

*Citation:*

Equilibria in the system Pb-S-O; the roasting reaction process, in:  
KNAW, Proceedings, 17 II, 1914, pp. 703-718

of the infra-red bands for three gases <sup>1)</sup>. This agreement appears from the foregoing table, in which the values of the three first mentioned gases are derived from MANDERSLOOT.

I hope soon to come back to the application of the used expressions to some other equilibria.

*Postscript.* During the correction of the proofs a treatise by O. STERN in the *Annalen der Physik* of June came under my notice, in which an expression is derived which shows close resemblance with that of Prof. VAN DER WAALS. Application on the iodine equilibrium can also here lead to a small moment of inertia, which is however considered improbable by STERN.

Amsterdam, Sept. 1914.

Anorg. Chem. Laboratory  
of the University.

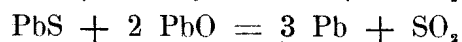
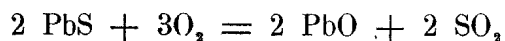
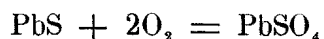
**Chemistry.** — “*Equilibria in the system Pb—S—O; the roasting reaction process*”. By Prof. W. REINDERS. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of Sept. 26, 1914).

#### *Introduction.*

1. The manufacture of galena into metallic lead is mostly carried out in this manner that the sulphide is first partially roasted and the mass then again strongly heated with unchanged or freshly added lead sulphide out of contact with air. Lead is then formed with evolution of SO<sub>2</sub>.

The reactions that take place in this process known under the name of “Rostreactionsarbeit” are generally given in the text-books as follows:



<sup>1)</sup> MANDERSLOOT. Thesis for the Doctorate. Utrecht. 1914.

For a proper insight into this process and to answer the question whether these reactions actually do take place it is necessary to study the equilibria between the different phases that may be formed therein.

After various older researches among which deserve to be mentioned those of H. C. JENKINS and E. H. SMITH <sup>1)</sup>, a systematic research as to these equilibria was carried out some years ago by R. SCHENCK and W. RASSBACH <sup>2)</sup>. They determined the equilibrium pressure of the sulphur dioxide evolved when three of the four phases PbS, PbSO<sub>4</sub>, PbO and Pb are heated together in an evacuated tube at 550° to 900°.

The conclusions which they drew from these measurements as to the nature of the equilibria occurring therein could, however, not be correct in many respects. Their idea has in fact been considerably modified in various subsequent publications thereon <sup>3)</sup>. But even the last concluding articles still contain many contradictions so that it is not plain what equilibria they have actually determined and which phases are stable in the presence of each other.

In the following will, therefore, be discussed (1) the different equilibria imaginable in this system and (2) the results will be communicated of researches which in consequence thereof have been carried out conjointly with Dr. F. GOUDRIAAN.

2. The equilibria between Pb and the compounds PbO, PbS, PbSO<sub>4</sub> and SO<sub>2</sub> may be considered as those in a system of three components, namely Pb, O, and S. The isotherm for the equilibria between the different phases can, then, be indicated by a triangle with these components as apexes. (See fig. 1).

Let us now first suppose that

- a. only the phases Pb, PbS, PbSO<sub>4</sub>, PbO and SO<sub>2</sub> are possible
- b. the gaseous phase is pure SO<sub>2</sub> and the lead phase pure lead.

In the last supposition we therefore neglect the small amount of PbS in the vapour and the solubility of PbS in molten lead; in the first supposition no notice is taken of the basic sulphates which according to the later researches of SCHENCK and RASSBACH <sup>4)</sup> occur as intermediate phases between PbSO<sub>4</sub> and PbO.

<sup>1)</sup> Journ. Chem. Soc. **71**, 666 (1897).

<sup>2)</sup> Ber. d. d. chem. Ges. **40**, 2185 (1907). Metallurgie **4**, 455, (1907).

<sup>3)</sup> Ber. d. d. chem. Ges. **40**, 2947 (1907); **41**, 2917 (1908). R. SCHENCK, Physikalische Chemie der Metalle.

<sup>4)</sup> Ber. d. d. chem. Ges. **41**, 2917, (1908).

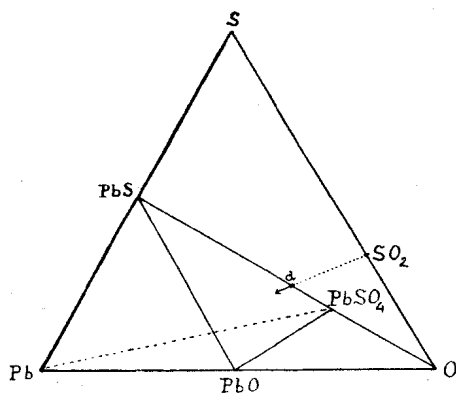


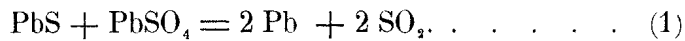
Fig. 1.

