ART. XXXV.—*The Sulphides of Zinc, Cadmium, and Mercury; their Crystalline Forms and Genetic Conditions;* by E. T. ALLEN and J. L. CRENSHAW. *Microscopic Study* by H. E. MERWIN.

INTRODUCTION.

MINERAL genesis in its fullest sense includes not only a knowledge of the limiting conditions outside of which a mineral can not exist, but a knowledge of the particular processes within the above limits by which the mineral is actually formed in the earth's crust. Concerning the first half of the problem,—the limiting conditions, the general relations of composition, temperature and pressure are pretty well understood, in so far as they have to do with equilibria. In equilibrium studies, however, *unstable forms* are commonly overlooked or avoided, but they must be taken account of in mineral genesis because many minerals are unstable forms. They differ from the unstable forms best known to chemists in their greater inertness; indeed, they often appear capable of unlimited existence at ordinary temperatures, though there is a potential difference between them and truly stable forms. For unstable forms an upper limit of temperature may be set, above which they can not exist. This is found experimentally by a determination of the lowest temperature at which, *under the most unfavorable conditions*, transformation into the stable form can be followed. We say "under the most unfavorable conditions," because the nature of the system in which the mineral undergoes transformation vitally affects the rate of the latter. Heating *alone*, i. e., without the addition of any solvent substance, is in general the condition most unfavorable to change. The velocity of the change would then be at a minimum and the temperature at which it first became noticeable would mark the upper limit of the actual existence of the mineral, above which it could never be formed.* This temperature is evidently not a sharp point, but it is, at least in some cases, a valuable limit in geology.

The effect of pressure on reversible changes is comparatively slight, in general, in systems containing no gaseous phase, though it may be considerable on minerals formed at great depths. In systems which contain a gaseous phase, the mass law affords us a guide to the influence of pressure. It may be noted here, by way of example, that in the formation of sulphides with hydrogen sulphide, a variation in the pressure of the latter only affects the quantity, not the nature of the solid phase, and while it would also condition the concentration

* Unstable forms may sometimes be obtained in the laboratory at temperatures where a slight disturbance is sufficient to effect their transformation, but it is hardly to be supposed that anything of this sort occurs in nature.

of the metal of the sulphide in the liquid phase, the absolute amount of the variation in most cases would be very small on account of the virtual insolubility of most mineral sulphides. Comparatively soluble sulphides like zinc sulphide are exceptional.

A comprehensive knowledge of necessary or even sufficient conditions of composition in mineral genesis is limited by the meagerness of what we know of chemical affinities. In practice, we must be content with the investigation of those systems which by reason of their simplicity or the light they are likely to throw on natural phenomena are especially promising. The method of procedure will depend materially on the class of minerals we have to study; e. g., if we have under consideration a *magmatic mineral*, the rock of which it is a constituent is a partial guide to the composition of the solution in which it crystallized, although it must not be forgotten that important volatile and soluble constituents may have escaped during the processes of rock formation. The best way to get light on the genesis of such a mineral is doubtless to study the behavior of systems made up of components, generally oxides, which we find in the rock. If, however, the mineral in question is a *vein mineral*, we have no similar indication of the composition of the original solution. Still, all lines of evidence indicate that the solution must have been aqueous and that the constituent elements of the mineral existed usually in more complex forms than those in the magmatic solutions. Thus the sulphur of a sulphide may have existed originally as hydrogen sulphide, soluble sulphides, sulphates or even more complex forms, while the metal doubtless occurred in the form of some salt. Now, while we might obtain valuable chemical information by the investigation of systems consisting of sulphur and the various metals, it would not be very helpful in the elucidation of geological processes. To get at the composition of the systems in which vein minerals have formed, we must rely rather on our knowledge of the composition of springs and mine waters and on our knowledge of general chemistry. At the same time, important subsidiary information may be obtained by the study of various other systems adapted especially to the case in hand.

The determination of the geological portion of the subject of mineral genesis might be left entirely to the geologist; but it will be evident to anyone that there are decided advantages in the study of these questions by a method of consultation between the laboratory and the field worker—a method which affords opportunities for mutual suggestion and criticism, and promises safer conclusions.

The necessary and sufficient conditions for the formation of the sulphides of zinc, cadmium, and mercury which are stated in these pages have been worked out with geological aid from

several members of the U. S. Geological Survey, who will be specially mentioned as occasion demands.

I. The Sulphides of Zinc: Sphalerite and Wurtzite.

The sulphide of zinc occurs in nature crystallized in two different forms, the common sphalerite, or blende, which belongs to the regular system and the comparatively rare wurtzite which belongs to the hexagonal system. Both are transparent and straw-colored* when pure and are distinguished from each other and from amorphous zinc sulphide by the presence or absence of double refraction† and by the magnitude of the indices of refraction. The latter for sphalerite is 2·37, which in sodium light is slightly less than that of wurtzite for the ray vibrating in the vertical axis, while the other index of the latter mineral is 2·35 (Merwin). These properties were determined on a very pure natural sphalerite from Sonora, Mexico, and on the wurtzite formed from it by heating to the proper temperature. The analysis of this mineral was as follows:

Zn	66·98
Fe	0·15
S	32·78
	99·91

The specific gravity of the two minerals was also determined on the same material by the pycnometer method at 25°.

Table I.

Specific gravities of Sphalerite and Wurtzite.

Sphalerite.[1]			Wurtzite.	
I. Sonora, Mex.	II. Same locality.		Formed by heating sphalerite	
mineral at 25° water at 25°	mineral at 25° water at 25°	mineral at 25° water at 4°	mineral at 25° water at 25°	mineral at 25° water at 4°
4·101	4·103	----	4·098	----
4·102	4·102	----	4·100	----
4·100	4·102	----	4·098	----
4·099	----	----	4·098	----
4·007	----	----	4·100	----
av. 4·100	av. 4·102	av. 4·090	av. 4·099	av. 4·087

[1] For the determination of sample I, only about 6·5 g. were used; for those of sample II, about 13 g. was available, and the latter values are subject to less error in consequence.

* The blende from Franklin, N. J., and from Nordmark, Sweden, is described as pure white. (Dana, A Textbook of Mineralogy, 1906, p. 61.) Our purest synthetic products have all been straw-color.

† For an interesting exception to isotropy in amorphous bodies see microscopic part of this paper, p. 383.

It appears from the above data that the specific gravities of sphalerite and wurtzite of identical composition are nearly the same, but that of wurtzite is very slightly lower.

Enantiotropic relation between Sphalerite and Wurtzite.

If sphalerite is heated to a temperature of about 1100° and cooled with moderate rapidity, i. e., to 100° inside of two hours, microscopic examination shows that it is completely transformed into wurtzite.* The heating curve, however, shows no break to indicate that any heat change has accompanied the transformation. A very careful test of this point was made as follows :†

FIG. 1.

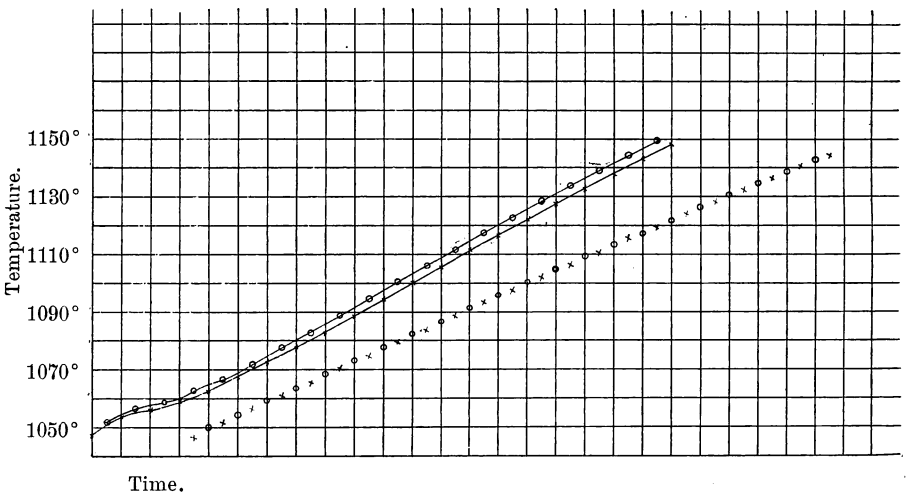

FIG. 1. Heating curves for sphalerite and wurtzite in the vicinity of the inversion point. × × Sphalerite, ○ ○ Wurtzite.

Two small cylindrical crucibles, one containing 10 g. sphalerite and the other 10 g. wurtzite, each provided with a calibrated thermoelement, were heated side by side in the same furnace, the temperature of the two elements being read alternately every half-minute. By reference to the curves in fig. 1, it is seen that those of the first pair are practically parallel ; those of the second pair are virtually identical, i. e., the temperature of the two crucibles, by reason of their position in the furnace, was a little closer together in the second case. Neither pair

* J. Weber heated small plates of sphalerite in a Bunsen flame and cooled quickly. He found they had become anisotropic. Zs. Kryst., xliv, 212, 1908. Biltz expressed the opinion that sphalerite might change to wurtzite without sublimation. Zs. anorg. Ch., lix, 273, 1908.

† See W. P. White, this Journal, xxviii, 488, 1909.

shows any lagging of one curve behind the other to indicate any absorption or evolution of heat in either substance.

The temperature interval which is included by the curves will be found by comparison with the sequel to lie *above* the true inversion point. It was found, however, by actual trials that the transformation was subject to hysteresis and, on comparatively rapid heating, occurred in this interval. The reaction sphalerite $\rightleftarrows$ wurtzite was proved to be reversible by long heating at selected temperatures (see below), and consequently there must be a heat absorption when sphalerite is heated; and further, since the change was found to be complete inside of a time interval of six minutes and a temperature interval of 70°, this effect must be quite small. The inversion point was determined with considerable accuracy by long heats at measured temperatures, after which the direction of the change was determined microscopically. The sluggish nature of the change from wurtzite to sphalerite made it possible to cool the former to room temperature without any transformation into sphalerite. By continually narrowing down the temperature interval on either side of which the transformation was reversed, the inversion point was determined within $\pm$ 5°.

The apparatus* used for most of the work consisted of a tube of Berlin porcelain 25^{mm} inside diameter and 500^{mm} long, closed at one end and glazed inside and out. The tube, which was held in a vertical position, was closed at the top by a doubly perforated graphite cover. Through the central orifice passed a glazed Marquardt tube of 6^{mm} internal diameter, also closed at one end, which protected the thermoelement. Attached to the closed end were one or more short tubes. also closed at one end, of the same size and material, which contained the zinc sulphide in the form of coarse powder. The large enclosing tube was traversed by a current of dry hydrogen sulphide, which entered by a second Marquardt tube open at both ends. The heating was done by a resistance furnace which surrounded the cylinder.

The thermocouple which was used for the final temperature measurements was calibrated after they were finished, at the silver point (960°).

By reference to Table II it will be seen that the inversion point of zinc sulphide may be located between 1015° and 1024°, i. e., 1020° $\pm$ 5°. As was mentioned above, the reversion of wurtzite to sphalerite is very slow. Instead of heating in an atmosphere of hydrogen sulphide, it was naturally more convenient in long continuous heats to use a vacuum apparatus.†

* Allen, Crenshaw and Johnston, this Journal, xxxiii, 195, 1912.
† Ibid., xxxiii, 210, 1912.

TABLE II.

Inversion of pure natural zinc sulphide.

	Time.	Temp. in mv.	Temp. in degrees	Result.
1	4 hrs.	9950 El. A.	1037	Wurtzite unchanged. Sphalerite about $\frac{1}{3}$ changed.
2	$3\frac{1}{4}$ "	9650 El. A.	1011	" unchanged.
3	4 "	9850 El. A.	1028	" slightly changed.
4	$4\frac{1}{4}$ "	9800 El. A.	1024	" very slightly changed.
5	$3\frac{3}{4}$ "	9750 El. A.	1020	Wurtzite slightly, if at all, changed. Sphalerite unchanged.
6	$9\frac{1}{3}$ "	9700 El. A.	1015	Sphalerite unchanged. Wurtzite partly changed.

In four hours at 800° there was no appreciable change in wurtzite. It required 66 hours, between 800° and 900°, to change the mineral entirely into sphalerite. In a repetition of the experiments, 48 hours were required for the change at 850°–900°, and again 40 hours at 850°–950°. For these experiments we used both the wurtzite formed by heating pure natural sphalerite and also some natural wurtzite crystals from the Hornsilver Mine near Frisco, Beaver Co., Utah, which behaved in the same way.

Effect of iron on the inversion point of zinc sulphide.

It is well known that the natural sulphide of zinc nearly always contains sulphide of iron (FeS), sometimes in quantities as high as 20 per cent or more. The effect of this common impurity on the inversion point was thought to be of interest, and accordingly several iron-bearing sphalerites which contained only small quantities of other impurities were carefully analyzed and tested thermally.

Ferrous sulphide lowers the inversion point of sphalerite strongly as the results in Table III show. From fig. 2 it will be seen that the inversion temperatures when plotted against the percentages of iron form a fairly regular curve. It ought to be noted, however, that blende containing other impurities besides iron sulphide does not always show a lower inversion temperature than pure sphalerite. Thus a blende from

TABLE III.

Influence of iron on the inversion temperature of sphalerite.

	I	II	III	IV	V
Locality	Sonora, Mex.	Scotland	Guipuzcoa, Spain	Queensland, Australia	Breitenbrunn, Saxony
Impurities: Quartz	----	0·33%	----	----	----
Impurities: Pyrite	----	----	----	----	3·0 %
Impurities: Copper	----	0·13	0·22	----	0·10
Impurities: Manganese	----	----	tr	0·20	1·05
Percentage of iron	0·15	1·43	5·47	10·8	17·06
Inversion temperature	1020°	998°	955°	919°	880°

Oporto, Portugal, containing 7·43 per cent iron, 0·68 per cent cadmium and traces of lead and silver, was tested repeatedly and found to have an inversion temperature of 1035° as compared to 1020° for pure sphalerite.

The specific gravities of these blendes were also determined and from them the specific volumes were calculated.

TABLE IV.

Influence of ferrous sulphide on the specific gravity of sphalerite.

	I	II	III	IV	V
Locality	Sonora, Mex.	Scotland	Guipuzcoa, Spain	Queensland, Australia	Breitenbrunn, Saxony
Percentage of iron	0·15%	1·43%	5·47%	10·8%	17·06
Sp. gr. at 25°	4·102	2·091	4·035	3·99†	3·970
Sp. gr. corrected	----	----	4·042*	----	3·946‡
Density $\frac{\text{mineral at } 25°}{\text{water at } 4°}$	4·090	4·079	4·030	3·98	3·935
Specific volume	0·2444	0·2451	0·2481	0·2513	0·2541

* Corrected for 0·33 per cent quartz, sp. gr. 2·65 (see Table III).

† Only 3·5 grms. were available for this determination ; hence the gravity is given only to the second decimal.

‡ Corrected for 3 per cent pyrite, sp. gr. 5·02 (see Table III), from which it was separated by dissolving in hydrochloric acid in a carbon dioxide atmosphere.

The impurities in these blendes are all small except in V, and we are certainly justified in correcting the gravities for quartz and pyrite in III and V, respectively, since these impurities are mechanically mixed, The specific volumes plotted in fig. 3 show a nearly rectilinear relation. The dotted line on the plot is drawn through the specific volumes of ZnS and

FIG. 2.

