times the quantity of reagents used above. These were carried through the reductor and their final corrected titers divided by 5. This figure, called the reagent correction, was added to the indicator correction, the combined value of which was subtracted from the glass sand titers.

The numerical results secured by this method compare favorably with those obtained by the Bureau of Standards using the gravimetric method described in the certificate of standardization. The method possesses advantages of speed and low cost, due to the elimination of the precipitation of iron, and the fact that, working with 2-g. samples, it is possible to use 30-cc. crucibles in place of liter platinum dishes. For practical work it is possible to shorten the procedure still further by elimination of one ignition without sacrificing undue accuracy.

The authors are grateful to Dr. Orin W. Rees for coöperation and helpful suggestions and to Mr. L. D. McVickers for gravimetric standardization of the ferric ammonium sulfate solution.

Summary

1. An attempt to determine small quantities of iron by reduction with silver followed by titration with ceric sulfate revealed an error attributable to the formation of hydrogen peroxide in the reductor.

2. By conducting the reduction in an atmosphere of hydrogen, thereby decreasing the reductor correction, and applying a correction for the indicator, it was possible to determine quantities of iron of the order of 1.5 mg. with a high degree of accuracy.

3. The method was found to be relatively rapid and not to require the use of large platinum dishes, thus possessing advantages of practical value.

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

Hydrogen Sulfide. The Heat Capacity and Vapor Pressure of Solid and Liquid. The Heat of Vaporization. A Comparison of Thermodynamic and Spectroscopic Values of the Entropy

BY W. F. GIAUQUE AND R. W. BLUE[1]

The entropy of hydrogen sulfide as determined by means of the third law of thermodynamics is of special interest since it has been shown[2] that the ordinary application of this method does not give the correct entropy for the analogous and important case of water. However, the low temperature calorimetric investigation reported here proves that the $\int_0^T C_p \, d \ln T$ does give the correct entropy for hydrogen sulfide. The correct value has been calculated by Cross[3] from the band spectrum data of this substance.

The calorimetric apparatus and methods were identical with those described in our paper[4] on nitrous oxide except that the amounts of hydrogen sulfide were measured by absorbing the gas in alkali and observing the increase in weight. This latter procedure is the same as that followed by Giauque and Wiebe.[5]

Preparation of Pure Hydrogen Sulfide.—Hydrogen sulfide was prepared by direct combination of the elements. Dry electrolytic hydrogen which had been freed from oxygen by means of a nickel catalyst and sulfur which was shown by analysis to contain no trace of selenium were used. The hydrogen was bubbled through liquid sulfur at 275–300°. This temperature range ensured the presence of a large excess of hydrogen in the resulting mixture. The mixed gases were passed over a nickel catalyst on pumice at 600°. The nickel catalyst may be superfluous but it was readily available and was included because of its effectiveness in the analogous reaction between hydrogen and oxygen. In the preliminary preparations the hydrogen sulfide contained considerable impurity which was undoubtedly hydrogen polysulfide. While this condition may have been due to faulty operation of the above system, it was very satisfactorily eliminated by passing the gas, prepared as above, through a quartz tube, filled with pumice, and heated to 800°. After the furnace temperatures became constant the gaseous mixture was passed through the preparation system for half an hour before any hydrogen sulfide was collected. A large trap in the preparation line was then cooled with liquid air[6] and the hydrogen sulfide was collected as the solid. About 200 cc. of liquid hydrogen sulfide was prepared in twenty-four hours. The effective length of the tube at 600° was about 100 cm., that at 800° was about 30 cm. and the diameters were roughly 2 cm.

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[1] Shell Research Fellow, Academic year 1931–1932.

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

[3] Cross, *J. Chem. Phys.*, **3**, 168 (1935).

[4] Blue and Giauque, THIS JOURNAL, **57**, 991 (1935).

[5] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

[6] In condensing materials of this sort in glass containers immersed in liquid air we consider it advisable to surround the glass by a close fitting easily removable case of thin metal. This is to prevent the formation of a potentially explosive mixture in case of accidental glass breakage.

