Jenkins[4] and Bell and Arnold.[5] The latter authors have shown in benzene solutions of concentrations from $M = 0.01$ to $M = 1.5$ trichloroacetic acid is completely associated. We assume, therefore, that under the conditions of our measurements all the acids were entirely present as dimers.

The three infra-red absorption bands which can be investigated in this solvent correspond to the frequencies ν_1, ν_2 and ν_3 of the previous paper. The first of these (ν_1) (which has been omitted in Fig. 1 to conserve space) is mainly due to the C–H valence vibration, but is also in part made up of overtone and combination vibrations from other parts of the molecule. Thus it occurs even in trichloroacetic acid, but considerably displaced and much weaker. The remaining two bands are to be attributed to vibrations within the ring formed by the union of the two single molecules. Attempts to measure some of these bands in the single molecules at high temperatures were unsuccessful on account of decomposition.

It may be seen by reference to Table I that the band ν_2 is shifted toward higher frequencies by groups recognized by the organic chemist as electronegative, while it is shifted to lower frequencies by groups electropositive in the same sense. The uniform shift in the chloroacetic acids discovered by Bennett and Daniels is confirmed. The effect of the weight of the groups may be seen by considering the monohalogen acids. Here the shift in the band decreases as the weight of the halogen increases until in iodoacetic acid it occurs in the same position as acetic. This suggests that there may be two opposing factors operative, one a weight factor and the other perhaps connected with the electron affinity or polarizability of the substituted group. It is noticeable that there is a correlation between the strength of the acid in aqueous solution and the position of this band. This is perhaps to be associated with changes in the contribution of ionic states to the energy of the molecule.

The remaining band, ν_3, is shifted in each case in the opposite direction, but the displacement is smaller. This behavior was observed also in the investigation on the effect of association.[2] It does not seem possible in the light of our present knowledge to give an exact interpretation of these band shifts although they seem too uniform to be fortuitous.

The author is grateful to Dr. Farrington Daniels for helpful suggestions and for continued interest in this problem.

Summary

1. The infra-red absorption spectra of acetic acid and eight substituted acetic acids have been measured in carbon tetrachloride solution. Certain uniform shifts in the absorption bands have been observed and correlated with other measurements.

MADISON, WISCONSIN RECEIVED MAY 5, 1936

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[4] Bury and Jenkins, *J. Chem. Soc.*, 688 (1934).

[5] Bell and Arnold, *ibid.*, 1432 (1935).

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

The Entropy of Water and the Third Law of Thermodynamics. The Heat Capacity of Ice from 15 to 273°K.

BY W. F. GIAUQUE AND J. W. STOUT

It has long been known to those interested in the accurate application of the third law of thermodynamics that measured entropy changes in reactions involving water did not agree with those calculated from low temperature heat capacity data. In early comparisons the inaccuracy of the available data seemed sufficient to explain the disagreement, but even after more accurate experiments were performed discrepancies still remained. The investigations of Wiebe, Johnston, Overstreet, and one of us[1] on the entropies of hydrogen chloride, hydrogen, oxygen and chlorine, combined with very accurate determinations of the heats of reactions

$$H_2 + {}^1/_2O_2 = H_2O$$
$$\text{and } 2HCl + {}^1/_2O_2 = H_2O + Cl_2$$

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[1] (a) Giauque and Wiebe, (HCl), THIS JOURNAL, **50**, 101 (1928); (b) Giauque and Johnston, (H_2), *ibid.*, **50**, 3221 (1928); (c) Giauque and Johnston, (O_2), *ibid.*, **51**, 2300 (1929); (d) Giauque, (H_2), *ibid.*, **52**, 4816 (1930); (e) Giauque and Overstreet, (HCl, Cl_2), *ibid.*, **54**, 1731 (1932).

made by Rossini[2] and various equilibrium data, including those relating to the reactions[3]

$$HgO + H_2 = Hg + H_2O$$
$$Hg + {}^1/_2O_2 = HgO$$

indicated that the $\int_0^T C_p d \ln T$ for water did not give the correct entropy. That this was so became a certainty when Giauque and Ashley[4] calculated the entropy of gaseous water from its band spectrum and showed that an entropy discrepancy of about one calorie per degree per mole existed. They presumed this to be due to false equilibrium in ice at low temperatures.

