2. The apparently strange behavior of the temperature coefficient of reaction rate in the decomposition of bornyl and menthyl sulfonates in certain solvents has been accounted for on the basis of autocatalysis by the resulting acid, and the general effect of the solvent upon these reactions has been shown to agree with predictions based on the character of the solvent.

PASADENA, CALIFORNIA

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

THE HEAT CAPACITIES OF ISOPROPYL ALCOHOL AND ACETONE FROM 16 TO 298°K. AND THE CORRESPONDING ENTROPIES AND FREE ENERGIES

BY KENNETH K. KELLEY[1]

RECEIVED NOVEMBER 28, 1928 PUBLISHED APRIL 5, 1929

The heat capacities of *iso*propyl alcohol and acetone have been studied by Parks and the author[2] from 70 to 298°K. Equilibrium measurements at several temperatures were also made for the reaction $CH_3CHOHCH_3$ = $CH_3COCH_3 + H_2$ in the gaseous state[3] in order to show that the third law of thermodynamics held, at least for all practical purposes, for this organic reaction. An exact test was not possible since heat capacity data for gaseous *iso*propyl alcohol and acetone were not available for extrapolating the results of the equilibrium measurements and since considerable uncertainty was involved in extending the heat capacity curves for crystalline *iso*propyl alcohol and acetone below 70°K. The present work, carrying the specific heat measurements to 16°K., was undertaken to remedy this latter defect. The temperature range covered before has been reinvestigated with increased accuracy and measurements have been obtained in the large temperature gaps which were omitted in the previous work. Details of the apparatus and methods used were given in a previous paper.[4]

Materials

*Iso*propyl Alcohol.—The best grade of *iso*propyl alcohol (99 to 100%) of the Special Chemicals Company was used. It was refluxed over lime for eighteen hours and carefully fractionated three times. The middle portion taken for the measurements had a volume of about 200 cc. and a boiling-point range of 0.03°. The density was d_4^{25} = 0.78095, while Brunel[5] found d_4^{25} = 0.78084 for 100% *iso*propyl alcohol. The density determination corresponds to 99.95% of alcohol on the basis of purity adopted by Parks and Kelley.

---

[1] National Research Fellow in Chemistry.

[2] Parks and Kelley, THIS JOURNAL, **47**, 2089 (1925).

[3] Parks and Kelley, *J. Phys. Chem.*, **32**, 734 (1928).

[4] Kelley, THIS JOURNAL, **51**, 180 (1929).

[5] Brunel, *ibid.*, **45**, 1336 (1923).

Acetone.—The acetone was an Eastman Kodak Company product. It was allowed to stand over calcium chloride for seven days, decanted off and carefully fractionated three times. The middle fraction used had a boiling point range of 0.05° and a volume of 150 cc. The density was $d_4^{25} = 0.78650$ which compares favorably with the values given in the literature.

The Specific Heats

In Tables I and II are given the results of the specific heat measurements expressed in 15° calories per mole (in vacuum). The same data are shown graphically in Figs. 1 and 2.

TABLE I

SPECIFIC HEATS OF *Iso*PROPYL ALCOHOL

1 mole = 60.06 g.

T, °K.	C_p g.-cal.$_{15}$°/mole	*T*, °K.	C_p g.-cal.$_{15}$°/mole	*T*, °K.	C_p g.-cal.$_{15}$°/mole
	Crystals				Liquid
19.49	1.936	82.27	11.28	188.45	25.82
23.82	2.749	90.44	11.99	193.02	26.05
26.88	3.413	99.62	12.71	202.32	26.47
29.99	4.041	107.33	13.66	212.82	26.85
34.03	4.791	115.05	14.49	224.07	27.56
38.68	5.612	123.91	15.25	235.26	28.31
43.02	6.341	131.95	15.98	246.54	29.57
46.90	6.928	136.26	16.19	258.40	30.67
51.04	7.524	144.56	17.16	274.48	32.07
55.41	8.090	153.08	18.06	280.26	33.68
68.51	9.788	161.11	19.01	286.76	34.49
72.44	10.21	165.98	19.42	292.84	35.79
77.64	10.84	170.46	20.24		

TABLE II

SPECIFIC HEATS OF ACETONE

1 mole = 58.05 g.

