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THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES

BY

ROGER C. WELLS

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THE FRACTIONAL PRECIPITATION OF SOME ORE-FORMING COMPOUNDS AT MODERATE TEMPERATURES.

By Roger C. Wells.

INTRODUCTION.

SCOPE OF THE INVESTIGATION.

The experiments described in this bulletin were made to aid in elucidating the chemistry of ore deposition. They were confined to aqueous solutions at moderate temperature, and they have shown the order of solubility of the compounds of each of the classes investigated—sulphides, hydroxides, carbonates, and silicates. The solubility of most of these compounds in water is so slight that its direct and accurate determination is difficult. The literature of the subject accordingly contains many determinations of their solubility by indirect physicochemical methods, and some of these are given in this bulletin in order that they may be compared with the results obtained in the experiments here reported. Three or four complications have been met in the otherwise simple relations of solubility, namely, that sulphides may act as reducing agents, that carbonates and silicates may precipitate hydroxides, and that solids may require considerable time to assume their most stable forms.

Considered chemically, the precipitation of an ore from a solution may require only a single condition—the constituents of the ore must be present in the solution in certain forms and in concentrations above certain minima. A closer examination of this requirement, however, shows that it is conjoined with other minor requirements, all more or less related in such a way that a certain lack of one may exist if another is more than fulfilled. A statement of the relative solubility of two metallic compounds based on the final table given in this paper (p. 45) need not, for example, correspond with the order of their deposition in nature, although the solubility of an ore has a direct relation to its deposition. The solubilities presented were determined by starting with solutions containing the competing metallic constituents in equal concentrations, whereas in nature the constituents occur in various concentrations and the deposition of ores is governed very largely by the mass law, a point that will be more fully discussed elsewhere in this bulletin.

The present experiments do not show the behavior of solutions that may exist in magmas or that may constitute magmatic exudations. Such solutions are not only at high temperature and pressure but some of them are also supposed to contain liquid carbon dioxide, chlorides, fluorides, and sulphides, together with water. As some of these compounds are mutually incompatible, the assumption that such solutions are a source of ore deposits requires a great deal of explanation, one of the first requirements being the ascertainment of groups of metallic and nonmetallic elements that can be appreciably compatible in such solutions. Though such solutions seem to have played important rôles in the deposition of certain ores, as indicated by geologic evidence, yet, as aqueous solutions at moderate temperatures form not only the solvent but the transporting medium and distributing agent of enormous quantities of metalliferous material, especially in the upper parts of the earth's crust, any generalizations that may be established with reference to such solutions will have wide application.

It is interesting to trace the cyclic courses of the various elements in the numerous operations that are going on unceasingly in the earth. The continents are elevated and eroded; the sediments consolidate and possibly fuse together anew to form new magmas; intrusions and extrusions are constantly occurring. The following quotation from T. Sterry Hunt well expresses the continuity of these processes:[1]

> We learn * * * that amid all the changes of the face of the globe the economy of nature has remained the same. We are apt, in explaining the appearances of the earth's crust, to refer the formation of ore beds and veins to some distant and remote period, when conditions very unlike the present prevailed; when great convulsions took place and mysterious forces were at work. Yet the same chemical and physical laws are now, as then, in operation; in one part dissolving the iron from the sediments and forming ore beds, in another separating the rarer metals from the ocean's waters; while in still other regions the consolidated and buried sediments are permeated by heated waters, to which they give up their metallic matters, to be subsequently deposited in veins. These forces are always in operation, rearranging the chaotic admixture of elements which results from the constant change and decay around us.

The courses of the valuable metals in these cycles, as well as those of the nonmetals most frequently associated with them, are of particular significance in respect to theories of ore deposition.

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[1] Hunt, T. S., Chemical and geological essays, chapter 12, pp. 235-236, 1878.

In discussions of the origin of ore deposits the nonmetallic constituents are frequently neglected. If an ore contains more than one element the term "source of the ore" is equivocal, as it is possible that the metal may have come from one source and the nonmetal from another. The presence of the nonmetallic constituent needed to precipitate the metallic constituent may in fact explain the presence or absence of an ore at a given locality. Moreover, the proportion of such a constituent may determine the character of the ore; for example, in a solution containing iron and sulphur an excess of sulphur may yield pyrite and an excess of iron may yield pyrrhotite. This essential factor must be borne in mind in considering the mode of formation of ores. In the treatment adopted in this bulletin the constituents discussed are primarily arranged according to the nonmetallic constituent that combines with the metal, the sulphides in one group, the carbonates in another, and so on; that is, all the possible compounds of each metal are not considered together. Both arrangements have advantages. The one adopted here is at least equal in value to that followed in the older method of studying all the salts of one metal together.

In making a laboratory investigation it may happen that the methods employed do not reproduce natural conditions closely. For instance, in studying the behavior of gold, platinum, and silver, soluble salts are used in the laboratory, whereas in nature soluble salts are rarely found, and the essential problem is to determine the conditions of solution and transportation of those metals rather than their precipitation. Frequently, however, the assumption is warranted that mixtures of soluble metallic salts in noteworthy concentrations may come under the influence of precipitating agents—such as sulphides, sulphates, carbonates, and hydroxides—and be in part or completely precipitated. The precipitating action of solids will differ from that of solutions only in respect to the concentration of the precipitant available and the rate of the action, the action approaching that of an extremely dilute precipitant in solution.

In considering precipitation several elemental concepts have wide applicability, such as the law of mass action, ionization, and the constant solubility product. For the benefit of those who may not have access to detailed treatises on these subjects it seems appropriate to explain these concepts briefly, in so far as they are applicable to the present investigation, an investigation of solutions in which partial precipitation occurs. The law of mass action accounts for the equilibria occurring in the solution, the ions determine in the most general way the properties of inorganic solutions, and solubility finds its best interpretation through the solubility product.

THE MASS LAW.

The law of mass action has very wide application. Suppose that in any homogeneous system at a definite temperature there is possible a general reaction or equilibrium [1] of the type.

$$mA+nB\ldots\ldots \rightleftharpoons xC+yD\ldots\ldots$$

then, according to the law of mass action,

$$K=\frac{c^x d^y\ldots\ldots}{a^m b^n\ldots\ldots}$$

where a, b, c, d represent the concentrations of the molecular species A, B, C, D, and K is a constant, the equilibrium constant. It follows from this relation that an increase in the concentration of any substance on one side of the equation must result in an increase in the concentration of the substances on the other side and a decrease in the concentration of the other substances on the same side.

IONS AND THE SOLUBILITY PRODUCT.

This is not the place to present arguments for and against the theory of electrolytic dissociation suggested by Arrhenius in 1887. Almost every recent work on chemistry shows abundantly the fruitfulness of the conception of ions and presents the generalizations based on it.[2] Moreover, the phenomena of electric conduction warrant the assertion that the existence of ions is not only theoretically possible but is practically demonstrated.

The statement that a substance "ionizes" in solution does not mean that it ionizes completely but only that its characteristic ions appear among the "molecular species" contained in the solution and are potential factors of chemical reactions. The written symbols for ions indicate the nature of their electric charges—that is, they show whether they are positive or negative; for example, H^+, Cl^-; for of course such ions are entirely different from free atoms. Moreover, every solution must contain equivalent numbers of positive and negative ions.

As "molecular species" contained in the solution the ions as well as the molecules may be considered with reference to the mass law. Such a consideration leads to the conception of the "dissociation constant."

Thus,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

gives

$$K=\frac{[H^+]\ [HCO_3^-]}{[H_2CO_3]}$$

the dissociation constant for the primary dissociation of carbonic acid.

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[1] The sign $\rightleftharpoons$ indicates that the reaction may occur in either direction, according to conditions, and, according to the usual interpretation, equilibrium is merely the condition attained when the rate of the two opposing reactions is equal.

[2] For example, see Stieglitz, Julius, The elements of qualitative analysis, The Century Co., 1911.

With respect to chemical precipitates it was early assumed that the concentration of the nonionized dissolved portion is not changed by the presence of other salts,[1] but it has since been discovered that large deviations from this rule may be shown by moderately concentrated solutions.[2] The great number of solutions in which it holds fairly well, however, warrants its consideration, especially as it leads to a principle of even wider applicability, namely, that of the constant solubility product.

The solubility product (S. P.) is the product (result obtained by multiplication) of the concentrations of the ions yielded by the precipitate in the solution, which must be exceeded before precipitation can occur. Dr. John Johnston, of the Geophysical Laboratory of the Carnegie Institution of Washington, has suggested to me the need of a simpler term than "solubility product" for the mathematical function under discussion. The words "solubility product" merely denote a number that is a characteristic property of each specific substance. The evaluation of these numbers is one of the constant aims of chemists. There will be as many powers in this product as there are ions formed from the salt under examination. Thus for a uni-univalent salt

$$\text{S. P.} = [B]\,[A]$$

in which [B] and [A] are the concentrations expressed as gram molecules or gram ions per liter. For unibivalent salts the solubility product takes the form

$$\text{S. P.} = [B]^2[A] \text{ or } [B]\,[A]^2$$

and so on for more complicated salts.

Therefore if to a precipitate in a saturated solution a salt having a common univalent ion is added, the concentration of the other ion or ions of the precipitate will be decreased. Recent investigations have shown, however, that the effect of the addition of a common bivalent ion is insignificant.[3] It is not yet clear whether these results indicate a failure of the theory or whether, as seems more likely, correct evaluations of the ionic concentrations have not yet been obtained. However, though in many solutions the relations are still considered only qualitatively, the more insoluble the precipitate considered the more certainly the theory appears to be substantiated.[4] An application of the principle to sulphides, hydroxides, and carbonates of the

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[1] Noyes, A. A., Ueber die gegenseitige Beeinflussung der Löslichkeit von dissociierten Körpern: Zeitschr. physikal. Chemie, vol. 6, p. 243, 1890.

[2] Arrhenius, S., Ueber die Aenderung der Stärke schwacher Säuren durch Salzzusatz: Idem, vol. 31, p. 224, 1899.

[3] Noyes, A. A., and Bray, W. C., The effect of salts on the solubility of other salts: Am. Chem. Soc. Jour., vol. 33, p. 1648, 1911.

[4] Harkins, W. D., The solubility of unibivalent salts in solutions of salts of different types: Am. Chem. Soc. Jour., vol. 33, p. 1827, 1911.

heavy metals would thus appear not wholly unwarranted, and some applications of it have therefore been made in this bulletin.

Of course it remains true that if a substance with no common ion is added to a solution the solubility of the precipitate is, in general, slightly increased, for a little of it goes to form every possible new species of molecule by metathesis; and furthermore the solubility of a substance, even in the presence of a common ion, may be greatly increased under special conditions on account of the formation of complex ions.

FRACTIONAL PRECIPITATION.

PREVIOUS INVESTIGATIONS.

Most of the separations made in analytical chemistry depend on pronounced differences in solubility and the use of an excess of reagent, but in geochemistry we have to consider associated substances whose solubility may differ but slightly and whose formation was due to fractional precipitation. A fractional precipitation is one in which only a part of the dissolved substances pass from solution to solid.