Water is a substance of such importance that we considered further experimental investigation to be desirable not only to check the above discrepancy but especially to see whether slow cooling or other conditions favorable to the attainment of equilibrium could alter the experimental result.

Apparatus.—In order to prevent strains in the resistance thermometer when the water was frozen a double-walled calorimeter, Fig. 1, was constructed. The outside wall was of copper, 0.5 mm. thick, 4.4 cm. o. d., and 9 cm. long. The inside copper wall, 0.5 mm. thick, was tapered, being 3.8 cm. o. d. at the bottom and 4.0 cm. o. d. at the upper end. The top of the inner container was made from a thin copper sheet, 0.2 mm. thick, which prevented the transmission of strains to the resistance thermometer. The neck for filling the calorimeter was in the center of this sheet. A series of thin circular slotted vanes of copper were soldered to the inner container, and the assembly forced inside the outer tube. A heavy copper plate, 1 mm. thick inside the inner wall, and 2 mm. thick between the walls, served as the bottom of both tubes. The thermocouple was soldered into tube D by means of Rose's metal.

A resistance thermometer-heater of No. 40 double silk covered gold wire containing about 0.1% silver was wound on the outside of the calorimeter. The resistance was 310 ohms at 290°K. and dropped to about 17 ohms at 15°K. The resistance thermometer was calibrated during the measurements by means of copper–constantan thermocouple No. 16 which had been compared with a hydrogen gas thermometer.[5] However one of the five parallel constantan wires in the thermocouple had accidentally been broken since the original calibration. This wire was discarded and after the completion of the measurements the thermocouple was compared with the oxygen and hydrogen vapor pressure thermometers.[5b] The thermocouple was also checked against the melting point, 54.39°K. and higher transition point, 43.76°K., of oxygen.[1c] On the basis of these comparisons a small correction to the original calibration was readily made.

Helium gas was introduced into the space between the two walls by means of a German silver tube, A. A similar German silver tube was soldered by means of Wood's metal into the cap, B. The sample, C, was transferred through this tube into the calorimeter, and helium gas at one atmosphere pressure admitted. The German silver tube was then heated and removed from the cap, leaving the hole sealed with Wood's metal. After the measurements on the full calorimeter had been completed, the calorimeter was heated to the melting point of the Wood's metal (72°C.) and the water completely pumped out without dismantling the apparatus. The heat capacity of the empty calorimeter was then measured.

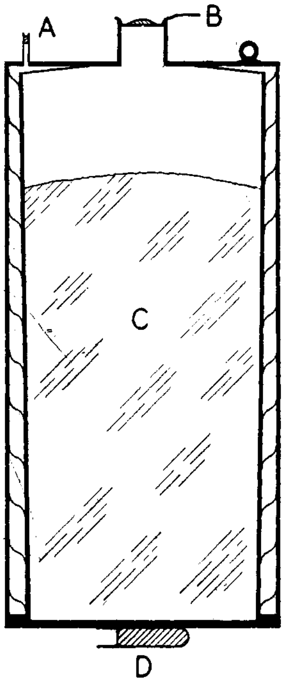

Fig. 1.—Calorimeter.

The remainder of the heat capacity apparatus, the method of making the measurements and calculations, and accuracy considerations were similar to those previously described.[1a,c]

Purification of Water.—Distilled water from the laboratory still was transferred into the vacuum-tight purification apparatus constructed from Pyrex glass. The apparatus was evacuated to remove dissolved gases, and flushed out several times with helium gas. The water was distilled into a receiving bulb, the first fraction being discarded. The calorimeter had previously been attached to the purification system and evacuated. When sufficient water had collected in the receiving bulb, it was transferred into the calorimeter. Helium gas at one atmosphere pressure was admitted to the calorimeter which was then sealed off as described above.

