

**FIRST REPORT ON INVESTIGATION OF
THE PLATE MATERIALS OF THE LEAD ACID CELL
COMPOUND FORMATION BETWEEN
LEAD MONOXIDE AND LEAD SULFATE**

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ABSTRACT

As the initial phase in the study of the active material of the plates of the lead-acid cell, the formulas of the compounds (basic sulfates) formed between PbO and PbSO₄ have been checked or established. The phase diagram for the melts of these substances shows formation of the compounds: PbSO₄·4PbO, PbSO₄·2PbO, and PbSO₄·PbO. A wet method of preparation leads to formation of the compounds: PbSO₄·4PbO, PbSO₄·PbO, and a hydrous compound tentatively assigned the formula: PbSO₄·3PbO·H₂O. X-ray methods of analysis support these formulas.

X-ray diffraction patterns have been recorded for these compounds for use in identification work.

The nature of the thermal decomposition products of PbSO₄·2PbO and the hydrous compound have been determined by X-ray analysis to be a mixture of PbSO₄·4PbO and PbSO₄·PbO in each case.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

AUTHORIZATION

NRL Problem No. C05-01.

FIRST REPORT ON INVESTIGATION
OF THE PLATE MATERIALS OF THE LEAD ACID CELL
Compound Formulation Between Lead Monoxide and Lead Sulfate

BACKGROUND OF PROBLEM

The lead-acid cell is composed of positive and negative plates immersed in an electrolyte. In the charged condition the active material of the positive plates consists of lead dioxide, while that of the negative is lead. Briefly, these plates are made in the following fashion: pure litharge (lead monoxide) (for positive plates) or a leady litharge (for negative plates), is mixed with water and sulfuric acid into a paste in definite amounts and under rather carefully controlled conditions and is immediately pasted into lead or antimonial lead grids, making a plate. The pasted plate is then subjected to one of several possible drying procedures or a combination of procedures, after which it is placed in a tank of relatively weak sulfuric acid and charged against a dummy electrode until the active material is substantially completely converted to lead dioxide for positive plates or to lead for negative plates. After this process, called forming, the plates may be assembled into individual cells or batteries which are then ready for use.

For years the battery industry has been making the active material of plates according to well-defined methods which have been arrived at primarily on the basis of experience. Thus, it has been found that by mixing lead oxide, sulfuric acid, and water in definite amounts and under controlled conditions, these ingredients may be made into pastes which have desirable properties in the mixing, pasting, drying, and forming processes, and which can be incorporated into cells or batteries which will give acceptable performance. However, very little is known about many of the fundamental chemical and physical-chemical processes which occur in the active material during the above-mentioned steps in plate-making, or about the basic reasons for the desirable or undesirable characteristics of pastes or active materials. The investigation of these processes is aimed at obtaining a knowledge of the factors which control the properties of the pastes and active materials. This knowledge should be of value in further development of the lead-acid cell.

In laying the groundwork for a study of this nature, it was decided to first determine the compounds which can be formed by lead monoxide and lead sulfate, inasmuch as such compounds might be formed in the mixing, drying, and forming processes. This report is concerned with this initial phase of the investigation: the determination of the formulas of the compounds which may be formed from PbO and PbSO_4 , their methods of preparation and means of identification.

No previous work has been done on this phase of the problem at this Laboratory but other work has been done along these lines at other institutions. Jaeger¹ and Schenck²

¹ F. M. Jaeger and H. C. Germs, *Z. anorg. allgem. Chem.* 119: 145-173 (1921).

² R. Schenck, *Metall u Erz.* 23: 408-420 (1926).

have made a phase study of the system PbO-PbSO_4 . Because the existence of a tetrabasic lead sulfate was indicated at this Laboratory by preliminary studies of melts of these substances, and such a compound was not reported by either of these investigators, it was decided to repeat the phase study. Clark³ gives wet methods of preparing some basic sulfates and he presents the X-ray data. After vainly trying to check his work, it was decided to attack the problem of wet-method preparations in a systematic fashion, adopting one of his methods of preparation.

THEORETICAL CONSIDERATIONS

Determination of the compositions of the compounds formed by the reaction between PbO and PbSO_4 in the molten conditions should be possible by thermal analysis such as has been done previously by Jaeger and by Schenck. The theory of this method is well outlined in the various physical chemistry texts and other books, for example Findlay's text on the phase rule.⁴ By studying the cooling curves of melts of various compositions of the two substances, data is obtained which enables a plot to be made of temperature vs composition. From this plot or phase diagram, the existence and composition of compounds of the two constituents can be determined readily.

Another means of determining the existence and composition of compounds is offered by X-ray analysis of a series of melts ranging from pure PbO to pure PbSO_4 (actually no melt of PbSO_4 is possible because it decomposes rapidly at temperatures considerably below its melting point). Since all chemical compounds give a characteristic diffraction pattern, a study of such a series of patterns should show the existence of compounds and their approximate composition. For example, in going through the series from pure PbO to pure PbSO_4 , and provided no compound were formed, the intensities of the lines of the PbO pattern should gradually decrease while those of the lines of the PbSO_4 patterns should gradually increase. At pure PbSO_4 the PbO lines would be completely gone from the pattern and only the pattern for PbSO_4 should be present. Suppose that a compound should be formed at 50 percent, composition PbSO_4 , then the lines of the PbO and PbSO_4 patterns would have faded out completely at 50 percent, being replaced entirely by the lines of the compound. Beyond 50 percent, the intensity of the lines of the pattern of the compound would gradually decrease and the PbSO_4 lines would gradually come in until at pure PbSO_4 only the pattern for PbSO_4 would be present. Therefore, for every compound that is formed in the series, the X-ray patterns of the series will go through a transition and evidently then, the number of new patterns that appear gives the number of compounds formed, and the percent compositions of the reactive materials at which these patterns reach their maximum intensity should provide data for calculating the compositions of the new compounds. Therefore, an X-ray diffraction examination of the melts from the phase study should help to confirm the thermal data as well as give the diffraction patterns for the compounds. X-ray analysis in conjunction with thermal data is a method in common use, especially in metallurgy, to help establish phase diagrams.⁵

It has already been shown that several wet methods are available for the preparation of the basic sulfates of lead. The simplest of these and probably the most suitable for a

³ G. L. Clark, J. N. Mrgudich and N. C. Schieltz, *Z. anorg. allgem. Chem.* **229**: 401-409 (1936).

⁴ A. Findlay, *The phase rule and its applications*; 7th Ed., Longmans, Green and Co. (1931).

⁵ C. S. Barrett, *Structure of metals, crystallographic methods, principles and data*; McGraw-Hill Book Co. (1943).

systematic study is to boil a water suspension of powdered PbO and PbSO₄ for specified lengths of time and in specified ratios of PbO to PbSO₄. Here again, if the ratio is varied from pure PbO to pure PbSO₄, the X-ray patterns of the series should indicate compound formation in the same way as described for the melts.

In general, solid compounds are most easily identified by their X-ray powder patterns, since each compound has its characteristic pattern. If compounds could be prepared in substantially pure form by the above methods, then the diffraction patterns obtained could serve as a means for identification of these compounds in future preparations of one kind or another, such as battery pastes. This would be particularly advantageous in a series of compounds like these, where, unless it is known that pure compounds are involved and the chemical composition of these is at least roughly known, chemical means of identification of the compounds would be next to impossible. In the case of mixtures of these compounds, not only is qualitative identification possible by X-ray methods, but under best conditions quantitative results of a limited precision are also obtainable. Therefore the X-ray method of identification would be in this case the most practical method to use, and for this reason, obtaining these patterns is an important part of the overall problem.

EXPERIMENTAL METHODS AND APPARATUS

Phase Study

For this work 100- to 130-gram mixtures of Baker's yellow lead monoxide (National Formulary quality) and Merck's reagent quality lead sulfate, ranging from pure PbO to a 50-50 mole percent mixture of the two were melted up in a platinum crucible in an electric furnace and then allowed to cool at a rate of 3 -5 per minute. The melts were stirred continuously with a motor-driven stirrer made from 90 percent platinum - 10 percent rhodium alloy thermocouple wire. The melts were usually seeded to prevent supercooling, since they had a tendency to supercool both at the inflection and the arrest in spite of efficient stirring. The temperature of the furnace was manually controlled by a Variac to which leads were run from the heating element. The temperature was measured by a platinum - 90 percent platinum 10 percent rhodium alloy thermocouple which was immersed, uninsulated in the melt. No protection was used for the thermocouple because nothing which was tested could resist the chemical action of the melts except the noble metals used in the work. Leads from the cold junction of the thermocouple ran to a voltage divider by means of which any desired portion of the potential generated by the thermocouple could be bucked out. This enabled the cooling curve in the vicinity of the melting point to be recorded on any desired range of a General Electric Recorder. The two-millivolt range was always used; this provided a 180° C temperature range, the zero of which could be adjusted by means of the voltage divider. The voltage divider circuit was equipped with a switch which allowed the thermocouple leads to be connected directly to a Rubicon 150-millivolt portable potentiometer to enable a more exact determination of the temperatures of inflections and arrests.

