

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

## THE HEAT CAPACITIES OF ETHYL AND HEXYL ALCOHOLS FROM 16°K. TO 298°K. AND THE CORRESPONDING ENTROPIES AND FREE ENERGIES

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In an earlier paper low temperature thermal data were given for methyl alcohol.<sup>2</sup> This paper presents similar results for ethyl and hexyl alcohols. The ethyl alcohol has been studied by Gibson, Parks and Latimer<sup>3</sup> and by Parks,<sup>4</sup> whose measurements go down to liquid-air temperature. The measurements here go to liquid-hydrogen temperatures and omit no large temperature intervals between determinations.

The apparatus and methods used have already been described<sup>2</sup> and need not be mentioned here.

### Materials

**Ethyl Alcohol.**—A good grade of ethyl alcohol was allowed to stand on a steam-bath over lime for one week and distilled. It was then put over lime for five days and redistilled. Finally, three fractionations were made, two with lime present and one with metallic calcium. The final product of about 500-cc. volume had a boiling point range of 0.03° and a density,  $d_4^{25}$ , 0.78520. This density corresponds to 99.96% ethyl alcohol if the impurity is assumed to be water. The data in the "International Critical Tables"<sup>5</sup> are the basis for this estimate.

**Hexyl Alcohol.**—The hexyl alcohol was a Kahlbaum product. It was dried with sodium carbonate and with lime and fractionated twice. The middle portion used, 50 cc. in volume, boiled at 157.0–157.1° (760 mm.). Its density was found to be  $d_4^{23.7}$ , 0.8165.

### The Specific Heats

The specific heat values expressed in 15° calories per mole are given in Tables I and II and plotted against the temperature in Figs. 1 and 2.

TABLE I  
SPECIFIC HEATS OF ETHYL ALCOHOL

1 mole = 46.05 g.					
T, °K.	Cal./mole	T, °K.	Cal./mole	T, °K.	Cal./mole
Crystals					
18.57b	1.458	27.05b	3.142	43.50	5.751
18.66a	1.456	27.48a	3.192	46.73	6.368
21.40b	1.906	29.51b	3.565	50.13	6.842
22.00a	1.986	30.43a	3.632	54.26	7.317
24.47b	2.586	32.81b	4.028	58.67	7.777
24.81a	2.619	36.49	4.567	62.62	8.274
		40.05	5.098	66.21	8.657

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<sup>2</sup> Kelley, *THIS JOURNAL*, **51**, 180 (1929).

<sup>3</sup> Gibson, Parks and Latimer, *ibid.*, **42**, 1547 (1920).

<sup>4</sup> Parks, *ibid.*, **47**, 338 (1925).

<sup>5</sup> "International Critical Tables," Vol. III, p. 116.

TABLE I (Concluded)

<i>T</i> , °K.	Cal./mole	<i>T</i> , °K.	Cal./mole	<i>T</i> , °K.	Cal./mole
68.27	8.896	40.75	5.790	102.87b	19.21
69.92	9.053	44.27	6.451	104.43a	19.23
73.15	9.241	47.82	7.077	104.93b	19.31
77.57	9.527	51.63	7.680	107.99b	19.16
81.71	9.872	55.92	8.196	108.21a	19.26
85.53	10.25	60.14	8.703		Liquid
90.11	10.56	64.28	9.232	163.51	20.74
92.51	10.71	70.76b	9.96	167.90	20.80
96.20	11.01	73.09a	10.21	172.22	20.88
100.06	11.29	75.07b	10.47	176.65	20.95
104.07	11.63	77.28a	10.72	181.23	21.16
108.76	11.91	78.80	10.83	185.57	21.22
113.56	12.28	79.07b	10.92	191.68	21.24
117.68	12.52	81.46a	11.25	192.61	21.26
121.86	12.88	82.82b	11.35	195.98	21.27
125.99	13.08	83.91c	11.49	197.34	21.31
130.18	13.18	85.83a	11.90	208.13	21.77
132.55	13.43	86.75b	12.03	212.94	21.80
	Glass	90.11a	12.76	217.64	22.23
18.19	1.830	90.47b	12.73	238.19	22.70
21.00	2.244	93.57b	14.22	260.56	23.77
23.11	2.728	94.09a	15.15	265.48	24.01
25.06	3.188	96.48b	18.40	271.02	24.41
27.19	3.655	97.63a	19.10	277.52	25.00
29.76	4.046	98.66b	19.07	288.95	25.91
33.12	4.542	100.78b	19.14	294.31	26.26
37.00	5.166	100.96a	19.11		

TABLE II  
SPECIFIC HEATS OF HEXYL ALCOHOL  
1 mole = 102.11 g.