The theoretic side of fractional precipitation was treated extensively by Berthollet over a century ago. As regards fractional precipitation Berthollet was correct in contending that the composition of the precipitate might be indefinite, and Proust's view as to the definite composition of the precipitate was correct in regard to pure simple chemical compounds. Berthollet held that the fundamental factors in chemical reactions are cohesion, elasticity, and mass relations, governing, respectively, solubility, volatility, and precipitation.

Fractional precipitation of the rare earths has long been familiar to chemists. In this way the constituents of the gadolinite earths were separated by Mosander;[1] praseodymium and neodymium were separated from the cerite earths by Welsbach; the constituents of the yttria earths were separated by Crookes;[2] and the sulphide of polonium by Curie.[3] Debus,[4] in 1853, made quantitative experiments on the fractional precipitations of barium and calcium carbonate, and Chizynski[5] later studied the phosphates of these two metals. Chroustchoff and Martinoff[6] studied the precipitation of sulphates and chromates by a barium salt and Küster and Thiel the fractionation of bromides and thiocyanates by silver nitrate.[7] Recently Golblum

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[1] Mosander, C. G., On yttria, terbium, and erbium: Philos. Mag., 3d ser., vol. 23, p. 252, 1843.

[2] Crookes, William, On the methods of chemical fractionation: Chem. News, vol. 54, pp. 131, 155, 1886.

[3] Curie, Sklodowska, Radioactive substances: Chem. News, vol. 88, p. 146, 1903.

[4] Debus, Heinrich, Ueber chemische Verwandtschaft: Liebig's Annalen, vol. 85, p. 124, 1853.

[5] Chizyński, Anton, Ueber die chemische Massenwirkung: Annalen der Chemie und Pharmacie, Suppl. Bd. 4, p. 226, 1865.

[6] Chroustchoff, P., and Martinoff, A., Des coefficients d'affinité chimique: Compt. Rend., vol. 104, p. 571, 1887.

[7] Küster, F. W., and Thiel, A., Ueber Gleichgewichtserscheinungen bei Fällungsreaktionen: Zeitschr. anorg. Chemie, vol. 33, p. 129, 1902.

and Stoffella[1] have studied the system involving lead carbonate and chromate.

The advantage of studying fractional precipitation for a theory of ore deposits is that the results show the net effect of all the factors that enter into play, including even unsuspected factors. Thus, if the salt of one metal is more hydrolyzed in solution than another, or if a metal has a tendency to form basic salts, the effect will be manifest in the fractionation.

An objection that may be made to many laboratory experiments is that chemical precipitates are formed instead of natural minerals. For some purposes this objection is valid; for others not. In general such experiments will shed light on the relations to be expected in the formation of minerals. In fact in many experiments it has been shown that in the course of a few hours the precipitate alters even at ordinary temperature into the mineral, as does lead sulphide.[2] In other experiments the rate of alteration is very slow, as Allen and Crenshaw have shown for zinc sulphide,[3] and solubility determinations are needed for the minerals as well as for the amorphous precipitates. I have, however, found, in every experiment in which the effect of time has been noted, that when equivalent quantities of two metallic salts are taken the experiment shows almost at once which of the two metals forms the more insoluble compound. There may be a decrease in solubility with time or a relative change in the solubilities on account of the very gradual development of the most stable compounds, but in no experiment did the metal first precipitated in excess later become the more soluble.

METHOD OF EXPERIMENTATION.

The metallic compounds will be discussed in the order of their solubility—sulphides, hydroxides and oxides, carbonates, bicarbonates, and silicates.

The procedure in the experiments on fractional precipitation was simple. A dilute solution containing two metallic salts in equivalent quantities was precipitated by reagent enough for one metal only. After a time an aliquot part of the mother liquor was analyzed and the composition of the precipitate was determined by difference. In some experiments the proportions were varied slightly, as noted.

Since the quantities of salts used are frequently expressed in equivalents a table has been prepared to assist in making conversions from units of weight to "equivalents." An equivalent is the molecular

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[1] Golblum, H., and Stoffella, G., Contribution à l'étude de l'affinité chimique: Jour. chim. physique, vol. 8, p. 135, 1910.

[2] Weigel, O., Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, p. 293, 1907.

[3] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury: Am. Jour. Sci., 4th ser., vol. 34, p. 358, 1912.

weight of a radicle (or atomic weight of an element that constitutes a radicle) reduced to a univalent basis. The equivalents thus calculated correspond to the usual chemical equivalents of salt radicles in aqueous solution referred to eight parts of oxygen. Of course, equivalent weights of salts may be taken in milligrams, grams, pounds, or tons, but wherever no qualification is expressed gram equivalents are always understood.

Table for computing "equivalents."

For weight given of—	Divide by—	For weight given of—	Divide by—
Ag	107.87	Mg	12.16
Al	9.033	Mn''	27.46
Ba	68.68	Na	23.00
Cd	56.20	Ni	29.34
Ca	20.03	Pb	103.59
Co	29.48	Zn	32.68
Cu	31.78	Cl	35.45
Fe''	27.92	CO_3''	30.00
Fe'''	18.61	HCO_3'	61.01
H	1.008	NO_3	62.01
Hg'	200.6	SO_4''	48.04
K	39.09	HSO_4'	97.08

SULPHIDES.

SOLUBILITY OF SULPHIDES.

As these experiments were made to determine the order of solubility of the compounds studied, it will be advantageous to present first such data as already exist on the subject.

The sulphides of the heavy metals are very insoluble. Although they are ordinarily considered quite insoluble their solubilities can be determined approximately by physicochemical methods, and, in fact it has been shown that mercuric sulphide is many thousandfold more insoluble than manganous sulphide. The solubility of the sulphides in water at 18° C. was determined by Weigel[1] by the conductivity method, but the determination of the solubility by this method is complicated by the fact that the exact nature of the dissolved substances must be known, and as the sulphides produce solutions differing in alkalinity the method could hardly be expected to yield more than mere approximations to the true solubility.

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[1] Weigel, Oskar, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, p. 293, 1907.

Solubility of the sulphides of the heavy metals in distilled water at 18° C. according to Weigel.

[Moles $\times 10^{-6}$ per liter.]

Crystallized sulphides.		Freshly precipitated (probably amorphous) sulphides.	
SnS	0.14	HgS	0.05
Ag_2S	0.55	Bi_2S_3	0.35
SnS_2	1.13	Ag_2S	0.55
Galena (from precipitated PbS)	1.18	As_2S_3	2.1
Galena (Freiberg)	1.21	CuS	3.51
Cu_2S	3.1	PbS	3.6
Zinc blende (artificial)	6.63	Sb_2S_3	5.2
Zinc blende (Santander)	6.55	CdS	9.00
Greenockite (artificial)	8.99	NiS	39.87
Millerite (artificial)	16.29	CoS	41.62
Wurtzite (artificial)	28.82	FeS	70.1
Pyrite (artificial)	40.84	ZnS	70.6
Pyrite (Freiberg)	48.89	MnS	71.6
Pyrrhotite	53.6		
MnS	54.5		

The solubility products of sulphides have been determined by other investigators from time to time.[1]

For a univalent, bivalent, and trivalent metal, respectively, the solubility products (S. P.) would be:

$$\text{S. P.} = [M^{+}]^2\,[S^{--}]$$
$$\text{S. P.} = [M^{++}]\,[S^{--}]$$
$$\text{S. P.} = [M^{+++}]^2\,[S^{--}]^3$$

The values of the solubility products already published were collected by Bruner and Zawadzki, who also calculated them from the heat of formation of the sulphide and the electrolytic potential of the metals and of sulphur. In the table below I have placed their calculated values of the solubility products, those found by the observer noted, and finally the "solubility of the sulphide in water" calculated from the solubility product. It will be noted that the solubilities in this table are far smaller than those obtained by Weigel.

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[1] Bernfeld, I., Studien über Schwefelmetallelektroden: Zeitschr. physikal. Chemie, vol. 25, p. 46, 1898. Knox, Joseph, A study of the sulphur anion and of complex sulphur anions: Faraday Soc. Trans., vol. 4, p. 48, 1908. Immerwahr, C., Beiträge zur Kenntnis der Löslichkeit von Schwermetallniederschlägen auf elektrochemischen Wege: Zeitschr. Elektrochemie, vol. 7, p. 478, 1901. Glixelli, S., Zur Theorie der H_2S Fällung der Metalle: Die Einwirkungen von Schwefelwasserstoff auf Zinksalze: Zeitschr. anorg. Chemie, vol. 55, p. 306, 1907. Lucas, R., Gleichgewichte zwischen Silbersalzen: Zeitschr. anorg. Chemie, vol. 41, p. 211, 1904. Bruner, L., and Zawadzki, J., Ueber die Gleichgewichte bei der Schwefelwasserstoffällung der Metalle: Zeitschr. anorg. Chemie, vol. 65, p. 136, 1910.

Solubility products of several sulphides and their solubility in water.

[Based on determined solubility product, if known; otherwise on solubility product calculated by Bruner and Zawadski.]

Sulphide.	Solubility product calculated.	Solubility product found.	Observer.	Solubility in water.
				Moles per liter (calculated).
MnS	7.0×10^{-16}		Bruner and Zawadski.	2.6×10^{-8}
Tl_2S	(4.5×10^{-23})	(4.5×10^{-23})	do	2.2×10^{-8}
FeS	7.0×10^{-22}	3.7×10^{-19}	do	1.9×10^{-11}
βZnS	6.0×10^{-24}	1.1×10^{-24}	Glixelli	1.0×10^{-12}
αZnS		5.0×10^{-26}	do	2.2×10^{-13}
NiS	7.0×10^{-25}		Bruner and Zawadski.	8.4×10^{-12}
CoS	1.5×10^{-26}		do	1.2×10^{-13}
PbS	2.1×10^{-28}	3.4×10^{-28}	do	1.8×10^{-14}
CdS	1.8×10^{-29}	5.0×10^{-29}	do	4.2×10^{-15}
Ag_2S	1.4×10^{-48}	4.8×10^{-53}	Lucas	2.3×10^{-18}
Ag_2S		1.5×10^{-50}	Bernfeld	1.9×10^{-17}
Ag_2S		3.9×10^{-50}	Knox	2.2×10^{-17}
CuS	7.0×10^{-45}	5.9×10^{-42}	Immerwahr	2.4×10^{-21}
CuS		1.2×10^{-42}	Knox	1.1×10^{-21}
HgS	[a] 2.0×10^{-52}	2.8×10^{-54}	do	1.7×10^{-27}
HgS	[a] 1.0×10^{-49}	6.7×10^{-48}	Immerwahr	2.4×10^{-24}

[a] Based on different heats of formation.

The order of solubility obtained from experiments on fractional precipitation should agree with the order of solubility given in the last column of the table. As a matter of fact, the agreement is excellent except for two metals, silver and cobalt. The discrepancy for silver requires explanation; that for cobalt is not surprising in view of the small difference between its solubility and those of the adjacent sulphides. The discrepancy for silver may be due to a failure of the principle of the solubility product, as silver sulphide is a unibivalent compound, or possibly to the precipitation of silver by sulphides in part as free metal. A study of the fractional precipitation of thallous sulphide would assist in deciding between these two possibilities. Weigel's series seems to place silver in its proper position, but it shows several discrepancies for other metals.

