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

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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

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[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).

and Burgess[3] on the heat of solution of aluminum in acid. Then in order to get the free energy, ΔF, and the electromotive force from the relation $\Delta F = -nEF = \Delta H - T\Delta S$, it is necessary to determine the entropy change, ΔS, for the reaction. The entropies of metallic aluminum and hydrogen gas are known and the experimental portion of this article consists in the determination of the entropy of Al^{+++} with respect to that of H^+. In order to accomplish this, the entropy, at 25°, of some aluminum salt and its entropy of solution must be measured. To permit an accurate evaluation of the free energy of solution, the salt must have a low solubility, must be capable of existing in stable equilibrium with its ions and should be definitely crystalline in character. An extended investigation indicated that no simple aluminum salt possessed such qualifications; amorphous modifications in metastable equilibrium with basic hydrates were predominant. However, the alkali metal alums, which have been thoroughly described in the literature, offered promise. Of these, the cesium alum, $CsAl(SO_4)_2\cdot 12H_2O$, has the lowest solubility ($M/70$ at 25°). It is easily obtained in a high degree of purity, is stable at room temperature with respect to its full quota of water,[4] and has been the subject of several solubility determinations over a wide temperature range.

The following measurements were made: (1) the heat capacity of cesium alum from 18 to 300° K.; (2) the freezing points of solutions of cesium and rubidium alums; and (3) the heat of solution of cesium alum.

The values in (1) were employed to calculate the entropy by the relation $S_{298} = \int_0^{298} C_p d \ln T$. The freezing point data were necessary in order to calculate the free energy of solution from the solubility. This free energy combined with the experimental heat of solution (3) sufficed to give the entropy of the aqueous solution of the salt.

Heat Capacity and Entropy of Cesium Alum

Material.—C. P. cesium alum was obtained from Eimer and Amend, containing 37.98% of H_2O; theoretical, 38.05%. Pycnometer determinations gave $d_4^{20} = 1.978$. The reported values are 1.984,[5a] 1.911[5b] and 1.93–1.96.[5c]

Apparatus.—Considerable attention was given to the design of a vacuum calorimeter suitable for measuring the heat capacity of solids from the triple point of hydrogen to room temperature. The present apparatus is expected to be so employed in this Laboratory over a period of years and it was eminently desirable to unite mechanical durability with ease of manipulation and delicacy of control. The general disposition of the apparatus is similar to that of Latimer and Hoenshel,[6] but the dimensions have been approximately doubled. This change decreases the possibility of electrical or

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[3] Richards and Burgess, THIS JOURNAL, **32,** 1176 (1910).

[4] Ephraim and Wagner, *Ber.*, **50,** 1103 (1917).

[5] (a) Spring, *Ber.*, **17,** 408 (1884); (b) Soret, *Compt. rend.*, 99, 867 (1884); (c) Hart and Huselton, THIS JOURNAL, **36,** 2082 (1914).

[6] Latimer and Hoenshel, *ibid.*, **48,** 19 (1926).

mechanical breakdown, increases the constancy of temperature control, accelerates evacuation by reason of the larger lead-in tubing, and facilitates assembly and take-down.

The more important newer characteristics are as follows (see Fig. 1). The calorimeter A of 115cc. capacity was wound with 300 turns of No. 40 D. S. C. gold wire (215 ohms at 25°). This wire was made by the Shreve Gold Products Company of San Francisco, from proof gold alloyed with 0.1% silver and drawn to No. 30 B. and S. gage through steel dies, washing with hot concentrated sulfuric acid after each draw. Diamond dies effected reduction to No. 40, and thorough annealing at 375° followed. This process is similar to that described by Giauque and Wiebe.[7] The entire winding gave a dR/dT of approximately 0.6 ohm/deg. from room temperature to 40°K. At 25° K. it fell to 0.4 and then rapidly diminished to 0.14 at 14°K.

