cal basis for the conclusion that the entropy of a perfect crystal of a pure substance vanishes at the absolute zero.

We, therefore, state the third law of thermodynamics as follows: *if the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero.*

It seems likely, however, that the difference between the entropy of a pure substance in a crystalline state and in an amorphous state may, in many cases, prove to be very small.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

ENTROPY CHANGES AT LOW TEMPERATURES. I. FORMIC ACID AND UREA. A TEST OF THE THIRD LAW OF THERMODYNAMICS.

BY G. E. GIBSON, W. M. LATIMER AND G. S. PARKS.

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The third law of thermodynamics, which states that the entropy of all pure crystalline substances at zero absolute temperature is zero,[1] offers a ready method for the determination of the free energy of compounds which cannot conveniently be investigated by determination of equilibrium or electromotive force. This is in general true of organic compounds. If the specific heats of a compound and of its elements at various temperatures are known, ΔS, the entropy of formation of the compound from its elements may be calculated. It is necessary then to know only the heat of formation ΔH in order to obtain the free energy ΔF from the relationship

$$\Delta F = \Delta H - T\Delta S \qquad (1)$$

The only organic compounds for which specific heat measurements at low temperatures have been made are benzene and oxalic acid, investigated by Nernst.[2] Calculation of the free energy of these compounds by the method indicated above, offers no check on the validity of the Third Law, since the free energies of these compounds have not been determined by other methods. From the equilibrium between water, carbon monoxide and formic acid, Branch[3] has calculated the free energy of formation of formic acid from its elements to be

$$\Delta F_{298} = -85{,}200 \text{ cal.}$$

From the work of Lewis and Burrows[4] on the equilibrium between am-

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[1] The exact statement of the third law has been discussed in the preceding paper by Lewis and Gibson.

[2] Nernst, *Ann. Physik*, [4] 36, 395 (1911).

[3] Branch, THIS JOURNAL, 37, 2316 (1915).

[4] Lewis and Burrows, *ibid.*, 34, 1575 (1912).

monia, carbon dioxide, water and urea the free energy of formation of urea may be calculated to be

$$\Delta F_{298} = -48{,}992 \text{ cal.}$$

The object of this investigation, then, is to determine the specific heat of formic acid and urea over the range of temperature from the boiling point of liquid air to 25°, and to compare the free energy calculated from these measurements with the values given above.

Experimental.

In principle the method of Eucken and Nernst[1] was employed in the measurements of the specific heats. A measured amount of heat was supplied by an electric current to the substance contained in a copper calorimeter, which was suspended in a vaccum in a silvered glass tube in order to diminish the conduction and radiation of heat to and from the surroundings. A thermocouple in the center of the calorimeter measured the rise in temperature.

The Calorimeter.—The poor thermal conductivity of the substances dealt with necessitated a calorimeter which gave uniform heating and rapid distribution of heat. After experimenting with several types of copper and glass calorimeters, a cylindrical copper calorimeter, of approximately 3.8 cm. diameter and 11.5 cm. length, with walls 0.05 cm. thick, was adopted. A heating coil of silk-wound Therlo wire, of 90 ohms resistance, was wound on a thin copper cylinder (2.2 × 10 cm.) which slipped through a circular slit in the bottom of the calorimeter, and fitted tightly in the annular space between 2 thin concentric copper cylinders, the upper ends of which were soldered together, while their lower ends were soldered to the edges of the circular slit in the bottom of the calorimeter. Heat could thus be supplied from the inside of the calorimeter without the troublesome sealing of insulated copper wires through copper walls, and with the added advantage of being able to slip the heating coil in and out. Copper vanes running from the sheath enclosing the heating coil gave rapid distribution of the heat throughout the calorimeter. The thermocouple was inserted through a small vertical copper tube 6 cm. long which was soldered through the center of the top of the calorimeter. The calorimeter was filled through an opening in the top which was then closed by means of solder. Hydrogen was introduced with the substance to aid in thermal distribution, and all joints were made gas-tight. The weight of the calorimeter varied from 73 to 97 g., and its heat capacity from 15 to 20% of that of the substance under investigation.

