

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

## THE HEAT CAPACITY OF METHYL ALCOHOL FROM 16°K. TO 298°K. AND THE CORRESPONDING ENTROPY AND FREE ENERGY

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The measurements of the heat capacities of aliphatic compounds made by Parks and his co-workers<sup>2</sup> have brought forth interesting regularities in the entropies and free energies of members of homologous series. They find that when the members are considered in the liquid state at 298.1°K. there is a definite entropy increase per CH<sub>2</sub> group of about 9 units, while the free energies have the same value within their limits of accuracy. The measurements upon which these conclusions are based do not go below liquid-air temperatures and consequently a very large and uncertain extrapolation is involved in the entropy calculations. It seemed desirable therefore to carry the measurements to liquid hydrogen temperatures in order to throw further light on these regularities. Also, in view of the important theoretical calculations<sup>3</sup> which are being made concerning the formation of aliphatic compounds from carbon monoxide and hydrogen under pressure, accurate values of the entropies of these compounds are now essential.

This paper contains results of measurements on methyl alcohol and will be followed later by data for other substances. Since little extra labor was involved in making the measurements from 90 to 298°K., this region, which Parks covered, was re-investigated and data were obtained for the intervals between his bath temperatures.

### Method and Apparatus

The method used has been described by others and the apparatus is of the general type used by them,<sup>4</sup> so that only a brief description seems necessary.

The calorimeter, which is of the design used by Parks, was made from copper tubing and is 6.5 cm. long and 3 cm. in diameter. It is equipped with 38 thin perforated copper disks which are in good thermal contact with the calorimeter walls. These disks are essential for the assurance of rapid heat distribution. A layer of rice paper

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<sup>2</sup> (a) Parks, *THIS JOURNAL*, **47**, 338 (1925); (b) Parks and Kelley, *ibid.*, **47**, 2089 (1925); (c) Parks and Anderson, *ibid.*, **48**, 1506 (1926); (d) Parks and Huffman, *ibid.*, **48**, 2788 (1926).

<sup>3</sup> (a) Kelley, *Ind. Eng. Chem.*, **18**, 78 (1926); (b) Smith, *ibid.*, **19**, 801 (1927); (c) Francis, *ibid.*, **20**, 277 (1928); (d) **20**, 283 (1928).

<sup>4</sup> (a) Gibson and Giauque, *THIS JOURNAL*, **45**, 93 (1923); (b) Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

saturated with Bakelite lacquer was baked on the outside and a bare gold resistance thermometer-heating coil of B. and S. gage No. 40 wire was wound on, the turns being separated by silk thread. The resistance of the coil at 22° is 140 ohms. The gold wire had been annealed previously at temperatures from 350 to 600° for four days. This coil serves both as a heater for the energy input and as a thermometer, as will be described later. Another layer of rice paper and Bakelite lacquer was applied over the coil and the outside covered with gold leaf to decrease radiation. A piece of small-diameter copper tubing one cm. long filled with Wood's metal was soldered to the bottom and serves as a holder for the thermocouple junction. The calorimeter is filled through a small copper tube silver soldered through the bottom. This tube is plugged with solder after filling the calorimeter.

The calorimeter hangs by linen threads inside a heavy metal block, the lower part of which is a copper cylinder of 1.1 kg. mass and the upper part solid lead of about 1.75 kg. mass. This block is equipped with a 260-ohm constantan heater and a thermocouple. All lead wires to external circuits and the calorimeter thermocouple are in good thermal contact with this block, thus minimizing the flow of heat along the wires into the calorimeter.

The block is suspended by heavy twine inside a brass container 21.5 cm. long and 7.5 cm. in diameter. A German silver tube hard soldered in the top of this container serves as support for the container, outlet for the heater lead wires and thermocouples and connection to the evacuating system. On top of this can about 3 kg. of lead is stacked, which together with the heavy block furnishes sufficient heat capacity to make it possible to obtain the entire specific heat curve from 16 to 298°K. without the use of temperature baths other than liquid hydrogen and liquid air. This implies, of course, that measurements be made continuously from about 200° to room temperature; with such a procedure the container warms at just about the right rate.

