INDUCED PRECIPITATIONS AND PROPERTIES OF METAL SULFIDES

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EXAMPLES OF INDUCED PRECIPITATIONS

It has been frequently observed that in separations of the metals of the second and third groups of the qualitative analysis scheme the metal sulfides of group II may cause the appearance of the sulfides of group III in the precipitate under conditions which would not allow the precipitation of the latter if present alone. Such phenomena have been vaguely referred to as examples of "induced" precipitation, and various cases have been investigated and discussed. Conflicting views as to the nature of the phenomena have resulted and the matter at present is in a state of considerable dispute.

Among the observations reported which are clearly defined examples of the above-mentioned effect, or which seem to have some bearing on the subject, the following may be briefly listed.

The case of the sulfides of copper and zinc has received much attention by workers in the field of analytical chemistry. It has been known for a long time that zinc sulfide is "carried down" by copper sulfide when precipitation by hydrogen sulfide takes place at such an acidity that zinc sulfide would not precipitate from solutions containing only zinc salts. A review of the literature reveals that notice was taken of the difficulty met with in separating zinc and copper by the sulfide method as early as the middle of the nineteenth century by Rivot and Boquet (62), Calvert (15), Spirgatus (72), and Grundmann (29). Further investigations regarding this pair have been made by Baubigny (7), Larsen (50), Berglund (8), Glixelli (26), Kolthoff and Van Dijk (45), Böttger and Druschke (11), and Kolthoff and Pearson (46).

Craig (16) found difficulty in recovering small quantities of cadmium in sulfide zinc ores, since in hydrochloric acid medium it was necessary to keep the acidity so high in order to prevent precipitation of the zinc that the cadmium was incompletely precipitated. The limiting acidity at which the separation could be effected was found to be 1.8 N in sulfuric acid,—an acidity far greater than that necessary to prevent precipitation

293

of zinc sulfide from solutions containing salts of that element alone. This behavior is related to the observation made by Treadwell and Guiterman (77) that zinc sulfide is carried down by cadmium sulfide.

Feigl (19) mentions that mercuric sulfide precipitated from an acid solution (acidity not given) in the presence of zinc ions contains about 3 per cent zinc sulfide. Related to the subject is the statement by Hillebrand and Lundell (36) that the separation of mercury from most members of the hydrogen sulfide group, based on the insolubility of mercuric sulfide in boiling dilute nitric acid, fails if the mercuric sulfide is brought down in solutions containing copper, cadmium, or zinc. It was found by the present authors that mercuric sulfide does have a tremendous promoting effect on the precipitation of zinc sulfide, and a detailed investigation of the phenomenon in the case of these two sulfides has been made (59).

The precipitation of zinc sulfide has also been found to be hastened by the sulfides of lead or tin (51) and by arsenic pentasulfide (21). From work being done at present in this laboratory by Mr. Griffith it may be stated that bismuth sulfide has a similar effect.

On the other hand, Funk (24) reports that manganese, cobalt, nickel, and iron are carried out of acetic acid solution with zinc sulfide by precipitation with hydrogen sulfide, even though those ions if present alone in acetic acid medium are not precipitated as sulfides. A similar observation as to the "induced" precipitation of the sulfides of nickel and cobalt with zinc sulfide has been made by Kato (40) and by Kling, Lassieur, and Lassieur (41).

Auger and Odinot (3) found that even at an acidity where stannic tin is incompletely precipitated by hydrogen sulfide, cobalt sulfide is found in the precipitate if precipitation takes place from a solution containing ions of both metallic elements. Divalent tin seemed to have no such effect. It also appears that iron sulfide is carried down from acid solution by stannic sulfide, and that nickel sulfide is brought down by stannous sulfide (21).

Berglund (8) reported that cadmium sulfide is carried down by copper sulfide in strongly acid solution.

Böttger and Druschke (11) found that even in 3 N nitric acid solution a precipitate of copper sulfide is contaminated with an appreciable amount of iron sulfide if precipitation takes place from a solution containing salts of both metals.

The above authors, in common with Manchot, Grassl, and Schneeberger (56) and Feigl (19), found that a much greater concentration of hydrochloric acid is required in the separation if mercuric chloride is present than that required to prevent precipitation of cadmium sulfide alone. Rosenbladt (64), too, found difficulty in effecting this separation. A similar phenomenon has been noted in the case of mercury and copper (21).

Thallous sulfide, which is not precipitated from mineral acid solution by the action of hydrogen sulfide, was found to be "carried down" by the sulfides of arsenic, antimony, tin, lead, mercury, and copper (13, 33, 40).

Tungsten sulfide, though easily soluble in alkali sulfides, owing to the formation of thiotungstates, is brought down by the addition of ammonium sulfide to a solution which contains, besides tungsten, other cations, such as manganese, which are precipitated by that reagent (21).

Platinum sulfide, while only incompletely precipitated by hydrogen sulfide from acid solution, nevertheless "induces" sulfide precipitation of metals not usually precipitated if present alone. This effect is especially marked in the case of iron (21).

Working in basic solution Feigl (20) found that the sulfides of cadmium, zinc, and manganese removed appreciable quantities of mercury from solutions of sodium mercuric sulfide (Na_2HgS_2). If manganous sulfide is precipitated with zinc sulfide or mercuric sulfide, the precipitate cannot be freed of manganese by treatment with acetic acid. Likewise if mercuric sulfide is precipitated on the sulfides of manganese, zinc, or cadmium and extracted with sodium sulfide, some mercury is left in the residue. This observation has been confirmed by the present authors.

INTERPRETATION OF THE INDUCED SULFIDE PRECIPITATIONS

The above list of instances where the "carrying down" effect would appear to be indicated serves to illustrate the wide occurrence of the phenomenon. It is not to be assumed, however, that all cases occur according to one general process or mechanism. Even in the case of one particular pair of metal sulfides there may be several effects involved which give rise to the composite effect designated as "induced" precipitation. Various theories have been advanced to explain the phenomenon in certain specific cases.

Bassett (6) proposes that in the precipitation of metallic sulfides from acid solution with hydrogen sulfide, amphoteric neutralization of the primarily formed hydrosulfides occurs, resulting in the formation of the sulfide precipitate from molecular complexes of the hydrosulfides with elimination of hydrogen sulfide. This theory in the case of sulfides is based on analogy with amphoteric neutralization processes proposed in regard to the hydroxides of copper and other metals. Bassett further suggests that such a mechanism is partly responsible for the readiness with which certain sulfides, notably copper, carry down from acid solutions sulfides of the third group such as zinc. There seems to be no definite proof, however, that the formation of sulfide precipitates involves amphoteric neutralization as proposed, or that contamination of a sulfide

precipitate of the second group by sulfides of the third group is even partially a consequence of such a mechanism.

Feigl (19, 20, 21) attempted to clear up the entire problem of induced precipitations among the sulfides by his Coördination Theory. Rejecting the ionic theory and the law of mass action as regards the precipitation of sulfides, he proposes that by virtue of the residual valences on the sulfur atoms the following types of coördination compounds may be obtained: (1) MS—SH$_2$, hydrosulfide; (2) MS—S, polysulfide; (3) M$_1$S—SM$_1$, isopolymer; (4) M$_1$S—SM$_2$, heteropolymer or mixed sulfide. Cases such as we are considering are then represented according to Feigl by type 4.

It is evident from consideration of this theory that Feigl assumes a condition of coprecipitation in all cases. Undoubtedly Feigl is wrong in his generalization, although the existence of compound formation among the sulfides cannot be successfully disputed. Examples in the case of copper and thallium, mercury and manganese, possibly in the case of copper and iron and others have been reported by various investigators (13, 81, 33, 35, 69). In general, however, Feigl's views have not been favorably received by other workers in the field.

By the powder method of x-ray analysis Böttger and Druschke (11) were unable to detect any evidence of compound formation in the sense of Feigl in the case of the sulfides of mercury and cadmium. In the later work of Böttger and Ahrens (1) the belief was again expressed that Feigl's theory could not explain the "carrying down" effect exhibited by these two sulfides.

Weiser (81) expresses the opinion that while the existence of mixed salts such as 2HgS·MnS cannot be denied, it is probable that most instances of contamination such as are here considered are due to adsorption phenomena.

Kolthoff and Pearson (46) concluded Feigl's theory to be untenable in the case of copper and zinc sulfides, and the same conclusion is just as strongly supported in the case of mercury and zinc (59).

Ruff and Hirsch (66) have vigorously attacked both the theory and experimental evidence cited by Feigl. They contend that the mass action law and solubility product principles are the decisive factors in separations of the sulfides, and that occlusion, adsorption, and mixed crystal formation are of only minor importance. In polemical papers Feigl (20) as well as Ruff (65, 66) defended their antagonistic viewpoints without changing any of their former statements. The contentions of Ruff and Hirsch are somewhat weakened, however, by lack of consistency and clarity in some of the explanations advanced by them to interpret Feigl's results and also by lack of experimental evidence in support of their own theories. These investigators have advanced the hypothesis that a protective coating of

the sulfide with the smaller solubility product may be formed about the sulfide with the larger solubility product. In order to explain the promoting effect of such substances as copper sulfide or mercuric sulfide on the precipitation of zinc sulfide, this theory necessitates the condition that the less soluble sulfide be deposited on the more soluble one. This condition is not realized in the instances mentioned, since it has been shown that the more insoluble sulfide is quantitatively precipitated in a pure form before any zinc sulfide enters the precipitate (46, 59). Böttger and Ahrens (1) concluded that the theory of Ruff and Hirsch was not acceptable as an explanation of the induced precipitation effect in the case of the sulfides of mercury and cadmium.

