chlorobenzene and nitrobenzene in the various solvents used leaves nothing to be desired. This agreement is shown amply in Table VI.

Summary

1. Using an electrical resonance method previously described, dielectric constant data have been obtained for carbon disulfide solutions of benzoic acid, phenol, cinnamic acid, iodine, naphthalene, anthracene, benzene, hexane, nitrobenzene and chlorobenzene, and for hexane solutions of benzoic acid, naphthalene, benzene, nitrobenzene and chlorobenzene. Corresponding density determinations have been made.
2. The data have been applied to the calculation of the electric moments of a majority of the solute molecules.
3. The data of this article prove that the molar polarization, and therefore the electric moment, of a solute molecule is independent of the non-polar solvent used.
4. The solvents benzene, carbon disulfide and hexane have been shown to be non-polar in character.

MADISON, WISCONSIN

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

THE ENTROPY OF HYDROGEN CHLORIDE. HEAT CAPACITY FROM 16°K. TO BOILING POINT. HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID

BY W. F. GIAUQUE AND R. WIEBE

RECEIVED OCTOBER 20, 1927 PUBLISHED JANUARY 5, 1928

The results presented in this paper were obtained in the first of a series of researches on low temperature calorimetry of condensed gases. This research, which was started in 1922, is in active continuation. It is hoped that the more important substances of simple structure which are gases under ordinary conditions will be investigated, or perhaps we should say re-investigated since data exist in many cases. In addition to the data presented in this paper, measurements on hydrogen bromide and hydrogen iodide have been completed but will not be available until the completion of the laborious calculations.

Our immediate purpose is the testing of the third law of thermodynamics and more particularly the comparison of the entropy, as obtained from this law, with that obtained from various theories with the assistance of spectroscopic data It seems almost unnecessary to state that such a purpose imposes severe requirements on the accuracy of the measurements.

Hydrogen chloride was selected because of the reliability of band spectra measurements and their interpretation for this substance. While the measurements were in progress the results of a similar investigation by Eucken and Karwat[1] and by Karwat[2] appeared. However, our experimental data are in considerable disagreement with those of the above authors, thus necessitating a different conclusion as to the interpretation. This confirms our previous conclusion regarding the desirability of new determinations in other cases.

Preparation of Hydrogen Chloride.—The preparation of pure anhydrous hydrogen chloride in large quantities proved to be one of the most difficult parts of the work. The amount required to fill the calorimeter was about 3.5 moles, and it was necessary to work with as much as 10 moles to allow for losses during the purification. At first the gas was prepared by the addition of sulfuric acid to sodium chloride in a system which had been evacuated. The gas was further dried by passing through sulfuric acid and through phosphorus pentoxide before condensation in a bulb cooled with liquid air. C. P. reagents only were used. Hydrogen chloride prepared in this manner had two properties which required further investigation; first, the condensed material was of a reddish pink color; second, on melting it was obviously impure since solid white particles could be seen in the colorless liquid.

Pink Hydrogen Chloride.—The most obvious assumption would be that some impurity caused the pink color but additional experiments did not support this explanation. The reddish pink color was obtained only when the condensation by liquid air took place *in vacuo*. When hydrogen chloride was passed into a condensation bulb which contained air and was left open to the atmosphere, the crystalline material was white. When the liquid air was removed from a bulb containing pink crystals, thus allowing the temperature to rise, the pink color disappeared abruptly, leaving white crystals. This occurred at a temperature very little above that of liquid air, probably within 10 or 20 degrees above the boiling point. Subsequent cooling in liquid air did not restore the pink color. The intensity of the color varied with the conditions, a greater intensity resulting when the gas was more slowly admitted to the condensation bulb. The possible sources of impurity were the reagents and stopcock grease. Since other reagents could be used, the following methods of preparation were carried out with stopcocks in the system.

$NH_4Cl + H_2SO_4$,	HCl dried with H_2SO_4 and with P_2O_5
HCl (aq.) + H_2SO_4,	HCl dried with H_2SO_4 and with P_2O_5
$NH_4Cl + H_3PO_4$,	HCl dried with P_2O_5 only
$NaCl + H_2SO_4$,	HCl dried with H_2SO_4 only

C. P. phosphorus pentoxide was available from several sources, and samples from some lots turned brown on treatment with concentrated H_2SO_4. Such material was not used, and we believe that the phosphorus pentoxide which was used for preparation purposes was of the highest quality.

---

[1] Eucken and Karwat, *Z. physik. Chem.*, 112, 467 (1924).

[2] Karwat, *ibid.*, 112, 486 (1924).

Pink hydrogen chloride was produced by each of the above methods, in one of which phosphorus pentoxide was carefully eliminated. Finally, a closed apparatus was constructed without stopcocks in which, after evacuation by a mercury diffusion pump and sealing off, sodium chloride and sulfuric acid could be mixed and the gas condensed in a bulb either after or before drying with phosphorus pentoxide. This also produced pink hydrogen chloride. One of the bulbs of this apparatus had purposely been made of thick glass with a thin spot on one side. It was found that in this case the material on the thin spot was pink while the remainder was white. This explains the effect produced by the presence of air, namely, that unless the inside wall of the vessel is kept practically at the temperature of liquid air the pink modification will not form. It was not possible to obtain the pink form in the calorimeter since the gas was necessarily liquefied first in the process of filling. There was a transition at 98.36°K. in the calorimeter but both forms are colorless, as could readily be observed by freezing the liquid and cooling the solid to about 83°K. in glass. It seems probable that the reddish pink material is an unstable crystalline form of hydrogen chloride. Since it was always mixed with some white material it may be presumed that the color of the pure unstable form would be considerably darker than the color observed. The existence of a third crystalline form is supported by the work of Simon and Simson,[3] who found by x-ray analysis that the form stable at the melting point had a face-centered cubic structure, while at the temperature of liquid air the observed twenty-eight characteristic distances prevented interpretation. In the above experiment the hydrogen chloride was examined on a metal plate on which it had been condensed *in vacuo* by liquid air. This may have resulted in the presence of two forms simultaneously. If such was the case an experiment in which a second exposure, made after the material has been allowed to warm somewhat above the temperature of liquid air and then been recooled, would result in the disappearance of approximately one-half of the characteristic distances. By difference this would enable the identification of both forms occurring in the mixture. It would also seem that the observed intensities might assist in the interpretation of the data as they are, unless chance provided two forms in nearly equal proportion. Simon and Simson did not include the data.

Pink hydrogen chloride has also been observed by Loeb[4] to whom we had suggested our technique of preparation.

Purity of Hydrogen Chloride.—As previously mentioned, hydrogen chloride prepared from sodium chloride and sulfuric acid and further dried with sulfuric acid and phosphorus pentoxide contained considerable

---

[3] Simon and Simson, *Z. Physik*, **21**, 168 (1924).