A pyrex Dewar 76 cm. long and with an inside diameter of 11 cm. was used to contain the temperature baths. This Dewar rests inside a Monel metal can 81 cm. by 16 cm. The top of this can, which is soldered on, is attached to the German silver tube before mentioned and is equipped with an inlet for liquid air or hydrogen, an outlet for the outgoing gas and a safety valve.

The liquid hydrogen is made with a liquefier similar to that described by Giaque and Wiebe and is transferred into the apparatus through a German silver Dewar tube.

Further heat insulation is given by a sheet iron case 100 cm. long and 40 cm. in diameter which is filled with silk floss.

The apparatus is attached by means of a de Khotinsky seal to a glass vacuum line and a pressure of  $10^{-6}$  mm. or better is maintained by a mercury diffusion pump backed by a Nelson oil pump.

### The Measurements

The instruments and the method of measuring the energy current and voltage are those described by Gibson and Giaque. The time of energy input was measured with a stop watch which was frequently calibrated against an accurate chronometer of the Department of Astronomy. The temperature rise was measured with the resistance thermometer. The latter was calibrated against the calorimeter thermocouple at intervals of 5 to 15° depending upon the temperature. Care was always taken to have the block and calorimeter within 0.5° of each other when these comparisons were made. Since the resistance was found to increase slightly with the time, it is necessary to make these calibrations for each

filling of the calorimeter. The graphical method of Giauque and Wiebe was used in handling these data.

The temperature scale used has been described.<sup>5</sup> The calorimeter thermocouple was compared at 28 points between 14 and 298°K. with one of the laboratory standard couples with conditions as nearly identical as possible with those under which the couple is used. The temperature measurements are considered accurate to 0.05°.

### Purification of Methyl Alcohol

The methyl alcohol was Mallinckrodt's "reagent quality." It was allowed to stand over lime for two weeks and carefully fractionated several times. The final product, 300 cc. in volume, had a boiling-point range of 0.01° and density  $d_4^{25} = 0.78675$ . The value interpolated from the data in "International Critical Tables"<sup>6</sup> is 0.78677, a fortuitous agreement. Also the melting point was very sharp, there being but little pre-melting, which indicates high purity.

### Heat Capacities

The heat capacities of methyl alcohol and the mean temperature of each determination are given in Table I and are shown graphically in Fig. 1.

TABLE I  
SPECIFIC HEATS OF METHYL ALCOHOL

Temp., °K.	$C_p$ , cal./mole	Temp., °K.	$C_p$ , cal./mole	Temp., °K.	$C_p$ , cal./mole
Crystals				Liquid	
18.80	1.109	97.22	10.23	181.09	16.77
21.55	1.512	111.14	11.23	185.10	16.67
24.43	1.959	114.82	11.48	189.06	16.77
27.25	2.292	117.97	11.64	192.97	16.79
30.72	2.829	118.79	11.64	196.77	16.78
34.33	3.437	121.44	11.75	210.34	16.97
37.64	3.962	125.37	12.18	221.69	17.08
40.87	4.427	129.38	12.28	235.84	17.41
43.93	4.840	133.71	12.64	256.34	17.70
48.07	5.404	147.86	12.97	267.01	18.13
56.03	6.425	152.29	13.69	273.58	18.30
59.53	6.845	153.98	14.12	277.81	18.46
63.29	7.252	157.08	92.5	285.15	18.70
69.95	8.001	157.46	283.4	292.01	19.11
73.95	8.392	159.58	17.92		
77.61	8.735	163.94	11.36		
81.48	9.001	164.14	11.29		
85.52	9.295	166.23	11.63		
89.29	9.693	167.65	11.68		
93.18	9.939				

<sup>5</sup> (a) Giauque, Buffington and Schulze, *THIS JOURNAL*, **49**, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

<sup>6</sup> Vol. III, p. 116.