Heat Insulation.—While the method of heat insulation was essentially that employed by Eastman and Rodebush[2] of this laboratory, it differed

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[1] Nernst, *Ann. Physik,* [4] 36, 395 (1911).

[2] Eastman and Rodebush, THIS JOURNAL, 40, 489 (1918).

somewhat in detail. The calorimeter was suspended by a silk thread from a lead block in the lower portion of a silvered tube, approximately 5.5 × 70 cm. The block was supported by a constriction in the tube, and its under and upper sides covered with a polished copper sheet. A few centimeters above the block a copper baffle was sprung into place, to cut down radiation to the block from above. The silvered tube extended to the bottom of a long Dewar vessel which was filled with the cooling mixture to well above the copper baffle. Radiation was further decreased by surrounding the calorimeter by a screen of thin polished copper foil insulated by fine glass points. Although some conduction of heat along the thermocouple and fine heating wires was unavoidable, this effect was reduced to a minimum by bringing the bundle of 8 insulated wires into good thermal contact with the lead block, and winding in helical form the portion, over 10 cm. long, between the block and the calorimeter. The Kraus[1] arrangement of double mercury vapor pumps, supported by a small oil pump, gave the necessary high vacuum. The connection between the top of the silvered tube and the vacuum line was made either by a large ground glass joint or a seal of de Khotinsky cement. The character of the electrical discharge produced in the tube by a small spark coil indicated the quality of the vacuum.

Measurements.—Heat was supplied to the calorimeter by means of an electric current from a battery of 14 Edison cells. The fall in potential across the terminals of the heating coil could be measured with an accuracy of at least 0.1% by means of a calibrated voltmeter. The current of 0.13 to 0.15 ampere was measured by a Leeds and Northrup potentiometer and a standard ohm. In runs above 150° K. the current was remarkably steady, but below this temperature there was a uniform decrease in current during each run, owing to the change in resistance of the fine copper leads during heating. This variation, about 0.5% in magnitude, was corrected for by averaging the readings taken at intervals of 30 seconds. As the voltmeter was in parallel with the heating coil in the calorimeter, it was also necessary to correct for the current passing through the voltmeter. It is believed that the error in the final value for the current through the heating coil was never more than 0.1%. The time for heating was 300 to 600 seconds, and this interval was measured with a stop-watch with an accuracy of 0.1% or better. Thus the maximum error in the amount of heat delivered to the calorimeter during any run should not exceed 0.3%; the average error was probably much less.

For the temperature measurements a single element copper-constantan thermocouple, calibrated from the 4-element couple of Eastman and Rodebush,[2] was used. Measurements of its e. m. f. were made with a

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[1] Kraus, THIS JOURNAL, **39**, 2183 (1917).

[2] Eastman and Rodebush, *ibid.*, **40**, 489 (1918).

modified White potentiometer[1] by which temperature differences could be measured accurately to 0.001° at 273° K. and 0.003° at 100° K. The increase in temperature during a run was from 3° to 6°. The temperature, T, and the rate of change of e. m. f. with change of temperature, dE/dT, were obtained from curves plotted for values calculated from the equation of Eastman and Rodebush:

$$E = 1/426,840 - 0.74097\ T^{1.837} - 17.45\ T.$$

Experimental Procedure.—The substances studied were extremely poor conductors of heat. Owing to this fact it was found that after each addition of heat to the contents of the calorimeter a period of 40 to 50 minutes elapsed before thermal equilibrium was complete. At the end of this time the temperature of the calorimeter became constant, provided that the difference between the calorimeter and its surroundings was not greater than 5° or 6° at 90° K., or than 0.5° at 270° K. Otherwise there existed a heating or cooling rate, the magnitude of which depended upon this temperature difference and upon the absolute temperature of the bath. In order to arrive at an accurate value for this rate, measurements of the temperature of the calorimeter were continued at minute intervals for 70 to 90 minutes after the cessation of the heating current. With these data a correction for the heating or cooling of the calorimeter during the period of the run was made, and the true temperature rise in the calorimeter, due to the heat added, could be computed within at least 1%. In about $^1/_6$ of the runs the final temperature was constant. In general the correction averaged 3 or 4% of the total increase, although in a few cases it rose as high as 8 or 10%.