When sufficient hydrogen sulfide had been collected the trap containing the solid hydrogen sulfide was isolated from the rest of the preparation line and evacuated with a mercury diffusion pump. The liquid air was then removed and the hydrogen sulfide was distilled, through a tube filled with phosphorus pentoxide, into a bulb cooled with solid carbon dioxide and ether. The liquid was then distilled three times, a fraction of 10 cc. or more being discarded at the beginning and at the end of each distillation. During the first of the above three distillations the gas was bubbled through 10–22 cc. of the distillate contained in an intermediate bulb. Also a larger end fraction was discarded in this case. Finally the distillate was solidified by cooling with liquid air and subjected to a high vacuum by means of a mercury diffusion pump. Three preparations, referred to as 1, 2 and 3, were used in the course of the measurements.

Assuming that the slight rise in heat capacity below the melting point is due to premelting, caused by a liquid-soluble solid-insoluble impurity, the amount of impurity was estimated to be less than one part in one hundred thousand. It was shown by observations on the preliminary preparation mentioned above that the most probable contamination, hydrogen polysulfide, does cause premelting.

The Vapor Pressure of Hydrogen Sulfide.—The vapor pressure measurements were made with the apparatus described in connection with nitrous oxide.[4] The calorimeter could be connected directly with the manometer for this purpose. The measurements were made on the material described as Preparation 2. In a preliminary study of the triple point pressure the pressure increased by about 0.5 mm. in twelve hours. This was not caused by leaks since the system was tested repeatedly both before and after this measurement and found to hold a vacuum of 10^{-5} mm. for several hours. Discoloration of mercury in a small manometer used for control purposes indicated that the pressure increase was due to the reaction $H_2S + Hg = HgS + H_2$. It appears that this reaction cannot be prevented without baking out the glass apparatus and this was not very practicable. The mercury menisci in the large manometer, used for measuring vapor pressures, were not distorted. To eliminate the possibility of error due to the presence of hydrogen it was necessary to remove the gas in the line leading to the manometer and some material from the calorimeter before each measurement. With this procedure the results were very satisfactory. With the assistance of a cathetometer the manometer was compared with a standard meter hung between the arms within the manometer case. All pressure observations are expressed in terms of international centimeters of mercury, using the data given in the "I. C. T."[7] The gravitational acceleration for this location was taken as 979.973 cm./sec.^{2} from the work of Sternewarte.[8] The standard acceleration of gravity was taken as 980.665 cm./sec.^{2}. The vapor pressure observations are satisfactorily represented by the equations

Solid hydrogen sulfide, 164.90 to 187.61°K.

$$\log_{10} P\,(\text{int. cm. Hg}) = -(1329/T) + 9.28588 - 0.0051263T \quad (1)$$

Liquid hydrogen sulfide, 187.61 to 213.17°K.

$$\log_{10} P\,(\text{int. cm. Hg}) = -(1145/T) + 7.94746 - 0.00322T \quad (2)$$

The observed and calculated values are given in Table I.

TABLE I

VAPOR PRESSURES OF HYDROGEN SULFIDE

Boiling point 212.77°K. 0°C. = 273.10°K.

T, °K	$P_{\text{obsd.}}$, int. cm. Hg.	$P_{\text{calcd.}}$	$T_{\text{obsd.}} - T_{\text{calcd.}}$
164.904	2.405	2.406	+0.004 Solid
168.470	3.417	3.417	+ .000 Solid
173.308	5.356	5.358	+ .004 Solid
177.888	8.003	7.998	− .008 Solid
182.844	12.041	12.025	− .017 Solid
187.61	17.389		Triple point
188.350	18.289	18.276	− .011 Liquid
190.506	21.078	21.073	− .004 Liquid
193.840	26.084	26.084	.000 Liquid
196.980	31.644	31.652	+ .004 Liquid
199.909	37.670	37.682	+ .006 Liquid
203.400	46.056	46.048	− .003 Liquid
206.575	54.893	54.892	− .000 Liquid
210.176	66.500	66.507	+ .002 Liquid
213.166	77.545	77.565	+ .004 Liquid