Manganin exhibits a nearly constant dR/dT at these lower temperatures, offering a means of eliminating the error introduced in estimating the mean dR/dT of the gold winding for a given ΔT in this region. The gold winding was therefore spaced at the center and $16^1/_2$ turns of No. 40 D. S. C. manganin (192 ohms at 25°) wound in the gap. The wire was further insulated from the calorimeter shell by a single layer of porous tissue paper saturated with bakelite lacquer and slowly baked to dryness, overheating being carefully avoided to prevent crackling. Exchange of thermal radiation was reduced by sheathing the calorimeter with 0.0005-inch gold foil.

For temperature calibration a copper–constantan thermocouple was located on the bottom of the calorimeter, the body of the junction entering a $^1/_{16}$-inch copper tube filled with Rose metal. For temperature control both the 4.6-kg. lead block B and the 1.4-kg. copper radiation shield C were equipped with resistance heaters proportioned to give an equal temperature rise at 80°K. The auxiliary lead block D was secured to the outer brass container E by three No. 10 brass machine screws. The evacuating tube F was of 0.75-inch Monel tubing 3.5 ft. long and carried the electrical leads. A vacuum of 10^{-6} mm. of mercury was maintained during the runs.

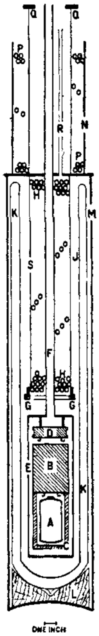

Fig. 1.

The built-in hydrogen liquefier consisted of a double-wound regenerative liquefying coil *H*, by-passed at the middle thirds, using 300 ft. of copper tubing (0.070 in. I. D., 0.125 in. O. D.). The superposed liquid air immersion pre-cooling coil *P* consisted of 40 ft. of copper tubing (0.125 in. I. D., 0.188 in. O. D.). Two special blow-out tubes were affixed thereto to clean out obstructions. Duplicate expansion valves *G* were provided, the valve stems extending to the hand wheels *Q*. The valves were connected by a circular 0.25-inch copper tube, designed to act as a trap for solid oxygen particles, thereby preventing plugging of the valve bore. The accumulated oxygen presents the hazard of electrostatic discharge due to crystal cleavage, igniting the hydrogen gas and solid oxygen. A recent explosion in one of the older liquefiers in this Laboratory might be so explained, although it is possible that the ignition was due to the sudden fracture of a circular *steel* tube leading to the valve. Copper is superior to steel under these conditions of repeated stress; its use offers a possible safeguard. Duplicate valves are advantageous; in case of "plugging" by solid oxygen or "freezing" by thermal contraction of the valve seat, the spare valve will as a rule be found free. Whether the accumulation of solid oxygen in the tube joining the valves is more likely to ignite than the constant stream of solid oxygen particles ejected through the valve at the beginning of liquefaction is most

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

uncertain, and indeed the amount, location and physical state of this troublesome impurity varies capriciously during each run. The hydrogen analyzed 0.03 ±0.01% of O_2 on leaving the compressor.

In operation, 3 or 4 liters of liquid hydrogen could be produced in two hours from a total circulation of 1270 cu. ft. of hydrogen gas at 1200 lb. pressure, sufficient to maintain a temperature below 18°K. for fourteen hours. The coil *H* was wrapped in a sheet S of Monel metal, this in turn being surrounded by a wool blanket in the space J. Thermal insulation was provided by the 36-inch Pyrex Dewar K, seated in a felt-lined wood block L. A vacuum-tight Monel can M served as container; when assembled the entire apparatus was lowered into a silk floss insulating case 4.5 ft. deep, 7 in. I. D., 14 in. O. D. Inlet and outlet tubes similar to the hydrogen return line R were provided for liquid air intake and blow-out, evacuation and outside control thermocouples. These are not shown for the sake of clarity.

