far as they could be without showing deviations of more than the experimental error from a linear course.

The method of calculating the initial velocity of hydrolysis consists in dividing the change in rotation for each sample of the hydrolyzing sucrose solution taken by the time in minutes after the start at which that sample was taken. The change in rotation for a given sample is the difference between the initial rotation of the hydrolyzing solution and the rotation of that sample after the addition of 5 cc. of sodium carbonate solution. This ratio was calculated for each sample and the mean taken as the velocity for that particular sucrose solution. This procedure made it quite essential to determine the initial rotation very accurately and this was found to be rather difficult in the more concentrated solutions where slight errors in weighing out samples (weighed to the nearest drop) were liable to make a considerable error in the observed rotation. So in addition to synthetic initials, made by mixing 3.125 cc. of invertase solution with 5.625 cc. of the carbonate solution and then adding 25.00 cc. of the original 250 cc. of sucrose solution made up for the hydrolysis, a sample was taken within three to six minutes after the start of the reaction and its rotation used as a basis for extrapolating back to find the rotation at zero time. The mean of these two, the synthetic and the extrapolated initials, was used as the true initial rotation.

Summary

The above study shows that the concentration of water is a factor in determining the magnitude of the velocity of hydrolysis of sucrose by invertase.

NEW YORK CITY

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

THE HEAT CAPACITY OF HYDROGEN BROMIDE FROM 15°K. TO ITS BOILING POINT AND ITS HEAT OF VAPORIZATION. THE ENTROPY FROM SPECTROSCOPIC DATA

BY W. F. GIAUQUE AND R. WIEBE

RECEIVED JUNE 18, 1928 PUBLISHED AUGUST 4, 1928

In a recent paper[1] we have shown that the entropy of hydrogen chloride as calculated with the assistance of spectroscopic data is in agreement with the value as obtained from measurements of heat capacity and the third law of thermodynamics. Here we shall present similar calorimetric data on hydrogen bromide and show, in this case, also, agreement between the two methods of obtaining the entropy.

Preparation of Hydrogen Bromide.—Hydrogen bromide was prepared directly from the elements. The hydrogen was prepared by electrolysis and the oxygen present

---

[1] Giauque and Wiebe, THIS JOURNAL, 50, 101 (1928).

by diffusion was reduced to 0.01% by means of a nickel catalyst. Analysis of the bromine used showed no trace of chlorine or of iodine.

Dry hydrogen was bubbled through liquid bromine and the resulting mixture passed over a platinum spiral supported on a quartz rod and electrically heated to about 600–700°. The reaction tube was immersed in water which boiled during the procedure. To prevent excessive lowering of the vapor pressure of the liquid bromine due to cooling by evaporation, it was found desirable to immerse the mixing flask in warm water. The hydrogen bromide and unreacted bromine were condensed in a trap by means of liquid air. When enough material, approximately ten moles, had been prepared, the collection line was evacuated and most of the bromine separated by a rough distillation. The remaining bromine was easily removed by means of mercury, which had previously been condensed on the walls of a bulb. A small amount of mercury in the bottom of a bulb had previously proved to be rather slow in its action. The hydrogen bromide was then distilled into a bulb containing an amount of phosphorus pentoxide sufficiently large to bring it into intimate contact with all of the liquid. The material was dried for about one week, the liquid state being retained by means of a bath made from solid carbon dioxide and ether. Following this the material was distilled several times, the middle fractions being retained.

Heat Capacity Measurements and the Data.—The heat capacity determinations were made in gold calorimeter II. This calorimeter has been described in our previous paper[1] which also includes a description of the experimental method; 3.05 moles of hydrogen bromide were used for the measurements. The data are given in Table I. The first column gives the run number, which is included because the chronological order of the measurements is of interest in connection with the transition phenomena.