The agreement shown in Table I is very satisfactory. The temperatures are given to 0.001° only because of the high relative accuracy. The absolute values may be in error by several hundredths of a degree. Points on each side of the triple point indicate that a melting point of about 187.60° would give better agreement. However, the melting point was carefully investigated with Preparations 1, 2 and 3 and 187.61° was obtained in each case. Preparation 1 was observed for nine hours with amounts from 8 to 50% melted, heat being added occasionally for this purpose. The resistance thermometer had an average deviation of only 0.006° over the above period. Similarly Preparation 2 was observed for eighteen hours with amounts ranging from 3 to 55% melted. The average deviation was 0.005° on the resistance thermometer. Preparation 3 was observed for thirty-one hours, with amounts from 3 to 60% melted, giving an average deviation of only 0.002°. The thermocouple had an average deviation of less than 0.01° in each case.

From Equation 2 the boiling point was determined as 212.77°K.

Table II contains a summary of measurements of the melting and boiling point temperatures for hydrogen sulfide.

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(7) "International Critical Tables," McGraw-Hill Book Co., New York, 1926.

(8) Sternewarte, Landolt, Börnstein and Roth, "Physikalische-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

TABLE II

MELTING AND BOILING POINT TEMPERATURES OF HYDROGEN SULFIDE

Melting point, °K.	Boiling point, °K.	Observer
188	....	Faraday[9] (1845)
...	211.3 (755 mm.)	Regnault[10] (1862)
...	209.6	Olzewsky[11] (1890)
190.2	212.7 (755.2 mm.)	Ladenburg and Krügel[12] (1900)
184	212 (733 mm.)	De Forcrand and Fonzes-Diacon[13] (1902)
...	212.9	McIntosh, Steele and Archibald[14] (1906)
190	...	Magri[15] (1907)
191	...	Bagster[16] (1911)
190.1	212.9	Cardoso and Arni[17] (1912)
189.5	213.3	Maas and McIntosh[18] (1914)
190.3	...	Baume and Georgitses[19] (1914)
187.6	...	Kemp and Denison[20] (1933)
187.60	...	Clusius[21] (1933)
187.7	...	Smyth and Hitchcock[22] (1934)
187.61	212.77	This research

The Transition of Hydrogen Sulfide.—There is a sharp transition in solid hydrogen sulfide at 103.52°K. and a region of considerable energy absorption principally between 126 and 127°K. In the latter case heat is absorbed almost, if not exactly, isothermally at 126.22°K. but an abnormal rise in heat capacity is evident for at least five degrees below this temperature. The situation appears to be similar to that observed by Simon[23] in the case of ammonium chloride and later found to exist in many hydrogen compounds such as hydrogen bromide, hydrogen iodide and methane. Pauling[24] has pointed out that rotation within the solid is undoubtedly the usual cause of such regions of high energy absorption in these substances. Our observations on hydrogen sulfide became of interest to J. D. Kemp and G. H. Denison,[20] who then carried out an investigation on the dielectric properties of hydrogen sulfide. They prepared pure hydrogen sulfide with the apparatus and procedure described above. Their results showed a dielectric constant characteristic of a non-polar substance below the isothermal transition at 103.52°, with a large dielectric increase at this temperature. No marked change was observed on passing through the region near 126°K. Kemp and Denison show that the magnitude of the dielectric constant in the solid above 103.52° is the same as that of liquid hydrogen sulfide.

Smyth and Hitchcock[22,25] have also carried out a dielectric investigation on hydrogen sulfide. Their results show a small and rather abrupt change near 126°K. and this is consistent with the marked increase in the heat capacity in this temperature region.

Although the above results do not provide an answer to the question concerning a discontinuous or rather abrupt loss of some molecular rotation near 126°K., they do show that the molecules can rotate without much restraint both below and above this temperature.