We shall see later how the deduced equilibria are being modified when we drop these simplifications.

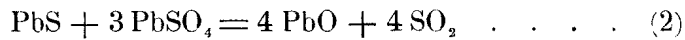
3. Let us imagine PbS heated at constant temperature between 600° and 800° in an enclosed space wherein a limited quantity of oxygen is forced. PbS is then partly converted into PbSO<sub>4</sub>.

The two phases will be capable of existing in the presence of each other and in an unchanged condition at a series of temperatures and pressures.

If on lowering the pressure this falls below a certain limit, one of the two following reactions will take place



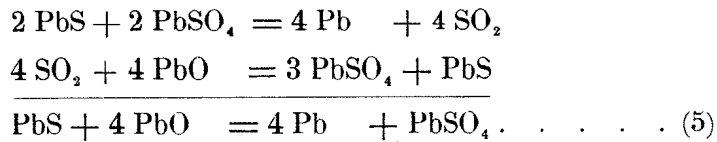
or



In both cases there are formed in addition to the two existing solid phases two new phases, namely fused Pb and SO<sub>2</sub>-gas, or solid PbO and SO<sub>2</sub>-gas. Hence, between these four phases a monovariant equilibrium will set in, which, at a constant temperature, is possible only at one special pressure. This will be *p*<sub>1</sub> or *p*<sub>2</sub>.

Only in a very special case, namely with an eventual transition point where the five phases PbS, PbSO<sub>4</sub>, PbO, Pb, and SO<sub>2</sub> might coexist, *p*<sub>1</sub> and *p*<sub>2</sub> are equal. As a rule, however, they are not and in consequence only one of the two monovariant equilibria can be stable.

For if *p*<sub>1</sub> > *p*<sub>2</sub> the reaction (1), in the presence of the five phases, will take place from the left to the right and the SO<sub>2</sub> formed act on PbO according to equation (2) in the direction ←. Hence, the two reactions together result in the following conversion:



This transformation takes place until one of the phases of the first member of the equation is used up, whilst the other with Pb

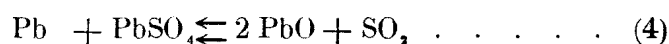
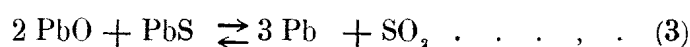
and  $\text{PbSO}_4$  is left.  $\text{PbS}$  and  $\text{PbO}$  are, therefore, not capable of existing side by side of each other.

If, conversely  $p_1 < p_2$  the different reactions take place in the opposite sense and  $\text{Pb}$  and  $\text{PbSO}_4$  recede from each other.

Hence, of the phase pairs  $\text{Pb} + \text{PbSO}_4$  and  $\text{PbS} + \text{PbO}$  only one can be stable, the other forms a metastable equilibrium.

Here we have a case quite similar to that occurring with reciprocal salt pairs where also only one of the two pairs can be stable.

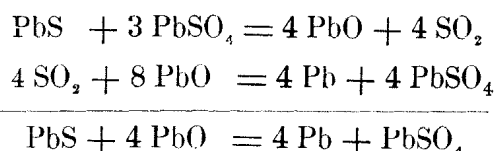
4. Let us now also consider the two other monovariant equilibria which may be assumed to exist with  $\text{SO}_2$ -vapour and which are indicated by the equations



In the case  $p_1 > p_2$ , it follows at once from the incompatibility of the phases  $\text{PbS}$  and  $\text{PbO}$  that the equilibrium (4) can be stable, but not equilibrium (3).

Moreover, we then must have  $p_3 > p_1$  for otherwise after the reaction (1) in the direction  $\rightarrow$  might follow the reaction (3) in the direction  $\leftarrow$  which reactions might jointly cause the conversion (5) in the direction  $\leftarrow$ , which is in conflict with the premiss.

Finally we shall have  $p_4 < p_2$ , for then the stable equilibrium may also be again attained by the reaction (2) in the direction  $\rightarrow$  followed by (4) in the direction  $\leftarrow$ , namely:



Hence, we get this result:

If  $\text{Pb} + \text{PbSO}_4$  forms the *stable* phase pair, then only the monovariant equilibria (1) and (4) are stable and  $p_3 > p_1 > p_2 > p_4$ .

If  $\text{PbO} + \text{PbS}$  form the *stable* phase pair, all the reactions occur in the opposite sense and only the monovariant equilibria (2) and (3) are stable, whereas then  $p_4 > p_2 > p_1 > p_3$ .

