REACTIONS IN FUSED SALT MEDIA—I. A STUDY OF THE BASIC LEAD CHROMATES

BY J. F. G. HICKS

Heintz,¹ working in this laboratory, prepared lead chromate and lead carbonate in a reaction-medium, or vehicle, of fused sodium chlorid. It was suggested² that the writer continue the investigation with a view to studying the mechanism of these fusion-reactions. The basic lead chromates offered an interesting problem, and were studied in some detail. Some analogies to hydrolysis have been noted, and the investigation would seem to throw some light on the mechanism of formation of certain "basic" salts.

The experimental work herein recorded is admittedly preliminary, and certain phases of the investigation are still in progress. With two possible exceptions ($\text{PbO} \cdot 4\text{PbCrO}_4$ and $\text{PbCrO}_4 \cdot 4\text{PbO}$) no new compounds are noted, nor was it originally intended to prepare any. However, it is thought that the mechanism of such reactions may be of interest.

Apparatus.—A "surface-combustion" furnace³ was used for the rapid fusion of sodium chlorid (m. p., 820°) where such fusions were of larger volume than 50 cc. No special heating-device was necessary for smaller fusions or for those of lower melting-points. Cooling-curve data were obtained by the use of a Pt/Pt-Rh thermo-couple.

Materials.—Sodium chlorid was first used as a solvent, but in the case of the "basic lead chromates" (*q. v.*) a 50–50 molar % mixture of sodium and potassium nitrates (eutectic at

¹ Chem. Engr. Thesis, Stanford University, 1920; unpublished.

² Acknowledgment for this suggestion and many others during the course of the investigation is here made to Profs. R. E. Swain and S. W. Young, of this laboratory.

³ Schein (with S. W. Young): "The Precipitation of Potassium Sulfate Fumes." Thesis for degree Chemical Engineer, Stanford University, 1920. Unpublished.

218°)¹ was used. This flux was selected because of its low melting point, and because of the marked interaction between sodium chloride flux and lead oxide (*q. v.*).

Procedure.—Components of reaction-mixtures were weighed out in multiples or fractions of mols. It was found advisable to pour the melted flux over the solid reaction-mixture, allow it to stand for a short time, and then gradually stir the whole mass. This procedure was evolved because the fused nitrates do not “wet” solid lead oxide readily; if the latter is added to the melted flux it floats, and is only stirred in with great difficulty, involving considerable loss of time.

Experimental.—Dried lead oxid (PbO) and an excess of anhydrous sodium chromate were mixed with dried sodium chlorid, fused, and the mass kept in a state of quiet fusion for ten minutes, and then poured into water. The characteristic “chrome yellow” resulted, and the reaction was nearly complete.

Anhydrous sodium dichromate is not suited to reactions of this type, the resulting precipitate being badly discolored (greenish brown), and containing compounds of trivalent chromium, as was indicated by the fact that the original yellow color could be restored by fusion (or boiling in water) with sodium peroxid. The presence of trivalent chromium may be accounted for by considering that sodium dichromate dissociates in sodium chlorid fusion, after which the dissociation product chromic anhydrid decomposes into chromium sesquioxid and oxygen, which oxygen oxidizes the PbO to PbO_2 , causing further discoloration. Potassium dichromate is also unsuited for these reactions, but is less objectionable than the sodium salt. Ordinarily, both sodium and potassium dichromate dissociate at temperatures well above that of these fusions (about 880°) when either is heated alone, but this dissociation apparently takes place at a much lower tempera-

¹ Landolt-Bornstein-Roth: “Physicalische-chemische Tabellen,” 4 Auflage, pp. 611-635.

ture in a solution of fused sodium chlorid. Chromic anhydrid decomposes at 250° .¹