While the solubility of sulphides is under consideration attention may be paid briefly to the enormous effect of changes in acidity on the precipitation of sulphides. This effect is due to the nature of the ionization of hydrogen sulphide, the sulphide ion concentration varying inversely as the square of the hydrogen ion concentration for a given concentration of total sulphide. As is well known, the precipitability of the sulphides varies so greatly that a complete separation of certain groups is possible. Thus in an acid solution hydrogen sulphide added to a dilute mixture of the sulphates of iron and copper precipitates almost wholly copper sulphide. This is not strictly a fractional precipitation, since in an acid solution of hydrogen sulphide the concentration of sulphide is probably not sufficient to exceed the solubility product of ferrous sulphide. A fractional precipitation would be obtained with a small amount of precipitant under conditions which would permit all the metals to be precipitated with an excess. With iron and copper sulphates, for example, a fractionation might be made with sodium sulphide, since an excess of sodium sulphide would precipitate both sulphides completely.

EXPERIMENTS WITH THE NITRATES OF COPPER AND LEAD.

The first experiments on this point showed that the composition of the precipitate depends a great deal on the manner of precipitation and time of standing. A mixture of the nitrates of lead and copper, partly precipitated with a solution of hydrogen sulphide in the cold and filtered within a short time, yielded a precipitate containing the sulphides of both metals, although copper was slightly in excess. On warming, however, copper sulphide was the chief product, being precipitated even at the expense of the lead sulphide first formed.

EXPERIMENTS WITH THE SULPHATES OF COPPER AND ZINC.

A good illustration of selective precipitation was obtained with mixtures of cupric sulphate and zinc sulphate, precipitated by ammonium sulphide. The data are given in the table below and the curves in figure 1. The evidence is very clear that even in alkaline solution more cupric sulphide is precipitated than zinc sulphide. The quantities of substances used are expressed in milligram equivalents. (See p. 12.) The solutions were dilute at the time of precipitation, the final volume being 40 cubic centimeters for the quantities stated in the table.

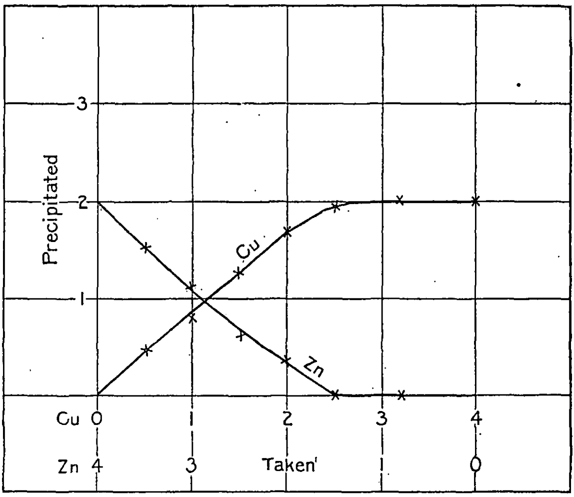

FIGURE 1.—Selective precipitation of copper before zinc by ammonium sulphide. The abscissæ represent the content of the solution in milligram equivalents of cupric sulphate and zinc sulphate before the addition of 2 milligram equivalents of ammonium sulphide; the ordinates represent the composition of the resulting precipitate.

Fractional precipitation of cupric and zinc sulphates by ammonium sulphide.

[2.00 milligram equivalents in each precipitation.]

Cupric sulphate taken.	Zinc sulphate taken.	Copper in precipitate.	Zinc in precipitate.
Milligram equivalents.	*Milligram equivalents.*	*Milligram equivalents.*	*Milligram equivalents.*
0.00	4.00	0.00	2.00
.50	3.50	.49	1.51
1.00	3.00	.87	1.13
1.50	2.50	1.29	.60
2.00	2.00	1.70	.41
3.00	1.00	1.97	.02
3.20	.80	2.05	.00
4.00	.00	2.00	.00

These results are stated fully as illustrations of relations which hold for most pairs of sulphides. Both precipitate together at first, then one largely redissolves, leaving the sulphide radicle in combination with a single metal.

These facts may find application in theories of the formation of ores. If large bodies of precipitable solutions come into sudden contact, an indefinite mixture of sulphides will be precipitated. On the other hand, if the solutions are somewhat warm or react slowly the sulphides tend to be precipitated in a definite succession.

WORK OF ANTHON AND SCHÜRMANN.

The precipitation of soluble salts of metals by the insoluble sulphides of other metals was studied long ago by Anthon.[1] He obtained the series silver, copper, lead, cadmium, iron, nickel, cobalt, and manganese. A sulphide of any one of these metals, he found, would be precipitated at the expense of the sulphide of one lower in the series. The subject was studied further in 1888 by E. Schürmann,[2] who enlarged the series as follows: Palladium, mercury, silver, copper, bismuth, cadmium, antimony, tin, lead, zinc, nickel, cobalt, ferrous iron, arsenic, thallium, and manganese. The experiments of Anthon and Schürmann lead to exactly the same conclusions as those on fractional precipitation. The further investigation of sulphides was therefore restricted to some of the side issues involved. (See pp. 18–23.)

Schürmann found that some of these transpositions, of which he studied a very large number, occurred more easily than others, particularly those where the metals are widely separated in the series. It was especially difficult to obtain complete transformations in the case of nickel sulphide treated with zinc sulphate and between thallium salts and the neighboring members of the series. The

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[1] Anthon, E. F., Jour. prakt. Chemie, vol. 10, p. 353, 1837.

[2] Schürmann, Ernst, Ueber die Verwandtschaft der Schwermetalle zum Schwefel: Liebig's Annalen, vol. 249, pp. 326–350, 1888.

behavior of iron was peculiar in that the sulphides of zinc, nickel, and cobalt formed at the expense of an excess of ferrous sulphide, but they were in turn dissolved when treated with ferrous sulphate. The positions of arsenic, tin, and antimony in the series are subject to qualifications depending on the valence of the metal.

This series for the order of solubility of sulphides has thrown great light on the development of sulphide ores.[1] It indicates the order of deposition of sulphides from a mixture of metallic salts when they compete under equal conditions for a sulphide. The first metals of the series will be precipitated first, leaving the solution richest in the last members; or, if solution is going on, the last members will tend, other things being equal, to go into solution first.

Schürmann was chiefly interested in determining the place of each metal in the series. He considered the series to represent the order of the "affinities" of the metals for sulphur. A more empirical statement is that it represents the order of the solubilities of the sulphides in water.[2]

If the mechanism of these reactions is considered according to present theories, we should have the following scheme of ionization in solution, for example, for the couple silver-copper:

$$\begin{array}{rcccc} Ag_2SO_4 & \rightleftharpoons & 2Ag^{+} & + & SO_4^{=} \\ & & + & & + \\ CuS & \rightleftharpoons & S^{=} & + & Cu^{++} \\ & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ & & Ag_2S & & CuSO_4 \end{array}$$

Since the solubility product of silver sulphide is smaller than that of copper sulphide, silver sulphide forms at the expense of copper sulphide, and the equilibrium lies well toward the right in the following equation:

$$Ag_2SO_4 + CuS \rightleftharpoons Ag_2S + CuSO_4$$

The actual relations may be more complex than the last equation indicates, because there may also be a reaction of oxidation and reduction, but the scheme shows the general relation. Every sulphide has a "solubility product"; that is, the product of the concentrations of its two ions, which must be exceeded before precipitation can occur. Conversely, if the concentrations of the ions of any sulphide are less than its solubility product the sulphide will dissolve. That Schürmann's series is very nearly the order of solubility of the sulphides in pure water is evident from a comparison of the last column in the table on page 14 with Schürmann's series on page 16.

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[1] Emmons, W. H., The enrichment of sulphide ores: U. S. Geol. Survey Bull. 529, p. 56, 1913.

[2] Wells, R. C., Econ. Geology, vol. 5, p. 7, 1910.

The idea of the solubility product allows us at once to explain certain facts noted by Schürmann and to predict others with reasonable confidence. For instance, it is not a matter of primary importance what acidic radicles are present in the solution as long as they do not form insoluble salts with the metals present. Again, the greater speed of adjustment of equilibrium for metals widely separated in the series accords with our present idea that the speed of reaction is a function of the remoteness of removal from equilibrium.

If we let K_1 and K_2 represent the solubility products of two sulphides involved in a fractional precipitation and write

$$K_1 = (M_1)\ (S)$$
$$K_2 = (M_2)\ (S)$$

where (M_1), (M_2) and (S) represent concentrations of metal 1, metal 2, and sulphide ions, then when equilibrium is established, since the sulphide ion is common, we should have

$$\frac{K_1}{K_2} = \frac{(M_1)}{(M_2)} \text{ or } \frac{(M_1)}{(M_2)} = K_3, \text{ a new constant.} \qquad (1)$$

That is, the ratio of the concentrations of the two metallic ions in a solution saturated with both sulphides should be a constant, independent of the quantity of sulphides but probably somewhat dependent on the temperature. Schürmann as a rule gave only qualitative results, and where he says one metal was "completely" separated from the other more exact research might show that a distribution occurs. As a matter of fact, however, the relation expressed by equation (1) above has not yet been experimentally illustrated in a quantitative way for sulphides.

A consideration of the solubility of sulphides helps to explain certain phenomena observed by Stokes.[1] He found that pyrite and marcasite are slightly attacked by a solution of alkali carbonate but much more completely when a carbonate of copper, lead, silver, or zinc is present. This is no doubt due in part to the greater insolubility of the sulphides of copper, lead, silver, or zinc, which form at the expense of the sulphide of iron in the pyrite and marcasite while the alkali dissolves the excess sulphur, the two concurrent reactions being much more effective than either singly.

COMPOUND SULPHIDES.

One of the objects in studying fractional precipitation was to gain light on the conditions of formation of compound sulphides, such as chalcopyrite. It is easy to perceive that the solubility of one sul-

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[1] Stokes, H. N., Experiments on the action of various solutions on pyrite and marcasite: Econ. Geology vol. 2, p. 19, 1907.

phide might be changed by the presence of a second in solution and that a compound sulphide might have an intermediate solubility, following the usual behavior as described by Van't Hoff for double salts. The sulphides are so insoluble, however, that no adequate study of their behavior over a wide range of conditions has as yet been made.

Grout[1] has suggested that compound sulphides may have been produced in some instances by the admixture of alkaline and acid solutions. This seems very probable. Malfatti[2] has described certain complex sulphides of iron of the formula $RFeS_2$ where R is a univalent radicle. But in chalcopyrite copper has usually been regarded as bivalent, if the formula is written CuS.FeS; to write it $Cu_2S.Fe_2S_3$ suggests trivalent iron. However that may be, if chalcopyrite could be formed by a simple precipitative reaction its formation would remove the constituents from a solution in definite proportions. Such removal would modify curves like those shown in figure 1 (p. 15) into lines with horizontal sections over certain regions. As no such horizontal sections were discovered in the fractional precipitation of copper and iron sulphide the conditions for the formation of chalcopyrite were not revealed by that method.[3] It was therefore concluded that the formation of chalcopyrite by a precipitative reaction at moderate temperature and pressure demands at least more precipitating sulphide than corresponds to the copper present; otherwise no iron will be precipitated. Further investigation of this subject is needed.