5. Starting from the mixture of  $\text{PbS}$  and  $\text{PbSO}_4$  (for instance  $a$  in fig. 1) we will, on withdrawal of  $\text{SO}_2$  travel either through the monovariant equilibria (1) and (4) (region  $\text{PbS}$ ,  $\text{PbSO}_4$ ,  $\text{Pb}$  and region  $\text{PbSO}_4$ ,  $\text{Pb}$ ,  $\text{PbO}$  of Fig. 1) or the equilibria (2) and (3) (region

PbS, PbSO<sub>4</sub>, PbO and region PbS, PbO, Pb) to finally retain the equilibrium Pb + PbS or Pb + PbO after eliminating the SO<sub>2</sub> as much as possible.

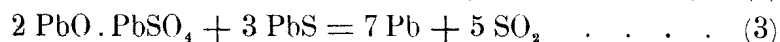
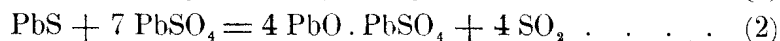
Hence, the reactions (1) and (3), which are generally quoted as taking place in the roasting reaction process cannot possibly indicate *both* stable equilibria.

Of the p-T-lines which SCHENCK and ROSSBACH determined by addition of PbSO<sub>4</sub>, PbS and Pb and of PbS, PbO and Pb one at least must, therefore, indicate an instable equilibrium or an equilibrium between phases other than those which were brought together in the reaction tube.

We will see later that both equilibria are metastable and that the pressure lines recorded by them relate to the equilibrium between other phases.

6. The supposition made in (2) sub *a* is not correct. Between PbSO<sub>4</sub> and PbO there still arrive three basic salts as intermediate phases, namely PbO.PbSO<sub>4</sub>, (PbO)<sub>2</sub>PbSO<sub>4</sub> and (PbO)<sub>3</sub>PbSO<sub>4</sub>. The first of these can be in equilibrium with PbSO<sub>4</sub>.

The four monovariant equilibria mentioned in (3) now become:



and the alternative found must read:

either Pb + PbSO<sub>4</sub> stable and then  $p_3 > p_1 > p_2 > p_4$  and only (1) and (2) stable,

or PbS + PbO.PbSO<sub>4</sub> stable and then  $p_3 < p_1 < p_2 < p_4$  and only (2) and (3) stable.

#### *Experimental.*

(conjointly with Dr. F. GOUDRIAAN).

7. In order to investigate which of these two phase pairs was stable and at the same time to know the SO<sub>2</sub>-pressure of the stable equilibrium, an intimate mixture of PbS and PbSO<sub>4</sub> (6—8 grams) was heated in a porcelain tube connected by means of a ground joint with a manometer and an air-pump.

The lead sulphide was precipitated from a solution of lead acetate with H<sub>2</sub>S and after washing, dried by heating in a current of nitrogen at 200°—300°.

The lead sulphate was precipitated from a solution of lead acetate with sulphuric acid and also dried at 300°.

The mixture was introduced in a porcelain boat. The remaining space in the reaction tube was occupied by a porcelain rod so as to render the gas-volume as small as possible and thus to accelerate the setting in of the equilibrium as much as possible.

The heating took place in an electric furnace. The temperature was measured with a Pt-PtRh thermocell and a galvanometer.

8. Although the reacting substances had been previously dried at 300° there still was evolved, on heating at 500°, in vacuo, a little moisture, which condensed in the colder part of the tubes and was removed by a repeated evacuation and gentle heating.

Subsequently the dissociation pressure was measured at different pressures between 500°—700°.

The equilibrium set in very rapidly so that when the temperature had been raised and more gas began to evolve there could generally not be noticed any change in pressure after 20—30 minutes. Then a further evolution of SO<sub>2</sub> was caused by a short heating at a somewhat higher temperature and after cooling to the original temperature the course of the absorption of the SO<sub>2</sub> was recorded. This also took place very rapidly. The equilibrium was thus attained from both sides and yielded figures which differed from each other at most 2 or 3 m.m. Also the same pressure again set in after an evacuation. The equilibrium is, therefore, independent of the total composition, which was confirmed by a change in the proportions of PbSO<sub>4</sub> and PbS.

The results are contained in table I. (Fig. 2 Curve I).

TABLE I.

7 PbSO <sub>4</sub> on 1 PbS		5 PbSO <sub>4</sub> on 1 PbS		3 PbSO <sub>4</sub> on 1 PbS	
<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
582°	26	604	50	590	30
606	56	634	100	620	72
630	94.5	660	185	670	222
655	156	688	346		
680	280				

After the tube had been evacuated a few times and a certain quantity of the dissociation product might thus have been formed,

and as it had been shown that always the old equilibrium again set in, the oven was allowed to cool and the tube was withdrawn.