Methyl alcohol has two crystalline forms with the transition at 157.4°K. The transition is not sharp but is of the type first found by Simon<sup>7</sup> for ammonium chloride and later for the other ammonium halides by Simon, Simson and Ruhemann.<sup>8</sup> Such maxima have also been investigated by Giaque and Wiebe<sup>9</sup> in the case of hydrogen bromide and by Millar<sup>10</sup> for manganous oxide. The methyl alcohol transition becomes perceptible at about 145°K. and is over at 160°K.

All attempts to supercool appreciably the high temperature form failed. The experiment which was tried several times consisted in having the block at about 85°K. while the calorimeter was heated *in vacuo* to temperatures well above the transition range and allowed to stand for some

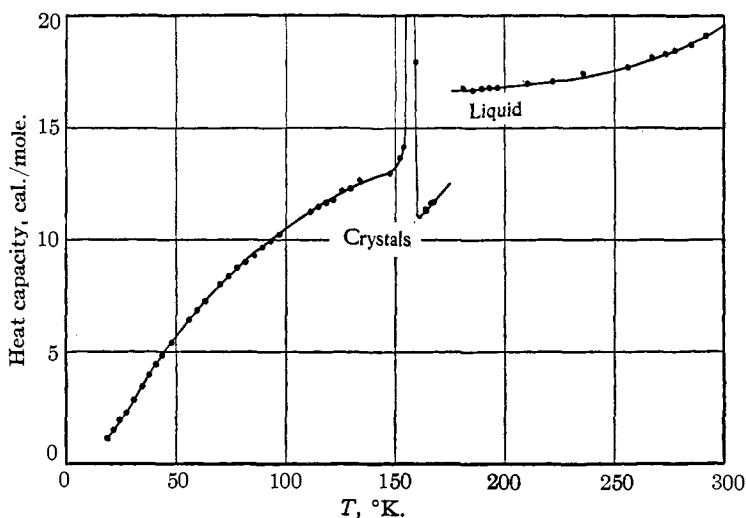


Fig. 1.—Heat capacity in calories per mole of methyl alcohol.

time. The vacuum was then broken with hydrogen and the calorimeter and contents cooled rapidly. Even with such temperature differences this form failed to supercool by more than 25° at most.

In making the calculations corrections were made for the heat interchange with the block (taking into account the source of error discussed by Giaque and Wiebe),<sup>11</sup> for the heat loss in the calorimeter heater lead wires, for the heat capacity of the small amount of solder used in plugging the calorimeter and for the heat capacity of the empty calorimeter itself. The latter was determined separately in the same manner as when full

<sup>7</sup> Simon, *Ann. Physik*, [4] **68**, 241 (1922).

<sup>8</sup> Simon, Simson and Ruhemann, *Z. physik. Chem.*, **129**, 339 (1927).

<sup>9</sup> Giaque and Wiebe, *THIS JOURNAL*, **50**, 2193 (1928).

<sup>10</sup> Millar, *ibid.*, **50**, 1875 (1928).

<sup>11</sup> Ref. 4 b, p. 109.

of methyl alcohol, being filled with hydrogen to increase the speed of heat distribution.

In converting joules to 15° calories the factor 4.185 adopted by "International Critical Tables"<sup>12</sup> was used. All weighings were reduced to a vacuum basis.

The accuracy of the results depends upon the temperature. Below 20° the error may be of the order of 1% due to the rapid decrease of the  $dR/dT$  for the resistance thermometer. Between 20 and 40° the error decreases to about 0.2% and remains such to about 130°. Between 130 and 200° the error increases to about 0.5%. Above 200° certain points may be in error by 1% due primarily to large corrections caused by increased radiation. These estimates do not apply to the determinations made in the transition range where the heat capacity is changing very rapidly and where thermal equilibrium is slow. Here the error may be as much as 3%. It is important to note, however, that these determinations are not used in the entropy calculation.

The specific heats are somewhat lower than those obtained by Parks. Above 200° part of this difference (0.5 to 1%) is due to the additional heat interchange correction discussed by Giauque and Wiebe which was made in the present work but not in that of Parks.