[4] Loeb, *Proc. Nat. Acad. Sci.*, **12**, 35 (1926).

impurity. It was noticed that the amount of impurity increased when the amount of phosphorus pentoxide used for drying was increased. After evaporation of the hydrogen chloride, there remained a white solid which melted near the ice point, and a test on a water solution of the material showed the presence of phosphate. It seems probable that the material was phosphorus oxychloride, $POCl_3$, which melts at 1.25° and may be prepared by the interaction of hot hydrogen chloride and phosphorus pentoxide.

The method finally adopted for drying made use of concentrated sulfuric acid followed by liquefaction in a bulb containing phosphorus pentoxide and maintained at a temperature of approximately 195°K. by solid carbon dioxide and ether for about a week. The liquid hydrogen chloride was intimately mixed with a large amont of phosphorus pentoxide. The liquid was then repeatedly fractionated, the middle fractions being retained.

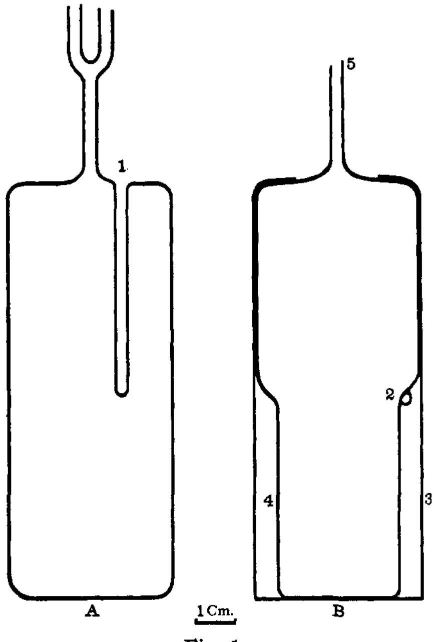


Fig. 1.

Apparatus for Vapor Pressures and for First Heats of Vaporization.—The apparatus used for temperature control was the same one used for calorimetric purposes by Gibson and Giauque,[5] except that the copper calorimeter was replaced by one of glass. Several glass containers were tried, none of which were very satisfactory since they often cracked when the hydrogen chloride was cooled to the temperature of liquid air. The first type tried is shown at A in Fig. 1. This type on two occasions broke at point 1 where the tube for holding the thermocouple was set into the container. Two glass tubes of about 2.5 mm. inside diameter are shown attached to container A. One of these was attached to a manometer while the other served as an inlet and outlet tube. When heat was introduced for the purpose of measuring the heat of vaporization it was found by means of the separate tube to the manometer that the pressure increase inside the calorimeter was less than 1 mm. of Hg and thereafter the second tube was discarded. The heater covered only the lower half of the glass vessel since it was desirable not to supply heat to the material which had been evaporated. For this reason only the material in the upper half of the calorimeter was used for heat of vaporization measurements.

The final glass calorimeter used is shown at B in Fig. 1. The thermocouple was placed in a long glass pocket shown at 2. The pocket was filled with paraffin to improve thermal contact. A copper sheath shown at 3 was shrunk on to the upper portion of B. This acted as a radiation shield for the number thirty constantan wire heater, shown at 4, returning radiated heat to the calorimeter. A thermocouple was also attached to

---

[5] Gibson and Giauque, This Journal, 45, 93 (1923).

the sheath. To assist heat conduction a heavy sheet of platinum was coiled and placed in the interior of the glass calorimeter. Platinum was used because the better conducting gold was not immediately available. The inlet tube was closely wound with a heater of number thirty constantan wire which could be used to avoid the presence of solid within the tube. The inlet tube was sealed to the protective copper cylinder by Rose metal at point 5, Fig. 1. The vapor pressures were measured by means of a manometer constructed of Pyrex glass tubing 2 cm. in diameter, and a Société Génévoise cathetometer accurate to a few hundredths of a millimeter and with a precision of 0.01 mm. A trap filled with thin gold foil protected the calorimeter against distillation of mercury from the manometer. The copper-constantan thermocouple used for the vapor pressure measurements was calibrated by means of the transition, melting and boiling point temperatures of hydrogen chloride. Our determination of these temperatures on the absolute scale will be described later in this paper.

Vapor Pressure Results.—The vapor pressures of solid hydrogen chloride are given in Table I. The pressures are expressed in international cm. of Hg. The calculated pressures given in the third column were obtained from the equation.

$$\log P(\text{cm. Hg}) = -\frac{1114}{T} - 1.285 \log T - 0.0009467T + 11.00500 \qquad (1)$$

The constants of equation (1) were chosen to fit the observed data.

TABLE I

VAPOR PRESSURES OF SOLID HYDROGEN CHLORIDE

T, °K.	$P_{\text{obs.}}$, international cm. of Hg	$P_{\text{calcd.}}$	$T_{\text{obs.}} - T_{\text{calcd.}}$
132.48	0.558	0.554	−0.05
132.82	.589	.580	− .12
135.20	.787	.797	+ .10
139.23	1.308	1.310	+ .01
143.00	2.044	2.041	− .01
145.77	2.782	2.783	.00
148.44	3.705	3.709	+ .01
154.29	6.692	6.710	+ .03
155.04	7.221	7.215	− .01
158.91	10.370 10.371	10.371	.00

The vapor pressure of solid hydrogen chloride has been measured by Henglein[6] who gives the equation

$$\log P_{(\text{mm. Hg})} = -\frac{1966.3}{T^{1.1600}} + 7.5030 \qquad (2)$$

and by Karwat[2] who gives an equation which is evidently in error since it does not reproduce his table of calculated data.

Henning and Stock[7] made one pressure measurement on the solid, namely, 7.56 cm. at 155.55°K. Equation (1), representing our data, gives 155.57°K. for the temperature corresponding to that pressure.

[6] Henglein, *Z. Physik*, **18**, 64 (1923).

[7] Henning and Stock, *Z. Physik*, **4**, 226 (1921).

Near the melting point Equation (1) gives values 0.16° lower than that of Henglein (2) and 0.44° lower than the calculated value of Karwat. In the region about 130°K. Equation (1) gives values 0.35° higher than that of Henglein (2) and 0.36° lower than the calculated value of Karwat. Henglein evidently failed to observe the melting point since he records a pressure of 12.22 cm. for the solid at 161.0°K.; whereas our measurements show a pressure of 10.371 cm. at the triple point, 158.91°K. In addition to our triple point pressure data recorded in Table I, two preliminary measurements, made about a year previous with a less precise cathetometer, had each given 10.370 ± 0.005 cm. Karwat's observed value was 10.344 cm. at 159.34°K.

The vapor pressure data on liquid hydrogen chloride are given in Table II. The calculated pressures given in the third column are obtained from the equation of Henning and Stock[7]

$$\log P_{(\text{mm. Hg})} = -\frac{905.53}{T} + 1.75 \log T - 0.005077T + 4.65739 \qquad (3)$$

The observed differences tabulated in Col. 4 show very close agreement of our data with those of Henning and Stock. Our temperatures may be in error by 0.05° in an absolute sense while having a higher relative accuracy.

The vapor pressure of liquid hydrogen chloride has also been measured by McIntosh and Steele.[8] However, their temperatures appear to be 0.3° too high near the melting point and about 2.0° too high at the boiling point.

