[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON AND DIVISION OF INDUSTRIAL RESEARCH, WASHINGTON STATE INSTITUTE OF TECHNOLOGY]

Phase Rule Investigation of the System Al_2O_3–SO_3–H_2O at 60°, Basic Region

BY JACK L. HENRY[1] AND G. BROOKS KING

During the course of development of a combined sulfuric–sulfurous acid leaching process for the extraction of alumina from clay, many problems have arisen. Important among these is the elimination of such impurities as silica, titania, iron and phosphorus from the basic aluminum sulfate produced by the process. The ratio of sulfate to alumina and also the physical characteristics of the product seem to depend to a large extent upon the conditions under which the basic salt is formed. In view of the fact that many basic aluminum sulfates have been reported in the literature, a systematic phase rule study seemed advisable to determine which of these are stable chemical individuals. Such a study has shed much light on the chemistry of the process and on the nature of the basic aluminum sulfate produced. Since a temperature range near 60° has been found most advantageous for the process,[2,3] the system was investigated at this isotherm.

Compounds reported in the literature which would be included in the over-all system, Al_2O_3–SO_3–H_2O are listed in Table I in terms of mole ratios of Al_2O_3 and SO_3 accompanied by a column giving the approximate number of different hydrates which have been reported for each of these compounds.

TABLE I

COMPOUNDS REPORTED IN LITERATURE

Mole ratio Al_2O_3	Mole ratio SO_3	Number of hydrates reported	Mole ratio Al_2O_3	Mole ratio SO_3	Number of hydrates reported
1	0	4	4	3	2
48	1	1	1	1	6
24	1	1	5	6	1
12	1	1	3	4	3
6	1	1	2	3	3
5	2	1	1	2	3
2	1	5	1	3	13
5	3	2	1	4	1
8	5	1	1	5	1
3	2	4	1	6	1

It is seen that at least thirty-nine basic aluminum sulfates have been reported as well as thirteen different hydrates of the normal salt and three acid salts. Many of these compounds are naturally occurring minerals, the composition of which has been established. That the entire fifty-five compounds listed exist as stable compounds is highly improbable. S. U. Pickering[4] regards most of the basic salts as mixtures with composition depending upon the conditions under which they are prepared, and considers those corresponding to naturally occurring minerals as true compounds. Mellor[5] states that many of the reported basic aluminum sulfates are no doubt intermediate stages in the hydrolysis of the normal sulfate. Many of the compounds cited have been prepared rapidly and no doubt under non-equilibrium conditions. Miller,[6] while investigating the effect of various ions on aluminum hydroxide, found that ions are carried down with the precipitate and are not removed by washing with water. He has suggested the possibility of a solid solution phenomenon. Charriou[7] has found that divalent ions could be removed by washing the precipitate with negative ions of equal or greater valence but not by monovalent ions. A. W. Thomas[8] explains the peculiar behavior of basic salts of aluminum sulfate on the basis of the Werner–Pfeiffer theory of olation. This theory provides a mechanism to account for the gradual increase in size of the hydrous oxide aggregates in solution. Haynes[9] states that adsorption takes place to a considerable extent when aluminum hydroxide is precipitated in the presence of foreign anions.

In view of these many possibilities, adsorption, formation of solid solutions or mechanical mixtures, and polymerization, it is not surprising that so great a number of basic aluminum sulfates has been reported. The question still remains as to what compounds exist in this system at 60° and atmospheric pressure as stable chemical individuals and over what concentration ranges they are stable. The acid region of the system Al_2O_3–SO_3–H_2O discussed previously[10] has shown the existence of four compounds stable under these conditions. This region is shown in Fig. 1 although the recalculated data are omitted.

In connection with the basic sector, Kremann and Huttinger[11] have studied the solubility of aluminum hydroxide in aluminum sulfate solutions over a wide range of concentrations at 20, 40 and 60°. They report the existence of three compounds corresponding to breaks in their solubility curves. $Al_2O_3 \cdot 3SO_3 \cdot 16H_2O$ (the normal

---

(1) Submitted in partial fulfillment of the requirements for the Ph.D. degree, the State College of Washington. Present address: Department of Chemistry, University of Nevada, Reno, Nevada.

(2) Redlich, *Ind. Eng. Chem.*, **38**, 1181 (1945).