It may be recalled that hydrogen bromide and hydrogen iodide have more than one such region of high heat capacity. Thus it seems necessary to assume that rotations about different axes are excited somewhat independently or that the population in different quantum levels connected primarily with the same type of motion undergoes rather abrupt changes with temperature.

It is well known from studies[26] of the imperfections of two component solutions that in many cases the effects are such as to be consistent with the idea that like molecules of each kind tend to associate with each other. This effect often leads to separation into two phases, each consisting principally of like molecules, when the solution is cooled to a sufficiently low temperature.

Somewhat similarly, in a one component system, molecules with zero, one or two units of rotation may differ sufficiently from each other so that an assemblage of molecules in a low energy state can repress the population increase of a higher quantum species as the temperature is increased. Finally, a temperature is reached where the re-

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(9) Faraday, *Phil. Trans.*, **135**, 170 (1845).

(10) Regnault, *Mem. Acad.*, **26**, 613 (1862).

(11) Olzewsky, *Bull. Acad. Cracovie*, **67**, 1890.

(12) Ladenburg and Krügel, *Ber.*, **33**, 637 (1900).

(13) De Forcrand and Fonzes-Diacon, *Compt. rend.*, **134**, 229, 281 (1902).

(14) McIntosh, Steele and Archibald, *Z. physik. Chem.*, **55**, 129 (1906).

(15) Magri, *Rend. Linc.*, [5] **16**, **1**, 518 (1907).

(16) Bagster, *J. Chem. Soc.*, **99**, 1222 (1911).

(17) Cardoso and Arni, *J. chim. phys.*, **10**, 504 (1912).

(18) Maas and McIntosh, *Trans. Roy. Soc. Can.*, [3] **8**, 65 (1914).

(19) Baume and Georgitses, *J. chim. phys.*, **12**, 250 (1914).

(20) Kemp and Denison, THIS JOURNAL, **55**, 251 (1933).

(21) Clusius, (a) *Z. Elektrochem.*, **39**, 598 (1933); (b) *Nach. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 171 (1933).

(22) Smyth and Hitchcock, THIS JOURNAL, **56**, 1084 (1934).

(23) Simon, *Ann. Physik.*, **68**, 241 (1922).

(24) Pauling, *Phys. Rev.*, **36**, 430 (1930).

(25) Hitchcock and Smyth, THIS JOURNAL, **55**, 1296 (1933).

(26) *E. g.*, Hildebrand, "Solubility," Reinhold Publishing Co., New York, 1936.

sultant unstable condition leads to the excitation of the new state or states in large amount, either within a short temperature interval or discontinuously. Available dielectric investigations in the cases of polar substances do not permit unambiguous interpretation as they have been made on masses of randomly oriented small crystals. The rather difficult investigation of the axial dielectric susceptibilities of single crystals seems to be one of the most fruitful means of obtaining detailed information on this matter.

It is of interest to note that Kemp and Denison checked our results for the melting and transition temperatures and the temperature of near isothermal energy absorption above 126° within their limit of accuracy, 0.1°.