Balarew (4) indicates that the "carrying down" of zinc sulfide by other sulfides may be explained by his theory of "inner adsorption." According to his view macro crystals having a mosaic structure are formed by the building on of primary building blocks or submicroscopic crystals to other such crystal entities to give rise to a network of capillaries within the crystal aggregate. It is in these capillaries that adsorbed material may then be held. It follows that, according to Balarew, the "carrying down" of zinc sulfide would then be a wholly capillary phenomenon, similar to the coprecipitation of potassium permanganate with barium sulfate. Balarew reports that he was unable to extract completely the zinc from a copper sulfide–zinc sulfide "mixed" precipitate even with strong hydrochloric acid. This result is contradictory to the results of Kolthoff and Pearson, as well as to those of Böttger and Druschke, and on the whole Balarew's experimental work in regard to the sulfides of copper and zinc seems to be somewhat questionable.

Böttger and Druschke (11) and also Ahrens (1), working with the pairs Cu–Fe, Cu–Zn, and Hg–Cd, seem to have regarded the phenomenon in all these cases as one of coprecipitation. They found surprising difficulty in extracting iron from the Cu–Fe "mixed" sulfide. Likewise cadmium could not be completely removed except by drastic treatment from a precipitate obtained by precipitating mercuric and cadmium sulfides together. A similar behavior has been noted by the present authors in the case of the sulfides of mercury and zinc. However, in harmony with the work of Kolthoff and Pearson, Böttger and Druschke were able to extract completely the zinc from corresponding Cu–Zn precipitates by treatment with 1 N hydrochloric acid solution, and they assumed the viewpoint that in the cases of Cu–Zn and Hg–Cd, at least, a kind of isomorphous replacement or mixed crystal formation had taken place. From the work of Ahrens on the Hg–Cd couple it was concluded that the coprecipitation effect was to be attributed to a mixed crystal formation. Böttger and Druschke explained the difference in ease of extraction of the more soluble

sulfides in the two respective cases as being a consequence of the extent to which the more insoluble sulfide was attacked by the acid. However, the behavior of the mixed precipitate of copper and iron sulfides as regards extraction is not consistent with this explanation.

The view is quite generally taken, though in many cases not definitely proven, that mixed crystal formation exists as a partial explanation of the phenomenon in many cases. Undoubtedly mixed crystal formation among the sulfides is of frequent occurrence, since the similarity in structure and ionic domains (both as to size and shape) exhibited by different sulfides makes this event seem highly probable. Mention of this effect in the instance of the sulfides of mercury and cadmium as reported by Böttger and Ahrens has already been made. X-ray evidence of mixed crystal formation in the cases of the sulfides of manganese and cadmium and of manganese and zinc has recently been offered by Schnaase (68). It was found that the former pair formed a continuous series of mixed crystals of the zinc blende type, and that a like series having the wurtzite structure was indicated. Under the conditions of precipitation employed in the case of the sulfides of manganese and zinc, a miscibility gap extending from about 20 to 84 atomic per cent manganese was indicated. Precipitates having compositions corresponding to this gap were found to consist of two separate phases having compositions corresponding to the above limits. Such mixed crystals were predominantly of the zinc blende type, although some having a wurtzite structure were also present. No indication of mixed crystal formation was found by Kolthoff and Pearson (46) in their work on the sulfides of copper and zinc. In the case of mercury and zinc sulfides again, evidence of a limited mixed crystal formation was obtained (59).

The above serves to illustrate the frequency with which the effect is encountered. However, it is believed that even in cases where mixed crystal formation does occur, this phenomenon may be a secondary effect and not of primary importance in the depiction of the mechanism by which "induced precipitation" takes place.

It is to be emphasized that in all the papers discussed the viewpoint was held that "induced precipitation" is a matter of coprecipitation. However this condition is not generally realized, since it has been definitely shown in the case of copper and zinc by Kolthoff and Pearson (46) and in the case of mercury and zinc by the present authors (59), that we are not dealing with a coprecipitation but with a postprecipitation. The sulfide with the smaller solubility product (copper sulfide or mercuric sulfide, respectively) primarily precipitates free from zinc, but on standing in the presence of a solution of a zinc salt containing an excess of hydrogen sulfide, more and more zinc sulfide enters the precipitate. From work now being

done in this laboratory by Mr. Griffith, it may be said that a similar statement can be made in the case of bismuth and zinc. The fact that the process involves postprecipitation is made evident by the following experimental data obtained in the investigation of the sulfides of mercury and zinc.

Mixtures of mercuric chloride and zinc sulfate in varying concentrations of hydrochloric acid and mixtures of mercuric perchlorate and zinc sul-

TABLE 1

Postprecipitation of zinc sulfide

25 ml. of 0.05 M HgCl$_2$; 25 ml. of 0.05 M ZnSO$_4$; acid as indicated

	TIME SHAKEN	KIND OF ACID	ACIDITY BEFORE PRECIPITATION	ZINC PRECIPITATED
	minutes		N	*per cent*
Blank*............	0	H$_2$SO$_4$	0.30	0
	0	H$_2$SO$_4$	0.30	65
	30	H$_2$SO$_4$	0.30	95
Blank*............	30	H$_2$SO$_4$	0.30	0
	0	H$_2$SO$_4$	1.05	15
	30	H$_2$SO$_4$	1.0	47
	30	H$_2$SO$_4$	2.0	8.0
	60	H$_2$SO$_4$	2.0	8.6
	60	H$_2$SO$_4$	4.0	0
Blank*............	30	HCl	0.30	0
	0	HCl	0.30	60
	30	HCl	0.30	85
	0	HCl	0.80	10.5
	30	HCl	0.80	22
	120	HCl	0.80	28
	0	HCl	1.0	6.8
	30	HCl	1.0	13
	0	HCl	1.5	1.6
	30	HCl	1.5	2.8
	0	HCl	1.75	0.5
	60	HCl	2.0	0

* The blanks contained 25 ml. of water in place of 25 ml. of 0.05 M mercuric chloride.

fate in dilute sulfuric acid were treated with hydrogen sulfide in such a way that a small part of the mercury remained in the solution. Upon analysis of the filtrate all of the zinc originally present was recovered, thus showing that zinc is not coprecipitated with mercuric sulfide.

The results in table 1, which are substantiated by a great number of experiments at other acidities and times of shaking, show conclusively that we are dealing with a postprecipitation of zinc sulfide on the surface of mercuric sulfide.

Precipitation was effected by a three-minute passage of the gas through the solution, and thereafter the contents of the flask were mechanically shaken under continuous passage of hydrogen sulfide over the solution for the time noted under "time shaken." After this period of shaking the mixtures were filtered, the precipitates washed four times with cold water, and the filtrates analyzed for zinc by the ferrocyanide method (46). The temperature was 25°C.

In showing the presence of a postprecipitation phenomenon, the above results are substantiated by the fact that the effect is qualitatively the same whether the zinc solution is added before or after precipitation of the mercuric sulfide.
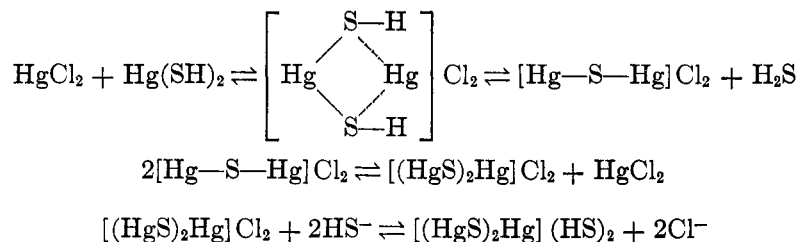
Thus it is shown that freshly precipitated copper sulfide or mercuric sulfide promotes the precipitation of zinc sulfide. This postprecipitation was attributed to the presence of an adsorbed layer of hydrogen sulfide on the copper sulfide and mercuric sulfide, respectively. From colloid chemical studies we know that the metal sulfides exert strongly adsorbent properties towards hydrogen sulfide, hydrosulfide ions, and sulfide ions. Hydrogen sulfide adsorbed on the surface of the metal sulfide has a much stronger tendency to ionize than has that which is present in the bulk of the solution. Thus the concentration of hydrosulfide or sulfide ions in the surface is much greater than in the bulk of the solution, and therefore the speed of precipitation of the more soluble sulfide is much greater at the interface than in the bulk of the solution. The confusing statements found in the literature are mainly to be attributed to the fact that it is generally assumed that the sulfides of the third group are not, or are incompletely, precipitated from weakly acid medium. The fact is overlooked that precipitation equilibrium is sometimes reached only after extremely long periods of standing. Thus, when a solution which is 0.05 M with respect to zinc sulfate and 0.5 N in sulfuric acid is saturated with hydrogen sulfide, no precipitation occurs for at least forty-five minutes or an hour. With increasing acidity the length of this so-called "induction" period rapidly becomes greater. Employing a solution which was 2 N in sulfuric acid and 1/16 M with respect to zinc sulfate, Glixelli (26) found that a precipitate was exceedingly slow to appear, but that after a period of two and one-half months precipitation had taken place to the extent of 25 per cent of the original zinc content and that after five months only about 50 per cent remained in solution. It is apparent that the solution tends to remain supersaturated with regard to zinc sulfide. In the presence of mercuric sulfide or copper sulfide, a promoted precipitation takes place by virtue of the presence of the adsorbed hydrogen sulfide.