TABLE I

HEAT CAPACITY OF HYDROGEN BROMIDE

Molecular weight, 80.924

Run no.	T, °K.	ΔT	C_p/mole in cal./deg.	Run no.	T, °K.	ΔT	C_p/mole in cal./deg.
20	15.72	2.097	1.831	15	95.12	4.214	9.90
21	17.81	1.692	2.160	16	98.71	4.024	10.21
22	19.75	2.039	2.615	17	103.09	4.497	10.79
23	22.32	3.002	3.010	18	107.44	4.155	11.52
24	25.49	3.641	3.459	45	109.30	3.239	11.86
25	30.16	4.704	3.955	19	111.47	3.806	12.58
26	34.58	3.922	4.415	53	113.31	.124	135
27	39.15	4.836	4.827	54	113.37	.021	1290
28	43.75	4.266	5.160	55	114.13	1.365	19.32
29	48.32	4.578	5.453	56	115.76	1.835	13.06
30	52.93	4.595	5.832	57	116.76	.132	239
31	57.80	4.978	6.171	58	116.86	.044	860
32	62.23	3.768	6.559	59	117.09	.394	74.1
1	65.67	4.718	6.877	46	118.99	3.344	10.79
4	68.96	4.367	7.291	60	120.76	4.643	10.80
2	70.68	5.086	7.460	47	122.71	3.966	10.86
5	73.63	4.683	7.951	61	125.48	4.488	10.93
3	75.60	4.473	8.323	48	127.31	4.555	10.99
6	80.03	3.882	9.368	62	130.06	4.383	10.96

Table I (*Concluded*)

Run no.	T, °K.	ΔT	C_p/mole in cal./deg.	Run no.	T, °K.	ΔT	C_p/mole in cal./deg.
7	83.49	2.807	10.86	49	132.41	5.267	10.98
9	84.62	3.319	11.50	63	135.89	4.986	11.03
8	86.15	2.359	13.10	50	139.02	7.490	11.08
10	86.79	.907	13.55	64	140.25	4.807	11.10
33	87.20	.830	14.51	65	145.61	5.437	11.19
11	87.69	.814	15.20	70	153.45	4.400	11.25
34	88.00	.741	16.36	71	158.03	4.252	11.40
35	88.68	.612	20.62	72	162.72	4.770	11.61
12	88.74	1.158	21.44	73	167.67	4.660	11.69
36	89.23	.446	29.08	74	172.86	4.466	11.91
38	89.39	.122	114	75	177.52	4.396	12.07
13	89.45	.241	190	76	182.09	4.259	12.32
37	89.49	.060	268		186.24	Melting point	
39	89.50	.029	483	66	189.93	5.330	14.20
40	89.53	.032	437	51	190.94	4.366	14.25
41	89.59	.075	187	67	195.08	4.182	14.21
42	90.01	.702	17.02	52	195.59	4.206	14.33
43	90.91	1.091	9.87	68	199.67	4.073	14.26
14	91.23	3.306	14.09	69	205.11	4.035	14.31
44	92.01	1.076	9.87		206.38	Boiling point	

The data are also shown graphically in Fig. 1. The heat capacity of hydrogen bromide has previously been measured by Eucken and Karwat[2] and their data have been included in Fig. 1 for comparison. The disagreement between the two pieces of work is large and is very similar to the disagreement previously observed in the case of hydrogen chloride.[1]

Excepting certain measurements in the transition ranges which will be referred to later, most of our data are accurate to two or three tenths of one per cent. Runs 70, 71 and 72 may be somewhat in error due to heat effects associated with accidental distillation effects in the connecting tube of the calorimeter. Runs 66, 67, 68 and 69 on the liquid were made under poor conditions of vacuum around the calorimeter. This resulted from the presence of a small variable pressure of water vapor which reduced the accuracy of the heat interchange corrections. Below 20°K. the measurements may be in error by one per cent. This is largely due to the rapid decrease of the dR/dT of the gold thermometer in this region.

The Transitions of Hydrogen Bromide.—The three high maxima indicate gradual transitions of the type observed by Simon[3] in the case of ammonium chloride. The measurements of heat capacity within the transition range were of two types. Some were designed to have as high an accuracy as possible for use in obtaining the entropy of the substance. Others, made in order to obtain information about the character of the transitions, had a small temperature rise and were thus necessarily less

---

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

[3] Simon, *Ann. Physik.*, **68**, 241 (1922).

accurate. The question of thermal equilibrium during measurement of such a transition naturally arises and we may say that while the process is one in which the measurements indicate that equilibrium is attained with difficulty, the evidence is against lack of equilibrium as a primary factor in preventing sharpness. For example, suppose that the transition is one that would occur sharply only if sufficient time were allowed. On cooling, a portion of the form stable at the higher temperature might fail to undergo the transition. When a sufficiently low temperature had been reached, the rate of approach to true equilibrium might easily become negligible. However, on heating to temperatures near to but below that of the true transition, it would be expected that a change