(3) "Recovery of Alumina from Clay," Bulletin Washington State Institute of Technology, Pullman, Washington, No. 203 (1949).

(4) S. U. Pickering, *J. Chem. Soc.*, **91**, 1981 (1907).

(5) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, Longmans, Green and Company, London, p. 336–339.

(6) L. B. Miller, *U. S. Public Health Reports*, **39**, 1502 (1924).

(7) Charriou, *Compt. rend.*, **176**, 679, 1890 (1923).

(8) A. W. Thomas, *Paper Trade Journal*, **100**, No. 9, 36 (1935).

(9) H. G. Haynes, *Pharm. Journal*, **158**, 446 (1947).

(10) Henry and King, THIS JOURNAL, **71**, 1142 (1949).

(11) R. Kremann and K. Huttinger, *Jahrbuch d. k. k. geol. Reichsanstalt. Wein*, **58**, 637–648 (1908).

sulfate), and $Al_2O_3{\cdot}2SO_3{\cdot}12H_2O$ (corresponding to the mineral, *alumian*) were found to be the stable phases in the less basic region. However, they were unable to obtain enough solid phase for analysis in the more basic part of the system and were therefore unable to determine the composition of the third compound. They suspect that it is $Al_2O_3{\cdot}SO_3{\cdot}9H_2O$ which corresponds to the mineral, *aluminite*. H. Bassett[12] has been conducting a study of the system Al_2O_3–SO_3–H_2O at 25°, but it is as yet unpublished.

The present paper treats the basic region of the system Al_2O_3–SO_3–H_2O at 60° over SO_3 concentrations from 5.10 to 22.02%.

Materials and Apparatus.—From preliminary experiments on the basic system, it was found that equilibrium in this range could not be attained in as short a period of time as in the acid system. Consequently a new thermostat bath was designed which would give satisfactory performance over several months of continuous operation at 60 ± 0.1°. This thermostat was fabricated from sheet aluminum and insulated by double walls which were filled with vermiculite. To reduce excess evaporation of the water at high temperatures, a tight aluminum cover was designed. The water level was kept constant by a float valve which was fed from a distilled water reservoir by a siphon system. The most unique feature lies in the external drive of the equilibrium tube rotor. This was accomplished by a stainless steel shaft passing entirely through the bath. The shaft is secured by brass bearings on either end and by brass thrust collars. The water seals consist of machined magnesium packing glands which are packed with 0.25-inch asbestos pump packing. To the outer end of the shaft is attached a 7.5-inch machined magnesium pulley which is driven by a V-belt from a fractional horsepower motor and Boston gear-reducer mounted beneath the supporting platform. The gear ratio and pulley ratio are designed to drive the equilibrium tube rotor at 16 r. p. m. The tubes are easily secured to and removed from the rotor by aluminum spring clamps. The rotor is designed to hold 24 tubes. Attached to the rotor are eight aluminum blades which provide mechanical agitation of the water in the bath. The bath is heated by two 750-watt stainless steel rod-type immersion heaters. Control circuits include a sealed mercury thermoregulator and a mercury plunger relay which is energized by current flow through a gas tetrode. Highly satisfactory results have been obtained for continuous operation up to six months.

An electrodialyzer was employed to purify the aluminum hydroxide used in synthesizing basic aluminum sulfate complexes. It consists of three rubber compartments separated by cellophane partition diaphragms. The aqueous suspension to be dialyzed was placed in the center compartment, and carbon electrodes in the two outer compartments. Provision is made for passage of wash water through the two outer compartments.

Mallinckrodt analytical reagent aluminum sulfate and ammonium hydroxide were used in the synthesis of all basic complexes.