A series of short heat capacity measurements were made in the temperature region immediately below the melting point in order to determine the pre-melting effect due to liquid-soluble solid-insoluble impurity. From these measurements it was calculated that the mole fraction of impurity was three parts in a million.

The Heat Capacity of Ice.—The results of the heat capacity measurements are given in Table I. The data are shown in Fig. 2.

In the calculations one 15° calorie was taken as equal to 4.1832 international joules. The calorimeter contained 72.348 g. of ice.

In order to allow time for the establishment of an equilibrium state in the solid, the ice was cooled

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[2] (a) (H_2O), *Bur. Standards J. Research*, **6**, 1 (1931); (b) (HCl), *ibid.*, **9**, 583 (1932).

[3] See summary by Eastman, Circular 6125, U. S. Dept. of Comm., Bur. of Mines (1929).

[4] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

[5] (a) Giauque, Buffington and Schulze, This Journal, **49**, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

very slowly. The following are temperatures reached at various times after the ice was frozen: 0 hours, 273.1°; 12 hours, 246°; 37 hours, 203°; 60 hours, 180°; 84 hours, 168°; 92 hours, 156°; 108 hours, 105°; 120 hours, 91°; 156 hours, 90°. The sample was then cooled from 90 to 68° in about three hours and the heat capacity measurements of series I taken. Next the calorimeter was cooled to the temperatures of liquid hydrogen at the following rate: 0 hours, 85°; 1.5 hours, 72°; 2 hours, 60°; 2.5 hours, 56°; 7 hours, 39°; (liquid hydrogen evaporated) 17.5 hours, 49°; 22 hours, 50° (more liquid hydrogen added); 23 hours, 41°; 27 hours, 13°. The measurements of series II were then made.

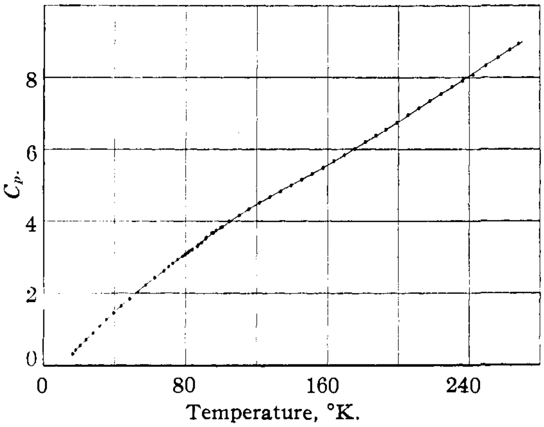

Fig. 2.—Heat capacity in calories per degree per mole of ice.

During this series of measurements which extended from 15°K. to the melting point, and covered a period of eighty hours, the calorimeter was under constant observation. To make certain that no unusual thermal situation was present in the solid near the melting point, the heat of fusion was determined at the end of the above series of measurements. The value obtained, 1436 cal./mole, agrees well with that which has been chosen for the entropy calculation.

TABLE I

HEAT CAPACITY OF ICE

(Molecular weight, 18.0156) 0°C. = 273.10°K.