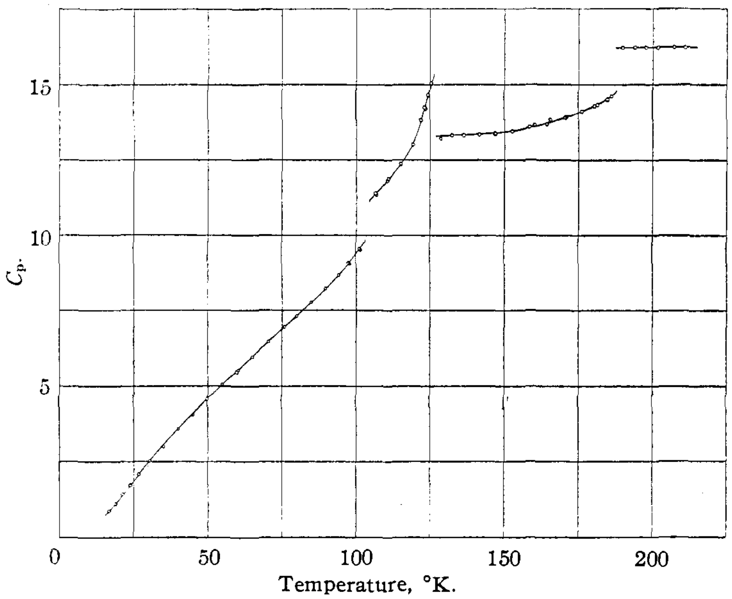

Fig. 1.—Heat capacity in calories per degree per mole of hydrogen sulfide.

Clusius[21] has since published a calorimetric investigation in which he agrees closely with the above temperatures.

In Table III we present the evidence that most of the energy is absorbed isothermally. The almost regular rise with percentage transformed may be somewhat illusory as the observations covered only a total period of four hours and it is our experience that many sharp transitions require a rather long time for equilibrium after an addition of energy. A very similar effect was observed on the sharp transition at 103.52°, with four additions of energy, during a period of six hours.

TABLE III

TEMPERATURES OF HIGH ENERGY ABSORPTION NEAR 126°K. IN HYDROGEN SULFIDE

Total energy added, %	Resistance thermometer, °K.	Thermocouple, °K.
10	126.210	126.21
30	126.218	126.22
60	126.225	126.23
80	126.240	126.24

In Table IV we summarize the available data on the above approximate temperature and on the transition temperature.

The Heat Capacity of Hydrogen Sulfide.—The heat capacity results are given in Table V. As usual we have corrected the results for vaporization, where the vapor pressure was large enough to produce an appreciable vaporization into the gas space above the substance. For this purpose the density of liquid hydrogen sulfide was taken from the work of McIntosh, Steel and Archibald.[14] The density of the solid at the melting point was estimated roughly as 1.1 g./cc. from an observation on a glass bulb. The energy measurements assumed that 1 calorie (15°) was equal to 4.185 absolute joules and 1.00042 absolute joules were equal to one international joule.

It is believed that the smooth curves represent the correct values of heat capacity to within 0.2% at all temperatures above 35°K. At 20°K. the error is not greater than 1%.

The heat capacity of hydrogen sulfide has been measured by Clusius[21] but a comparison cannot be made since the preliminary publication is in graphical form.

TABLE IV

SUMMARY OF TRANSITION TEMPERATURE DATA OF HYDROGEN SULFIDE

0°C. = 273.10°K.

Transition temperature, °K.	Principal temperature of high energy absorption, °K.	Observer
103.5	126.3	Kemp and Denison (1933)
103.6	126.2	Clusius (1933)
103.1	126.4	Hitchcock and Smyth (1933)
103.52	126.22	This research

In Table VI the results are summarized by points taken from smooth curves through the data.

The Heats of Fusion and Transition.—The measurements of the heats of fusion and transi-

TABLE V

HEAT CAPACITY OF HYDROGEN SULFIDE

Molecular weight 34.076. 0°C. = 273.10°K.