Before elaborating on some of the interesting phenomena observed in studies of the postprecipitation effect, the mechanism of the precipitation of sulfides and the aging of metal sulfides will first be considered.
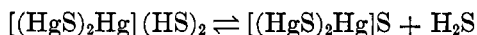
THE MECHANISM OF THE PRECIPITATION OF SULFIDES

The subject of sulfide precipitation in general presents difficulties in interpretation. Smith (70) calculated that 5 ml. of a 0.2 N hydrochloric acid solution which is 0.1 M with respect to hydrogen sulfide contains 3 $\times$ 10^{20} non-ionized molecules of hydrogen sulfide, 15 $\times$ 10^{13} hydrosulfide ions (SH^-), and only one sulfide ion (S^{--}). In the precipitation of a very insoluble sulfide such as mercuric sulfide from acid solution by hydrogen sulfide, it would seem impossible for equilibrium to be established in the time in which it is if sulfide ions were directly involved in the reaction. From the considerations mentioned it would seem probable that sulfide precipitation involves the reaction of hydrosulfide ions to give first the hydrosulfide of the metal which, by secondary loss of hydrogen sulfide, results in the formation of the sulfide itself. This view is in harmony with the belief that peptized sulfides are hydrosulfides. While Smith believes that if sulfide formation is to be viewed from an ionic standpoint the hydrosulfide ion rather than the sulfide ion should be regarded as the active precipitating agent, he, like Feigl, tends to favor a non-ionic theory for the process. In a paper by Smith and Semon (71) the opinion is advanced that the precipitation of heavy metals as sulfides will eventually be regarded in the light of the coördination theory of Werner. From their work with mercury salts these authors are led to favor a theory embracing the formation of intermediary hydrosulfide compounds. The presence of excess hydrogen sulfide in freshly precipitated material is explained as its being present partially in the hydrosulfide form, probably as decomposition product of hypothetical, unstable, intermediate hydrosulfide compounds. In the light of the existence of known addition products of salts with sulfides, both organic and inorganic, and in view of the fact that compounds are often present in solution too unstable or relatively too soluble for isolation, Smith and Semon deduce the occurrence of addition reactions analogous to the combination of salts with alkyl sulfides, in which the hydrogen sulfide itself assumes the rôle of the organic sulfide (or mobile hydrogen in place of the alkyl radical). Their observations regarding intermediary compounds in the case of mercury is thought to bear out this contention. It is pointed out that the assumption of hydrosulfide compounds is supported by the existence of analogous hydroxide compounds, the hydrogen being more mobile in the case of the hydrosulfides. To illustrate the formulation of sulfide precipitation under such a theory, we may cite the case of the reaction taking place when hydrogen sulfide is passed into a solution of mercuric chloride. Smith describes the mechanism of the reaction by first assuming the formation of an addition product such as $[(H_2S)_nHg] HgCl_4$ which, after conversion into the hydrosulfide, $Hg(SH)_2$, may again react with a molecule of mercuric chloride and subse-

quently result in the precipitation of mercuric sulfide as indicated by the
following series of equilibria.

$$HgCl_2 + Hg(SH)_2 \rightleftharpoons \left[Hg \underset{S-H}{\overset{S-H}{<>}} Hg \right] Cl_2 \rightleftharpoons [Hg-S-Hg] Cl_2 + H_2S$$

$$2[Hg-S-Hg] Cl_2 \rightleftharpoons [(HgS)_2Hg] Cl_2 + HgCl_2$$

$$[(HgS)_2Hg] Cl_2 + 2HS^- \rightleftharpoons [(HgS)_2Hg] (HS)_2 + 2Cl^-$$

and more slowly

$$[(HgS)_2Hg] (HS)_2 \rightleftharpoons [(HgS)_2Hg]S + H_2S$$

Rather than attributing to a simple adsorption mechanism the inaccuracies found to be due to the coprecipitation of other substances such as chlorides in the determination of mercury by direct precipitation of the sulfide, Fenimore and Wagner (22) suggest that such a theory of intermediate compound formation as outlined above is a more likely interpretation. Weiser and Durham (82), on the other hand, concluded that a like contamination of cadmium sulfide by chloride was due to an adsorption phenomenon.

It should be realized that the assumption of the intermediate formation of coördination compounds is not strictly necessary to explain the rapid precipitation of various metal sulfides. It is true that in the case mentioned by Smith only one sulfide ion was present in 5 ml. of solution, according to the calculation. However, one should not attribute an *absolute* significance to such an "absurdly small concentration." In doing so one would infer that on dividing the 5-ml. portion into two parts, one part would contain one sulfide ion and the other would be free of sulfide ions. This conclusion would, of course, be absurd. In dealing with a reversible reaction such as the dissociation of hydrosulfide ions into sulfide and hydrogen ions,

$$HS^- \rightleftharpoons H^+ + S^-$$
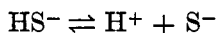
it must be realized that in a given time a certain fraction of the hydrosulfide ions dissociate and that under equilibrium conditions the hydrogen and sulfide ions combine with the same speed to form hydrosulfide ions. We may say that a concentration of one sulfide ion per 5 ml. of solution means that practically all the sulfide ions are present in the associated state and that, averaged over a given time interval, only a very few are present as free ions. In other words, the concentration term in equilib-

rium reactions is a statistical expression which denotes the *probability* that the dissociation and association products are present at a certain concentration at a given instant. If, in a dissociation process, the concentrations of the reaction products are such that they seem realizable according to our general conceptions (e.g., in the dissociation of 0.1 N acetic acid) we attribute to the concentrations an *absolute* significance. However, with regard to a system in kinetic equilibrium the concentration is a *relative* concept or, in other words, the concentration is an *abstract* mathematical expression.

According to the above one cannot definitely conclude that the rapid precipitation of metal sulfides in acid medium cannot occur by direct combination of metal and sulfide ions. Many sulfide ions may be formed per second by dissociation of hydrogen sulfide or hydrosulfide ions, most of which, however, disappear with the same speed by recombination with hydrogen ions. In the presence of metal ions which give rise to the formation of slightly soluble sulfides there is a possibility that the sulfide ions formed by dissociation react with the metal ions before they have a chance to associate again with hydrogen ions. Whether such a description of the mechanism is correct is impossible to say, since the individual speeds of reaction are unknown. It also seems possible that the metal sulfide might be formed directly by effective collisions of metal ions with hydrogen sulfide molecules or hydrosulfide ions without assuming the formation of intermediate compounds. Since the speed of formation of metal sulfides in acid medium is inversely proportional to the *square* of the hydrogen-ion concentration, a direct reaction between metal ions and hydrogen sulfide molecules may be excluded from consideration. On the basis of this fact a direct reaction between metal ions and hydrosulfide ions or sulfide ions is possible.

The exact mechanism of the precipitation of metal sulfides in acid medium is immaterial from the viewpoint of the mass action law. This law can be applied to all cases as long as the system is in a state of reversible equilibrium. Various authors (14, 19, 26) have overlooked this simple fact and have been led to express doubt as to the reversibility of the reaction

$$Me^{++} + H_2S \rightleftharpoons MeS + 2H^+$$
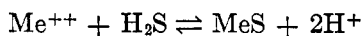
and to point out apparent contradictions to the mass action law in the case of sulfide precipitations. However, explanations based upon assumptions which are contrary to the law of mass action must result in failure to fulfill their purpose.

Many metal sulfides tend to form supersaturated solutions. This may be explained partly by the relatively large difference in solubility of ex-

tremely small nuclei and crystals of larger size, but mainly by the slow formation of nuclei and the small speed of crystallization. It is well known that relatively weakly acid solutions of zinc, cobalt, and nickel do not precipitate by treatment with hydrogen sulfide in a reasonable length of time, even though the solubility product has been exceeded to a rather large extent. Recognition of the fact that during such a period the system is in a state of supersaturation is of the utmost importance in a study of the promoting effect of certain sulfides on the precipitation of more soluble sulfides. The fact that zinc sulfide, for example, is not quickly and completely precipitated unless the hydrogen-ion concentration is quite low, but that precipitation takes place on long standing from solutions that are quite strongly acid has been shown by various workers (2a, 12, 45) besides Glixelli, to whose experiments reference has been made in a previous paragraph. The phenomenon, often referred to as involving an "induction period," seems not to have been considered from the standpoint of supersaturation by Glixelli.