Clearly, if the correction for temperature difference during a run is so large, it becomes very important to maintain the surroundings at a fairly constant temperature which does not differ very much from that of the calorimeter itself. After considerable experimentation it was found that by regulating the amount of liquid air in the long Dewar tube successful runs could be made with liquid air as a cooling agent between 85° and 140° K. By boiling liquid air under reduced pressure, a bath temperature of about 71° to 75° K. could be obtained and maintained for several hours. Temperatures between 170° and 250° K. could be obtained easily by means of a mixture of solid carbon dioxide and acetone, while a mixture of ice and salt proved suitable between 255° K. and room temperature.

Pure formic acid and urea purchased in the open market were used. Without further purification of the formic acid its specific heat was found to rise abnormally with temperature in the interval beginning 18° below the melting point. Following Schlesinger,[2] the acid was twice distilled over boron sesquioxide at 20° C. and 6 mm. pressure in a glass apparatus

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[1] Randall, Bichowsky and Rodebush, This Journal, **38**, 1266 (1916).

[2] Schlesinger and Coleman, *ibid.*, **38**, 271 (1916).

free from rubber connections, and then twice recrystallized *in vacuo.* Even when so purified the specific heat was found to be abnormally high, a few degrees below the freezing point.

Specific Heats.

TABLE I.—FORMIC ACID.

Temperature. ° K.	C_p per g.	C_p per g. atom.
71.0	0.157	1.45
73.3	0.163	1.50
76.6	0.163	1.50
77.7	0.165	1.52
82.0	0.168	1.55
86.0	0.174	1.60
89.0	0.174	1.60
90.0	0.179	1.66
90.3	0.182	1.68
94.0	0.188	1.73
176.3	0.270	2.48
180.0	0.273	2.51
184.5	0.282	2.59
196.0	0.292	2.69
205.0	0.297	2.73
237.0	0.328	3.02
243.2	0.339	3.12
248.0	0.348	3.20
250.5	0.344	3.17
253.0	0.352	3.24
257.0	0.353	3.25
270.0	0.372	3.42
275.0	0.459	4.22
286.0	0.506 (liquid)	4.66 (liquid)
288.0	0.517 (liquid)	4.77 (liquid)
291.5	0.510 (liquid)	4.69 (liquid)

Experimental Results.—The results of the measurements made are shown in Tables I and II. As a typical example of the way in which the values given were obtained, the data for one of the runs with formic acid are given in detail.

Voltage at terminals of heating coil, 12.66 volts.

Current, 0.1177 ampere.

Time, 310.4 seconds.

Total heat supplied, $12.66 \times 0.1177 \times 310.4 \times 0.2391 = 112.09$ cal.

Initial potentiometer reading....... 5786.88 microvolts.

Final potentiometer reading........ 5696.00 microvolts.

Difference........................ 90.88 microvolts.

Average T, corresponding to average potentiometer reading, 82° K.

Corresponding $\dfrac{dE}{dT}$, 17.97 microvolts.

Heat capacity of calorimeter, at 82° K, 3.76 cal.

Heat supplied to calorimeter........ $3.76 \times \dfrac{90.88}{17.97} = 19.00$ cal.

Heat supplied to formic acid........ 112.09 — 19.00 = 93.09 cal.
Weight of formic acid.............. 109.66 g.
C_p of formic acid per g............. $\frac{93.09}{109.66} \times \frac{17.97}{90.88} = 0.168$ cal./deg.
C_p per mol....................... 7.73 cal./deg.
C_p per mean gram atom............ 1.546 cal./deg.

The heat capacity of the calorimeter, as determined experimentally, was on the average 2% higher than that calculated for the same mass of pure copper from the values given by Nernst and Lindemann.[1]

Table II.—Urea.