T, °K.	C_p g.-cal.$_{15}$°/mole	*T*, °K.	C_p g.-cal.$_{15}$°/mole	*T*, °K.	C_p g.-cal.$_{15}$°/mole
	Crystals				Liquid
17.77	1.899	93.44	14.98	180.31	28.04
20.99	2.661	100.74	15.76	180.40	27.97
23.98	3.290	107.65	16.63	180.78	28.06
27.05	4.112	114.81	17.55	185.02	27.96
30.68	4.952	119.09	18.10	189.23	27.74
34.24	5.863	121.56a	18.93	199.19	27.77
37.55	6.613	125.58	19.79	209.31	28.17
41.07	7.429	125.61a	19.92	218.41	28.27
47.38	8.607	129.45	19.73	228.14	28.19
54.90	9.977	129.85a	19.78	242.75	28.34
61.34	11.12	133.30	19.19	258.47	28.69
67.03	11.91	143.62	19.55	272.88	29.31
70.47	12.34	151.08	19.77	282.59	29.37
74.31	12.90	158.89	19.99	296.99	29.80
78.41	13.40	163.34	20.10		
82.18	13.81	126.59x	18.55		
86.15	14.16	130.64x	18.74		

The *iso*propyl alcohol curves have no abnormalities and require no discussion. In the case of the acetone a curious hump occurs with the maximum at about 126°K. There can be little doubt but that some sort of a transition in the crystals involving a small energy change occurs here, for after passing through this region the material was kept at about 150°K. overnight, then rapidly cooled to 123° and the two determinations marked "x" in Table II and in Fig. 2 were obtained. During these two determinations the substance must have been in the high temperature form but supercooled somewhat. Immediately afterward the substance was further cooled to 118°K. and allowed to stand for several hours, after which the three determinations marked "a" in Table II were made. These three measurements agree very well with the previous ones around the hump and are about one calorie per mole higher than those marked "x," showing that on further cooling the substance passes into the low temperature form. A similar case has been discovered by Millar[6] in the heat capacity curve for manganese dioxide.

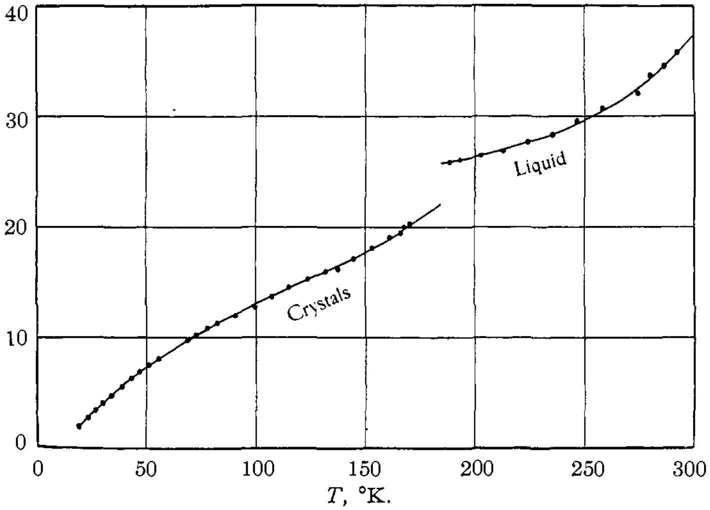

Fig. 1.—Heat capacity of *iso*propyl alcohol in calories per mole.

This phenomenon was missed in the work of Parks and Kelley since no measurements were made between 110 and 150°. A warming curve was taken through this region but was not accurate enough to indicate an increase in heat capacity of only 5%, though undoubtedly a transition involving a large energy change could not have escaped notice.

The facts or even a theory to explain the various types of transitions which have been found in specific heat curves would be very interesting but needless to say both are lacking at present.