All of the electrical measurements were made with the set-up described by Gibson and Giauque.[8]

Thermocouples.—Nine thermocouples measuring 305 cm. from ice to cold junction were made up of three parallel No. 30 D. S. C. constantan wires and one No. 36 D. S. C. copper. They were then calibrated against the laboratory standard couple No. 17[9] with Mr. R. T. Milner. All nine couples showed similar characteristics, the average deviation from the standard being +2.5 microvolts at 16° K., rapidly falling to +0.5 microvolt at 100° K. and maintaining such a value to room temperature. A couple designated as No. 1C9 was selected for its particularly uniform behavior and used as standard throughout the measurements. All temperatures are expressed in terms of the hydrogen thermometer.[9,10]

Operation of Calorimeter.—The specific heat measurements were made as follows. The block and radiation shield were adjusted to the mean temperature of the run; sufficient energy was then supplied over a period of several minutes (usually ten) to heat the calorimeter five or six degrees. The method of measurement and calculation was similar to that of Gibson and Giauque,[8] and included the smaller correction terms for apparent heat effect in the resistance thermometer winding described by Giauque and Wiebe.[11] Over half of the runs were timed with the automatic device described by Johnston[12] with an accuracy of 0.003 sec. The remainder were timed with a stop watch, the observer's error averaging ±0.2 sec.

Results.—The data are summarized in Table I.

The points fall on a smooth curve (Fig. 2) with an average deviation of less than 0.25%, excepting (1) those in the range 210–230° K., where water vapor adsorbed on the metallic surfaces of the apparatus always causes a temporary disturbance while being pumped off; and (2) the two measurements at the ice point, where the presence of 0.05 g. of uncombined water would completely account for the observed deviation from the smooth curve. The effect of this amount of water on the observed heat capacity at any other point is less than one-tenth the estimated experimental error. It is important to be aware of this phenomenon when investigating hydrated salts.

[8] Gibson and Giauque, THIS JOURNAL, **45,** 93 (1923).

[9] Giauque, Buffington and Schulze, *ibid.*, **49,** 2343 (1927).

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

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

[12] Johnston, to be published.

TABLE I

HEAT CAPACITY OF CESIUM ALUM

$CsAl(SO_4)_2 \cdot 12H_2O = 568.10$

T, °K.	Spec. ht. cal./g./-deg.	Molal ht. cap., cal./mole/-deg.	T, °K.	Spec. ht., cal./g./-deg.	Molal ht. cap., cal./mole/-deg.	T, °K.	Spec. ht., cal./g./-deg.	Molal ht. cap., cal./mole/-deg.
18.71	0.0129	7.35	94.20	0.1051	59.69	192.82	0.1882	106.91
21.26	.0146	8.29	99.62	.1098	62.38	198.19	.1925	109.36
23.70	.0214	12.16	104.61	.1150	65.33	205.72	.1955	111.08
27.23	.0244	13.84	109.24	.1189	67.54	210.20	.1980	113.47
30.25	.0291	16.50	113.61	.1254	71.24	215.83	.2091	118.81
31.31	.0308	17.49	117.80	.1270	72.14	221.86	.2124	120.69
32.65	.0329	18.68	122.52	.1323	75.13	227.88	.2122	120.56
36.13	.0379	21.53	127.68	.1363	77.42	233.78	.2208	125.44
39.77	.0434	24.68	132.57	.1379	78.36	239.29	.2247	127.67
44.17	.0494	28.05	137.90	.1428	81.13	245.25	.2275	129.22
48.60	.0546	31.03	143.63	.1488	84.54	251.62	.2321	131.88
52.87	.0606	34.40	149.03	.1518	86.23	257.77	.2356	133.86
57.71	.0663	37.64	154.17	.1569	89.12	263.77	.2409	136.83
62.68	.0721	40.93	159.43	.1603	91.06	(269.44)	(.2530)	(143.75)
67.57	.0780	44.31	164.62	.1642	93.28	(275.30)	(.2522)	(143.25)
72.63	.0834	47.35	169.46	.1684	95.68	281.30	.2521	143.24
75.88	.0868	49.28	176.26	.1745	99.15	286.73	.2544	144.50
80.07	.0912	51.80	181.56	.1796	102.04	292.42	.2578	146.45
84.84	.0956	54.30	187.12	.1840	104.54	297.84	.2586	146.91
89.26	.0996	56.58						

The entropy of cesium alum at 298° K. was found by plotting C_p against log T, multiplying the area under the curve by 2.3026 (Fig. 3).