Basic Lead Chromates.—Two such compounds, PbO.PbCrO_4^2 and PbO.2PbCrO_4^3 are described in the literature. The former has been prepared by the alkaline hydrolysis (NaOH) of lead chromate, or by fusing the same compound with potassium nitrate, and the latter, together with lead chromate, "by allowing solutions of lead nitrate and potassium chromate to diffuse into one another."⁴ Both are described as red compounds. The former was readily prepared as described (see analysis 1, Table II) but it was not found possible to prepare the compound PbO.2PbCrO_4 by the method given. A mixture of one mol lead oxid and two of lead chromate was fused with the nitrate flux, and yielded a scarlet-red mass, which analysis showed to contain:

		Theory for PbO. 2PbCrO_4
PbO	75.08%	76.98%
CrO ₃	24.90%	23.02%
	99.98%	100.00%

If a 50–50 molar % mixture of lead oxid and lead chromate were allowed to interact in fused sodium chlorid solution, a substance closely approximating the composition PbO.PbCrO_4 resulted. If the melted fusion were poured into water, the resulting precipitate was of a deep orange color; if allowed to cool slowly, it was red. The equilibrium diagram (*q. v.*) points to the cause of this difference in color as partial dissociation of the "basic lead chromate" at the temperature of the bath. Analyses showed:

¹ Roscoe and Schorlemmer: "Treatise on Chemistry," 5th edition, 2, p. 1029.

² Cox: Jour. Am. Chem. Soc., 28, 12, 1902; Zeit anorg. Chem., 50, 232.

³ Roscoe and Schorlemmer: "Treatise on Chemistry," 5th edition, 2, pp. 1033–1034.

⁴ See note (3).

I. Poured into water (orange)		II. Slowly cooled (red)	Theory for $\text{PbO} \cdot \text{PbCrO}_4$
PbO	81.91%	81.26%	81.69%
CrO ₃	17.91%	18.67%	18.31%
	99.82%	99.93%	100.00%

A 50-50 molar % mixture of sodium and potassium nitrates was used as the vehicle for subsequent attempts to prepare "basic lead chromates, on account of its relatively low melting point (eutectic at 218°). Beside the red substance $2\text{PbCrO}_4 \cdot \text{PbO}$, three other red substances were prepared in the nitrate flux; they approximated the compositions $\text{PbO} \cdot \text{PbCrO}_4$, $2\text{PbO} \cdot \text{PbCrO}_4$ and $3\text{PbO} \cdot \text{PbCrO}_4$, respectively; whether slowly or rapidly cooled, the red color persisted. Their analyses follow:

TABLE I

	PbO	CrO ₃
1. PbCrO_4 , nitrate flux, 225° - 230° , 90 minutes	80.37%	19.60%
1a. $\text{PbCrO}_4 + \text{PbO}$, nitrate flux, same conditions	81.86%	18.14%
Theory for $\text{PbCrO}_4 \cdot \text{PbO}$	81.69%	18.31%
2. $\text{PbCrO}_4 + \text{PbO}$, nitrate flux, 100 minutes	88.26%	11.74%
Theory for $2\text{PbO} \cdot \text{PbCrO}_4$	87.00%	13.00%
3. $\text{PbCrO}_4 + \text{PbO}$, nitrate flux, 200 minutes...	90.21%	9.83%
Theory for $3\text{PbO} \cdot \text{PbCrO}_4$	89.82%	10.08%

Insofar as analysis is concerned, there is little difference between the red substances prepared by (1) alkaline (NaOH) hydrolysis of lead chromate, (2) fusion of lead chromate with nitrate flux, (3) fusion of lead chromate and lead oxid (50-50 molar %) with nitrate flux, (4) fusion of lead chromate and lead oxid (same mixture) with sodium chlorid flux, and the orange substance prepared by fusion of the same mixture of lead chromate and lead oxid in sodium chlorid flux, but poured quickly into cold water. Comparative analyses follow:

TABLE II

	PbO	CrO ₃
I. PbCrO ₄ +10% NaOH, boiled 1 hour (red) .	80.52%	19.41%
II. PbCrO ₄ +nitrate flux, 225°-230°, 30 minutes (red).....	80.37%	19.60%
III. PbCrO ₄ +PbO, nitrate flux, 225°-230°, 10 minutes (red).....	81.86%	18.14%
IV. PbCrO ₄ +PbO, sodium chlorid flux, 10 minutes (880°) slowly cooled (red)..	81.26%	18.67%
V. PbCrO ₄ +PbO, sodium chlorid flux, 10 minutes (880°) quickly poured into cold water (orange).....	81.69%	17.91%
VI. Theory for PbCrO ₄ .PbO.....	81.69%	18.31%

A consideration of the above, and the differences in method of preparation renders the mechanism of reaction and the constitution of the compounds (phase-relations (*q. v.*) clearly indicate the compound PbCrO₄.PbO) important questions. That I is an hydrolysis-product can scarcely be doubted; the reaction forming it would, of course, be ionic. The others (II-V) may be products of a reaction similar in mechanism to hydrolysis, but there is nothing to show how the molecules PbO and PbCrO₄ are afterward combined. If the reactions are similar in mechanism to hydrolysis, it follows that there will be an interaction between the ions of solvent and solute, hence we must, on this assumption, consider at least this much of the process of formation of basic lead chromates an ionic reaction. There is no reason to believe that the fused nitrates behave any differently from any other flux or solvent (see tests on used flux), hence the general name "solvolysis" for this type of reaction is proposed;¹ it would of course include hydrolysis and ammonolysis. Apparently the color and composition of a given red basic lead chromate prepared as above depend solely upon the time allowed for solvolysis. An inspection of Table I will indicate that the PbO might even be omitted; that the formation of a given red substance depends upon the removal of CrO₃, which would require a longer time without the added PbO.

¹ Suggested by E. C. Franklin.

All this would tend to show that the red substances are produced in two steps: (1) lead chromate solvolyzes; (2) it combines with PbO. This does not carry one very far in the way of an explanation, nor does it decide whether the red substances are constituted:

The logical conclusion would be that the substances were either "higher order" compounds (1, 2) or the lead salt of a chromic acid containing four hydroxyl-groups, i. e., an ordinary "valence compound" (3). Such a chromic acid would correspond to what might otherwise be termed a "hydrate" of the ordinary chromic acid, i. e., $\text{H}_2\text{CrO}_4 \cdot \text{H}_2\text{O}$ (H_4CrO_5). This "hydrate" of chromic acid is strictly analogous to one of those known for sulfuric acid.^{1,2} It must also be borne in mind, that beside the two structure-possibilities already mentioned one must include the possibility that these red compounds are true basic salts. Such conception excludes the possibility of other than the ordinary chromic acid, but not the "higher order compounds" already referred to. Again, from the standpoint of the Phase Rule, any composition is possible, depending on temperature, pressure and concentration. None of the explanations offered are satisfactory for a substance of the composition $3\text{PbO} \cdot \text{PbCrO}_4$ nor are they sufficient to enable the prediction of such a compound. A study of the freezing-point diagram, (*q. v.*) however, does not reveal any such compound; at that composition there is indicated a solution of $\text{PbCrO}_4 \cdot \text{PbO}$ and $\text{PbCrO}_4 \cdot 4\text{PbO}$ in each other.

¹ Pickering: Jour. Chem. Soc., **57**, 1339 (1895).

² See Stearns and Young: Jour. Am. Chem. Soc., **38**, 10, 1953, footnote 1. These observers arrived at a similar conclusion concerning the salts of "orthosulfuric" acid. The present conclusion as to "orthochromic" acid was reached independently and without knowledge of the work of Stearns and Young. Dr. Stearns called the writer's attention to the same in the course of a conversation some three months later.