### The Transition Heat

For the purpose of obtaining the entropy, since specific heat measurements in the transition range could not be made accurately, it was necessary to determine the total heat required to bring one mole of methyl alcohol from a temperature below the transition range to a temperature above it and also to determine what might be called the "mean temperature" of the transition. The latter was determined by the method used by Gibson and Giauque for the melting point of glycerol and also the mean temperature of the hump was read from the  $C_p$  vs.  $T$  plot. The average of these two values is 157.4°K. Parks reported 161.1°K. for the temperature of transition. The difference between these values is easily explained. Parks measured the temperature during the course of the heat of transition measurements by means of a thermocouple immersed in a central, longitudinal well. This well was soldered to the top of his calorimeter so that it was joined by metal to the calorimeter walls. In the present work with the thermocouple attached to the outside of the calorimeter it was impossible to decide upon any temperature from data taken during a heat of transition measurement since in an ordinary specific heat determination where energy was being supplied slowly a temperature head of from 3 to 5° was built up on the calorimeter walls due to the poor thermal conductivity of the substance in this region. The head was appreciably

<sup>12</sup> Vol. I, p. 24.

larger when heat was supplied rapidly, as is done in determining the heat of transition.

The quantity designated "heat of transition" in Table II is the total heat before mentioned from which has been subtracted the area under the "normal" heat capacity curves which were extrapolated to 157.4°K.

TABLE II  
HEAT OF TRANSITION, CAL./MOLE

Temp.	1st result	2nd result	Mean
157.4°K.	153.8	154.9	154.3

### Melting Point and Heat of Fusion

The melting point and heat of fusion were determined by the methods of Gibson and Giauque. Both values check those of Parks very closely. Table III contains these data.

TABLE III  
HEAT OF FUSION, CAL./MOLE

Temp.	1st result	2nd result	3rd result	Mean
157.22°K.	757.2	757.2	756.5	757.0

### The Entropy

The entropy,  $\int_{16.5}^{298.1} dQ/T$ , was calculated in the usual manner.

The entropy below 16.5°K. was obtained by extrapolation, using the Debye function with  $\Theta = 138$ . This procedure in obtaining a value of 0.26 E. U. per mole can certainly cause no appreciable error. The calculations are tabulated below.

TABLE IV  
ENTROPY OF METHYL ALCOHOL

0-16.5°K.	extrapolation	0.26
16.5-157.4	crystals	14.18
154.3/157.4	transition	0.98
157.4-175.22	crystals	1.24
757.0/175.22	fusion	4.32
175.22-298.1	liquid	9.28
$S_{298.1}$ for 1 mole of CH <sub>3</sub> OH		30.3 ± 0.2 E. U.

This value is 2.3 E. U. lower than that obtained by Parks; however, 1.9 units of this difference is the error in Parks' extrapolation below 90°K. (that is, about 20% of his extrapolated value). This error is due to the use of the well-known "n" formula of Lewis and Gibson.

### The Free Energy

The free energy of formation of methyl alcohol at 298.1°K. may now be calculated from the thermodynamic equation,  $\Delta F = \Delta H - T\Delta S$ .

The heat of combustion of methyl alcohol was determined by Richards and Davis.<sup>13</sup> Their value when recalculated in terms of the 15° calorie, taking into account the slight error pointed out by Verkade and Coops,<sup>14</sup> corresponds to 170,760 cal. per mole at constant pressure (weighing in vacuum). This result is for the heat of combustion measured at about 291°K. and must be corrected to 298.1°K. by means of the necessary specific heats. This correction is 110 cal. per mole, making the heat of combustion at 298.1° become 170,650 cal. per mole. Combining this latter result with the best values for the heats of formation at 298.1°K. of carbon dioxide and water,<sup>15</sup> one obtains -60,260 cal. for the  $\Delta H_{298.1}$  in the above equation.