By microscopic examination of the lean Butte ores J. F. Simpson has shown that the pyrite contains the copper as the copper minerals chalcocite, bornite, chalcopyrite, and enargite, and that of such minerals chalcopyrite is the oldest.[4] Graton and Murdock have reached similar conclusions after an examination of many specimens from other localities.[5] The typical minerals of enrichment processes appear to have been formed by the progressive alteration of one mineral into another, not strictly a fractional precipitation, although the fractionating tendency is revealed by the removal of the iron and the increasing deposition of copper. For the formation of the compound sulphides by enrichment the iron sulphide is already present. Of course, chalcopyrite may also result from magmatic differentiation, but for aqueous solutions we can not avoid the conclusion that its formation

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[1] Grout, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, 1913.

[2] Malfatti, H., Beiträge zur Kenntnis des Eisensulfids: Zeitschr. anal. Chemie, vol. 48, p. 352, 1909.

[3] For details see Econ. Geology, vol. 5, p. 1, 1910.

[4] Simpson, J. F., The relation of copper to pyrite in the lean copper ores of Butte, Mont.: Econ. Geology, vol. 3, p. 635, 1908.

[5] Graton, L. C., and Murdock, Joseph, The sulphide ores of copper: Am. Inst. Min. Eng. Bull., May, 1913, pp. 741–812.

indicates the presence of an excess of available sulphide beyond the requirements of the copper. Briefly, a small amount of a soluble sulphide, say sodium sulphide, acting on a considerable quantity of ferrous and cupric sulphates does not produce chalcopyrite but only copper sulphide.

REDUCING ACTION OF SULPHIDES.

Besides taking part in purely metathetic reactions both soluble and insoluble sulphides may act as reducing agents. This action may be referred to the slight electroaffinity of sulphur, which produces the partial reaction:

$$S^{--} = S + 2\ominus$$

This reaction has a strong tendency to occur whenever it can be linked with a reaction of positive ions yielding positive electricity. For example, we are familiar with the action of hydrogen sulphide in acid solution on ferric salts:

$$2FeCl_3 + H_2S = 2FeCl_2 + S + 2HCl$$

If the reaction is considered to be essentially one between ions we have:

$$2Fe^{+++} + S^{--} = 2Fe^{++} + S \qquad (2)$$

This reaction shows the neutralization of the positive and negative charges and the precipitation of free sulphur.

The application of the reducing tendency of sulphide ions here suggested and illustrated should lead to interesting conclusions with other than iron salts. With cupric salts, for example, we should expect that the sulphide ions would tend to reduce cupric ions, along the line of the following equation:

$$2Cu^{++} + S^{--} = 2Cu^{+} + S \qquad (3)$$

Data on this possibility are scanty. Several investigators[1] have called attention to the fact that hydrogen sulphide produces in a solution of cupric sulphate a precipitate in which there is some free sulphur and a deficit in the amount of combined sulphur required by the formula CuS. According to Schweizer, there is usually about 7.2 per cent cuprous sulphide (Cu_2S)—that is, if the complex is interpreted as a mixture of cupric and cuprous sulphide—but, according to the more recent work of Clark, if such a precipitate is filtered off and digested for a long time with a solution of hydrogen sulphide

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[1] Thomsen, Julius, Ueber die Zusammensetzung des auf nassem Wege gebildeten Schwefelkupfers: Deutsche Chem. Gesell. Ber., vol. 11, p. 2043, 1878. Ditte, A., Action du sulfure de cuivre sur le sulfure de potassium: Compt. Rend., vol. 98, p. 1429, 1884. Brauner, Bohuslav, Action of hydrogen sulphide on cupric salt solutions: Chem. News, vol. 74, p. 99, 1896. Schweizer, E., Diss., p. 34, Erlangen, 1908. Clark, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ., Diss., p. 106, 1914.

in water the residue after removal of free sulphur contains about 71 per cent cuprous sulphide.

The study of the ionic reaction suggested by equation (3) as a possible equilibrium governed by the mass law is rendered difficult by the fact that sulphur and the two sulphides of copper are very insoluble. Of the different concentrations in equation (3) that of Cu^{++} will be determined by the solubility product of cupric sulphide and that of Cu^{+} by the solubility product of cuprous sulphide. The concentration of free sulphur may presumably be varied from zero to that of a saturated solution of sulphur. The concentration of sulphide ions, S^{--}, may be varied most widely, both by changes in total concentration and by the use of alkaline solutions in which the ionization of hydrogen sulphide is enormously increased. The use of an alkaline solution also serves to keep the concentration of free sulphur, S, below that of a solution saturated with sulphur on account of the formation of alkali polysulphide.

If we increase the concentration of the sulphide ions, S^{--}, there should be an increase in the cuprous ion concentration, Cu^{+}, if equation (3) is significant, and presumably more cuprous sulphide might then be precipitated.

A number of experiments were made, directed wholly toward securing a precipitate with a high percentage of cuprous sulphide, especially by the use of alkaline solutions. The results are summarized in the following table. The precipitations were made hot by adding the cupric sulphate to the alkaline sulphide. The precipitate was washed by decantation, finally with alcohol and ether, well pressed between filter papers, and dried over sulphuric acid.

Action of alkaline soluble sulphide solutions on cupric sulphate.

Experiment.	Gram equivalents taken per liter of the mixture.			Percentage of Cu_2S in precipitate.
	$CuSO_4$.	Na_2S.	NaOH.	
126	0.091	0.091	0.017	18.3
127	.059	.112	.022	31.1
128	.035	.069	.130	47.6
130	.001	.002	.200	55.8
131	.016	.155	.146	61.8
129	.014	.028	.158	69.3
	$CuCl_2$			
132	.05	.10	.10	49.8

These results prove that the immediate precipitate produced by alkaline sulphides contains a much higher percentage of cuprous sulphide than that formed by hydrogen sulphide in acid solutions. The results strengthen the supposition that the equilibrium shown in equation (3) determines the composition of the precipitate to some extent, since the sulphide ion concentration varies with the alkalinity.[1] It appeared impossible, however, by this method to obtain a precipitate of pure cuprous sulphide. The experiments of Ditte show that a concentrated solution of potassium sulphide will convert copper entirely into the cuprous state, but he says that a dilute solution is without effect.[2] My experiments seem to modify Ditte's conclusions. The further solution of the problem would seem to require a more careful study of the reversibility of the action with respect to variations in the concentrations of sulphide ions and free sulphur.

The reducing action of sulphide ions on other metallic salt solutions has not been studied.

ELECTRIC ACTIVITY IN SULPHIDES.

Since insoluble metallic sulphides are conductors of electricity the equalization of chemical differences, especially differences in degree of oxidation, can take place through electric action over appreciable distances. Thus the deposition of such metals as gold, silver, and copper may occur at one end of a conducting filament while the oxidation of a sulphide or any other oxidizable substance is occurring at the other end of the system constituting the metallic portion of the circuit. The associations of products produced in this way will naturally be different from those produced under conditions of thorough admixture. Further, not only will dissimilar sulphides and metals manifest reciprocal influences on each other through electric activity but effects from active solutions will be transmitted as far as the complete circuits extend. I have discussed these matters in detail elsewhere[3] and need refer to only one phase of the subject further in this connection.

In studying chalcocite enrichment A. C. Spencer has reached the conclusion that the change of pyrite or chalcopyrite to chalcocite may be considered as an alteration involving a series of steps, or perhaps even a continuous progression through indefinite compounds or mixtures of iron-copper sulphides. He succeeded in bringing about the change of chalcopyrite at least into chalcocite through bornite and covellite in several artificial ways. One of these ways consisted in touching the specimens immersed in cupric sulphate by an iron nail. Since there is every reason to believe that the iron affected the sulphides through electric action it seems worth while to quote his account of this experiment as an illustration of possible electric action.[4]

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[1] Knox, Joseph, A study of the sulphur anion and of complex sulphur anions: Faraday Soc. Trans., vol. 4, p. 47, 1908.

[2] Ditte, A., Compt. Rend., vol. 98, p. 1429, 1884.

[3] Wells, R. C., Electric activity in ore deposits: U. S. Geol. Survey Bull. 548, 1914.

[4] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 629, 1913.

The colors * * * referred to above may be readily obtained by another simple procedure, and the observer can hardly fail to conclude that the colors obtained indicate the formation of the minerals bornite, covellite, and chalcocite. If any member of the series chalcopyrite, bornite, covellite is touched by a piece of iron while it is immersed in a cupric sulphate solution the mineral changes color almost instantly and in a short time becomes coated with the mineral next above it in the series. The brilliant indigo of covellite changes to the dull gray so characteristic of chalcocite, bornite assumes a blue color unmistakably like that of covellite, and chalcopyrite takes on a bronzy hue resembling that of bornite. Furthermore, within a very short time the bronze plating on chalcopyrite gives place to or is hidden by a film of covellite; then within an hour or so the surface turns to a chalcocite gray, and finally metallic copper is deposited. When pyrite is used in place of a cupriferous sulphide the effect of the iron is sufficient to throw down metallic copper rather quickly, but by scraping away the metal and again placing the mineral in contact with iron in the solution it is possible to obtain deposits of copper sulphides. In this way spots having somewhat the same color as chalcopyrite and others bronzy like bornite may be developed on pyrite along with unmistakable films of covellite and of chalcocite. If copper is used instead of iron the results are essentially the same with chalcopyrite, bornite, and covellite. For instance, covellite may be coated with chalcocite by contact with copper in a solution of cupric sulphate. It is obvious that the speed of reaction may be varied by employing different metals as inductors, or by employing minerals to cause electrolytic action. Very pleasing results have been obtained by placing in a solution of cupric sulphate a polished specimen of intergrown chalcopyrite and pyrrhotite. Here a pinkish bronze color resembling that of bornite appeared within a few days, but gradually changed to purple, deep purple, and finally to indigo blue. On the most reactive grains the covellite color was fully developed in about eight weeks, but the surface in general became blue only after 12 weeks, and even then certain areas were still bronzy. At the end of four months no gray color had developed to indicate the formation of chalcocite, but the color was a paler blue than that of natural covellite.

It may be suggested that the results described, which were obtained under ordinary temperatures, may actually epitomize the course of reaction between the primary sulphides and copper salts held in oxidized solutions penetrating from the surface. Even if the means employed to produce the results in a short time are not comparable with those involved in natural processes, perhaps the conditions under which the experiments were made may be considered to be less unnatural than those prevailing in mineral syntheses effected under high temperatures.

SUMMARY OF RESULTS OF EXPERIMENTS WITH SULPHIDES.

1. The concentration of the sulphide ion is so greatly affected by change of acidity that this change is the principal factor determining the precipitation of sulphides.

2. The solubility of the several sulphides, however, differs so greatly that complete separations by fractional precipitation are possible; for example, copper from zinc.

3. A mixture of two metallic salts yields, by fractional precipitation, an initial precipitate containing the sulphides of both metals, but as a rule, if the mixture is heated or is permitted to stand, one sulphide largely or wholly redissolves.

4. The order of precipitation, beginning with the metal that separates first, is palladium, mercury, silver, copper, bismuth,

cadmium, antimony, tin, lead, zinc, nickel, cobalt, ferrous iron, arsenic, thallium, manganese.