Methods of Preparation of the Basic Sulfates of Lead

Dry Method-- Samples were prepared by melting mixtures of PbO and PbSO₄ in a platinum crucible, according to the description given for the melts used in the phase study. In fact, the solidified melts from the phase study were used for the subsequent X-ray analyses.

Wet Method-- Suspensions of about 10-gram mixtures of the system PbO--PbSO₄ in 2 to 3 liters of water were allowed to boil from 7 to 8 hours. Stirring may be preferable, but only the natural stirring of the boiling mixture was used here. The mixtures then filtered and dried in an oven at 75° C overnight.

The X-Ray Apparatus

The apparatus used was the North American Philips X-ray spectrometer, on which the slit system and counting circuit had been modified along the general lines of a design worked out in the Physical Optics Section of this Laboratory. These modifications resulted in a much greater intensity and somewhat better resolution than the original instrument could produce. The better performance was due chiefly to two reasons: first, the slit system and sample position were arranged to take advantage of a focussing principle which uses the focal spot on the target of the X-ray tube as the beam source (the theory of this arrangement is described in NRL Report H-2517⁶), and second, a much improved counting circuit was employed which avoids saturation effects. A copper target tube operating on 35 kv and 6.8 milliamperes was used as the source of the radiation.

Sample Preparation

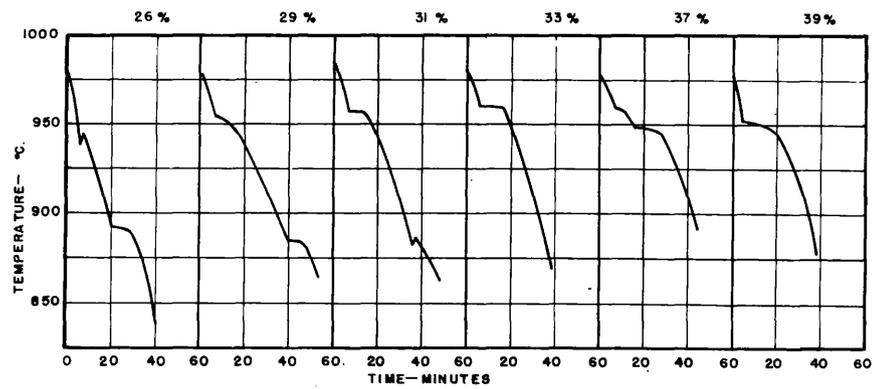
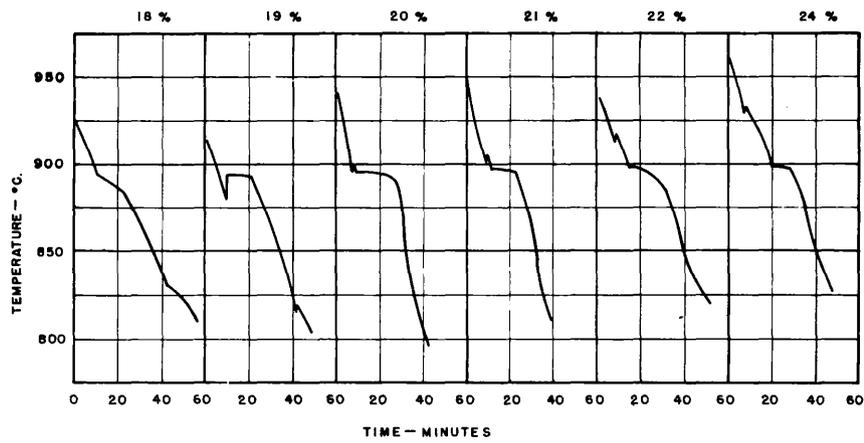
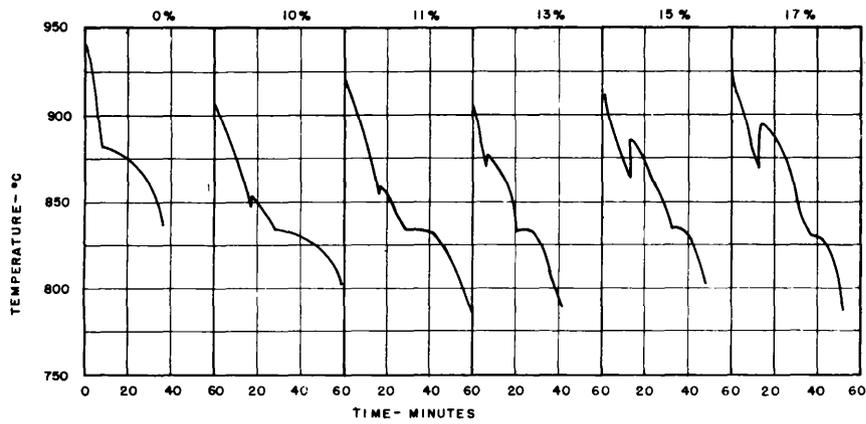
The crystals resulting from the melts of the phase study were ground for about one-half hour by hand using a mortar and pestle. The resulting powder was pressed into a disc one inch in diameter and about one-eighth inch thick, at a pressure of about 5000 pounds per square inch. The discs were mounted on a glass slide and the X-ray diffraction pattern obtained. The same treatment, except for grinding, was given the dried powders obtained by the wet method. These were not ground because the particle size was very small and grinding for periods up to one-half hour resulted in no change in the pattern. The pressed-pellet technique was preferred over a technique which would give a truer intensity pattern, in spite of the strong possibility of orientation effects, because the resulting surface of the pellet was almost mirror-like and resulted in a considerable increase in the overall intensity of the pattern together with a slightly smaller and smoother background.

EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

The Phase Study

In Figures 1, 2, 3, and 4, are given the cooling curves for melts of the various compositions measured. Table I presents the temperatures of the inflections and arrests. Figure 5 gives the phase diagram obtained from the cooling curves and compares it with the diagram obtained by Jaeger. From Figure 5 it can be seen that except for the range between about 10 mole percent and 27 mole percent PbSO_4 , the data obtained in this work checks that of Jaeger and of Schenck very well. However, this data definitely shows compound formation at 20 mole percent PbSO_4 rather than at 25 mole percent as the previous investigations showed. The reason for this disagreement is not apparent but might possibly be due to insufficient data in the range 15-25 mole percent PbSO_4 in the earlier work. Both sets of data indicate compound formation also at $33 \frac{1}{3}$ mole percent and 50 mole percent PbSO_4 , the temperatures for arrests and inflections checking within one or two degrees centigrade. The dibasic compound has an arrest in its cooling curve at 450°C . This corresponds to a decomposition of the dibasic lead sulfate into a mixture of the mono- and tetrabasic lead sulfates as has been shown by Jaeger. This will be demonstrated later from the X-ray pattern of the decomposition product.

⁶ L. S. Birks, Geiger counter technique for x-ray diffraction Part IV. Detailed consideration of experimental conditions, NRL Report H-2517, 20 April 1945.



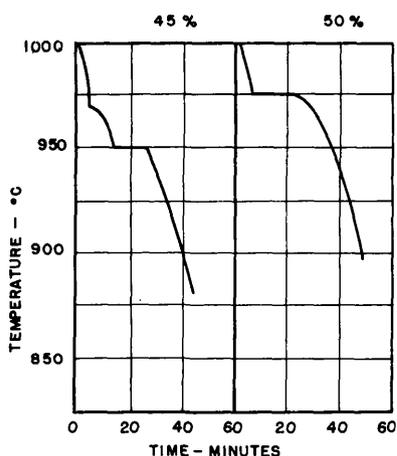


Fig. 4 - Cooling Curves:
Range 45-50 Mole % PbSO_4

TABLE I

Data from the Phase Study

PbSO_4 (Mole %)	Inflection ($^{\circ}\text{C}$)	Arrest ($^{\circ}\text{C}$)
0	---	878
10	853	834
11	860	835
13	878	835
15	888	835
17	895	832
18	893	830
19	893	820
20	899	895
21	903	895
22	915	895
24	928	895
25	940	895
26	945	893
28	954	892
29	956	888
31	960	886
33	---	961
37	957	950
39	---	950
45	972	950
50	---	975