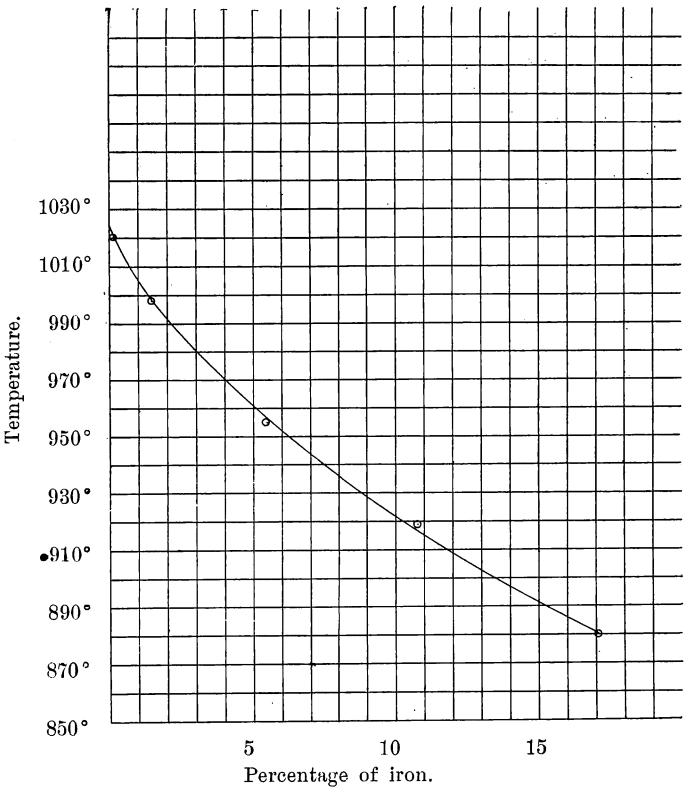

FIG. 2. Influence of iron on the inversion temperature of sphalerite.

FeS.* If we compare this with the locus of the actual specific volumes of the natural blendes, it is evident that the solution of ferrous sulphide by sphalerite (ZnS) must be attended by a marked expansion.

For the relation of the indices of refraction of these solutions to their composition see microscopic part.

* See Allen, Crenshaw and Johnston, this Journal, xxxiii, 198, 1912.

The effect of solvents on the inversion point of ZnS.

When wurtzite is heated in a medium of molten chloride of sodium it changes to sphalerite much more rapidly than when heated in vacuo or in an atmosphere of hydrogen sulphide. Not only did the wurtzite change in the solid state, but new dodecahedrons of the refractivity 2·37 were formed. As the

FIG. 3.

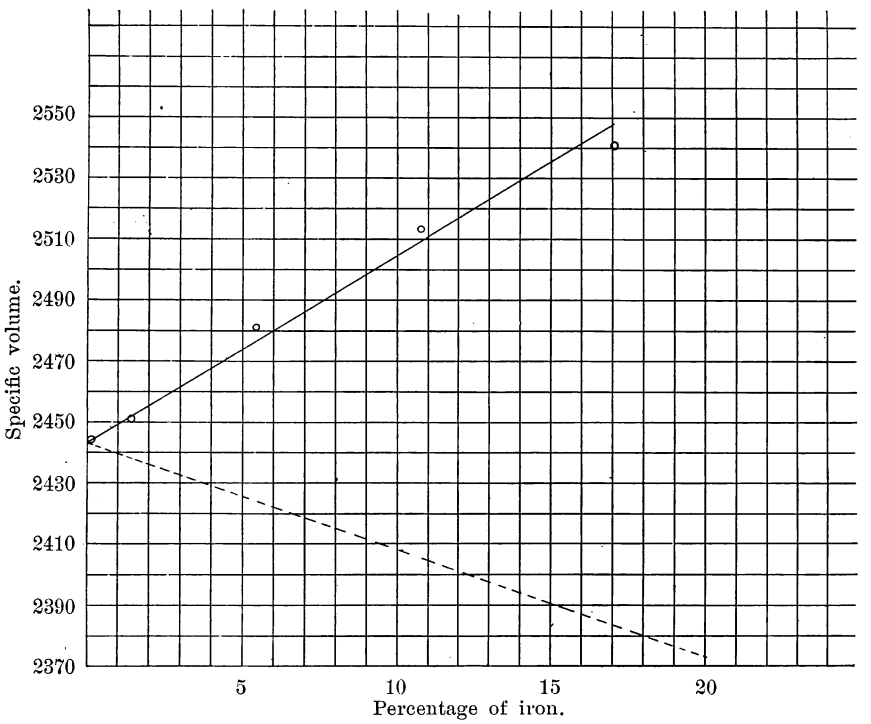

FIG. 3. Influence of iron on the specific volume of sphalerite.

surface of the salt was left open to the air a little zinc oxide of lower refractive index than wurtzite was detected by the microscope. The aqueous solution of the sodium chloride gave strong tests for zinc and sulphate. This indicates the reaction $2NaCl + ZnS = ZnCl_2 + Na_2S$. The reversion of the reaction in the colder parts of the charge may have caused the deposition of the crystals which are the stable form at that temperature. In a platinum tube protected from the air by a slow stream of carbon dioxide, wurtzite was almost completely changed to sphalerite in 30 hours and excellent small dodecahedrons were obtained. Pure amorphous zinc sulphide in 46

hours crystallized from the same solvent in still larger crystals. The temperature in nearly all these experiments was very near the melting point of sodium chloride, slightly above 800°. Schneider* formed crystalline zinc sulphide by heating 1 part of pure dry amorphous zinc sulphide with 12 parts potassium carbonate and 12 parts sulphur. A repetition of this experiment confirmed Schneider's statement. Larger crystals than those from sodium chloride were obtained in this way at about 400°. Both dodecahedrons and tetrahedrons were observed.

Thermal behavior of ZnS above its inversion point.

Cussak † states that zinc sulphide melts at 1064°. No other investigator has ever observed the melting of zinc sulphide, though several have obtained wurtzite as a sublimation product.‡ The results of Hautefeuille are especially interesting since he obtained well-characterized hemimorphic crystals like those of nature by subliming zinc sulphide in a bed of alumina. We found zinc sulphide volatile enough at about 1000° to form small crystals of wurtzite in a few hours. Several grams were sublimed in well-formed crystals of considerable size between 1200° and 1300°. We observed no melting under any circumstances at atmospheric pressure. The experiment was tried of dipping a tube containing zinc sulphide quickly into a furnace heated to 1550°. It was thought that if this temperature were above the melting point, deorientation might go on faster than volatilization, but no certain indication of melting was found.

Zinc sulphide from aqueous solutions.

It has been shown in the foregoing pages that zinc sulphide may exist in two enantiotropic forms; β-ZnS, or sphalerite, stable below 1020°, and α-ZnS, or wurtzite, stable above 1020°. Nevertheless the latter as well as the former may be crystallized at comparatively low temperatures from aqueous solutions, and the necessary conditions for the formation of each are of the highest interest to chemical geology. Zinc sulphide is surprisingly difficult to crystallize below 200° and it is safe to say neither sphalerite nor wurtzite has been obtained heretofore in the wet way.

Sphalerite from aqueous solutions.

Several investigators claimed to have obtained sphalerite from water solutions. Baubigny§ is said to have formed

* Jour. prakt. Chem. (2), viii, 33, 1874.

† N. J. Min. 1899, I, Referate 196.

‡ Deville and Troost, C. R., lii, 920, 1861. Sidot, ibid., lxii, 999, 1866; lxiii, 188, 1866. Hautefeuille, ibid., xciii, 824, 1881. Mourlot, ibid., cxxiii, 54, 1896. Biltz, loc. cit.

§ Fouquée et Levy, Synthèse des Min. et Roches, Paris, 1882, 298.

blende by heating to 80°, in a sealed tube, an acid solution of zinc sulphate, saturated with hydrogen sulphide. We prepared many products in a similar way and none of them ever showed an index of refraction greater than about 2·25, which is characteristic of amorphous zinc sulphide.

Villiers * states that the precipitate from *alkaline* zinc solutions by hydrogen sulphide, though amorphous ordinarily, is crystallized by certain influences, e.g. by the presence of a large excess of ammonium chloride in the solution from which it is precipitated. Heat also transforms the gelatinous precipitate into a distinctly granular state, in which, though it does not show any appearance of crystallinity, it is probably cubic because it possesses a decidedly lower solubility than the gelatinous mass at first formed. Precipitates which we obtained in this way were also amorphous.

Stanek † believed he had obtained a crystalline product when he heated amorphous zinc sulphide with colorless ammonium sulphide to 150°—200°, in sealed tubes.

Senarmont ‡ states that by heating the amorphous sulphide in sealed tubes with hydrogen sulphide under a pressure of several atmospheres he obtained blende. The last-named investigators (Stanek and Senarmont) give no proof of their claims except the appearance of the product. Their experiments, repeated by us more than once, gave nothing but amorphous sulphide. No crystal outlines appeared under the microscope, and when the grains were coarse enough to admit of the measurement they showed a refractivity of 2·2 to 2·3 instead of 2·37. Having failed to accomplish our purpose by any methods given in the literature, we experimented with alkali sulphides in sealed tubes with the result that only amorphous products were obtained at first and when the tubes were heated for long periods or at higher temperatures (250° and above) they were so badly attacked, that the method was temporarily abandoned. Meanwhile other methods were tried.

Action of sodium thiosulphate on Zinc salts.

Our success with the use of thiosulphate in the preparation of the mercuric sulphides gave us some hope that it might prove satisfactory here. Sodium thiosulphate in excess shows no action on zinc salts in the cold, but on heating to 100° the zinc is quantitatively precipitated in dense form, which under the microscope appears in spherical aggregations. This is amorphous, however. Though in one instance there seemed to be slight double refraction as if from wurtzite, the refractive index was too low. The principal reaction here, gives rise only

* C. R., cxx, 189, 498, 1895. † Zs. anorg. Ch., xvii, 117, 1898.
‡ Ann. Ch. Ph., xxxii, 129, 1851.

to neutral products, though by a secondary reaction we have usually a very little sulphur dioxide formed. The reaction is the same as with ferrous * salts with excess of thiosulphate, and was worked out in the same way, i.e. weighed quantities of the substances were introduced in solution into glass tubes which were exhausted of air, sealed and heated to a certain temperature. On cooling, the precipitate was filtered and washed with water, then with alcohol and dried in the air. The sulphur in it was removed by carbon disulphide. The filtrate was diluted to a definite volume and aliquot parts tested for zinc, free acid and finally unchanged thiosulphate by a standard iodine solution. The following table (Table V) shows the results obtained compared with those calculated for the reaction $4Na_2S_2O_3 + ZnSO_4 = 4Na_2SO_4 + ZnS + 4S$.

TABLE V.

Action of $Na_2S_2O_3$ on zinc salts.

No.	$ZnSO_4.7H_2O$ taken	$Na_2S_2O_3.5H_2O$ taken	Water	Temperature	ZnS + S		ZnS		$Na_2S_2O_3.5H_2O$ consumed	
					Found	Cal.	Found	Cal.	Found	Cal.
1	2·000g	8·000g	75cc	100°	1·59	1·57	·67	·68	6·99	6·95
2	2·000g	8·000g	"	"	1·56	"	·67	"	6·76	"
3	2·000g	8·000g	"	"	1·51	"	·68	"	6·35	"
4	2·000g	8·000g	"	"	1·59	"	·70	"	7·04	---

Some secondary reaction evidently affects the quantity of thiosulphate consumed, but a fuller investigation was not deemed advisable. Small quantities of sulphurous acid are formed, but not enough to cause the variations in 2 and 3. In No. 4, which was heated longer than usual (several days), a little hydrogen sulphide was formed, doubtless according to the equation $Na_2S_2O_3 + H_2O = Na_2SO_4 + H_2S$, which we have elsewhere established. The excess of thiosulphate would thus be reduced.

Attempt to form Sphalerite in other ways.

A number of other methods for the synthesis of sphalerite were tried in which zinc sulphide would be precipitated or crystallized in neutral or alkaline solution. Thus hydrogen sulphide was brought into contact with zinc carbonate and zinc bicarbonate; and amorphous zinc sulphide was heated with a solution of sodium bicarbonate. In every case, no matter how slow the reaction, only amorphous sulphide was obtained. It will,

* Allen, Crenshaw and Johnston, this Journal, xxxiii, 185, 1912.

therefore, not be necessary to describe the experiments in detail. Two other experiments of a negative nature may also be mentioned here. The behavior of metallic zinc in saturated sulphurous acid solution gave only amorphous sulphide in rather large grains—of refractivity 2·2—2·3. On account of the weak nature of this acid it was thought sphalerite might possibly be formed. The action of powdered marcasite on zinc chloride in an atmosphere of carbon dioxide gave no sulphide of zinc.

Formation of Sphalerite by precipitation with alkali sulphides.

The precipitate from zinc salts by alkali sulphides in the cold, or under ordinary conditions at a boiling temperature, shows no indications of crystallinity. However, when pretty concentrated solutions of the soluble sulphides act on amorphous zinc sulphide at higher temperatures, sphalerite is obtained. As previously stated, experiments with concentrated alkaline solutions gave much trouble. The glass tubes were so badly attacked that the products obtained in them were quite impure, greatly increasing the difficulties of microscopic analysis, while at 300° the tubes were sometimes eaten entirely through. The difficulty was finally overcome by putting the solutions into platinum tubes which were then set inside of glass tubes, the latter being afterwards sealed. Satisfactory platinum tubes which are not so expensive as to be prohibitive may be fashioned from foil by the use of the oxyhydrogen blowpipe. Ours had a diameter of about 15^{mm} and a total capacity of about 40^{cc}.

In our first successful experiment amorphous zinc sulphide was put into a tube of Jena combustion glass* with sodium sulphide of about 20 per cent concentration; the tube and its contents were heated 3 days in a steel bomb at 350°. Small though good crystals of sphalerite, both octahedrons and tetrahedrons, were obtained. Again, amorphous zinc sulphide was heated in a platinum tube sealed inside a glass tube, as described above, with potassium sulphide of about 35 per cent at 200° for 11 days. Minute tetrahedrons of sphalerite were obtained. A solution of 10 per cent potassium sulphide heated with amorphous zinc sulphide in a similar manner at 200° for two months† gave a product which was entirely crystallized in minute isotropic crystals with evident faces but rather rounded edges. A second experiment with 10 per cent sodium sulphide lasting six weeks at 100° failed to yield any crystals. Thus we find, as we should expect, that the lower the temperature and the more dilute the reagent the longer is the time required to

* Out of a large number of experiments with glass tubes, this was the only one in which the product could be recovered.

† By mistake the temperature was dropped to 100° for a part of the period.

produce recognizable crystals. *It is a notable fact that sphalerite only was obtained by this method, never wurtzite.*

Zinc sulphide from acid solutions.

When zinc sulphide is precipitated by hydrogen sulphide from solutions which are either neutral or acid at the start, at temperatures ranging from the ordinary up to 200°, the product is always amorphous so far as our observation goes. The double tube method, which proved so satisfactory in the formation of some other sulphides, did not generate hydrogen sulphide at a rate slow enough to give crystals. True, the products were frequently, though not always, doubly refracting, and for some time we were misled into the belief that they were wurtzite, but the measurement of their refractive index later on showed that they were in all probability amorphous and that the double refraction was caused by strains produced in the hardening of precipitates originally gelatinous. (See microscopic part.) Experience in qualitative analysis might lead one to believe that zinc salts could not be precipitated by hydrogen sulphide from solutions containing much free acid. As a matter of fact precipitates are obtained from rather strong acid solutions, provided only sufficient time is allowed, as Glixelli* has proved.

Table VI shows our own results on this point. In it are given the times which elapsed after hydrogen sulphide was introduced, before a precipitate was observed, and the composition of solutions after ten days' standing. The concentration of the zinc was 0·2 N at the beginning in all the solutions except the last; the hydrogen sulphide was kept at a pressure of approximately one atmosphere, by uncorking the flasks and passing in fresh gas from time to time, while the concentration of the sulphuric acid varied as stated in the table. The experiments were carried out at room temperature. It will be noted that a partial precipitation was obtained in the above manner from solutions which contained about 5 per cent sulphuric acid at the start, and nearly 6 per cent at the end of the experiment. With a higher initial concentration of zinc or a higher pressure of hydrogen sulphide, precipitation would naturally be obtained from solutions containing still more acid. The text-books commonly assume equilibrium in these systems and use them as examples of the mass law. Preliminary work on the subject has convinced us that such is not the case. In fig. 4 are plotted the concentrations of zinc in solution as they vary with the concentration of sulphuric acid, after the precipitation with one atmosphere of hydrogen sulphide has apparently ceased. If one begins with the same precipitate, adding different concentrations of acid and maintaining the hydrogen sulphide at one atmosphere, different results are obtained.