TABLE II

VAPOR PRESSURES OF LIQUID HYDROGEN CHLORIDE

T, °K.	$P_{\text{obs.}}$, international cm. of Hg	$P_{\text{calcd.}}$	$T_{\text{obs.}} - T_{\text{calcd.}}$
158.91	10.371	10.357	−0.02
164.62	16.29	16.26	− .03
169.28	22.98	22.93	− .03
173.95	31.71	31.72	.00
178.53	42.81	42.83	+ .01
181.84	52.64	52.65	.00
185.17	64.34	64.29	− .01
188.41	77.48	77.47	.00
191.96	94.39	94.28	− .02
195.93	116.51	116.33	− .03

Calorimetric Apparatus.—The copper sheathed glass apparatus used for the vapor pressure measurements could have been used for heat capacity measurements. However, it was known from the experience of others in this Laboratory that glass calorimeters were unsatisfactory, principally because the poor thermal conductivity decreases the accuracy with which small temperature intervals can be measured. For this

[8] McIntosh and Steele, *Z. physik. Chem.*, **55**, 129 (1906).

reason no heat capacity measurements were made with the glass apparatus, although measurements of the heat of vaporization were made by a method which avoided the necessity of high precision in the measurement of temperature. This will be discussed later in this paper. The major purpose of the glass calorimeter had been for the acquisition of experience before proceeding to the construction of a more elaborate apparatus.

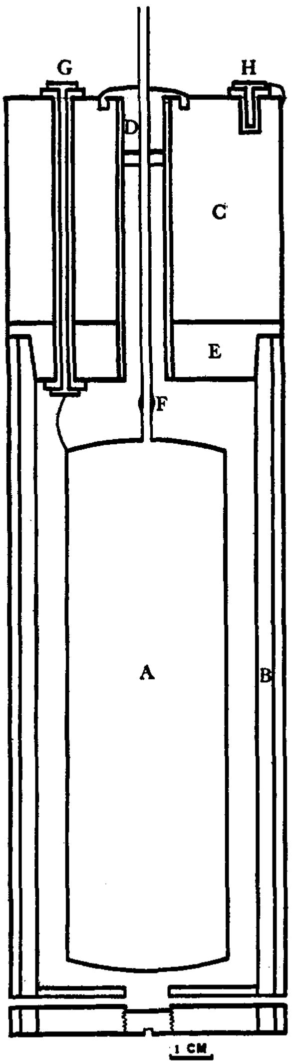


Fig. 2.

For purposes of identification we shall in future papers refer to the calorimeter described below as gold calorimeter II. This calorimeter is shown in Fig. 2. The cylindrical calorimeter A was made from gold sheet 0.75 mm. in thickness, with welded seams. The height was 12 cm. and the diameter 3.75 cm. Twelve radial vanes were placed inside to assist in attaining temperature equilibrium. The gases were introduced through a glass tube, of inside diameter about 2.5 mm., which was sealed to a short platinum tube, extending from the top of the calorimeter, by means of a lead and a cobalt-lead glass seal. The glass inlet tube was wound with a heater similar to that used in the glass calorimeter. A combined resistance thermometer-heater[9] was used for measuring temperature intervals and introducing energy. This was made of gold since it was to be wound on the gold calorimeter, thus minimizing strain due to temperature change. A gold thermometer had previously been used by Keesom and Onnes.[10] The gold from which the thermometer wire was made contained 0.175% of silver, which was desirable, since Onnes and Clay[11] have found that the presence of silver prevents the resistance from falling to small values at low temperatures. This was advantageous since the wire was also used for heating. The gold was drawn to a diameter of 0.025 cm. (B. and S. No. 30) through steel dies, being washed with nitric and sulfuric acids after every pull, as recommended by Onnes and Clay.[11] Diamond dies were then used to reduce the diameter to 0.008 cm. (B. and S. No. 40). The wire was annealed after the last pull and then doubly insulated with silk. The construction of the thermometer-heater was as follows. The sides of the gold calorimeter were coated with Bakelite lacquer and baked at 110° for thirty minutes. The wire was then wound on, impregnated with Bakelite lacquer and dried for one week. The exterior was then coated with gold leaf to minimize radiation. Following this the calorimeter was heated to 120° for a few minutes.

---

[9] Eucken, *Physik. Z.*, 10, 586 (1909).

[10] Keesom and Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 143 (1914).

[11] Onnes and Clay, *ibid.*, No. 99c (1907).

The thermometer-heater was divided into two approximately equal parts. The total was used in all measurements except for the determinations of the heat of vaporization, in which case the lower half was used for energy input. The total resistance at room temperature was about 350 ohms and decreased to about 81 ohms at 15° K. From the results of Onnes and Clay we had expected the resistance to be less than 30 ohms at 15° K. At each end and in the center of the thermometer a lead wire of size B. and S. No. 30 copper was attached and brought into good thermal contact with the calorimeter to prevent possible gold-copper thermo-electric effects. This wire was connected to the thermometer terminals by means of 2.5 cm. of B. and S. No. 40 copper wire. One of the thermometer terminals is shown at G, Fig. 2.

The calorimeter was suspended by means of the glass connecting tube which was fastened to the protective cylinder C by means of Rose metal, shown at D, Fig. 2. The Rose metal also greatly diminished heat leak along the glass tube from above.

The protective cylinder consisted of 1750 g. of lead located in the upper portion, while the exterior walls and the lower portion of the cylinder consisted of 1850 g. of copper. . The other details, such as the electrical connections and heaters for the protective cylinder, the vacuum-tight joint in the steel container for the apparatus, the high vacuum system, apparatus and methods for the electrical measurements necessary for the determination of energy and temperature were essentially the same as those described by Gibson and Giauque.[5]

The temperature of the protective cylinder and that of the steel container were obtained by means of thermocouples. The protective cylinder was suspended from the cover of the steel container by means of heavy string.

A hydrogen liquefier was located directly above the steel container. The interchanger was made from 160 meters of copper tubing of 0.2 cm. inside diameter and walls 0.05 cm. thick. The steel container and the interchanger were enclosed in a large Pyrex glass Dewar tube of about 11 cm. inside diameter and 74 cm. inside depth. The expansion valve of the liquefier could be controlled by a valve stem leading out of the apparatus. An insulated tube was included by which warm hydrogen could be blown on the valve in case of stoppage by solidified air which might accidentally get inside the hydrogen cycle. By this device the valve could be warmed sufficiently within a minute and without warming the interchanger to any great extent. Proper care in keeping the hydrogen pure made it unnecessary to make much use of the valve warmer, but it has proved valuable on several occasions. The large Dewar tube was enclosed in a vacuum-tight Monel Metal container which could be immersed in liquid air, although this was ordinarily unnecessary even when hydrogen was being liquefied. Directly above the cover of the Monel Metal container was a precooling coil consisting of about 15 meters of copper tubing similar to that in the interchanger. The precooling coil could be immersed in liquid air which, after evaporation, was utilized to surround the exterior of the whole apparatus with cold air, thus making unnecessary the immersion referred to above. In addition to the interchanger and precooler already referred to, there was a pre-interchanger to interchange heat between the temperature of liquid air and that of the room. This pre-interchanger consisted of 40 meters of copper tubing in each of four parallel tubes to eliminate a large pressure drop. The general plan of the liquefier and hydrogen cycle was similar to that described by Latimer, Buffington and Hoenshel.[12]

The hydrogen compressor delivered about 0.45 cubic meter (16 cubic feet) of hydrogen per minute at 160 atmospheres. A cast iron gas meter of large capacity in the hydrogen return line was very valuable for control purposes. A vacuum pump with a displacement of 4.25 cubic meters (150 cu. ft.) per minute was used to reduce

---

[12] Latimer, Buffington and Hoenshel, THIS JOURNAL, **47**, 1571 (1925).

the temperature of the liquid air or liquid hydrogen by evaporation at low pressures. This pump would reduce the pressure to 2.5 cm. of mercury.