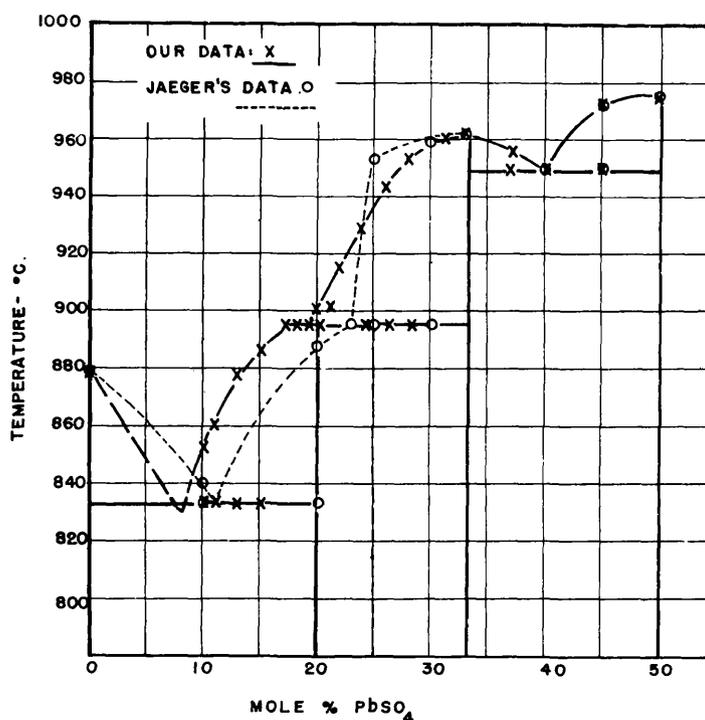


Fig. 5 - Phase Diagram: System PbO-PbSO_4

X-Ray Patterns of Compounds Prepared by the Dry Method

The X-ray data on the melts (dry method) is given in Table II where line positions and relative intensities are given for the following melts: pure PbO , 20 mole percent PbSO_4 , 33 1/3 mole percent PbSO_4 and 50 mole percent PbSO_4 . Their recorded patterns are shown in Figure 6. Actually patterns of melts in steps of from 1 to 5 percent, from pure PbO to 50 mole percent PbSO_4 were examined. These show that new patterns with maximum line intensities occur at about 20 percent, 33 1/3 percent, and 50 percent PbSO_4 . All this data is not included in the report because of its cumbersome nature. Instead, in Table III the intensity values of

several strong lines of each compound are given as a function of concentration of PbSO_4 . These should be sufficient to illustrate the basis of the general argument, without presenting excessive data. At any rate, the X-ray method of examining the series of melts places compound formation at about the same compositions as the thermal analyses, thus providing a check on the results. Thermal analysis is in this case the more exact method for locating these compositions.

The patterns for the melts are not entirely pure, each possibly being contaminated to some extent with each of the other basic sulfates and the 20 percent melt also with PbO . This is especially the case for the dibasic and possibly the tetrabasic, with the monobasic probably being the most nearly pure. To illustrate this it can be observed plainly from

the pattern of the dibasic lead sulfate (33 1/3 percent PbSO₄) (Figure 6) that the strongest line of each of the tetrabasic and monobasic are present indicating some contamination of the dibasic with each of these. This is probably to be expected in this case since the dibasic decomposes into both these compounds at 450° C and possibly even quenching doesn't prevent this decomposition entirely. Another contributing factor to the possibility of impurity in these patterns is the fact that these compounds are all to a greater or lesser extent dissociated in the melt and if cooling should take place too rapidly and without efficient stirring, contamination of the one compound with the others might be expected. However, it is quite evident that there are three distinct patterns other than those of pure PbSO₄ (Figure 8) and pure PbO resulting from the melts. The compositions at which the intensities of the lines of these patterns reach their maxima are not inconsistent with the compositions for compound formation as shown by the phase diagram.

TABLE II

X-ray Data on Compounds Prepared by Dry Method
(Intensities Relative to Strongest Line of Pattern)

Pure PbO*		20 Mole % PbSO ₄		33 1/3 Mole % PbSO ₄		50 Mole % PbSO ₄	
d	I	d	I	d	I	d	I
5.8	.15	7.9	.11	7.8	.10	6.1	.02
4.9	.06	3.22	1.00	5.8	.10	5.8	.10
3.04	.11	3.09	.15	3.75	.05	4.4	.01
2.92	1.00	3.04	.11	3.47	.10	3.68	.01
2.79	.06	2.92	.13	3.22	.60	3.47	.01
2.50	.40	2.87	.20	2.96	1.00	3.32	.10
1.99	.06	2.66	.20	2.92	1.00	3.16	.03
1.96	.30	2.30	.11	2.87	.70	2.93	1.00
1.86	.05	2.04	.11	2.69	.05	2.84	.10
1.85	.02	1.94	.19	2.37	.50	2.46	.02
1.71	.08	1.86	.11	2.35	.50	2.42	.02
1.63	.02	1.82	.13	2.29	.10	2.33	.02
1.52	.05	1.72	.18	2.22	.05	2.26	.04
1.46	.35	1.68	.15	2.11	.15	2.21	.06
1.287	.02	1.64	.17	2.06	.20	2.05	.08
1.251	.04	1.61	.21	1.96	.40	1.96	.50
1.173	.06	1.59	.15	1.89	.05	1.90	.01
		1.58	.15	1.86	.05	1.84	.10
		1.55	.05	1.82	.25	1.75	.06
		1.422	.05	1.79	.40	1.72	.05
		1.361	.11	1.74	.10	1.71	.04
		1.282	.12	1.73	.20	1.67	.01
		1.268	.17	1.68	.20	1.66	.01
		1.257	.12	1.62	.05	1.64	.02
		1.222	.08	1.56	.30	1.61	.02
		1.155	.12	1.52	.20	1.60	.01
				1.51	.10	1.51	.11
				1.44	.10	1.49	.01
				1.426	.06	1.47	.08
				1.329	.02	1.445	.04
				1.316	.02	1.435	.07
				1.298	.02	1.352	.01
				1.245	.05	1.305	.02
				1.235	.05	1.281	.02
				1.210	.02	1.228	.01
				1.178	.02	1.210	.02
				1.167	.20	1.177	.08
						1.169	.04
						1.151	.01
						1.133	.01

* This is a mixture of the tetragonal and orthorhombic forms.

TABLE III

Intensity Variations with PbSO₄ Concentration of Some Strong Lines of Compounds Formed in the Melts

d	Intensities in Scale Divisions									
	Concentration of PbSO ₄ (Mole %)									
	0	10	15	20	25	30	33 1/3	35	40	50
5.8	7.5	4.0	1.0							
3.6								0.6	2.2	
3.32								3.4	5.0	
3.22		7+	7+	7+	7+	5.4	4.4	4.2	2.0	
3.11								1.0	1.2	2.0
2.96				3.0	7+	7+	7+	7+		
2.93								6.8	6.8	7+
2.87		2	3.0	5.4	7+	7+	7+	7+	3.2	7+
2.66		2	3.4	3.8	2.6	1.0				
2.51	7+	7+	1.2							
2.42									0.6	2.0
2.37				0.8	1.4	4.3	4.2	2.0	0.4	
2.26								0.8	1.4	3.0
2.21							0.4	1.0	1.4	3.6
2.06				1.2	1.8	1.4	2.2	2.0		
2.05									4	4.2
1.86	2.8	1.8	0.8							
1.79					1.2	3.2	3.0	1.4	0.4	
1.64		0.3	1.6	2.2	1.0					
1.61			2.0	3.4	3.4	0.8				
1.56				0.4	0.4	2.4	2.4	2.0	0.6	
1.52	2.4	2	0.8							
1.44					0.6	1.2	3.0	1.6	0.8	3.6
1.268		0.6	1.2	1.4	0.8	0.4				
1.177								0.4	1.2	2.4
1.173	4.4	0.4								

The fact that the dibasic compound decomposes at 450° C into a mixture of the tetrabasic and the monobasic has been mentioned and this is shown in Figure 7 where the pattern of a sample of dibasic which had been held at a temperature of 410° C for about thirty-six hours is given. Patterns of the 20 percent and 50 percent melts are given for comparison. The "d" values for the decomposition products are given in Table IV along with a comparison with matching values for the tetra- and monobasic lead sulfates. The decomposition probably is not easily reversible since the decomposed material was held at 550° C for forty-eight hours without bringing about any change in the pattern.