* Zs. anorg. Ch., lv, 297, 1907.

More work on this subject is under consideration, but the results given show well enough that hydrogen sulphide will *in time* precipitate zinc from solutions which are quite strongly acid.

FIG. 4.

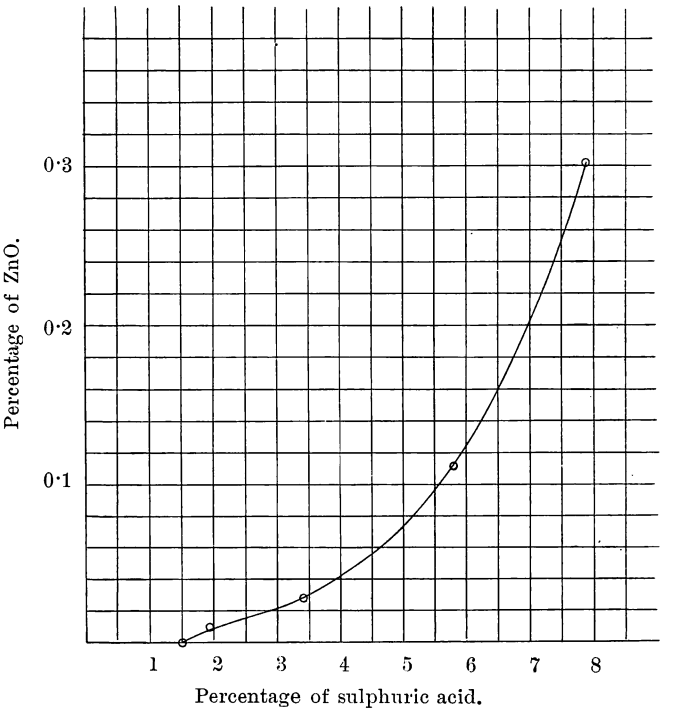

FIG. 4. Influence of free acid on the precipitation of zinc sulphide.

Crystalline zinc sulphide from acid solutions.

A great number of experiments have been made with the purpose of preparing crystalline zinc sulphide from acid solutions at *low* temperatures, yet so far without success. This seems very remarkable when we consider how slowly the sulphide forms in strong acid solutions (see Table VI), and we have as yet no explanation for it. At temperatures of 250° and upward, by the use of the double-tube method * crystalline products can be obtained. The results are sufficiently interesting to be stated in detail. In all the experiments the source of hydrogen sulphide was about 6 g. $Na_2S_2O_3 . 5H_2O$ in 15–20^{cc} water, which was placed in the outside tube. The inside

* Allen, Crenshaw and Johnston, this Journal, xxxiii, 174, 1912.

TABLE VI.

The action of hydrogen sulphide on 0·2N$ZnSO_4$, with varying concentration of H_2SO_4.

No.	H_2SO_4		Approx. time before ppt. began	Zn in solution after 10 days		H_2SO_4 after ppt.	
	Normality	Per cent		Normality	Per cent	Normality	Per cent
1	0·1	0·49	1 min.	0·0000	0·000	0·300	1·47
2	0·2	0·98	5 min.	0·0031	0·010	0·398	1·95
3	0·5	2·45	25 min.	0·0089	0·029	0·691	3·39
4	1·0	4·90	a few hours	0·0338	0·111	1·183	5·80
5	1·5	7·36	no ppt. after 2 days	-----	----	----	----
6*	1·5	7·36	3 days	0·0923	0·302	1·609	7·89

* Concentration of $ZnSO_4$ in No. 6 was increased to 0·214 N after 2 days.

tube* in each case contained 10–15cc of 10 per cent $ZnSO_4.7H_2O$. The time in all cases was 2 to 3 days. The concentration of the sulphuric acid in the latter solutions and the temperature to which the tubes were heated varied in the different experiments.

Exp. 1. Temperature 300°—10% H_2SO_4 used. The product consisted of spherulitic aggregates, all doubly refracting and having the refractive index of wurtzite.

Exp. 2. Temperature 300°—7·5% H_2SO_4. Crusts and spherules consisting of felted fibers which were unquestionably wurtzite sometimes surrounded by amorphous sulphide, indicating that the precipitate first formed was amorphous. 5–10 per cent of more transparent irregular masses of isotropic substance having the refractive index of sphalerite.

Exp. 3. Temperature 300°—5% H_2SO_4. The product consisted of globules with crystal faces growing out of them. Nearly all were isotropic and showed the refractive index of sphalerite, though there was perhaps 5 per cent of doubly refracting wurtzite.

Exp. 4. Temperature 300°—4% H_2SO_4. About 30 per cent amorphous sulphide, the rest wurtzite.

Exp. 5. Temperature 300° — 1% H_2SO_4. The product showed crystalline faces and was apparently isotropic. Practically all of it had the index of sphalerite, though there were a few pieces of amorphous material.

Exp. 6. Temperature 250°—5% H_2SO_4. The product consisted almost entirely of large spherules showing both radial

* A platinum tube was used.

fibers and felted fibrous structure. Inside of some were nuclei of amorphous material, indicating again that the precipitate was at first amorphous. Crystalline material all wurtzite.

Exp. 7. Temperature 250°—2·5% H_2SO_4. Both large and small spherules, the last in clustered form and amorphous, the large ones mostly doubly refracting and crystalline wurtzite.

Exp. 8. Temperature 350°—5% H_2SO_4. Possibly 30 per cent wurtzite, the rest sphalerite.

Exp. 9. Temperature 350°—10% H_2SO_4. Perhaps 80 per cent wurtzite, the rest sphalerite.

Exp. 10. Temperature 350°—2·5% H_2SO_4. Most of the product consisted of small spherules, of which about 30 per cent was amorphous, the rest felted aggregates of wurtzite.

Exp. 11. Temperature 250°—1% H_2SO_4. Consisted almost wholly of irregular granules, much of it isotropic and having the refractive index of sphalerite. In strong light considerable of it shows double refraction and the index of wurtzite.

Exp. 12. Temperature 300°—2·5% H_2SO_4. All apparently isotropic irregular forms having the index of sphalerite.

TABLE VII.

Influence of temperature and acid concentration on the crystalline form of Zinc sulphide.

Temperature	Percentage of H_2SO_4					
	1·0	2·5	4·0	5·0	7·5	10·0
350°	----	70% wurtzite.	----	30% wurtzite.	----	80% wurtzite.
300°	no wurtzite; very little amorphous sulphide.	no wurtzite.	70% wurtzite; rest amorphous sulphide; no sphalerite.	5% wurtzite.	90% wurtzite	100% wurtzite.
250°	much sphalerite as well as wurtzite.	all wurtzite and amorphous sulphide.	----	all wurtzite and amorphous sulphide.	----	----

The results of these experiments are summarized in Table VII. When all the data are carefully compared, it will be seen that temperature and acid concentration appear to be the two fac-

tors which determine the product; and if we omit two experiments out of the twelve done at three different temperatures, we find the following regularity: For a given temperature the higher the acid concentration the greater is the quantity of *wurtzite* found in the product, and for a given acid concentration the higher the temperature the greater is the quantity of *sphalerite* found in the product. More work ought to be done on this point, but the above conclusion gains support from the fact that the same rule proved true in the case of the disulphides of iron.* There the quantity of *pyrite* increased with the temperature for a given acid concentration, and the quantity of *marcasite* increased with the acid concentration for any given temperature. When it is remembered that pyrite and sphalerite are *stable* forms, while marcasite and wurtzite are *unstable*, the analogy becomes striking.

In one respect this synthetic work on sphalerite and wurtzite may appear inadequate to the geologist, viz., the temperature of formation. Field observation points to lower temperatures in many instances than the lowest at which we have succeeded in forming these minerals. Although it would be highly desirable to obtain positive results at lower temperatures, it may be pointed out that there is nothing in our knowledge of the minerals to indicate anything more than *continuous* changes in the necessary conditions as the temperature falls. We must admit, however, that the temperature interval is still too long to extrapolate accurately, so that we might predict, for example, what concentration of acid would be necessary at ordinary temperature to give rise to pure wurtzite. Since even quite dilute solutions of soluble sulphides and zinc salts always give an immediate amorphous precipitate at the ordinary temperature, and since amorphous sulphides are seldom met with in nature, we are constrained to believe that the natural sulphides which have been deposited even as low down as 100°, must have been crystallized from very dilute solutions indeed and therefore exceedingly slowly.

The genesis of the natural sulphides of zinc.

The sphalerite of deep veins has in all probability been formed from hot solutions, and the latter are generally alkaline, as we know both from field observation of hot springs and from our knowledge of the hydrolysis of alkali silicates, like the feldspars, with hot water. In accord with this we have found that alkaline solutions always give rise to sphalerite, never to wurtzite.

The conditions under which the sphalerite of the Mississippi Valley region was deposited have been much discussed by

* Allen, Crenshaw and Johnston, loc. cit., p. 179.

geologists. We may call attention, in this connection, to the fact that sphalerite can be formed from acid as well as alkaline solutions. If the temperature is as high as 300°, only sphalerite seems to be deposited from solutions containing 1 per cent of free sulphuric acid, while only a few per cent of wurtzite is formed when the concentration of acid is as high as 5 per cent. However, when the temperature drops to 250° a solution containing as much as 2·5 per cent acid deposits practically pure wurtzite. In other words, from 350° down to 250°, which is as low as we have been able to get crystalline products, the lower the temperature the smaller is the percentage of acid required to give pure wurtzite. Unfortunately we cannot say what that percentage may be at ordinary temperature, because we cannot imitate the slow rate of crystallization which presumably proceeds in nature. But certainly sphalerite may be what geologists call a secondary mineral if the temperature and acid concentration fall within certain limits. On the other hand, to judge from the synthetic work wurtzite can never be anything but a secondary mineral,* since we have obtained it only from acid solutions. Our knowledge of natural wurtzite is still rather limited. Mr. B. S. Butler of the U. S. Geological Survey has acquainted us of an interesting occurrence of this mineral, to which he has given careful study. In the Hornsilver Mine near Frisco, Beaver Co., Utah, wurtzite seems to be undoubtedly a product of secondary sulphide enrichment. The original ore, still fresh in the lowel levels, contains galena, pyrite and sphalerite, a little chalcopyrite, and possibly other copper minerals. The upper part of the deposit has been largely oxidized to sulphates, minor quantities of carbonates and other secondary minerals forming also. Octahedral cavities in the rock bear testimony to the former presence of pyrite, which, though plentiful lower down, has now disappeared from the oxidized zone. Below this lies a zone of secondary sulphide enrichment carrying secondary (reprecipitated) chalcocite, covellite, and wurtzite in large quantities, much of the last named precipitated around original sphalerite cores. The chemistry of these processes must have involved first the oxidization of the sulphides of zinc, copper, and iron to sulphates, and since the original ore contained pyrite, the oxidized solution must have contained sulphuric acid. As this solution moved downward, the sulphuric acid gradually decomposed the more soluble sulphides of the unoxidized ore with the formation of sulphates and hydrogen sulphide. At greater depths, after the oxygen of the solution was entirely used up and the acid reduced, the sulphides were reprecipitated. The difficultly soluble sulphides of copper would readily precipitate on the more

* At least, it can form only from acid solutions.

easily soluble sulphide of zinc. Of course the sphalerite could not have precipitated wurtzite directly out of the solution since wurtzite should be the more soluble of the two, but when the acid in the solution had become sufficiently neutralized or used up in any way whatever, the hydrogen sulphide present would precipitate the zinc after the less soluble sulphides of copper.

In this instance, therefore, the formation of wurtzite is well explained by our synthetic experiments and it will be interesting to learn whether other occurrences of wurtzite may not be similarly explained. It appears quite possible that wurtzite may often have been taken for sphalerite on account of the general similarity between the two and the lack of careful examination.

The origin of "schalenblende," which seems to consist of alternate layers of the two forms of zinc sulphide, is difficult to explain, but the suggestion is made that some systematic alternation of conditions may have resulted in the periodic neutralization of a slightly acid solution.

II. The Sulphide of Cadmium.

So far as present knowledge goes, sulphur forms with cadmium only* the monosulphide, CdS. Schiff† claimed that a pentasulphide was precipitated from solutions of cadmium salts by potassium pentasulphide, but Buchner‡ proved that the precipitate thus formed was merely a mixture of the monosulphide with sulphur. Cadmium sulphide occurs in nature only as the mineral greenockite which crystallizes in the hexagonal system, but at least two other crystalline forms have been reported as laboratory products.§ From several points of view it is of interest to know whether these forms actually exist—especially whether there is one of regular symmetry analogous to sphalerite, the common sulphide of zinc, and a systematic investigation of the question was, therefore, undertaken.

Thermal behavior of Cadmium sulphide.

A sample of amorphous cadmium sulphide was first heated in a current of hydrogen sulphide in the manner previously described in this paper (p. 345). The sulphide was raised to a temperature of about 1000° and held there for two hours. After cooling, it was submitted to a microscopic examination, when it was found to be entirely crystalline. Individuals were

* See Follenius, Zs. anal. Ch., xiii, 411, 1874.
† Liebig's Ann., cxv, 68; J. B. Ch., 1860, 84.
‡ Chem. Ztg., xi, 1087, 1107, 1887.
§ Lorenz, Ber,, xxiv, 1501, 1891. Klobukow, J. pr. Chem. (2), xxxix, 412, 1887. Beyerinck, N. J., 1897-8, Beilage Bd. xi, 432.

naturally not well developed in the mass, though there were some well-formed prisms which had evidently crystallized direct from the vapor. The whole product was identified by its optical properties as greenockite. This mineral has been formed* by others at high temperatures and its volatility has been noted.† Heating and cooling curves were determined on the product crystallized as above, the same apparatus being used. No break was found anywhere from ordinary temperature to 1000° to indicate any physical transformation whatever. These results, however, can not safely be regarded as conclusive, because the effects which accompany definite physical changes are sometimes too small to be thus detected. Furthermore, unstable forms are often capable of existence under certain conditions, while they would not be found under circumstances like those described above.

Lorenz‡ states that he obtained beautiful crystals of cadmium sulphide by vaporizing metallic cadmium in a strong current of hydrogen sulphide. The preparation was examined by Prof. Groth, who found in it simple crystals of greenockite, and also twinned forms in large number, which he regarded as monoclinic. Lorenz accounted for two crystal forms in the same preparation by the supposition that the temperature varied greatly in different parts of the mass. We made two preparations by this method. The largest crystals, which surpassed 20^{mm} in length, were made by heating in a resistance furnace a porcelain tube which enclosed the boat containing the metal. When the boiling point of cadmium was reached the galvanometer indicated a temperature of 780°, which held constant about ten minutes. After heating half an hour longer, during which the hydrogen sulphide was passed in rapidly, the furnace was cooled down. The product so obtained and also a previous one made by heating with an ordinary blast lamp, contained many twinned crystals, as well as simple prisms of greenockite. It would be easy to mistake these forms for monoclinic twins, but a careful study of them by Dr. Merwin (Microscopic Study) has shown conclusively that they are hexagonal, twinned after two different pyramids.

