suddenness is reminiscent of a change of state, although there is nothing comparable to a heat of fusion and two phases are never present. The middle point of this transition region has been found to be associated with a viscosity of the order of  $10^{13}$  or  $10^{14}$  poises in a number of cases.<sup>8</sup>

For secondary butyl alcohol this transition centers around 115°K. The corresponding temperatures in the cases of other simple glass-forming compounds have been found as follows: 3-methylhexane 88°; ethyl alcohol 94°; *n*-propyl alcohol 98°; propylene glycol 159°; glycerol 185°; lactic acid 204°; glucose 282°; boron trioxide 510°. Among the organic compounds the mean temperature of the transition evidently rises with increasing polarity and increasing molecular weight, the former factor being the more important. However, at present there seems to be no way of quantitatively determining this temperature in advance of experiment.

<sup>7</sup> Some preliminary heat capacity values for this heptane were published in a general study of the nine isomeric heptanes by Huffman, Parks and Thomas, *J. Am. Chem. Soc.* **52**, 3241 (1930).

<sup>8</sup> Parks and Spaght, *Physics* **6**, 69 (1935).

<sup>6</sup> White, *Am. J. Sci.* **47**, 1 (1919).

TABLE IV.  $C_v$  values in cal. per degree for 3-methylhexane.

$T(^{\circ}\text{K})$	$C_p$ per mole	$C_p - C_v$ per mole	$C_v$ per mole	$T(^{\circ}\text{K})$	$C_p$ per mole	$C_p - C_v$ per mole	$C_v$ per mole
82	20.9	0.6	20.3	200	44.3	6.6	37.7
92	39.7	2.7	37.0	250	47.9	8.7	39.2
100	39.9	2.9	37.0	290	51.9	10.6	41.3

In the case of the lactic acid the *mixed glass*, which presumably represents a greater variety of molecular composition, exhibits a distinctly more gradual transition than the *acid glass*, as may be seen in Fig. 3. This result is in agreement with the previous studies on mixed alcohol glasses.<sup>1</sup>

Some interesting points come out in the case of the nonpolar 3-methylhexane if we deal with  $C_v$  instead of the experimentally measured  $C_p$  values. The molecular volume ( $V$ ) and the coefficients of isothermal expansion ( $\alpha$ ) and compressibility ( $\beta$ ) have been reported for this compound at 20°C by Edgar and Calingaert.<sup>9</sup> By use of the thermodynamic relationship

$$C_p - C_v = \alpha^2 VT / \beta$$

we then find  $C_v = 41.3$  cal. per mole at 290°K. Taking the quantity  $\alpha^2/\beta$  above the transition region as constant with temperature, we have then derived the additional values given in columns 3 and 4 of Table IV. The lone value for  $C_p - C_v$  below the transition region constitutes a somewhat cruder guess, based on fragmentary data concerning the change of  $\alpha$  and  $\beta$  for the analogous case of glucose.<sup>1b</sup>

The tabulated data show that  $C_v$  changes relatively little for the liquid heptane above 92°K, and its order of magnitude can be readily accounted for. If we neglect the vibrations of the hydrogen atoms attached to carbon, which are generally regarded as negligible below 250°K, there are left twenty-one degrees of freedom for the heptane molecule. Postulating only harmonic vibrational motion within the liquid, we thus obtain for the upper limit of  $C_v$  21 $R$  or 41.7 cal./deg., which is merely 4.7 to 0.4 calories higher than the actual values above 92°K. The much lower  $C_v$  value of 20.3 cal./deg. at 82° may

be interpreted either on the basis of a very rapid decline of the heat capacity associated with these vibrational degrees of freedom consequent to a rapid increase in their characteristic frequencies within the temperature interval 92°–82°, or perhaps to the actual loss of some of these degrees of freedom with lowering temperature. Of course this glass at 82°K, which is the apparent lower edge of the transition region, must be regarded as a comparatively inert material. Thus on the assumption of a characteristic frequency of the order of  $10^{13}$  per second (which seems plausible in view of Andrews' studies on several organic crystals<sup>10</sup>) we have estimated that the average heptane molecule acquires between the absolute zero and 82°K only about one quantum of energy, distributed between these twenty-one degrees of freedom.

Throughout this discussion the interval of 10° or so, in which the specific heats rise suddenly, almost discontinuously, has been termed the *transition region*. Previous studies in this series<sup>1, 11</sup> have shown that the character of the curve here depends upon the way in which the heating is carried out and to some extent upon the thermal history of the glass. With the Nernst method the transition in organic materials becomes somewhat more abrupt with increased annealing during the initial formation of the glass and also with enlargement of the time intervals between successive heat capacity determinations. Such considerations make very plausible the earlier suggestion of Gibson and Giauque<sup>12</sup> that "if it were possible to obtain a glass free from strain at all temperatures, the liquefaction would occur at a definite temperature"; and recently several students of the glass problem, including Berger<sup>13</sup> and Tammann,<sup>14</sup> have adopted this notion of a *transformation point* (analogous to the melting point of a crystal) separating the glassy and viscous liquid conditions. This idealization of the transition region into a transformation point certainly fits in with the conception of a glass as

<sup>10</sup> Andrews, Chem. Rev. **5**, 533 (1928); *Colloid Symposium Annual*, Vol. 7 (John Wiley and Sons, New York, 1930), pp. 119–128.