Analogous behavior as regards such an "induction" period has been pointed out by Baubigny (7), Glixelli (26), Thiel and Ohl (76), and others in the cases of cobalt and nickel sulfides and in the precipitation of cadmium sulfide by Krishnamurti (48). Apparently the induction period in the case of cobalt and nickel may be very long, since under certain conditions of acidity Baubigny found that precipitation was still taking place after a couple of months. Likewise in the case of zinc sulfide a very prolonged induction period may be experienced, while in the case of cadmium sulfide Krishnamurti found that equilibrium was attained within six hours.

Besides demonstrating the increase in the length of the induction period with increasing acidity, Glixelli, whose work provides an admirable statement of the facts to be considered in studies involving promoting effects on the precipitation of zinc sulfide, showed that it was decreased (speed of precipitation of zinc sulfide increased) by the presence of copper sulfide, zinc sulfide, and silica gel. It may be considered as a substantiation of a theory involving surface phenomena, that the effect which zinc sulfide had on the promotion of its further precipitation depended on the nature of the product used, increasing in the order indicated: ignited < aged < fresh. The adsorption of hydrogen sulfide on the given products would increase in like order. In the same work the self-promotive nature of the process (precipitation of zinc sulfide) was clearly shown. Other conditions being equal, precipitation proceeded to a much greater extent in an experiment in which the precipitated zinc sulfide was allowed to accumulate than in one in which the precipitate was successively removed. Kolthoff and Pearson (46) further found that a number of finely divided substances (powdered glass, barium sulfate, sulfur, charcoal, talc, etc.) seemed

to have a definite, though slight, promoting effect on the precipitation of zinc sulfide.

THE SOLUBILITY OF METAL SULFIDES

Kolthoff (44) pointed out that there is tremendous confusion in the literature with regard to the solubilities and solubility products of metal sulfides. Their solubilities in pure water are so small that they cannot be determined by direct measurements. It is difficult, if not impossible, to obtain precipitated sulfides in a pure form and to prevent air oxidation when shaken with water. Moreover, the carbon dioxide content of the water has a large effect on the solubility. The values determined by Weigel (80) and cited in most texts should therefore be rejected. Mainly on the basis of the experimental work of Bruner and Zawadsky (13), Moser and Behr (60), and others, Kolthoff (44) has calculated the solubility products of precipitated metal sulfides. A summary is given in table 2 in which pL is the negative logarithm of the solubility product L, and K is the reaction constant as given in the following equations:

$$[Me^{++}] = K \frac{(H^+)^2}{(H_2S)}$$

or (for Ag$_2$S, Tl$_2$S, and Hg$_2$S)

$$[Me^+] = \sqrt{K \frac{(H^+)^2}{(H_2S)}}$$

[Me] represents the metal-ion concentration in a solution saturated with hydrogen sulfide and the metal sulfide at a hydrogen-ion concentration of 1.

It must be realized that quite generally the solubility of a metal sulfide depends upon its age and the manner of preparation. After the particles have grown to a certain size and are present in the stable modification, the solubility represents a constant and the solubility product principle can be applied to the calculation of the solubility under various conditions. Freshly precipitated sulfides as a rule are not present in the stable form, and therefore exhibit a higher solubility than aged products. These statements will be further enlarged upon in the next chapter. For the above reasons the data given in table 2 cannot be considered entirely conclusive.

THE AGING OF METAL SULFIDES

Upon aging of precipitated metal sulfides in the supernatant liquid agglomeration of the particles occurs, resulting in a decrease of the total surface of the precipitate. This, for example, is demonstrated by the experiments of Freundlich and Schucht (23) with mercuric sulfide obtained

by flocculation of a sol. A large amount of mercuric sulfide sol was mixed with an appropriate amount of neufuchsin (or auramine) solution so that coagulation was complete. The mixture was then stirred in such a way

TABLE 2

Solubilities and solubility products of metal sulfides

METAL SULFIDE	L	pL	K	[Me]	OBSERVER
MnS (flesh colored?)	7.0×10^{-16}	15.16	6.3×10^{6}	6.3×10^{7}	Bruner and Zawadsky (13)
MnS (green)	6.2×10^{-22}	21.21	5.6	5.6×10^{1}	Moser and Behr (60)
FeS	3.7×10^{-19}	18.43	3.4×10^{3}	3.4×10^{4}	Bruner and Zawadsky
FeS	2.6×10^{-22}	21.58	2.4	2.4×10^{1}	Moser and Behr
Tl$_2$S	7.0×10^{-23}	22.16	6.4×10^{-1}(?)	2.5	Bruner and Zawadsky
Tl$_2$S	1.2×10^{-24}	23.92	1.1×10^{-2}	3.3×10^{-1}	Moser and Behr
α-ZnS	8.0×10^{-26}	25.10	7.3×10^{-4}	7.3×10^{-3}	Schaefer (67)
α-ZnS	5×10^{-26}	25.3	4.5×10^{-4}	4.5×10^{-3}	Glixelli (26)
α-ZnS	6.9×10^{-26}	25.16	6.3×10^{-4}	6.3×10^{-3}	Moser and Behr
β-ZnS	1.1×10^{-24}	23.96	About 10^{-2}	10^{-1}	Glixelli
CoS	1.9×10^{-27}	26.72	1.7×10^{-5}	1.7×10^{-4}	Moser and Behr
NiS	1.1×10^{-27}	26.96	1.0×10^{-5}	1.0×10^{-4}	Moser and Behr
CdS (from CdCl$_2$)	7.1×10^{-28}	27.15	6.5×10^{-6}	6.5×10^{-5}	Bruner and Zawadsky
CdS (from CdSO$_4$)	5.1×10^{-29}	28.29	4.6×10^{-7}	4.6×10^{-6}	Bruner and Zawadsky
PbS	3.4×10^{-28}	27.47	3.1×10^{-6}	3.1×10^{-5}	Bruner and Zawadsky
Bi$_2$S$_3$	1.6×10^{-72}?	71.8?	3.5×10^{-3}?	3.5×10^{-2}?	Bernfeld (9)
CuS	6.9×10^{-41}	40.16	6.3×10^{-19}	6.3×10^{-18}	Immerwahr (37)
CuS	1.2×10^{-42}	41.92	1.1×10^{-20}	1.1×10^{-19}	Knox (42)
CuS	3.5×10^{-42}	41.46	3×10^{-20}	3×10^{-19}	Jellinek and Czerwinski (39)
Ag$_2$S	1.8×10^{-50}	49.74	1.6×10^{-29}	4×10^{-14}	Bernfeld
Ag$_2$S	2.3×10^{-51}	50.64	2.1×10^{-29}	1.45×10^{-14}	Lucas (55)
Ag$_2$S	3.9×10^{-50}	49.41	3.6×10^{-28}	6×10^{-14}	Knox
Ag$_2$S	1.2×10^{-50}	49.92	1.1×10^{-28}	3.3×10^{-14}	Jellinek and Czerwinski
Ag$_2$S	5.7×10^{-51}	50.24	5.1×10^{-29}	2.2×10^{-14}	Jellinek and Czerwinski
Average Ag$_2$S	1×10^{-50}	50.00	9×10^{-29}	3×10^{-14}	Average
Hg$_2$S	1×10^{-47}	47.0	0.9×10^{-25}	0.95×10^{-12}	Immerwahr (average)
HgS	3×10^{-54}	53.5	2.7×10^{-32}	2.7×10^{-31}	Knox

that the precipitate was kept suspended in the liquid. From time to time a portion was taken out, the mercuric sulfide removed by centrifuging, and the concentration of the dyestuff determined colorimetrically. Employing this procedure they found that the concentration of the dyestuff in

the solution increased with the time; they concluded therefrom that the phenomenon was one of reverse adsorption accompanying the change of mercuric sulfide from an amorphous to a more crystalline form, exhibiting an instance in which a substance has a greater adsorption capacity in the former than in the latter condition. They further found indication that the process was self-promoting and that the addition of crystalline particles of mercuric sulfide to the mixture described above accelerated the reverse adsorption. The effect of temperature on the process was found to be very great. The results of Freundlich and Schucht are not entirely convincing. The rather general observation has been made in this laboratory that the presence of such adsorbed dyestuffs prevents further "aging" of precipitates (47).