Calibration of Resistance Thermometer.—The resistance thermometer was calibrated by means of standard copper-constantan thermocouple No. 18 which had been calibrated in terms of a hydrogen gas thermometer by Giauque, Buffington and Schulze[13] and a hydrogen vapor pressure thermometer by Giauque, Johnston and Kelley.[14] The thermocouple was used under as nearly as possible the same conditions as those existing in the original calibration. Since it was very important to carry out the calibration while the measurements were in progress, this was our invariable procedure. The high precision of the resistance thermometer enabled the measurement of small temperature intervals with an accuracy unattainable with the thermocouple alone. The absolute temperatures given are believed to be accurate to 0.05°. The resistance thermometer calibration data were treated by a graphical method which consisted of plotting deviations from a linear equation, except at the temperatures of liquid hydrogen where a large plot of resistance against temperature proved to be more convenient.

Measurement of Heat Capacities.—The method of calculating energy input, heat transfer from the surroundings and temperature rise was similar to that used by Gibson and Giauque.[5] However, we have investigated more thoroughly a small source of error in the measurement of an increment of temperature. The necessity for a correction to the temperature rise observed on the resistance thermometer arises in the following manner. Excepting the lowest temperatures of measurement, the protective cylinder was maintained at a temperature slightly above the final temperature attained in a heat capacity determination. This was in order to avoid distillation from the calorimeter into that portion of the inlet tube in thermal contact with the protective cylinder. Thus at all times the calorimeter was receiving a small amount of heat from its surroundings. It is obvious that any sort of thermometer located on the exterior of the calorimeter would record a temperature above that of the average temperature since the distribution of heat requires a thermal head. Favorable location of a thermometer in the interior of a calorimeter might reduce this effect, but would make it nearly impossible to apply a correction. The necessary data for making the correction were supplied by the measurements of current and voltage during energy input. From these data the resistance and therefore the temperature of the thermometer-heater wire at any time during energy input could be calculated. The average temperature of the calorimeter at the corresponding time was known. The rate of energy input being known, it was possible to

[13] Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927).

[14] Giauque, Johnston and Kelley, *ibid.*, 49, 2367 (1927).

determine the relation of thermal head to energy flow. This permitted the estimation of the thermal head due to an observed heat leak. In gold calorimeter II this correction was usually about one-tenth of one per cent. or less, and did not exceed three-tenths of one per cent. When this correction is not made the heat capacity results will be high. This is general for any temperature relation of calorimeter and its surroundings, provided the temperature of the surroundings is constant during a measurement. A calorimeter with poor heat conductivity will have a relatively large correction of this sort. This is particularly true when such a calorimeter is made of glass. The thermal head between the thermometer-heater wire and the average location of heat capacity in gold calorimeter II was ordinarily about one degree or less during energy input. This temporary rise in the external temperature of the calorimeter was considered in correcting for the heat received from the surroundings.

During the heat capacity measurements a small amount of material evaporated into the unfilled volume of the calorimeter and into the line. It was necessary to record the pressure at the beginning and end of each heat capacity determination in order to correct for the heat absorption accompanying this effect.

The density of solid hydrogen chloride has been determined by Simon and Simson,[3] while that of liquid hydrogen chloride has been determined by Baumé and Perrot.[15]

Heat Capacity Data.—The heat capacity data of hydrogen chloride are given in Table III. The first column contains the absolute temperature and the second column the heat capacity in calories per mole per degree.

TABLE III

HEAT CAPACITY OF HYDROGEN CHLORIDE

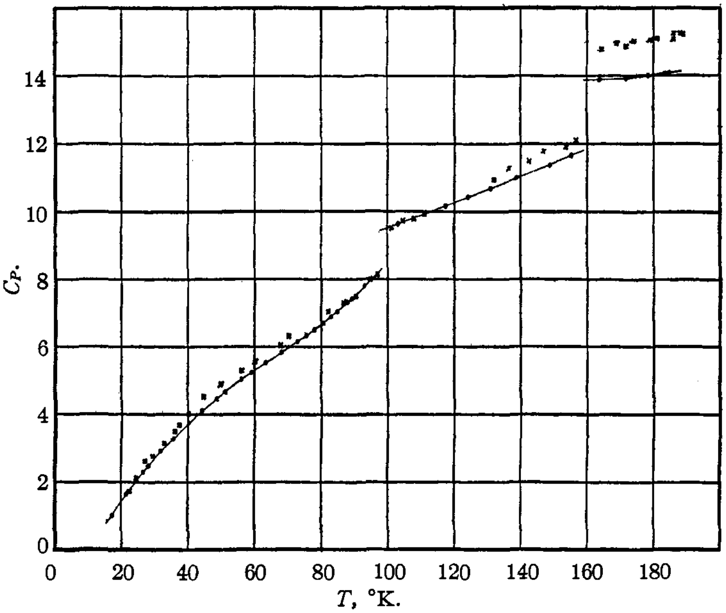
Molecular weight, 36.456

T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.
17.29	1.031	67.85	5.848	117.30	10.14
21.34	1.637	72.63	6.159	123.92	10.46
24.71	2.066	75.46	6.329	131.18	10.67
26.85	2.330	77.65	6.526	138.79	10.95
28.10	2.491	80.25	6.712	148.90	11.34
31.89	2.943	82.63	6.894	155.06	11.65
35.82	3.393	84.69	7.053	158.91	Melting point
39.95	3.794	87.70	7.327	163.72	13.89
44.20	4.132	88.79	7.410	171.45	13.95
48.62	4.472	92.83	7.786	171.74	13.95
51.23	4.677	92.96	7.849	178.64	14.01
56.01	5.070	98.36	Transition	185.20	14.07
58.94	5.231	103.01	9.64	188.07	Boiling point
63.31	5.550				

---

[15] Baumé and Perrot, *J. chim. phys.*, 12, 225 (1914).