Methods of Synthesis.—Several methods of synthesis were attempted in preliminary studies. Most of these were found to be unsatisfactory. The method of dissolving freshly precipitated aluminum hydroxide in aluminum sulfate solution used by Kremann and Huttinger[11] seemed to offer more promise than other methods tried. This method was perhaps first described as early as 1810 by J. L. Gay-Lussac.[13] In order to produce a complex free from any substances other than aluminum oxide, sulfur trioxide and water it was necessary to produce a highly purified aluminum hydroxide. This was finally accomplished by precipitating the aluminum hydroxide from aluminum sulfate solution of known concentration with a slight excess of ammonia and electrodialyzing the suspension for two hours. The dialysis was carried on with constant agitation at 30 volts d. c. Wash water was passed through the apparatus at the rate of 40 to 60 ml. per minute. It was found that after two hours the suspension in the dialyzer contained less than 0.01% NH_4^+. The suspension was then filtered on a Buchner filter, washed several times, and then carefully removed from the filter paper in the form of a flat cake. Since the paste had to be used immediately, control samples of paste were previously analyzed to determine the composition and batch-to-batch consistency. This cake was then thoroughly mixed with a spatula. Since the composition of the paste thus produced is known approximately, it was possible to weigh out quantities and introduce them into tubes containing calculated amounts of aluminum sulfate and water to make a complex of approximately known composition.

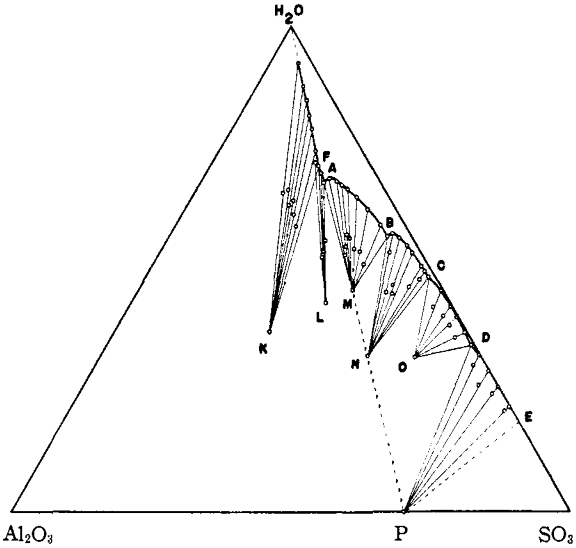

Fig. 1.—System Al_2O_3–SO_4–H_2O at 60°: K = $Al_2O_3{\cdot}SO_3{\cdot}6H_2O$, L = $Al_2O_3{\cdot}2SO_3{\cdot}11H_2O$, M = $Al_2O_3{\cdot}3SO_3{\cdot}16H_2O$, N = $Al_2O_3{\cdot}3SO_3{\cdot}9H_2O$, O = $Al_2O_3{\cdot}6H_2O{\cdot}15H_2O$, P = $Al_2O_3{\cdot}3SO_3$.

Methods of Analysis.—Aluminum was determined gravimetrically as aluminum oxide, by ignition at 1150°. The sulfate was determined gravimetrically as barium sulfate. In many cases the solid phase dissolved in 1:1 hydrochloric acid solution only after being held near the boiling point for fifteen to twenty minutes.

Solubility Determinations.—Various weight ratios of dialyzed aluminum hydroxide, aluminum sulfate and water were placed in glass tubes of 50-ml. capacity. The charged tubes were well stoppered and cotton-filled caps secured over the stoppers to hold them in place. The aluminum hydroxide dissolved completely in all cases except in those complexes which contained less than about 4 g. of aluminum sulfate per 40 g. total weight. Whereas the resulting solutions were slightly turbid, they contained no undissolved lumps of paste. Two grams of electrodialyzed aluminum hydroxide paste was used in most of the complexes. The tubes were then secured to the rotor and rotated in the bath at 60° until equilibrium had been established. Samples of the liquid phase were removed at intervals and analyzed for aluminum oxide to determine the progress in attainment of equilibrium.

Once equilibrium had been established, the tubes were removed from the rotor and placed on the rack where they were kept at 60° without agitation until the solid and liquid phases had separated. This done, samples of liquid were pipetted into weighing bottles, weighed and treated

---

(12) Personal communication (see M. P. Applebey), *J. Soc. Chem. Ind.*, **56**, 139–146T (1937).

(13) J. L. Gay-Lussac, *Ann. chim. phys.*, **74**, 193 (1810).

for analysis. The solid phase was quickly placed on a vacuum filter plate where a large amount of the liquid was removed within a few seconds. The semi-dried solid was then placed in weighing bottles, weighed, dissolved and treated for analysis. The method of wet-residues[14] was employed throughout.