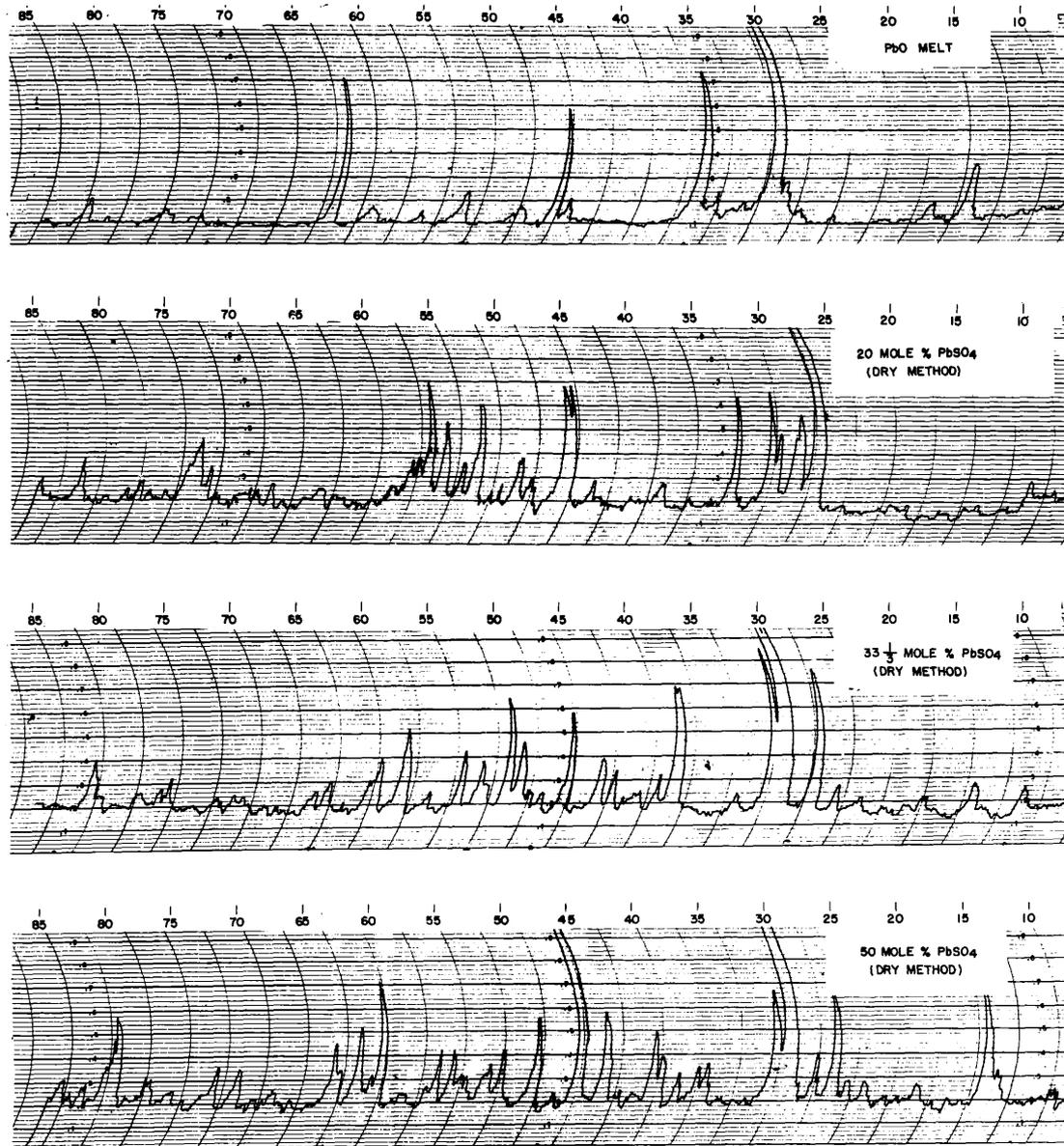


Fig. 6 - Patterns for Compounds Prepared by the Dry Method

X-Ray Patterns of Compounds Prepared by the Wet Method

The patterns for compounds prepared by the wet method seem to be purer as evidenced by the sharpness of the transitions and the lack of persistence of lines beyond ranges where they should not be. Examination of the patterns in 5 percent steps from pure PbO to pure PbSO₄ shows compound formation at 20 percent, 25 percent, and 50 percent PbSO₄. The X-ray data for the patterns at these compositions is given in Table V and the patterns recorded are shown in Figure 8. In Table VI are given the intensity values for strong lines of each compound as a function of concentration, and here it is quite evident that lines of

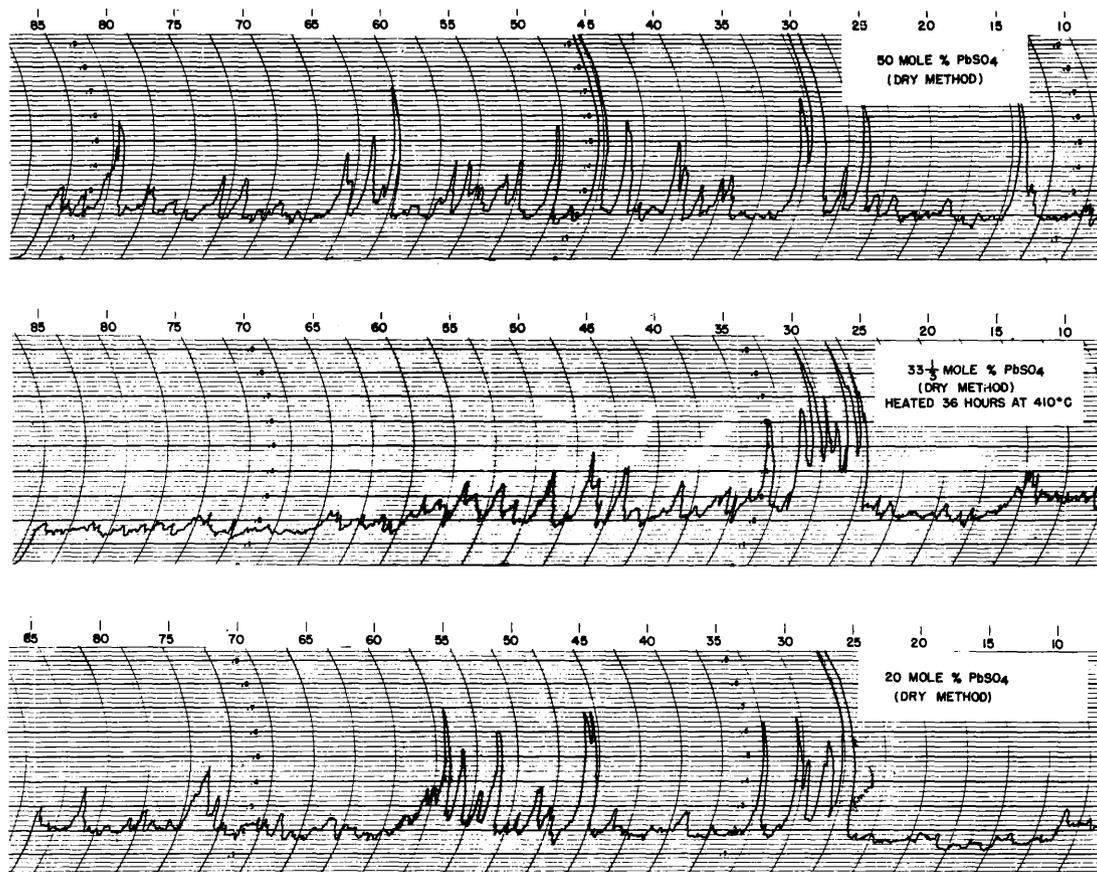


Fig. 7 - Decomposition Products of Dibasic Lead Sulfate

the tetrabasic pattern do not persist above 25 percent, while lines of the compound formed at 25 percent do not persist above 50 percent or below 20 percent.

A comparison of the 20 percent and 50 percent patterns with the patterns for the same compositions from the melts shows that these patterns are substantially the same, with differences in intensity explainable possibly on the basis of different crystal habit due to different methods of preparation and possibly to the method of preparation of the samples for mounting in the sample holder of the X-ray spectrometer. Impurities, especially in the melt for the 20 percent compound may be contributing some extra lines to that pattern. This comparison is made in Table VII and in Figure 9. Evidently tetrabasic lead sulfate and monobasic lead sulfate can be prepared by either method used in this work. Furthermore, the fact that the maximum intensities for these two patterns occur near 20 percent $PbSO_4$ and near 50 percent $PbSO_4$ coincides closely with the data from the thermal analyses and the X-ray data on the melts.