---

[6] Millar, This Journal, **50**, 1875 (1928).

The specific heat of liquid acetone first decreases slightly just above the melting point and then increases, similarly to the behavior of water. This is usually attributed to association effects.

In an earlier paper[4] involving similar data for methyl alcohol a somewhat detailed discussion of the accuracy of the measurements was given which will also apply to the present results.

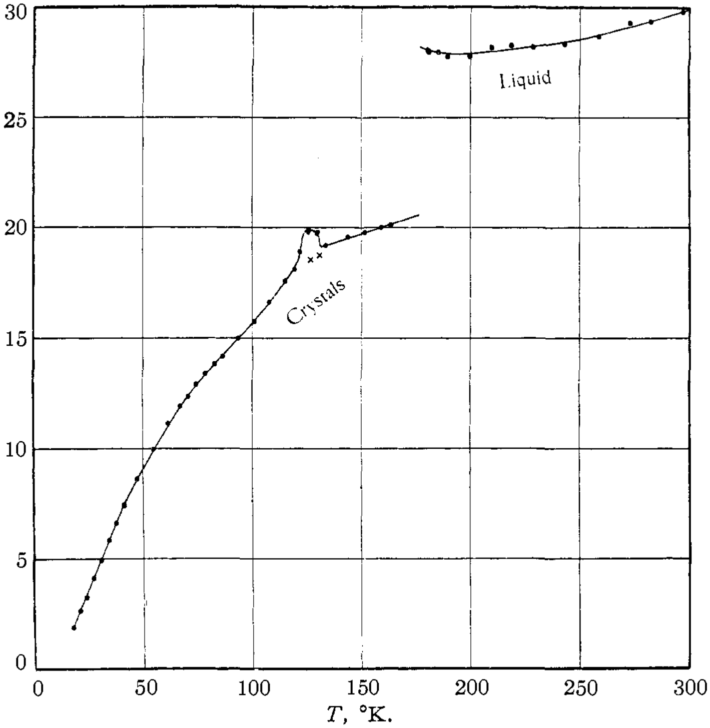

Fig. 2.—Heat capacity of acetone in calories per mole.

The Fusion Data.—The heats of fusion and the temperature of fusion were measured and the results appear in Table III.

TABLE III

HEATS OF FUSION OF *Iso*PROPYL ALCOHOL AND ACETONE

Substance	T, °K.	Heat of fusion in g.-cal.$_{15°}$ per mole 1st result	2nd result	mean
*Iso*propyl alcohol	184.67	1283	1285	1284
Acetone	176.62	1364	1368	1366

The mean values for the heats of fusion are considered accurate to 0.5% or better.

The Entropies.—The values of the entropies at 298.1 °K. were calculated. The heat capacity curves for the crystalline substances were extrapolated from the initial temperatures of the lowest measurements to 0°K. by means of Debye functions with $\Theta = 108$ for *iso*propyl alcohol and $\Theta = 101$ for acetone. The results appear in Table IV.

TABLE IV

ENTROPIES

*Iso*propyl alcohol			Acetone		
0–16°K. (extrap.)	crystals	= 0.47	0–16°K. (extrap.)	crystals	= 0.56
16–184.67	crystals	= 21.61	16–176.62	crystals	= 24.67
1284/184.67	fusion	= 6.95	1366/176.62	fusion	= 7.73
184.67–298.1	liquid	= 13.99	176.62–298.1	liquid	= 14.90
$S_{298.1}$ for 1 mole of liquid = 43.0(±0.3) E. U.			$S_{298.1}$ for 1 mole of liquid = 47.9(±0.3) E. U.		

The entropy under the hump in the acetone crystals curve in excess of that due to the "normal" specific heat is 0.1 E. U. per mole.

The Free Energies.—The free energies of formation from the elements of the two substances may be calculated from the third law of thermodynamics and the thermodynamic equation, $\Delta F = \Delta H - T\Delta S$.