<i>T</i> , °K.	Cal./mole	<i>T</i> , °K.	Cal./mole	<i>T</i> , °K.	Cal./mole
		Crystals		Liquid	
18.28	1.695	85.38	17.35	229.64	46.75
23.36	2.823	94.59	18.70	240.19	48.06
27.11	3.819	103.26	19.95	250.73	48.81
30.72	4.782	111.54	21.23	260.70	50.00
35.36	6.103	120.31	22.43	270.57	51.77
40.41	7.473	128.66	23.86	280.56	54.78
44.92	8.670	136.78	24.71	290.01	55.56
49.19	9.739	145.82	25.77		
55.82	11.38	154.09	26.85		
60.97	12.68	162.65	27.64		
66.33	13.89	171.69	28.51		
71.01	14.78	180.86	29.77		
76.52	15.80				

Ethyl alcohol may be obtained at low temperatures in either the crystalline or the glassy state. At hydrogen temperatures the curves for glass

and crystals are nearly parallel but are converging slightly. At 50°K. the increase in slope of the glass curve over that of the crystals is easily perceptible in the figure. Between 90 and 96°K. the heat capacity of the glass undergoes a rapid increase of over 50%. This phenomenon is typical of heat-capacity curves for glasses and has been previously studied for ethyl alcohol by Gibson, Parks and Latimer<sup>3</sup> and by Parks,<sup>4</sup> for glycerin by Simon<sup>6</sup> and by Gibson and Giauque,<sup>7</sup> and for propyl alcohol and propylene glycol by Parks and Huffman.<sup>8</sup> When the ethyl alcohol glass is warmed to 110°K. crystallization invariably begins. This is similar to

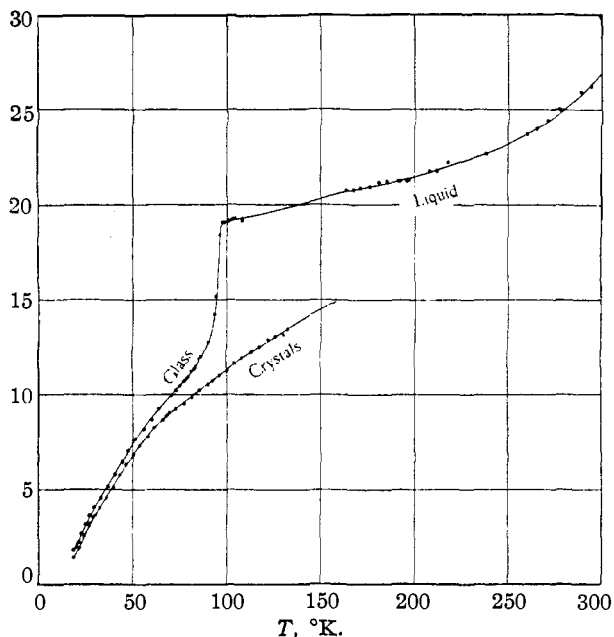


Fig. 1.—Heat capacity of ethyl alcohol in calories per mole.

the behavior of propyl alcohol glass.<sup>8</sup> For this reason no measurements are given between 110° and the melting point temperature of the crystals. Parks and Huffman<sup>8</sup> found that the shape of the curve in the region of the rapid rise depended upon the previous history of the glass, that is, upon the annealing. Therefore care was taken in this work always to prepare the glass in the same manner. This was done by breaking the vacuum with approximately the same pressure of hydrogen (1 cm. of mercury) each time and then cooling as rapidly as possible to the temperature of liquid air. Two sets of measurements which are in complete agreement

<sup>6</sup> Simon, *Ann. Physik*, [4] **68**, 241 (1922).

<sup>7</sup> Gibson and Giauque, *THIS JOURNAL*, **45**, 93 (1923).