Preparation No.	1	2	3
Amount in moles	2.7444	2.8841	2.9098

T, °K.	ΔT	C_p cal./deg./mole	Preparation
16.97	1.799	0.835	II
19.07	1.875	1.103	II
21.41	2.442	1.427	II
24.07	2.544	1.731	II
26.84	2.893	2.082	II
30.43	4.109	2.527	II
35.03	5.053	3.015	II
40.00	4.891	3.581	II
45.04	5.113	4.061	II
50.05	4.908	4.592	II
54.95	4.934	5.064	II
59.90	4.943	5.496	II
60.49	2.862	5.542	I
65.08	5.316	5.981	II
70.62	5.595	6.484	II
75.97	5.062	6.951	II
80.12	4.797	7.314	I
84.88	4.693	7.766	I
89.71	3.537	8.240	I
93.67	4.215	8.647	I
97.50	4.520	9.096	II
97.81	3.888	9.076	I
101.29	2.933	9.564	II
101.48	3.318	9.533	I
103.52	Transition		
106.59	3.718	11.40	I
107.05	3.800	11.35	II
110.65	4.017	11.83	I
110.65	4.017	11.83	I
111.00	3.941	11.90	II
115.00	4.428	12.38	I
119.33	4.090	13.09	I
121.97	1.969	13.81	II
123.33	3.780	14.24	I
123.51	1.028	14.19	II
124.53	0.992	14.65	II
125.47	0.862	15.34	II
126.22	Region of high energy absorption		
128.55	2.329	13.22	II
132.41	5.208	13.34	II
136.49	4.558	13.32	I
141.56	5.261	13.36	I
147.02	5.439	13.39	I
152.79	5.198	13.51	I
158.48	5.701	13.60	I
160.21	4.818	13.65	III
164.44	5.785	13.69	I
165.60	5.098	13.83	III
170.54	5.836	13.90	I
171.04	4.922	13.92	III
176.31	4.724	14.10	III
176.38	5.121	14.09	I
180.61	4.801	14.28	I
181.65	4.519	14.32	III
185.00	1.325	14.50	III
186.36	1.309	14.61	III
187.61	Melting point		
189.95	3.642	16.21	III
194.03	3.543	16.22	III
197.81	3.471	16.22	III
201.83	3.891	16.25	III
207.14	4.375	16.30	III
210.99	4.324	16.31	III
212.77	Boiling point		

TABLE VI

HEAT CAPACITY OF HYDROGEN SULFIDE

Molecular weight 34.076. 0°C. = 273.10°K.

Values taken from smooth curves through data

T, °K.	C_p cal./deg./mole	T, °K.	C_p cal./deg./mole
20	1.25	125	15.02
30	2.48	130	13.25
40	3.56	140	13.33
50	4.56	150	13.45
60	5.51	160	13.65
70	6.43	170	13.92
80	7.31	180	14.26
90	8.26	185	14.53
100	9.36	190	16.21
105	11.25	200	16.26
110	11.79	210	16.31
120	13.27		

tion of hydrogen sulfide are summarized in Table VII. As noted above the heat absorption occurring near 126 is not strictly isothermal. Therefore we have given the total heat absorbed in the region from 126 to 127°K. Since the calorimetric observations do not prove that a change in phase has taken place, we prefer not to present the data in the form of a heat of transition. However,

TABLE VII

HEATS OF TRANSITION AND FUSION OF HYDROGEN SULFIDE

Molecular weight 34.076

Transition at 103.52°K.

Temperature interval	Corrected total heat input per mole	$\int C_p\, dT$/mole	ΔH cal./mole
103.154–105.498	393.19	25.73	367.5
102.889–104.684	387.15	19.16	368.0
102.758–105.050	392.92	24.53	368.4
		Mean	368.0 ± 0.3
Total heat absorbed between 126 and 127°K.			
125.286–127.878	143.71	22.69	121.0
125.650–127.733	136.44	15.17	121.3
124.961–127.378	142.40	20.95	121.4
125.644–127.267	130.43	9.09	121.3
		Mean	121.3 ± 0.1
Fusion at 187.61°K.			
187.256–189.930	610.60	42.66	567.9
187.095–189.583	608.00	39.42	568.6
187.252–189.104	596.90	29.38	567.5
187.098–188.468	589.80	21.36	568.4
		Mean	568.1 ± 0.4

the data have been presented in a manner that permits this calculation to be made if a phase change can be proved.

Clusius[21] has given the heat of transition as 362.1 cal./mole and the heat of fusion as 568.3 cal./mole.

The Heat of Vaporization of Hydrogen Sulfide.—The heat of vaporization was measured calorimetrically at constant pressure, as described previously.[5] The data are summarized in Table VIII. We have included the work of other observers for comparison. A value calculated from the vapor pressure data as represented by Equation 2 has been included but is given no weight in comparison to the more accurate calorimetric values. This latter value was calculated by assuming that Berthelot's equation of state represents the gas imperfection. The critical constants used are quoted later.