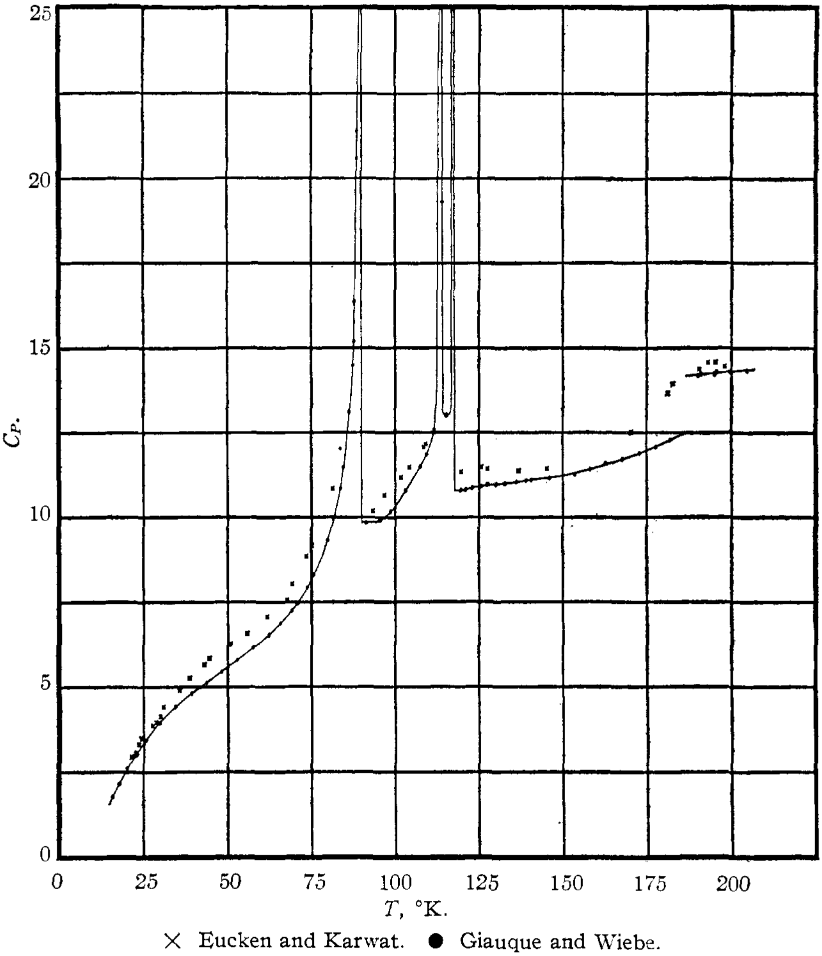

Fig. 1.—Heat capacity in calories per mole of hydrogen bromide.

toward equilibrium would proceed with the evolution of heat, but this was not observed. It would be rather surprising if equilibrium could not be attained with sufficient rapidity to show a heat effect at temperatures within a degree or two of what might be called the transition temperature.

The two maxima near 115°K. were first noted by observing the rate of change of current with time while energy was being introduced. This was possible since the gold thermometer-heater used for introducing the energy increased in resistance as the temperature rose. The rate of change dropped to a small value at the first maximum, then increased and having maintained the increased rate for some time, it again decreased at the second maximum. These effects might result from unusual changes in thermal conductivity but the heat capacity measurements in this region eliminate that possibility. Measurements 55 and 56 between the two maxima cover a range of over three degrees of low heat capacity. It is probable that the molal heat capacity is lower than 13 cal. per degree, since the temperature rise in these two measurements was too large to give true differential values in this region.

It is difficult to decide whether the curve should be discontinuous on the high temperature side of the transitions. Measurements 55 and 59 supply little evidence on this question in the case of the two close maxima. However, measurements 41, 42 and 14 indicate a continuous drop in the case of the lower transition.

It may be noted from the run order during the transitions, particularly the lower transition, that the values fall on a smooth curve even when the measurements are taken in somewhat erratic order.

It seems plausible that such transitions may be due to internal changes in the molecular structure, as has been suggested by Simon and Simson,[4] who found, by x-ray analysis, that the similar behavior of ammonium chloride was not accompanied by a change in crystal form. Simon, Simson and Ruhemann[5] have found similar maxima in the heat capacities of the other ammonium halides.