In calculating  $\Delta S_{298.1}$ , the entropy of graphitic carbon was taken as 1.3 E. U. per g. atom,<sup>16</sup> that of hydrogen as 29.6 units per mole,<sup>17</sup> and for oxygen 48.9 units per mole.<sup>18</sup> The result is  $\Delta S_{298.1} = -54.6$  E. U.

Substituting these values in the equation, the free energy of formation of liquid methyl alcohol is found to be,  $\Delta F_{298.1} = -44,000$  cal. per mole.

The relation of these results to the thermodynamics of the synthetic methyl alcohol process will be considered elsewhere.

In conclusion the author wishes to thank Mr. G. F. Nelson for the excellent mechanical construction of the apparatus, Professor W. F. Giauque for many helpful suggestions and Professor G. S. Parks of Stanford University for his interest and encouragement.

### Summary

1. The specific heat of methyl alcohol has been determined from 16 to 298°K.
2. The transition between the two crystalline forms was found to be of the ammonium chloride type and the heat of transition and temperature were determined.
3. The temperature and heat of fusion were determined.
4. The entropy of methyl alcohol was found to be  $30.3 \pm 0.2$  units per mole.

<sup>13</sup> Richards and Davis, *THIS JOURNAL*, **42**, 1599 (1920).

<sup>14</sup> Verkade and Coops, *Rec. trav. chim.*, **46**, 903 (1927).

<sup>15</sup> The heat of formation of water accepted by "International Critical Tables" is -68,380 cal. at 18°, which would give -68,320 cal. at 25°. The heat of combustion of  $\beta$ -graphite determined by Roth and Naeser is -94,270 cal. at about 18° (*Z. Elektrochem.*, **31**, 461 (1925)). The correction for temperature here is negligible due to the fact that CO<sub>2</sub> has the same specific heat as C + O<sub>2</sub>. This value is considered better than the one selected by "International Critical Tables" previous to the appearance of Roth and Naeser's work.

<sup>16</sup> Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 464.

<sup>17</sup> See Ref. 4 b, p. 121.

<sup>18</sup> Giauque and Johnston, personal communication.

5. The free energy of formation from the elements of liquid methyl alcohol at 298°K. was obtained as  $-44,000$  cal. per mole.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES OF COPPER CATALYSTS PREPARED FROM  
PRECIPITATED HYDROXIDE.  
II. COMPARISON OF SODIUM HYDROXIDE AND AMMONIA  
AS A PRECIPITATING AGENT

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In order to obtain copper of the highest purity, the catalysts discussed in the preceding paper were prepared from the hydroxide precipitated from copper nitrate with ammonia. While this method of preparation was useful for a study of the temperature effect, it was apparent that the resulting copper catalysts, on the whole, possessed very low activity.<sup>1</sup> In this respect, as well as in appearance, they resembled the clear, red, very compact metal with low catalytic power which Sabatier<sup>2</sup> prepared by calcination of copper nitrate and subsequent reduction with hydrogen. No doubt both these types of catalysts owe their large particle size and low activity to their high purity, which does not leave any foreign matter to interfere with the crystallization of the metal during reduction.

Reduction of the ammonia precipitated product with hydrogen gave the same low activity that was obtained when using methanol vapor. On the other hand, highly active catalysts were prepared by reduction of the tetra cupric hydroxide precipitated from a boiling copper nitrate solution with sodium hydroxide.<sup>2</sup> This copper, in contrast to that resulting from precipitation with ammonia, was a light violet-colored metal with all the appearance of possessing a smaller particle size.

### Experimental Work

These observations pointed to a promoter effect of the small amount of sodium salts which undoubtedly were occluded in the copper hydroxide precipitated with sodium hydroxide. To test this supposition the experiments reported in Table I were made.

Two hundred grams of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) was dissolved in 1500 cc. of water and from this solution the hydroxide was precipitated either with ammonium hydroxide or with sodium hydroxide, as indicated in the table. In each case the hydroxides were heated at 220° in a stream of nitrogen for four hours prior to reduction

<sup>1</sup> Frolich, Fenske and Quiggle, *THIS JOURNAL*, **51**, 61 (1929).

<sup>2</sup> Sabatier, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 58.