T,°K.	ΔT	C_p cal./deg./mole	Series
16.43	1.403	0.303	II
18.37	1.729	.410	II
20.78	2.964	.528	II
24.20	3.815	.700	II
28.05	3.596	.883	II
31.64	3.578	1.065	II
35.46	4.073	1.251	II
39.62	4.242	1.449	II
43.96	4.469	1.641	II
48.52	4.571	1.837	II
52.98	4.361	2.014	II
57.66	5.041	2.203	II
62.63	5.228	2.418	II
67.83	4.910	2.612	II
70.61	5.403	2.723	I
73.01	5.737	2.821	II
75.60	4.638	2.922	I
78.51	4.991	3.016	II
79.98	4.133	3.070	I
81.44	5.538	3.115	III
82.42	4.860	3.163	IV
83.72	5.438	3.191	II
83.94	3.765	3.199	I
86.66	4.893	3.286	III
87.25	4.756	3.336	IV
89.20	5.557	3.389	II
91.32	4.394	3.488	III
91.93	4.651	3.532	IV
94.93	5.233	3.649	II
95.85	4.649	3.660	III
97.37	6.234	3.724	IV
99.57	4.778	3.814	II
100.69	4.980	3.832	III
104.69	5.497	3.985	II
110.13	5.373	4.136	II
115.84	6.031	4.315	II
121.74	5.908	4.489	II
127.54	5.813	4.655	II
133.50	6.005	4.808	II
139.48	5.952	4.978	II
145.43	5.928	5.135	II
151.43	6.240	5.306	II
157.48	5.837	5.466	II
163.52	5.851	5.653	II
169.42	5.908	5.842	II
175.36	5.996	6.007	II
181.25	5.678	6.185	II
187.20	5.983	6.359	II
192.96	5.658	6.530	II
199.11	6.133	6.710	II
205.32	6.309	6.935	II
211.56	6.554	7.119	II
217.97	6.200	7.326	II
224.36	5.935	7.519	II
230.08	6.068	7.711	II
236.19	6.101	7.887	II
242.40	6.795	8.048	II
249.31	6.903	8.295	II
256.17	6.591	8.526	II
262.81	6.303	8.732	II
267.77	4.465	8.909	II

In the heat capacity measurements between 85 and 100°K., the attainment of temperature equilibrium in the solid was much less rapid than at other temperatures. This observation is of considerable interest and some of its implications will be discussed below.

To study possible effects due to rapid cooling the sample was cooled from 273.1 to 90° in four hours. The heat capacities in series III were then measured. Slow equilibrium was again encountered, and the heat capacities were not significantly different from those previously obtained.

To determine whether the ice was being transformed from an unstable to an equilibrium condition at an appreciable rate, measurements extending over several hours each were made of the rate of temperature drift at 60, 72, 78 and 85°K. After correcting for the known heat interchange with the surroundings, the rate of evolution of heat due to internal changes was zero within the limits of experimental error. An amount of 0.0008 calorie per mole per minute could have been detected.

The calorimeter was allowed to stand for four days at temperatures between 60 and 80° before taking the measurements in series IV. Again the measurements were not significantly different from those previously obtained.

In Table II are listed the values of the heat capacity at even temperatures as read off a smooth curve through the observations. These values are compared with those of previous investigators. A review of the measurements prior to 1913 has been given by Dickinson and Osborne.[6] Of these the measurements of Nernst and co-workers are most important. The values used for comparison in Table II are calculated from an equation proposed by Nernst, Koref and Lindemann[7] as representing these data. Pollitzer[8] made measurements between 20 and 90°K. His measurements were plotted and a smooth curve drawn through them to give the values compared in Table II. The very accurate work of Dickinson and Osborne[6] between 0 and −40°C. has been calculated from an equation proposed by these authors. Maass and Waldbauer[9] and Barnes and Maass[10] have measured the total change in heat content from various low temperatures to 25°C., and from the results have proposed equations for the specific heat of ice. Simon[11] lists values for the heat capacity of ice from 10°K. to the melting point.

Professor Simon[12] informs us that, of the values listed in the "Handbuch der Physik," only the one at 10°K. is based on the results of his own measurements. The heat capacities at higher temperatures were calculated from the work of earlier observers. The experimental results of Simon[12] are in excellent agreement with the continuation of the curve drawn through our measurements. We have included in Table II a value for the heat capacity of ice at 10°K. picked from a smooth curve through Simon's data.

TABLE II

HEAT CAPACITY OF ICE

(Molecular Weight, 18.0156) 0°C. = 273.10°K.