Heats of Fusion and Transition.—The heat of fusion was found to be 575.1 cal. per mole. Eucken and Karwat[2] obtained 616 and 623. The discrepancy is about the same as was found in the case of hydrogen chloride.

It is not possible to obtain heats of transition in the ordinary sense. The amounts of energy added over the various regions of principal heat absorption are tabulated in Table II.

Purity of the Hydrogen Bromide.—The previously described method of preparation of the hydrogen bromide left very little possibility of appreciable impurity. It is, however, worth noting that the absence of pre-melting effect in the heat capacity measurements below the melting

---

[4] Simon and Simson, *Naturwissenschaften*, **38**, 880 (1926).

[5] Simon, Simson and Ruhemann, *Z. physik. Chem.*, **129**, 339 (1927).

TABLE II

HEAT ABSORBED IN TRANSITION REGIONS OF HYDROGEN BROMIDE

Temp. intervals, °A.	Heat absorbed, cal./mole
87.37–92.19	124.7
87.39–93.21	133.5
110.97–120.38	256.3
112.35–117.25	204.3
112.39–114.86	93.3
115.04–118.31	122.1

point is the best evidence for the absence of an impurity which could affect the various measurements. This observation is especially important in that it eliminates the effect of impurity as an appreciable factor in the gradual transitions.

Melting and Boiling Point Temperatures.—The melting point was determined by introducing energy at intervals and waiting for equilibrium. Sufficient energy to melt about one-fourth of the substance at a time was added until fusion was complete. The material was then resolidified and the procedure repeated a week later. The first series covered a period of thirty hours, the second series twenty-four hours. The deviation between extremes was 0.06° on both the thermocouple and on the resistance thermometer. The average deviation from the mean was 0.02° on each. The melting point temperature was found to be 186.24 ± 0.05°K.

The measurements of pressure made in connection with the determination of the heat of vaporization gave the temperature of the boiling point as 206.38 ± 0.05°K.

A summary of the melting and boiling point temperatures obtained by various observers has been collected in Table III.

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF HYDROGEN BROMIDE

Melting point, °K.	Boiling point, °K.	Observer
186	......	(1845) Faraday[6]
184.6	208.2 (738.2 mm.)	(1896) Estreicher[7]
186.9	205.0 (755.4 mm.)	(1900) Ladenburg and Krügel[8]
187	204.4	(1906) McIntosh and Steele[9]
...	203.0	(1910) Estreicher and Schnerr[10]
185.1	206.0	(1923) Henglein and Roth[11]
186.24 ± 0.05	206.38 ± 0.05	Giauque and Wiebe

Heat of Vaporization.—The heat of vaporization was determined by both Methods I and II as described for the hydrogen chloride measure-

---

[6] Faraday, *Phil. Trans.*, **135,** 161 (1845).

[7] Estreicher, *Z. physik. Chem.*, **20,** 605 (1896).

[8] Ladenburg and Krügel, *Ber.*, **33,** 637 (1900).

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

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

[11] Henglein and Roth, *Z. Physik,* **18,** 64 (1923).

ments.[1] In Method I, the evolution of hydrogen bromide from the calorimeter and energy input were measured simultaneously. In Method II, the total amount of material evaporated by the introduction of a definite amount of energy was measured. Most of the measurements were made in gold calorimeter I, which has not previously been described. It was practically identical with gold calorimeter II, except for a 0.5 mm. wall thickness. It was equipped with two thermocouples, one on the bottom and one in the middle of the side. A constantan heater wound on the lower half was used instead of the gold thermometer-heater later placed on gold calorimeter II. The data are given in Table IV.

TABLE IV

HEAT OF VAPORIZATION OF HYDROGEN BROMIDE

Boiling point, 206.38°K. Molecular weight, 80.924

HBr evap., moles	Type of run	Time of energy input, min.	ΔH at 760 mm. of Hg, cal./mole
Gold Calorimeter II			
0.3218	I	75	4214
.3143	II	75	4206
.3125	II	75	4216
.3087	II	75	4208
Mean			4211 ± 4
Gold Calorimeter I			
.2987	I	75	4212
.2983	I	75	4218
.2980	I	75	4205
0.2977	I	75	4208
.2902	I	75	4211
.2895	I	75	4207
.2697	I	75	4207
.2806	I	120	4206
.2804	I	120	4206
.2810	I	120	4208
Mean			4209 ± 3
Value selected			4210 ± 4

The values of the heat of vaporization obtained by various observers are given in Table V.