Temperature. ° K.	C_p per g.	C_p per g. atom.
86.4	0.239	1.79
90.0	0.235	1.76
90.0	0.244	1.83
90.3	0.243	1.82
96.5	0.252	1.89
97.0	0.244	1.83
104.0	0.249	1.87
107.5	0.259	1.94
128.1	0.285	2.13
198.5	0.343	2.57
199.6	0.340	2.55
201.4	0.338	2.54
204.7	0.345	2.59
204.7	0.346	2.59
208.2	0.344	2.58
223.9	0.377	2.83
244.2	0.382	2.87
274.0	0.428	3.21
275.0	0.425	3.19
277.5	0.430	3.22
295.5	0.463	3.47
298.0	0.459	3.44
300.3	0.460	3.45

The specific heats of liquid formic acid agree with the following values given by Landolt and Börnstein: 18° to 56°, 0.522 cal.; 57°, 0.515 cal.; 17° to 82°, 0.532 cal. per degree per g. In the value given for the solid, formic acid seems to have been confused with lauric acid. The value 0.321 cal. for urea is certainly in error.

Calculation of Entropy and Free Energy.

Formic Acid.—Assuming the entropy at absolute zero to be zero, the entropy at 298° K. is given by the equation

$$S_{298} = \int_0^{298} \frac{dQ}{T}. \qquad (3)$$

Thus for formic acid we may write

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[1] Nernst and Lindemann, *Z. Elektrochem.*, 17, 817 (1911).

$$S_{298} = \int_{0}^{281.5} \frac{C_p\,(\text{solid})\,dT}{T} + \frac{\Delta H\ \text{fusion}}{281.5} + \int_{281.5}^{298} \frac{C_p\,(\text{liquid})\,dT}{T}. \qquad (4)$$

The values of the integrals may readily be obtained by plotting C_p as ordinates against $ln\ T$ as abscissas, the entropy then being the area under the curve. If, as in the present case, the curve is not known at lower temperature, some interpolation formula must be used. It has been shown from existing data for many substances which crystallize in the regular system that

$$C_v = f\,(T/\theta), \qquad (5)$$

where T is the absolute temperature, θ is a characteristic constant for each substance and f is the same function for different substances. Likewise, Lewis and Gibson[1] suggest for all other solids

$$C_v = f\,(T^n/\theta^n), \qquad (6)$$

where f is the same function as before, and n is less than unity.

The latter formula agrees well with the values for formic acid and has been employed in the entropy calculations. To obtain the values of C_v, corresponding to the experimental C_p, use is made of the thermodynamic equation

$$C_p - C_v = T\beta^2V/41.8\alpha \qquad (7)$$

where v is the molecular volume and α and β are respectively the coefficients of cubical compressibility and thermal expansion. Although α and β have not been determined for solid formic acid, a good estimate may be obtained by comparing values of similar substances. $C_p - C_v$ is thus calculated to be 0.4 cal. per atom at 270° K. from the estimated values $\beta = 7.0 \times 10^{-4}$ and $\alpha = 30 \times 10^{-6}$. The difference at 71° K. may be obtained from the equation of Lindemann and Magnus,[2]

$$C_p - C_v = aT^{3/2}, \qquad (8)$$

to be 0.05 cal. per atom.

For a detailed description of the method of calculating entropies from Equation 6, reference is made to the paper of Lewis and Gibson.[3] Adopting their notation we obtain for solid formic acid

$$n = 0.350 \qquad \theta = 270 \qquad \log 281.5/\theta' = 0.0063$$

$$S_{v281.5} = 4.72 \text{ per atom.}$$

Adding the value of $S_p - S_v = 0.14$, which was obtained from the area between the C_p and C_v curves, we have $S_{p281.5} = 4.86$ per atom or 24.30 per mol. For the heat of fusion we shall adopt Berthelot's[4] value, 2420 cal. at 281.5° K. The corresponding entropy of fusion is 8.60.

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[1] Lewis and Gibson, THIS JOURNAL, **39**, 2555 (1917).

[2] Lindemann and Magnus, *Z. Elektrochem.*, **16**, 269 (1910).

[3] Lewis and Gibson, *loc. cit.*

[4] *Compt. rend.*, **78**, 716 (1874).