5. Attempts to form chalcopyrite by fractional precipitation of ferrous and cupric sulphate were unsuccessful.

6. Soluble sulphides may act as reducing agents. This action affects the composition of precipitates of copper sulphide and may explain the anomalous position of silver in the precipitation series.

7. At one stage of the action produced by an admixture of sulphides and metallic salts electric activity may determine the products formed.

HYDROXIDES.

PREVIOUS WORK.

Only a few experiments are found in the literature on the fractional precipitation of the common metallic hydroxides. Mills and Smith,[1] in working on nickel and cobalt, found a very narrow margin of difference in precipitability, but this is probably one of the most difficult pairs to separate, although my own experiments indicate that manganese and magnesium are similarly close together. Fink[2] obtained the precipitation series copper, zinc, nickel, cobalt, manganese, and magnesium for the hydroxides of these metals. Pickering[3] studied the partial precipitation of copper sulphate solutions only by calcium hydroxide, but this was not strictly a fractionation.

SOLUBILITY OF HYDROXIDES.

The preliminary data available in regard to the solubility of the hydroxides at room temperatures of 20°–25° C., are as follows:

Solubility of hydroxides.

	Gram equivalents per liter.
$Zn(OH)_2$	6.0×10^{-6}
$Cd(OH)_2$	8.7×10^{-6}
$Mn(OH)_2$	3.0×10^{-5}
Ag_2O	4.6×10^{-5}
$Pb(OH)_2$	9.3×10^{-5}
$Fe(OH)_2$ (Lamb[4])	2.7×10^{-5}
$Mg(OH)_2$	7.5×10^{-4}
HgO	2.5×10^{-4}
$Ca(OH)_2$	4.5×10^{-2}
$Sr(OH)_2$	1.3×10^{-1}
$Ba(OH)_2$	4.6×10^{-1}

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[1] Mills, E. J., and Smith, J. J., Researches in chemical equivalence: Roy. Soc. Proc., 5th ser., vol. 29, p. 181, 1879.

[2] Fink, R., Ueber die Affinität der Vitriolmetalle zur Schwefelsäure: Deutsche chem. Gesell. Ber., vol. 20, p. 2106, 1887.

[3] Pickering, S. U., The chemistry of Bordeaux mixture: Chem. Soc. Trans., vol. 91, p. 1989, 1907; vol. 97, p. 1852, 1910.

[4] Lamb, A. B., The potential of iron calculated from equilibria measurements: Am. Chem. Soc. Jour., vol. 32, p. 1218, 1910.

FRACTIONAL PRECIPITATION OF HYDROXIDES.

By the procedure used in the study of the sulphides the hydroxides of the important metals were fractionally precipitated as follows: To a dilute solution containing two metallic salts in equivalent quantity, heated nearly to boiling, was added a dilute solution of sodium hydroxide sufficient to precipitate one metal only. The sodium hydroxide contained some barium hydroxide, used to free it from carbonate. Oxidizable salts were precipitated in an atmosphere of hydrogen. The precipitate was kept at a temperature close to 100° for several minutes and finally filtered off. An aliquot portion of the filtrate was analyzed and the composition of the precipitate was thus determined. In general one metal was precipitated to a greater extent than the other, and after working out a number of pairs it was found possible to arrange the metals in a series, which may be termed the hydroxide precipitation series. Although in the experiments with the sulphides the proportions in the precipitate were determined, in nearly every experiment with the hydroxides the results were limited at first to the determination of the order in the series. This order was found to be as follows:

Order of solubility of hydroxides.

1. Ferric hydroxide.
2. Aluminum hydroxide.
3. Cupric hydroxide.
4. Zinc hydroxide.
5. Lead hydroxide.
6. Nickelous hydroxide.
7. Silver hydroxide.
8. Ferrous hydroxide.
9. Manganous hydroxide.
10. Magnesium hydroxide.
11. Calcium hydroxide.

The pairs determined are shown in the next table.

Pairs of metals compared in fractional precipitation of hydroxides.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.
113	Ferric hydroxide	Aluminum.
111	do	Copper.
112	Aluminum	Do.
97	Copper	Zinc.
98	do	Lead.
109	do	Nickel.
112	do	Ferrous hydroxide.
96	do	Magnesium.
100	Zinc	Lead.
10	do	Nickel.
102	do	Ferrous hydroxide.
99	Lead	Silver.
	do	Magnesium.
106	Nickel	Silver.
	do	Ferrous hydroxide.
101	Silver	Magnesium.
103	Ferrous hydroxide	Do.
105	do	Do.
109	Manganese	Calcium.
110	Magnesium	Do.

It will be seen that the precipitation series does not follow the solubility series very closely. Possibly some of the solubility determinations are incorrect, or the matter of hydrolysis may not have been sufficiently considered. However that may be, it is significant that the precipitation series may be correlated with a heat effect, namely with the heat of the reaction

Sodium hydroxide+metallic sulphate=metallic
hydroxide+sodium sulphate.

These heats of reaction are shown in the table below.

Order obtained for the heat of reaction of sodium hydroxide with metallic sulphates.

M	1.	2	M	1	2
Hg^{++}		11.78	Pb		4.79
Hg^{+}		10.57	Zn	3.99	3.77
Fe^{+++}	10.05		Cd	3.59	3.56
Ag		8.24	Co	3.35	3.13
Cr	7.47		Fe^{++}	3.23	3.01
Cu	6.47	6.25	Ni	2.64	2.42
Al	5.19		Mn	2.45	2.23

1. $NaOHaq+M(SO_4)_{1/2}aq=Na(SO_4)_{1/2}aq+MOH$.
2. $NaOHaq+MNO_3aq=NaNO_3aq+MOH$.

Although the order here shown does not yet agree exactly with the order obtained in the fractional precipitations the agreement is closer than that between the precipitation series and the order of the solubilities determined directly (p. 24).

FERROUS AND CUPRIC HYDROXIDES.

For the purpose of studying one fractionation in greater detail the precipitation of iron and cupric hydroxides was studied over a wide range of concentrations. The fractionations in the table below were carried out with ammonium hydroxide as the precipitant. The results are also plotted in figure 2. Dilute solutions were used for

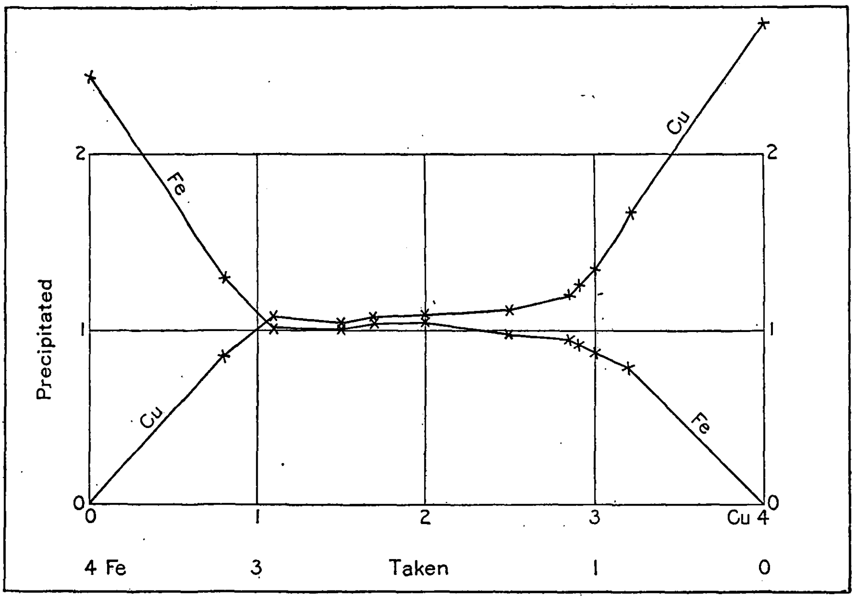

FIGURE 2.—Apparent selective precipitation with ferrous and cupric sulphates. The abscissæ represent the content of the solution in milligram equivalents of ferrous and cupric sulphate before the addition of 2 milligram equivalents of ammonium hydroxide, the ordinates the composition of the resulting precipitate.

these precipitations, the final volume in every experiment being 40 cubic centimeters for the quantities stated in the table.

Precipitation of ferrous and cupric sulphate by ammonium hydroxide (milligram equivalents).

Cupric sulphate taken.	Ferrous sulphate taken.	Copper in precipitate.	Iron in precipitate.	Color of precipitate.
0.00	4.00	0.00	2.43	Pale green.
.80	3.20	.80	1.30	Black.
1.10	2.90	1.08	1.01	Do.
1.50	2.50	1.03	1.01	
1.70	2.30	1.08	1.05	Brownish.
2.00	2.00	1.09	1.07	
2.50	1.50	1.12	.97	
2.85	1.15	1.20	.95	Orange.
2.90	1.10	1.26	.91	Do.
3.00	1.00	1.33	.87	Do.
3.20	.80	1.66	.68	
4.00	.00	2.75	.00	Green.

These results show a very peculiar selective precipitation. At the extreme concentrations basic salts are precipitated. Although it seemed at first as if the results indicated the formation of a precipitate containing one atom of iron to one of copper, it was afterward concluded that the oxidation of the ferrous salt had not been wholly prevented, and in fact that it could not be wholly prevented on account of the presence of cupric sulphate. As a result of this oxidation ferric hydroxide was precipitated instead of ferrous hydroxide, and therefore the assumption of the formation of a complex compound is unwarranted.

Similarly solutions of cupric sulphate and ferrous sulphate in varying proportions were precipitated hot out of access of air by sodium hydroxide.

Precipitation of ferrous and cupric sulphate by sodium hydroxide (milligram equivalents).

Ferrous sulphate taken in 250 cubic centimeters.	Cupric sulphate taken in 250 cubic centimeters.	Iron precipitated by 4 milligram equivalents of sodium hydroxide.	Copper precipitated.
1.50	6.50	1.15	....
4.00	4.00	1.78	....
6.20	1.80	2.03	1.79

These results show that the copper has a greater tendency to precipitate where equal amounts of both salts are present, and this tendency causes the practical removal of the copper where it is the minor constituent. What looks like evidences of the formation of a molecule $FeCu(OH)_4$ may again be due simply to unpreventable oxidation of a portion of the ferrous salt.

Recently Curtman and St. John[1] have studied the sensitiveness of the hydroxide reactions for the common metals. They find an order of sensitiveness which differs considerably from the precipitation series here deduced, but it appears that their results are based on optical effects, such as the visibility, color, and density of the precipitates, so that an exact agreement is not to be expected.

SUMMARY OF RESULTS OF EXPERIMENTS WITH HYDROXIDES.

1. The precipitation series obtained for the hydroxides, beginning with the most insoluble compound, is as follows: Ferric hydroxide, aluminum, cupric hydroxide, zinc, lead, nickel, silver, ferrous hydroxide, manganous hydroxide, magnesium, calcium.
2. The series is very nearly the same as that for the heat required for the formation of the hydroxides, namely: Mercury, ferric hydroxide, silver, copper, aluminum, lead, zinc, cadmium, cobalt, ferrous hydroxide, nickel, manganese.
3. When cupric and ferrous salts are precipitated together by a soluble hydroxide the iron tends to appear as ferric hydroxide, and this fact explains the apparent exceptional precipitation of the two metals together as hydroxides in spite of the fact that cupric hydroxide is more insoluble than ferrous hydroxide.