In addition to agglomeration a perfection and growth of the crystals of the metal sulfides occur, as is evidenced by a sharpening of the interference lines in x-ray diffraction patterns. Various metal sulfides may be obtained in a state usually designated by the term "amorphous," but may become definitely crystalline on aging in the supernatant liquid. The tendency for the sulfides of the Zn–Cd–Hg family to come down in microcrystalline form increases with increasing atomic number. Böhm and Niclassen (10) report that zinc sulfide precipitated at 0°C. from solutions of zinc sulfate was amorphous, but that after being digested on a water bath for several days an x-radiogram of the product showed sharp interference maxima, indicating that crystallization had taken place. These crystals are submicroscopic since Allen, Crenshaw, and Merwin (2a) found no microscopic evidence of crystal structure of zinc sulfide precipitated and digested under ordinary laboratory conditions. The precipitation of zinc sulfide takes place on long standing from solutions quite strongly acid. Even under such conditions (very slow precipitation at higher acidities), the product contains no crystals of such a size as to be easily visible with a microscope, although such a product, or one obtained by aging, contains larger particles and is much less soluble than zinc sulfide precipitated rapidly at low acidities. In agreement with the observations of Böhm and Niclassen, the present authors found that under the conditions of radiography employed a precipitate of zinc sulfide (from slightly acid solution which had been filtered off and dried immediately after a short precipitation period) gave only a few very faint and diffuse interference maxima, whereas a precipitate which had been aged at room temperature in the supernatant liquid for a period of a month gave a clear and distinct diffraction pattern. A similar contrast in the patterns obtained using fresh and aged mercuric sulfide was noted, though it was indicated that the period of aging necessary before a distinct diffraction diagram could be obtained was shorter in the case of mercuric sulfide than in the case of zinc

sulfide. Apparently aging, in the sense of increased perfection of the ag-
glomerates, does not take place in the dry condition at room temperatures,
since the "fresh" precipitates after being kept in the dry condition for two
years still gave diffraction patterns consisting of only faint, broad bands
with no sharply defined lines in evidence. Under the microscope at a
magnification of 440 diameters the aged zinc sulfide appeared to consist
mainly of compactly cemented clusters of very small crystals. The
clusters were not easily broken up and their appearance and behavior sug-
gested that recrystallization and cementing together had taken place, with
the result that the clusters themselves behaved as crystalline entities.
The crystals of which these clusters were made up were so small that it
was barely possible to distinguish individuals and no crystal faces were
apparent. Qualitatively much the same may be said concerning the ap-
pearance of the aged mercuric sulfide, though in the precipitates inves-
tigated, which were aged for such periods of time and under such conditions
as to exclude any appreciable transformation to the trigonal form, the
clusters did not seem to be cemented together as firmly nor to as great an
extent as in the case of the aged zinc sulfide. The characteristics of the
fresh precipitates were rather indefinite, and nothing much can be said
about such precipitates, except that the result of clumping together was
not as apparent and no indication of the presence of individual crystals
could be derived. Such agglomerates as were present were easily broken
up,—more so than in the case of the aged products.

Quite generally the growth and perfection of the particles on aging is
accompanied by a decrease of the solubility. This observation has been
made in the case of zinc sulfide by a number of investigators, including
Glixelli (26), Bruner (12), Bruni and Padoa (14), and the present authors.
It was found (59) that of two zinc sulfide precipitates from slightly acid
solution, one of which was freshly prepared and the other a well-aged
product, the respective solubilities in 2 N sulfuric acid saturated with
hydrogen sulfide were approximately 0.035 M and 0.005 M with respect to
zinc. Moreover, the dependence of the solubility of individual sulfide
precipitates upon the conditions under which they are formed has been
remarked upon by various investigators. Jeffreys and Swift (38), in
investigating the precipitation of zinc sulfide and its separation from other
elements, concluded that the hydrogen-ion concentration was the domi-
nant factor governing the form and solubility of the product. Glixelli
(26) prepared two zinc sulfide precipitates, one which he designated as
α-ZnS, from acid medium, and the other (β-ZnS) by precipitation with a
slight excess of sodium sulfide from a solution of zinc sulfate. The pre-
cipitates designated in this way are not to be confused with the wurtzite
and zinc blende forms of zinc sulfide which are also designated as α- and

β-ZnS, respectively. It was found that of the two precipitates the one prepared from basic solution was about 4.6 times more soluble than the one obtained from acid medium by precipitation with hydrogen sulfide. However, on continued contact with acid solution retaining the evolved hydrogen sulfide the solubility of the β-ZnS precipitate gradually decreased and approached that of the α-ZnS precipitate (Glixelli's notation). It follows that precipitates of zinc sulfide formed under varying conditions are not sharply definable from one another, as would be the case of polymorphic substances, and it is apparent that the "solubility" of such products as Glixelli's β-ZnS and the fresh precipitate described in regard to the work of the present authors has little significance, since the precipitate is not present in the stable solid state. Glixelli also reports that zinc sulfide prepared at low temperatures (0°C.) is more soluble than that obtained at higher temperatures. In connection with these studies regarding the dependence of solubility upon the method of preparation, it was also found that the β-ZnS precipitate held water (concluded to be held in an adsorbed state) more tenaciously than the product formed from acid solution. In the interpretation of these results Glixelli favors an explanation which construes the difference in behavior of the two preparations as due to differences in particle size. The above results reported by Glixelli have been confirmed in general by Krokowski (49). Some question arises, however, as to the extent which adsorption of zinc sulfate on the precipitated zinc sulfide might explain the effects observed, since both investigators prepared zinc sulfide from solutions of the sulfate. Work and Odell (83) found that such adsorption was very appreciable in the case of zinc sulfide prepared by the addition of sodium sulfide to zinc sulfate solutions. The conditions under which the latter investigators worked were, however, particularly favorable for the occurrence of such an effect.

In accordance with the observation that the solubility of zinc sulfide preparations depends upon the hydrogen-ion concentration of the solution from which precipitation takes place, Krokowski found that the solubility of the product increased according to the following series. (1) ZnS precipitated with hydrogen sulfide from zinc sulfate solution; (2) ZnS precipitated with hydrogen sulfide from zinc acetate solution; (3) ZnS precipitated with ammonium sulfide from zinc sulfate solution; and (4) ZnS precipitated with hydrogen sulfide from ammoniacal zinc sulfate solution.

That the sulfides of cobalt and nickel after being precipitated and allowed to stand for some time are relatively insoluble in dilute mineral acids, even though these sulfides will not readily precipitate from even very dilute acid solution, is a generally recognized fact. This case has been investigated in some detail by Hertz (34), Thiel and Ohl (76), and Thiel and Gessner (75). The latter workers found that different methods

of preparation and treatment of nickel sulfide precipitates lead to products which differ immensely as to the extent to which they are attacked by hydrochloric acid. Thiel and Gessner were led to postulate the existence of different "modifications" of nickel sulfide roughly designated as the α-, β-, and γ-forms, corresponding to more or less definite solubilities in hydrochloric acid of a given strength. They advanced the belief that the different preparations differed in the extent of polymerization and that differences in solubility were to be attributed to this condition. Considering a given nickel sulfide preparation Thiel and Gessner designated as the α-modification that portion which was quickly and easily soluble in cold 2 N hydrochloric acid, this form actually being soluble in 0.01 N acid. After removal of the α-NiS by this treatment a more or less stationary state was reached, as measured by the concentration of dissolved nickel realized by further extraction with cold 2 N acid. Upon treatment with hot 2 N hydrochloric acid, however, another portion of the precipitate was rather easily and quickly removed until again a stationary state was obtained. The portion thus removed, being easily soluble in hot 2 N acid, was designated as β-NiS and the remainder, which could be readily dissolved only by the addition of an oxidizing agent, was characterized as γ-NiS. Apparently conversion of the more soluble preparations to the less soluble condition may readily be brought about. The solubility of precipitated nickel sulfide decreases markedly merely on standing in contact with acid solution. In pure water the effect is less. Higher temperatures seem to hasten the transition.

In addition to a growth of the crystals, the latter upon aging may be transformed to a different crystalline modification. In the case of zinc sulfide two different crystal forms are known to exist in nature. The regular form, or zinc blende, is by far the more abundant and is the stable form at ordinary temperatures, passing to the hexagonal or wurtzite form at or above the conversion point of 1020°C. (value given by Allen and Crenshaw (2a)). The solubility of wurtzite is given by Gmelin (27) as being about 4.3 times that of zinc blende. Wyckoff (84) gives the lattice constant of the zinc blende form as being 5.43 A.U. The values reported in the literature show some deviation from this figure, ranging from 5.395 ±0.005 (18, 25) to 5.437 ±0.004 (53). This disagreement may be due to small amounts of impurities such as iron sulfide in the natural specimens chosen for the various investigations.

Levi and Fontana (54) investigated four zinc sulfide precipitates prepared similarly to the series previously listed in reference to Krokowski's work. Their aim was to determine the crystal form of such precipitates, using the powder method of x-ray analysis, and also to examine the precipitates for the dimensions of the granules. They found that the pre-

cipitates all had the blende structure and that the granules of the four preparations had practically identical dimensions (about 20 A.U.). On the basis of their results Levi and Fontana make the statement that the differing behavior of zinc sulfide precipitates must be due to differences in states of agglomeration rather than to differences in crystal form or particle size. To be complete the statement should be further augmented by a definition of what is meant by "state of agglomeration."