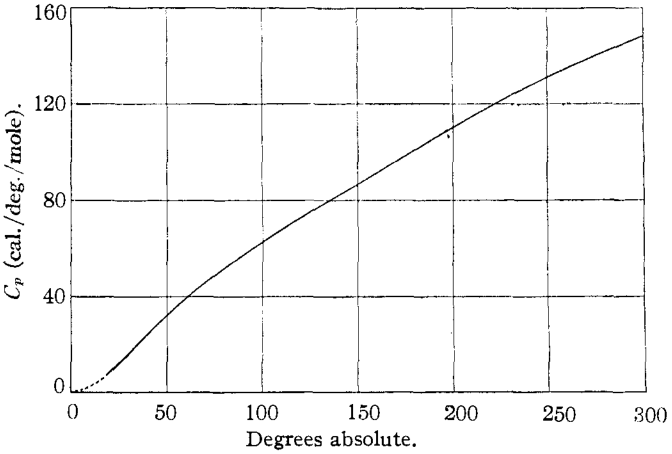


Fig. 2.—Molal heat capacity of cesium alum.

The curve was graphically extrapolated from the lowest measurement at 18.71 down to 10° K. A large scale plot was then drawn for this region and composite "Debye curves" were computed for the entropy due to Cs^+, Al^{+++}, $SO_4^=$ and $12H_2O$. The cesium alum curve was then extended parallel to the sum of the latter, giving the heat capacity to 3°. Below this point the Debye T^3 rule was assumed to be valid. These figures are summarized in Table II. The estimated accuracy is to within 0.5%.

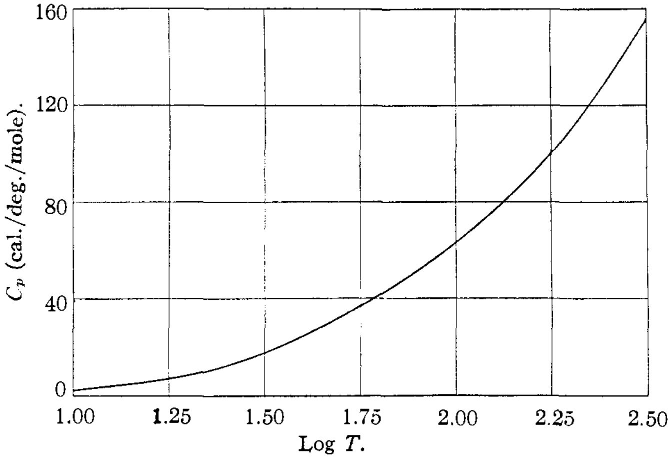


Fig. 3.—Molal entropy of cesium alum.

TABLE II

ENTROPY OF CESIUM ALUM

T, °K.		E. U.
0–3	Debye T^3 Rule	0.067
3–10	Calcd. extrapolation	1.082
10–18	Graphical extrapolation	2.647
18–298.1	Graphical from data	160.051
		163.847

Entropy of cesium alum at 298.1° K. = 163.85 E. U.

Activity and Free Energy of Solution of Cesium Alum

The freezing point lowering of dilute solutions of cesium and rubidium alum was measured in the apparatus of Randall and Vanselow,[13] using the fifty junction thermo-element. In this way a temperature difference of 0.00005° could easily be observed. The measurements were carried out on a nearly saturated solution, gradually diluted over the desired range. The concentrations were determined by gravimetric analysis.

To evaluate the free energy of solution at 298.1°K., the activity of the aqueous salt must be determined for the corresponding concentration. The freezing points of dilute solutions of cesium alum were first measured, the results being shown in Fig. 4 and Table III. As a check both upon

[13] Randall and Vanselow, THIS JOURNAL, **46**, 2418 (1924).

the method and the behavior of cesium alum, a similar series of determinations was made on rubidium alum. The points fall smoothly on the same straight line within the limits of experimental error. The activity coefficient at the 25° saturation concentration is then obtained without extrapolation, since saturated rubidium alum at 0° has about the same molality as cesium alum at 25°.

