

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

THE EXISTENCE OF TETRAHYDRATED SODIUM SULFATE IN MIX-CRYSTALS WITH SODIUM CHROMATE.

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Dekahydrated sodium chromate and sodium sulfate form mix-crystals in almost all, if not all, proportions. The present note proves that the tetrahydrate of sodium chromate also is capable of isomorphously dissolving sodium sulfate, in spite of the fact that $\text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ does not exist by itself.

The induced crystallization of one salt by a second, in the otherwise unattainable form of hydration of the second, is well known in several other instances: for example, the crystallization of cupric sulfate heptahydrate, $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$, with ferrous sulfate heptahydrate.¹ Nevertheless, cases of this kind are not so numerous as to make the addition of another to their number superfluous: hence the publication of the present brief paper, which records a side-issue of a comprehensive investigation of the sulfate-chromate equilibrium.

That mix-crystallization occurs with sodium chromate tetrahydrate might be inferred from the fact that sodium sulfate is eliminated only very slowly during recrystallization of the tetrahydrate of sodium chromate.²

This conclusion was strongly supported by preliminary analysis of crystals of tetrahydrated sodium chromate obtained from warm solutions of sodium chromate containing considerable sodium sulfate, which had been washed four times with a pure saturated solution of sodium chromate while the crystals were stirred with the washing liquid. After crushing and air-drying to the first visible trace of efflorescence, 0.8712 g. of these crystals lost 0.2695 g. (or 30.93%) of water on complete dehydration: and 7.06% of sodium sulfate was found in the residue. The theoretical water content for this mixture if both salts were present in the form of tetrahydrate would be 30.96%, or almost exactly that found.

Evidence that the sulfate thus found was not due to remaining mother liquor was afforded by the fact that the second and fourth wash-solutions contained approximately identical percentages of sulfate. It was necessary to make sure, however, that separate crystals of partly dried ordinary Glauber's salts were not present. Therefore in subsequent trials not only the crystallization but also the filtering, washing with pure saturated

¹ Marignac, *Ann. Mines*, 9, 1 (1856); also Lecoq de Boisbaudran, *Ann. chim. phys.*, 18, 246 (1869). See also Stortenbeker, *Z. physik. Chem.*, 16, 250 (1895); and Rctgers, *ibid.*, 16, 580 (1895), and 15, 571 (1894).

² T. W. Richards and G. L. Kelley, *Proc. Am. Acad.*, 47, 173 (1911).

chromate solution and drying were conducted about 32.4°. The final drying of the crystals was accomplished by allowing them to stand over dil. sulfuric acid of such concentration that its vapor pressure was slightly less than that of the solution of sodium chromate saturated at the same temperature. Six separate crops of crystals were prepared from different solutions and treated in this way before analysis. Sample 2 consisted of short, fine powdery crystals; Samples 3 and 4, of fine needles; Samples 5 and 6, after drying to constant weight, were afterwards crushed and again placed in the desiccator. Sample 7 was exposed to an atmosphere dry enough to dehydrate crystals containing 10 molecules of water. Samples 8 and 9 consisted of very large, clear crystals crystallized at 23° and picked out carefully by hand.

TABLE I.
Analysis of Tetrahydrated Mix-crystals.

Sample.	Weight crystallized salt. G.	Weight water. G.	Na ₂ SO ₄ in anhydrous residue. %.	Per cent. of water.	
				Observed. %.	Calc. for 4H ₂ O for both salts. %.
2	1.2785	0.3985	5.08	31.2	30.9
3	2.3503	0.7335	3.25	31.2	30.9
4	2.0832	0.6635	2.97	31.8	30.8
5	0.8716	0.2703	3.25	31.0	30.9
6	1.5546	0.4821	2.97	31.0	30.8
7	1.4003	0.4323	3.07	30.9	30.9
8	1.5940	0.5010	8.58	31.4	31.0
9	1.7098	0.5296	4.39	31.0	30.9

In every case except No. 4 (in which the fine needles had apparently not been adequately dried), the amount of water was within the usual limit of error in such cases. If all the sulfate in Expt. 8 had been dehydrated, the percentage of water found would have been 35.9, instead of 31.4. There can thus be no question that sodium sulfate crystallizes with sodium chromate in the form of tetrahydrate, Na₂SO₄·4H₂O. The effect of the dissolved sulfate on the crystal angles would be a matter of interest, but time was lacking for its study.

The distribution of sodium sulfate between the crystals and their mother liquor was approximately determined by analysis of mother liquors from new tetrahydrate crystals as follows.

TABLE II.		
Na ₂ SO ₄ in dried crystals. %.	Na ₂ SO ₄ in dried salt from liquid. %.	Temperature of formation. °C.
4.39	10.38	23
2.97	8.00	33

These make no pretension to great accuracy, but show roughly that the sulfate under these conditions is distributed between the crystals and the salts in solution in the ratio 1:2.5, approximately. This is, of course,

a far smaller proportion of sulfate in the crystals than in the case of decahydrate, but is quite enough to account for the difficulty in eliminating sodium sulfate from chromate by crystallization as tetrahydrate.

When sodium sulfate was in large excess, in repeated trials, no crystallization could be induced by inoculating the saturated mixture with the crystal of the tetrahydrate above the transition temperature of sodium sulfate, and below this temperature only crystals of the decahydrate could be made to form. Thus under these conditions the tetrahydrate is so much more soluble than the phases containing more sodium sulfate as to be incapable even of meta-stable existence.

Summary.

In brief, this paper shows that crystals of $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ dissolve sodium sulfate as $\text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (a form otherwise unknown) to the extent of somewhat less than half the quantity corresponding to the same weight of sodium chromate in the supernatant solution.

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THE SOLUBILITIES OF ACIDS IN AQUEOUS SOLUTIONS OF OTHER ACIDS.

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The factors controlling addition-compound formation in systems of the type $\text{HX}:\text{HY}$ have been investigated in an earlier article.¹ It has been established that a weak acid in the presence of a strong acid behaves as a base, the stability of the resultant "salt" depending upon the difference in acidic strengths. Precisely the same factors are operative in determining the hydration of an acid in aqueous solution, the extent of compound formation between acid and water increasing uniformly with the strength of the acid.² When we come to consider the three-component system $\text{HX}:\text{HY}:\text{H}_2\text{O}$, the equilibria involved are naturally more complicated. By investigation of the solubility curve for one acid HX in solutions containing increasing concentrations of the second acid HY , however, we can obtain valuable evidence with regard to the existence and stability of compounds between the two acids in aqueous solution. The problem resembles in certain respects one already taken up in a previous paper³—the effect of other chlorides upon the solubility of silver chloride in water—but is obviously considerably more intricate in view of the wide variations possible in the solubilities and in the ionization constants of the two acids selected.

¹ Kendall, *THIS JOURNAL*, **36**, 1722 (1914).

² Kendall, Booge and Andrews, *ibid.*, **39**, 2303 (1917).

³ Kendall, Davidson and Adler, *ibid.*, **43**, 1496 (1921).