TABLE III

HIGH-TEMPERATURE HEAT CONTENT OF $Ba(NO_3)_2$ (CAL. PER MOLE)

T, °K.	$H_T - H_{298.16}$ Exptl.	$H_T - H_{298.16}$ Eqn. 3	Deviation	% Deviation
411.1	4,434	4,454	+20	+0.4
448.9	6,077	6,098	+21	+ .3
496.2	8,230	8,223	− 7	− .1
549.8	10,788	10,756	−32	− .3
626.1	14,549	14,560	+11	+ .1
693.5	18,101	18,112	+11	+ .1
769.9	22,339	22,346	+ 7	.0
820.8	25,299	25,289	−10	.0
862.1	28,363	(premelting)		

TABLE IV

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	$Mg(NO_3)_2$		$Ca(NO_3)_2$		$Ba(NO_3)_2$	
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole
350	1,821	5.63	1,962	6.07	1,947	6.00
400	3,782	10.81	3,958	11.40	3,963	11.39
450	5,866	15.77	6,053	16.32	6,132	16.49
500	8,153	20.58	8,340	21.14	8,410	21.29
550	10,569	25.19	10,687	25.61	10,799	25.84
600	13,118	29.62	13,151	29.90	13,234	30.08
650			15,738	34.04	15,780	34.15
700			18,409	38.00	18,453	38.11
750			21,139	41.76	21,218	41.93
800			23,974	45.42	24,070	45.61
850					27,007	49.17

Table IV is a compilation, at 50° intervals, of the heat content and entropy above 298.16°K. of magnesium nitrate, calcium nitrate, and barium nitrate. These values have been derived from smoothed curves drawn through points representing the experimental data.

Summary

High-temperature heat content measurements of magnesium nitrate, calcium nitrate, and barium nitrate were made from about 100° up to as high a temperature as was permitted by the thermal stability of each substance.

Heat content and specific heat equations, adequately representing the experimental data, have been derived for each nitrate.

The entropy increments above 298.16°K., at 50° intervals, have been tabulated along with smoothed values of the heat contents.

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[CONTRIBUTION FROM RESEARCH LABORATORIES, MUTUAL CHEMICAL COMPANY OF AMERICA]

Crystallized Basic Zinc Chromates

BY O. F. TARR, MARC DARRIN AND L. G. TUBBS

The yellow pigment which is ordinarily produced by the reaction of acidified zinc oxide and potassium bichromate is known as zinc yellow. For almost a century there has been controversy as to whether it is a definite chemical compound, an adsorption complex or a mixture. The great variation in analyses and impurities, the selective solution of CrO_3 and K_2O, and a lack of crystalline form, led Mellor[1] to consider the various suggested formulas as representing adsorption products rather than a pure chemical compound. Although recent investigators[2,3] have reported some analyses corresponding fairly closely to molecular proportions of the combined oxides, and the major evidence[2,4] indicates the probable existence of the compound, $K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$, no prior investigator has reported the preparation of a pure crystallized compound. The authors obtained well-defined crystals having analyses corresponding to simple molecular proportions by the following procedure.

Basic Potassium Zinc Chromate

Preparation.—Zinc yellow having an analysis corresponding to the formula $K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$ was prepared by the direct reaction between an aqueous suspension of zinc oxide and a solution of potassium tetrachromate,[5] thus

$$4ZnO + K_2Cr_4O_{13} + 3H_2O \longrightarrow K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$$

On separation and drying the zinc yellow appeared to be a non-crystalline powder. When suspended in water it slowly underwent partial decomposition, releasing into solution a mixture of K_2CrO_4 and $K_2Cr_2O_7$. Equilibrium was reached when the concentration of dissolved chromate and bichromate was equivalent to about 15 g. of $K_2Cr_2O_7$ per liter.

Ten grams of the above zinc yellow was suspended in a solution containing 22.5 g. of $K_2Cr_2O_7$ in 1500 ml. of water, and brought into solution at room temperature by the addition of a minimum amount of nitric acid. This solution was slowly neutralized at 80° without mechanical agitation, with a solution containing 5 g. of potassium hydroxide and 20 g. of potassium chromate per liter. Heat was applied at the edge of the beaker and the caustic solution was added dropwise to the rising convection current. After the addition of about 300 ml., which required from six to twenty-four hours, small crystals could be seen

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(1) W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1931, Vol. 11, p. 279.

(2) A. A. Brizzolara, R. R. Denslow, and S. W. Rumbel, *Ind. Eng. Chem.*, **29**, 656–657 (1937).

(3) I. V. Riskin and G. Pugacheva, *J. Appl. Chem.* (U. S. S. R.), **12**, 1780–1785 (1939).

(4) M. Gröger, *Sitzber. Akad. Wien*, **113**, 155 (1904).

(5) O. F. Tarr and Marc Darrin, U. S. Patent Appl., Ser. 403,707 (1941).

in the convection stream, with larger, well-defined, transparent yellow crystals (Fig. 1) settling out loosely on the bottom of the beaker. The *p*H of the reaction solution at this time was 6.4. When the reaction was continued to a higher *p*H (about 6.7) an additional yield was obtained of smaller crystals of the same system and class. The analysis was the same for all crystals and the zinc yellow from which they were obtained. Reaction periods extending over several weeks, also long standing at various temperatures, did not increase the size of single crystals—although some agglomerates were formed. Increasing the speed of neutralization resulted in a decrease in the size of the crystals, down to the precipitation of a powder similar to the original zinc yellow.