The composition of the compound which occurs at 25 percent $PbSO_4$ is not known with certainty. It seems to be a hydrate as shown by the fact that it loses water on heating at 280°C. Actually it decomposes at as low as 210°C, but 280°C is given as a temperature at which the substance will decompose rapidly and completely. A quantitative analysis for water loss of all samples from 20 percent to 50 percent was run and the results are

TABLE V

X-Ray Data on Compounds Prepared by the Wet Method
(Intensities Relative to Strongest Line of Pattern)

20 Mole % PbSO ₄		25 Mole % PbSO ₄		50 Mole % PbSO ₄		Pure PbSO ₄		Hannawalt Index on PbSO ₄	
d	I	d	I	d	I	d	I	d	I
8.1	.30	9.8	.3	6.2	.2	4.20	0.44	4.26	0.80
3.25	1.00	6.1	.02	5.8	.1	3.82	0.22	3.80	0.28
3.11	.03	5.8	.02	4.4	.02	3.59	0.18	3.61	0.08
3.04	.02	4.85	.08	3.67	.80	3.44	0.20	3.47	0.08
2.87	.30	4.24	.08	3.47	.10	3.31	0.88	3.33	0.60
2.67	.02	3.68	.07	3.33	1.00	3.20	0.56	3.21	0.40
2.31	.10	3.54	.10	3.22	.10	2.99	.85	3.00	1.00
2.04	.20	3.27	1.00	3.16	.10	2.74	0.25	2.75	0.32
1.94	.15	3.12	.20	2.95	1.00	2.68	0.22	2.68	0.32
1.72	.25	2.96	.02	2.84	.30	2.61	0.10		
1.68	.02	2.92	.02	2.57	.05	2.39	0.20	2.40	0.12
1.64	.08	2.88	.08	2.46	.25	2.25	0.20	2.27	0.12
1.61	.20	2.82	.08	2.42	.70	2.22	0.08		
1.437	.08	2.69	.10	2.39	.25	2.19	0.10		
1.364	.08	2.49	.10	2.34	.05	2.16	0.22	2.16	0.16
1.345	.01	2.44	.22	2.26	.12	2.06	0.69	2.06	1.00
1.269	.08	2.21	.01	2.22	.10	2.03	1.00	2.02	0.40
1.255	.06	2.14	.08	2.11	.05	1.97	0.40	1.97	0.20
1.156	.20	2.07	.15	2.05	.40	1.87	0.08	1.87	0.04
		1.97	.10	1.96	.12	1.79	0.40	1.78	0.12
		1.94	.05	1.91	.15	1.74	0.06	1.73	0.06
		1.84	.05	1.84	.50	1.70	0.25	1.70	0.12
		1.81	.05	1.76	.10	1.64	0.05	1.65	0.04
		1.77	.08	1.72	.10	1.62	0.30	1.61	0.20
		1.68	.06	1.67	.15	1.57	0.02	1.57	0.04
		1.63	.25	1.66	.15	1.49	0.25	1.490	0.16
		1.57	.10	1.64	.05	1.465	0.15		
		1.53	.05	1.57	.20	1.435	0.10		
		1.51	.06	1.51	.05	1.427	0.10		
		1.394	.05	1.48	.20	1.401	0.10		
		1.354	.02	1.47	.20	1.390	0.08		
		1.255	.05	1.445	.20	1.366	0.20		
		1.248	.05	1.435	.15	1.338	0.08		
		1.218	.03	1.380	.02	1.324	0.06		
		1.192	.03	1.360	.05	1.220	0.20		
				1.306	.10	1.182	0.15		
				1.232	.10	1.162	0.10		
				1.213	.05	1.143	0.08		
				1.174	.10				

TABLE IV

X-Ray Data on Decomposed Dibasic Lead Sulfate
(Intensities Relative to Strongest Line of Pattern)

Decomposition Product		Matching Lines from: Tetrabasic Monobasic	
d	I	d	d
6.1	.14		6.1
5.8	.07		5.8
4.4	.03		4.4
3.69	.03		3.68
3.32	.85		3.32
3.22	1.00	3.22	
3.18	.20		3.16
3.10	.60	3.09	
3.03	.70	3.04	
2.94	1.00		2.93
2.87	0.70	2.87	
2.65	0.60	2.66	
2.58	.12		2.46
2.46	.12		2.42
2.41	.10		2.33
2.33	.05		2.26
2.26	.20		
2.11	.05		
2.05	.40	2.04	2.05
1.97	.30		1.96
1.94	.50	1.94	
1.84	.30		1.84
1.76	.10		1.75
1.72	.20	1.72	1.72
1.67	.15		1.68
1.64	.20		1.64
1.61	.10	1.61 ^r	1.61
1.60	.10	1.59	1.60
1.57	.10		
1.55	.05	1.55	1.51
1.51	.05		
1.43	.08	1.422	1.435
1.345	.02		1.352
1.267	.08	1.268	

TABLE VI

Intensity Variations with PbSO₄ Concentration of Some Strong Lines of
Compounds Formed from the Wet Method

d	Intensities in Scale Divisions									
	Concentration of PbSO ₄ (Mole %)									
	0	10	15	20	22	25	30	40	45	50
9.8					9+	9+	9+	9+	9+	
8.1		3.4	5.4	9	2.4					
6.2								1	1.6	2.0
5.0	8	1.8	0.8							
4.85					1.0	1.6	3.0	1.6	1.0	
3.54					1.0	2.0	2.0			
3.27					9+	9+	9+	9+	9+	1.6
3.25		9+	9+	9+						
3.11	9+	5.8	4.4	1.0	1.4	4.0	4.0	2	1.4	
2.95							1.8	2.4	3.0	5.4
2.87		4.2	6.2	7.2	5.4	1.8				
2.69					1.4	2.0	2.0	1.2	0.8	
2.51	9+	9+	9							
2.44					4.2	9+	9+	8.0	4.0	
2.31		0.8	1.4	1.8	1.0	0.2				
2.26							0.4	1.0	1.4	2.0
2.22							0.4	0.6	0.8	1.4
1.87	3.4	2.2	0.8							
1.72		3.4	4.0	5.8	3.4	2.4	0.4			
1.63		0.2	1.0	1.6	5.0	9+	9+	8	6	
1.61		2.2	2.6	4.0	2.6	2.6				
1.55	5.4	3.0	1.4							
1.436		0.8	1.0	1.0	0.6	0.4		0.2	0.6	1.0
1.364		0.2	0.6	1.2	0.4	0.2				
1.156		0.2	1.2	1.8	1.0	0.4				