The reaction product was strongly caked and of a *lighter colour* than the original mixture of PbS and PbSO<sub>4</sub>. Here and there were visible granules with a strong metallic lustre so that at first the suspicion was raised that lead had formed as a reaction product. On closer examination by means of a magnifying glass these granules proved to be very beautifully formed crystals of "galena" which had deposited, besides in the reaction mass, also against the porcelain boat and the extremity of the porcelain rod. The analysis showed this to be perfectly pure PbS, whilst in the reaction product itself not a trace of free lead could be detected.

Hence, no lead has formed so that the reaction product must be *basic lead sulphate*.  $PbS + PbO.PbSO_4$  form the stable phase pair,  $Pb + PbSO_4$  the metastable one.

9. This was confirmed by the following experiment:

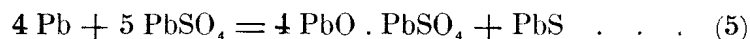
An intimate mixture of PbSO<sub>4</sub> and finely divided lead scrapings in the proportion of 10 PbSO<sub>4</sub> to 1 Pb was heated in an evacuated and sealed tube for 3 hours at 600°.

The product obtained gave with hydrochloric acid a very distinct evolution of H<sub>2</sub>S.

A weighed quantity was now heated in a small flask with strong hydrochloric acid and the gas expelled collected in an ammoniacal solution of hydrogen peroxide. This solution was boiled for a while, then acidified, and the resulting H<sub>2</sub>SO<sub>4</sub> precipitated as BaSO<sub>4</sub>.

Five grams of mixture containing originally 0,380 gram of Pb, yielded 0,040 gram of BaSO<sub>4</sub>, equivalent to 0,041 gram of PbS.

According to the equation:



0,142 gram of Pb has been required for this 0,041 gram of PbS.

Although the lead has not yet entirely disappeared, a considerable quantity of the same has been converted into PbS<sup>1)</sup>.

10. The pressures observed almost entirely agree with the values found by SCHENCK and RASSBACH for the mixture of PbS + PbSO<sub>4</sub> + Pb as well as for PbS + PbSO<sub>4</sub> + PbO. They conclude that the pressures

<sup>1)</sup> Afterwards it came to our knowledge that also JENKINS and SMITH (l.c. p. 691) had already made an experiment from which this is shown. They heated a mixture of equal molecular quantities of Pb and PbSO<sub>4</sub> in a porcelain crucible at dull red heat for half an hour; from the residual mass could be expelled with HCl a quantity of H<sub>2</sub>S corresponding with 1,41% of sulphur.



relate to the equilibrium between the first three phases and that the second trio is not stable. From the preceding it follows that both equilibria are metastable and that the pressures recorded relate to the equilibrium  $\text{PbS}, \text{PbSO}_4, \text{PbO} \cdot \text{PbSO}_4, \text{SO}_2$ .

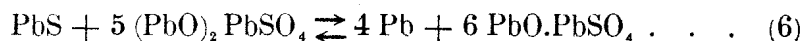
The fact that the lead present exerts so little influence on the equilibrium pressure proves that reaction (4), which should lead to a higher pressure  $p_4$  and the reactions (1) and (3) in the direction  $\leftarrow$  which should lower it either compensate each other or, in comparison with the reaction (2) proceed so slowly that they do not perceptibly alter the pressure. Probably the more finely divided lead is soon converted and the remaining lead, united to larger drops, offers such a small surface of attack that it can react but very slowly.

11. When now from the  $\text{PbS} + \text{PbSO}_4$  so much  $\text{SO}_2$  has been abstracted that all has passed into  $\text{PbS} + \text{PbO} \cdot \text{PbSO}_4$ , the equilibrium has become divariant. The residual phases will be capable of existing by the order of each other in a series of pressures  $< p_2$ .

If, however, the pressure falls below a definite limit, a third condensed phase appears. Two phases are concerned here, namely  $\text{Pb}$  and  $(\text{PbO})_2 \cdot \text{PbSO}_4$ .

As noticed in the case  $\text{PbS} + \text{PbSO}_4$ , only one of the two can be in stable equilibrium with  $\text{PbS}$  and  $\text{PbO} \cdot \text{PbSO}_4$ .

This depends on which of the phase pairs  $\text{PbS} + (\text{PbO})_2 \cdot \text{PbSO}_4$  and  $\text{Pb} + \text{PbO} \cdot \text{PbSO}_4$ , which can be converted into each other by double decomposition:



is stable.

12. In order to investigate this an intimate mixture of finely divided lead scrapings and basic lead sulphate in the molecular proportion of 3:1 was heated for three hours in an evacuated and sealed tube at  $670^\circ$ — $680^\circ$ .

The  $\text{PbO} \cdot \text{PbSO}_4$  had been prepared by the moist process, according to D. STRÖMHOLM<sup>1)</sup>, by digesting finely powdered  $\text{PbSO}_4$  with a 1—2%  $\text{NH}_3$ -solution. The analysis of the product obtained gave 84.88%  $\text{PbO}$ , theory for  $\text{PbO} \cdot \text{PbSO}_4$  84.79%.