CARBONATES.

PREVIOUS WORK.

In 1853 Debus[2] published some quantitative experiments on the fractional precipitation of barium and calcium carbonate. Although some of his conclusions are faulty, an examination of his results shows that calcium competing with barium is precipitated to a greater extent than barium by a soluble carbonate. No other experiments on the fractional precipitation of carbonates have come to my attention except those reported in 1882 by Mills and Bicket[3] on the fractional precipitation of nickel and manganous sulphates and nickel and cadmium sulphates by a slight deficiency of sodium carbonate. Their experiments clearly show that cadmium is precipitated to a greater extent than nickel and that nickel is precipitated to a greater extent than manganese under equal terms of competition. Their experiments were made in the cold and no time was allowed for any possible readjustment. Other experiments by them on the separate precipitability of these salts show that rather complex precipitates are obtained.

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[1] Curtman, L. J., and St. John, A. D., Am. Chem. Soc. Jour., vol. 34, p. 1679, 1912.

[2] Debus, H., Ueber chemische Verwandtschaft: Liebig's Annalen, vol. 85, p. 124, 1853.

[3] Mills, E. J., and Bicket, J. H., Researches on chemical equivalence: Philos. Mag., 5th ser., vol. 13, pp. 169, 177, 1882.

T. Sterry Hunt[1] states that a gypsum solution loses no calcium to crystalline dolomite or crystalline carbonate of magnesium; and that even in the presence of carbon dioxide very little magnesium is taken into solution; but with hydrated magnesium carbonate or hydrate of magnesium there is considerably more magnesium dissolved.

To determine the behavior of certain heavy metals with an excess of carbon dioxide at ordinary temperatures Raikow studied the action of that gas on their hydroxides.[2] He found that basic carbonates were formed with glucinum and yttrium, that acid carbonates were formed with magnesium, thallium, nickel, and cobalt and slightly with manganese and ferrous iron, and that all the other carbonates were normal. His results do not include any statement of the solubility or insolubility of the carbonates so formed, although they indicate that with an excess of carbon dioxide only silver, cadmium, mercurous, lead, and copper salts among the common elements form insoluble precipitates to any great degree of completeness.

SOLUBILITY OF CARBONATES.

The preliminary data available in regard to the solubility of the carbonates are as follows:

Solubility of carbonates in pure water.

	Temperature. °C.	Gram equivalents per liter.	Authority.
$PbCO_3$	18	1.6×10^{-5}	M. Pleissner.[a]
$FeCO_3$	15	6.2×10^{-5}	J. von Essen.[b]
$ZnCO_3$	15	1.7×10^{-4}	Do.
$BaCO_3$	16	1.9×10^{-4}	
$CaCO_3$ (calcite)	16	2.6×10^{-4}	T. Schloesing.[c]
$CaCO_3$ (aragonite)	15	3.4×10^{-4}	J. von Essen.[b]
	25	2.86×10^{-4}	J. Kendall.[d]
	100	3.56×10^{-4}	Do.
	15	3.0×10^{-4}	R. Abegg.[e]
	25	3.06×10^{-4}	J. Kendall.[d]
	100	3.80×10^{-4}	Do.
$SrCO_3$	15	3.2×10^{-4}	J. von Essen.[b]
$CoCO_3$	15	4.4×10^{-4}	Do.
$MnCO_3$	15	4.6×10^{-4}	Do.
$NiCO_3$	15	4.7×10^{-4}	Do.
$MgCO_3$	15	2.4×10^{-3}	Do.
Tl_2CO_3	15	1.7×10^{-1}	
Li_2CO_3	15	3.7×10^{-1}	
Na_2CO_3	15	2.6	

[a] Ueber die Löslichkeit einiger Bleiverbindungen in Wasser: Arbeiten aus dem Kaiserl. Gesundheitsamt, Bd. 26, Heft 3, Berlin (Julius Springer), 1907.
[b] Recherches expérimentales sur la solubilité des carbonates et des bicarbonates, Thesis, Geneva, 1897.
[c] Compt. Rend., vol. 74, p. 1555, 1872.
[d] Philos. Mag., vol. 23, p. 958, 1912.
[e] Abegg, R., Handbuch der anorganischen Chemie, Bd. 2, Abt. 2, p. 157, 1905.

The uncertainty of some of these data is illustrated by the figures for silver carbonate, which does not appear in the table. Cox[3]

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[1] Chemical and geological essays, p. 107, 1878.

[2] Raikow, P. W., Weitere Untersuchungen über die Einwirkung der Kohlensäure auf die Hydrate der Metalle: Chem. Zeitung, vol. 31, p. 55, 1907.

[3] Cox, A. J., Ueber die Löslichkeitsverhältnisse einiger schwerlöslicher Silbersalze: Zeitschr. physikal. Chemie, vol. 46, p. 11, 1903.

gives 17 parts per million, whereas Moissan[1] gives 30 at 15° C. Moissan states that this is increased to 1,040 parts per million when the water is saturated with carbon dioxide. Discrepancies in many of the determinations are probably due to the fact that the acidity of the solutions was not exactly controlled. Even the slight amount of carbon dioxide in the air increases the solubility of carbonates enormously.

EFFECT OF HYDROLYSIS.

Owing to hydrolysis hydroxides, not carbonates, are precipitated with aluminum, ferric, and chromic salts. "Basic carbonates" are precipitated under ordinary circumstances with zinc, nickel, cobalt, copper, and mercuric salts, and boiling removes the carbon dioxide from these salts to a greater or less extent. When hydrolysis is not so pronounced or the hydroxide is more soluble, normal carbonates are formed as with calcium, manganese, ferrous iron, cadmium, silver, lead, and mercurous salts; these are unchanged on boiling, but the carbonates of lead, mercury, and silver are changed to basic carbonates in time. Lead carbonate suspensions become alkaline at 70° according to Abegg.

For carbonates the chief hydrolytic reaction would be

$$CO_3^{--} + HOH = HCO_3^- + OH^-$$

and to a less extent

$$HCO_3^- + HOH = H_2CO_3 + OH^-$$

The degree of hydrolysis of sodium carbonate at 24.1° is shown below for the concentrations stated, the degree expressing the percentage of total sodium present in the form of the hydroxide.

Hydrolysis of sodium carbonate at 24.1° C.

Moles Na_2CO_3 per liter	0.1900	0.0940	0.0477	0.0238
Per cent hydrolysis	2.12	3.17	4.87	[2] 7.10

The hydrolysis of sodium carbonate may be increased by boiling the solution and the removal of carbon dioxide as follows, starting with a normal solution:[3]

Hydrolysis of sodium carbonate produced by boiling.

Time of boiling (hours)	1.25	3.5	6.0	8.5	23.3	38.0
Remaining Na_2CO_3 (per cent)	96.7	94.6	92.7	91.4	87.0	83.8
NaOH formed (per cent)	3.3	5.4	7.3	8.6	13.0	17.2

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[1] Moissan, H., Traité de chimie minérale, vol. 5, p. 580, 1904–1906.

[2] Shields, John, Ueber Hydrolyse in wässerigen Salzlösungen: Zeitschr. physikal. Chemie, vol. 12, p. 167, 1893.

[3] Küster, F. W., and Grüters, Max, Ueber den Zerfall von gelöster Soda in Kohlendioxyd und Natriumhydroxyd: Deutsche chem. Gesell. Ber., vol. 36, p. 748, 1903.

EXPERIMENTS WITH CARBONATES AT ORDINARY TEMPERATURE.

In making fractional precipitations of carbonates two metallic salts were precipitated by less than their chemical equivalent of soluble carbonate and the ratio of the metals in the precipitate determined.

The first precipitations were made in flasks which stood at the temperature of the laboratory and were shaken from time to time. The analyses were carried out by difference—that is, by analyzing an aliquot part of the solution after filtering off the precipitates and subtracting the quantities found from the quantities taken. The general scheme of this ionization and reaction in solution may be illustrated by a mixture of zinc sulphate, calcium sulphate, and sodium carbonate, as follows:

$$\begin{array}{rccc} \mathrm{(Zn,Ca)SO_4} = & \mathrm{(Zn,Ca)^{++}} & + & \mathrm{SO_4^{--}} \\ & + & & + \\ \mathrm{Na_2CO_3} = & \mathrm{CO_3^{--}} & + & \mathrm{2Na^+} \\ & \| & & \| \\ & \mathrm{(Zn,Ca)CO_3} & & \mathrm{Na_2SO_4} \end{array} \tag{4}$$

Since, in the fairly dilute solutions used, the soluble salt, in this experiment sodium sulphate, plays an insignificant part, the scheme may be simplified even further, as follows:

$$\mathrm{(Zn,Ca)^{++} + CO_3^{--} = (Zn,Ca)CO_3} \tag{5}$$

Information can be gained in the first place by considering what will happen when equivalent quantities of the two metals are present, with just enough carbonate for one, and afterward by noting whether the result so found is changed for other proportions of the metals.

From equation (5) it is evident that the equilibrium to be determined may be obtained by precipitating both the metallic salts with a soluble carbonate or by treating a carbonate of one metal with a soluble salt of the other metal. The first method was chiefly used, and the results are presented below.

In these results the radicles and metals are expressed in milligram equivalents, an equivalent being equal in milligrams to the molecular weight of the metal or radicle reduced to a univalent basis. The solution was made up to 1 liter in every experiment, or was calculated to that basis.

Preliminary results of experiments with carbonates at 25° C., with equivalent quantities of two metals present and carbonate enough for one.

Quantity taken (milligram equivalents). Quantity precipitated (milligram equivalents).

Experiment 4.

$ZnSO_4$	8.0	Zinc	6.52
$CaSO_4$	8.0	Calcium	None.
Na_2CO_3	8.0		
Time, 17 days.			

Experiment 5.

$CdSO_4$	20.0	Cadmium	15.5
$ZnSO_4$	20.0	Zinc	4.5
Na_2CO_3	20.0		
Time, 19 days.			

Experiment 6.

$FeSO_4$	10.0	Iron	6.25
$CaSO_4$	10.0	Calcium	None.
Na_2CO_3	10.0		
Time, 3 days.			

Experiment 7.

$CuSO_4$	10.0	Copper	5.30
$FeSO_4$	10.0	Iron	5.35
Na_2CO_3	10.0		
Time, 2 days.			

Experiment 8.

$CuSO_4$	8.0	Copper	6.84
$ZnSO_4$	8.0	Zinc	.76
Na_2CO_3	8.0		
Time, 26 days.			

Prescott and Johnson[1] state that calcium carbonate has no action on zinc salts at ordinary temperature. Since the above experiment shows a considerable precipitation of the zinc—to be exact, 6.52 milligram equivalents in 8 or 81.5 per cent in 17 days—it appears that the duration of the experiment is a factor to be considered. This was confirmed by further experiments, in which finely powdered calcite was introduced into zinc sulphate instead of precipitating the two salts with sodium carbonate.

In one experiment (No. 12) 8 milligram equivalents of calcite were introduced into 8 milligram equivalents of zinc sulphate in a liter. The flask was shaken occasionally at room temperature. After 2 days 16.5 per cent of the zinc was precipitated, and after 24 days 81.2 per cent was precipitated.