Values taken from smooth curve through observations

T,°K.	C_p, cal./deg./mole	Deviations previous results—This research, % Nernst 1910	Pollitzer 1913	D. and O. 1915	M. and W. 1925	B. and M. 1930
10[13]	0.066					
20	.490		−13.3			
30	.984		− 0.8			
40	1.466		+13.1			
50	1.896		+ 4.1			
60	2.304		+ 2.8			
70	2.701	+ 8.5				
80	3.075	+ 4.4	+ 6.6			
90	3.448	+ 1.3	− 0.4		−29.6	
100	3.796	− 0.6			−22.4	
110	4.130	− 1.9			−16.8	
120	4.434	− 2.3			−11.8	
130	4.728	− 2.4			− 7.6	
140	4.993	− 1.8			− 3.8	
150	5.265	− 1.5			− 0.8	
160	5.550	− 1.4			+ 1.3	
170	5.845	− 1.5			+ 2.5	
180	6.142	− 1.5			+ 3.4	
190	6.438	− 1.5			+ 3.9	
200	6.744	− 1.5			+ 3.9	−2.1
210	7.073	− 1.7			+ 3.3	−0.9
220	7.391	− 1.7			+ 2.6	− .1
230	7.701	− 1.3		−0.5	+ 1.9	+ .3
240	8.013	− 0.4		− .2	+ 0.9	+ .2
250	8.326	+ 1.3		+ .1	− 0.3	− .4
260	8.642	+ 6.1		+ .3	− 1.6	−1.3
270	8.960	+43.8		+ .5	− 3.2	−2.6

The Entropy of Water.—Values of the heat of fusion, heat capacity of the liquid and heat of

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(6) Dickinson and Osborne, *Bull. U. S. Bur. Standards*, **12**, 49 (1915).

(7) Nernst, Koref and Lindemann, *Sitzber. Berlin Akad. Wiss.*, 247 (1910).

(8) Pollitzer, *Z. Elektrochem.*, **19**, 513 (1913).

(9) Maass and Waldbauer, THIS JOURNAL, **47**, 1 (1925).

(10) Barnes and Maass, *Can. J. Research*, **3**, 205 (1930).

(11) Simon, "Handbuch der Physik," Vol. X, 1926, p. 363.

(12) Simon, personal communication. Measurements of the heat capacity of ice between 9 and 13°K. were made in 1923 by Simon, but the results have not as yet been published. Since these values are of considerable interest in connection with the present investigation, we are, with Professor Simon's kind permission, presenting them here.

HEAT CAPACITY OF ICE BETWEEN 9 AND 13°K. MEASUREMENTS OF F. SIMON

T, °K.	9.47	9.88[a]	10.46	11.35	11.55[a]	12.10	12.85
C_p cal./deg./mole	0.056	0.063	0.075	0.096	0.102	0.118	0.141

[a] Obtained in an independent second experiment.

(13) Calculated from data of Simon, see Ref. 12.

vaporization of water are so accurately known that further investigation was unnecessary.

The heat of fusion of ice has been accurately determined by a number of workers. The measurements prior to 1913 have been critically summarized by Dickinson, Harper and Osborne,[14] who also made a number of measurements of the heat of fusion both by an electrical method and by the method of mixtures. Dickinson and Osborne[6] measured the heat of fusion in an aneroid calorimeter, using electrical heating. The measurements in which energy was introduced electrically were recalculated by us on the basis of 1 int. joule = 4.1832 calories (15°). A weighted average of all the reported values yields 1435.7 cal./mole with an estimated accuracy of ±0.9 cal./mole, for the heat of fusion.

Fiock[15] has reviewed the measurements of the heat of vaporization of water and compared them with the results of determinations at the Bureau of Standards[16] extending down to 50°. All measurements were converted into international joules. Of the data considered by Fiock, those of Griffiths, of Smith and of Henning contained measurements in the neighborhood of 25°C. Giving equal weight to the result of each of the above three observers and to the value extrapolated from the Bureau of Standards measurements, and taking 1 calorie (15°) = 4.1832 int. joules, we obtained an average value of 10,499 ± 3 (av. dev.) calories/mole for the heat of vaporization of water at 25°.

The "I.C.T." values for the heat capacity of liquid water[17] were plotted against the logarithm of the absolute temperature and integrated graphically to obtain the entropy between 0 and 25°. The value for the vapor pressure at 25° was also obtained from the "I.C.T."[18] Using Berthelot's equation of state and thermodynamics it can be shown that the entropy correction[1a] to the ideal gas state is almost negligible in this case The critical constants[19] used were $T_c = 647.1$°K. and $P_c = 217.7$ atm.

