sodium, and no compounds of the chiolite type are formed by the first-mentioned metals. The structures for all these compounds are based on aluminum fluoride octahedra, arranged in chains for penta-fluoaluminates and layers for tetrafluoaluminates. Chiolite is similar to the tetrafluoaluminates except that one octahedron in every four is replaced by a sodium ion. While the ionic radii of potassium, rubidium and univalent thallium lie within the limits 1.33 to 1.60 Å., it is evident that the much lower value (0.95 Å.) for sodium is incompatible with the tetra- or penta-fluoaluminate structures. On the other hand, the ionic radii of potassium, rubidium, etc., are apparently too great to enable these ions to occupy the positions of missing aluminum fluoride octahedra, as occurs with sodium ions in the chiolite lattice.

Compounds such as NaAlF₄·H₂O and Na₂AlF₅, described by Yatlov,⁸ are thus mixtures of chiolite with aluminum fluoride and cryolite, respectively. Samples 1 (cryolite) and 4 (chiolite) represent attempts to obtain sodium penta-fluo-aluminates by his methods. Yatlov also claimed that sodium tetra-fluoaluminate dissolved in water to give solutions of the same composition as the solid, but this is at variance with the observations of the present authors. A washed sample of the tetra-fluoaluminate made according to his directions gave diffraction patterns for chiolite only and had the sodium-aluminum ratio of 1.33 (sample 7). It is most probable that the so-

called tetra-fluoaluminate (NaAlF $_4$ ·H $_2$ O) is a mixture of chiolite (1 mole) with aluminum fluoride trihydrate (2 moles), a combination which reduces to the empirical formula NaAlF $_4$ ·1.2H $_2$ O.

Conclusions

In precipitates obtained from aqueous solutions, the only sodium fluoaluminates which can be detected by X-ray diffraction methods are cryolite and chiolite. Although both compounds contain combined water (>5%), the crystal structures are the same as those of the corresponding anhydrous compounds obtained in the binary melt, aluminum fluoride-sodium fluoride, except for a small increase in the volume of the unit cell in the case of chiolite. The compounds NaAlF4·H2O and Na2AlF5, previously mentioned in the literature, are probably mixtures of chiolite with aluminum fluoride and cryolite, respectively.

Summary

A study has been made of the sodium fluoaluminates precipitated from aqueous solutions. Examination of X-ray diffraction patterns has shown that the only fluoaluminates obtained are cryolite (Na₃AlF₃) and chiolite (Na₅Al₃F₁₄). Variation in the chemical position (as shown by sodium-aluminum ratios) is caused by admixture of chiolite with either cryolite or hydrated alumium fluoride. No evidence has been found for the existence of penta- or tetra-fluoaluminates of sodium.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Heat of Formation and Free Energy of Chlorous Acid

By B. J. FONTANA AND WENDELL M. LATIMER

The free energy of chlorous acid as quoted by Latimer¹ was based upon the Bichowsky and Rossini² value for the heat of formation of the acid. These authors used the heat of solution of chlorine dioxide (g) in water obtained by Booth and Bowen³ and assumed that the heat resulted from the reaction

 $2ClO_2(g) + H_2O = HClO_3(aq.) + HClO_2(aq)$

However, Bray⁴ made a careful study of the distribution of chlorine dioxide between water and carbon tetrachloride in the presence of H⁺ and ClO₃⁻ and concluded that the water solution was practically unhydrolyzed. It seemed desirable, therefore, to obtain a new value for the heat of formation of chlorous acid and to recalculate the free energy values. The general experimental

- (1) Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 48.
- (2) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 181
 - (3) Booth and Bowen, J. Chem. Soc., 127, 342 (1025)
 - (4) Bray, Z. physik. Chem., 54, 583 (1906)

procedure adopted was the determination of the heat of solution of NaClO₂ and the heat of reduction by iodide.

Experimental

Analysis of NaClO₂(s).—We are indebted to Mr. Herbert Fleischman for a sample of NaClO₂ of unusual purity for this material. The compound was analyzed by dissolving 0.1-g. samples in ~ 300 cc. of ~ 0.1 M potassium iodide, 0.03 M sulfuric acid (or perchloric acid) solution. The liberated iodine was titrated with standard S₂O₃-after standing five to ten minutes.

Average of four analyses gave 43.60 ± 0.03 milliequivalents per gram (98.6% of theoretical).

Calorimetric Measurements.—The calorimeter used was that of Latimer and Zimmerman⁵; however, a new copper resistance thermometer and manganin heater were constructed. The resistance thermometer measuring circuit of Pitzer⁶

- (5) Latimer and Zimmerman, This Journal. 61, 1550 (1939)
- (6) Pitzer, ibid., 59, 2365 (1937)

was retained, but the heater measuring circuit was simplified by use of a Rubicon Type B potentiometer.