In another experiment (No. 9) precipitated calcium carbonate, which had been previously dried and heated, was digested at 20°–25° for 3 hours with dilute zinc sulphate. No zinc was precipitated.

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[1] Prescott, A. B., and Johnson, O. C., Qualitative chemical analysis, 5th ed., p. 179, 1903.

These results show that hasty chemical experiments may lead to greatly mistaken conclusions in geologic investigations. At ordinary temperature several days are required to show the effect; and, in fact, it is not certain that equilibrium was attained in these experiments, but it is certain that calcium carbonate will precipitate considerable zinc in time, even at ordinary temperatures. On the other hand, too long continuation of experiments in glass vessels introduces an uncertainty on account of the slow production of basic salts due to the action of the glass.

The fact that in the first experiment with zinc sodium carbonate was added, whereas in those just mentioned calcite was used, necessitates a consideration of the varieties of calcium carbonate. It is generally true that a freshly precipitated substance is more soluble than the same substance after the lapse of time. With some substances this is due to the size of the particles, with others to the crystalline form, and these facts must be considered in precipitations with solids. As regards calcium carbonate, W. Meigen[1] has shown that when calcium chloride solutions are precipitated by sodium carbonate aragonite separates, in globules at low temperatures, in needles at high temperatures, and that on standing under some conditions this aragonite passes into calcite. Since aragonite is more soluble than calcite, it would be expected to have a slightly greater precipitating power on solutions of metallic salts than calcite. Meigen has shown that this is the case. This study has been continued by his students.[2]

Similar conclusions can be drawn from my own experiments with freshly precipitated calcium carbonate. As a variation of the fractionation in one experiment (No. 13), the calcium sulphate was first precipitated with its equivalent of sodium carbonate, then, without filtration, zinc sulphate was added, and in 2 hours 17.6 per cent of the zinc was precipitated. With the calcium carbonate which had been previously dried and heated no zinc was apparently precipitated, even in 3 hours, but after 24 days the zinc was practically all precipitated.

The conclusion from all the experiments with zinc and calcium at ordinary temperature is that calcium carbonate in any form will ultimately precipitate a considerable amount of zinc from zinc sulphate solutions but that the metathesis takes time to occur. Moreover, it occurs slowly with well-dried calcium carbonate, more quickly with aragonite than with calcite, and most quickly with freshly precipitated calcium carbonate.

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[1] Naturf. Gesell. Freiburg im Breisgau Ber., Bd. 30, p. 64, 1903.

[2] Gassner, L., Weitere Beiträge zur Kenntniss des kohlensauren Kalks: Inaug. Diss., Freiburg im Breisgau, 1906.

These results immediately suggest new experiments concerning the action of calcium carbonate on salts of iron, aluminum, chromium, cobalt, nickel, and manganese. It is held in qualitative analysis that a suspension of freshly precipitated calcium carbonate will precipitate ferric, aluminum, and chromic salts in the cold, but have no action on ferrous, cobalt, nickel, manganese, and zinc salts. Chromic salts are said to precipitate more slowly than aluminum or ferric salts.[1]

According to Meigen's researches,[2] a hundredfold excess of calcite precipitated a 0.045 normal solution of manganese to the extent of 2.9 per cent in 72 hours at 17°, and aragonite precipitated 70.2 per cent under the same conditions.

In experiment 21 calcite was tried with nickel sulphate; 5.10 milligram equivalents of nickel sulphate and 4 milligram equivalents of sodium sulphate in 500 cubic centimeters of water were shaken occasionally with 4 milligram equivalents of powdered calcite for 17 days. The precipitate then showed 0.36 milligram equivalents of nickel and 3.89 milligram equivalents of calcium. Hence the precipitation of the nickel by calcite after 17 days was slight, only about 7 per cent of the whole quantity, but experiment 87 shows that time is an important factor in this action and that eventually nickel is very largely if not completely precipitated.

Magnesium carbonate, like calcium carbonate, is known to exist in several forms which differ in solubility and which must therefore also differ in their capacity for precipitating other carbonates. The most soluble form is the trihydrate, $MgCO_3.3H_2O$. A liter of pure water saturated with this salt contains 0.23 gram of magnesium and 0.42 gram carbon dioxide at 20°, according to Auerbach,[3] in the absence of any excess of carbon dioxide. I have found its solubility under atmospheric conditions, that is, its solubility in water in equilibrium with air containing the normal amount of carbon dioxide, to be somewhat greater, namely, 0.36 gram magnesium per liter, total carbon dioxide 1.01 gram per liter. Amorphous magnesite was found to be much less soluble than this. No experiments were made with crystallized magnesite, which is rather difficult to obtain.

Other fractional experiments were made, beginning with experiment 22, the results of which, together with the preceding experiments, are shown in the following table, all results corresponding to a volume of 1 liter. In most experiments 8 milligram equivalents of sodium carbonate were used, but a few variations were made, as follows: Experiment 32, 10.28; experiment 34, 8.80; experiment 39, 8.30; experiments 71 and 74, 16 milligram equivalents of sodium carbonate.

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[1] Prescott, A. B., and Johnson, O. C., Qualitative chemical analysis, 5th ed., p. 154, 1903.

[2] Op. cit., p. 83.

[3] Auerbach, F., Zeitschr. Elektrochemie, vol. 10, p. 161, 1904.

Summary of fractional precipitations of carbonates at ordinary temperature.

Experiment.	Quantity of mixture taken (milligram equivalents per liter).		Duration of experiment (days).	Quantity of the metal found in precipitate (milligram equivalents).	
4	8 $ZnSO_4$	8 $CaSO_4$	17	6.52 zinc	Tr. calcium.
5	20 $CdSO_4$	20 $ZnSO_4$	19	15.5 cadmium	4.5 zinc.
6	10 $FeSO_4$	10 $CaSO_4$	3	6.25 iron	Tr. calcium.
7	10 $CuSO_4$	10 $FeSO_4$	2	5.30 copper	5.35 iron.
8	8 $CuSO_4$	8 $ZnSO_4$	26	6.84 copper	0.76 zinc.
22	8 $Pb(NO_3)_2$	8 $AgNO_3$	4	8.00 lead	0.08 silver.
23	8 $Pb(NO_3)_2$	8 $Cd(NO_3)_2$	6	8.00 lead	0.42 cadmium.
24	8 $Zn(NO_3)_2$	8 $Pb(NO_3)_2$	6	7.96 lead	Tr. zinc.
25	8 $AgNO_3$	8 $HgNO_3$	24	2.28 silver	7.98 mercury.
26	8 $AgNO_3$	8 $Cd(NO_3)_2$	4	0.30 silver	7.18 cadmium.
27	8 $ZnSO_4$	8 $NiSO_4$	10	5.00 zinc	1.50 nickel.
28	8 $AgNO_3$	8 $Zn(NO_3)_2$	8	1.60 silver	3.96 zinc.
29	8 $FeSO_4$	8 $NiSO_4$	1	4.20 iron	3.06 nickel.
30	8 $FeSO_4$	8 $Zn(NO_3)_2$	1	2.66 iron	2.64 zinc.
31	8 $Cd(NO_3)_2$	8 $HgNO_3$	11	3.54 cadmium	7.36 mercury.
32	8 $MnSO_4$	8 $CaSO_4$	2	6.56 manganese	1.64 calcium.
33	8 $NiSO_4$	14.54 $MgSO_4$	5	5.94 nickel	Tr. magnesium.
34	8 $NiSO_4$	8 $MnSO_4$	9	4.04 nickel	3.80 manganese.
39	8 $AgNO_3$	8 $MnSO_4$	7	3.98 nickel	5.76 manganese.
41	8 $AgNO_3$	8 $CaSO_4$	7	6.80 silver	1.56 calcium.
42	8 $CaSO_4$	8 $MgSO_4$	8	1.60 calcium	1.12 magnesium.
55	8 $HgNO_3$	8 $Pb(NO_3)_2$	6	3.50 mercury	0.75 lead.
60	8 $CuSO_4$	8 $CdSO_4$	8	7.24 copper	0.20 cadmium.
64	8 $NiSO_4$	8 $AgNO_3$	6	3.16 nickel	2.96 silver.
71	16 $ZnSO_4$	16 $MnSO_4$	(a)	11.96 zinc	8.96 manganese.
74	16 $MnSO_4$	16 $CaSO_4$	(b)	14.80 manganese	5.70 calcium.
78	8 $ZnSO_4$	8 $CdSO_4$	15	1.26 zinc	2.34 cadmium.
87	8 $NiSO_4$	8 $CaSO_4$	800	7.99 nickel	1.80 calcium.
90	20 $Fe(NO_3)_2$	20 $Pb(NO_3)_2$	1	2.40 iron	19.0 lead.
91	20 $Fe(NO_3)_2$	20 $Cu(NO_3)_2$	1	10.65 iron	10.20 copper.
92	20 $FeSO_4$	20 $CdSO_4$	1	2.90 iron	11.6 cadmium.
93	20 $ZnSO_4$	20 $FeSO_4$	1	15.80 zinc	4.2 iron.

[a] 18 hours. [b] 1 hour.

The results show that very rarely was a complete separation effected in the fractionation in the time allowed; in most of the experiments both metals were found in the precipitate and filtrate. The separations are far less sharp than those obtained with sulphides. The precipitation series deduced from these experiments is shown in the table below. The numbers in the third column indicate the ratio, in equivalents, of the predominating metal to the one in smaller amount in the precipitate. Not all the experiments have been made which could be made; conversely some of the orienting experiments were later seen to show little except that the two metals were widely separated in the series.

Precipitation series deduced from the experiments on fractional precipitation of carbonates and relative precipitation of the two metals.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.	Ratio of major to minor constituent.
55	Mercury	Lead	Large.
31	do	Cadmium	2.1
25	do	Silver	3.5
59	Lead	Copper	Large.
90	do	Iron	6.5
23	do	Cadmium	19.0
24	do	Zinc	Large.
22	do	Silver	100.0
7, 91	Copper	Iron	1.0
8	do	Zinc	9.0
60	do	Cadmium	36.0
78	Cadmium	Zinc	1.9
92	do	Iron	4.0
67	do	Nickel	2.8
26	do	Silver	25.0
28	Zinc	do	2.5
27	do	Nickel	3.3
4	do	Calcium	6.5
71	do	Manganese	1.3
93	do	Iron	3.7
7	Iron	Copper	1.0
30	do	Zinc	1.0
29	do	Nickel	1.4
6	do	Calcium	6.3
34	Nickel	Manganese	1.1
33	do	Magnesium	Large.
87	do	Calcium	Do.
64	do	Silver	1.1
32, 74	Manganese	Calcium	4.0
41	Silver	do	4.4
42	Calcium	Magnesium	1.4

Incidental to the determination of relative solubility the experiments showed that metallic silver was precipitated with ferrous and manganous salts and there was also a very slight darkening of the precipitate with nickelous salt. The exact position of silver is therefore in some doubt, but it is certainly below zinc.

The positions of manganese and nickel are inconsistent with the recorded solubilities. Either the solubility of manganese carbonate should be less than that of calcium carbonate or there was oxidation of the manganese salt in experiment 70. Nickel shows a similar discrepancy.