The cadmium which we used in the formation of the sulphide was of known composition; the total impurities were Pb = ·086 per cent, Fe = ·002 per cent. The sulphide was,

*Deville & Troost obtained it by heating the amorphous sulphide to a white heat in a current of hydrogen; also by heating together $CdSO_4$, BaS and CaF_2 in equal quantities; C. R., lii, 920, 1861. Mourlot sublimed cadmium sulphide in the arc furnace; C. R., cxxiii, 54, 1896.

†Biltz states that greenockite begins to sublime about 980°; Zs. anorg. Ch., lix, 273, 1908.

‡Loc. cit.

therefore, tested for these impurities only, and then used for a determination of the density. No lead was found, though ·02 per cent of residue remained after driving off the volatile acid of the chloride with sulphuric acid. There was also a trace of iron which probably came from the reagents. Nearly 10 g. of material were used in the gravity determination. At 25° the value 4·833 was obtained. After finer crushing, to eliminate possible air bubbles, a second determination gave 4·835, proving that porosity was negligible—a conclusion confirmed by the microscope. From the above value we obtain the density $\frac{\text{mineral at } 25°}{\text{water at } 4°} = 4{\cdot}820$. The value of this constant given in the text-books depends on meager data and is, doubtless, too high.*

At a much lower temperature, well developed prisms (about 1^{mm} maximum length) were obtained by Schüler's† method—i. e. by heating‡ the amorphous sulphide with a flux consisting of equal parts of potassium carbonate and sulphur.§ These prisms were also hexagonal. They probably dissolve a small percentage from the flux, since Merwin finds $\epsilon_{Li} = 2{\cdot}447$ as compared with 2·45 for greenockite prepared by heating the amorphous sulphide in hydrogen sulphide.

Cadmium sulphide from acid solutions.

Failing to get any evidence of the existence of any other sulphide of cadmium than the ordinary greenockite by dry methods, experiments on aqueous solutions were undertaken. When acid solutions of cadmium salts are precipitated by hydrogen sulphide, the product may be either amorphous or crystalline—the result depending on the rapidity of precipitation, the acidity of the solution, its cadmium concentration, temperature, etc., as it is with zinc salts. By the use of the double tube, a device already referred to (p. 355), hydrogen sulphide was generated slowly, and comparatively large prisms (about $0{\cdot}5^{mm}$ long) were obtained. The composition of the solution in the inside tube was 2 g. $CdSO_4.8/3H_2O$ + 20 cc. 30%H_2SO_4; the outside tube contained 9 g. $Na_2S_2O_3.5H_2O$ + 20 cc. water. The duration of the experiment was three days at 180°. The crystals were undoubtedly greenockite, though the index of refraction, ϵ_{Li}, was slightly lower than that of the purest product, being 2·440 instead of 2·456. This is accounted for

* Thus Dana (Text-book of Mineralogy, 6th ed., 1906) gives 4·9 — 5·0.

† Lieb. Ann., lxxxvii, 40, 1853.

‡ The temperature in one experiment was 365°.

§ Much amorphous residue remained after dissolving out the flux with water, perhaps from a decomposition of a compound of the cadmium and potassium sulphides.

by the probable presence of cadmium sulphate in the crystals, a hypothesis which is in accord with the well known tendency of this substance to occlude salts from the solution in which it is precipitated.

In other experiments carried out in a similar way, the crystals of the product were smaller. When amorphous cadmium sulphide was heated in a sealed tube with 30 per cent sulphuric acid at 200° for two days, the product consisted of spherulitic aggregations of small *doubly refracting prisms.* Again hydrogen sulphide was passed into a boiling solution which contained 1 g. $CdSO_4.8/3H_2O$ in 50 cc. 30 % H_2SO_4. After the air had been entirely replaced from the flask, the latter was connected with the hydrogen sulphide generator and allowed to cool. Most of the product crystallized during the cooling. It consisted of spheroidal lumps of amorphous material shot through with *doubly refracting needles.* The crystals of the two last-named products showed *parallel extinction* though they were too small for a determination of the refractive index.

We also prepared crystalline cadmium sulphide by the method of Geitner,* which consists in heating the metal with sulphurous acid in sealed tubes. Cadmium chips were sealed up in a tube of Jena combustion glass with a solution of sulphurous acid, saturated at room temperature. The tube was heated to 200° for two days. The crystals of the product were of such size that it was possible to determine the crystal system. They were *hexagonal.*

Cadmium sulphide from alkaline solutions.

If cadmium sulphide behaves like zinc sulphide, its closest analogue, we should expect a different product to crystallize from alkaline solutions, perhaps a regular form similar to sphalerite. In the first place we repeated Stanek's† experiments—heating the amorphous sulphide with excess of colorless ammonium sulphide in a sealed tube to 150°–200°. We used in our experiment 1/2 g. $CdSO_4$. 8/3 H_2O with excess of colorless ammonium sulphide, prepared from concentrated ammonia. The sealed tube was heated three days at 200°. Microscopic examination of the product showed that it was all crystallized in *doubly refracting needles showing parallel extinction.* In a repetition of this experiment, larger crystals were obtained; they were well-formed *hemimorphic* prisms, undoubtedly greenockite. On the other hand, no crystalline product was obtained with sodium or potassium sulphides. Orange-colored sulphide of cadmium remained unchanged, when heated at 200° for two days with dilute solutions of potassium (3·5 per cent) or sodium

* Liebig's Ann., cxxix, 350. J. B. Ch., 1864, 140.
† Zs. anorg. Ch., xvii, 1898.

(2 per cent) sulphide. Concentrated solutions of these reagents change the orange-colored sulphide to a bright yellow color. This is caused by a subdivision of the particles of the latter (see p. 391). Thus 0·1 g. $CdSO_4.8/3H_2O$ was dissolved in a little water and enough sodium sulphide was added to make a solution of about 13 per cent concentration. The mixture was then poured into a platinum tube and the latter was set inside of a larger glass tube, which was then sealed. After 8 days at a maximum temperature of 260°, no crystals had been formed. In a similar way about half a gram of the amorphous cadmium sulphide was heated with an excess of 20 per cent sodium sulphide for 7 days at a maximum temperature of 275°. Again no crystals were obtained. We may therefore infer that cadmium sulphide is more soluble in ammonium sulphide than it is in the alkali sulphides, while with zinc sulphide the opposite is true.

We conclude from the foregoing that no regular form of cadmium sulphide is obtained from alkali sulphide solutions, and that the analogy with zinc does not hold.

Effect of Sodium thiosulphate on soluble Cadmium salts.

The crystal form of the precipitate thrown down by sodium thiosulphate from cadmium sulphate solutions was also investigated. The principal reaction with excess of reagent is the same as that with zinc, mercuric and ferrous salts. There is evidently a secondary reaction producing a little sulphurous acid, and reducing the amount of thiosulphate consumed. The sulphide also sticks obstinately to the glass and occludes a little sulphate, making it difficult to obtain quantitative results, though the latter are good enough to prove that the chief reaction *with excess* of thiosulphate is $4Na_2S_2O_3+CdSO_4 = 4Na_2SO_4+CdS+4S$. The following data were obtained in sealed tubes at 100°:

TABLE VIII.

Action of $Na_2S_2O_3$ on $CdSO_4$.

	Taken			$Na_2S_2O_3.5H_2O$		CdS + S		CdS	
	$CdSO_4.8/3H_2O$	$Na_2S_2O_3.5H_2O$	H_2O	Used up	Cal.	found	Cal.	found	Cal.
1	1·000g	5·006g	75-1000cc	3·44	3·87	0·98	1·06	0·54	0·56
2	"	"	"	3·56	3·87	----	----	----	----

A product obtained under the same conditions was examined by the microscope. It was too fine to identify; it consisted of small orange-colored doubly refracting crystals. Such properties as could be determined, therefore, agreed with greenockite.

Explanation of color differences in Cadmium sulphide.

Cadmium sulphide is a well-known artist's color, and varies from lemon-yellow to orange-red according to the method by which it is prepared. Follenius,* having proved that there was but one sulphide of cadmium, came to the conclusion that these different tints were due to the variable quantity of occluded impurities which he found the sulphide contained. Buchner† appears to have disproved this. He gives no quantitative data, but asserts that he has examined many hundred preparations and finds that sulphide of different tints may contain the same quantity of impurities while variable amounts of the latter occur in sulphide of the same tint. Buchner describes two different "forms" of cadmium sulphide, the methods of preparing which are not very clearly given, one of which is lemon-yellow, the other "almost as red as minium." Most products, he says, are mixtures of these two forms. Solutions containing little free acid give with hydrogen sulphide a yellow precipitate which becomes orange when it is heated in acid or alkaline solutions. Buchner asserts that he has never found crystals in any preparation of cadmium sulphide. He regards the orange or "β-form" a polymer of the yellow or "α-form" because it always has a higher density. Later Klobukow obtained from Buchner a large number of products and sought to prove whether their difference in color was due to chemical or physical differences. He confirmed Buchner's statements regarding the density of the two supposed modifications. At 17°–17·5°, after drying at 105°–107°, the yellow form gave specific gravities varying from 3·906 to 3·927, while the orange form showed specific gravities which varied from 4·492 to 4·513. These and other preparations were also examined microscopically by Prof. Haushofer. He found them generally doubly refracting, but makes no specific statements regarding extinction angles, indices of refraction or other constants, except that the crystals of the "α-form" were not crystallographically well determined. He regarded the "α-form" as identical with greenockite, while the "β-products" probably contained both regular and monoclinic forms.

Our experiments confirm Buchner's experimental observations in almost all respects, but a microscopic examination of products of many different hues, made in several ways, prove that the differences in color are primarily dependent on the

* Loc. cit. † Loc. cit.

amorphous or crystalline nature of the substance and on its state of division; and in a minor degree on the nature of its surface, etc.

1st. The *crystals* vary from clear yellow, in tufts of hair-like needles, to brownish yellow in the larger ones, but *the powder of all specimens is orange.* Still, there is no doubt that all are the same crystalline form; the different colors are due to the relative amounts of light transmitted and reflected.

2d. Amorphous cadmium sulphide shows all tints from lemon yellow to orange red. Light yellow products are obtained by precipitating cold solutions of low cadmium concentration by hydrogen sulphide, or by precipitating cadmium solutions with the alkali sulphides. The microscope shows that the globules of these amorphous precipitates are all very small and of similar magnitude.

The deep orange precipitates are obtained by precipitating hot acid cadmium solutions with hydrogen sulphide, or by long boiling of cadmium solutions with excess of thiosulphate. When the first method is used, a high concentration of acid gives a deeper-colored product. The orange amorphous cadmium sulphide is made up of larger aggregates than the yellow —sometimes fifty times as great in diameter. (See microscopic part.) A very illuminating experiment on this subject was carried out as follows: To about 200 cc. water 4 g. NaCl, 10 g. $Na_2S_2O_3.5H_2O$ and 2 g. $CdSO_4.8/3H_2O$ were added. The solution was heated to boiling and kept in ebullition for some hours, hot water being added from time to time. Precipitation began almost at once. After about an hour a little of the lemon yellow product was removed and examined microscopically. The particles were too small to measure. After 2½ hours the product had much increased in quantity, but was still light yellow. The microscope showed that it was made up of clear globules about $\cdot001^{mm}$ in diameter. Gradually the precipitate grew denser and darker in color until after 4 or 5 hours it had all settled to the bottom, and showed a bright orange color. This product contained particles of all sizes up to $\cdot05^{mm}$ in diameter.

Another piece of evidence in point is this: the light yellow precipitate formed by the action of ammonium sulphide on a cadmium salt retains the same color after the system has been heated, though the product is now all crystalline greenockite. When, however, the latter is ground in a mortar it becomes orange in color. This proves quite conclusively that the difference in color has no connection with another crystalline form. Klobukow gives a much lower density for the yellow products than for the orange, viz., 3·906 – 3·927 against 4·492 – 4·513. This looks like a specific constant, but it must

be remembered that the density of the products would be changed a great deal by varying intermixtures of crystalline sulphide which Haushofer says was present in these products, and also by occluded salts. Furthermore, in our experience very fine powders are apt to give densities several per cent lower than the same substance in a coarser form.

In view of all the facts Buchner's hypothesis of polymerization appears untenable.

Change in color of Cadmium sulphide with rising temperature.—When cadmium sulphide is heated, its color becomes progressively darker, until at the full heat of the Bunsen burner, 800°–900°, it is dark red. On cooling, however, it regains its former color. This behavior is entirely similar in character to that of mercuric sulphide (see p. 379), and like that of the latter is to be attributed to a varying absorption of light with rising temperature rather than to a reversible transformation, for the change is perfectly gradual. To avoid the formation of oxide, the experiments were made in evacuated tubes of Jena combustion glass. At 450° the amorphous sulphide had entirely crystallized in two days' time.

Only one sulphide of Cadmium.—We find no convincing evidence either in the literature or in our own experiments that cadmium sulphide crystallizes in more than one form. We have crystallized it by every method we could devise and have obtained greenockite in every case, or where in some instances the crystals were too small to identify, what properties could be determined agreed with greenockite.

III. The Sulphides of Mercury.

There are two sulphides of mercury occurring naturally, the well-known cinnabar and the much rarer metacinnabar. In addition to these there is another form, probably hexagonal, not known in nature. All have the same composition, HgS.

Cinnabar, σ-HgS, is readily formed in the wet way by the action of the soluble alkali sulphides on the amorphous black sulphide of mercury. The most satisfactory preparation method is to heat the latter in a sealed tube at 100° with concentrated ammonium sulphide. In a short time the product changes to a vermilion color, but it is best to continue the action for 24 hours to insure a thorough transformation.

The amorphous mercuric sulphide which we used in our work was carefully analyzed. It contained no other metal than mercury except a trace of iron. A small quantity of free mercury and some chlorine, probably in the form of $HgCl_2.2HgS$,

were present, but both the latter are removed by ammonium sulphide.*

Any form of mercuric sulphide dissolves readily in concentrated solutions of sodium (20% Na_2S, and 35% K_2S were actually used) or potassium sulphide. If the sulphide of mercury is kept in excess, the product is much darker than the vermilion powder formed by ammonium sulphide. The difference is solely one of division. The darker product consists of crystals easily recognized by the naked eye. These, when ground in the mortar, are scarcely distinguishable from the vermilion powder made from ammonium sulphide, while the optical properties as determined by the microscope are identical. The alkali sulphides form with mercuric sulphide two compounds $HgS.2M_2S$ and $HgS.M_2S$. The latter, we may mention in passing, is easily formed in long hair-like needles of dark green color, when the alkali sulphide solution is evaporated. Individually developed crystals of cinnabar are formed by the solvent action of dilute solutions of the alkali sulphides on mercuric sulphide. The black amorphous sulphide is always the first product when mercuric salts are precipitated by alkali sulphides, but on digestion with the latter at 100°, it gradually passes into cinnabar. Much interest attaches to the fact that *cinnabar only is obtained from these alkaline solutions.* (See p. 380.) Numerous experiments were made with mercuric chloride and dilute solutions of sodium or potassium sulphide or polysulphide between 100° and 200°. The experiments were made in sealed tubes and were continued several days. Many of the experiments were discontinued before the amorphous black sulphide was all crystallized, but *metacinnabar was never observed and cinnabar was always found.*

Effect of sublimation on Vermilion, HgS.