<sup>8</sup> Parks and Huffman, *J. Phys. Chem.*, **31**, 1842 (1927).

were made in this region and are distinguished in Table I by "a" and "b." The point marked "c" was obtained just prior to cooling the glass to liquid-hydrogen temperature.

In the region of the rapid rise the thermal conductivity is poor and the corrections for heat interchange with the surroundings are abnormally large due to the long equilibrium period at the end of each determination. However, equilibrium was rapid below  $90^\circ$  and above  $100^\circ$ . To test the accuracy obtained in this range a determination was made starting at  $86.02^\circ$  and ending at  $103.14^\circ$ . The heat necessary to raise the temperature of the calorimeter and contents through this interval was 273.7 calories,

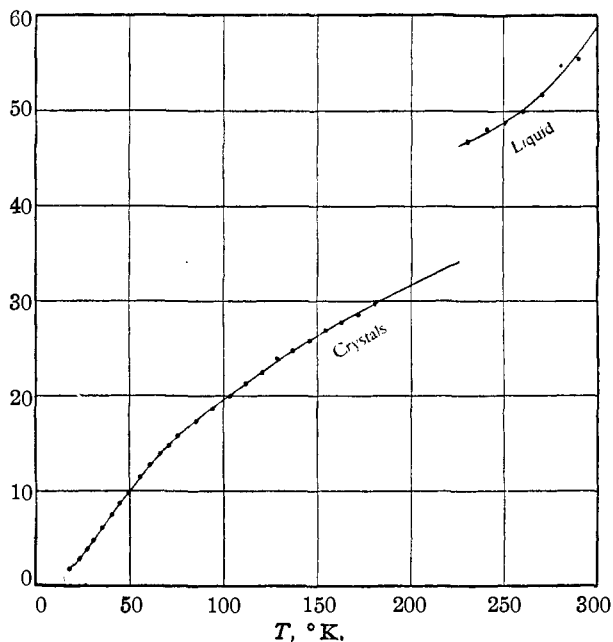


Fig. 2.—Heat capacity of hexyl alcohol in calories per mole.

while the graphical calculation from the  $C_p$  vs.  $T$  plot gave 275.2 calories, a difference of 0.55%. It seems safe to say, therefore, that the accuracy obtained for the glass in this region is about 0.5% less than that for the crystals.

Two sets of determinations were made on the ethyl alcohol crystals below  $35^\circ\text{K.}$  and are in very good agreement. Above  $158.6^\circ\text{K.}$  this alcohol was liquid.

Except for the short interval on the ethyl alcohol glass which has already been discussed, the specific heat measurements have the same accuracy as that given for those on methyl alcohol. That is, "the accuracy of the results depends upon the temperature. Below  $20^\circ$  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."

The hexyl alcohol was studied in the crystalline and liquid forms only, since it showed no appreciable tendency to form the glass. It melts at 225.8°K. Its specific heat curves are normal in all respects.

### The Temperatures and Heats of Fusion

The temperatures and heats of fusion were measured by the methods used by Gibson and Giauque<sup>7</sup> for glycerin. Near the melting point the specific heats of both substances showed considerable increases, which were assumed to be due to premelting caused by small amounts of impurities, and consequently the usual practice of considering the heat involved in excess of the "normal" heat-capacity curves for the crystals as part of the heat of fusion was followed. The mean values in Table III are considered accurate to 0.5%. The result for ethyl alcohol is about 1% higher than the mean of Parks' measurements.

TABLE III  
HEATS OF FUSION

Substance	Temp., °K.	Heat of fusion, Cal. per mole			Mean
		1st result	2nd result	3rd result	
Ethyl alcohol	158.5	1200.8	1200.3	1198.5	1200
Hexyl alcohol	225.8	3679	3672	....	3676

### The Entropies

The entropy from 0°K. to the initial temperature of the lowest measurement was obtained by extrapolation using Debye functions with  $\Theta$ 's as

TABLE IV  
ENTROPIES  
Ethyl Alcohol

0-16°K. (extrap.) crystals = 0.45	0-16°K. (extrap.) glass = 0.67
16-158.5 crystals = 16.20	16-158.5 glass + liq. = 20.94
1200/158.5 fusion = 7.57	158.5-298.1 liquid = 14.18
158.5-298.1 liquid = 14.18	$S_{298.1} - S_0$ glass = 35.8
	$S_0$ glass = 2.6 E. U. per mole

$S_{298.1}$  for one mole of liquid  $C_2H_5OH$  = 38.4 = 0.3 E. U.