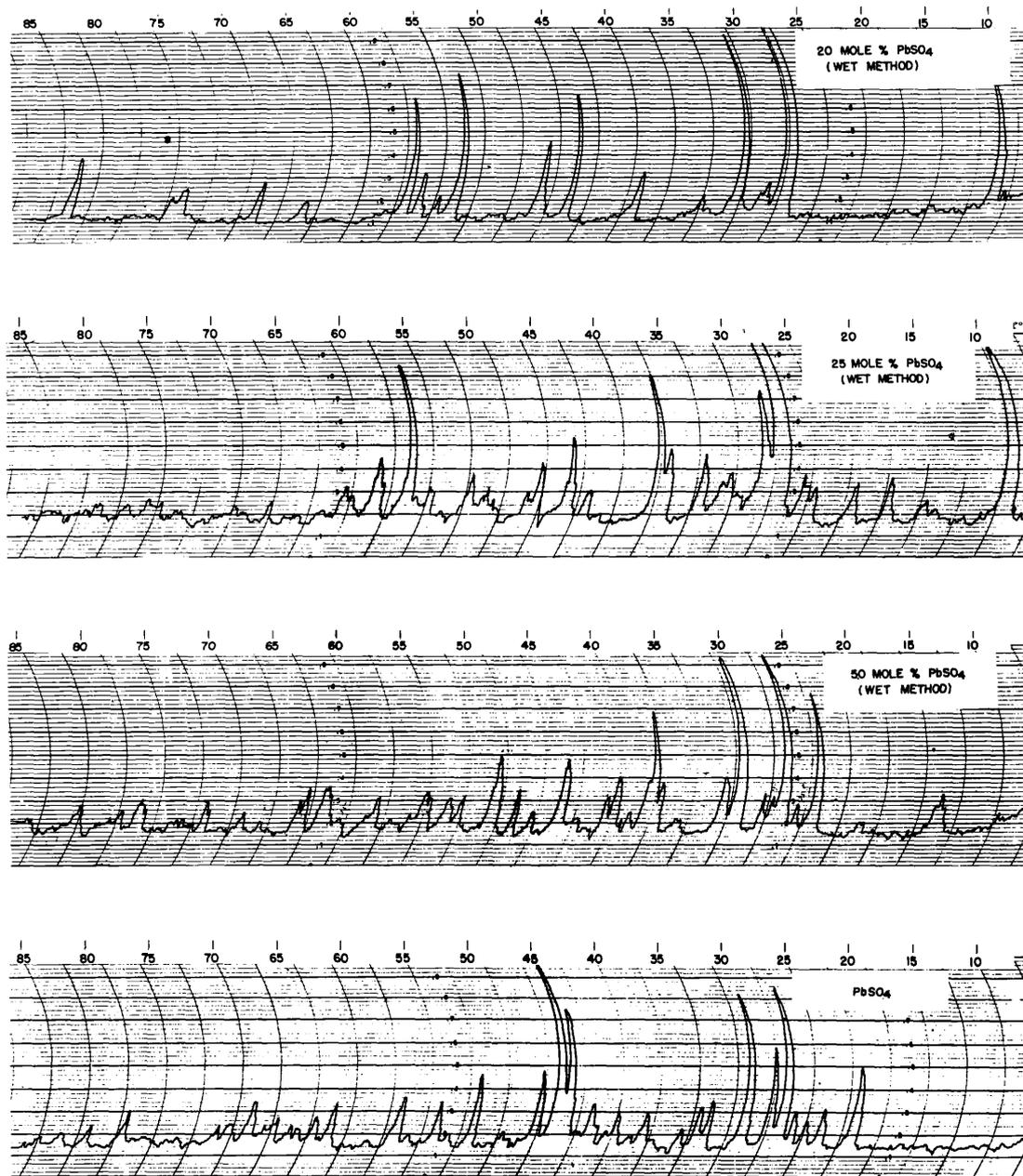


Fig. 8 - Patterns for Compounds Prepared by the Wet Method

tabulated in Table VIII and graphed in Figure 10. It can be seen that the maximum water loss occurs very close to 25 mole percent PbSO₄ as should be the case for a hydrate of that composition. The amount of water in the sample at 25 mole percent corresponds to about 10 percent less than the theoretical amount for the monohydrate of tribasic lead sulfate (PbSO₄·3PbO·H₂O). Therefore this compound will be referred to by that name tentatively only. When it breaks down under heating it forms a mixture of the mono- and the tetrabasic lead sulfates, as might be expected since the phase diagram doesn't show the

TABLE VII

Comparison of Data for the Tetra- and Monobasic Lead Sulfates
Prepared by Both Methods

(Intensities Relative to Strongest Line of Pattern)

20 Mole % PbSO ₄				50 Mole % PbSO ₄			
Dry Method		Wet Method		Dry Method		Wet Method	
d	I	d	I	d	I	d	I
7.9	.11	8.1	.30	6.1	0.2	6.2	.20
3.22	1.00	3.25	1.00	5.8	.10	5.8	.10
3.09	.15	3.11	.03	4.4	.02	4.4	.02
3.04	.11	3.04	.02	3.68	.01	3.67	.80
2.92	.13			3.47	.01	3.47	.10
2.87	.20	2.87	.30	3.32	.10	3.33	1.00
2.66	.20	2.67	.02			3.22	.10
2.30	.11	2.31	.10	3.16	.03	3.16	.10
2.04	.11	2.04	.20	2.93	1.00	2.95	1.00
1.94	.19	1.94	.15	2.84	.10	2.84	.30
1.86	.11					2.57	.05
1.82	.13			2.46	.02	2.46	.25
1.72	.18	1.72	.25	2.42	.02	2.42	.70
1.68	.15	1.68	.02			2.39	.25
1.64	.17	1.64	.08	2.33	.02	2.34	.05
1.61	.21	1.61	.20	2.26	.04	2.26	.12
1.59	.15			2.21	.06	2.22	.10
1.58	.15					2.11	.05
1.55	.05			2.05	.08	2.05	.40
1.422	.05	1.437	.05	1.96	.50	1.96	.12
1.361	.11	1.364	.08	1.90	.01	1.91	.15
		1.345	.02	1.84	.10	1.84	.50
1.282	.12			1.75	.06	1.76	.10
1.268	.17	1.269	.08	1.72	.05	1.72	.10
1.257	.12	1.255	.06	1.71	.04		
1.222	.08			1.67	.01	1.67	.15
1.155	.12	1.156	.20	1.66	.01	1.66	.15
				1.64	.02	1.64	.05
				1.61	.01		
						1.57	.20
				1.51	.11	1.51	.05
				1.49	.01	1.48	.20
				1.47	.08	1.47	.20
				1.445	.07	1.445	.20
				1.435	.02	1.435	.15
						1.380	.02
				1.352	.01	1.360	.05
				1.305	.02	1.306	.05
				1.228	.01	1.232	.10
				1.210	.02	1.213	.05
				1.177	.08	1.174	.10

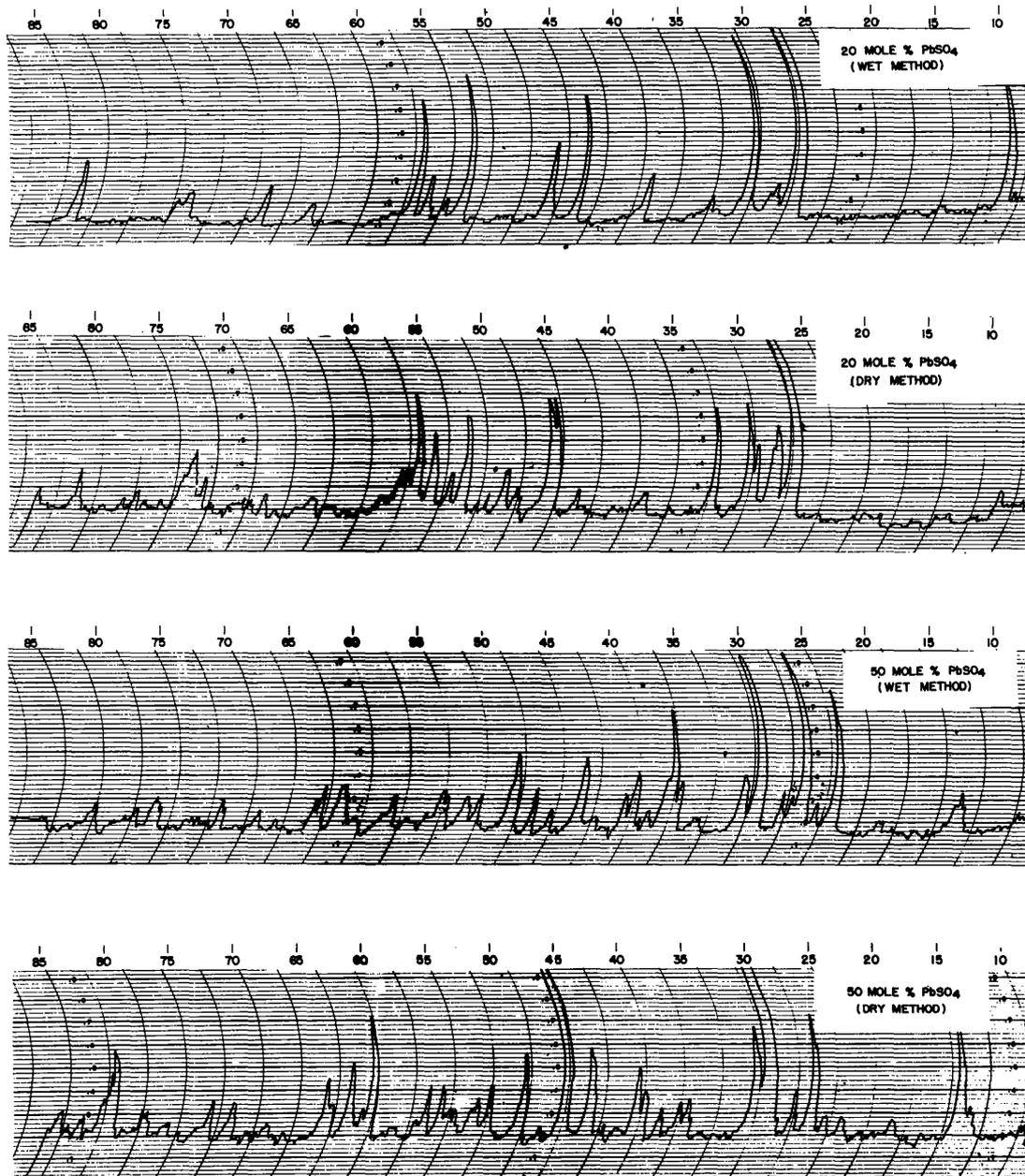


Fig. 9 - Comparison of Tetra- and Monobasic Lead Sulfates Prepared by Both Methods

existence of a tribasic lead sulfate. The pattern for the decomposed material is recorded in Figure 11 and compared with the patterns for the mono- and tetrabasic lead sulfates. The X-ray data is tabulated in Table IX.

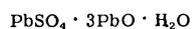
Evidently the dibasic lead sulfate is not capable of being formed by the wet method, since there is no pattern in the series corresponding to that of the dibasic compound as formed from the melt. This is, of course, to be expected since the dibasic lead sulfate is unstable below 450°C .