Discussion of Results

After ten to twenty days, tie-lines in the region of high mole ratios of sulfur trioxide to aluminum oxide were fairly consistent, whereas those in the region of lower mole ratios were quite erratic. Behavior of tie-lines in the latter region would suggest either that equilibrium had not been attained or that possibly a continuous series of solid solutions prevailed. Although Kremann and Huttinger[11] had stated that in their study saturation was obtained in approximately three days, it was felt here that the complexes should be allowed more time in case equilibrium conditions had not been achieved. It was found that the reaction began to accelerate after twenty days and that not until after fifty days did the liquid show no further change in composition in most cases. In the more basic region samples had not reached equilibrium after four months.

Data for the system are given in Table II and shown graphically in Fig. 1. The acid system curves which have been fully discussed before[10] are now shown as curves AB, BC, CD and DE. A pronounced distortion of the shape and position of the solubility curves is noted with the change of units.

TABLE II

SYSTEM Al_2O_3–SO_3–H_2O, BASIC REGION, AT 60°

Solution, wt. %		Residue, wt. %		Solid[b] phase	*p*H of solution	Dev. in % Al_2O_3 by algebraic extrapn.
Al_2O_3	SO_3	Al_2O_3	SO_3			
10.04	22.02	15.80	28.26	L		−0.31
9.71	20.61	17.19	29.09	L		+ .08
9.59	20.46	17.59	29.55	L		+ .06
9.58	19.00	17.60	29.13	L[a]	2.58	− .06
9.50	18.58	18.06	29.54	L[a]-	2.59	+ .02
9.38	19.23	19.41	24.29	L + K	2.53	
9.17	18.97	19.35	22.43	K	2.47	− .54
8.43	17.42	19.23	21.64	K	2.68	− .62
8.26	17.20	19.63	21.55	K	2.78	+ .62
7.27	15.23	19.50	20.78	K	2.78	− .58
6.85	14.33	18.85	20.00	K	3.00	− .17
6.24	13.21	20.06	20.22	K	2.95	− .50
5.92	12.59	17.38	18.61	K	3.04	− .62
5.20	10.99	20.17	19.33	K	3.05	− .10
4.86	10.34	18.67	18.11	K	3.13	+ .42
3.97	8.41	17.18	16.39	K	3.20	+ .62
2.46	5.10	18.47	15.95	K	3.55	+ .55

[a] = Metastable. [b] L = $Al_2O_3 \cdot 2SO_3 \cdot 11H_2O$; K = $Al_2O_3 \cdot SO_3 \cdot 6H_2O$.

Data for the basic system include *p*H values for most of the liquid phases. Only two solid phases have been found in this region. Considering first the solubility curve FA in Fig. 1, it is seen that $Al_2O_3 \cdot 2SO_3 \cdot 11H_2O$ is the solid phase in equilibrium with solutions ranging in sulfur trioxide content from approximately 22 to 19.2%. The parallel nature of the tie-lines here makes it difficult to establish the exact degree of hydration of the salt by graphical extrapolation. However, the results obtained by algebraic extrapolation[15] seem to favor the 11-hydrate over the 12-hydrate reported by Kremann and Huttinger.[11] They found the solubility curve to extend from about 20 to 6% sulfur trioxide at 60°. From evidence shown in the present work it appears that they were working under non-equilibrium conditions throughout the greater portion of their study. Algebraic extrapolation showed an average deviation in per cent. aluminum oxide of +0.27 for the 10-hydrate, −0.04 for the 11-hydrate and −0.33 for the 12-hydrate. $Al_2O_3 \cdot 2SO_3 \cdot 11H_2O$ was mentioned briefly by H. Bassett[16] who stated that the compound is well crystallized and readily soluble in cold water with slow further hydrolysis. Undoubtedly this is the same compound here reported, for the salt herein described is white in color, readily soluble in water, after which it undergoes hydrolysis. The salt corresponds to the mineral "alumian."

For the solubility curve commencing at F and proceeding toward the water apex, $Al_2O_3 \cdot SO_3 \cdot 6H_2O$ is found to be the stable solid phase. This again is not in agreement with Kremann and Huttinger,[11] who suspected the naturally occurring mineral aluminite, $Al_2O_3 \cdot SO_3 \cdot 9H_2O$, to exist in this range. Although aluminite was expected here, algebraic extrapolations of the data indicated the 6-hydrate, which has an entirely different X-ray diffraction pattern from aluminite. The average deviation in per cent. aluminum oxide was +1.36 for the 5-hydrate, −0.05 for the 6-hydrate and −1.42 for the 7-hydrate. The compound $Al_2O_3 \cdot SO_3 \cdot 6H_2O$ is quite insoluble in water and appears as a soft white powder. Under 600 diameters the crystals appear rod-shaped. A compound corresponding to this composition was reported in 1888 by C. Bottinger[17] to be formed when aluminum sulfate was heated with sodium chloride in a sealed tube at 140°.