The question as to whether zinc sulfide precipitates entirely in the blende form from acid solution under the action of hydrogen sulfide does not seem to be entirely settled. It is generally accepted that only the more stable blende form is precipitated from alkaline solution (2a, 81). As mentioned above, Levi and Fontana found only the blende form to be precipitated from solutions of the sulfate and acetate. Since it is not easy to distinguish between crystals of the zinc blende and zinc oxide type by x-ray methods, a small amount of the wurtzite form might easily have escaped detection. Allen, Crenshaw, and Merwin (2a) found by microscopic examination of crystals formed in sealed tubes in the presence of the supernatant liquid at temperatures between 200°C. and 400°C. that from acid solution both wurtzite and zinc blende forms were produced. From their investigations concerning the sulfides of zinc, iron, cadmium, and mercury they drew the general conclusion that the higher the temperature the greater the quantity of stable form produced, while the higher the acidity of the solution from which precipitation takes place, the greater the quantity of the unstable form. The acid concentration required to give pure marcasite or wurtzite (unstable forms of FeS_2 and ZnS, respectively, at ordinary temperatures) falls with the temperature, being close to neutrality for marcasite at ordinary temperatures. They conjecture that the same statement probably holds for wurtzite (2b). This latter supposition as regards the formation of wurtzite is supported, however, neither by the work of Levi and Fontana (54) nor by the work conducted by the present authors. We found that a precipitate of zinc sulfide formed and aged in a solution 0.4 N in sulfuric acid and saturated with hydrogen sulfide consisted, according to x-ray analysis, mainly of crystals of the blende structure, though some indication was afforded by microscopic examination that the wurtzite form was also present to an extent roughly estimated to be in the neighborhood of 1 per cent. The microscopic examination cannot, however, be considered as conclusive evidence. In spite of the confusion in the literature regarding the question, it seems to be indicated by a review of the investigations carried out that in precipitation from acid solution the obtainment of both modifications of zinc sulfide is possible, and it may be said with equal justification that the form assumed under ordinary laboratory conditions is predominantly that of zinc blende.

Mellor (57a) lists four different forms in which mercuric sulfide may exist. Three of these are crystalline, while black amorphous mercuric sulfide is given as the fourth form. Of the three crystalline forms reported, the existence of two, namely α-HgS or ordinary red cinnabar and α'-HgS or black metacinnabarite, is unquestioned; they have been known for a long time to exist in nature. Cinnabar, having a trigonal structure, is the most commonly occurring natural form and is the most stable modification at ordinary temperatures, while the cubical (zinc blende type) structure of black metacinnabarite is the form usually assumed by mercuric sulfide precipitated from acid solutions of mercuric salts with hydrogen sulfide. The statement is made by Allen and Crenshaw (2a) that cinnabar is the stable modification at all temperatures up to the sublimation temperature (580°C.), but the later work of Rinse (61) tends to refute this. From vapor pressure data the latter finds that a transition point is indicated at 386 ± 2°C., above which temperature the black form is the stable modification. The third crystalline form listed by Mellor is the supposed new form reported by Allen and Crenshaw (2a), which is also a red hexagonal form but differing from ordinary cinnabar and not found in nature. Allen and Crenshaw based their report of the existence of this modification on evidence gained by microscopic examination. Kolkmeijer, Bijvoet, and Karssen (43), employing the powder method of x-ray investigation, found none of the preparations of mercuric sulfide described by Allen and Crenshaw to contain crystals different from the ordinary black and red forms.

The structure of red, trigonal cinnabar has been determined by Mauguin (57), using the Bragg method of x-ray analysis by which the dimensions of the unit cell were determined to be: $a = b = 4.15$ A.U., $c = 9.51$ A.U. It was found that with a slight deviation the particles were arranged on a rhombohedral lattice. The work was later confirmed by Kolkmeijer (43) and coworkers, using the powder method of x-ray analysis.

The structure and properties of natural and artificial black metacinnabarite have been investigated by various workers (31, 43, 53). There is entire agreement that the black form usually precipitated from acid solution is identical in structure with that of naturally occurring metacinnabarite, the atoms of mercury and sulfur being arranged on a face-centered cubic lattice of the zinc blende type. The edge of the unit cell is reported by Wyckoff (84) to be 5.84 A.U., this value being in good agreement with the work of various investigators, including our own. The diffraction patterns of the black and red modifications of mercuric sulfide show striking agreement, in that the lines appearing on a pattern produced with metacinnabar also appear in the case of the trigonal modification. There are, however, many more lines obtainable in the latter case. This similar-

ity in certain line positions is attributed by Kolkmeijer, Bijvoet, and Karssen (43) to the complete equality of dimensions in the octahedral and basal planes of the two respective modifications

$$\left(\frac{a_{black}}{\sqrt{2}} = 4.14 \text{ A.U.} = a_{red}\right)$$

Böhm and Niclassen (10) report that mercuric sulfide precipitated at 0°C. gives at once a sharp interference pattern. In our work it was found that, while under the conditions of radiography used the fresh precipitate gave no sharp interference maxima, yet the period of aging necessary for the precipitate to assume a condition making possible a clear pattern was rather short. Apparently freshly precipitated mercuric sulfide which is rapidly formed tends to be of a more crystalline nature than a correspondingly "fresh" precipitate of zinc sulfide, which is formed relatively slowly from acid solution. An explanation of this rather surprising observation undoubtedly involves consideration of the relative magnitudes of orientation and agglomeration velocities (in the sense of Haber (30)) attendant to the formation of the respective precipitates. It may be experimentally shown that the crystallization velocity of zinc sulfide is relatively very small.

Since the red, cinnabarite form of mercuric sulfide is the more stable at ordinary temperatures it is to be expected that it will be formed upon aging of the black precipitate. Actually the observation has been generally made that the red modification is readily formed by digestion of the black gel with soluble alkali sulfides. Weiser (81) expresses the opinion that this process consists in the solution of the black form with subsequent precipitation of the less soluble, red hexagonal form. There is no definite proof, however, that such a mechanism is the actual case. According to Allen and Crenshaw, black "amorphous" mercuric sulfide is always formed first by the action of alkali sulfides on mercuric salts, but cinnabar only is obtained when the precipitate is digested with alkaline solution. Furthermore they report that cinnabar is formed from the other modification by application of heat alone or by heating the precipitate with 30 per cent sulfuric acid solution (2a). Our own experiments have shown that alkalinity is not a necessary condition for the formation of the red form, but the transformation occurs upon aging in the supernatant liquid at room temperature even in quite strongly acid medium. However, if the sulfide is precipitated from a neutral solution of the perchlorate and allowed to age in the resulting supernatant liquid saturated with hydrogen sulfide, transformation to the trigonal form, as indicated by the change in color of the precipitate, may be detected within a few hours and is appar-

ently complete within a day or two, whereas in more strongly acid solution the change is much retarded, a week or so being necessary for the change to become apparent at an acidity of 2 or 3 N in sulfuric acid. Proof of this transformation and the identity of the crystal forms involved was obtained by x-ray methods as well as by visual observation of the color changes taking place (59). If aging is conducted at higher temperatures (70°C.) the transformation is much accelerated, being complete within an hour or so in case the only acid present is that formed by the precipitation reaction, and if ammonia has also been added to the supernatant liquid (ammonium sulfide formed), the time necessary for complete conversion is further reduced to a matter of ten minutes or so. Transformation in case the precipitate was suspended in pure water or in dilute ammonium hydroxide was not detected. From these observations it appears that conversion from the cubic to the hexagonal form is promoted by low hydrogen-ion concentration, high concentration of hydrogen sulfide (or sulfide ion), and by higher temperatures, at least within a moderate range, of the supernatant liquid in which aging takes place. The presence of certain substances in solution, such as potassium iodide and sodium acetate, was found to retard the transformation, as did likewise the presence of post-precipitated zinc sulfide.

Evidence of the reverse change, namely from the red to the black form, does not seem to have been observed with the same degree of certainty. Observations have been reported by Allen and Crenshaw (2a), Spring (73), and Rinse (61), which indicate that heating the red precipitate may result in the formation of a black product which reassumes a red color if cooled slowly, but which remains black if cooled rapidly after being heated to a sufficiently high temperature. Assuming that the black color denotes the presence of the metacinnabarite form, these results support Rinse's conclusion that the regular modification is stable above 386°C. and are not in agreement with the statement made by Allen and Crenshaw to the effect that cinnabar is the stable form at all temperatures up to the sublimation point of 580°C. Roloff (63) concluded that the red sulfide changed to black through the action of light. The change depended on the presence of moisture, taking place more rapidly in alkaline medium than in pure water. No change took place in acid medium.

Proof that in the above-observed instances there is an actual change from the hexagonal to the cubic modification rests on the assumption that the respective colors are uniquely characteristic of the crystal forms. Milligan (58) found that either β-CdS (cubic) or α-CdS (hexagonal) may be yellow or red, depending on the physical character of the precipitate. Likewise in the case of mercuric sulfide a difference in color may not necessarily signify a change in crystal modification.

Freshly precipitated cadmium sulfide has been shown (10, 58, 78) to exist as the above-mentioned two modifications, depending on the method of preparation. Milligan (58), investigating this observation more in detail, found that the β-CdS tends to be precipitated from cadmium sulfate solutions and under some conditions from the nitrate solutions, especially if the latter are hot and distinctly acid in reaction. The α-CdS tends to be formed from the chloride, bromide, and iodide solutions, but these precipitates may also contain some of the β-modification. The formation of two different crystal modifications is thus indicated, and the possibility of transformation of one form to the other on aging is evident.