The heating of the mixture  $\text{Pb} + \text{PbO} \cdot \text{PbSO}_4$  yielded apparently a but little changed product. It gave, however, a slight sulphide reaction. Thus it seemed that the mixture selected did not form the

<sup>1)</sup> Zeitschr. f. anorg. Chem. **38**, 429 (1904).

stable phase pair. We must, however, consider that the lead phase need not be pure Pb, but may contain dissolved PbS and hence there exists the possibility that the PbS found was present, not as a free phase, but as a solution in the molten Pb.

The amount of PbS was, therefore, determined quantitatively.

From two grams of the mixture were obtained 17,4 mg. of  $\text{BaSO}_4$  corresponding with 17,8 mg. of PbS. For the formation of 17,8 mg. of PbS according to reaction (6) are required 70 mg. of Pb. Before the heating 2 grams of the mixture contained 1,082 grams of lead. Hence, there remains 1,022 gram of Pb, which in 100 grams contains  $\frac{17,8}{1022} \times 100 = 1,77$  grams of PbS.

From the observations of FRIEDRICH and LEROUX<sup>1)</sup> it follows that the lead solution saturated with PbS at  $680^\circ$  contains 2,5% PbS. Hence the PbS will be present in the heated mixture not as a free phase, but as a solution in Pb, and  $\text{Pb} + \text{PbO.PbSO}_4$  will form the stable phase pair.

13. This conclusion was further confirmed by the dissociation experiments, starting from a mixture of PbS and  $\text{PbO.PbSO}_4$ .

These experiments were conducted in a manner similar to that in the case of PbS and  $\text{PbSO}_4$ . The  $\text{SO}_2$ -evolution started at  $680^\circ$ . The equilibrium set in quite as easily as with  $\text{PbS} + \text{PbSO}_4$  and could be determined readily from both sides. Also, after removal of larger quantities of  $\text{SO}_2$ , the same equilibrium pressure was again always obtained. In order to prevent fusion the mass was not heated above  $800^\circ$ .

The results obtained are united in table II (Fig. 2, Curve II).

TABLE II.

$t$	$p$
712	27.5
740	63
750	78
753	87.5
770	123
790	233

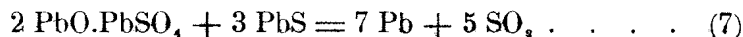
<sup>1)</sup> Metallurgie 2, 536 (1905).

These values correspond very well with the pressures found by SCHENCK and RASSBACH with a similar mixture and with a mixture of PbS + PbO which has been heated above 800° and then cooled.

On opening the apparatus it appeared that the reaction product, although not fused, had strongly caked: the porcelain boat was strongly attacked and on the rod a sublimate of very beautiful PbS-crystals had again deposited. It was not doubtful that the reaction mass contained *metallic lead*; there could be found large, soft paper-marking and malleable particles. Finally, it was proved by extracting a portion of the reaction product first a few times with ammonium acetate and then with lead acetate. All the PbSO<sub>4</sub> and PbO then dissolves. The residue was treated with fuming HNO<sub>3</sub>, which converts the PbS quantitatively into PbSO<sub>4</sub>. After expelling the HNO<sub>3</sub> and filtering off the PbSO<sub>4</sub>, any Pb formed eventually as Pb(NO<sub>3</sub>)<sub>2</sub> must be present in the filtrate.

The filtrate gave a strong lead reaction. The reaction mass thus contains metallic lead.

Hence *Pb + PbO.PbSO<sub>4</sub>* are the stable phase pair and the pressures measured relate to the reaction:

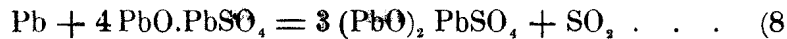


14. From the above it follows that with a sufficient excess of basic lead sulphate the end of reaction (7) will be a mixture of PbO.PbSO<sub>4</sub> and Pb. (In the latter, however, a little PbS will still be dissolved).

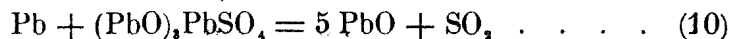
This equilibrium is divariant and, on a sufficient reduction of pressure, will pass into a monovariant equilibrium.

The third condensed phase occurring therein cannot be a second metallic phase for the solution of PbS in Pb already present is mixable with pure lead in every proportion.

Hence, it must be the basic sulphate (PbO)<sub>2</sub>.PbSO<sub>4</sub> which follows the PbO.PbSO<sub>4</sub> and the reaction occurring is indicated by the following equation:



The monovariant equilibrium of this reaction will in turn be followed by still two other monovariant equilibria wherein occur the reactions represented by the equations:



In these reactions *primary formed lead therefore disappears* on behalf of PbO until, finally, only Pb + PbO is left.