TABLE VIII

HEAT OF VAPORIZATION OF HYDROGEN SULFIDE

Boiling point, 212.77°K. Molecular weight, 34.076

Moles evaporated	Time of energy input, min.	ΔH at 760 mm. cal./mole
0.26023	60	4463
.26067	60	4461
.20843	50	4464
		Mean 4463 ± 4
Calculated from vapor pressure equation (2), assuming a Berthelot gas		4451
De Forcrand and Fonzes-Diacon[13] (1902)		4230
Elliott and McIntosh[27] (1908)		4655
Schnerr[28] (1910)		4498
Maas and McIntosh[18] (1914)		4586

The Entropy of Hydrogen Sulfide.—The calculation of the entropy from the experimental data by means of the equation $S = \int_0^T C_p \, d \ln T$ is summarized in Table IX. The correction for gas imperfection was made by combining thermodynamics with Berthelot's equation of state.[5]

$$T_c = 373.5°\text{K.}^{28} \quad P_c = 88.9 \text{ atm.}^{29}$$

$$\Delta S = S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c \quad (3)$$

$$= 0.10 \text{ E. U. at the boiling point}$$

The band spectrum of hydrogen sulfide has been accurately measured and interpreted by Cross.[30]

TABLE IX

THE ENTROPY OF HYDROGEN SULFIDE

Molecular weight 34.076

0–16°K. Debye function $hc\nu/k = 136$	0.255
16–103.52°K., graphical	7.648
Transition 368.0/103.52	3.554
103.52–126°K., graphical	2.482
ΔH 126–127°K. 121.3/126.22	0.961
127–187.61°K., graphical	5.322
Fusion 568.1/187.61	3.028
187.61–212.77°K., graphical	2.049
Vaporization 4463/212.77	20.98
Entropy of actual gas at boiling point	46.28 ± 0.1 E. U.
Correction for gas imperfection	0.10
Entropy for ideal gas at boiling point	46.38 ± 0.1 E. U.

He has also published[3] the results of free energy, entropy and heat capacity calculations based on his spectroscopic data. During the course of his investigation he kindly offered to include an entropy value corresponding to our measured boiling point temperature. His spectroscopic values are included in Table X. The spectroscopic constants used were 2.667, 3.076, 5.845 × 10^{-40} g. cm.^{2} for the moments of inertia and $\nu_\sigma = 1260$ cm.$^{-1}$ and $\nu_\pi = \nu_\sigma = 2620$ cm.$^{-1}$ for the fundamental vibrational frequencies.

TABLE X

COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC ENTROPIES OF HYDROGEN SULFIDE

Temperature, °K.		212.77	298.1
Spectroscopic	Absolute	49.195	51.905
	Less nuclear spin entropy	46.441	49.151
Experimental	Actual gas	46.28 ± 0.1	....
	Corrected to ideal state	46.38	49.10

The experimental value given for 298.1°K. was obtained by using the spectroscopic data for the gas above the boiling point. As usual the low temperature extrapolation of the experimental data did not include the nuclear spin entropy so that comparison should be made between rows two and four in Table X.

It will be seen that the experimental value obtained from the calorimetric data and the third law of thermodynamics is in excellent agreement with that derived from the band spectrum.

We wish to thank Mr. Roy Overstreet for assistance with the experimental work.

Summary

The heat capacity of solid and liquid hydrogen sulfide has been measured over their respective ranges from 16°K. to the boiling point.

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(27) Elliott and McIntosh, *J. Phys. Chem.*, **12**, 163 (1908).

(28) Schnerr, "Ueber die Verdampfungswärme, etc.," Freiburg, **1910**.

(29) Cardoso, *Gazz. chim. ital.*, **51**, I, 153 (1921); also Pickering, *Bur. Standards Sci. Papers*, **31**, No. 541 (1926).

(30) Cross, (a) *Phys. Rev.*, **46**, 536 (1934); (b) **47**, 7 (1935).

