transfer of one. The second wave corresponds to an irreversible reduction.

2. The half-wave potential of the first wave in 0.01 to 0.1 *N* hydrochloric acid is -0.18 v. (*vs.* S.C.E.). Its value is independent of the uranyl concentration and is hardly affected by the acidity of the solution or the concentration of potassium chloride. The half-wave potential of the second wave is -0.92 v.; it is independent of the uranium and hydrochloric acid concentration in the solution. The independency of both half wave potentials of the acidity indicates that hydrogen ions are not involved in the electrode reactions. An explanation of this fact has been presented.

3. The diffusion coefficient of the UO_2^{++} at 25° ion has been calculated to be 0.62×10^{-5} cm.^{2} sec.$^{-1}$. This corresponds to a mobility of the uranyl ion of 46.5 ohm^{-1} sec.^{2}.

4. Uranous uranium in 0.1 *N* HCl gives one reduction wave corresponding to a reduction of U^{4+} to U^{3+}. The half wave potential is equal to that of the second uranyl wave.

5. For the polarographic determination of uranyl it is recommended that the first diffusion current be measured at a potential of -0.5 v. (*vs.* S.C.E.) in 0.01 to 0.1 *N* hydrochloric acid. The solution contains $10^{-4}\%$ thymol as an eliminator of the maximum. The diffusion current was found proportional to the uranyl concentration in a range between 5×10^{-4} and 4×10^{-3} *M*. Ferric iron is made harmless by warming the solution at 50° for ten minutes with an excess of hydroxylamine hydrochloride.

6. Use is made of the catalytic effect of uranium upon the polarographic reduction of nitrate. An empirical procedure has been developed which allows the polarographic determination in a concentration range between 2×10^{-7} and 3×10^{-5} *M*.

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[CONTRIBUTION OF THE COÖPERATIVE X-RAY LABORATORY, UNIVERSITY OF PITTSBURGH]

X-Ray Diffraction Studies of Anhydrous Sodium and Potassium Ferric Sulfates. I. The Disulfates and Trisulfates[1]

BY RICHARD C. COREY[2] AND S. S. SIDHU[3]

When a mixture of sodium or potassium sulfate and ferric oxide is exposed to dry sulfur trioxide, the entire system being at 538°, a change of phase occurs. This transition is indicated by an increase in weight and a noticeable change in color of the reaction product. For a given mixture the equilibrium percentage increase of weight is constant for partial pressures of sulfur trioxide between 0.15 to 0.50 mm. Neither sodium nor potassium sulfate, nor ferric oxide alone undergoes any such changes under the same conditions of temperature and range of partial pressures of sulfur trioxide. An X-ray diffraction pattern of the reaction product is entirely different from either of the original constituents.

This paper gives (1) the identification of the unknown phase formed, and (2) the methods for the preparation of the anhydrous alkali metal ferric sulfates and their X-ray diffraction data used for the identification of the newly formed phase.

Experimental

Alkali metal ferric disulfates and trisulfates were prepared by two methods. In the first method the sulfates were crystallized from solution and heated to a relatively high temperature, and in the second method they were obtained from a solid–solid reaction between the anhydrous salts at a high temperature.

The equations for the reactions involved in the first method are as follows

$$M_2SO_4 + Fe_2O_3 + 3H_2SO_4 \longrightarrow 2MFe(SO_4)_2 + nH_2O \quad (1)$$

$$3M_2SO_4 + Fe_2O_3 + 3H_2SO_4 \longrightarrow 2M_3Fe(SO_4)_3 + nH_2O \quad (2)$$

where $M = Na$ or K

Reagent grade anhydrous Na_2SO_4, K_2SO_4, Fe_2O_3 and concentrated H_2SO_4 in the proper mole proportions were mixed in water, evaporated to dryness and the final product heated to a constant weight at 300°. The proportions that were used are given in Table I.

TABLE I

MOLE PROPORTIONS OF ANHYDROUS Na_2SO_4, K_2SO_4, Fe_2O_3 AND SO_3 FOR PREPARATION OF ALKALI METAL FERRIC SULFATES

Compound	Materials used	Moles	Wt. %
$NaFe(SO_4)_2$	Na_2SO_4	1	26.2
	Fe_2O_3	1	29.5
	SO_3	3	44.3
$KFe(SO_4)_2$	K_2SO_4	1	30.7
	Fe_2O_3	1	27.8
	SO_3	3	41.5
$Na_3Fe(SO_4)_3$	Na_2SO_4	3	51.6
	Fe_2O_3	1	19.3
	SO_3	3	29.1
$K_3Fe(SO_4)_3$	K_2SO_4	3	56.7
	Fe_2O_3	1	17.3
	SO_3	3	26.0

For each mole of sulfur trioxide required, 55 ml. of concentrated sulfuric acid was used. This amount was slightly in excess of the stoichiometric requirement, but it was used to minimize hydrolysis.