Evidence shows that this compound is stable at 60° over a very wide range of liquid compositions, extending from 19.2 to less than 5% sulfur trioxide. Time required to establish equilibrium exceeded forty days in all cases and reached one hundred and twenty days in the region of 8 to 10% sulfur trioxide. In the region between the water apex and about 5% sulfur trioxide the time required was so excessive that the work was not continued. Both solubility curves in the basic region show metastable extensions at their intersection.

Approximately twelve basic aluminum sulfates

---

(14) Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

(15) Hill and Ricci, THIS JOURNAL, **53**, 4305 (1931).

(16) H. Bassett, "Quarterly Reviews of the Chemical Society," Vol. I, No. 3, 246 (1947).

(17) C. Bottinger, Mellor, *loc. cit.*, Vol. V, p. 338.

shown in Table I would lie in the region covered by the solubility curves discussed. It is apparent that these reported compounds are not stable chemical individuals at 60° and atmospheric pressure.

In addition to the equilibrium study of the basic region of the system Al_2O_3–SO_3–H_2O, it is of interest to view the make-up of the basic system before equilibrium has been attained. After hydrolysis had proceeded for two to three weeks, analysis showed a solubility curve displaced slightly toward the aluminum oxide apex from the stable curve associated with the solid $Al_2O_3 \cdot SO_3 \cdot 6H_2O$. Tie-lines on this curve had a pronounced divergent nature, such that the mole ratios of the solid phases varied considerably from one another. The range over which these diverging tie-lines extend corresponds to a mole ratio of aluminum oxide to sulfur trioxide in the solid phase of 1 to about 0.3. The solid phase in this region showed no X-ray diffraction pattern. It is obvious from this that a basic aluminum sulfate of nearly any composition could be produced under non-equilibrium conditions by merely varying the proportion of the reactants. Undoubtedly many of the thirty-nine basic aluminum sulfates given in Table I have been produced under similar non-equilibrium conditions. These non-equilibrium solids vary in physical form. Over a short region of liquid composition near 4% aluminum oxide and 6% sulfur trioxide the solids are quite granular, while on either side of this range the solids are slimy and difficult to filter. Microscopic examination shows that the solid is made up of very small transparent spheres, the granular nature of some of the solids being due to the presence of the spheres in the form of large clusters.

The granular basic aluminum sulfate produced by the alumina-from-clay extraction process was found to have the same physical properties as these non-equilibrium solids and showed no X-ray diffraction pattern.

Over a portion of the non-equilibrium range tiny rod-shaped nuclei were observed to be formed after approximately twenty days. Once this nucleation had taken place, the crystallization of the compound $Al_2O_3 \cdot SO_3 \cdot 6H_2O$ proceeded for a period of several days until the mass was composed entirely of the crystals.

X-Ray diffraction patterns were studied for each of the solid phases using Cu K-α-1 radiation. Relative intensities of the lines were estimated by comparison with a standard sodium chloride pattern of known intensity relationships and *d* values calculated from the Bragg equation. The diffraction data are given in Table III. Lines of relative intensity less than 0.1 have been omitted.

TABLE III

X-RAY DIFFRACTION DATA:

Intensity	*d*	Intensity	*d*	Intensity	*d*
A. COMPOUND $Al_2O_3 \cdot 2SO_3 \cdot 11H_2O$					
0.9	6.77	0.2	2.70	0.3	1.84
.8	5.72	.6	2.60	.4	1.79
.9	4.94	.6	2.54	.2	1.76
.9	4.47	.4	2.43	.2	1.74
.2	4.33	.2	2.39	.2	1.71
.2	4.17	.1	2.33	.2	1.66
1.0	4.01	.1	2.27	.2	1.62
1.0	3.69	.1	2.24	.2	1.57
0.1	3.48	.1	2.24	.1	1.55
.3	3.36	.3	2.14	.2	1.52
.3	3.21	.4	2.10	.1	1.49
.3	3.11	.4	2.00	.1	1.46
.7	2.87	.3	1.89	.1	1.38
		.1	1.86		
B. COMPOUND $Al_2O_3 \cdot SO_3 \cdot 6H_2O$					
0.9	7.75	0.5	3.31	0.1	2.00
.6	6.73	.4	3.09	.4	1.96
.3	5.97	.2	2.97	.1	1.92
.3	5.67	.1	2.89	.5	1.87
.2	5.35	.3	2.83	.2	1.79
.9	4.64	.1	2.78	.2	1.75
1.0	4.40	.5	2.61	.1	1.71
0.2	4.24	.1	2.51	.5	1.63
.1	4.07	.1	2.46	.2	1.58
.1	3.90	.3	2.27	.1	1.55
.1	3.77	.3	2.21	.1	1.48
.6	3.69	.1	2.18	.1	1.46
.5	3.41	.5	2.12		

X-Ray patterns of several complexes near the water apex which failed to reach equilibrium within four months show lines of new individuals. The lines are very diffuse and of low intensity, however. Nothing can be said of these compounds at this time. Several investigators[18,19] have found that whereas freshly precipitated aluminum hydroxide shows no X-ray pattern, a pattern corresponding to the mineral hydrargillite, $Al_2O_3 \cdot 3H_2O$, is found from the aged precipitate. Goudriaan[20] has found $Al_2O_3 \cdot 3H_2O$ to be the stable phase in the aluminum oxide-rich portion of the ternary system Al_2O_3–Na_2O–H_2O at 25°. Hydrargillite is probably the stable phase at one extreme of the system under discussion.

Acknowledgment.—The authors wish to acknowledge their indebtedness to several persons for their aid in the project: to M. F. Adams for many helpful suggestions; to S. A. Duran for assistance in making X-ray diffraction studies, and to Sidney Finch for assistance in design and construction of the thermostat bath.

Summary

The system Al_2O_3–SO_3–H_2O, basic region, has been investigated at 60° and at atmospheric

---

[18] R. Fricke, *Z. anorg. chem.*, **166**, 244 (1927).

[19] Huttig and Wiggenstein, *ibid.*, **171**, 323 (1928).

[20] F. Goudriaan, *Proc. Acad. Amsterdam*, **23**, 129 (1920), *Rec. trav. chim. phys. bas.*, **41**, 82 (1922).

pressure over sulfur trioxide concentrations from 5.10 to 22.02%. Two stable solid phases have been found to exist in this range: $Al_2O_3 \cdot SO_3 \cdot 6H_2O$ and $Al_2O_3 \cdot 2SO_3 \cdot 11H_2O$. Equilibrium has been attained over the entire region studied. The investigation has given evidence that many basic aluminum sulfates reported in the literature are not stable chemical individuals at 60° and atmospheric pressure.

PULLMAN, WASHINGTON RECEIVED JUNE 17, 1949

[PUBLICATION NO. 57 OF THE RESEARCH LABORATORIES, MUTUAL CHEMICAL COMPANY OF AMERICA]

Double Alkali Chromates of Some of the Transition Elements

BY WINSLOW H. HARTFORD AND KEITH A. LANE

An important group of compounds of this type was first described by Gröger.[1] Although variously formulated in subsequent literature, they possess the oxide formula $M^{i}_2O \cdot 4M^{ii}O \cdot 4CrO_3 \cdot 3H_2O$. Salts were described where M^{i} and M^{ii} were potassium and zinc, potassium and copper, potassium and cadmium, potassium and cobalt, NH_4 and cadmium, and NH_4 and cobalt, respectively. The "zinc yellow" of commerce has recently been identified as being composed principally of $K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$; the situation having been clarified by published analyses[2,3] and preparation of the compound in well-defined crystals by Tarr, Darrin and Tubbs.[3] These workers also prepared the sodium zinc salt in a state of purity by reaction of sodium tetrachromate solution on a suspension of zinc oxide, a method yielding a finely divided product suitable for use as a pigment,[4] but not entirely free from zinc oxide or susceptible of easy examination to determine uniformity.

Because of the probability of preparing additional compounds of this general type, attempts were made to prepare unlisted compounds of sodium, ammonium and potassium with cadmium, cobalt, copper, nickel and zinc.