The above results are shown graphically by means of the points with the connecting curve in Fig. 3. The results of Eucken and Karwat are plotted as crosses. The measurements are in agreement at the temperatures of liquid hydrogen and of liquid air, but at all other temperatures the values of Eucken and Karwat are higher. It is difficult to explain such large discrepancies as those indicated. It appears that the temperature scale of Eucken and Karwat was somewhat in error, since they record the transition temperature as 98.75°K. as compared with our 98.36 ± 0.05°K., while Karwat gives the melting point as 159.34°K. as compared with our 158.91 ± 0.05°K. However, since the results deviate in only one direction it is improbable that the difficulty can be primarily due to an inaccurate temperature scale. Even an approximate knowledge of the extremes of the temperature range investigated would mean that if some results were too high others would necessarily be made too low. It does not seem possible to attribute the unsystematic deviations to incorrect standards of e.m.f. or resistance necessary for the energy measurements. Our standards were either calibrated by the U. S. Bureau of Standards or compared with standards newly received from the Bureau both before and after the experiments. Our standard of time was obtained from the astronomical observatory of this University. We believe that the error in the results of Eucken and Karwat is due primarily to the



× Eucken and Karwat. ● Giauque and Wiebe.

Fig. 3.—Heat capacity in calories per mole of hydrogen chloride.

use of too small an amount of material, and secondarily due to the use of a poorly conducting glass calorimeter. The amount of hydrogen chloride used by Eucken and Karwat was about 0.17 mole, whereas 3.72 and 3.57 moles were used in our experiments.

Nearly all of our measurements fall within 0.1 or 0.2% of a smooth curve through the points. A few are off by about 0.5%. A smooth curve through the data should represent the heat capacity to an accuracy of about 0.2%, except in the case of the lowest measurement where, as the result of a poor vacuum and other experimental difficulties, the value may be in error by over 1%.

Transition Temperature and Melting Point Temperature.—Both the transition and the melting point temperatures were very sharp. Each was observed over a period of several days with occasional small input of energy and return of equilibrium. The temperature of the protective cylinder was maintained very closely at the same temperature as the calorimeter during these measurements. At the transition temperature the resistance thermometer showed an extreme variation of 0.02° over a period of seventy hours, while during the same time interval the thermocouple varied over a range of 0.05°. The transition temperature was 98.36 ± 0.05°K.

At the melting point an extreme variation of 0.01° was observed on the resistance thermometer over a period of seventy hours, while the thermocouple varied over a range of 0.06°. The melting point temperature was 158.91 ± 0.05°K.

Heats of Fusion and of Transition.—The heat of fusion and that of transition were measured in the usual way of starting the heat input at a temperature somewhat below the melting or transition temperature and ending the input when the temperature had risen somewhat above. A correction for the $\int C_p dT$ was applied. The results are given in Table

TABLE IV

HEAT OF TRANSITION OF HYDROGEN CHLORIDE

ΔH in Calories per Mole

Temp., °K.	G. and W.	Average	E. and K.	Average
98.36	284.2	284.3	290.0	293.8
	284.2		291.7	
	284.5		293.2	
			299.2	

HEAT OF FUSION OF HYDROGEN CHLORIDE

Temp., °K.	G. and W.	Average	E. and K.	Average
158.91	476.5	476.0	504.5	504.5
	475.6		506.5	
			505.5	
			504.5	
			502.5	

IV in the column headed G. and W. The results of Eucken and Karwat[1] are included for comparison.

Karwat[2] has calculated the heat of fusion from his measurements of the vapor pressure of solid hydrogen chloride combined with those of Henning and Stock on the liquid. He obtains the value 498.2 cal. per mole, in fair agreement with the calorimetric value of 504.5 obtained by Eucken and Karwat. A similar calculation based on our vapor pressure data leads to a value of 462 cal. per mole. However, we can expect no high accuracy from this calculation and we give it no weight as compared with our calorimetric value of 476.0. In the above calculation the equation of Berthelot was assumed in correcting for the imperfection in the gas state. The above correction lowered the value only by about three calories below the value which would have been obtained on the assumption of a perfect gas.

Measurement of the Heat of Vaporization.—The amount of material evaporated was obtained by absorption in a solution of 30% sodium hydroxide. The gas was bubbled through a small mercury trap in the bottom of the absorption bulb. The absorption solution was protected by two U-tubes, each containing on one side calcium chloride and on the other soda lime. One of the U-tubes was removable for weighing.

Two methods of measurement were employed. The first one designated as I in the tables was as follows. Two identical absorption bulbs were attached to a line leading from the calorimeter in such a way that a three-way stopcock controlled the flow of gas. The heating current was turned on and the stopcock opened into one of the absorption bulbs. After several minutes a steady state was reached and the stopcock was turned to direct the flow of gas into the other bulb. At the same time a calibrated stopwatch was started. The pressure remained constant to one millimeter. The second method, designated II in the tables, was as follows. With one absorption bulb on the line and the stopcock closed, the warming rate was observed as in a heat capacity determination. Then at a predetermined time the current was turned on, the stopwatch started, and shortly after this the stopcock was opened. At the end the current was turned off and after the flow of gas had practically ceased the stopcock was closed and the warming rate again taken. In both methods a correction for heat received from the surroundings during a run was made on the assumption of Newton's law of heat transfer and our knowledge of the temperature of the exterior of the calorimeter. In gold calorimeter II the external temperature was obtained as an average of the wall, by means of the thermometer-heater, of the bottom, by means of the attached thermocouple, and of the top, from the evaporation temperature as indicated by the pressure. The external temperature was about one degree above the evaporation temperature. The temperature of the protective cylinder and that of the steel container were kept above the evaporation temperature to prevent condensation. The container temperature was controlled by means of solid carbon dioxide condensed on its surface. The temperature of the solid carbon dioxide was controlled by reduced pressure. The hydrogen chloride was evaporated in amounts of from 10 to 15 g. for each determination. Only the liquid above the heater was used for this purpose. The determinations made with gold calorimeter II utilized the material on which the measurements of heat capacity had been made. The initial and final pressures were observed for each determination and a small correction was made for the amount of material in the line volume which was known by calibration. From the known density of liquid hydrogen chloride the correction for the volume of the liquid replaced by gas could be made. Method II involved a knowledge of the heat capacity of calorimeter and substance.

We feel more confidence in Method II, and the results obtained by this method show a smaller deviation from the mean than do those obtained by Method I. The results on the heat of vaporization at one atmosphere are given in Table V. The actual evaporation pressures were slightly above one atmosphere, but a small correction has been made to allow for this. Method I was used only with the glass calorimeter which was somewhat of a handicap, although the copper sheath and the coiled platinum sheet in the interior removed most of the disadvantages of the glass type of apparatus. The agreement, to one calorie, of the average values obtained from the two different methods and calorimeters must be regarded as fortuitous. In the measurements with the glass calorimeter the rate of evaporation was varied by a factor of more than three without producing any systematic deviation of the results. Also, the total amount of material within the calorimeter seemed to produce no appreciable effect. The slow evaporation rate of less than one-third mole per hour, which was used in the final measurements, eliminated the possibility of any appreciable loss due to spray. Observation on exposed glass bulbs of similar cross section, and a rate of evaporation many times that of any used, showed that evaporation proceeded without the formation of visible bubbles.