The entropy between 10 and 273.10°K. was obtained by graphical integration of the measured heat capacities. The entropy between 0 and 10°K. was calculated by means of the Debye equation, using $h\nu/k = 192$. A summary of the entropy calculation is given in Table III.

TABLE III

CALCULATION OF ENTROPY OF WATER

0–10°K., Debye function $h\nu/k = 192$	0.022
10–273.10°K., graphical	9.081
Fusion 1435.7/273.10	5.257
273.10–298.10°K., graphical	1.580
Vaporization 10499/298.10	35.220
Correction for gas imperfection	0.002
Compression $R \ln 2.3756/760$	−6.886
Cal./deg./mole	44.28 ± 0.05

The value of the entropy given in Table III may be compared with that calculated from spectroscopic data. Giauque and Ashley[4] utilized the preliminary molecular constants of water as given by Mecke and Baumann[20] to determine the entropy of water. Later Gordon[21] recalculated the thermodynamic quantities for water using the revised moments of inertia of Freudenberg and Mecke.[22] He obtained $S^\circ_{298.1} = 45.10$ cal./deg./mole. The difference between the spectroscopic and calorimetric values is 0.82 cal./deg./mole.

The Problem of the False Equilibrium in Ice.—To account for the discrepancy between the calorimetric and spectroscopic values for the entropy of water Giauque and Ashley[4] offered an explanation based on the assumption that the ortho and para molecular states, which are known to exist in gaseous water, had persisted in the crystalline state at low temperatures. The situation was assumed to be similar to that which accounts for the entropy discrepancy in the case of solid hydrogen.[1b,d] The ortho water was assumed to have non-polar clockwise and counter clockwise rotations in ice, since the dielectric constant of ice at low temperatures corresponds to that of non-polar substances. This leads to a calculated discrepancy of $^3/_4 R \ln 2 = 1.03$ cal./deg./mole.

We have had many interesting private discussions with Professor Linus Pauling who has consistently objected to the ortho-para explanation. During the course of the present investigation Pauling[23] offered an alternative explanation based

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[14] Dickinson, Harper and Osborne, *Bull. U. S. Bur. Standards*, **10**, 235 (1914).

[15] Fiock, *Bur. Standards J. Research*, **5**, 481 (1930).

[16] (a) Osborne, Stimson and Fiock, *ibid.*, **5**, 411 (1930); (b) Fiock and Ginnings, *ibid.*, **8**, 321 (1932).

[17] "International Critical Tables," McGraw-Hill Book Co., New York, Vol. V, 1926, p. 113.

[18] "I. C. T.," Vol. III, p. 211.

[19] "I. C. T.," Vol. III, p. 248.

[20] Mecke and Baumann, (a) *Naturwiss.*, **20**, 657 (1932); (b) *Phys. Z.*, **33**, 833 (1932).

[21] Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

[22] Freudenberg and Mecke, *Z. Physik*, **81**, 465 (1933).

[23] Pauling, (a) personal communication; (b) THIS JOURNAL, **57**, 2680 (1935).

on the random orientation of hydrogen bonds in ice. Crystal structure investigations have shown that each oxygen atom is surrounded by four equivalent oxygen atoms. Although the positions of the hydrogen atoms have not been determined experimentally it seems reasonable to assume that they are located on lines joining adjacent oxygens. Since the oxygen–oxygen distance is considerably greater than twice the separation which is characteristic of an oxygen–hydrogen linkage, it has been assumed by Bernal and Fowler[24] that each oxygen is joined to two close and two distant hydrogen atoms. At higher temperatures the bond directions of the close or distant hydrogen atoms of a given oxygen are a matter of chance. We quote from the paper of Bernal and Fowler. "Therefore it is quite conceivable and even likely that at temperatures just below the melting point the molecular arrangement is still partially or even largely irregular, though preserving at every point tetrahedral coördination and balanced dipoles. In that case ice would be crystalline only in the position of its molecules but glass-like in their orientation. Such a hypothesis may be still necessary to explain the dielectric constant and the absence of pyroelectricity."