Again in the case of manganese sulfide, Schnaase (68) reports the identification by x-ray methods of three different crystal modifications. The green sulfide designated as α-MnS, having a cubic, sodium chloride structure, is the stable modification. The red sulfide may consist of two different crystal forms designated as the β-modifications. One of these, the β-cubic form, has a cubic, zinc blende type of structure, while the other, the β-hexagonal modification, is of the wurtzite type. The identity of the crystal form assumed by a precipitate of manganese sulfide is again found to be dependent upon the method of preparation. Under conditions leading to the formation of the red sulfide it was concluded by Schnaase that the β-cubic and β-hexagonal modifications are simultaneously formed and hence always appear together in the precipitate. Predominance of one or the other depends again on the method of preparation. The β-cubic form predominates if a strong alkali sulfide such as sodium sulfide is used as the precipitating agent, while the β-hexagonal form occurs in the greater proportion if precipitation is effected by ammonium sulfide. All precipitates are, however, converted to the crystal form characteristic of the green sulfide after shorter or longer periods of time, at low or high temperatures, and in the dry or wet condition. The reverse process, namely the formation of the red form from the green, has never been observed (68).

THE AGING OF A MIXTURE OF METAL SULFIDES

When the precipitation of a metal sulfide takes place in the presence of another freshly formed metal sulfide and the resulting "mixed" precipitate is subjected to an aging process in the supernatant liquid, a mixed crystal formation may occur, the extent of which is dependent upon the similarity in size and shape of the ionic domains in the respective crystal lattices. Referring again to the case of the sulfides of mercury and zinc, it has been previously mentioned that both substances when precipitated from acid medium consist of submicroscopic crystals having the zinc blende type of lattice. The lattice constants of mercuric and zinc sulfides may be taken as 5.84 and 5.40 A.U., respectively.

In connection with their work with alkali halides, Havighurst, Mack, and Blake (32) state the rule that, if two substances have similar crystal structures, complete miscibility is possible if the difference in lengths of the cube edges is less than 5 per cent of the average value of the respective lattice constants: i.e.

$$\delta = \frac{a_1 - a_2}{1/2(a_1 + a_2)} < 0.05$$

However, partial miscibility may exist for values of δ up to as high as about 0.10. It seems possible that these limits may vary with the kind of ions or atoms present. Barth and Lunde (5) found that complete miscibility is possible in the case of the halides of certain heavy metals (Cu^I, Ag, and Tl), even though the difference in lattice constants may be considerably greater than the limits set by Havighurst and coworkers for the case of the alkali halides. Considering the cubic modifications of the sulfides of zinc and mercury, we find that δ has a value equal to 0.078. From this we should expect that at least a limited mixed crystal formation is possible.

The manner in which the lattice constant of the solvent will be affected by the presence of the solute atoms (or ions or molecules) may be quantitatively predicted in certain cases. Havighurst and coworkers (32) reason that solid solution may take place in two different ways:

1. Interstitial type. The solute atoms are crammed in between the solvent atoms and as a result always cause an enlargement of the unit cell regardless of the size of the solute atoms. Only partial miscibility can exist in such cases. The solute and solvent atoms need not be alike either chemically or in regard to their size and shape. The system C–Fe is considered an example of such a solid solution. No case has been recorded of interstitial solution in the case of salts, and it may be assumed that these considerations do not apply to systems of metal sulfides.

2. Substitutional type. In this case it is assumed that there is a more or less regular substitution in the space lattice of the solvent atoms by the solvent atoms (or ions). At least in the case of salts the prerequisites as to chemical similarity and approximate equality in size and shape of the ionic domains must be fulfilled before solid solution of this type may take place. The assumption is made that the change in lattice parameters is a continuous function of the concentration of the solute. In the case of wholly miscible systems, at least, the relationship has been found to be practically linear, but exceptions to this might be expected to occur in systems of two salts with a common ion, wherein the dissimilarity in ionic domains is such as to make the components only partially miscible in each

other (32). This latter consideration may be of significance in regard to the system ZnS–HgS. From their work with alkali and ammonium halides Havighurst, Mack, and Blake formulated the following quantitative expression for this general rule of additivity as applicable to systems crystallizing in the cubic system

$$a^n = (a_2^n - a_1^n)x + a_1^n$$

where a is the lattice constant of the solid solution, a_2 and a_1 are the respective lattice constants of the components, and x is the mole fraction of the component having the lattice constant a_2. Values for n of 1 (79), 3, and 8 (28) have been suggested, but the above-named authors found a value of 1 or 3 to be most consistent with their results.

Substituting the known values of the lattice constants of zinc blende and metacinnabar and the lattice constant experimentally determined by the authors (59) for a precipitate obtained by the action of hydrogen sulfide on a solution containing both zinc and mercuric salts (5.79 A.U.) in the above equation we find a value of about 0.12 for the mole fraction of zinc sulfide present in the mixed crystal. The possibility must be kept in mind, however, that, owing to the large difference in the size of ionic domains found in this case, there may be strains set up in the lattice which might partially controvert the law of additivity.

The question as to how the atoms of the respective components are distributed in a mixed crystal seems still to be an open one. Among others, the view was taken by Tamman (74) that the atoms (or ions) of solute are regularly distributed throughout the solvent lattice. Laue (52), on the other hand, from consideration of x-ray diffraction phenomena asserts that the solute atoms (or ions) must be distributed in an entirely random fashion. He points out that were regular distribution in the sense of Tamman the case, there would be a regular periodicity in the lattice which should give rise to new, weak interference lines on the diffraction diagram. Neither Vegard (79), nor Havighurst, Mack, and Blake (32), investigating mixed crystals in systems of the alkali and ammonium halides, nor Barth and Lunde (5), working with the halides of copper, silver, and thallium, were able to detect any such periodicity required by Tamman's assumption. As pointed out by Davey (17), such lines have never been found in the case of a mixed crystal, although they have been found in the case of certain systems such as (a) 0.25 mole Si and 0.75 mole Fe (corresponding to the possible compound Fe_3Si) and (b) 0.50 mole Pd and 0.50 mole Cu (PdCu), and others where likewise a chemical compound is indicated. From these considerations Davey concludes that uniform distribution of the components of a solid solution is evidence of a definite chemical compound, and

that the ions of the same sign in a mixed crystal are arranged in an entirely random fashion.

In regard to the proof of the existence of solid solution or mixed crystal formation by x-ray methods, caution should be used in the interpretation of results. In dealing with systems of two components we may have a single phase corresponding to complete solubility of one component in the other, or we may have two phases corresponding either to total immiscibility or to limited miscibility. In case two solid phases are present and both are composed of crystals of appropriate size and of random orientation, it is usually easy to demonstrate their existence by obtaining at a single exposure two diffraction patterns, one from each of the solid phases. If the crystals of one of the phases are very small or very imperfect, the diffraction pattern due to their presence may be composed of only a few very broad and indistinct lines. In such an event the presence of a second phase may easily escape detection by x-ray methods. If solution has taken place the diffraction pattern of the particular phase in question should resemble that of the pure solvent with the lines somewhat displaced, corresponding to an increase or decrease in the lattice constant. Davey (17) points out that a change in the lattice constant, although always found in solid solutions when the concentration of the solute is sufficiently great, is not basic evidence of solid solution or mixed crystal formation. However, it is an indication of such a phenomenon which is well supported by theory. The fallacy of assuming complete solubility of one component in the other solely on the basis that only a single diffraction pattern is obtained is evident. The possibility must always be considered that a second phase may actually be present and that under more favorable conditions its existence could be demonstrated. Also, it should be born in mind that a second phase, though present, may not be in such a condition as to give a distinguishable diffraction pattern. These considerations are especially pertinent to the system mercuric sulfide–zinc sulfide. Only a single diffraction pattern was obtained from each of two precipitates containing 48 and 39 mole per cent of zinc sulfide, respectively. The lattice constants found for the precipitates were identical within experimental error. The diffraction pattern obtained was similar to that of pure mercuric sulfide. The degree of alteration of the lattice constant indicated, however, that the mixed crystal contained zinc sulfide only to the extent of about 12 mole per cent. To account for the remainder of the zinc sulfide present in the precipitate there are two possibilities open. Either there is a second phase consisting of pure zinc sulfide, or one consisting of a solid solution of mercuric sulfide in zinc sulfide. The latter possibility represents a case in which we have two solid phases, each of which is a mixed crystal, mercuric sulfide being the predominant component of one and hence the solvent,

while zinc sulfide is the solvent in the second phase. It is a general rule that if A dissolves in B then B dissolves in A, but the degree of solubility of A in B is no criterion of the degree of solubility of B in A. Allowing for the possibility of such a second phase in which zinc sulfide is the solvent, the concentration of mercuric sulfide in that phase may be very low. In any event, whether the second phase consisted of pure zinc sulfide or a mixed crystal of mercuric sulfide in zinc sulfide, the condition of the crystals was such as to allow no diffraction pattern to be obtained from that phase. A precipitate consisting of 21 mole per cent mercuric sulfide which had been aged three days gave a diffraction pattern so indistinct and of so few lines that it was uninterpretable. The diffraction pattern obtained with a precipitate produced by the long time action (one month) of hydrogen sulfide on a 2 N sulfuric acid solution originally containing salts of both zinc and mercury contained two very weak lines which could not be explained on the assumption of a single solid phase consisting of a mixed crystal of zinc sulfide in mercuric sulfide. Excluding these two lines from consideration it was found that the pattern obtained from this precipitate which contained 39 mole per cent zinc sulfide could be interpreted according to such an assumption and led to a value for the lattice constant of 5.79 A.U. The presence of the two lines is indicative of a second solid phase, but because of their indefinite character it is impossible to say whether they may have been due to the presence of pure zinc sulfide or to a second type of mixed crystal, the possibility of which has been discussed.