#### Hexyl Alcohol

0-15°K. (extrap.) crystals = 0.43
15-225.8 crystals = 37.82
3676/225.8 fusion = 16.28
225.8-298.1 liquid = 14.10

$S_{298.1}$  for one mole of liquid  $C_6H_{13}OH$  = 68.6 = 0.4 E. U.

follows: 109 for ethyl alcohol crystals, 94 for ethyl alcohol glass and 104 for hexyl alcohol crystals. The extrapolated values are small so that this procedure can cause no appreciable errors in the  $S_{298}$  values given in Table IV. The entropy between the temperature at the start of the lowest determination and 298.1°K. was obtained in the usual manner.

The value 2.6 E. U. is obtained for the entropy of ethyl alcohol glass at 0°K. Parks<sup>4</sup> obtained 1.79 E. U. but the difference is almost entirely due to the error made in extrapolating from 90 to 0°K. by means of the "n" formula of Lewis and Gibson.<sup>9</sup> In the case of the ethyl alcohol crystals this formula causes an error of 3.7 E. U. or 28% in the extrapolated value.

### The Free Energies

The free energies of formation of the compounds at 298.1°K. were calculated by means of the fundamental thermodynamic equation,  $\Delta F = \Delta H - T\Delta S$ .

In obtaining  $\Delta H$  for ethyl alcohol the heat of combustion measured by Richards and Davis<sup>10</sup> was used, namely, 7110 Cal. (18°) per g. (in air) at constant volume. This value was corrected to 15° calories, to vacuum weighing and to constant pressure, with 327,340 Cal. per mole as the result. Since this measurement was made at about 291°K. a further correction of -180 Cal. is necessary to correct it to 298.1°K., which gives 327,160 Cal. per mole. For hexyl alcohol the value, 9314 Cal. (15°) per g. (in air) at constant volume, obtained by Verkade and Coops<sup>11</sup> was similarly corrected, the result being 951,540 Cal. per mole (measured at 292.6°K.) or 951,200 Cal. per mole at 298.1°K. These values when combined with the heats of formation of carbon dioxide and water at 298.1°K. which were adopted in previous work<sup>2</sup> give the values of  $\Delta H_{298.1}$  in Col. 3 of Table V.

The values of  $\Delta S_{298.1}$  given in the fourth column of Table V are based upon the measured entropies and the values 1.3 units per gram atom for carbon, 29.6 units per mole for hydrogen and 48.9 units per mole for oxygen, the sources of which were also given in the earlier paper. Col. 5 contains the free energies of formation of the compounds at 298.1°K.

TABLE V  
THERMAL DATA

The 15° Calorie is used throughout

Substance	Heat of combustion at 298.1°K.	$\Delta H_{298.1}$	$\Delta S_{298.1}$	$\Delta F_{298.1}$
Ethyl alcohol	327,160	-66,340	- 77.4	-43,300
Hexyl alcohol	951,200	-92,660	-170.8	-41,700

<sup>9</sup> Lewis and Gibson, *THIS JOURNAL*, **39**, 2554 (1917).

<sup>10</sup> Richards and Davis, *ibid.*, **42**, 1599 (1920).

<sup>11</sup> Verkade and Coops, *Rec. trav. chim.*, **46**, 903 (1927).

### Discussion

Parks and his co-workers<sup>12</sup> have shown that in an homologous series of normal saturated aliphatic compounds there is an increase in entropy of about nine units per  $\text{CH}_2$  group if the substances are considered in the liquid state at  $298.1^\circ\text{K}$ ., while the free energies of formation from the elements have the same value. The present work bears out these conclusions qualitatively. If the entropy of methyl alcohol,  $30.3 \pm 0.2$  E. U. per mole, previously reported<sup>2</sup> is compared with the values in Tables IV, it may be seen that the entropy difference between methyl and ethyl is 8.1 units and between ethyl and hexyl alcohols 30.2 units, or on the average about 7.7 units per  $\text{CH}_2$  group. A similar comparison of the free energies shows differences of 700 Cal. between methyl and ethyl and 1600 Cal. between ethyl and hexyl or a change of about 500 Cal. per  $\text{CH}_2$  group.