The behavior of a 50–50 molar % mixture of lead oxid and lead chromate in fused sodium chlorid solution is also worthy of notice. As has been previously noted, when the fusion containing such a mixture is poured into water, an orange-colored mass results; allowed to cool slowly, it is red. As the compositions of the red and orange substances are very nearly identical (Table II), the difference in color would seem to indicate a partial dissociation at the temperature of the bath (about 880°), that is $\text{Pb}_2\text{CrO}_5 \rightleftharpoons \text{PbO} + \text{PbCrO}_4$ occurs, and the sudden chilling “fixes” the system in this condition. Hence the orange-colored mass might be looked upon as a mixture of lead oxid and lead chromate, and the red mass as a definite compound, Pb_2CrO_5 . The freezing-point diagram verifies the assumption of dissociation at higher temperatures because:

1. The compound $\text{PbCrO}_4 \cdot \text{PbO}$ is clearly defined (C_3) in equilibrium chart.

2. The maximum C_2 in the freezing-point curve occurs at 65–35 molar % instead of at 66.7–33.3 molar % as would be expected, and which latter corresponds to the compound $2\text{PbCrO}_4 \cdot \text{PbO}$ already known.¹ The shifting of this maximum can be explained in terms of such a dissociation.

3. Boiling the orange-colored mass with 10% sodium hydroxid solution for 48 hours did *not* produce the red substance, which apparently indicates that the dissociation-product PbO dissolves more readily in 10% NaOH solution than the dissociation-product PbCrO_4 . Boiling with more concentrated NaOH solution simply dissolves the entire substance.

In attempting to secure experimental evidence of the mechanism of formation of these “basic lead chromates,” the following facts were brought out:

1. A random mixture of lead oxid and lead chromate, heated to fusion without flux, and slowly cooled, yielded a red product.

2. A 50–50 molar % mixture of lead oxid and lead chro-

¹ Pogg. Ann., 28, 162.

mate treated in the same manner yielded a red product containing 81.67% PbO and 18.28% CrO₃.

3. One mol lead oxid and five of sodium chlorid were fused and kept in a state of quiet fusion for two hours. 99.4% PbO was solvolized to PbCl₂.

4. One mol lead chromate and five of sodium chlorid were treated as in 3. A muddy-brown to orange mass resulted, which analyzed as follows:

Solvolysis residue		Theory for PbCrO ₄
PbO	70.20%	68.73%
CrO ₃	29.80%	31.27%

showing that 8.25% of the original CrO₃ had been removed by solvolysis. The brown mass closely approximates the composition 17PbO.16CrO₃, to which theory assigns

PbO	70.32%
CrO ₃	29.68%

An inspection of the freezing-point diagram reveals no such compound; the ratio 17:16 is so nearly 1:1 (50-50 molar %) that none should be expected.

5. PbCrO₄ was treated for an hour with nitrate flux (fusion poured on solid PbCrO₄) at 225°-230° without stirring. After solidification, the upper layer was bright yellow in color and the lower a bright red. Samples of the yellow solid dissolved quickly and completely in water at room temperatures, and reacted strongly for (CrO₄)⁼ but not for Pb⁺⁺ as was to be expected from its dissolving without precipitation of PbCrO₄. The lower bright red layer contained.

PbO	73.10%
CrO ₃	26.80%

showing the removal of 14.3% of the original CrO₃ by solvolysis. This red substance closely approximates the composition 5PbO.4CrO₃; that is, 4PbCrO₄.PbO, represented by the point C₁ in the diagram.

6. A similar experiment, though lasting for two hours, was tried, yielding a bright red substance containing

PbO 80.36%

CrO₃ 19.51%

showing the removal of 37.6% of the original CrO₃ by solvolysis. This composition approximates 11PbO.6CrO₃ (i. e., 6PbCrO₄.5PbO), not shown to exist; it is probably a solution of PbCrO₄.PbO and 2PbCrO₄.PbO in each other.¹ (See diagram.)