TABLE V

HEAT OF VAPORIZATION OF HYDROGEN BROMIDE

Heat of vaporization, cal./mole	Method	Observer
4160	Vapor pressure	(1906) McIntosh and Steele)[9]
4130	Direct	(1908) Elliott and McIntosh[12]
3939	Direct	(1910) Estreicher and Schnerr[10]
3953	Vapor pressure	Estreicher and Schnerr
4405	Vapor pressure	(1923) Henglein and Roth[11]
4210 ± 4	Direct	Giauque and Wiebe

The value given by McIntosh and Steele is not corrected for gas imperfection. The vapor pressure value given by Estreicher and Schnerr is calculated from the data of McIntosh and Steele and includes a correction for gas imperfection. The value given by Henglein and Roth is uncorrected and would fall near our value if a reasonable correction were applied. The corresponding difference was 180 calories in the case of hydrogen chloride.

---

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

The Entropy of Hydrogen Bromide from the Third Law.—The entropy was calculated graphically by plotting heat capacity against the logarithm of temperature. The graphical method presented some difficulty in the transition ranges so the following procedure was used. The graph included all heat capacity up to sixteen calories per degree per mole. From the total heat input over the transition range and a plot of heat capacity against temperature, the energy represented by the area under each maximum and above 16 cal. per degree was calculated. The value of 16 cal. per degree was selected only for convenience. Since this energy was added over a narrow temperature range in each case, single temperatures could be chosen as divisors in order to obtain the respective entropy changes. The temperatures were chosen as a center of gravity on a $(C_p - 16)$ against T plot.

The temperatures and heats obtained are given in Table V. They are, of course, not to be taken as temperatures or heats of transition.

The extrapolation below 14.5°K. was carried out by means of the Debye function with an $h\gamma/k = 92$. The consideration of Einstein functions in addition seemed to offer little further advantage. The low temperature heat capacity measurements show a definite tendency to approach six calories per degree per mole as was the case with hydrogen chloride. This indicates that the molecules, having lost some of their degrees of freedom, are acting with sufficient approximation in the manner of a monatomic solid. Thus no great error would be expected in the extrapolated amount of one half entropy unit per mole.

The detail of the entropy calculation is given in Table VI.

Table VI

Calculation of Molal Entropy of Hydrogen Bromide Gas

0–14.5 °K., extrapolation	0.546	14.5–186.24 °K., graphical	17.27
Transition 63.4/89.2	.711	Fusion 575.1/186.24	3.097
Transition 78.8/113.4	.695	Liquid	....
Transition 85.7/116.8	.734	186.24–206.38 °K., graphical	1.464
"Transitions" are $\int(C_p-16)dT$	...	Vaporization 4210/206.38	20.40
		Entropy at the boiling point	44.9 ± 0.1 E.U.

The critical pressure of hydrogen bromide has not been measured, which makes it difficult to determine the decrease in entropy due to the imperfection of the actual gas at its boiling point. However, the amount must be nearly the same as that for hydrogen chloride, which was estimated as 0.1 cal./deg. per mole. This value is very uncertain.

The Entropy of Hydrogen Bromide from Spectroscopic Data.—The entropy of hydrogen bromide may be calculated by combining the Sackur equation with the equation.

$$S_{R+V} = R\left[\ln \Sigma_m\Sigma_n p_{m,n}\, e^{-\frac{E_{m,n}}{kT}} + \frac{1}{kT}\,\frac{\Sigma_m\Sigma_n p_{m,n}\, E_{m,n}\, e^{-\frac{E_{m,n}}{kT}}}{\Sigma_m\Sigma_n p_{m,n}\, e^{-\frac{E_{m,n}}{kT}}}\right]_0^T$$

where S_{R+V} is the contribution made to the entropy by the rotation and vibration of the molecules. $E_{m,n}$ is the energy of the state having m and n as its rotation and vibration quantum numbers, respectively. While $p_{m,n}$ is the corresponding *a priori* probability of the state, $p_{m,n}$ was taken equal to $2m$. A full discussion of the above calculation may be found in connection with the similar calculation for hydrogen chloride.[1]

The values for the various energy levels of the hydrogen bromide molecule were obtained from the work of Czerny[13] on the pure rotation band of this substance and from the earlier work of Kratzer[14] on the first rotation-vibration band.