The heat of combustion data of Richards and Davis<sup>10</sup> and of Verkade and Coops<sup>11</sup> show a definite increment of about 156,000 Cal. per  $\text{CH}_2$  group in the alcohol series from methyl to decyl. The first of these differences is somewhat large and upon this basis Verkade and Coops think that Richards and Davis' value for methyl alcohol is low by 0.1%. If this claim should prove true, the free energy difference between methyl and ethyl alcohols would be reduced to 500 Cal. It is obvious, of course, that if regular differences appear in the consecutive values of any two of these properties (free energies, entropies and heats of combustion) they must appear in the third.

If the free energy difference per  $\text{CH}_2$  group found here persists throughout the series, then the higher alcohols are thermodynamically less stable toward the elements than are the lower.

For all practical purposes the author certainly would not hesitate to employ these differences in the calculation of the entropies and free energies of the normal alcohols, propyl, butyl and pentyl.

It is interesting to compare the entropy of ethyl alcohol glass at  $0^\circ\text{K}$ . reported with the available data for other glasses. Table VI contains these values.

TABLE VI  
ENTROPIES OF GLASSES AT  $0^\circ\text{K}$ .

Quartz glass	Ethyl alcohol	Propyl alcohol	Glycerol
0.9	2.6	3.1 (?)	4.6

The data for quartz glass and glycerol were calculated by Simon and Lange.<sup>13</sup> The value for propyl alcohol is that of Parks and Huffman<sup>12d</sup> corrected as well as possible for the error made in extrapolating below  $86^\circ\text{K}$ .

<sup>12</sup> (a) Parks, ref. 4; (b) Parks and Kelley, *THIS JOURNAL*, **47**, 2089 (1925); (c) Parks and Anderson, *ibid.*, **48**, 1506 (1926); (d) Parks and Huffman, *ibid.*, **48**, 2788 (1926).

<sup>13</sup> Simon and Lange, *Z. Physik*, **38**, 227 (1926).

It thus appears as would be expected that the entropy of the glass at 0°K. increases with the complexity of the molecule.<sup>14</sup>

### Summary

1. The specific heats from 16 to 298°K. of ethyl alcohol crystals, glass and liquid and of hexyl alcohol crystals and liquid have been measured.
2. The heats of fusion and the temperature of fusion have been determined.
3. The entropies and free energies of ethyl and hexyl alcohols at 298° K. and the entropy of ethyl alcohol glass at 0° K. have been calculated.
4. Regularities in the thermal data for the normal saturated aliphatic alcohols have been discussed.

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## CATALYTIC EFFECT OF RUTHENIUM SALTS ON THE REDUCTION OF PERCHLORIC ACID BY HYDROBROMIC ACID

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### Introduction

It is well known that both dilute and moderately concentrated solutions of perchloric acid are remarkably unreactive with most reducing agents, although the thermodynamic tendency for the acid to act as an oxidizing agent is undoubtedly very great. Its great power as an oxidizing agent is shown only when the acid is hot and concentrated. Under such conditions the lower valence compounds of osmium and ruthenium are oxidized to the tetroxides.<sup>1</sup> In dilute solutions of perchloric acid the only reducing agents mentioned in the literature as reacting with it are trivalent titanium, trivalent molybdenum and bivalent chromium,<sup>2</sup> the reactions in all three cases being measurably slow. It is to be noted that these three reducing agents have not only a very high reduction potential but have also high reaction rates with most oxidizing agents.

It was found by Dr. Robert H. Dalton in this Laboratory that bromine is evolved on heating mixtures of perchloric and hydrobromic acids containing small amounts of ruthenium chloride, while in the absence of ruthenium no such effect is observed. Subsequent experiments showed that the

<sup>14</sup> See Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, pp. 137-138.

<sup>1</sup> Noyes and Bray, "Qualitative Analysis for the Rare Elements," Macmillan Co., New York, 1927, p. 17.

<sup>2</sup> Bredig and Michel, *Z. physik. Chem.*, **100**, 124 (1922).