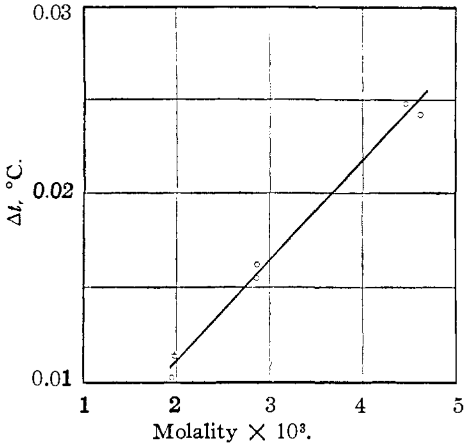
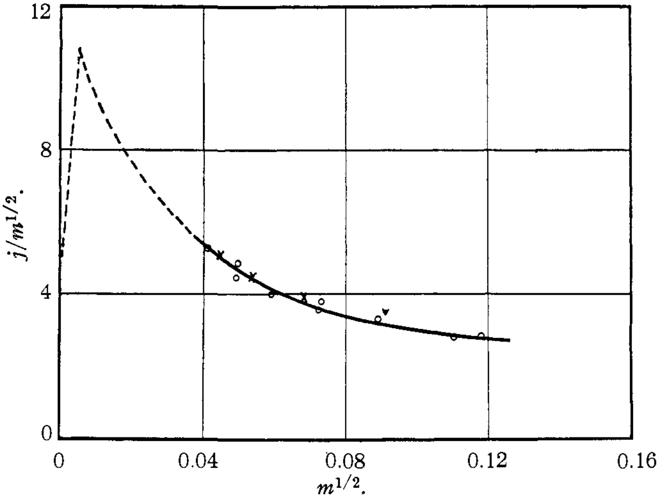


Fig. 4.—Freezing point lowering of cesium alum.

The activity coefficient was graphically calculated from the expression $\ln \gamma = -j - 2 \int_0^m (j/m^{1/2})\mathrm{d}(m^{1/2})$, which may be simply derived from the Duhem equation.[14] The limit, $j/m^{1/2} = 5.05$ when $m^{1/2} = 0$, was deduced from the Debye-Hückel theory; the segment of the curve between this point and that corresponding to the most dilute solution capable of measurement was drawn in agreement with the best data available for comparable valence types, as shown in Fig. 5. The sharp maximum in



○ Rubidium alum; × cesium alum.

Fig. 5.—Activity function.

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[14] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 286.

this curve should, of course, be rounded off, but as the area difference is not large we have left it in this limiting form.

The activity coefficients so established are valid at 25° if the heat of dilution is negligible. Experimental verification was made by diluting 200 cc. of saturated solution at 25° to one-tenth its concentration. A Beckmann thermometer sensitive to 0.001° indicated no measurable temperature difference.

The results are shown in Table III. It may be noted that the freezing points are somewhat lower than those obtained for potassium alum and sodium alum by Jones and Mackay.[15] No definite interpretation can be made in view of the uncertainty of the values of these investigators. The values of γ for rubidium alum and cesium alum fall about 25% below the curve calculated from the table of individual ionic activities given by Lewis and Randall,[16] using their figures for Cs^+, Al^{+++} and SO_4^{--}. The two curves are nearly identical in shape; the numerical agreement is adequate, taking cognizance of the specific differences entering into any given combination of ions.