Pauling assumes further that when ice is cooled to low temperatures, it fails to attain the ordered arrangement which would correspond to zero entropy. He shows that the discrepancy corresponding to the above lack of order would be $R \ln 6/4 = 0.806$ cal./deg./mole. This is in very close agreement with the experimentally determined discrepancy of 0.82 ± 0.05 cal./deg./mole.

However, it should be pointed out that in two previous cases, carbon monoxide[25] and NNO[26] where random molecular orientations led to entropy discrepancies, the experimental discrepancy was a few tenths of a unit lower than the calculated value due to partial attainment of an ordered state. If this were the case in ice, the ortho-para explanation might be correct. However, we consider that the explanation advanced by Pauling is the more plausible as well as being in better agreement with the experimental results.

It is of interest to note that MacDougall and Giauque[27] investigated ice from 0.2 to 4°K. and found no appreciable heat capacity in this region.

One of the purposes of the present work was to investigate the possibility of more complete attainment of equilibrium. We have mentioned above that various experiments, in which ice was cooled slowly or rapidly to low temperatures, or was allowed to stand for long periods of time at low temperatures, resulted in heat capacities which were not appreciably different in the various series of measurements. At temperatures between 85 and 100°K. the attainment of thermal equilibrium in the solid was very much less rapid than at other temperatures. For this reason the heat capacity measurements in this region are somewhat less accurate than the others. This slow equilibrium presumably is due to the initial stages of excitation of some new degrees of freedom. From the value of the heat capacity this evidently is connected with motion of the hydrogen atoms. At temperatures below the region of slow equilibrium the dielectric constant[28] is of the order of magnitude characteristic of a non-polar substance. At higher temperatures the dielectric constant rises rapidly and the orientation time of the dipole decreases. From this it would appear that the new degrees of freedom referred to above are associated with the dipole orientation mechanism.

From the temperature drift experiments at 60, 72, 78 and 85°K. it appears that no great change in the heat content would be expected if ice were kept at these temperatures for a considerable period of time.

We may mention in passing that low temperature heat capacity measurements on some of the high pressure forms of ice would undoubtedly lead to correct values for the entropy of water.

It is perhaps worth noting that while the theory of random bond orientation would lead to the same discrepancy, $R \ln 3/2 = 0.806$ cal./deg./mole in both hydrogen and deuterium oxides, the theory of molecular rotation in ortho states of water would lead to different values for the calculated discrepancy. For hydrogen oxide the value is $3/4\, R \ln 2 = 1.033$, for deuterium oxide, $1/3\, R \ln 2 = 0.459$ cal./deg./mole. Although we believe the latter theory to be less plausible it will be of interest to make the comparison when measurements on deuterium oxide become available.

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(24) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(25) Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932).

(26) (a) Clusius, *Z. Elektrochem.*, **40**, 99 (1934); (b) Blue and Giauque, THIS JOURNAL, **57**, 991 (1935).

(27) MacDougall and Giauque, *ibid.*, **58**, 1032 (1936).

(28) "I. C. T.," Vol. VI, page 78.

We wish to thank Mr. C. C. Stephenson for assisting with the experimental work.

Summary

The heat capacity of ice has been measured between 15 and 273°K.

It has previously been shown by Giauque and Ashley that a discrepancy exists between the spectroscopic value of the entropy and the $\int_0^T C_p \, d \ln T$ for water.

The purpose of the present investigation was to make an accurate determination of the discrepancy.

With the assistance of the well-known values for the heats of fusion and vaporization of water we find that the $\int_0^T C_p \, d \ln T = 44.28 \pm 0.05$ cal./deg./mole for H_2O (g.) at one atmosphere and 298.1°K. The spectroscopic value is 45.10 leading to a discrepancy of 0.82 cal./deg./mole. This is in excellent agreement with the theoretical discrepancy 0.806 calculated by Pauling on the assumption of random orientation of hydrogen bond directions in ice.