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TABLE II

X-RAY DIFFRACTION DATA FOR ANHYDROUS ALKALI METAL FERRIC SULFATES

$K_3Fe(SO_4)_3$		$Na_3Fe(SO_4)_3$		$KFe(SO_4)_2$		$NaFe(SO_4)_2$	
d	I/I_0	*d*	I/I_0	*d*	I/I	*d*	I/I
7.40 (2)	S	6.82 (3)	S	7.98 (1)	VS	8.28	W
5.06	W	4.38	W	4.65	W	7.35 (1)	VS
4.25	W	4.04	S	3.94	M	3.78	M
3.61	W	3.59	W	3.78	M	3.49	W
3.29 (1)	VS	3.41	W	3.54	M	3.08	VW
2.07	W	3.20 (1)	VS	3.33	VW	2.97	VW
2.80 (3)	S	3.07 (2)	VS	3.18	VW	2.81 (2)	VS
2.69	VW	2.97	VW	3.01 (2)	VS	2.77 (3)	S
2.54	VW	2.88	W	2.88 (3)	S	2.61	W
2.46	M	2.75	M	2.65	M	2.41	M
2.36	W	2.49	M	2.62	M	2.12	M
2.22	S	2.42	M	2.43	S	2.03	W
2.09	W	2.27	S	2.31	W	1.98	VW
2.05	M	2.16	W	2.18	W	1.89	W
1.99	VW	2.06	S	2.14	M	1.85	VW
1.91	W	2.01	W	2.04	VW	1.80	S
1.87	VW	1.97	W	1.98	W	1.73	W
1.79	W	1.91	S	1.96	W	1.67	S

d = Interplanar spacing in ångströms; I/I_0 = estimated relative intensity; V = very, S = strong, M = medium. W = weak. Three strongest lines are indicated in order of decreasing intensity by (1), (2) and (3).

The equations for the reactions involved in the second method are

$$M_2SO_4 + Fe_3(SO_4)_3 \longrightarrow 2MFe(SO_4)_2 \qquad (3)$$

$$3M_2SO_4 + Fe_2(SO_4)_3 \longrightarrow 2M_3Fe(SO_4)_3 \qquad (4)$$

Na_2SO_4, K_2SO_4 and $Fe_2(SO_4)_3$ were first heated separately to constant weight at 370° in an atmosphere of nitrogen to remove combined water and any excess sulfur trioxide that might have been present. These salts were powdered to −200 mesh and then intimately mixed in the mole proportions necessary for the formation of the respective compounds desired, and heated at 538° in evacuated sealed Pyrex tubes for twenty-four hours.

X-Ray diffraction patterns of a series of samples of each compound, disulfate or trisulfate showed that only those compounds prepared according to the methods described above gave one set of diffraction lines. A sample with an excess of any one of the original constituents gave a diffraction pattern consisting of the lines of the compound plus the lines of the particular constituent. It was thus established that the four compounds for which diffraction data are given in Table II, were not mechanical mixtures of different constituents, nor were they solid solutions of one salt in another.

The X-ray diffraction pattern of the reaction product obtained from a mixture of sodium or potassium sulfate, ferric oxide and sulfur trioxide at 538° checked exactly with that of the synthetically prepared anhydrous sodium or potassium iron trisulfate. The phase formed under the above conditions is obviously an alkali metal iron trisulfate; no disulfate was observed. The trisulfate phase is formed regardless of the alkali metal sulfate and ferric oxide ratio in the original mixture. This suggests that the reaction which occurs is

$$3M_2SO_4 + Fe_2O_3 + 3SO_3 \longrightarrow M_3F(SO_4)_3 \qquad (5)$$

Summary

The phase formed by the reaction of mixtures of alkali metal sulfates and ferric oxide with sulfur trioxide at 538° is of the $M_3Fe(SO_4)_3$ type regardless of the alkali sulfate to iron oxide ratio in the original mixture. No disulfates were formed under these conditions.

Alkali metal ferric disulfates and trisulfates may be prepared by (a) recrystallization from a solution and subsequent heating to a high temperature to affect dehydration, and (b) by a solid–solid reaction at a high temperature.

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