TABLE VIII

Water Content of Samples Prepared by Wet Method
In Concentration Range 20-50 Mole % PbSO_4

Mole % PbSO_4	Wt. % H_2O
20.0	0.19
21.5	1.29 1.28
23.5	1.77 1.70
25.0	1.77* 1.77
27.5	1.63 1.56
30.0	1.38 1.37
32.5	1.12 1.17
35.0	0.99 0.97
37.5	0.77 0.77
40.0	0.61 0.62
42.5	0.49 0.48
45.0	0.22 0.24
47.5	0.19 0.11
50.0	0.08

* This represents 0.89 mole % based on formula:



DISCUSSION OF ERRORS

Phase Study

The most important factor in the phase study is the temperature of the arrests and inflections as a function of concentration. The method of placing the unprotected thermocouple directly in the melt might possibly lead to some error. The thermocouple was not calibrated. In view of the excellent checks obtained in this work for the melting points of the pure PbO , the dibasic lead sulfate, and the monobasic lead sulfate, as well as the agreement of several eutectic temperatures compared with the data of Jaeger and of Schenck, it is concluded that those thermocouple factors are unimportant in this case. This is especially true since the point to be established by this work is the composition at which compound formation takes place in the range 20 percent-25 percent PbSO_4 , and it is not an attempt to establish extremely accurate temperatures.

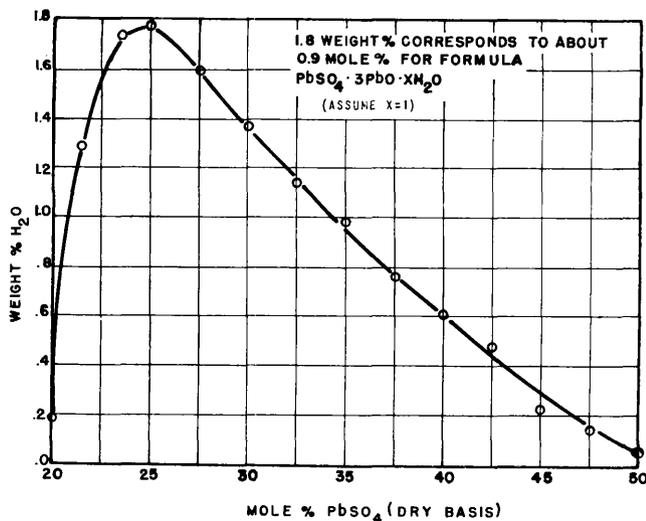


Fig. 10 - Water Content of Wet Method Samples

TABLE IX

X-Ray Data for Decomposed Hydrus Compound

Decomposition Product		Matching Lines from: Tetrabasic Monobasic	
d	l	d	d
3.68	.05		3.68
3.33	1.00		3.33
3.22	.30	3.22	
3.10	.30	3.09	
3.04	.30	3.04	
2.94	.10		2.93
2.86	.10	2.87	
2.72	.10		
2.67	.20	2.67	
2.60	.05		
2.55	.05		2.57
2.42	.05		2.42
2.28	.05		2.26
2.12	.02		2.11
1.99	.05		
1.96	.10		1.96
1.94	.15	1.94	
1.85	.15	1.86	1.84
1.71	.10	1.72	1.71
1.68	.02	1.68	1.67
1.65	.10	1.64	1.66
1.61	.10	1.61	1.61
1.57	.02	1.58	
1.53	.02	1.55	1.51
1.48	.05		1.47

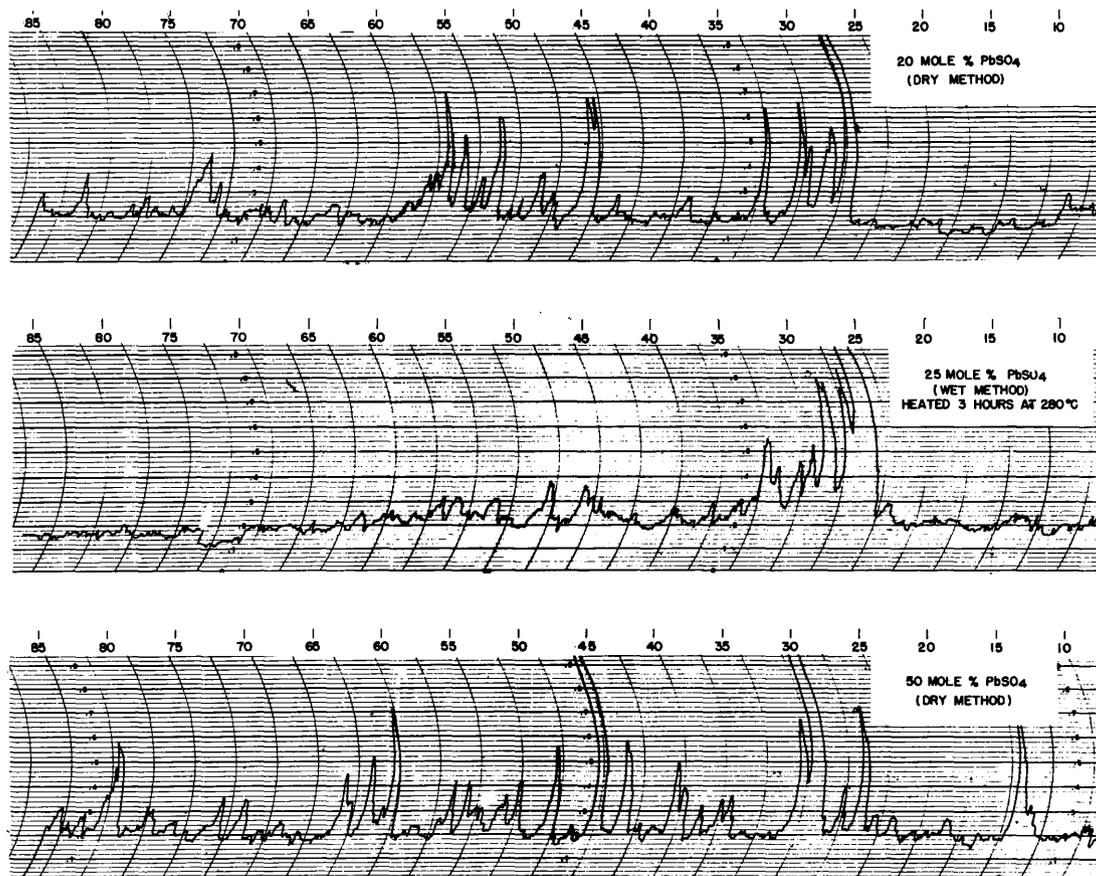


Fig. 11 - Decomposition Product of the Hydrus Compound

Care must be taken to keep the melts free of any oxidized material such as fire brick or the alundum rod supporting the thermocouple wires, since these materials as well as other oxides dissolve readily in the melts.

Because PbSO₄ decomposes well below its melting point, and because casual observation showed that PbO was distilling onto the colder parts of the furnace, these factors had to be examined for the possible effect of changing the concentration from that for which the melts were made up. To evaluate these factors, first 100 grams of pure PbO was held at 1010° C for thirty minutes, cooled, and reweighed. No appreciable weight change could be detected on a balanced sensitive to 0.01 gram. Second, 100 grams of PbSO₄ was held at temperatures of 850°, 930°, and 1010° C for periods of thirty minutes. Weight changes indicating decomposition were negligible in the first two instances, but at 1010° C the weight change was such as to indicate that 4.2 percent of the PbSO₄ decomposed, if the reaction is:



Thus in melting up the original components care should be undertaken to keep the temperature as low as possible, especially when working with melts around 50 percent. This could be easily done if the constituents were first boiled up together since compounds are formed which melt easily, thus avoiding the necessity for higher heating to enable the molten PbO to take the PbSO₄ into solution.

The melts apparently attack the platinum crucible and the platinum-rhodium alloy to some extent, as is evidenced by a grayish color on the solidified melt at the melt-crucible interface. After several meltings, however, the weight change of the crucible is less than 1 part in 2000, so that the reaction apparently is not fast enough to be serious for this work.

Most of the compositions for which cooling curves were run were checked at least twice for temperatures of inflections and arrests, and most of those in the range 15-25 percent PbSO_4 were checked three times. Checks to within $\pm 2^\circ \text{C}$ were always obtained and more frequently checks to within $\pm 1^\circ \text{C}$ were obtained.

The X-Ray Apparatus

The magnitude of the error in "d" values is worked out in Appendix I, where calibration data for four different runs with the same sample of NaCl are reported. These runs were interspersed throughout the period in which PbO- PbSO_4 patterns were recorded. There is a constant average correction to be applied to the angle 2θ across the scale. Originally the adjustments to the apparatus were made by setting the goniometer arm at the exact angle where the $75^\circ 18'$ line of NaCl should come in and then adjusting the slits and sample position to give maximum intensity of this line. The constant correction seemed to be necessary as a result of lag in the recording mechanism. However, once this correction is applied, the resulting precision is quite acceptable as shown by the calculations in Appendix I. The reliability of this data is well within the limits consistent with ordinary requirements for identification work. This method was adopted instead of using NaCl as an internal indicator for several reasons. First, the reliability of data is evidently good; second, a decrease in intensity of the lines of the pattern would result from admixture with NaCl; and third, the number of lines in these patterns is already large.