TABLE III

FREEZING POINT LOWERING

Molality	Cesium Alum F. p. lowering, °C.	Molality	Rubidium Alum F. p. lowering, °C.
0.00456	0.0243	0.01236	0.0598
.00287	.0158	.00787	.0413
.00197	.0108	.00527	.0286
		.00343	.0198
		.00242	.0139
		.00170	.0099

Activity Coefficients for Rubidium and Cesium Alum

Molality	0.001	0.002	0.004	0.006	0.008	0.010	0.01167	0.01403	0.01690
γ	.462	.406	.353	.310	.276	.251	.233	.217	.200

The last three values of γ correspond to the saturated cesium alum at 20, 25 and 30°, respectively. An additional check was obtained from the experimental heat of solution (see below). Assuming a constant second derivative of the curve $\ln \gamma m$ against $1/T$ between 20 and 30°, it is found that $\gamma\ 0.01690/\gamma\ 0.01167 = 0.84$; from Table III, $\gamma\ 0.01690/\gamma\ 0.01167 = 0.86$.

The effect of the solute on the activity of the water, a twelfth-power factor, was calculated to be less than 25 cal./mole in terms of ΔF.

Heat of Solution of Cesium Alum.—Since it is a difficult matter to evaluate accurately ΔH of solution from the temperature solubility curve, even where activity corrections are applied, the direct experimental determination was carried out with Dr. F. D. Rossini in the accurately

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[15] Jones and Mackay, *Am. Chem. J.*, **19**, 83 (1897).

[16] Ref. 14, p. 382.

calibrated apparatus described by Randall and Rossini.[17] It was found that $\Delta H_{298\cdot 1} = +13{,}560$ cal./mole, the estimated accuracy being ±25 cal./mole.

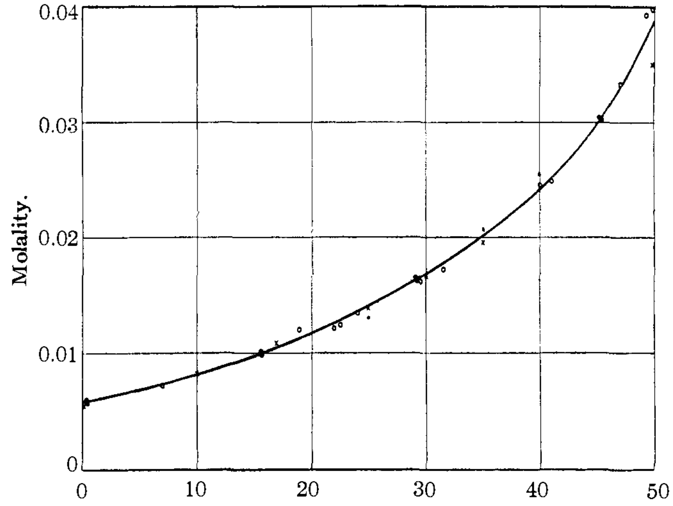
Entropy of Aluminum Ion

The entropy of aluminum ion may now be calculated. Writing the solubility reaction as

$$\mathrm{CsAl(SO_4)_2{\cdot}12H_2O = Cs^+ + Al^{+++} + 2SO_4^{--} + 12H_2O}$$

$\Delta F^\circ_{298\cdot 1} = -RT \ln K = -1363.7 \log 4(\gamma m)^4 = -5454.8 \log (1.4142)(0.217)(0.01403) = +12{,}910$ cal./mole.

The solubility, m, of cesium alum[18] has been accurately determined by Berkeley and confirmed by others, as illustrated by Fig. 6.



● Berkeley; ○ Hart and Huselton; △ Locke; × Setterberg.

Fig. 6.—Solubility of cesium alum.

Then employing our experimental value for the heat of solution, $\Delta H_{298\cdot 1} = +13{,}560$ cal./mole, we obtain for the entropy of solution

$$\Delta S^\circ_{298\cdot 1} = \frac{\Delta H - \Delta F}{T} = +2.18 \text{ E. U.}$$

We may now write for the entropy of Al^{+++}

$$S_{Al^{+++}} = \Delta S_{(sol)} + S_{\text{Cs alum (solid)}} - 12S_{H_2O\ (liq.)} - 2S_{SO_4^{--}} - S_{Cs^+}$$

The first two terms on the right have been obtained above. The entropy of H_2O has been computed from the specific heat of ice given from 9 to

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[17] Randall and Rossini, to be published.