When the red powder which is formed by the action of ammonium sulphide is sublimed in an evacuated glass tube, the sublimate is quite black. If the layer on the walls of the tube is very thin, i. e. was cooled with sufficient rapidity, it is *entirely* black, but in thick layers the product is practically all coarsely crystallized cinnabar coated with a thin layer of the black sulphide. Whether this coating is amorphous or crystalline metacinnabar, it is impossible to say. Ground in a mortar the product is liver-colored like some ores of mercury. If, now, the ground sample is treated with a few cubic centi-

* The original amorphous sulphide always left a small residue of metallic mercury when the sulphide was dissolved by sodium or potassium sulphide solution, while the red product formed from it showed none when treated in the same manner. The chlorine in the original product volatilized as mercuric chloride when heated in an evacuated glass tube.

meters of strong sodium sulphide solution and allowed to stand for a short time, the black material is completely removed. After the addition of a little water the product is filtered and then washed with more and more dilute sodium sulphide solution, so as to prevent the precipitation of the dissolved HgS, and finally with water. This treatment would also remove free sulphur in case any had formed by dissociation of some HgS, during the process of sublimation. The product is now digested with warm dilute nitric acid to remove any free mercury,* washed with water, alcohol and ether and thoroughly dried in a vacuum desiccator containing sulphuric acid. This product showed, under the microscope, all the properties of cinnabar in much larger crystals than the original powder. Table IX shows the specific gravities of various preparations of cinnabar before and after sublimation.

TABLE IX.

Specific gravities of cinnabar at 25°.

Sublimed and purified.		Vermilion powder.	
Prep. I.	Prep. II.	Prep. I.	Prep. II.
8·200	8·198	8·191	8·186
8·198		8·190	
		8·188	
		8·188	
		8·187	

Careful experiments have shown that the vermilion powder contains a little carbonaceous matter as well as about 0·02 per cent of sulphide of iron. The sublimed product is purer and its constants are to be regarded as more reliable.

The density of the pure cinnabar, $\frac{\text{Mineral at } 25°}{\text{Water at } 4°}$ would be therefore 8·176. The lower refractive index directly measured is, $\omega_{Li} = 2{\cdot}85$. The double refraction is 0·35, making the higher index $\epsilon_{Li} = 3{\cdot}20$. (See microscopic part.)

The behavior of mercuric salts with soluble thiosulphates.

Before going further it will be well to explain the interesting chemical behavior of mercuric salts with soluble thiosulphates, which is somewhat complicated. Three solid phases may be obtained from such solutions which contain from 0—25 per cent by weight of total salts. For the purposes of this investigation it was thought unwise to carry the concentrations farther. It was found that the chemical reactions depended entirely on the ratios between the salts, while the phase which separated was also dependent on the degree of dilution.

* A very high specific gravity (8·7) of one product prepared without digesting with nitric acid was strong indication of the presence of mercury.

The facts may be clearly presented by means of a triangular diagram, from an inspection of which we can see the relation of the solid phases to the composition of the solutions out of which they crystallize, but it must be understood that the phases do not represent equilibrium relations, though the relations are constant. The diagram (fig. 5) refers only to 10

FIG. 5.

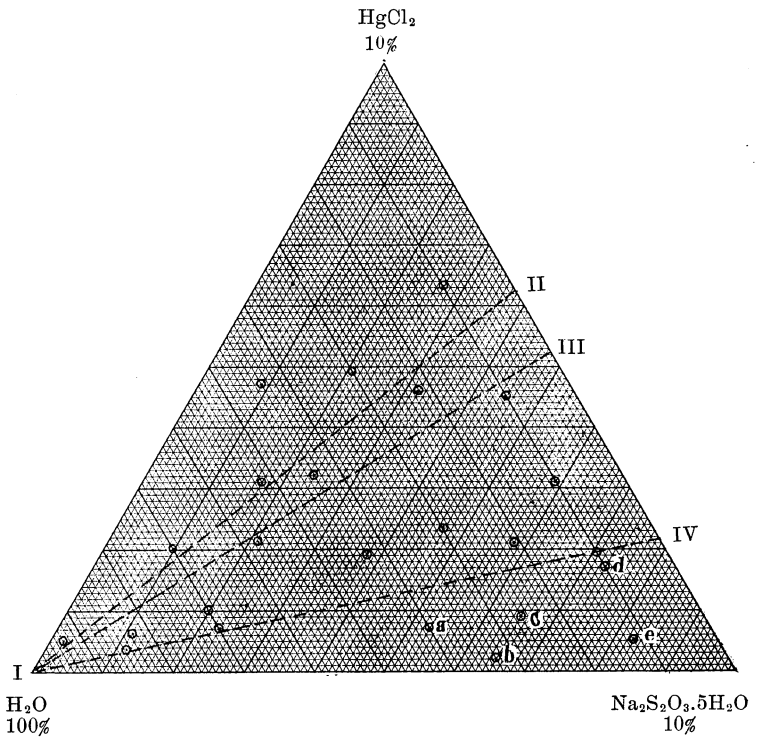

FIG. 5. The action of sodium thiosulphate on mercuric chloride in solutions of varying composition.

per cent solutions. All the solutions plotted contain a constant quantity of sodium chloride (2 g. per 100^{cc}), it having been found that the decomposition of sodium mercuric chloride proceeds much more slowly than that of mercuric chloride and better crystals appear to be obtained by the use of it.

1. All solutions lying in the field above the line I,II precipitate white mercuric chlorosulphide, $HgCl_2.2HgS$. It will be observed that the line I,II includes all solutions in which the ratio of $HgCl_2$ to $Na_2S_2O_3$ is as 3 mol : 2 mol while all solu-

tions in the field alluded to contain more mercuric chloride than this ratio. The chemical reaction which will be proved below is:

$$2H_2O+3HgCl_2+2Na_2S_2O_3=HgCl_2.2HgS+4NaCl+2H_2SO_4$$

2. All solutions lying in the field included between I,II and I,III precipitate mixtures of $HgCl_2.2HgS$ and black HgS, apparently amorphous. All solutions on the line I,III contain $HgCl_2$ and $Na_2S_2O_3$ in the ratio 1 mol: 1 mol. The chemical reaction is $H_2O + Na_2S_2O_3 + HgCl_2 = 2NaCl + H_2SO_4 + HgS$ (black).

3. All solutions lying between the lines I,III and I,IV precipitate, *in the beginning, black* HgS, though later a red precipitate may be obtained.

4. The line I,IV includes all solutions in which the ratio of $HgCl_2$ to $Na_2S_2O_3$ is 1 mol: 4 mol. The principal reaction is $HgCl_2 + 4Na_2S_2O_3 = 2NaCl + 3Na_2SO_4 + 4S + HgS$. The mercuric sulphide precipitated here is, in the beginning, a deep red modification which the microscope shows is not cinnabar but a new form, appearing transparent and orange-colored under the microscope and having lower indices of refraction than cinnabar. It should be stated here that the precipitation of this phase continues until the dilution of the supernatant liquid has fallen to about 1 per cent of mercuric chloride, when the black form in crystalline condition begins to come down with it.

Proof of the above reactions.—1. The reaction $3HgCl_2 + 2Na_2S_2O_3 + 2H_2O = HgCl_2.2HgS + 4NaCl + 2H_2SO_4$. A solution containing 2·0 g. NaCl, 1·64 g. $HgCl_2$ and 1·000 g. $Na_2S_2O_3.5H_2O$ in 100 to 200^{cc} water was boiled for a short time and filtered. No gas escaped during the process. The curdy yellowish precipitate was carefully washed, and the filtrate and washings were diluted to 250^{cc}. This solution was free from mercury, gave a strong acid reaction with litmus and a decided reaction for sulphate with barium chloride.

0·2011 g. pure dry sodium carbonate required of this solution 120·6^{cc} for neutralization, using methyl orange as an indicator. 0·386 g. H_2SO_4 found. 0·394 g. H_2SO_4 cal. from the above equation.* In a second experiment 20 g. NaCl, 1·65 g. $HgCl_2$ and 1·000 g. $Na_2S_2O_3.5H_2O$ in about 200^{cc} water were boiled and filtered as before.† The filtrate was diluted to 500^{cc}. It contained no mercury, no thiosulphate and was strongly acid as before. No sulphur dioxide was evolved during the reaction. 0·3006 g. Na_2CO_3 required for neutralization 348·5^{cc} solution, using as indicator phenol phthalein at boiling temperature. Total H_2SO_4 found 0·3991. Cal. from equation ·3955. Thor-

* It will be remembered that the thiosulphate has the formula $Na_2S_2O_3.5H_2O$.

† It may be the slight excess of mercury was absorbed by the precipitate.

oughly washed precipitates made in the above way were dried and analyzed. In all of them a small excess only of mercuric chloride was used, since a large excess gave finely divided precipitates difficult to wash.

	Found.			Cal. for $HgCl_2.2\,HgS$.
	1.	2.	3.	
Hg	81·51	----	----	81·58
Cl	----	9·37	----	9·41
H_2O	·44	----	·48	----

2. The reaction $H_2O + HgCl_2 + Na_2S_2O_3 = 2NaCl + HgS + H_2SO_4$. 1·000 g. $HgCl_2$ and 2·0 g NaCl were dissolved in water and added to a solution of 0·920 g. $Na_2S_2O_3.5H_2O$, the total volume after all was added being 150cc. A curdy yellow precipitate was obtained in the cold, probably mercuric thiosulphate, which on boiling turned black. A careful test of the precipitate for chlorine revealed not more than a trace. In a second experiment a solution containing 1·10 g. $HgCl_2$, 2·0 g. NaCl and 1·000 g. $Na_2S_2O_3.5H_2O$ in 150cc water was boiled for a short time and filtered. The filtrate and washings were diluted to 250cc. The resulting solution contained no mercury but was strongly acid. 0·2024 g. pure dry Na_2CO_3 required 119·4cc of solution for neutralization, using as indicator phenol phthalein at boiling temperature. Total H_2SO_4 found = 0·3921. Cal. from the equation 0·3951. In a duplicate experiment a solution identical with the first was prepared, washed and filtered. The filtrate and washings were diluted to 250cc as before. 0·2029 g. pure dry Na_2CO_3 required 119·5cc solution for complete neutralization. Total H_2SO_4 found = 0·3927. Cal. from the equation 0·3951.

3. The reaction $HgCl_2 + 4Na_2S_2O_3 = HgS + 4S + 2NaCl + 3Na_2SO_4$. This is the principal reaction at 100° in sealed tubes when the thiosulphate is present in sufficient excess. The solution is generally, however, slightly acid, and when it is boiled in an open vessel considerable sulphur dioxide is evolved. All the mercury is precipitated, and in two distinct layers. The bottom layer, which of course, precipitated first, is bright red and consists of the new hexagonal mercuric sulphide which we will call β'-HgS;* the upper layer consists of a mixture of this form with metacinnabar, α'-HgS. The total precipitate when mixed has a puce color almost exactly like lead peroxide. It contains the α'-HgS and β'-HgS in approximately equal quantities, as was estimated by matching the color with various mixtures of the pure substances.

* We will use the symbol σ to designate the stable form and for monotropic forms the symbols α', β' to distinguish them from enantiotropic forms, for which the unaccented letters are commonly used.

As evidence of the above reaction we give the following data:

TABLE X.

Action of $HgCl_2$ on a large excess of $Na_2S_2O_3$.

	$HgCl_2$ taken	$Na_2S_2O_3.5H_2O$ taken	NaCl taken	H_2O taken	$Na_2S_2O_3.5H_2O$ used	$Na_2S_2O_3.5H_2O$ Cal.	HgS + S found	HgS + S Cal.	HgS found	HgS Cal.
1.	1·000g	5·000g	2·0g	75cc	3·66	3·66	1·32	1·32	·86	·85
2.	1·000g	5·000g	2·0g	75cc	3·56	3·66	1·29	1·32	·82	·85

The data were obtained in the manner described on p. 352, i. e., the excess of thiosulphate was obtained by titrating an aliquot part of the filtrate with iodine; the total weight of the precipitate, washed with alcohol and dried, was then taken, and finally the weight of the sulphide was found after extracting the precipitate with carbon disulphide, washing out the excess with ether, and drying.

Metacinnabar, a'-HgS. The metacinnabar of nature, when pure, is entirely black and crystalline and is generally regarded as an isometric mineral, though crystallographic data are meager. We have obtained black crystalline mercuric sulphide by only one method, viz., by the action of an excess of sodium thiosulphate on sodium mercuric chloride *in dilute solution.* By reference to the previous pages (pp. 371-372) it will be seen that moderately concentrated solutions (10%–25%) of total salts containing the substances in the ratio $HgCl_2:4Na_2S_2O_3$ give first a red precipitate, which continues to form until the concentration of the mercuric chloride is approximately 1 per cent, when the black crystalline sulphide separates with the red. The solutions *a*, *b*, *c*, *d*, *e* (fig. 5) precipitated a mixture of the two forms from the outset. The formation of the red modification may be entirely inhibited, however, by the addition of sulphuric acid to the solution before boiling. In six different experiments where the concentration of the mercuric chloride remained constant, 1 g. : 700cc H_2O, and the thiosulphate varied from 2 g. to 20 g., the addition of 4 drops 30% H_2SO_4 entirely prevented the formation of the transparent red sulphide. This was proved by microscopic examination of the products. On the other hand, if the acid was omitted, all the other conditions remaining constant, a large quantity of the red form (β'-HgS) was intermixed. For the preparation of the black a'-HgS in

portions large enough for a specific gravity determination, we used the following solution: 6 g. $HgCl_2$; 60 g. NaCl; 12 g. $Na_2S_2O_3 . 5H_2O$ in 4l. of water. 10^{cc} 30 per cent sulphuric acid was added and the solution boiled till precipitation was complete. More than a proportional quantity of acid was thus required for the larger volume of solution. The precipitate, after thorough washing, was dried with alcohol and ether; then the sulphur was removed by repeated digestion with carbon disulphide, washed with ether, and dried by heating in vacuo to 250°. It contained only a trace of occluded salt. A weighed portion dissolved in aqua regia and changed to chloride with excess of hydrochloric acid was precipitated with hydrogen sulphide. The filtrate was evaporated to dryness and finally heated to redness in a tarred platinum dish and weighed. Three-tenths of a milligram of sodium sulphate in one gram substance = 0·03 per cent was thus obtained. Of course this does not prove the original form of the sodium to have been sulphate, though it probably was. The sulphide was tested for water by heating in an atmosphere of carbon dioxide, till it was largely volatilized, the water being absorbed by calcium chloride. Of course precautions were taken to guard against driving the sulphide vapor over into the absorption tube, and when the apparatus was cold, the carbon dioxide was removed by dry air. No water was found. Under the microscope the product was apparently all crystalline, though it was impossible to say that there was no intermixture of amorphous sulphide.

The slow precipitation of mercuric sulphate or chloride in strongly acid solution by hydrogen sulphide was also tried for the preparation of this form. The device referred to on p. 355 was used for the purpose. The products obtained in this way showed no crystal faces, and being opaque it was impossible to say whether they were crystalline or not. Similar products were also obtained by the action of sulphur and sulphuric acid on metallic mercury in closed tubes containing an atmosphere of hydrogen sulphide. At high temperatures, 200° and 300°, respectively, some cinnabar was obtained by both the last two methods.

Properties of α′-HgS. The opacity of the black mercuric sulphide made optical tests on it impossible. The attempt to prepare measurable crystals of it was futile and therefore our product could not be certainly identified with metacinnabar. The following facts, however, make the identity highly probable. Both minerals are entirely black when pure, even in a powdered condition. Natural metacinnabar is regarded as tisometric; the laboratory product was obtained from thiosulphate solutions in the form of bars crossed at right angles like the principal axes of a cube, suggesting skeleton crystals of the

regular system. The specific gravities of several products made in this way at 25° were,

I	II	III	IV	V	Average
7·592	7·586	7·642	7·588	7·568	7·60

The variation in these determinations is, perhaps, to be accounted for by the presence of some amorphous sulphide in varying quantity. The microscope was unable to decide this point.

The best determinations of the specific gravity of the natural mineral are close to 7·7. G. E. Moore,* who first described and named the mineral, said that the specific gravity varied from 7·701 to 7·748 "owing to intermixed cinnabar." Genth and Penfield,† who obtained the number 7·706 on a specimen of metacinnabar from San Joaquin, Orange County, California, say: "Color iron-black, but many pieces show already a change into ordinary cinnabarite both by a good lens and the reddish black powder which some of the particles yield on pulverizing." It is probable, therefore, that these values are somewhat high; on the other hand, it is possible that the values obtained on the laboratory product are somewhat low, since it was impossible to prove that the latter was free from amorphous material. True, Moore calls the mineral amorphous, but no other investigator confirms him. On heating alone or more rapidly with ammonium sulphide or dilute sulphuric acid, the metacinnabar passes over into cinnabar. This is true for both the natural and the synthetic mineral (see p. 377).