7. PbO, treated exactly as in (5) and (6), yielded a *perfectly* white upper layer of solidified flux completely and readily soluble in water at room-temperatures, and reacting for neither Pb⁺ nor (NO₂)⁻. The lower layer of lead oxid consisted of a yellow and a red zone and contained 97.0% PbO; the original PbO contained 99.52%. Calculated to Pb₃O₄, this "loss" of PbO would mean very nearly one molar % of that compound formed in the course of fusion, so that apparently the fusion product is 99PbO.Pb₃O₄. But the assumption of the formation of Pb₃O₄ must include reduction of nitrate to nitrite (for this experiment), and no nitrite was found; hence, another explanation for the red substance must be sought for. PbO exists in two modifications:² (1) yellow, orthorhombic, (litharge); (2) red, tetragonal (massicot). The former is stable up to 620° and is completely transformed into the latter at 720°.³ This explains the reddening of the PbO at the *bottom* of the vessel (local heating, mass not stirred), also the lack of evidence of oxidation of lead and reduction of nitrate, already referred to. This seems a logical explanation in view of the persistent and pronounced arrest in all of the cooling-curves (except pure PbCrO₄) at 625° (*q. v.*), indicated by the line HH' in the diagram, (*q. v.*). The line NN' may also represent the transformation from the red modification to another form, since NN' corresponds to 720°.

A consideration of (5) would lead one to expect a "solvolytic" reaction such as: $\text{PbCrO}_4 + \text{KNO}_3 + \text{NaNO}_3 \rightleftharpoons \text{Pb}(\text{NO}_3)_2 +$

¹ Cox: Jour. Am. Chem. Soc., **28**, 12, 1902.

² Hintze: Handbuch der Mineralogie, **1**, 1934 (1915).

³ Ruer: Zeit. anorg. Chem., **50**, 265 (1906).

NaKCrO_4 , which should be an ionic reaction. If this were the sole process of mechanism, treatment of the yellow solid flux with water should lead to a reversal of the above reaction. But no precipitation of lead chromate results, and the aqueous solution of this yellow flux will precipitate Pb^{++} from its solutions. Since lead nitrate begins to decompose at temperatures above 205° ¹ it would appear that the PbO formed as a result of such decomposition interacts with the PbCrO_4 already present. A consideration of (7) would show that Pb^{++} is present in the white flux in lower concentration than that sufficient to exceed the solubility-product of PbS ($=4.2 \times 10^{-28}$) (H_2S test used here for Pb^{++}), and hence if we consider the white flux to be thus free from Pb^{++} ($<4.2 \times 10^{-14}$), we can scarcely consider that the second phase of the reaction is an ionic reaction. While the writer is inclined to the belief that all reactions are ionic, the results recorded would seem to indicate that it need not of necessity follow that such must be the case under all conditions.²

Freezing-Point Diagram.—In order to definitely settle the true state of affairs in the system lead chromate-lead oxid, the freezing-point diagram was plotted from cooling-curve data obtained from a series of fused mixtures of the two compounds (without flux), the mixtures progressively differing in composition by 5 molar %. The resulting diagram was checked against photomicrographic evidence. With the exception of pure PbO and 55–45 molar % $\text{PbCrO}_4 + \text{PbO}$, the specimens were much too soft to permit of good polishing. The surfaces of the other specimens “dragged” and “pitted” to a high degree, and photomicrographs were obtained with difficulty. The freezing-point curves and diagram follow:³

¹ Van Nostrand's Chemical Annual, 1918, p. 178.

² See W. A. Noyes: Jour. Am. Chem. Soc., 42, 11, 2174 (1920), footnote 2. The writer reached the same conclusion independently some six months prior to the appearance of this article.

³ Due acknowledgment is here made to Prof. C. F. Tolman, Geology Department, Stanford, for the use of apparatus and for valuable assistance in the preparation of photomicrographs; also to Messrs. L. E. Porter and M. K. Rouse for assistance in preparing the specimens.