Experiments have been described in which ice was cooled slowly or rapidly to low temperatures or was allowed to stand for long periods of time at low temperatures. No difference in the thermal properties of ice was observed in these experiments.

BERKELEY, CALIF. RECEIVED MARCH 30, 1936

[CONTRIBUTION FROM THE NATIONAL RESEARCH INSTITUTE OF CHEMISTRY, ACADEMIA SINICA]

Pyrimidine Research. Synthesis of 4-Methyl-5-*n*-butylcytosine

BY YUOH-FONG CHI

In this paper is described a method of synthesizing 4-methyl-5-*n*-butylcytosine (VII), which is prepared as its hydrobromide from 2-ethylmercapto-4-methyl-5-*n*-butylcytosine (VI) by hydrolysis with concentrated hydrobromic acid. The free base (VII) is liberated from its hydrobromide by neutralizing with ammonia. For the preparation of 2-ethylmercapto-4-methyl-5-*n*-butylcytosine (VI), the starting point is the corresponding 6-oxypyrimidine, 2-ethylmercapto-4-methyl-5-*n*-butyl-6-oxypyrimidine (II). This is treated with phosphorus oxychloride to form the corresponding 6-chloropyrimidine (V), and the latter then heated with alcoholic ammonia at 170–180° to give the desired 2-mercapto-6-amino derivative (VI).

2 - Ethylmercapto - 4 - methyl - 5 - *n* - butyl-6-oxypyrimidine was prepared according to the general method of Wheeler and Liddle.[1] Ethyl *n*-butylacetoacetate is first condensed with thiourea in the presence of sodium ethylate to give 2-thio-4-methyl-5-*n*-butyl-6-oxypyrimidine (I), which is then treated in the presence of sodium ethylate with ethyl bromide to give 2-ethylmercaptopyrimidine (II). Alkylation of the latter with methyl iodide gives the corresponding 2-methylmercapto compound (III), and with ethyl chloroacetate to give ethyl 4-methyl-5-*n*-butyl-6-oxypyrimidine-2-thioglycolate (IV).

$$\mathrm{HNCSNHC(CH_3){=}C(\textit{n}\text{-}C_4H_9)CO}$$

I

$$\mathrm{HNC(SC_2H_5){=}NC(CH_3){=}C(\textit{n}\text{-}C_4H_9)CO}$$

II

$$\mathrm{HNC(SCH_3){=}NC(CH_3){=}C(\textit{n}\text{-}C_4H_9)CO}$$

III

$$\mathrm{HNC(SCH_2COOC_2H_5){=}NC(CH_3){=}C(\textit{n}\text{-}C_4H_9)CO}$$

IV

$$\mathrm{NC(SC_2H_5){=}NC(CH_3){=}C(\textit{n}\text{-}C_4H_9)CCl}$$

V

$$\mathrm{NC(SC_2H_5){=}NC(CH_3){=}C(\textit{n}\text{-}C_4H_9)CNH_2}$$

VI

$$\mathrm{NCONHC(CH_3){=}C(\textit{n}\text{-}C_4H_9)CNH_2}$$

VII

Experimental Part

2 - Thio - 4 - methyl - 5 - *n* - butyl - 6 - oxypyrimidine I.—Twenty-six grams of sodium was dissolved in 500 cc. of absolute alcohol and 210 g. of ethyl *n*-butylacetoacetate and 94 g. of thiourea added to the solution. This was then heated on a water-bath for ten hours and the excess of alcohol removed by heating under diminished pressure. The crude sodium salt of the desired pyrimidine was dissolved in water and the solution acidified with acetic acid, when the thiopyrimidine separated. It crystallized from hot water in needles, melting at 197–198°. The yield was 144 g.

Anal. Calcd. for $C_9H_{14}ON_2S$: N, 14.14. Found; N, 14.03, 13.98, 14.00.

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[1] Wheeler and Liddle, *Am. Chem. J.*, **40**, 547 (1908).