Methods of Preparation of Compounds and Sample Preparation

By the methods used to produce the compounds studied, there is no absolute guarantee that the melts and suspensions gave pure compounds at the concentrations which should correspond to compound formation. Since equilibrium processes are involved in the preparation of the compounds, contamination of these compounds each by the others might be expected to be the rule. This would probably be especially true of the tetra- and dibasic lead sulfates prepared from the melts for reasons mentioned previously.

In a method of investigation using X-ray analyses such as has been pursued here, the strong lines of any compound may be ascribed to it with a high degree of probability. As the intensity of the lines of a compound decrease they may be ascribed to that compound with a lesser and lesser degree of probability until very weak lines may not necessarily correspond to the compound at all, if not pure. Therefore, in an investigation such as this, where there is no existing criterion for purity, and where the compounds give diffraction patterns of considerable complexity, the possibility of assigning lines wrongly to a compound should not be overlooked. In view of this, lines which are only of a relative intensity of 0.02 or over are quoted in the conclusion as being characteristic of the compounds. From a study of the intensity variations of the lines in these series, the lines should be assignable to the pattern of any one compound for the most part with accuracy. Furthermore, the intensity variations in the patterns of the boiled suspensions are so clean cut that it is probable that the patterns recorded for these samples represent substantially pure compounds.

Another source of difficulty arises from the method of sample preparation for analysis

which lends itself quite readily to producing orientation of the grains⁷ and consequently variation in intensity of the lines. Variations in intensity may also be produced by the chemistry of the crystal growth. The two methods of preparation do lead to crystals of considerably different sizes and it is not certain that the grinding procedure in the case of the melts will produce particles of the same shape and size and tendency toward orientation under pressure as those obtained by the wet method. At any rate, large differences in intensities in the lines of these patterns (compare the patterns shown in Figure 9) make the comparison of these patterns difficult. Superposition of the patterns of the monobasic sulfate of both methods shows almost line for line correspondence as far as position goes and the same is true of the tetrabasic patterns, except that the tetrabasic melt has some extra lines which may be due to impurities such as PbO or the dibasic compound. In Table V the pattern for PbSO_4 is compared with that of the Hannawalt Card Index to illustrate these variations in intensity.

All of these factors mentioned lead to difficulty in reading and separating the lines into patterns characteristic of the compounds and make possible incorrect assignment of lines to compounds. However, it is believed that the method used in following the variation in line intensity with composition enables the patterns to be separated with a fair degree of accuracy in the case of the boiled suspensions, so that the "d" values finally quoted for the patterns of the compounds are probably almost completely correct for those compounds. The intensities, because of the method of sample preparation, may be at considerable variance with those which would be given by a true powder pattern where orientation effects are completely absent.

The complete answer to the problem of X-ray patterns of these compounds would be given by a structure determination, whereupon the line positions and intensities could be calculated and experimental values matched against them. Some independent guide for the purity of these compounds would also provide completely accurate powder patterns, but as the situation now exists, the X-ray patterns of the boiled suspensions probably furnish the best comparison for judging the purity of subsequent preparations of these compounds.

These patterns, for any given method of preparation of compound or sample, are very reproducible. Most of these patterns have been recorded two or three times from different preparations of the same composition by the same method, producing only minor variations in intensity of lines and variations in "d" values not outside the limits of experimental error.

CONCLUSIONS AND SUMMARY

Three compounds may be formed by melting PbO and PbSO_4 in the ratios indicated by their formulas: $\text{PbSO}_4 \cdot 4\text{PbO}$, $\text{PbSO}_4 \cdot 2\text{PbO}$, and $\text{PbSO}_4 \cdot \text{PbO}$. This is shown by the phase diagram of the PbO- PbSO_4 system and is supported by X-ray studies of the solidified melts. The dibasic lead sulfate is unstable below 450° C and decomposes on heating into a mixture of the tetrabasic and the monobasic lead sulfates.

Three compounds may be formed by boiling water suspensions of PbO and PbSO_4 in the proper ratio. Two of these are assigned the formulas $\text{PbSO}_4 \cdot 4\text{PbO}$ and $\text{PbSO}_4 \cdot \text{PbO}$ as a result of: (1) X-ray pattern studies of the system PbSO_4 -PbO, and (2) comparisons with the X-ray patterns of melts of the same compositions. The third compound apparently is a hydrate and on the basis of the available data is tentatively assigned the formula

⁷ C. S. Barrett, *op. cit.*

TABLE X

Characteristic X-Ray Data for the Basic Sulfates of Lead

Tetrabasic Lead Sulfate		Hydrous Compound		Dibasic Lead Sulfate		Monobasic Lead Sulfate	
d	I	d	I	d	I	d	I
8.1	.30	9.8	.30	3.75	.05	6.2	.20
3.25	1.00	4.85	.08	2.96	1.00	5.8	.10
3.11	.03	4.24	.08	2.87	.70	4.4	.02
3.04	.02	3.54	.10	2.69	.05	3.67	.80
2.87	.30	3.27	1.00	2.37	.50	3.47	.10
2.67	.02	3.12	.20	2.35	.50	3.33	1.00
2.31	.10	2.82	.08	2.29	.10	3.16	.10
2.04	.20	2.69	.10	2.11	.15	2.95	1.00
1.94	.15	2.49	.10	2.06	.20	2.84	.30
1.86	.11	2.44	.22	1.96	.40	2.46	.25
1.72	.25	2.21	.01	1.82	.25	2.42	.70
1.68	.02	2.14	.08	1.79	.40	2.39	.25
1.64	.08	2.07	.15	1.74	.10	2.34	.05
1.61	.20	1.97	.10	1.73	.20	2.26	.12
1.59	.15	1.77	.08	1.68	.20	2.22	.10
1.58	.15	1.68	.06	1.56	.30	2.05	.40
1.437	.05	1.63	.25	1.52	.20	1.96	.12
1.364	.08	1.57	.10	1.426	.06	1.91	.15
1.269	.08	1.51	.06	1.245	.05	1.84	.50
1.255	.06	1.394	.02	1.235	.05	1.76	.10
1.156	.20	1.345	.02	1.167	.20	1.72	.10
		1.255	.05			1.67	.15
		1.248	.05			1.66	.15
		1.218	.03			1.64	.05
		1.192	.03			1.57	.20
						1.51	.05
						1.48	.20
						1.47	.20
						1.445	.20
						1.435	.15
						1.360	.05
						1.306	.10
						1.232	.10
						1.213	.05
						1.174	.10

$\text{PbSO}_4 \cdot 3\text{PbO} \cdot \text{H}_2\text{O}$. This compound decomposes on heating at 280°C into a mixture of the tetrabasic and the monobasic lead sulfates.

The "d" values of those lines considered to be characteristic of the compounds concerned are tabulated in Table X, together with their relative intensities as recorded from the patterns for the wet method (boiled) suspensions, except for the dibasic lead sulfate, where, of course, the pattern from the melt must be used.

* * *

APPENDIX I

Experimental 2θ Values for NaCl Sample

Run. No.	Line Positions					
1.	31°48'	45°37'	56°40'	66°24'	75°21'	84°07'
2.	31°50'	45°30'	56°45'	66°20'	75°20'	84°05'
3.	31°43'	45°30'	56°33'	66°18'	75°18'	84°08'
4.	31°48'	45°36'	56°40'	66°20'	75°25'	84°05'
Avg.	31°47'	45°33'	56°40'	66°21'	75°22'	84°06'

Overall average deviation: $\pm 2.3'$

Comparison of Calculated and Experimental Values of 2θ

2θ Calc.	2θ Expt.	Diff.
31°42'	31°47'	5'
45°27'	43°33'	6'
56°28'	56°40'	12'
66°14'	66°21'	7'
75°18'	75°22'	4'
84°00'	84°06'	6'
	Avg.	6.7'

Thus 6.7' should be subtracted from the 2θ experimental values to get correct "d" values. The precision of these "d" values is then given by calculating the precision of "d" from the above average deviation and the equation:

$$n\lambda = 2d \sin\theta. \text{ Using an average deviation of } \pm 4',$$

the results are:	2d	d	d_{\pm}
	20°	4.425	± 0.015
	40°	2.248	± 0.004
	60°	1.538	± 0.002
	80°	1.196	± 0.001