The freezing-point curve XY shows four well-defined maxima (C_1, C_2, C_3, C_4) corresponding respectively to the compounds $4\text{PbCrO}_4 \cdot \text{PbO}$, $2\text{PbCrO}_4 \cdot 4\text{PbO}$,¹ $\text{PbCrO}_4 \cdot 4\text{PbO}$ ¹ and $\text{PbCrO}_4 \cdot \text{PbO}$. Apparently the first and fourth of this series have not been reported in the literature. While the point C_2 indicates a concentration of 65–35 molar % $\text{PbCrO}_4 \cdot \text{PbO}$, it is believed that the apparent location of this point is somewhat in error, and that it should correspond to the concentration 66.7–33.3 molar %, i. e., to the compound $2\text{PbCrO}_4 \cdot \text{PbO}$, already known. It will also be noted that the slope of the curve C_2E_2 (upper section) is very steep, so that a slight error in reading would displace the point C_2 sufficiently to cause its apparent location as recorded on the diagram. In the event that the location of the point C_2 is correct, its location with respect to the concentration corresponding to the compound $2\text{PbCrO}_4 \cdot \text{PbO}$ could be explained by considering that the dissociation

commences at a temperature below the melting point of the

Fig. 1

¹ See notes 2 and 3, p. 547.

compound $2\text{PbCrO}_4 \cdot \text{PbO}$. Photomicrographic evidence apparently confirms this supposition.

Fig. 2

It is to be noted that the diagram fails to show any other compounds than the four mentioned; this would indicate that the other red substances prepared were solutions of these compounds in each other. It is possible that the slight breaks in those portions of the freezing-point curve marked C_2E_2 and E_3C_4 may be due to the decomposition of other compounds, or perhaps to the influence of the solid eutectics at e_1 in the first case and e_2 in the second. There may be some relation between the break in E_3C_4 and the abrupt ending of the line GG' at G' . Photomicrographic evidence is lacking in both instances.

The diagram also shows three well-defined eutectics (E_1, E_2, E_3), the influence of the second being noticeable throughout almost the entire system (see AA') due, perhaps, to the additional influence of the solid eutectic at e_1 , both E_2 and e_1 occurring at the same concentration. The influence of the eutectics E_1 and E_3 is indicated by the lines OO' , PP' ,

respectively. There are two eutectics (e_1 , e_2) in the solid phase, the influence of each being indicated by the lines MM' , NN' , respectively. The line GG' may indicate that the eutectiferous material is immiscible with the other phases present.

The well defined and very regular lines CC' , DD' and FF' (and also GG') can be interpreted as indicating transitions in the solid phase; this in analogy to the transition between the two crystalline forms of PbO (*q. v.*) indicated by the line HH' . They may also indicate immiscibility in the liquid state at the indicated temperatures.¹ It will be noted that the line GG' contains the eutectic e_1 , and that the eutectics E_2 and e_1 occur at the same concentration, altho observations taken at shorter intervals than 5 molar % might easily indicate a shift of these and other points.

The lines BB' and CC' are so close together (10° – 15° only) in the diagram that there seems to be a reasonable doubt as to the authenticity of one of them; BB' is therefore dotted in the diagram. Perhaps a single line at 1010° would approximate the facts better; yet the halts in the cooling curves indicate a slight but definite change at BB' .

The abrupt ending of the lines AA' , BB' , CC' , DD' , FF' may be explained by considering that the concentration of PbO has reached sufficient magnitude to prevent the settling-out of the phases bounded by these lines at the temperatures and concentrations indicated, i. e., that the phases are now miscible. Observations with mixtures differing by less than 5 molar % concentration might prove of value in fixing the ending of these lines. The abrupt ending of GG' has already been discussed. The same explanation might be offered for the apparent break between the points G' and I . One could reasonably expect a continuous line from G to I' , but the cooling curves indicate no points of arrest between the temperatures indicated by the points G' and I , thus furnishing no

¹ This is known to be true for many alloys. See Hindrichs: *Zeit. anorg. Chem.*, **59**, 414 (1908); Lewkonja: *Ibid.*, 293; Desch: "Metallography," 2d edit., appendix, Table III, pp. 402-3.

evidence of the state of the equilibrium under these conditions of temperature and concentration. A possible connection between the abrupt ending of the line GG' and G' and the slight break between E₃ and C₄ has already been indicated. A similar explanation might be offered for the fact that there is a break in C₄Y at the same concentration as that indicated by the point I', altho this break may also be related to the solid eutectic at e₂, as was pointed out for the break in C₂E₂ in connection with the solid eutectic at e₁.