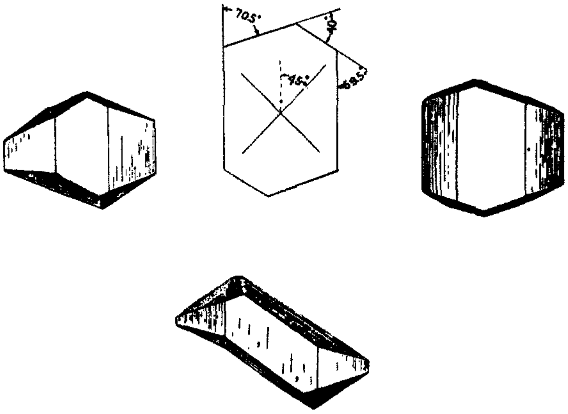

Fig. 1.—Basic potassium zinc chromate crystals.

Description.—The crystals (Fig. 1) were small, elongated, doubly-terminated, transparent yellow plates, belonging to the triclinic system, pinacoidal class. These crystals were hard but very friable. Maximum size observed for a single crystal was 10 × 50 × 90 μ; plane angles of crystal outline measured 70.5°, 40°, 69.5°; crystals were strongly birefringent but not pleochroic. Indices of refraction were very high, being in the neighborhood of 2.0; extinction angle was about 45°, and oblique to the length of the crystal. One of the optic axes was oblique to the plate making an angle of about 21° with the normal to the plate. Dispersion was extreme, and greater at the red end of the spectrum than at the violet. Specific gravity, d^{25}_4 3.47. The crystals were soluble in alcohol, slightly soluble in water with partial decomposition to a less soluble product, and readily soluble in acids or ammonium hydroxide. They were stable in air at room temperature but lost water slowly above 100°.

Anal. Calcd. for $K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$: K_2O, 10.8; ZnO, 37.2; CrO_3, 45.8; H_2O, 6.2. Found: K_2O, 10.7; ZnO, 37.3; CrO_3, 45.4; H_2O, 6.5.

Basic Sodium Zinc Chromate

Riskin and Pugacheva[3] prepared a large variety of zinc yellows containing sodium oxide as replacement for potassium oxide, but no evidence has been presented of the existence of the pure sodium compound. By a method similar to that employed in making the potassium compound, the authors obtained quantitative yields of a new crystallized compound directly from the reaction

$$4ZnO + Na_2Cr_4O_{13} + 3H_2O \longrightarrow Na_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$$

Under the microscope at 350 diameters the product appeared as small, highly refractive, transparent yellow, diamond-shaped plates, or short prisms; specific gravity, d^{25}_4 3.24. General properties were similar to those of the potassium compound. Analysis corresponded quite closely to the formula, $Na_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$, as regards ratio of sodium oxide to zinc oxide to chromic anhydride; but the crystals were a little higher in water than $3H_2O$, probably due to difficulty of complete drying without decomposition.

Anal. Calcd. for $Na_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$: Na_2O, 7.4; ZnO, 38.7; CrO_3, 47.5; H_2O, 6.4. Found: Na_2O, 7.4; ZnO, 38.3; CrO_3, 46.9; H_2O, 7.3.

Basic Ammonium Zinc Chromate

The ammonium compound was prepared in the same general manner as the potassium compound, but it was more difficult to obtain well-defined crystals. In preparing crystals of the ammonium compound it was found best to use a higher concentration and a little lower *p*H (5.3 to 5.7). Under the microscope at 350 diameters the crystals appeared as small, highly refractive, transparent yellow prisms, having a low order of symmetry. The product, however, did not consist entirely of crystals of this type. Mixed with these prismatic crystals were a few thin, transparent, yellow, hexagonal plates. All crystals were too small or too friable to separate by mechanical means. There was some variation in the analyses of crystals from different batches of the ammonium compound. The analysis of a typical batch of these crystals corresponded fairly closely to the formula, $(NH_4)_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$, as regards percentages of zinc oxide and chromic anhydride; but the crystals were higher in ammonia with a corresponding decrease in water.

Anal. Calcd. for $(NH_4)_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$: ZnO, 39.2; CrO_3, 48.1; $(NH_4)_2O$, 6.2; H_2O, 6.5. Found: ZnO, 39.8; CrO_3, 47.5; $(NH_4)_2O$, 8.0; H_2O, 4.6.

Alkali-Earth Compounds

The corresponding alkali-earth compounds were not obtained by the described method. When a solution of calcium tetrachromate, or magnesium tetrachromate, was substituted for potassium tetrachromate, the product was a basic zinc chromate containing only a trace of alkali earth.

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Summary

By the preparation of new, well-defined, crystals of a series of basic zinc chromates in which the oxides are combined in simple molecular proportions, it is shown that some of these products are definite chemical compounds, verifying the belief of the majority of prior investigators.

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