β′-HgS. It has already been stated that the precipitation of solutions of sodium mercuric chloride by sodium thiosulphate in the proportion $HgCl_2 : 4Na_2S_2O_3$ yields a beautiful red sulphide differing from cinnabar. If the product is to be free from *α′*-HgS, it should be filtered before precipitation is complete. For this reason it is wise to begin with pretty concentrated solutions, 10 to 25 per cent of total salts, and interrupt the operation while the product is still bright red. It has been found by actual test that the addition of a fraction of 1 per cent of black HgS to the *first precipitate which forms* (the two being thoroughly mixed in a dry condition), can readily be detected by the eye. A microscopic examination in this case was futile. Judging by the color test, the following conditions gave a product about 99·5 per cent pure. Two solutions of 400^{cc} each were prepared; one containing 40 g. NaCl and 34·4 g. $HgCl_2$, the other 125·6 g. $Na_2S_2O_3.5H_2O$. The solutions should be filtered if not perfectly clear, and the sodium mercuric chloride solution is then added gradually, with

* This Journal, iii, 36, 1872.
† Ibid., xliv, 383, 1892.

constant mixing, to the thiosulphate solution. The mixed solution should not contain a trace of precipitate. The product is now brought as rapidly as possible to boiling. After about 12 minutes the precipitate is rapidly filtered on a hot water filter and washed thoroughly with hot water. The temperature of the solution should not be allowed to fall materially during the process. In that case a further precipitate containing some black HgS is formed, as may be seen by the color. When the filtrate has reached room temperature, the further precipitation becomes very slow. If now the supernatant liquid is raised again to boiling, the β'-HgS is again formed. After the precipitate has been dried by alcohol and ether, the free sulphur is removed by carbon disulphide. That the substance is really a sulphide of mercury will be seen from the following analysis :

HgS	=	98·49
Cl	=	·10
Na_2SO_4	=	·23
H_2O	=	1·14
		99·96

A weighed portion of the substance was dissolved in caustic alkali, and the solution treated for a short time with hydrogen sulphide. A slight excess of dilute sulphuric acid was then added, and finally a slight excess of ammonia. The mercuric sulphide was then collected, freed from sulphur, and weighed according to Treadwell.*

The water and sodium sulphate were determined by the methods described for the α'-compound. The chlorine was doubtless present as sodium chloride, and the remainder of the sodium was probably in the form of sodium sulphate. If we calculate the chlorine and the sodium in this way it would change the above results only a trifle. The greater quantity of impurity found here than in the α'-HgS is due, no doubt, to the higher concentration of salts in the solution which one must use in order to obtain the β'-form. The determinations of density and refractive indices were made on preparations which had been heated to 250° in vacuo for some hours. Determinations of the water and sodium as sulphate in two of them were as follows :

I		II	
H_2O.	Na_2SO_4	H_2O.	Na_2SO_4
0·37 & 0·46	0·49	----	0·33%

These powders were apparently homogeneous as observed by the microscope, but they were quite fine and somewhat vari-

* Quantitative Analysis, translation by Hall, p. 135.

able in specific gravity. The following are the determinations of this property at 25°:

I	II	III	IV	Average
7·221	7·215	7·179	7·199	7·20

The refractive indices in lithium light were found to be 2·58 and 2·82 (Merwin). There can be no doubt that this is a new form of mercuric sulphide with properties quite different from

FIG. 6.

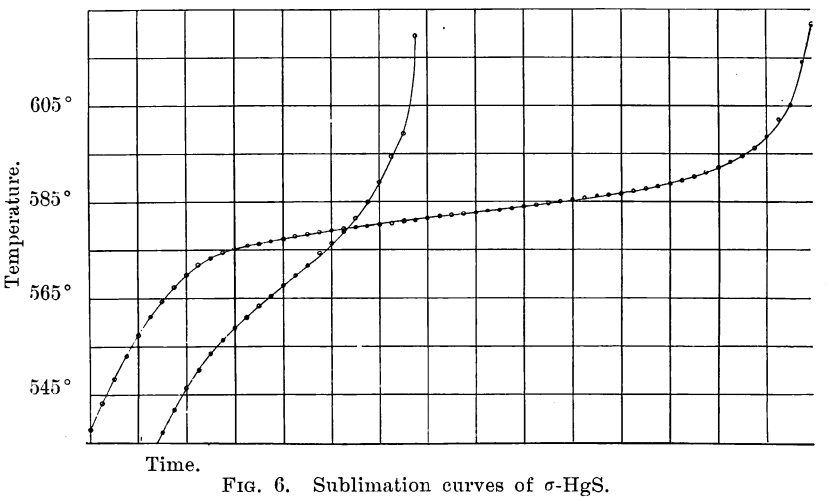

FIG. 6. Sublimation curves of σ-HgS.

cinnabar, though the color of the powder is not to be distinguished from ordinary vermilion.

Relation of the mercuric sulphides to one another.

Like zinc and cadmium sulphides, mercuric sulphide volatilizes without melting at atmospheric pressure. The pressure reaches one atmosphere at about 580°, as may be seen from the curves in fig. 6. In these experiments the sulphide was heated in an atmosphere of hydrogen sulphide. Cinnabar is the stable form over the whole temperature range up to the volatilization point. That the other two forms are both monotropic is proved by the following facts. At 100° both α'-HgS and β'-HgS are changed into cinnabar with ammonium sulphide solution, while at 200° the same change takes place very slowly in sealed tubes with 30 per cent sulphuric acid. At 400°, 450°, 500°, and 550°, both are transformed into cinnabar when heated alone in evacuated glass tubes. The heating was done in a stirred nitrate bath. Table XI shows the results.

TABLE XI. Thermal behavior of mercuric sulphide.

σ-HgS-Cinnabar				α′-HgS-Metacinnabar				β′-HgS			
Temperature	Time	Other conditions	Result	Temperature	Time	Other conditions	Result	Temperature	Time	Other conditions	Result
100°	1d	with $(NH_4)_2S$	unchanged	100°	--	with $(NH_4)_2S$	all changed to cinnabar	100°	½d	with $(NH_4)_2S$	Apparently all changed to cinnabar
----	--	----	----	200°	2d	"	95% changed to cinnabar	200°	--	with 30% H_2SO_4	Slow change to cinnabar
----	--	----	----	200°	4½d	with 30% H_2SO_4	about 10% changed to cinnabar	--	--	----	----
400°	5d	Heated alone in vacuo	< 1% α′-HgS	400°	5d	Heated alone in vacuo	small percentage changed to cinnabar	400°	5d	Heated alone in vacuo	Had the color of a mixture of 35% α′ HgS + 65% cinnabar
450°	5d	"	about 1% α′-HgS	450°	5d	"	95% changed to cinnabar	450°	5d	"	Had the color of a mixture of 15% α′-HgS + 85% cinnabar
500°	3d	"	< 1% α′-HgS	500°	3d	"	More than 99% changed to cinnabar	500°	3d	"	More than 99% changed to cinnabar
----	--	----	----	570°	3d	"	More than 99% changed to cinnabar	--	--	----	----

The thermal behavior of these substances is confusing. In the first place, cinnabar turns black as the temperature rises. This is not due to any transformation, but merely to a variation in the absorption of light with changing temperature, for after it has been heated to 325° for many hours, cinnabar quickly regains its color on cooling. If, however, the temperature is carried to 445°, or perhaps to a lower point, the color remains permanently black. This was first interpreted to mean a transformation into metacinnabar, but a microscopic examination failed to disclose anything but cinnabar, while by grinding in a mortar the black color was found to be due merely to a thin coating. By matching the tint of a ground sample of heated cinnabar with a ground mixture of the red and black sulphides, the former was found to contain 1 per cent or less of the black sulphide. The same final product was obtained whatever form of mercuric sulphide was heated, provided the temperature was as high as 500° and no further change was found on heating to 550°. This is difficult to explain satisfactorily. Possibly the coating is due to a condensation of the vapor to the black form. The volume of the tubes was about $0{\cdot}5^{cc}$ and the weight of the sulphide taken was half a gram. On the assumption that the tubes were filled with undissociated vapor at one atmosphere, they would have contained $\frac{116 \times {\cdot}09^{mg}}{2} = 5{\cdot}2^{mg}$ of sulphide vapor, and if this were all condensed on the surface of the sulphide, the mixture would have contained 1 per cent of black sulphide. Apparently little or none condensed on the glass at 500°. Even if the vapor pressure were only half an atmosphere, the results would still be of the right order of magnitude. The results on the β'-HgS, while conclusive, regarding the relation between it and cinnabar, do not settle the relative stability of the two unstable forms. With ammonium sulphide the β'-HgS appears to be transformed more slowly than the α'-form, though it is very difficult to detect small grains of cinnabar in a matrix of the former. Again, if we were to judge from the behavior of the β'-HgS when heated in evacuated tubes we might conclude that it passed through the α'-form in its transformation to cinnabar. (See Table XI.) This would make the β'-form the least stable which might be expected from the fact that it is not found in nature. However, the *apparently* large percentage of the black sulphide in the β'-HgS during the early stages of its transformation, may be nothing more than a surface coating on the numerous little grains, which in grinding still remain black because they escape the crushing action of the pestle. At the end of the transformation the β'-HgS has always changed into comparatively large cinnabar crystals in which, of course, the surface is greatly reduced.

The black coating should be thicker here if our explanation is correct, but the grinding process might well give a powder of a redder hue. We found, in accord with this supposition, that a very pure vermilion powder (unsublimed cinnabar) also gave, on heating, a product which was considerably darker after it was ground than a product formed by heating coarser cinnabar.

Whether our explanation be correct or not, it remains certain that metacinnabar and the new β'-HgS are both monotropic forms, while cinnabar is stable.

Genetic conditions of the natural mercuric sulphides.—The evidence for the geologic view that cinnabar is a product of alkaline solutions is convincing. The close and constant association of the mineral with igneous rocks is significant, while in two well-known localities, Steamboat Springs, Nev.,* and Sulphur Bank, Cal., it seems to be in the process of deposition from alkaline waters at the present day. Posepny† states that in the former locality pyrite is apparently forming with it. Cinnabar is thus undoubtedly a primary mineral. In some cases also it appears to be secondary, since mercurial tetrahedrite oxidizes readily to sulphates, and the descending solution seems to be precipitated as cinnabar on other sulphides at lower levels (Lindgren). Metacinnabar, on the other hand, is regarded as a characteristic secondary mineral. It was found near the surface in the Knoxville district, Cal., and has not been found lower down. A large part of the ore in the Baker Mine and in the upper levels of the Reddington Mine were metacinnabar.‡ Melville§ describes an occurrence of metacinnabar in the New Almaden mines, Santa Clara Co., Cal., where cinnabar and quartz are intimately mixed, while metacinnabar is crystallized on the quartz and is "certainly subsequent to it."

The metacinnabar of Idria, according to Schrauf, ‖ is far younger than the cinnabar which underlies it and has apparently been formed since the opening of the mines. It occurs here in hemispherical crystal aggregates which suggest to Schrauf that they may have formed by the action of hydrogen sulphide on the globules of metallic mercury which invariably accompany the cinnabar. Schrauf refers here to the experiments of Fleck, which lead him to believe that the metacinnabar formed in the presence of sulphuric acid. It is a noteworthy fact that metacinnabar is commonly associated with marcasite, at least in this country.¶

* W. P. Blake, this Journal (2), xvii, 438, 1854.

† Trans. Min. Eng., p. 228, 1893.

‡ Becker, U. S. G. S. Monograph 13, p. 284.

§ This Journal, xl, 293, 1890.

‖ Ueber Metacinnabarite von Idria und dessen Paragenesis. Jahrb. der k. k. geolog. Reichs., xli, p. 379-399, 1891. N. J. Min. 1893, I, referate 465.

¶ Becker, loc. cit., p. 285. Penfield, this Journal, xxix, 452, 1885.

Let us see how these field observations agree with the facts worked out in the laboratory. First, it was found that cinnabar very readily forms at moderately low temperatures (80°-100°) by the action of dilute alkali sulphide solutions on mercuric salts. Ippen* obtained good crystals at 45° in two months. Never under any conditions have we observed metacinnabar as a product of alkaline solutions.

Black crystalline mercuric sulphide was obtained by the slow precipitation of mercuric salts in acid solutions by the action of soluble thiosulphate. The crystals were not measurable and being opaque could not be positively identified. However there were some indications that they were regular and the identity of the two appears probable. The association of natural metacinnabar with marcasite in the deposits of the western United States is important in this connection because both are regarded by geologists as characteristic secondary minerals, i. e., they were precipitated directly or indirectly by the action of hydrogen sulphide from solutions which had been formed by the oxidation of sulphides near the surface. Such waters would of course contain the metals in the form of sulphates, and also free sulphuric acid if pyrite or any other sulphide of that chemical type were one of the minerals oxidized.

Marcasite has already been formed synthetically from such a solution. †

Chemical and geological relations of deep-seated and surface waters.

The difference in chemical character between "ascending" and "descending" natural waters is well known. As previously stated, our knowledge of the composition of hot springs, and the chemical behavior of common minerals with hot water, lead to the conclusion that the former class must be generally alkaline. Chlorides, bicarbonates and sulphides, especially of the alkali metals, are the characteristic constituents. On the other hand, surface waters in the vicinity of sulphides naturally contain sulphates as oxidation products and are generally acid on account of the frequency of pyrite and marcasite.

Now it is a remarkable fact that the crystalline form of a number of minerals is determined by the acid or alkaline nature of the solutions from which they crystallize. We find three pairs of minerals, pyrite and marcasite (FeS_2), sphalerite and wurtzite (ZnS), and cinnabar and metacinnabar (HgS), one member of which crystallizes from acid solutions only, the other member from alkaline solutions as well. Furthermore it is

* Tscher. Mitt., xiv, 114, 1895.

† Allen, Crenshaw and Johnston, this Journal, xxxiii, 179, 1912.

always the stable form which comes out of the alkaline solutions, while the unstable is obtained only from the acid solutions. The alkaline solutions never give rise to any other than the stable forms, while the acid solutions may give rise to either stable or unstable or both, according to conditions.

This statement is subject to only one qualification, viz., our synthetic black crystalline mercuric sulphide was not positively identified as metacinnabar though it was probably that.

We find in chemical literature one well attested instance of the same rule. Schoch * finds two crystalline oxychlorides of mercury of the composition $HgCl_2.2HgO$. One of these is red and changes readily into the other, which is black by the action of solutions of alkali carbonate or chloride. The latter form is therefore the stable one, at any rate at low temperatures. The conditions for the formation of these two bodies are essentially identical, except that for the preparation of the red form *(unstable)* the solution must be slightly *acid* while for the black form *(stable)* the solution must be slightly *alkaline.*

The geologic evidence so far as it is at hand seems to agree remarkably well with the above facts. Sphalerite, pyrite and cinnabar are primary minerals; marcasite, metacinnabar and apparently wurtzite are characteristic secondary minerals. As explained above, pyrite, sphalerite and cinnabar may be formed from acid solutions by hydrogen sulphide under certain conditions, consequently we are not surprised to find that they may be secondary as well as primary. There is one fact concerning the occurrence of marcasite and metacinnabar which should be mentioned. Both are sometimes associated with calcite. Whether or not they are paragenetic is a doubtful question. (Lindgren.) If the calcite is not subsequent to the sulphides one would be led to suspect that the original solution must have contained bicarbonates and sulphates. The synthetic work would lead us to expect pyrite from such a solution; still the quantity of free acid required for pure marcasite is very small *at low temperatures* and it may be that the reaction $FeSO_4+H_2S+S=FeS_2+H_2SO_4$ would produce marcasite when the initial concentration of acid was no greater than it is in calcium bicarbonate solutions. It would probably be difficult to verify or refute this by experiment. We are usually obliged to work in the laboratory at higher temperatures and in more concentrated solutions than nature does, in order to get any crystals at all in our limited periods of time.