TABLE V

HEAT OF VAPORIZATION OF HYDROGEN CHLORIDE

Boiling point, 188.07° K. Molecular weight, 36.456

Moles of HCl evaporated	Type of run	Time of energy input in min.	ΔH at 760 mm. Hg in cal./mole	Remarks
0.3621	I	29	3858	
.4000	I	40	3852	Pyrex glass calorimeter
.2848	I	60	3871	
.2769	I	60	3871	
.2717	I	75	3857	
.2729	I	75	3854	
.3068	I	75	3851	
Mean			3859 ± 9	
0.3316	II	80	3859	
.3083	II	80	3866	Gold Calorimeter II
.3192	II	80	3851	
.4746	II	120	3861	
.4683	II	120	3862	
Mean			3860 ± 4	Best value

The heat of vaporization of hydrogen chloride has been determined directly or by calculation from vapor pressure measurements by a number of observers. While the accuracy of these various results is such that they can be given no weight, we include them as Table VI for the sake of completeness.

Table VI

Previously Published Values of Heat of Vaporization of Hydrogen Chloride

ΔH, cal./mole	Method	Observer
3540	Indirect	McIntosh and Steele[8] (1906)
3560	Direct	Elliott and McIntosh[16] (1908)
3601	Direct	Estreicher and Schnerr[17] (1910)
4040	Indirect	Henglein[6] (1923)

In the two indirect determinations given above the gas was assumed to be perfect. This assumption leads to serious error in such calculations. For example, if we make use of the algebraically convenient equation of state of Berthelot

$$PV = RT\left[1 + \frac{9PT_c}{128P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]$$

combined with the thermodynamic equation $\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V}$, the density of liquid hydrogen chloride as given by Baumé and Perrot,[15] namely 1.706–0.00276T, and the equation of Henning and Stock which is in agreement with our data for the vapor pressure of liquid hydrogen chloride, we obtain the value of 3881 cal. per mole. Considering the assumption, this value compares favorably with our direct determination of 3860. However, we hasten to add that this approximate agreement should be taken to indicate that Berthelot's equation happens to represent the deviation of hydrogen chloride from the gas law rather than as a confirmation of our value for the heat of vaporization. The similar use of van der Waals' equation leads to a more inaccurate value of 3932 cal./mole.

Eucken and Donath[18] have by an ingenious and apparently quite accurate method obtained heats of condensation to the solid form for a number of gases. They state that their data on hydrogen chloride are somewhat more inaccurate than those on other substances, due to a slight amount of reaction with the metal apparatus. They give the value 4594 ± 7 cal. per mole at 156°K. Using our various calorimetric data, and assuming that Berthelot's equation may be used with the thermodynamic equation,[19]

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

to give the deviation of the heat content of the gas from that of the ideal state, we obtain a value of 4580, which is in satisfactory agreement with

---

[16] Elliott and McIntosh, *J. Phys. Chem.*, 12, 163 (1908).

[17] Estreicher and Schnerr, *Bull. intern. acad. sci. Cracovie*, A, 345 (1910).

[18] Eucken and Donath, *Z. physik. Chem.*, 124, 181 (1926).

[19] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 163.

the value of Eucken and Donath when it is considered that our use of Berthelot's equation involved a correction amounting to 25 cal. per mole.

The Entropy of Hydrogen Chloride from the Third Law.—The entropy of hydrogen chloride was obtained in the usual manner by graphical integration of the equation $S = \int_0^T C_p \mathrm{d} \ln T$ plus the entropy changes accompanying each change of state. In extrapolating below the lowest temperature of measurement we have made use of the Debye function with an $h\gamma/k = 128$. In doing so it has been assumed that at the lower temperatures the absorption of energy is determined by but one characteristic frequency. This assumption is based on the fact that the low temperature data show a tendency to approach a value asymptotically of about six calories per degree per mole. This may be noted in Fig. 2. It is plausible that at low temperatures molecule units in the crystal may be vibrating in a manner similar to that of a monatomic solid. The data agree quite well with the Debye function up to a temperature of 40°K. While we recognize the arbitrariness of the above procedure, the absolute error should be small on a total extrapolated amount of 0.30 entropy units. A summary of the entropy calculation is given in Table VII.

TABLE VII

CALCULATION OF ENTROPY OF HYDROGEN CHLORIDE

Solid stable below 98.36°K.	Cal. per deg. per mole
0 to 16°K., extrapolation	0.30
16 to 98.36°K., graphical	7.06
Transition 284.3/98.36 =	2.89
Solid stable above 98.36°K.	...
98.36 to 158.91°K. graphical	5.05
Fusion 476.0/158.91 =	3.00
Liquid	...
158.91 to 188.07°K., graphical	2.36
Vaporization, 3860/188.07 =	20.52
Entropy of hydrogen chloride gas at boiling point =	41.2 ± 0.1 E. U.

Since we are about to compare the above value of the entropy with that obtained from theories assuming a perfect gas, it will be necessary to consider the effect due to the imperfection of hydrogen chloride gas. We have previously shown that Berthelot's equation of state gives the molal volume of hydrogen chloride gas with considerable accuracy. Since reliable data of state are lacking, we can do no better than to use Berthelot's equation in the calculation of this correction. Combining this with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ we obtain for the entropy change accompanying expansion from one atmosphere to zero pressure

$$\Delta S = -R\left[\int_{P=1}^{P=0} \mathrm{d} \ln P + \frac{27T_c^3}{32T^3P_c}\int_{P=1}^{P=0} \mathrm{d}P\right]$$

The entropy change accompanying compression from zero pressure to an ideal state of one atmosphere (fugacity = 1) is given by

$$\Delta S = -R \int_{P=0}^{P=1} \mathrm{d} \ln P$$

Combining, it is found that the entropy of a Berthelot gas is lower than that of ideal gas by an amount of $R27T_c^3P/32T^3P_c$. For hydrogen chloride at its boiling point this amounts to 0.10 cal./deg. per mole.

Theoretical Calculation of the Entropy of Hydrogen Chloride from Spectroscopic Data.—The entropy of a gas may be considered to consist of two parts, first, that resulting from the volume and the translational motion of the molecules and, second, that resulting from all the other degrees of freedom. It is best not to separate the treatment of these latter degrees of freedom, since the absorption of energy by one often has an appreciable effect on the others.

The first portion may be obtained from the Sackur equation[20] where

$$S = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V + S_0$$

S = entropy per mole, R = gas constant per mole, M = the molecular weight, V = the molal volume and S_0 = a constant. The form of this equation has been supported by considerable data. There are, however, two theoretical methods of evaluating S_0 which lead to nearly the same value and yet are apparently irreconcilable since each makes use of natural constants known to a considerable degree of accuracy. Neither is free from questionable assumption. The first method[20,21,22] makes use of quantum assumptions and statistical mechanics. The second method is used by Lewis[23] and is based on the theory of ultimate rational units proposed by Lewis and Adams.[24]

The expression for the constant as determined by Tetrode is

$$S_0 = R \ln \frac{(2\pi k)^{3/2}\, e^{1/2}}{h^3\, N^{5/2}} = -11.06$$

The expression obtained from U. R. U. is

$$S_0 = R \ln \frac{k^{3/2}\, C^3}{N^{5/2}(4\pi l)^6} = -11.38$$

where e is the base of natural logarithms, h is Planck's constant, c the velocity of light and l the elementary electronic charge.