15. Pressures appertaining to the first monovariant equilibrium were obtained by starting from a mixture of Pb and  $\text{PbO} \cdot \text{PbSO}_4$ .

Not until  $700^\circ$  an evolution of gas was perceptible. The equilibrium sets in with much greater difficulty than in the first two cases; generally two or three hours were required. Probably this is due to the fact that the metal conglomerates and thus offers but a small contact surface with the basic salt. It is also very certain, however, that the greater vapour tension of the PbS will have strongly promoted the setting in of the previous equilibria of which PbS was one of the active phases. The equilibrium could again be attained from both sides.

The following pressures were measured (Fig. 2 Curve III):

TABLE III.

$t$	$p$
750'	36.5
771	61
789	98

The tube was subsequently evacuated at  $789^\circ$  and the equilibrium pressure again determined. This proved to be unchanged. Even on

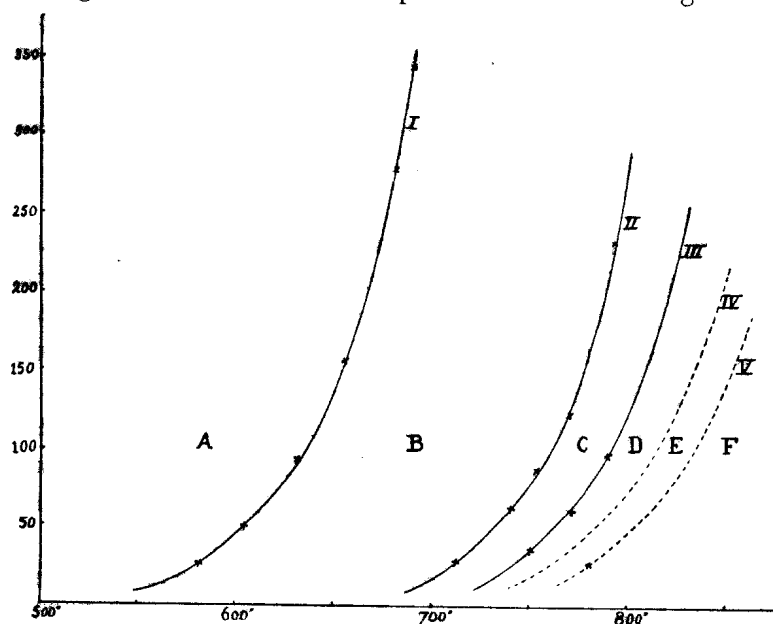


Fig. 2.

evacuating a second time the pressure reverted to its old value. The pressures measured therefore relate to a purely monovariant equilibrium.

16. Without opening the apparatus the experiments were now continued with the same mixture at  $789^{\circ}$ . The tube was, therefore, evacuated for the third time and then again a few times and each time the equilibrium pressure was again measured. It now appeared that the old pressure no longer set in, but that a lower pressure was attained and the more so when more  $\text{SO}_2$  had been withdrawn. In succession were found 93, 75, 61, 54, 41, 34, and 28 m.m.

This different behaviour can be explained in two ways.

1. The equilibrium is no longer monovariant, but divariant. Instead of three solid phases there are only two, one of which possesses a variable composition. This phase might be a very basic sulphate with a variable content in PbO. The fusion diagram PbO —  $\text{PbSO}_4$  of SCHENCK and RASSBACH gives, however, but little support to this conception.

2. The pressures measured are not true equilibria pressures, but indicate a stationary condition.

For if, on evacuating, the pressure falls below the equilibrium pressure of equilibrium (9) the basic sulfate  $(\text{PbO})_2 \text{PbSO}_4$  can decompose still further and give rise to the formation of  $(\text{PbO})_3 \text{PbSO}_4$ .  $\text{Pb} + \text{PbO} \cdot \text{PbSO}_4$  then strive, according to reaction (8) towards the pressure  $p_s$ ,  $(\text{PbO})_3 \text{PbSO}_4 + \text{SO}_2$  according to reaction (9), however, in the direction  $\leftarrow$  towards  $p_p$ . And when finally both reactions take place with equal velocity, we obtain an apparent equilibrium at a pressure between  $p_s$  and  $p_p$  and dependent on the quantities of the different phases.

It is even possible that PbO is also formed and that reaction (10) thus takes place simultaneously.

17. The second assumption was the most probable one. In order to test it more closely a mixture of Pb and  $(\text{PbO})_3 \text{PbSO}_4$  was heated in the pressure tube. From this mixture PbO only can be formed as the third phase so that only one reaction, that of the monovariant equilibrium (10), should be possible.

$(\text{PbO})_3 \cdot \text{PbSO}_4$  was obtained by fusion of 1  $\text{PbSO}_4$  with more than 3 PbO. As porcelain is strongly attacked by PbO, the mixture was heated in a magnesia boat previously heated and saturated with lead oxide.