A transition was found at 103.52°K. and a region of large energy absorption, possibly ending in a transition, was found near 126°K. The abnormal rise in heat capacity extended for many degrees below this temperature but a large proportion of the energy was absorbed nearly isothermally at 126.22°K.

The melting and boiling points were found to be 187.61 and 212.77°K., respectively.

The heat of transition at 103.52 is 368.2 cal./mole. The total heat absorption between 126 and 127°K. is 121.3 cal./mole. The heat of fusion is 568.1 cal./mole. The heat of vaporization is 4463 cal./mole at the boiling point.

The vapor pressure of solid and liquid hydrogen sulfide was measured and the results are represented by the equations:

Solid hydrogen sulfide, 164.90 to 187.61°K.

$$\log_{10} P\,(\text{int. cm. Hg}) = -(1329/T) + 9.28588 - 0.0051263T$$

Liquid hydrogen sulfide, 187.61 to 213.17°K.

$$\log_{10} P\,(\text{int. cm. Hg}) = -(1145/T) + 7.94746 - 0.00322T$$

The experimental data and the third law of thermodynamics have been used to calculate the molal entropy of the gas at the boiling point. The value found, 46.38 ± 0.1 E. U., is in excellent agreement with the spectroscopic value, 46.441 E. U. calculated by Cross. Each of the above values neglects the nuclear spin entropy.

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The Freezing Points of Aqueous Solutions. X. Dioxane and its Mixtures with Lithium, Sodium and Potassium Chlorides[1]

BY GEORGE SCATCHARD AND MARJORIE ALLEN BENEDICT

Debye and McAulay's application of the Born theory to the interaction of electrolytes and non-electrolytes in dilute solutions[2] indicates that the sodium ion should be more effective in salting out non-electrolytes than the potassium ion and that the lithium ion should be considerably more effective than the sodium ion. Debye's later theory,[3] which takes into account the variations from random distribution, indicates very much smaller differences, though in the same order. The experimental measurements of the salting out of non-electrolytes, on the other hand, disagree as to whether the sodium ion or the potassium ion is the more effective, but generally make the lithium ion much the least effective of the three. Since these measurements have been made at rather high concentrations of salt, and sometimes also of non-electrolyte, the following measurements were made of the freezing points of aqueous solutions of mixtures of each of the three chlorides with dioxane in order to obtain the limiting law at low concentrations with which the theories might be tested.

Dioxane was chosen as the non-electrolyte solute because it has a very large effect on the dielectric constant and also because its simple ether structure makes any specific chemical action improbable. Since dioxane–water mixtures are finding so much use in physico-chemical studies, and because such an ether might well be expected to be only slightly miscible with water, the study of the freezing points of dioxane solutions without added salt is also of importance.

Materials and Procedure

The salts were prepared as in earlier papers in this series.[4] The sodium and potassium chlorides were weighed into the mixtures as the dried salts, and the lithium chloride was weighed as an analyzed concentrated solution. All water used was from the laboratory conductivity water still.

Commercial dioxane ($C_4H_8O_2$) was refluxed eight hours with one-tenth its weight of concentrated hydrochloric acid, decanted from the acid layer, shaken with enough sodium hydroxide pellets to neutralize the acid and dried with calcium chloride and then with sodium, being refluxed during the drying with sodium.[5] It was then fractionated twice through a Davis column, the middle two-thirds being retained. By comparison with water in a carefully designed boiling point apparatus with a closed atmosphere of helium[6] and a Beckmann thermometer, the

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[1] From a thesis submitted in October, 1935, by Mrs. Marjorie Allen Benedict in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] P. Debye and J. McAulay, *Physik. Z.*, **26**, 22 (1925).

[3] P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

[4] G. Scatchard and S. S. Prentiss, THIS JOURNAL, **55**, 4355 (1933).

[5] B. D. Kribben, Thesis, M. I. T., 1933; C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934).

[6] J. A. Beattie, J. M. Gaines, Jr., and B. E. Blaisdell, unpublished.