<sup>11</sup> Thomas and Parks, J. Phys. Chem. **35**, 2091 (1931).

<sup>12</sup> Gibson and Giauque, J. Am. Chem. Soc. **45**, 95 (1923).

<sup>13</sup> Berger, J. Am. Ceram. Soc. **15**, 647 (1932).

<sup>14</sup> Tammann, Zeits. f. anorg. allgem. Chemie **190**, 48 (1930).

<sup>9</sup> Edgar and Calingaert, J. Am. Chem. Soc. **51**, 1540 (1929).

an amorphous solid,<sup>15</sup> or a fourth state of matter<sup>16</sup>—a conception that has much to be said for it from the purely practical standpoint of classifying our knowledge of the properties of glasses. Other investigators, however, consider that a glass is simply an undercooled liquid of great viscosity; and some adherents of this theory, notably Littleton<sup>17</sup> and Morey<sup>18</sup> in recent years, maintain that with *true* internal equilibrium within the glass at all temperatures the transition in a property, such as specific heat, must become more gradual and apparent discontinuities will disappear. The attainment of such complete internal equilibrium in glasses at the lower temperatures would presumably require long periods of time—months or even years. Accordingly, a thorough test of these opposing views of the transition region, which are both plausible in their way, is probably impossible in the case of heat capacity data because calorimetric procedures, at least at the present day, do not permit accurate measurements over such periods of time.

The present study also throws some light upon the nature of organic glass-forming materials. All three of the substances here investigated contained dextro and laevo molecules in equal numbers. The secondary butyl alcohol and 3-methylhexane could not be crystallized; the lactic acid, which probably forms a racemic compound, exhibited only a moderate tendency to crystallize. Apparently in many types of compounds, and notably in the hydrocarbons, the presence of the two varieties of molecules with equal intermolecular forces and energy contents strongly militates against any crystallization process. In the case of some very polar organic liquids, ethyl alcohol for example, a somewhat comparable variety of molecular species may undoubtedly be attained through a variable association of the ultimate molecular units; but this association, being rather temporary in character, produces a glass which more readily crystallizes.

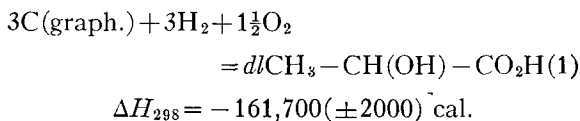
### The entropy and free energy of *dl*-lactic acid

The heat capacity data for the lactic acid

provide a basis for a calculation of its molal entropy and free energy at 298.1°K by means of the third law of thermodynamics.

By application of the extrapolation method of Kelley, Parks and Huffman<sup>19</sup> to the data for the crystals in Table II, the entropy increase between the absolute zero and 90° was estimated as 11.51 e.u. (cal. per degree) per mole. According to Borsook, Huffman and Liu<sup>3</sup> the melting point of pure *dl*-lactic acid is 289.9°K, i.e., about 0.8° higher than that found by us with acid of somewhat lower purity. The entropy increase for the crystals between 90° and 289.9°K, calculated from the data in Table II, is 23.62 e.u. The molal entropy of fusion is  $(30.1) \times (90.05)/289.9$  or 9.36 e.u. From the heat capacity values in Table II the entropy increase of the liquid between 289.9° and 298.1° is found to be 1.44 e.u. Addition of these various increments then yields  $S_{298}^{\circ} = 45.9(\pm 1.0)$  e.u. for the molal entropy of *dl*-lactic acid in the liquid state.

By using 326,000 cal., a revision by Kharasch<sup>20</sup> of the value of Emery and Benedict for the heat of combustion of lactic acid at constant pressure, in conjunction with the values 68,310 cal. and 94,240 cal.<sup>21</sup> for the heats of combustion of hydrogen and graphitic carbon, respectively, we find for the process



Taking for the atomic entropies<sup>21</sup> 1.36 e.u. for carbon, 15.615 e.u. for hydrogen and 24.52 e.u. for oxygen, we next find  $\Delta S_{298}^{\circ} = -125.4$  e.u. (cal. per degree) for this process. By the fundamental thermodynamic relation,  $\Delta F = \Delta H - T\Delta S$ , we then obtain  $\Delta F_{298}^{\circ} = -124,300(\pm 2300)$  cal. for the free energy of formation of a mole of liquid *dl*-lactic acid from its elements. The uncertainty in this last value can be greatly reduced when a more reliable combustion value for lactic acid becomes available.

<sup>15</sup> Warren, Rev. Sci. Inst. **4**, 520 (1933).

<sup>16</sup> Parks and Huffman, Science **64**, 363 (1926).

<sup>17</sup> Littleton, Ind. Eng. Chem. **25**, 748 (1933).

<sup>18</sup> Morey, J. Am. Ceram. Soc. **17**, 315 (1934).

<sup>19</sup> Kelley, Parks and Huffman, J. Phys. Chem. **33**, 1802 (1929).

<sup>20</sup> Kharasch, Bur. Standards J. Research **2**, 390 (1929).

<sup>21</sup> Parks and Light, J. Am. Chem. Soc. **56**, 1512 (1934).