The result of the measurement at  $780^{\circ}$  was  $p = 23$ , after evacuation at the same temperature again 22 m.m., then at  $800^{\circ}$ , 38 and after evacuation successively 30, 22, 16 m.m. Thus no constant equilibrium is attained.

On opening the pressure tube nearly all appeared to have been

fused and run through the boat although the temperature had not got above  $800^{\circ}$ , whereas the eutecticum of  $\text{PbO}$  and  $(\text{PbO})_3 \cdot \text{PbSO}_4$ , according to SCHENCK and RASSBACH is at  $820^{\circ}$ . Probably the  $\text{MgO}$  is attacked by the  $\text{PbSO}_4$ . The want of a suitable material which is attacked neither by  $\text{PbO}$  nor by  $\text{PbSO}_4$  or  $\text{Pb}$  at this high temperature renders a correct determination of dissociation pressures for reaction (9) and (10) a matter of great difficulty.

If we accept the value of 20 mm. at  $780^{\circ}$  as the correct one for the equilibrium (10), the  $p$ - $T$ -line for this equilibrium would then run as indicated by line V in fig. 2.

The  $p$ - $T$ -line of equilibrium (9) then lies between III and V and is indicated schematically in Fig. 2 by line IV.

18. Although from the preceding it is evident that  $\text{PbS}$  and  $\text{PbO}$  cannot be coexistent, a few experiments were made nevertheless in order to confirm this opinion.

SCHENCK and RASSBACH in all their publications consider the equilibrium  $\text{PbS}$  and  $\text{PbO}$  to be stable although in their dissociation experiments it had already been shown that with such a mixture reproducible pressures were not always obtained, for instance if the temperature had been raised to above  $800^{\circ}$ . They also noticed the formation of sulphate, but assume that this can only be formed at a high temperature and then remains intact on sudden cooling to the dissociation temperatures.

We have now heated an intimate mixture of  $\text{PbO} + \text{PbS}$  for some hours at  $600$ — $700^{\circ}$  in an evacuated and sealed tube.

The reaction product perceptibly contained sulphate. This was estimated quantitatively by boiling a weighed quantity of the product with aqueous sodium hydroxide and then passing  $\text{CO}_2$ . The  $\text{PbSO}_4$  present is then converted into  $\text{PbCO}_3$ . After filtering and acidifying the filtrate the sulphate was precipitated as  $\text{BaSO}_4$ . A check analysis was also made on a portion of the mixture that has not been subjected to heating, under exactly the same conditions of boiling etc.

Mixture of 4 mols. $\text{PbO}$ to 1 mols. $\text{PbS}$ . Temperature $670$ — $680^{\circ}$				
Time of heating	0	$1\frac{1}{2}$	3	6 hours
Gram of $\text{BaSO}_4$ per gram of mixture	0,0498	0,0758	0,1000	0,1121
Additional sulphate formed on heating at $680^{\circ}$				
in gram of $\text{BaSO}_4$ per gram of mixture	—	0,0260	0,0502	0,0623

If the mixture had been converted completely into basic sulphate

according to the equation  $5 \text{PbO} + \text{PbS} = \text{PbO} \cdot \text{PbSO}_4 + 4 \text{Pb}$ , 1 gram of the mixture should have yielded 154 mg. of  $\text{BaSO}_4$ . Hence, a large proportion of the  $\text{PbO} + \text{PbS}$  has been converted.<sup>1)</sup>

The pressures which SCHENCK and RASSBACH observed with a mixture of  $\text{Pb} + \text{PbO} + \text{PbS}$  do, therefore, probably not relate to an equilibrium of these three phases with  $\text{SO}_2$ , but to another equilibrium.

By a comparison of their observations with our measurements it appears that on heating at temperatures below  $800^\circ$  this is the equilibrium:  $\text{Pb} + \text{PbO} \cdot \text{PbSO}_4 + (\text{PbO})_2 \text{PbSO}_4$ , and on heating above  $800^\circ$  and then cooling, the equilibrium:  $\text{Pb} + \text{PbS} + \text{PbO} \cdot \text{PbSO}_4$ .

Also below  $800^\circ$  however, this latter equilibrium sets in, which with a sufficient excess of  $\text{PbS}$  is the most stable, as shown from the following experiment:

A mixture of 4 mols. of  $\text{PbO}$  to 1 mol. of  $\text{PbS}$  was heated in a pressure tube. The evolution of gas started at  $660^\circ$ . After evacuation the following change in pressure was observed at  $750^\circ$ .

time in min.	pressure
0	5
7	14
20	26
34	33
42	35
70	41
100	44
160	53
220	65
280	74
340	81
400	83
460	83

The pressure thus rises rapidly to  $\pm 38$  m.m. and then increases gradually to 83.