[18] (a) Berkeley, *Trans. Roy. Soc. London*, **203A**, 189 (1904); (b) Setterberg, *Ann.*, **211**, 100 (1882); (c) Locke, *Am. Chem. J.*, **26**, 180 (1901); (d) Hart and Huselton, THIS JOURNAL, **36**, 2082 (1914).

273.1°K. by Simon[19] in a tabulation in advance of formal publication. His measurements at the ice point show the influence of pre-melting. The extraordinarily precise data of Dickinson and Osborne[20] is used in this range. At lower temperatures the two series coincide exactly. Callendar's work[21] on the specific heat of water has been used for the range 0–25°.

The Simon curve compares favorably up to 210°K. with that derived from the earlier work of Nernst and of Pollitzer.[22] The value of Dickinson and Osborne is used for the heat of fusion, $\Delta H = 1436.6$ cal./mole. The calculation of the entropy of water at 298.1°K. follows in Table IV.

TABLE IV

ENTROPY OF WATER

	E. U.
0–10°K. Debye T^3 Rule	0.02
10–273.1 Graphical	9.06
Entropy of fusion, 1436.6/273.1	5.26
273.1–298.1 Graphical	1.58
$S°_{298.1} =$	15.92 ±0.02 E. U.

For the entropy of sulfate and cesium ions we have 9 and 27.9, respectively. The sulfate value is from the paper by Latimer and Buffington[2a] and that for cesium is calculated from the expression deduced by these authors relating the entropy of solution of gas ions and the ionic radius. Although this expression is empirical, the excellent agreement shown by the other alkali metal ions warrants confidence in its accuracy.

Substituting these values in the equation given above, we find for the entropy of Al^{+++} at 298.1°K. in a hypothetical one-molal solution, $S_{Al^{+++}298.1} = -70.9$ cal./deg./mole.

Potential of the Aluminum Electrode

The entropies of $^1/_2H_2$ and Al, as calculated by Lewis, Gibson and Latimer,[23] are 14.7 and 6.82, respectively. The recent work of Cornish and Eastman[24] changes the hydrogen value to 14.6. Using our value for the entropy of aluminum ion, we find for the reaction,

$$Al + 3H^+ = Al^{+++} + 3/2H_2;\ \Delta S = -70.9 + 43.8 - 6.8 = -33.9 \text{ cal./deg.}$$

$\Delta H°$ from the work of Richards and Burgess[3] is -127.0 k. cal., whence $\Delta F°_{298} = \Delta H°_{298} - T\Delta S°_{298} = -116{,}900$ cal./mole and $E° = -\Delta F/NF = 116{,}900/(3 \times 23{,}074) = +1.69$ v.

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[19] Simon, "Handbuch der Physik," Julius Springer, Berlin, **1926**, Vol. X, p. 363.

[20] Dickinson and Osborne, *U. S. Bur. Stand. Sci. Papers*, 248, **1915**.

[21] Callendar, *Proc. Roy. Soc. London*, **86A**, 254 (1912).

[22] (a) Nernst, *Sitzb. preuss. Akad. Wiss.*, **1910**, 262; (b) Pollitzer, *Z. Elektrochem.*, **19**, 513 (1913).

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

[24] Cornish and Fastman, *ibid.*, **50**, 627 (1928).

Discussion of Results

The probable error is rather difficult to estimate. The electrode potential changes about 0.01 volt per 700 cal. change in ΔF, and we believe the free energy is known with this accuracy. The largest uncertainty appears to exist in the extrapolation of the freezing point data to obtain the activity coefficient. The largest numerical quantity is evidently the heat of solution of aluminum metal in acid. For Richards' determination, -127.0 k. cal., with hydrochloric acid in 200 moles of water a correction might be made for the heat of dilution, but this is certainly much less than other errors involved in the determination. Richards' value, -126.0 k. cal., for a more concentrated solution, that is, for $HCl \cdot 20H_2O$ is substantiated by the work of Biltz and Hohorst,[25] who give 125.1 k. cal. for $HCl \cdot 8.8H_2O$.