There is no recent determination of the heat of combustion of *iso*propyl alcohol. Richards and Davis[7] have determined accurately the heat of combustion of the normal propyl alcohol and from this has been subtracted 5700 cal. per mole, which is the difference between the heats of combustion of the *iso*- and *n*-propyl alcohols found by Zubow.[8] Richards and Davis' value was corrected to 15° calories. The result of this procedure is 477,300 cal. per mole for *iso*propyl alcohol at 291°K. For the sake of consistency this value was corrected to 298°K., though the accuracy does not warrant it. Emery and Bennedict's[9] value for the heat of combustion of acetone has been utilized, correction being made to vacuum weighing and to 298°K. The final values appear in Col. 2 of Table V.

TABLE V

THERMAL DATA

The 15° g. calorie is used throughout

Substance	Heat of combustion at 298.1°K.	$\Delta H_{298.1}$	$\Delta S_{298.1}$, E. U.	$\Delta F_{298.1}$
*Iso*propyl alcohol	477,100	−79,000	−103.7	−48,100
Acetone	430,500	−57,300	− 69.2	−36,700

Column 3 contains the values of $\Delta H_{298.1}$ which were calculated using the best available values for the heats of formation of carbon dioxide and water.[4] Column 4 contains the value of $\Delta S_{298.1}$ calculated from the experimental entropies of this paper and the entropies of the elements pre-

---

[7] Richards and Davis, THIS JOURNAL, **42**, 1599 (1920).

[8] Zubow's values have been recalculated by Swietoslawski, *ibid.*, **42**, 1092 (1920).

[9] Landolt, Börnstein, Roth, Scheel, "Tabellen," **1923**.

viously adopted.[4] In Col. 5 are the free energies of formation from the elements.

Discussion

The differences between the entropy values given here and those reported by Parks and Kelley[2,3] are largely due to the error in extrapolating the heat capacity curves by means of the "*n*" formula as was done in earlier work. The use of this formula below 90°K. causes an error of 2.1 E. U. or 17% in the extrapolation for *iso*propyl alcohol and 4.2 E. U. or 25% in the extrapolation for acetone. Similar results were reported for methyl alcohol[4] and for ethyl alcohol.[10]

We are now in a position to recalculate the entropy of the reaction, $CH_3CHOHCH_3(l) = CH_3COCH_3(l) + H_2(g)$, at 298.1°K. with considerably greater accuracy than was obtained by Parks and Kelley from their heat capacity measurements. We find $\Delta S_{298.1} = 47.9 + 29.6 - 43.0 = 34.5$ E. U.[11] while Parks and Kelley from the equilibrium measurements obtained 35.9 E. U. These values agree as well as could be expected in view of the fact that no heat capacity data for gaseous *iso*propyl alcohol are available, so that a very accurate extrapolation of the results of the equilibrium measurements to 298°K. is not possible. Using the value of $\Delta H_{298.1} = 17{,}430$ cal. obtained by Parks and Kelley, the free energies of this reaction corresponding to the above entropy values are, respectively, 7150 cal. and 6720 cal.

Summary

1. The specific heats of *iso*propyl alcohol and acetone from 16 to 298°K. have been measured.

2. The heats and temperatures of fusion were determined.

3. The entropies and the free energies of formation from the elements have been calculated for 298°K.

4. The entropy and free energy of the reaction $CH_3CHOHCH_3(l) = CH_3COCH_3(l) + H_2(g)$ at 298°K. have been recalculated using the present thermal data and the third law of thermodynamics. These results are compared with previously reported data obtained by studying equilibria.

BERKELEY, CALIFORNIA

---

[10] Kelley, THIS JOURNAL, **51**, 779 (1929).

[11] In a recent paper Giauque and Johnston [*ibid.*, **50**, 3221 (1928)] consider that the entropy of hydrogen should be increased by 4.39 E. U. at 298.1°K. However, it is possible that only 1.63 E. U. of this need be considered for chemical reactions (Giauque, personal communication). Such a change would increase the third law value of the entropy of this reaction to 36.1 E. U., which agrees better with the equilibrium measurements.