The value obtained for the entropy of the ideal gas at the temperature of the boiling point is 44.92 or 44.60 cal./deg. per mole, corresponding, respectively, to the use of the Tetrode or Lewis constant for the Sackur equation. The entropy has also been calculated for a temperature of 298.1°K. (25°C.). The results of the above calculations are compared with the third law values in Table VII.

TABLE VII

COMPARISON OF SPECTROSCOPIC AND THIRD LAW VALUES OF THE ENTROPY OF HYDROGEN BROMIDE

	Spectroscopic		Third law	
T, °K.	Tetrode constant	Lewis constant	Actual gas	Corrected to ideal state
206.38	44.92	44.60	44.9±0.1	45.0
298.1	47.53	47.21	....	47.6

The third law value given at 298.1°K. was obtained by adding the spectroscopic difference between 206.38 and 298.1°K. to the 45.0 cal./deg. per mole obtained at 206.38°K.

The value for the chemical constant obtained in the paper of Eucken, Karwat and Fried[15] is given in terms of entropy in the German edition of Lewis and Randall[16] as $S_{\mathrm{HBr}} = 48.99 \pm 0.3$ E. U. at 298°K., which is 1.5 E. U. higher than the value obtained with the assistance of spectroscopic data.

Our measurements support the Tetrode rather than the Lewis constant for the Sackur equation. The close agreement supports the third law of thermodynamics.

[13] Czerny, *Z. Physik*, **44,** 235 (1927); **45,** 476 (1927).

[14] Kratzer, *ibid.*, **3,** 289 (1920).

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

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

Summary

The heat capacity of solid and liquid hydrogen bromide has been measured from 14.7 °K. to its boiling point.

Three regions of very high heat capacity were found in the solid state. These appear to be transitions of an internal molecular nature which do not occur at a definite temperature. The melting point is 186.24 ± 0.05° K. The boiling point is 206.38 ± 0.05°K.

Calorimetric determinations of the heat of fusion and of the heat of vaporization have been made.

The entropy of hydrogen bromide has been calculated from the experimental data and the third law of thermodynamics.

The entropy due to the rotational-vibrational energy has been calculated from the energy levels of the molecule as obtained from band spectra. This amount added to the entropy as given by the Sackur equation with the Tetrode constant agrees with the value obtained from the third law thus supporting this law.

BERKELEY, CALIFORNIA

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

THE HEAT CAPACITY AND ENTROPY OF CESIUM ALUM FROM 18 TO 300° ABSOLUTE. THE ENTROPY OF ALUMINUM ION. THE POTENTIAL OF THE ALUMINUM ELECTRODE FROM THERMAL DATA

BY WENDELL M. LATIMER AND BERNARD S. GREENSFELDER

RECEIVED JUNE 19, 1928 PUBLISHED AUGUST 4, 1928

The direct measurement of the potential of the aluminum electrode is a task of singular difficulty. The literature[1] abounds in discordant results and contradictory explanations of their disparity. It has therefore seemed desirable to make an independent evaluation from thermal data with respect to the reaction

$$Al + 3H^+ = Al^{+++} + 3/2H_2$$

employing values for the entropies of aqueous ions in the manner developed by Latimer and Buffington.[2]

The heat of this reaction, ΔH, is known from the precise work of Richards

---

[1] (a) Buff, *Ann.*, **102,** 265 (1857); (b) Neumann, *Z. physik. Chem.*, **14,** 217 (1894); (c) Kahlenberg and Montgomery, *Trans. Am. Electrochem. Soc.*, **36,** 285 (1919); (d) Kremann and Müller, *Z. Metallkunde*, **12,** 289 (1920); (e) Heyrovsky, *J. Chem. Soc.*, **117,** 27 (1920); (f) Müller and Hölz, *Z. anorg. Chem.*, **121,** 103 (1921); (g) Dhar, *Z. anorg. Chem.*, **119,** 75 (1921); (h) Smits and Gerding, *Z. Elektrochem.*, **31,** 304 (1925); (i) de Gruyter, *Rec. trav. chim.*, **44,** 937 (1925).

[2] (a) Latimer and Buffington, THIS JOURNAL, **48,** 2297 (1926); (b) Latimer, *ibid.*, **48,** 2868 (1926); (c) Latimer, *J. Phys. Chem.*, **31,** 1267 (1927).