It will be interesting to see whether other similar cases of polymorphism (or isomerism) exist where the crystal form is determined by the chemical composition of the solution.

* Am. Chem. Jour., xxix, 335, 1903.

It may also well be that the acidity or alkalinity of solutions will be found to determine the *composition* of minerals in certain cases. Thus chemical experience shows that the mineral chalcopyrite $CuFeS_2$ can be prepared synthetically out of alkaline solutions, while it is a matter of common knowledge that copper is *separated* from iron by hydrogen sulphide in acid solutions.

Geologists regard chalcopyrite in certain occurrences as a secondary mineral. It would be premature to enter upon a chemical discussion of this question at present; the case suffices to illustrate our meaning. Enough work has already been done to show that the difference in chemical character between acid and alkaline solutions, therefore in general between deep-seated and surface solutions, is of vital importance in geochemistry.

IV. Microscopic Study.

Zinc Sulphide.

Amorphous.—If examined immediately after being rapidly precipitated in a pulverulent form, the particles of zinc sulphide are spherical, and have diameters of ·0002 to ·0005^{mm} (2 to 5μ). If the precipitation is slow and the solution is agitated, the particles increase in size, and after standing in contact in the solution may aggregate into clusters or crusts, indicating that they are semi-fluid. In fact, the aggregates when compressed under a cover-glass flatten and break open like a stiff jelly. Though jelly-like, the globules contain very little water. On several occasions such masses after being pressed have been observed to become distinctly doubly refracting (probably crystalline). When formed very slowly in acid solutions without agitation—as in the double tube method—the precipitate is: (1) partly in the form of compact, stratified crusts having a decided double refraction with a parallel to the surface, (2) partly in globules resembling spherulites, and having a parallel to the surface. These crusts and spherules are hardened to the point of being gritty and brittle, yet their refractive indices* are far lower than those of the crystalline forms of zinc sulphide, sphalerite and wurtzite. The results of a large number of measurements are tabulated below.

Pure sphalerite	$n_{Li} = 2{\cdot}34$
Pure wurtzite	$e_{Li} = 2{\cdot}35$
	$w_{Li} = 2{\cdot}33$
Amorphous:	
Stiff jelly	$n_{Li} = 2{\cdot}18-2{\cdot}25$
Doubly refracting globules	$n_{Li} = 2{\cdot}18-2{\cdot}24$

* Measured under the microscope in mixtures of amorphous sulphur and selenium. See this Journal, xxxiv, 42, 1912.

Different layers of the hardened amorphous product may have very different refractive indices, perhaps indicating different compositions. The double refraction shown by this amorphous material is probably caused by the strains induced in these nonhomogeneous masses during the process of hardening. At temperatures above 200° these amorphous crusts and spherules soon become partly or wholly crystalline, that is, the resulting product has the refractive index, η_{Li}, of 2·34.

Sphalerite.—The isometric crystalline form of zinc sulphide, sphalerite, was produced from solutions and molten salts in the following typical habits: at about 800° from molten sodium chloride it occurred in the form of distorted dodecahedrons about 0·1^{mm} long; at 350° from a concentrated solution of sodium sulphide, dodecahedrons and tetrahedrons 0·01^{mm} in diameter appeared; at 200° for 11 days in a similar solution, tetrahedrons alone appeared. The refractive index of these crystals for lithium light determined under the microscope was found to be 2·340 ± ·005. Out of acid solutions definite crystals were not observed, but side by side were seen, in some preparations, spherules and crusts of amorphous zinc sulphide, and similarly shaped masses having no double refraction and the high refractive index. The latter were in some cases covered with minute facets. It appears that an amorphous precipitate is at first formed and that this subsequently crystallizes, probably after having hardened.

Wurtzite.—The hexagonal form, wurtzite, separated from solutions in three extreme habits: (1) Prismatic, hemimorphic crystals strongly striated across the prism faces, and reaching 0·8^{mm} in length, were produced in the double tube in an acid solution after 2 days at about 375°. (2) Crystals, tabular parallel to the base and modified by a different pyramid on each end, occurred with these prisms. (3) Hardened amorphous globules from acid solutions at high temperatures become transformed into coherent masses of very small doubly refracting grains having the mean refractive index of wurtzite. In two cases distinctly radial-fibrous forms, having the characteristics of wurtzite elongated parallel to the prism, were seen. This structure is found in the natural schalenblendes. Experience has shown that these aggregates, immersed in methylene iodide and viewed in ordinary light, may appear entirely isotropic, but mounted in a red mixture of sulphur and selenium having about the same refractive index as the aggregates, they are distinctly doubly refracting in artificial light.

Wurtzite produced by sublimation may appear in slender needles or small stout prisms. Such crystals made from pure zinc sulphide were used for determining the refractive indices under the microscope. The values obtained are as follows:

$\omega_{Li}=2{\cdot}330$, $\epsilon_{Li}=2{\cdot}350$, $\omega_{Na}=2{\cdot}356$, $\epsilon_{Na}=2{\cdot}378$. An independent measurement of $\epsilon-\omega$ on the prisms gave ·019 for Li-light and ·020 for Na-light.

Observations on natural Sphalerite and Wurtzite.

Samples from more than twenty different occurrences of natural zinc sulphide minerals were studied optically. With a prism of the light amber-colored sphalerite from Sonora the refractive indices for Na-light and Tl-light were accurately determined on a spectrometer. The values obtained were $2{\cdot}3688 \pm {\cdot}0001$ and $2{\cdot}3990 \pm {\cdot}0002$. Although this material is the purest natural sphalerite obtainable (containing only 0·22 per cent FeS) the impurity is sufficient to raise the refractive index ·0006 for Na-light and ·0007 for Tl-light (page 386). The refractive index of pure sphalerite, probably correct within ±·0002, therefore, is $\eta_{Na} = 2\ 3682$, $\eta_{Tl} = 2{\cdot}3983$.

The dispersion of the Sonora sphalerite was determined from measurements on two prisms, a goniometer and monochromatic illuminator being used. The illuminator was standardized by observations on the following lines: Li, Na, Tl, Sr (blue).

Wave-length	Refractive Index
420	2·517
434	2·493
486	2·436
535	2·399
589	2·369
630	2·353
671	2·340
760	2·320

The effect of dissolved FeS upon the refraction constants of Sphalerite and Wurtzite.—Natural blendes may contain as much as thirty per cent of FeS. Ferriferous blendes are deeply colored, but in very thin flakes they are a clear orange-brown by transmitted light. The blende from Saxony containing 28·2 per cent of FeS absorbs light in gradually increasing amounts from the red end of the spectrum to about 450$\mu\mu$, where it is practically opaque. The wurtzite formed by heating this blende is somewhat lighter in color, but is not distinctly pleochroic in any part of the spectrum. Its average refractive index is very near the refractive index of the blende —was observed to be ·005 less—and its double refraction about ·02. The mutual optical relations of sphalerite and wurtzite are thus not sensibly altered by the presence of large amounts of FeS.

The absolute values of the refractive indices are greatly increased by FeS. The following table shows the character of

the change for sphalerite. The same values apply to wurtzite also, within the limits of error of the determinations of refractive index—probably about ±·005, due to lack of homogeneity of the blende and to observational errors. The analyses and densities given in the table are by Allen and Crenshaw.

Locality	% FeS (MnS)	d	n_{Li}	n_{Na}	$\frac{n-1}{d}$		$\frac{n-1}{d}$ Calculated for FeS.	
					Li	Na	Li	Na
Sonora	0·2	4·090	2·34	2·37	·328	·335		
Spain	8·6	4·023	2·36	2·40	·338	·348	·442	·488
Australia	17·	3·98	2·38	2·43	·346	·358	·436	·471
Saxony	28·2	3·935	2·395	2·47	·355	·373	·427	·470

Assuming that the FeS is dissolved troilite having a density of 4·78, the average refractive index of troilite calculated on the assumption of an additive relation is 3·08 for Li-light and 3·25 for Na-light. However, if the formula $\frac{n^2-1}{n^2+2} \times \frac{1}{d}$ is used in making a similar calculation, the refractive index for Li-light is 4·7. So great a discrepancy indicates that the additive relation of the refraction constants does not hold in this case, or that it is some form of FeS other than troilite that is present in the blende. The latter alternative appears more likely, for mix-crystals of troilite and sphalerite should have intermediate densities, whereas ferriferous blende has a lower density than either of these minerals. A close agreement between the formulas, the observed densities and refractive indices is obtained by assuming that the FeS in the blendes has a density of 3·8 and an average refractive index of 2 8 for Li-light.

Etch-figures and anomalous double refraction.—Triangular etch-figures on a cleavage surface of sphalerite heated in $ZnCl_2$ are sketched in fig. 7, C (p. 389).

Pressure at a point develops double refraction which may become permanent. Fig. 7, D and E, show doubly refracting areas on a cleavage surface around a point at which pressure was applied. The positions of the plate are 45° apart, the lines Cl representing a cleavage direction.

The tooth-like irregularities on fracture surfaces of sphalerite may be distinctly doubly refracting.

Optical and crystallographic relations between Sphalerite and Wurtzite.

The development of double refraction is the only conclusive evidence we have of the change of sphalerite to wurtzite by heating. Inasmuch as the transformation is slow, its progress can be studied. In ferriferous blendes transformation appears to be most rapid, starting usually at a single point in a grain and progressing so that the final product has like orientation throughout. In grains of the purest sphalerites, the wurtzite usually begins developing at more than one point and in different orientations. The structure produced is an intergrowth of lamellæ of wurtzite, each lamella having its principal axis parallel to one of trigonal axes of the sphalerite grain.* It is evident that the strength of the double refraction of a grain thus transformed will be conditioned by the relative development of the four possible sets of lamellæ. J. Beckenkamp† has considered that lamellæ of wurtzite may develop parallel to the trapezohedron of sphalerite. Such lamellæ would outcrop on a cleavage face parallel or normal to cleavages or bisecting the acute angle between cleavage surfaces. All of the outcropping planes would be oblique to cleavage planes. No lamellæ of this sort were seen in the large number of preparations examined during this investigation.

In material furnished by Mr. B. S. Butler, from Beaver Co., Utah, prismatic crystals of wurtzite from a brecciated vein have fragments of sphalerite as nucleii. The traces of the prismatic cleavage of the wurtzite and of the cleavage of the sphalerite appear to be parallel. The wurtzite cleaves parallel to the second order prism.

Beckenkamp has discussed in detail the very close crystallographic relations of sphalerite and wurtzite. With these are now correlated the very slight changes in optical properties, volume, and energy content accompanying the inversion of these minerals.

Cadmium Sulphide.

Amorphous.—The flocculent precipitate of cadmium sulphide is yellow while moist, but it dries to an orange powder which is lumpy and nearly opaque to transmitted light. The lumps can be consolidated by pressure—as by grinding forcibly in a mortar or by compressing on a microscope slide under a cover-glass—into transparent films, some of which become crystalline during and after the compression. The progress of crystallization may be slow, several hours being required for

* Hautefeuille (loc. cit.) recognized this relation.

† Zs. Kryst., xliv, 243, 1908.

the induced radial—or parallel—fibrous structure to attain its apparent maximum double refraction.

The pulverulent precipitate is bright yellow when first formed, and may remain yellow when dry. Conditions which cause aggregation or great increase in size of the particles produce orange-colored powders. The physical characters of powders of various colors are considered in a succeeding section. Amorphous cadmium sulphide has not been observed in a hard, brittle, doubly refracting form like zinc sulphide. When it exhibits double refraction its refractive index approaches the refractive index of greenockite (crystalline CdS).

The tendency to crystallize is much greater in some preparations of amorphous cadmium sulphide than in others. This has been observed particularly when these preparations have been embedded in the mixtures of sulphur and selenium preparatory to obtaining refractive indices. Large clear globules and lumps from dried flocculent precipitates have not crystallized under this condition, but lumpy aggregates of minute globules such as have been formed by heating the latter in strong solutions of sodium sulphide crystallize readily. However, the crystals are oriented at random, and are so minute that only a very strong light reveals their double refraction. On account of the pores in these aggregates their refractive indices could not have been determined were it not for the fact that compressing and moving them about in the viscous mixture causes their surfaces to consolidate into transparent films.*

Crystalline.—By whatever method produced, the crystals of cadmium sulphide as seen in the microscope were prismatic with parallel extinction, elongation c, pure yellow color, and very faint or imperceptible pleochroism. Crystals from the preparations with molten alkali polysulphide were identified as greenockite by goniometric measurements. Three prismatic, hemimorphic crystals about 1^{mm} long furnished the following data: the prism angles varied between 59 and 61°; 9 angles from the prism to a pyramid varied between 26° 10′ and 28° 15′; five of these angles giving the sharpest signals were included between 27° 45′ and 28° 15′; the base terminating the end bearing this pyramid was dull; a steeper pyramid with dull faces terminated the other end. The pyramid measured corresponds to $20\bar{2}1$ of greenockite.

The observed refractive indices of these prisms for lithium light are $\epsilon = 2{\cdot}447$, $\omega = 2{\cdot}425$. The crystals from cadmium sulphate, slowly precipitated by hydrogen sulphide, gave a

* It was at first thought that these films might have taken up appreciable amounts of the constituents of the mixture, but this is not the case.

value for ϵ of 2·44. Hexagonal crystals of greenockite from sublimed cadmium sulphide have a slightly higher refractive index, $\epsilon = 2{\cdot}456$. The lower refractivity of the crystals formed in contact with salts is attributed to dissolved impurities, for no other optical differences were observed.

The sublimate produced by heating cadmium in hydrogen sulphide contains crystals of greenockite of four very different habits: filaments and needles, stubby prisms, twins after

FIG. 7.

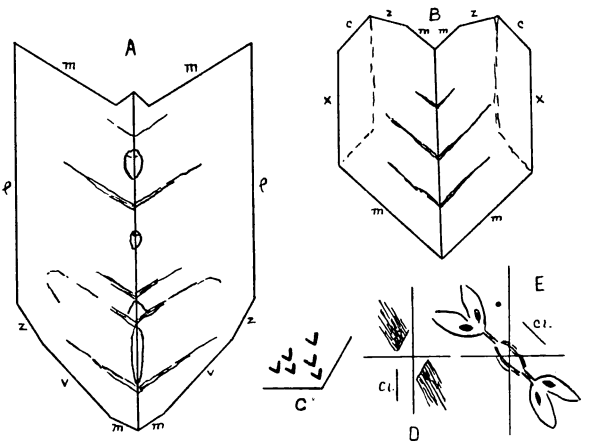

FIG. 7. A, B, Greenockite twin. C, etch figures on sphalerite. D, E, doubly refracting areas on sphalerite.

$10\bar{1}1$, and twins after $20\bar{2}3$. The drawings (fig. 7), made from microscopical studies show the twins. By the elongation of twins like A, feather-like crystals are produced. The angles measured are as follows: $x(10\bar{1}1) : c(0001) = 43°$; $m(10\bar{1}0) : x(10\bar{1}1) = 47°$; $m(10\bar{1}0) : z(20\bar{2}1) = 28°$; $m(10\bar{1}1) : v(40\bar{4}1) = 15°$; $\rho(20\bar{2}3) : v(40\bar{4}1) = 43°$; $v(40\bar{4}1) : z(20\bar{2}1) = 11°$.