Experimental

All compounds were first investigated by dropwise addition of the alkali chromate solution to a boiling solution of the appropriate metal oxide or carbonate in excess chromic acid. Products were filtered off, washed with cold water, alcohol and ether, and dried in warm air. This method was modified on occasion by the addition of alkali nitrates or acetates to the heavy metal oxide–chromic acid solution to change concentrations of alkali ion.

Further investigation of conditions of precipitation was made by addition of alkali dichromates to heavy metal acetates to provide a buffered solution, and also by the dropwise addition of both alkali chromate and heavy metal dichromate solution to a solution which could be maintained at desired values of hexavalent chromium, alkali salt, heavy metal and hydrogen-ion concentration.

The following well defined, previously undescribed compounds were obtained:

Sodium Copper Chromate.—Dropwise addition of 3.3 molal sodium chromate solution to a boiling solution of 40 g. of cupric oxide and 150 g. of chromium trioxide in 200 g. of water gave a maroon crystalline precipitate. Precipitation started at a *p*H of about 1 and was complete at a *p*H of 4, when substantially all the copper was precipitated and no further precipitate was noted on further addition of chromate. The product was mostly crystalline aggregates although an occasional diamond-shaped single crystal 0.005 to 0.01 mm. in length, was seen. Calculated for $Na_2O \cdot 4CuO \cdot 4CrO_3 \cdot 3H_2O$: Na_2O, 7.43; CuO, 38.15; CrO_3, 47.94; H_2O, 6.47. Found: Na_2O, 7.31; CuO, 38.27; CrO_3, 47.68; H_2O, 6.34; density, d^{30}_{4} 3.57.

To check further the chemical individuality of this material, analyses were made of precipitate removed from the reaction mixture as the precipitation progressed. The following results were obtained at various *p*H values:

*p*H	CrO_3 content of precipitate, (theory 47.94)
~1	47.42
2.52	48.98
3.56	47.53
3.97	47.38

All precipitates were similar in color and crystalline appearance to the product described above.

The product was also obtained by dropwise addition of two solutions, one containing 86 g. of cupric carbonate (57% CuO) and 150 g. of chromium trioxide in 400 g. of water, the other 3.9 molal sodium chromate solution, to a boiling solution of 250 g. of sodium dichromate dihydrate in 500 g. water. When the *p*H was such that Cu^{++} was present in the solution in appreciable quantity, as shown by a brownish tinge to the solution, crystals were readily obtained, which were identical with those obtained above, but much larger in size. Single crystals were obtained having a length of 0.16 mm. when the *p*H was maintained between 2.6 and 3.1. The crystals are maroon, highly refracting, transparent, tabular, and diamond shaped, with an acute angle of about 63° as measured on the microscope stage. They contained 47.51% CrO_3.

When concentration conditions are such that Cu^{++} is not present in solution, a brown amorphous precipitate is obtained, much lower in CrO_3 and sodium content. This is apparently the previously reported[5] hydrous basic chromate, $3CuO \cdot CrO_3 \cdot xH_2O$. It dissolves immediately from the double salt crystals when the *p*H is lowered and the Cu^{++} concentration increased.

The reaction as described above was also carried out at room temperature. The product consisted of smaller crystals than the above, but still was similar in appearance and analysis; CrO_3 = 47.38%.

Sodium Cobalt Chromate.—Dropwise addition of 3 molal sodium chromate solution to a boiling solution of 59.5 g. of cobaltous carbonate and 150 g. of chromium trioxide in 300 g. of water yielded a crop of gray-black

---

(1) M. Gröger, *Sitzber. Akad. Wien*, **112**, 263 (1903); **113**, 155 (1904); *Z. anorg. Chem.*, **49**, 196 (1906); **58**, 412 (1908).

(2) A. A. Brizzolara, R. R. Denslow and S. W. Rumbel, *Ind. Eng. Chem.*, **29**, 656 (1939).

(3) O. F. Tarr, M. Darrin and L. G. Tubbs, THIS JOURNAL, **66**, 929 (1944).

(4) O. F. Tarr and M. Darrin, "Process of Preparing Zinc Yellow Pigments," U. S. Patent 2,415,394, February 4, 1947.

(5) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, p. 261, Longmans, Green and Co., New York, 1931.