complete. This is as close agreement as could be expected.

Summary

The iodine concentration during a sensitized decomposition of gaseous diethyl ether, acetaldehyde, propionaldehyde, ethylene oxide, methyl alcohol, methyl formate, formaldehyde and probably many others, is very low.

The decompositions proceed through definite chemical reactions rather than collision activation processes.

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

The Heat Capacity and Entropy of Barium Chloride Dihydrate from 15 to 300°K. The Heat of Solution of Barium Chloride Dihydrate. The Entropy of Barium Ion

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The method of calculating the entropy of barium ion which has been used up to the present[1] involves directly the entropies of chloride, thallous and nitrate ions, and indirectly the entropies of silver, bromide and iodide ions. Since the entropy of chloride ion is known with greater precision than that of thallous and nitrate ions, a method of calculating barium ion directly from chloride ion has long been considered desirable. The recent careful work of Tippetts and Newton[2] on the thermodynamics of aqueous barium chloride solutions has now made such a calculation feasible. In the present paper we have determined the following properties of barium chloride dihydrate: (1) the entropy, (2) the heat of solution in water, and (3) the solubility in water. Combining these data we have calculated the entropy of barium ion in aqueous solution.

Material.—A c. p. grade of barium chloride was crystallized three times from redistilled water. It was then dried in a desiccator over partially dehydrated barium chloride dihydrate. Since the sample was found by analysis to have more than the theoretical amount of water, it was dried at 105°, then rehydrated in a desiccator containing water. After analysis showed that the sample had taken up more than the theoretical amount of water, the sample was again dried over partially dehydrated barium chloride dihydrate. This cycle was repeated once again before a sample containing the theoretical amount of water was obtained.

Heat Capacity Measurements.—The experimental method was that of Latimer and Greensfelder.[3] The apparatus was slightly modified from that used in previous work. The block employed to ensure a uniform temperature environment for the calorimeter was replaced by a new block, which was machined very carefully so as to provide better contact between the two halves of the block. The inner surface of the block was gold plated and polished, and reduced considerably the corrections necessary for heat interchange due to radiation. The approximate values of ΔT used in the measurements were: 1.2° up to 20°K., 2–3° up to 50°K., 3–6° up to 180°K, and 6–9° up to 300°K. In calculating the heat capacities one calorie was taken equal to 4.1833 int. joules, and the molecular weight of barium chloride diphydrate was taken as 244.317. Measurements were made on a sample of 192.845 g. (weight *in vacuo*). The results are given in Table I and shown as a function of temperature in Fig. 1.

TABLE I

MOLAL HEAT CAPACITY OF BARIUM CHLORIDE DIHYDRATE

$T.$, °K.	C_p Cal./mole/deg.	$T.$, °K.	C_p Cal./mole/deg.
14.87	1.06	112.10	22.87
16.18	1.27	117.92	23.53
17.24	1.49	123.62	24.16
20.00	2.04	129.49	24.94
23.16	2.73	135.64	25.81
25.69	3.36	141.68	26.46
28.14	3.97	147.84	27.09
30.21	4.51	153.76	27.65
32.13	5.05	160.01	28.21
34.87	5.89	166.86	28.77
37.98	6.82	173.45	29.34
40.45	7.39	180.25	29.95
42.91	8.26	187.15	30.63
48.02	9.63	193.41	31.06
51.15	10.57	200.27	31.63
54.60	11.54	207.32	32.11
58.06	12.51	214.06	32.57
61.78	13.38	221.02	32.97
66.12	14.45	229.72	33.45
69.82	15.35	236.41	33.78
70.78	15.58	244.76	34.58
73.92	16.31	254.54	35.02
78.67	17.33	263.58	35.33
83.68	18.31	272.18	36.01
89.08	19.30	281.17	36.48
94.72	20.26	287.97	36.65
100.61	21.21	297.07	37.09
106.37	22.00	301.28	37.13

(1) Latimer, Schutz and Hicks, J. Chem. Phys., **2**, 82 (1933).

(2) Tippetts and Newton, THIS JOURNAL, **56**, 1675 (1934); Newton and Tippetts, *ibid.*, **58**, 280 (1936).

(3) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).

Entropy of Barium Chloride Dihydrate.—The entropy was calculated by graphical integration of a plot of C_p against log T, combined with an extrapolation at low temperatures using the Debye specific heat equation. The calculation is summarized in Table II.