The extinction angles measured from the trace of the twinning (and composition) planes are 43° and 32°. The latter angle was measured accurately more than forty times on several twins, with variations less than 1°. The value $32° \pm 10'$ was obtained. For greenockite the calculated angle is 31° 58′. Poorly developed twins of this type may represent the supposed monoclinic modification of cadmium sulphide.

Optical properties of pure Greenockite.

The chief optical properties of pure greenockite may be inferred from the upper curves of fig. 8. It is uniaxial—positive

for the colors from red to blue-green and negative from blue-green to blue, the wave-length for which it is isotropic being about 523 $\mu\mu$. Above 500 $\mu\mu$ (toward the violet), absorption is so strong that the double refraction has not been measured. By transmitted light, therefore, clear crystals are pure yellow. Plates 0·02^{mm} thick are opaque for all the blue and the violet light that can be obtained from a 20-ampere arc through a monochromatic illuminator. The ordinary ray is more strongly absorbed in the green than the extraordinary ray, for which reason the mineral is pleochroic. In white light the pleochroism is not perceptible in single crystals, but in thin twin crystals it may be seen by contrast in the two parts.

A closer study of the light-absorption of greenockite shows that below (toward the red) wave-length 519 $\mu\mu$ there is very little absorption for ω, and from 517 to 511 it increases to nearly complete opacity. For ϵ absorption begins near 512 and increases similarly to 506. The change of optical sign is the natural accompaniment of the more rapid increase in refractive index of ω than of ϵ near this region of absorption.

The refractive indices for several different wave-lengths in the red and orange were measured under the microscope. The results are plotted on the diagram. The values for sodium and lithium lights with a probable error of $\pm$ ·003 are as follows: ϵ_{Na}=2·529; ω_{Na}=2·506; ϵ_{Li}=2·456; ω_{Li}=2·431. The values used for the curves in the yellow and green are extrapolated on the basis of the absorption, and of the following values for double refraction obtained by measurements on prisms ·03 to ·04^{mm} thick, in monochromatic light.

671 (Li) = ·025	527 = ·006
589 (Na) = ·023	523 = ·000
547 = ·018	518 = −·006
535 (Tl) = ·013	516 = −·016

Color of Cadmium sulphide.

The color of a substance as seen by reflected light depends upon the character and relative amounts of light reflected directly from external surfaces and indirectly from internal surfaces, that is, after having passed into the substance and reflected out. The quality of the light reflected in each case depends upon the refractive and absorptive powers of the substance, and upon the character (plainness, size, brightness) of the reflecting surfaces.

Greenockite.—This mineral absorbs all the blue and violet and part of the green of the spectrum, and freely transmits the rest. When the greenockite grains seen in mass have diameters of 0·2 to 1·0 or more and are bounded by plane, bright faces, a comparatively large amount of blue light is

directly reflected and a small amount of red, orange, yellow and green are reflected after passing through the surface layer of crystals. The combined effect of all the reflected light is a lustrous, dark, yellow to yellowish-green color, or dark citrene. Similarly, plane-faced bright crystals, but having diameters of ·01^{mm} or less reflect about the same amount of blue light directly, but they reflect much more of that which has penetrated the surface. The resulting color is a brilliantly pure yellow. Massed crystals of the size of the last but with dull faces have a light yellow-brown or citrene color. A powder consisting of crystalline grains of which the surfaces are mostly bright but not plane, such as is formed by grinding, is invariably a brilliant orange color. In this case there is less direct reflection, and much of the light finally reflected from the interior has penetrated deeper and thus lost more green and yellow than in a powder having plane-faced fragments. Combinations of the physical conditions described cause variations between the extreme colors enumerated.

The colors of dry, *amorphous cadmium sulphide* may be explained in much the same way. The amorphous sulphide, however, absorbs more strongly in the yellow and green than does the crystalline. By transmitted light its color is orange-yellow in films ·01^{mm} thick, and yellow in films ·001^{mm} thick.

The globules of which the pulverulent amorphous sulphide consists may have bright surfaces or surfaces dulled by wrinkles. In the former case the colors are most brilliant and pure. Powders consisting of separate globules ·0001 to ·001^{mm} in diameter are bright yellow with a tinge of orange; powders having globules ·004 to ·007^{mm} in diameter, or compact aggregates of smaller globules, are bright orange-colored. (See Table XII.)

The lumpy aggregates of dried flocculent precipitates have a duller orange color, owing to a less complete reflection of the light which enters the powder.

The characteristics of amorphous precipitates formed in various ways are given in Table XII, and the dispersion curve for the purest material at hand is shown in fig. 8.

A precipitate made by treating a 10 per cent solution of $CdSO_4$ + 20% H_2SO_4 with H_2S at boiling contained a few per cent of bright orange-yellow globules ·004 to ·007^{mm} in diameter. These were cell-like, having a more highly refracting wall about ·001^{mm} thick.

Another precipitate made by heating for 2 days at 200°, 2 g. of amorphous CdS in a closed tube with 10 per cent HCl, was covered with a very thin film of indefinitely doubly refracting material having a much redder color than any other preparation examined.

Mercuric Sulphide.

Amorphous.—The tendency to aggregate into spherical masses, which is so marked in amorphous cadmium and zinc sulphides, has not appeared in amorphous mercuric sulphide.

Crystalline.—At least three crystalline modifications of HgS have been prepared. Of these, cinnabar crystallizes best, in sharply-bounded nearly equi-dimensional, red, hexagonal prisms

FIG. 8.

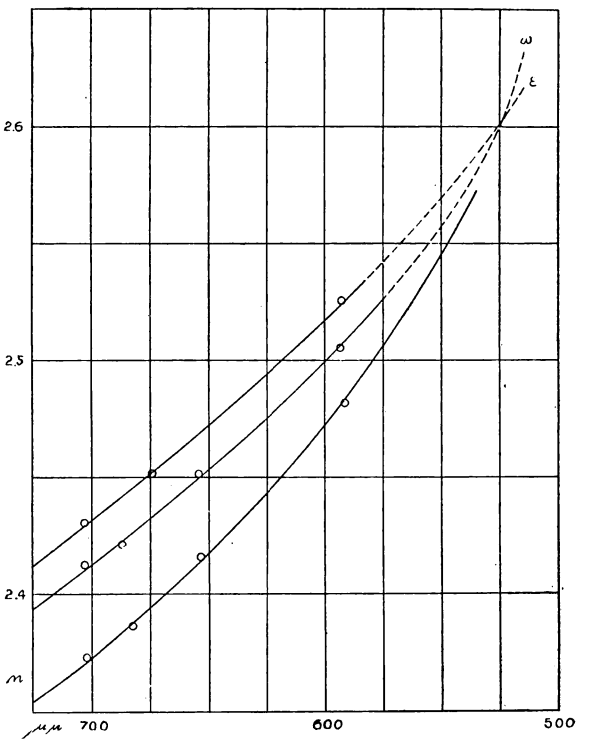

FIG. 8. Dispersion of greenockite and of amorphous cadmium sulphide.

or tables having very strong positive double refraction and very high refractive indices. The index ω of crystals formed by sublimation was approximately matched under the microscope in Li-light with a glassy mixture of Sb_2S_3. and As_2S_3. and found to be equal within the limits of error (about $\pm 0{\cdot}02$) to ω of natural cinnabar, i. e., 2·81; ϵ_{Li}, which is 3·14, is too high to be determined microscopically.

The new form, *β′-HgS*, is prismatic in habit and has not been produced in crystals exceeding ·003^{mm} in diameter and ·03^{mm} in length. These crystals always taper toward the ends

TABLE XII.

Method of preparation	Size of particles mm	Refractive index n_{Li}	Color	Remarks
Sodium thiosulphate in closed tube	·004 and less	2·38	Nearly pure orange	The purest orange examined
Do	·001—·003	2·32	Orange	Globules aggregated
H_2S cold	·0005		Orange-yellow	Clustered
H_2S and hot 5% HCl	·004		Orange	
H_2S and hot 28% H_2SO_4	·008		Deep orange	Aggregated
Boiled several hours with sodium thiosulphate	·007—·001	2·28±	Bright orange	
H_2S in the cold	·0005—·001		Yellow	
Na_2S, closed tube	·001	2·40	Yellow	
Commercial powder heated dry at 500°	·0006		Yellow	
Commercial powder Sample 1	Compact aggregate	2·38—2·39	Dull orange	
Sample 2	Do	2·37	Do	

and have no distinct faces. They are commonly aggregated into stellate groups. In color they are not distinguishable from cinnabar, and like cinnabar are optically uniaxial and positive, but their refractive indices are lower and double refraction not so strong. ω of several lots of crystals was determined for wave-length about 650 $\mu\mu$. Monochromatic light could not be used advantageously on account of weak illumination and diffraction, but for the mean wave-length of the narrow band of the spectrum transmitted by the sulphur-selenium mixture in which the crystals were imbedded, the value of ω was found to be 2·60 to 2·61, the larger value being for the purest crystals. The dispersion of the crystals is not accurately known, but it appears to be about equal to that of the sulphur-selenium mixtures used Therefore, for Li-light ω = about 2·58; ϵ-ω = ·24 ± ·03 according to several determinations on prisms of measured thickness.

The third modification, α', is probably identical with the mineral metacinnabar, but positive identification is not possible on account of the minute size and poor development of the artificial crystals, and on account of the meager and conflict-

ing data on the crystallography of metacinnabarite. Crystals of this form are black, and when typically developed have six spindle-shaped rays, apparently equal and meeting at right angles. These characteristics indicate skeletal growth parallel to the axes of the cube. But numerous rays are present in some cases, and though the six can usually be distinguished, the exact relations of the intermediate rays are uncertain. None of the rays exceed ·01^{mm} in length.

In several preparations—previously described—black prisms were found which, in all but two cases, were shown to consist of transparent double salts coated with amorphous mercuric sulphide. In the two cases no satisfactory determination could be made.

Summary.

1. The two sulphides of zinc are enantiotropic: β-ZnS or sphalerite is stable below 1020°, where it is transformed into α-ZnS or wurtzite. Sphalerite has a density of 4·090, $\left(\frac{\text{mineral at } 25°}{\text{water at } 4°}\right)$. Wurtzite has a density very slightly less, viz., 4·087. The determinations were made on a very pure analyzed sphalerite, and the wurtzite formed by heating it to the proper temperature. The refractive indices of these forms for sodium light are: sphalerite, n, = 2·3688; wurtzite, ω, = 2·356, ϵ = 2·378.

2. Iron sulphide in solution lowers the inversion point of sphalerite strongly and in a nearly regular manner. The inversion temperatures of four analyzed ferruginous sphalerites, the highest containing 17 per cent of iron, were determined. The specific volumes of these sphalerites varied almost rectilinearly with the percentage of iron. The volume increases with the latter, although the specific volume of ferrous sulphide is only about 85 per cent as great as that of zinc sulphide. The refractive indices for sodium light of both sphalerite and wurtzite are raised 0·0033 for each per cent of ferrous sulphide.

3. Crystals of wurtzite of considerable size were obtained by sublimation at about 1200°–1300°. Small dodecahedrons of sphalerite were obtained from molten sodium chloride at a little above 800°, while larger dodecahedrons as well as tetrahedrons crystallized from molten potassium polysulphide at about 350°. From aqueous solutions both sphalerite and wurtzite were obtained at temperatures between 200° and 400°. Below about 200° the products were amorphous. From solutions of alkali sulphides (alkaline solutions), *only sphalerite* formed; both dodecahedrons and tetrahedrons were obtained. From acid solutions of zinc salts hydrogen sulphide precipitates at 250° and above, both sphalerite and wurtzite. In nearly all cases (10 out of 12 experiments) so far as experiments have

gone, temperature and acid concentration have proved the definitive factors. The higher the temperature for a given acid concentration the greater is the percentage of sphalerite (the stable form) crystallized; and the higher the acid concentration for a given temperature the greater is the percentage of wurtzite (the unstable form) crystallized.

Quantitative work has shown previously that the same rule holds for the disulphide of iron. Here the *stable* form is *pyrite* and the *unstable*, *marcasite*.

4. A preliminary study was made of the precipitation of zinc by hydrogen sulphide from solutions of variable acid concentration.

5. We have obtained only one sulphide of cadmium, the mineral greenockite, whatever method was used in its preparation. Very pure large crystals were prepared by Lorenz' method, viz., the action of hydrogen sulphide on cadmium vapor. The density of these crystals, $\frac{\text{mineral at } 25^\circ}{\text{water at } 4^\circ}$, was 4·320. The refractive indices were found to be $\epsilon_{Na} = 2{\cdot}529$, $\omega_{Na} = 2{\cdot}506$.

The various hues of different preparations of cadmium sulphide do not depend, as has been claimed, upon different allotropic forms; they depend first on whether the substance is crystalline or amorphous. The color of the amorphous products depends chiefly on the size of the grains, the yellow products consisting of more minute particles, but it is also influenced by the nature of the surface of the individual grains, and their forms.

6. Mercuric sulphide exists in three different crystalline forms, viz.: cinnabar, σ-HgS, which is readily prepared by digesting any other form of mercuric sulphide with a solution of ammonium sulphide or alkali sulphide; metacinnabar, α'-HgS, which is precipitated from *dilute* acid solutions of mercuric salts by sodium thiosulphate; and a new crystal form, β'-HgS, which is obtained from *more concentrated* neutral solutions of mercuric salts in a similar way.

The density of cinnabar, $\frac{\text{mineral at } 25^\circ}{\text{water at } 4^\circ}$, $= 8{\cdot}176$.

The specific gravity of α'-HgS at 25° averaged 7·60 as compared to about 7·7 for the natural mineral. For reasons stated in the text the latter figure is doubtless too high.

β'-HgS has only been obtained in the form of a fine crystalline powder, having practically the same color as vermilion. It is hexagonal. The specific gravity at 25° averaged 7·20. The indices of refraction for 650 $\mu\mu$ were: $\omega_{Li} = 2{\cdot}61$, $\epsilon_{Li} = 2{\cdot}85$.

7. Cinnabar is the stable form of mercuric sulphide at all temperatures up to its sublimation point, which is about 580°.

The other two forms change into it, either by heating alone or more readily in the presence of solvents like concentrated ammonium sulphide or 30 per cent suphuric acid. The absorption of light by cinnabar increases markedly with rising temperature, but it regains its color on cooling after long heating at 325°. Heated above 400° it becomes permanently black. This is not an inversion as some have supposed; the cinnabar contains only about 1 per cent or less of a thin coating of the black sulphide which perhaps is caused by condensation of the vapor.

8. Amorphous cadmium sulphide is so fluid, that during precipitation small particles may aggregate into globules 0·005 to 0·01^{mm} in diameter which remain permanently plastic. Amorphous zinc sulphide aggregates similarly but the globules may harden, either without crystallizing, or by crystallizing. In the former case they simulate doubly refracting spherulites owing to the development of strains in a wholly amorphous substance; in the latter case double refraction is due to wurtzite.

9. Comparing the genetic relations of the minerals sphalerite, wurtzite, cinnabar and metacinnabar with the genetic relations of pyrite and marcasite, we find certain remarkable regularities. The *stable forms*, sphalerite, cinnabar and pyrite are always obtained by crystallization from alkaline solutions (solutions of the alkali sulphides), while the *unstable forms* wurtzite, metacinnabar and marcasite are obtained from acid solutions only. The stable forms also may be crystallized from acid under certain conditions. Of these temperature and acid concentration appear to be the important ones.

Certainly with pyrite and marcasite and in all probability with sphalerite and wurtzite, the higher the temperature the greater is the percentage of the stable form obtained, while the higher the acid concentration at any temperature the greater is the percentage of the unstable form obtained. These facts appear to agree remarkably well with the field evidence which relates to the genesis of the natural minerals, while they give new significance to the general geologic distinction between deep-seated and surface waters in nature.

10. None of the sulphides of the group zinc, cadmium, mercury melts at atmospheric pressure.

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