The values adopted for all fundamental and derived constants used in this paper are those given in the International Critical Tables.[25]

---

[20] Sackur, *Ann. Physik*, **36**, 968 (1911).

[21] Tetrode, *ibid.*, **38**, 434 (1912).

[22] Ehrenfest and Trkal, *Proc. Akad. Sci. Amsterdam*, **23**, 162 (1920).

[23] Lewis, *Phys. Rev.*, [2] **18**, 121 (1921).

[24] Lewis and Adams, *ibid.*, [2] **3**, 92 (1914).

[25] International Critical Tables, Vol. I, p. 16.

The second portion of the entropy is obtained from the spectroscopically determined possible energy states combined with some assumption as to the distribution of the molecules between these various possible states. The first calculation of this kind utilizing the actual energy levels is due to Hicks and Mitchell.[26] Their calculation is based on a choice of *a priori* probabilities, 2, 4, 6, etc., which now appear to be incorrect. Also, they neglected to include the zero point entropy of R ln 2 which results from a weight of 2 for the initial state. Hicks and Mitchell unnecessarily used a laborious method in calculating the entropy. This was due to their failure to observe that theoretical equations of the type concerned can be integrated exactly even when the actual quantum states are used. Since they had calculated values of the heat capacity at various temperatures, they obtained that fraction of the entropy concerned by graphical integration of $S = \int_0^T C \, \mathrm{d} \ln T$. It will be shown in the following paragraphs that the calculation of entropy from spectroscopic data involves less expenditure of labor than is necessary to obtain the heat capacity at a single temperature and, moreover, involves the use of summations which are common to both calculations. The value of this observation will be more apparent to those who undertake the labor required for calculations of this type.

In addition to translational energy, hydrogen chloride has, at ordinary temperatures, nearly fully excited rotational energy and a small amount of vibration. The integration required in the calculation of the rotational entropy of a rigid molecule has been performed by Urey[27] graphically, and by Tolman and Badger,[28] who substituted the limitation of rigidity before carrying out the integration. Hicks and Mitchell have tabulated the total energy above the zero point state for a sufficient number of the rotation levels accompanying zero, one and two units of vibration. Following the usual nomenclature, we designate, by Em,n, the energy corresponding to the state having m and n as its rotational and vibrational quantum numbers, respectively. The rotational-vibrational heat capacity is then shown by Hicks and Mitchell to be

$$C_{R+V} = \frac{N}{kT^2}\left[\frac{\Sigma m \Sigma n \; pm,n \; E^2m,n \; e^{-\frac{Em,n}{kT}}}{\Sigma m \Sigma n \; pm,n \; e^{-\frac{Em,n}{kT}}} - \left(\frac{\Sigma m \Sigma n \; pm,n \; Em,n \; e^{-\frac{Em,n}{kT}}}{\Sigma m \Sigma n \; pm,n \; e^{-\frac{Em,n}{kT}}}\right)^2\right]$$

where pm,n is the *a priori* probability, k is Boltzmann's constant, and N is Avogadro's number. As is well known, an expression of this type may be written as

---

[26] Hicks and Mitchell, THIS JOURNAL, **48**, 1520 (1926).

[27] Urey, *ibid.*, **45**, 1445 (1923).

[28] Tolman and Badger, *ibid.*, 45, 2277 (1923).

$$C_{R+V} = \frac{R}{T^2}\,\frac{\mathrm{d}^2 \ln Q}{\mathrm{d}\left(\frac{1}{T}\right)^2}$$

where Q represents the distribution function $\Sigma m \Sigma n\ pm,n\ e^{-\frac{Em,n}{kT}}$; for example, see Reiche.[29] Then using the same integral as that used by Tolman and Badger

$$S_{R+V} = \int_0^T \frac{R}{T^2}\,\frac{\mathrm{d}^2 \ln Q}{\mathrm{d}\left(\frac{1}{T}\right)^2}\,\mathrm{d}\ln T$$

$$= R\left[\ln Q - \frac{1}{T}\,\frac{\mathrm{d}\ln Q}{\mathrm{d}\left(\frac{1}{T}\right)}\right]_0^T$$

$$= R\left[\ln \Sigma m \Sigma n\ pm,n\ e^{-\frac{Em,n}{kT}} + \frac{1}{kT}\cdot\frac{\Sigma m \Sigma n\ pm,n\ Em,n\ e^{-\frac{Em,n}{kT}}}{\Sigma m \Sigma n\ pm,n\ e^{-\frac{Em,n}{kT}}}\right]_0^T$$

It may be observed that the only assumption concerning *pm,n* and *Em,n* is that they are independent of temperature. The above method also holds if an electronic transition is included in the energy absorption. In summing the above series we have used the *a priori* probabilities 1, 3, 5, 7, etc., corresponding to the respective quantum states $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$, etc. Each vibrational state has been given unit weight; thus *pm,n* is essentially *pm*. The use of $pm = 2m$ is supported by the intensity measurements of Bourgin[30] on the absorption spectrum of hydrogen chloride. He shows that his data correspond with the above weights in agreement with the requirements of the wave mechanics theory of Schrödinger.

Kemble[31] has carried out a re-analysis of the data of Colby, Meyer and Bronk[32] on the infra-red absorption bands of hydrogen chloride. He presents the results in the form of equations with estimates of the probable error of the coefficients. From these equations, which apply to the lighter isotope, may be obtained the energies of the various states with which we are concerned. We have used these more accurate values in preference to the data as tabulated by Hicks and Mitchell. It is particularly important to have accurate values for the energies of the first few states.

A consideration of the isotope effect on the rotational-vibrational entropy shows that the use of the data for the lighter isotope leads to a value which is low by only 0.0016 cal./deg. per mole.

With the above data and method we have calculated the value of the entropy of ideal hydrogen chloride at the temperature of its boiling point,

---

[29] Reiche, *Ann. Physik.* **58**, 657 (1919).

[30] Bourgin, *Phys. Rev.*, **29**, 794 (1927).

[31] Kemble, *J. Optical Soc. Am.*, **12**, 1 (1926).

[32] Colby, Meyer and Bronk, *Astrophys. J.*, **57**, 7 (1923).

188.07°K. The value obtained is 41.45 or 41.13 cal./deg. per mole corresponding, respectively, to the use of the Tetrode or Lewis constant for the Sackur equation. A similar calculation has been made for a temperature of 298.1°K. (25°C.). These results are compared with the experimental values in Table VIII. We believe that our experimental value for the actual gas at 188.07°K. is accurate to about 0.1 cal./deg. per mole. This is based on the assumption of no appreciable error in the 0.3 entropy units extrapolated. We hesitate to estimate the accuracy with which Berthelot's equation gives the correction from the actual to the ideal state Fortunately this correction is small. The necessity for this correction may be eliminated by obtaining the entropy of the gas through use of the vapor pressure and entropy of the solid. At these lower pressures the error introduced by the use of such an equation as that of Berthelot is negligible. Such a calculation, making use of vapor pressure equation (1) at the melting point temperature, 158.91°K., leads to a value of 41.2 E. U. for the entropy of ideal hydrogen chloride at 188.07°K. A similar calculation starting at 132°K. leads to a value of 41.3 E. U.