TABLE II
MOLAL ENTROPY OF BARIUM CHLORIDE DIHYDRATE

0–14.87°K.	Debye extrapolation	0.39
14.87–298.1°K.	Graphical from data	48.19 ± 0.1
	Entropy at 298.1°K.	48.58 E. U.

Heat of Solution of Barium Chloride Dihydrate.—The measurements of the heat of solution were made in a calorimeter which consisted of a vacuum-walled flask of about one-liter capacity fitted with a stirrer, resistance thermometer, and device for introducing a weighed quantity of salt into the water by breaking two gold foil seals. The resistance thermometer consisted of about 45 ohms of platinum wire and also served as a heater for determining the heat capacity of the calorimeter and contents. The values obtained for the heat of solution of one mole of barium chloride dihydrate in 400 moles of water at 298.1°K. were 4412 and 4427 cal. If we combine the average value, 4420 cal., with the known heat of dilution of barium chloride solutions at 298.1°K.[4,5] we obtain for the heat of solution at infinite dilution, $\Delta H° = 3955$ cal./mole.

Free Energy and Entropy of Solution of Barium Chloride Dihydrate.—The solubility of barium chloride at 298.1°K. was determined by evaporating weighed portions of the saturated solution to dryness and weighing the anhydrous barium chloride, after heating to constant weight at 150°. Equilibrium in the saturated solution was approached from both sides by saturating at higher temperatures and at lower temperatures than 298.1°K. The solubility in moles of anhydrous salt per 1000 g. of water was found to be 1.788. The activity coefficient of barium chloride has been determined by Tippetts and Newton[2] from both e. m. f. measurements and vapor pressure measurements. Using their results we find for the saturated solution $\gamma = 0.4418$ and $a_1 =$

0.9021 (a_1 = activity of water). For the reaction

$$BaCl_2 \cdot 2H_2O(s) = Ba^{++} + 2Cl^- + 2H_2O(l)$$
(hypothetical one molal solution) (1)

$\Delta F° = -1363.8 \log 4(\gamma m)^3 a_1^2 = -280$ cal. $\Delta H° = 3955$ cal. $\Delta S° = (\Delta H° - \Delta F°)/T = 14.20$ E. U.

Entropy of Barium Ion.—The entropy of chloride ion is 13.5 E .U.[1] The entropy of water calculated from the spectroscopic value for the perfect gas[6] and the entropy of condensation of the perfect gas to liquid water[7] is 16.77 E. U. The entropy of barium ion is given by the expression

$S°_{Ba_{++}} = S_{BaCl_2 \cdot 2H_2O} + \Delta S° - 2S°_{Cl^-} - 2S_{H_2O} =$
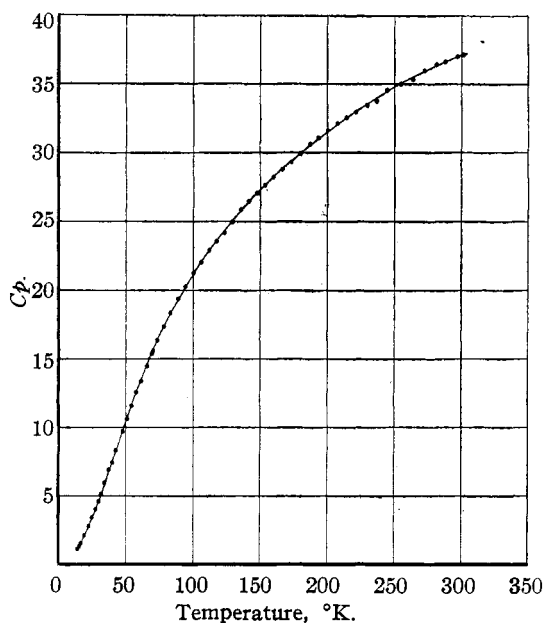$48.58 + 14.20 - 27.0 - 33.54 = 2.2$ E. U.

Fig. 1.—Molal heat capacity of barium chloride dihydrate.

Summary

The heat capacity of barium chloride dihydrate has been measured from 15 to 300°K., and the entropy of the salt determined by graphical integration. The solubility and heat of solution of barium chloride dihydrate in water has been determined at 298.1°K. Combining these data with other data already available, the entropy of barium ion has been determined.

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(4) Richards and Dole, THIS JOURNAL, **51**, 794 (1929).
(5) Lange and Streeck, Z. physik. Chem., **A152**, 1 (1931).
(6) Gordon, J. Chem. Phys., **2**, 65 (1934).
(7) Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936). The value here quoted is consistent with that selected by these authors after a review of the existing data.