In connection with the above, mention may be made of the mineral guadalcazarite—(Hg, Zn) (S, Se), 10 mole per cent ZnS—which has been investigated by Hartwig (31), and found by him to be isomorphous with metacinnabarite and zinc blende and to have a lattice constant of 5.781 ±0.006 A.U. It is to be noted that this naturally occurring mineral has an apparent lattice constant nearly identical with the synthetic product described above. Moreover, its composition is about that indicated by our researches as corresponding to the mixed crystal present in the precipitate obtained by the long time aging of a mixture of mercuric and zinc sulfides precipitated from acid medium in the presence of an excess of hydrogen sulfide.

Analogous to the presumed existence of mixed crystals in the case of the sulfides of mercury and zinc is the previously mentioned case of mixed crystal formation in the cases of Mn–Cd sulfides and Mn–Zn sulfides as reported by Schnaase (68). All three of these sulfides may assume both the zinc blende and the wurtzite structure. The respective lattice constants for the zinc blende forms of zinc sulfide, manganous sulfide, and cadmium sulfide may be taken as 5.40 A.U., 5.60 A.U., and 5.82 A.U. It may be inferred from this that conditions for mixed crystal formation

in the case of the pairs mentioned fulfill the requirements previously cited. From the work of Böttger and Druschke (11) and of Ahrens (1) there is evidence that in the case of mercuric sulfide and cadmium sulfide mixed crystals are formed on aging the mixed precipitate. Owing to the close similarity of lattice constants of these two respective sulfides, proof of the phenomenon by x-ray methods is practically impossible.

It may be mentioned here, in connection with the above, that it is extremely difficult if not impossible to extract completely the zinc from the (Hg–Zn)S "mixed" precipitates with dilute hydrochloric acid. This at least shows that the zinc sulfide is intimately associated with the mercuric sulfide. Likewise Böttger and Druschke and Ahrens encountered the same effect in the (Hg–Cd)S "mixed" precipitate.

POSTPRECIPITATION OF ZINC SULFIDE WITH MERCURIC SULFIDE AND COPPER SULFIDE, RESPECTIVELY

In connection with the general discussion of postprecipitation given in a previous chapter of this paper, it is of interest to consider some of the phenomena in a more detailed manner. The system CuS–ZnS was studied by Kolthoff and Pearson (46) and that of HgS–ZnS by Kolthoff and Moltzau (59). In both cases it could be shown that the adsorbed hydrogen sulfide was mainly responsible for the occurrence of postprecipitation of zinc sulfide. Thus an inhibition of the effect was observed on partly replacing the hydrogen sulfide adsorbed on the surface of the copper sulfide or mercuric sulfide by organic substances containing polar sulfur groups. Cysteine was found to be especially effective.

In general, it was found that the amount of zinc sulfide postprecipitated in a given time decreases with increasing acidity. For the same acid normality less postprecipitation was observed with hydrochloric than with sulfuric acid, since the activity of the hydrogen ions in hydrochloric acid solution is greater than that in sulfuric acid solution of the same normality.

In the presence of copper sulfide obtained by hot precipitation or by aging at room temperatures, more zinc sulfide is precipitated than in the presence of a fresh precipitate of copper sulfide obtained by cold precipitation from sulfuric acid medium. Aged precipitates of copper sulfide obtained by either hot or cold precipitation have practically the same promoting effect on the precipitation of zinc sulfide. The promoting effect of such aged precipitates is much greater than that of the fresh precipitate of copper sulfide obtained by precipitation in the cold, but less than that of the precipitate freshly prepared from hot solution. The method of preparation of the copper sulfide, i.e., whether from neutral or acid solution, has also been shown to be of influence in the promotion of precipitation of

zinc sulfide. These effects are thought to involve changes in the extent of surface of copper sulfide on aging.

When postprecipitation of zinc sulfide is brought about through the presence of freshly precipitated mercuric sulfide the resulting "mixed" precipitate, though apparently quite as black as pure mercuric sulfide, is more slimy and much more difficult to filter. Upon aging of the mercuric sulfide precipitate a marked decrease in its ability to promote the precipitation of zinc sulfide is to be observed. Precipitates aged at room temperature, whether precipitated from hot or cold solution, exhibit the same promoting ability. A certain "aged" condition of a mercuric sulfide precipitate is probably reached more quickly at higher than at lower temperatures, owing partially, at least, to an increased tendency towards transformation to the trigonal form at higher temperatures. Mercuric sulfide aged in acid solutions exhibits a slightly greater promoting action on the precipitation of zinc sulfide than that aged in more nearly neutral medium. This again is undoubtedly related to an increased tendency to assume the cinnabar structure at low hydrogen-ion concentration.

In studying the effect of acidity on the postprecipitation of zinc sulfide with mercuric sulfide it was found that at higher acidities the amount of zinc sulfide entering the precipitate in a given time falls off much more slowly with increasing acidity than is to be expected on the basis of solubility principles, while at lower acidities this abnormality is not as pronounced. Employing freshly precipitated mercuric sulfide it was found that an appreciable quantity of zinc, its magnitude depending upon the acidity, enters the solid phase within the first thirty minutes or so after saturation with hydrogen sulfide, and that thereafter precipitation of zinc sulfide takes place much more slowly until a point corresponding to the solubility of well-aged zinc sulfide is reached. At lower acidities the presence of a very small amount of mercuric sulfide will lead to the precipitation of relatively large amounts of zinc sulfide within a period of time of such length that no precipitate would be obtained from a solution of a zinc salt alone. At higher acidities (2 N in sulfuric acid) the amount of zinc sulfide entering the precipitate in a given, relatively short time of shaking closely approximates a direct proportionality with the amount of fresh mercuric sulfide present. Keeping constant the acidity and the amount of mercuric sulfide present, and varying the original concentration of zinc in solution, it was indicated that the amount of zinc carried down from solution was more or less directly proportional over a limited range to the concentration of zinc salt in solution.

These results were interpreted as clearly indicating that the process by which zinc sulfide appears in the precipitate under the promoting action of mercuric sulfide at acidities where it alone would not precipitate (at least

not in the same time) involves an adsorption phenomenon as well as precipitation of zinc sulfide in the ordinary sense. During the initial period of precipitation adsorption is the primary process to be considered and is mainly responsible for the appearance of zinc sulfide in the precipitate during that period, although precipitation in the ordinary sense also occurs to account for the slower but continued disappearance of zinc ions from solution. At higher acidities, where the rate of true precipitation is relatively slow, the rôle played by adsorption is emphasized, as evidenced by the experimental results reviewed above, while at lower acidities true precipitation takes place so rapidly and to such an extent that the adsorption effect is largely overshadowed. This adsorption process involves an exchange mechanism whereby the zinc ions replace the hydrogen of the hydrogen sulfide adsorbed on the surface of the mercuric sulfide. It has been shown experimentally by shaking a well-washed, freshly prepared precipitate of mercuric sulfide with a neutral solution of zinc sulfate, under which condition the hydrogen sulfide is retained by the mercuric sulfide in an adsorbed state, that an appreciable quantity of zinc ions leaves the solution and is replaced by an equivalent amount of hydrogen ions. The presence of other substances, such as strychnine or aluminum ions, which also act as counter ions on the surface of the mercuric sulfide, leads to a decrease in the adsorption of zinc ions. Likewise the presence of strychnine in acid solution saturated with hydrogen sulfide inhibits the "carrying down" of zinc sulfide by mercuric sulfide.

The greater tendency to ionize exhibited by the adsorbed hydrogen sulfide over that exhibited by the hydrogen sulfide present in the bulk of the solution is cited as an explanation of the increased reactivity of zinc ions to form zinc sulfide at the surface of the mercuric sulfides. According to the theory advanced there is a competition between hydrogen ions and zinc ions for adsorption as counter ions. Increasing the ratio of zinc-ion concentration to hydrogen-ion concentration twofold would make conditions twice as favorable for adsorption of zinc ions. This consideration readily affords an explanation of the decrease in adsorption effect with acidity and of the observation that at a given high acidity the amount of zinc ion disappearing from solution is more or less proportional to the concentration of zinc in solution.

In this paper emphasis has been placed upon the fact that in the cases of CuS–ZnS (46) and HgS–ZnS (59) we are dealing with a postprecipitation effect. Work now being done in this laboratory by Mr. Griffith shows that the same type of phenomenon is exhibited by the sulfides of bismuth and zinc. It is not, however, to be inferred from the foregoing discussion that the presence of a sulfide of the third group in a sulfide precipitate of the second group is always to be attributed to a postprecipitation effect.

It may be possible to find cases of definite coprecipitation, although they have not so far been observed in work done in this laboratory.

It is planned to make a more exhaustive and systematic study of the entire field.

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