The first pressure falls on the  $p$ - $T$ -line of  $\text{Pb} + \text{PbO} \cdot \text{PbSO}_4 + (\text{PbO})_2 \text{PbSO}_4$ , the second on that of  $\text{Pb} + \text{PbS} + \text{PbO} \cdot \text{PbSO}_4$ .

Similarly was found with a fresh mixture on heating at  $790^\circ$  a

<sup>1)</sup> The high result of the sulphate content in the check experiment is very striking, because both the  $\text{PbO}$  and the  $\text{PbS}$  employed were free from sulphate. Evidently the conversion of  $\text{PbS} + \text{PbO}$  into sulphate takes already place at the boiling heat in the aqueous solution, from which it follows that also at the ordinary temperature  $\text{PbS}$  and  $\text{PbO}$  are not stable in each other's presence.

first halt at  $\pm 100$  m.m. and then a slow rise to 236 m.m. Both pressures are again situated on the above cited  $p$ - $T$ -lines.

### CONCLUSION.

19. Summarizing it thus appears that on abstraction of  $\text{SO}_2$  from a mixture of  $\text{PbS}$  and  $\text{PbSO}_4$ , the subjoined monovariant equilibria are successively met with, which are indicated in fig. 3 by the regions I, II, III, IV and V.

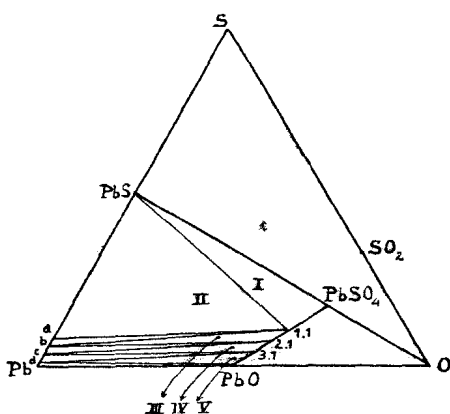
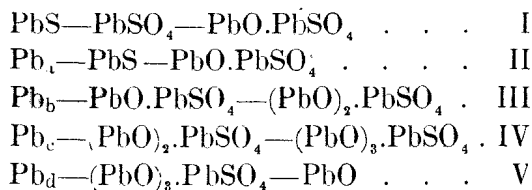


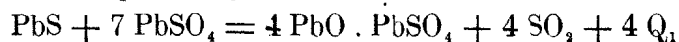
Fig. 3.

Therein region *A* is the existential region of  $\text{PbS} + \text{PbSO}_4$

„	„	<i>B</i>	„	„	„	„	„	$\text{PbSO}_4 + \text{PbO} \cdot \text{PbSO}_4$
„	„	<i>C</i>	„	„	„	„	„	$\text{PbO} \cdot \text{PbSO}_4 + \text{Pb}$
„	„	<i>D</i>	„	„	„	„	„	$(\text{PbO})_2 \text{PbSO}_4 + \text{Pb}$
„	„	<i>E</i>	„	„	„	„	„	$(\text{PbO})_3 \text{PbSO}_4 + \text{Pb}$
„	„	<i>F</i>	„	„	„	„	„	$\text{PbO} + \text{Pb}$

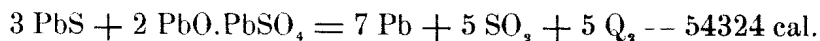
Hence, at the temperatures and pressures of region *F* all the sulphur will have been expelled from the roasting material.

20. By substituting the values found in table 1 first series in the equation  $\log p = -\frac{Q}{4,571 T} + C$  and combining the equations thus obtained in pairs,  $Q_1$  was calculated for the reaction:

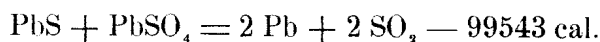
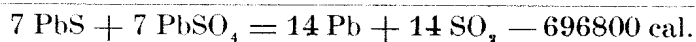
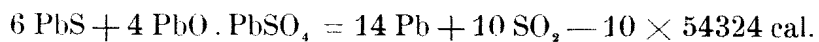




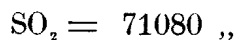
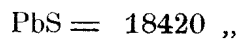
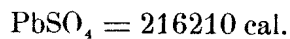
and as mean value was found  $-38390$  cal. Applying the same principle to the  $p$ - $T$ -values of table 2 we found as the mean value for  $Q_2$  in the reaction:



In order to check these figures we eliminate the unknown heat of formation of the basis sulphate from these equations:



From the molecular heats <sup>1)</sup>



the calculation for the above reaction at  $20^\circ$  gives  $-92470$  cal.

The agreement is tolerable.

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Technical University.*

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<sup>1)</sup> LANDOLT. BÖRNSTEIN, Phys. Chem. Tabelle 1912, 870 and 853.

**(November 27, 1914).**