While this method eliminates an uncertain correction, we believe our first method to be more reliable. Fortunately both methods lead to the same value. The "experimental" value given for 298.1°K. was obtained by adding the theoretical difference between 188.07°K. and 298.1°K. to the 41.3 cal./deg. per mole obtained at 188.07°K.

TABLE VIII

COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES OF THE ENTROPY OF HYDROGEN CHLORIDE

	Theoretical		Experimental	
T, °K.	Tetrode constant	Lewis constant	Actual gas	Corrected to ideal state
188.07	41.45	41.13	41.2 ± 0.1	41.3
298.1	44.64	44.32	......	44.5

Eucken, Karwat and Fried[33] have summarized the available data on condensed gases in terms of chemical constants. They have been recalculated in the form of absolute entropies in a chapter added, by the translator, to the German edition of "Thermodynamics" by Lewis and Randall.[34]

The value given for the work of Eucken and Karwat[1] on hydrogen chloride is 45.4 E. U. at 298.1°K., for which these authors had expressed an accuracy of ±0.2 E. U., which definitely placed it in disagreement with the theoretical values.

The close agreement of our experimental and theoretical values is very good evidence, not only for the validity of the theoretical considera-

---

[33] Eucken, Karwat and Fried, *Z. Physik*, 29, 1 (1924).

[34] "Thermodynamik und die freie Energie chemischer Substanzen," von Lewis und Randall, übersetzt von Redlich, Julius Springer, Wien, 1927.

tions as closely approximating the actual properties of the substance, but also for the third law of thermodynamics.

Tests of the Third Law.—We shall test the third law, first by means of the reactions

$$\begin{array}{llll}
\text{(a)} & \tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl\,(aq); & \Delta F^\circ_{298} = & -31{,}375 \\
\text{(b)} & HCl\,(aq) = HCl\,(g); & \Delta F^\circ_{298} = & 8{,}604 \\
\hline
\text{(c)} & \tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl\,(g); & \Delta F^\circ_{298} = & -22{,}771^{35}
\end{array}$$

The free energy change of (b) is taken from the manuscript soon to be published by Randall and Young, who have reconsidered the available data, while that of (a) is taken from Lewis and Randall[36] and corrected by use of the data given by Randall and Young. The heat of reaction, ΔH, for (c) is given as 22,000 cal. by both Thomsen and Berthelot. From the relation $\Delta F = \Delta H - T\Delta S$ we find $\Delta S_{298} = 2.6$ E. U. for reaction (c). The entropy of one-half a mole of chlorine gas as given by Gerke[37] is $\tfrac{1}{2}S_{Cl_2} = 27.1$ E. U. Bakhuyzen[38] gives a value for $\tfrac{1}{2}S_{H_2}$ at low temperatures which leads to 14.8 E. U. at 298°K. From these data $S_{HCl} = 44.5$ in exact agreement with our experimental value. Such close agreement is undoubtedly fortuitous. The principal uncertainty lies in the ΔH value given by Thomsen and by Berthelot, while the other data used may be in error by an amount corresponding to several tenths of an entropy unit.

The second test makes use of the reactions

$$\begin{array}{llll}
\text{(d)} & \tfrac{1}{2}H_2 + HgCl = Hg + HCl\,(0.1\,M); & \Delta F = & -\ 9{,}175 \\
\text{(e)} & HCl\,(0.1\,M) = HCl\,(g); & \Delta F = & 11{,}604 \\
\hline
\text{(f)} & \tfrac{1}{2}H_2 + HgCl = Hg + HCl(g): & \Delta F = & 2{,}429
\end{array}$$

The free energy changes of (d) and (e) are both given by Randall and Young. Their new measurements on the mercury-calomel electrode show that the older determinations are in error due to the effect of dissolved oxygen. The ΔH for (d) is given as —8291 by Lewis[39] who measured temperature coefficients of a cell utilizing this reaction. We have calculated the heat of reaction (e) from the measurements of Wrewsky and Sawaritzky[40] and find the value 17,660 cal. for $H_{HCl\,(g)} - \overline{H}_{HCl\,(0.1\,M)}$ where $\overline{H}$ refers to the partial molal heat content of hydrogen chloride in solution. Lewis and Gibson[41] give the entropy of liquid mercury $S_{Hg} = 17.8$ E.U., and that of calomel $S_{HgCl} = 23.2$. Thus we find $S_{HCl} = 43.5$ as against our measured value of 44.5. The difference is well within the limits

---

[35] The data used for the two tests of the third law have not been corrected by use of the I. C. T. constants since the difference is not important in this case.

[36] Lewis and Randall, ref. 19, p. 502.

[37] Gerke, THIS JOURNAL, **44**, 1684 (1922).

[38] Bakhuyzen, *Z. physik. Chem.*, **111**, 57 (1924).

[39] Ref. 19, p. 392.

[40] Wrewsky and Sawaritzky, *Z. physik. Chem.*, **112**, 90 (1924).

[41] Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

of accuracy of the various data, the greatest uncertainty being in the heat of solution of hydrogen chloride. The older value of 17,300 found by Thomsen for this reaction would more than double the discrepancy. This again emphasizes the observation of Lewis, Gibson and Latimer[42] that as more accurate data are obtained the discrepancies from the third law are reduced.

We express our appreciation to J. A. Roebling Sons Co. for insulating the delicate gold wire, to W. J. Cummings for the glass blowing, particularly of the metal-glass seal which so successfully withstood temperature changes, and to G. F. Nelson, who was responsible for the mechanical construction of the apparatus. This assistance contributed in no small measure to the success of our experiments.

Summary

The heat capacity of the two solid forms and of liquid hydrogen chloride has been measured from 16°K. to its boiling point.

The transition temperature is 98.36 ± 0.05°K., the melting point 158.91 ± 0.05°K. and the boiling point 188.07 ± 0.05°K.

Calorimetric determinations of the heats of transition, fusion and vaporization have been made.

The vapor pressures of both solid and liquid have been measured.

What is believed to be a third crystalline form of hydrogen chloride, with a reddish pink color, has been observed.

The entropy of hydrogen chloride gas has been calculated from the calorimetric data. It has also been calculated from spectroscopic data and the Sackur equation.

The procedure for the calculation of entropy from the energy levels of a molecule as given by band spectra is discussed.

The calculated and theoretical values agree well, thus supporting not only the theoretical method but also the third law of thermodynamics.

The third law has been tested by means of two series of reactions and is further confirmed within the limits of accuracy of the data.

BERKELEY, CALIFORNIA

---

[42] Lewis, Gibson and Latimer, THIS JOURNAL, **44**, 1008 (1922).