The lines KK' and LL' are inserted (provisionally) in the diagram solely for the purpose of making that diagram correspond with the evidence offered by the two cooling curves containing halts at this temperature; repeating the observations with concentrations differing by very small molar percentages might furnish additional evidence. No explanation is offered for these two short lines.

The line HH' represents the transition from the yellow form of PbO to the red form; this is usually given at 620°,¹ but the observations here recorded repeatedly show 625°. The yellow form of PbO crystallizes in the orthorhombic system² (mineral litharge)³ and the red in the tetragonal² (mineral massicot, recently reported).³ This could be due to slight error in reading or in fixing the calibration-curve for the thermo-couple. It is not a large error -0.8%.

Summary

Reactions in fused salt media can be brought about in such a way as to yield products analogous to those prepared from the same initial reacting substances in aqueous solution. A few typical reactions have been studied.

The chief difference between these reactions and their analogues in aqueous solution lies in the lower velocity of the

¹ Hintze: *Handbuch der Mineralogie*, 1, 1934 (1915). Groth: *Chemische Crystallographie*, 1, 76 (1906). Geuther: *Ann. Chem.*, 219, 56 (1883).

² Larsen: *Am. Mineralogist*, 2, No. 2, p. 8 (1917).

³ Wherry: *Ibid.*, p. 19.

former, most likely due to the relative insolubility of the reacting substances in the several fluxes experimented with, as compared to water.

In several cases, at least, there is an interaction between the fused salt flux, or solvent, and the solute dissolved therein. So far as the investigation goes, this interaction is analogous to hydrolysis or ammonolysis; the general term "solvolytic" is proposed, intended to include all such interactions.

While the above analogy would indicate that "solvolytic" reactions are ionic in mechanism, the second phase of the reaction forming "basic lead chromates" would point to a reaction not ionic in mechanism. It may be a purely "molecular" (addition) reaction, resulting in the formation of "higher order" compounds. Such a conclusion will satisfactorily explain the slowness of the reactions described, aside from the low solubility of the solutes in the fused salt media.

While at least one basic lead chromate may be prepared by a wet reaction (alkaline hydrolysis) which is admittedly ionic in mechanism, it does not necessarily follow that the basic lead chromates formed in fused salt reaction-media are formed by a wholly analogous process. At least two new "basic chromates" prepared by the latter method have not been prepared in the wet way, and one other, reported as being so prepared, resisted extended attempts to so prepare it. It could be readily prepared by the fusion-method. The existence of the four basic lead chromates is verified by a study of the system lead oxid-lead chromate. Other supposedly basic lead chromates are shown by the same means to be either mixtures or solutions of these compounds in each other.

Lead salts of "orthochromic acid" are shown not to exist. While the salt Pb_2CrO_5 may be a salt of a "monohydrate" of the ordinary chromic acid, it could equally well be a true basic salt or a "higher order" compound, so far as the present investigation is concerned.

At the temperature of the experiments the stable form of PbO is yellow in color. This, combining with yellow lead

chromate, yields red compounds, all of which points to higher order compounds. The red compound formed by alkaline hydrolysis of normal lead chromate could well be considered a basic salt, but the addition of lead oxid and lead chromate molecules to form a higher order compound might as easily take place in aqueous solution as in the nitrate flux used to form a red compound of very closely the same composition.

The reddening of PbO in the nitrate flux has been shown to be due to change in crystalline form, and not to the formation of Pb_3O_4 , as might at first be supposed.

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