Taking 4.72 as the mean specific heat per atom of liquid formic acid, we obtain for the liquid

$$\Delta S = (\log 298 - \log 281.5) \times 4.72 \times 2.3 \times 5 = 1.30$$

and

$$S_{298} \text{ liquid} = 24.30 + 8.60 + 1.30 = 34.2$$

Thomsen[1] obtained for the heat of combustion of formic acid 69,400 cal. calculated for the vapor at 18° C. Figuring the heat of vaporization at 18° to be 6300 cal. the heat of combustion of the liquid becomes 63,100 cal. Berthelot[2] gives 61,700 cal. Although the difference, 1400 cal., leads to some uncertainty, we shall accept the mean value 62,400 cal. For the heat content of the products of combustion we shall use the values

$$H_2O = 68{,}275 \text{ cal.}^3 \text{ and } CO_2{}^4 = 94{,}250 \text{ cal.}$$

Then for the reaction

$$H_2 + O_2 + C = HCOOH\ (l) \qquad (1)$$

$$\Delta H_{298} = -100{,}100 \text{ cal.}$$

For the entropies of hydrogen, oxygen and carbon, Lewis and Gibson[5] have calculated 15.9 ± 1, 24.1 ± 1 and 1.3, respectively.

$$\Delta S_{298} = 34.2 - 31.8 - 48.2 - 1.3 = -47.1.$$

Hence $\Delta F_{298} = -100.100 + 298 \times 47.1 = -86.070$ cal., a difference of 870 cal. from the value obtained by Branch[6] by means of equilibria measurement.

Since S_{298} for water (16.8), and carbon monoxide (45.55), are also given by Lewis and Gibson, we may calculate ΔF_{298} for the reaction

$$H_2O + CO = HCOOH.$$

Using the value for heat of formation[7] of carbon monoxide as —26,140 cal. and water as given above,

$$\Delta H_{298} = 100{,}100 - (-68{,}275 - 26{,}140) = -5685 \text{ cal.}$$

$$\Delta S_{298} = 34.2 - 16.8 - 45.55 = -28.15$$

$$\Delta F_{298} = -5685 + 298 \times 28.15 = 2705 \text{ cal.,}$$

a difference of 1275 cal. from the value obtained by Branch.

Considering the uncertainty of the heats of combustion and some of the values used in calculating the entropies of the elements, the agreement of the free energies obtained by the 2 different methods is very satisfactory and certainly well within the experimental error. If, in place of the mean

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[1] Thomsen, "Thermochemistry." Longmans, Green and Co., 1908, p. 373.

[2] Berthelot, *Ann. chim. phys.*, [6] 28, 126 (1893).

[3] Lewis and Randall, THIS JOURNAL, 36, 1969 (1914).

[4] Lewis and Randall, *ibid.*, 37, 488 (1915).

[5] Lewis and Gibson, *loc. cit.*

[6] Branch, *loc. cit.*

[7] Lewis and Randall, THIS JOURNAL, 37, 458 (1915).

value for the heat of combustion, we had taken Thomsen's value, 63,100 cal., we find for the formation from the elements

$$\Delta F^\circ_{298} = -85,370 \text{ cal.},$$

a difference of 170 cal. from Branch, and for the formation from water and carbon monoxide

$$\Delta F^\circ_{298} = 3415 \text{ cal.},$$

a difference of 575 cal.

Urea.—The C_p curve for urea is flatter than that for formic acid and hence a greater portion of its entropy lies below liquid air temperatures. For this reason experimental errors in C_p and doubtful approximations in the value of $C_p - C_v$ lead to rather large uncertainties in the entropy as calculated by the "n formula." It is hoped that these uncertainties may shortly be cleared up by measurements at liquid hydrogen temperatures. From the data given in Table II we calculate $S_{298} = 41.0 \pm 2$ entropy units, using