Two measurements of the heat of solution of 0.4977 and 0.4647 g. samples of NaClO₂ in 1000 ml. of water gave

NaClO₂(s)
$$\longrightarrow$$
 ClO₂⁻ + Na⁺
 $\Delta H_{298} = +1.15 \pm 0.07 \text{ cal./g.}$
= +0.10 ± 0.01 kcal./mole

No correction is necessary for hydrolysis since this amounts to only $\sim 0.001\%$ in pure water.

Three measurements of the heat of reaction of NaClO₂(s) with the iodide ion under the same conditions used for analysis were made (25.0°):

TABLE I

Initial
$$\begin{cases} (HClO_4) = 0.0300 \ M \\ (KI) = .1097 \ M \end{cases}$$

NaClO₂(s), Calories, obs. Cal./g. $-\Delta H_{200}$

1 0.4658 536.2 1152.4 105.72
2 .4690 540.6 1153.9 105.85
3 .4613 531.0 1152.2 105.70

Av. 105.76 ± 0.06

Using the equilibrium constant of Jones and Kaplan⁷ for the reaction $I_3^- \rightarrow I_2(aq.) + I^ K_{298} = 0.00140$, one calculates that under the conditions of the calorimetric runs above the fraction of the total iodine produced which is in the form of triiodide is 0.986. Hence the above ΔH corresponds to the reaction

$$4H^{+} + ClO_{2}^{-} + 5.972 I^{-} \longrightarrow 1.972 I_{2}^{-} + 0.028 I_{2}(aq.) + Cl^{-} + 2H_{2}O \Delta H_{298} = -105.76 \text{ kcal.}$$
 (1)

Calculations

Heats of Formation of HClO₂ and Cl₂O-.— If one subtracts the sum of the following heats from equation (1)

This gives for

$$2H_2 + ClO_2^- \longrightarrow Cl^- + 2H_2O \quad \Delta H_{298} = -159.12 \text{ kcal.}$$

Using the Bichowsky and Rossini heats of formation C1⁻, -39.54 kcal., and $2H_2O_1$, -136.64kcal., one obtains for the heat of formation of ClO_2^- , $\Delta H_{298} = -17.18$ kcal.

Combining this with the heat of ionization, -3.50 kcal., obtained by Barnett, 11 the heat of formation of chlorous acid is $\Delta H_{298} = -13.68$ kcal. This value is in remarkable agreement with that calculated by Bichowsky and Rossini, -13.8 kcal. However, we are of the opinion as expressed above, that the assumptions of these authors are unjustified and that the agreement is purely accidental.

Free Energy of Formation of HClO₂ and ClO₂. -From the entropy of formation of ClO₂-, 67.2 cal./deg., as given by Latimer1 and the free energy of dissociation of the acid by Barnett,11 2.67 kcal., one obtains for the free energy of chlorous acid, $\Delta F_{298}^0 = 0.23$ kcal. and for ClO_2^- , $\Delta F_{298}^0 = 2.90$ kcal. These free energies may be used to revise the potential diagram given by Latimer with the following results

Eo acid solution

HCIO
$$\frac{-1.65}{-1.47}$$
 HCIO₂ $\frac{-1.29}{-1.47}$ CIO₃-

E° basic solution
$$\frac{\text{C1O}^{-}}{-0.45} \frac{-0.35}{-0.45} \frac{\text{C1O}_2^{-}}{-0.35} \frac{\text{C1O}_3^{-}}{-0.45}$$

It is somewhat surprising that the disproportionation of ClO₂ in alkaline solution is slow in view of the 0.3 volt potential favoring the reaction.

Summary

The heat of reduction of ClO₂ by iodide has been measured and the data used to calculate the heats of formation of ClO_2^- and chlorous acid; the values are -17.18 and -13.68 kcal., respectively. These heats combined with the entropy data give for the free energies of formation of ClO_2^{-} , ΔF_{298}^0 2.90 kcal., and $HClO_2$, ΔF_{298}^0 0.23 kcal.

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⁽⁷⁾ Jones and Kaplan, This Journal, 50, 1845 (1928).

⁽⁸⁾ Bichowsky and Rossini, ref. 2, page 26, with correction as suggested by Shomate, ibid., 65, 785 (1943).

⁽⁹⁾ Bichowsky and Rossini, ref. 2, page 25.

⁽¹⁰⁾ From change of equilibrium constant with temperature. Jones and Kaplan, This Journal, 50, 1845 (1928)

⁽¹¹⁾ Barnett, Ph.D. thesis, University of California, 1935. Two values were given by Barnett. -4.10 and -3.50, but the latter was favored by him.