Among the direct determinations of the aluminum electrode, that of Heyrovsky[26] appears to be the most reliable. He employed the electrode sat. Al amalg. $\| \times m$ $AlCl_3$, and obtained the value $+1.337$ volts, which he believed corresponded to the reaction, $Al + 3H_2O = Al(OH)_3 + 3/2H_2$. This could be checked against our value if the solubility product of aluminum hydroxide were accurately known. For this quantity we find 4×10^{-18} by Remy and Kuhlmann[27] and 10^{-33} by Heyrovsky.[28] Whence we may write

		Volts
$Al + 3H_2O$	$= Al(OH)_3 + 3/2H_2$	1.337
$Al(OH)_3$	$= Al^{+++} + 3OH^-$	-0.344 or -0.650
$3H^+ + 3OH^-$	$= 3H_2O$	0.828
$Al + 3H^+$	$= Al^{+++} + 3/2H_2$	$+1.821$ or $+1.515$

Our value, $+1.69$ volts, falls as a close mean.

The free energy of the reaction $Al + 3H_2O = Al(OH)_3 + 3/2H_2$, has been calculated by Drossbach[29] from the reaction heats and entropies, and agrees with the potential found by Heyrovsky.

A correction, estimated from the data of Denham[30] as $+0.004$ volt, might be applied on the assumption of hydrolysis to $Al(OH)^{++}$. However, the stoichiometrical hydrolysis may be considered as due to the distributed polarization of the water molecules, and it then would be as unsuitable to attempt to specify an appropriate equilibrium constant as it is to define a dissociation constant for a strong electrolyte. For this reason no correction has been made and the hydrolysis effect is thus included in the standard state of hypothetical unit molal aluminum ion which corresponds to the experimental activities.

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Summary

The heat capacity of cesium alum, $CsAl(SO_4)_2 \cdot 12H_2O$, has been measured from 18 to 300°K.; the molal entropy at 298.1°K. is computed to be 163.8 cal./deg.

The activity of dilute solutions of rubidium and cesium alums has been determined from freezing point measurements.

The entropy ($H^+ = 0$) of Al^{+++} in hypothetical 1 M solution at 298.1°K. has been determined as -70.9 cal./deg./mole.

The electrode potential at 298.1°K. of aluminum, $Al = Al^{+++} + 3E^-$, has been calculated from thermal data to be $+1.69 \pm 0.01$ volts.

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[CONTRIBUTION FROM SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE]

THE TRANSITION TEMPERATURE OF CARBON TETRACHLORIDE AS A FIXED POINT IN THERMOMETRY

BY JAMES C. MCCULLOUGH AND HARRIS E. PHIPPS[1]

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An enantiotropic or reversible transition has been discovered when carbon tetrachloride is cooled below its freezing point. This solid–solid transition is a change from the cubic to the monoclinic system and takes place at $- 48.54 \pm 0.02°$. The hold in the time–temperature curve (Fig. 1) is of approximately the same duration as that at the freezing point. With proper precautions the transition temperature is as constant as the freezing temperature. Since the freezing point of carbon tetrachloride is given as a fixed point in thermometry,[2] the transition point should be equally valuable. The purification of one substance would thus serve to fix two points on the thermometer scale, saving the purification of a second material, such as chlorobenzene.

No reference has been found in the literature indicating that more than one solid form of carbon tetrachloride has been known at atmospheric pressure. Tammann,[3] working with high pressures, at one time believed that he had found three solid forms. Later, in "Kristallisieren und Schmel-

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[1] This paper represents part of the work done by Mr. Phipps in meeting the requirements for the degree of Master of Arts.

[2] (a) "International Critical Tables," Vol. I, p. 54; (b) Timmermans and Martin, *J. chim. phys.*, **23**, 747–787 (1926).

[3] Tammann, "Kristallisieren und Schmelzen," E. Barth, Leipzig, **1903**, p. 222.