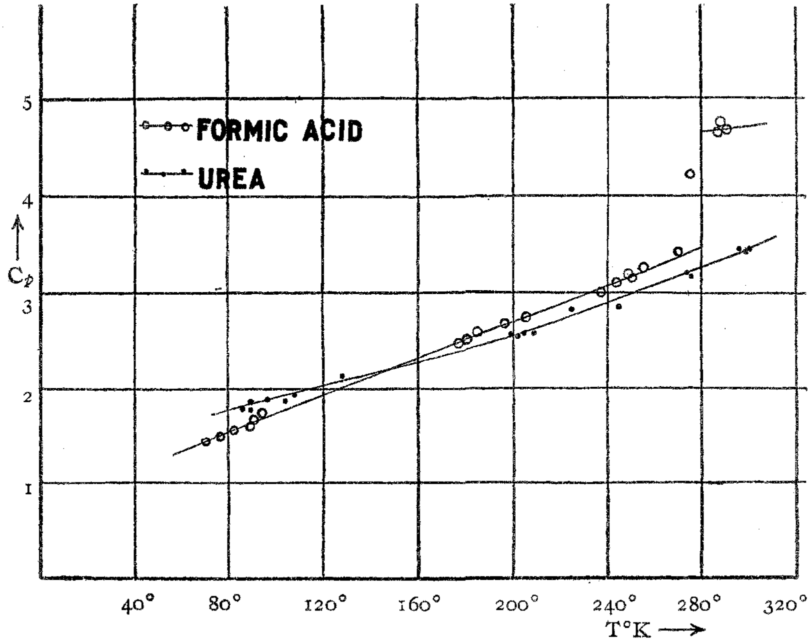

Fig. 1.—Specific heat of formic acid and urea (per gram atom).

$$n = 0.345 \qquad \theta = 245.$$

The Lewis and Gibson values for the entropies of the elements of urea are: C, 1.3; O, 24.1 ± 1; N, 22.8 ± 1; H, 15.9 ± 1. Thus for the reaction

$$C + 0.5O_2 + N_2 + 2H_2 = CON_2H_4(s)$$

$$\Delta S_{298} = 41.0 - (1.3 + 24.1 + 45.6 + 63.6) = -93.6 \pm 9.$$

For the heat of combustion of urea Berthelot[1] gives 151,600 cal. and Stohmann[2] 152,300 cal. The deviation from its mean value 151,950 is 350 cal. Using the values for the heats of formation of water and carbon dioxide given above, the heat of formation of urea from its elements is

$$\Delta H_{298} = 151{,}950 - 2 \times 68{,}275 - 94{,}250 = -78{,}850 \text{ cal.},$$

and the free energy of formation of urea from its elements is

$$\Delta F_{298} = -78{,}850 + 298 \times 93.6 = -50{,}960 \pm 3350 \text{ cal.}$$

Lewis and Burrows[3] found from measurements of equilibrium for the reaction

$$2NH_3(g) + CO_2(g) = CON_2H_4(s) + H_2O(1);\ \Delta F = -1772 \text{ cal.}$$

This gives for the free energy of formation of urea from its elements

$$\Delta F_{298} = -48{,}992 \text{ cal.},$$

using for the free energy of formation of $NH_3(g)$, $CO_2(g)$ and $H_2O(l)$ the respective values —4740 cal., —94,360 cal. and —56,620 cal.

Summary.

The specific heats of formic acid and urea have been measured over the temperature range 75° K. to 298° K., and their entropies and free energies have been calculated.

The values for the free energies agree within the experimental error with values calculated from equilibrium data. A check upon the validity of the third law of thermodynamics as applied to organic compounds has thus been obtained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

ENTROPY CHANGES AT LOW TEMPERATURES. II. ETHYL AND PROPYL ALCOHOLS AND THEIR EQUAL MOLAL MIXTURE.

BY G. E. GIBSON, G. S. PARKS AND W. M. LATIMER.

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In a previous paper[4] Lewis and Gibson have discussed the applicability of the third law of thermodynamics to processes of solution. They conclude that the entropy of a solution should always exceed at the absolute zero the sum of the entropies of the pure crystalline constituents. They also suggest that the transition from a pure crystalline substance to the same substance in the form of glass may be accompanied by an increase in entropy. The object of the present investigation is to obtain additional experimental data suitable for testing these conclusions.

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[1] Berthelot and Petit, *Ann. chim. phys.*, [6] **20**, 113 (1889).

[2] Stohmann and Langbein, *J. prakt. Chem.*, **44**, 380 (1891).

[3] Lewis and Burrows, THIS JOURNAL, **34**, 993 (1912).

[4] Lewis and Gibson, *ibid.*, **42**, 1529 (1920).