The experiments further throw doubt on the solubility of ferrous carbonate given on page 29, although it must be said that the fractionations with ferrous sulphate were not very satisfactory. The difficulty was partly due to the ready oxidizibility of ferrous sulphate and partly to the apparent tendency of iron to enter into double compounds containing an atom of iron to one of the other metal. There is also a tendency toward the formation of bicarbonates, which is considered on page 37.

The heats of precipitation for the metallic carbonates are so small that no apparent regularity exists in the relation between the heats and the positions in the precipitation series.

RESULTS OF EXPERIMENTS WITH BICARBONATES.

The effect of basic carbonates on the fractionations and the elimination of this effect will now be considered. If in any precipitation of carbonate a hydroxide of one of the metals possesses such a small solubility that the hydrolysis of the carbonate would result in exceeding the solubility product of the hydroxide, more or less "basic salt" will be formed. These precipitates are ordinarily considered to be indefinite mixtures of hydroxide and carbonate, but it seems highly probable that either a pure carbonate, a hydroxide, or a definite basic salt would result if time were allowed for the attainment of equilibrium, for it has been shown that many days are often required for the attainment of a stable state at ordinary temperatures. This is another instance where the duration of the experiment determines the final product.

It is possible that a basic carbonate of one metal might form at the same time as a bicarbonate of another metal. There is some evidence of this in experiments 87, 92, and 93. In experiment 92 the mother liquor showed 1.1 milligram equivalents of HCO_3^-, and in experiment 93 it showed 5.3 milligram equivalents of HCO_3^- per liter.

In order to ensure that carbonates alone were being precipitated the experiments might have been carried out in the presence of a certain excess of carbon dioxide. As a much simpler means to the same end, however, a number of experiments were made with sodium bicarbonate as precipitating agent. The only difficulty encountered in this procedure was the rather large solubility of the bicarbonates of certain metals. The experiments were as follows:

Fractional precipitations with sodium bicarbonate.

Quantity taken (milligram equivalents).		Quantity precipitated (milligram equivalents).	
Experiment 35.			
$CuSO_4$	8.0	Copper	6.08
$ZnSO_4$	8.0	Zinc	5.84
$NaHCO_3$	8.0		
Time, 9 days.			
Experiment 36.			
$CdSO_4$	8.0	Cadmium	5.46
$ZnSO_4$	8.0	Zinc	1.60
$NaHCO_3$	8.0		
Time, 3 days.			
Experiment 37.			
$HgNO_3$	8.0	Mercury	7.54
$Zn(NO_3)_2$	8.0	Zinc	None.
$NaHCO_3$	8.0		
Time, 20 hours.			

Fractional precipitations with sodium bicarbonate—Continued.

Quantity taken (milligram equivalents).		Quantity precipitated (milligram equivalents).	

Experiment 38.

$Pb(NO_3)_2$	8.0	Lead	7.82
$Cu(NO_3)_2$	8.0	Copper	0.16
$NaHCO_3$	8.0		
Time, 3 days.			

Experiment 44.

$ZnSO_4$	8.1	Zinc	0.70
$FeSO_4$	8.0	Iron	4.36
$NaHCO_3$	8.0		
Time, 24 hours.			

Experiment 45.

$ZnSO_4$	8.1	Zinc	2.14
$NiSO_4$	8.0	Nickel	0.82
$NaHCO_3$	9.0		
Time, 8 days.			

Experiment 46.

$ZnSO_4$	8.0	Zinc	1.06
$AgNO_3$	8.0	Silver	2.90
$NaHCO_3$	8.0		
Time, 8 days.			

Experiment 47.

$AgNO_3$	8.0	Silver	3.70
$MnSO_4$	8.0	Manganese	4.32
$NaHCO_3$	8.0		
Time, 11 days.			

Experiment 48.

$ZnSO_4$	40.0	Zinc	12.1
$FeSO_4$	40.0	Iron	21.2
$NaHCO_3$	40.0		
Time, 20 hours.			

Experiment 51.

$FeSO_4$	32.0	Iron	9.16
$MnSO_4$	32.0	Manganese	21.92
$NaHCO_3$	22.0		
Time, 1 day.			

Experiment 52.

$CuSO_4$	8.0	Copper	5.64
$CdSO_4$	8.0	Cadmium	0.40
$NaHCO_3$	8.0		
Time, 5 days.			

Experiment 53.

$HgNO_3$	8.0	Mercury	Nearly all.
$Pb(NO_3)_2$	8.0	Lead	Trace.
$NaHCO_3$	8.0		
Time, 5 days.			

Fractional precipitations with sodium bicarbonate—Continued.

Quantity taken (milligram equivalents).		Quantity precipitated (milligram equivalents).	
Experiment 54.			
$HgNO_3$	8.0	Mercury	Nearly all.
$Cd(NO_3)_2$	8.0	Cadmium	Trace.
$NaHCO_3$	8.0		
Time, 4 days.			
Experiment 57.			
$CdSO_4$	8.0	Cadmium	7.60
$MnSO_4$	8.0	Manganese	5.96
$NaHCO_3$	8.0		
Time, 5 days.			
Experiment 72.			
$ZnSO_4$	16.0	Zinc	6.84
$MnSO_4$	16.0	Manganese	10.24
$NaHCO_3$	16.0		
Time, 18 hours.			
Experiment 88.			
$NiSO_4$	16.0	Nickel	1.88
$CaSO_4$	16.0	Calcium	0.20
$NaHCO_3$	16.0		
Time, 5 days.			

Summary of results of fractional precipitation with sodium bicarbonate at 15°–20° C., arranged in the order of solubility deduced from the experiments.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.	Ratio of major to minor constituent.
53	Mercury	Lead	([a])
54	do	Cadmium	([a])
37	do	Zinc	([a])
38	Lead	Copper	49.0
52	Copper	Cadmium	14.0
50	do	Ferrous iron	1.6
35	do	Zinc	1.0
57	Cadmium	Manganese	1.3
49	do	Ferrous iron	6.4
36	do	Zinc	3.4
89	do	Silver	92.0
51	Manganese	Ferrous iron	2.5
72	do	Zinc	1.5
46	Silver	do	2.7
44, 48	Ferrous iron	do	1.7
45	Zinc	Nickel	2.6
88	Nickel	Calcium	9.4
	Calcium		
	Magnesium		

[a] Chiefly mercury.

From these results it appears that when bicarbonates are used instead of carbonates the principal changes are that ferrous iron, zinc, and nickel fall below silver in the series.

EXPERIMENTS WITH CARBONATES AT HIGHER TEMPERATURES

At 100° C. bicarbonates are no longer stable at low pressures, although the last traces of carbon dioxide are held very tenaciously by solutions containing calcium or magnesium salts. Under high pressures of carbon dioxide and at elevated temperatures the bicarbonates would no doubt persist. The compounds stable under these conditions, however, and their solubilities remain to be determined. A few solubilities have been measured in solutions saturated with carbon dioxide at a pressure of a few atmospheres, but mostly at ordinary temperatures. The crystallization of dolomite at 150° C. has been noted. Of course many of the metallic carbonates become basic as the temperature rises, as has already been stated, and some lose carbon dioxide on boiling. Hence in most of the experiments the precipitation was made cold and the flask and contents then heated to 60°–80° C.

In experiment 16 a solution containing 5.43 milligram equivalents of cadmium sulphate and 5.43 milligram equivalents of zinc sulphate was precipitated with 5.43 milligram equivalents of sodium carbonate in a volume of 250 cubic centimeters. After boiling three hours the precipitate contained 4.76 milligram equivalents of zinc and 0.60 milligram equivalents of cadmium.

In experiment 18 a solution containing 8 milligram equivalents of nickel carbonate was boiled one hour with 8 milligram equivalents of calcium sulphate. No nickel dissolved.

In experiment 20 a solution containing 8.81 milligram equivalents of cadmium sulphate and 8.81 of nickel carbonate was boiled five hours in the presence of 8.81 milligram equivalents of sodium sulphate. A small amount of cadmium was precipitated.

In experiment 66 the attempted fractionation of manganese sulphate and silver nitrate resulted in a reduction of the silver salt and oxidation of the manganese.

In experiment 70 the precipitate formed from the sulphates of manganese and calcium turned brown in about a quarter of an hour, showing a slight oxidation of the manganese.

Further results follow.

Fractional precipitations with sodium carbonate at 60°–80° C.

Quantity taken (milligram equivalents).		Quantity precipitated (milligram equivalents).	
Experiment 78.			
$Hg(NO_3)_2$	16. 0	Mercury	8. 88
$Pb(NO_3)_2$	16. 0	Lead	5. 2
Na_2CO_3	16. 0		
1 hour at 60° C.			
Experiment 79.			
$Pb(NO_3)_2$	16. 0	Lead	10. 24
$Cu(NO_3)_2$	16. 0	Copper	6. 68
Na_2CO_3	16. 0		
1 hour at 80° C.			
Experiment 80.			
$Ag(NO_3)_2$	12. 0	Silver	11. 00
$MgSO_4$	12. 0	Magnesium	. 40
Na_2CO_3	12. 0		
1 hour at 70° C.			
Experiment 82.			
$ZnSO_4$	16. 0	Zinc	13. 80
$FeSO_4$	16. 0	Iron	4. 72
Na_2CO_3	16. 0		
1 hour at 70° C.			
Experiment 83.			
$CdSO_4$	16. 0	Cadmium	14. 32
$FeSO_4$	16. 0	Iron	2. 04
Na_2CO_3	16. 0		
1 hour at 70° C.			
Experiment 84.			
$FeSO_4$	16. 0	Iron	0. 68
$NiSO_4$	16. 0	Nickel	10. 0
Na_2CO_3	18. 0		
1 hour at 70° C.			
Experiment 85.			
$CaSO_4$	12. 0	Calcium	Undetermined.
$FeSO_4$	12. 0	Iron	8. 44
Na_2CO_3	12. 0		
1 hour at 70° C.			
Experiment 86.			
$CuSO_4$	16. 0	Copper	9. 08
$FeSO_4$	16. 0	Iron	6. 72
Na_2CO_3	16. 0		
1 hour at 70° C.			

These results are collected in the following table:

Summary of results of fractional precipitation with sodium carbonate at 60°–80° C., arranged in the order of solubility deduced from the experiments.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.	Ratio of major to minor constituent.
78	Mercury	Lead	1.7
76	do	Copper	4.5
59, 62, 79	Lead	do	1.5
15	Copper	Cadmium	3.6
86	do	Ferrous	1.4
17	do	Silver	2.1
77	Zinc	Cadmium	1.1
82	do	Iron	2.9
67	Cadmium	Nickel	2.7
83	do	Iron	7.0
84	Nickel	do	15.0
73	do	Calcium	10.0
65	do	Silver	17.0
94	do	Manganese	1.0
85	Iron	Calcium	
95	Manganese	do	Chiefly manganese.
75	Calcium	Silver	1.5
80	Silver	Magnesium	27.0
	Magnesium		

The results at higher temperatures show only minor changes from the series at ordinary temperatures. Zinc appears above cadmium, probably owing to the formation of oxide. Nickel appears above iron, but as there is some doubt about their relative positions in the series at ordinary temperatures, this change is not to be emphasized. This shows that the experiments at ordinary temperatures yield conclusions of fundamental significance.

In experiment 86 the ferrous iron was partly oxidized, presumably at the expense of cupric sulphate. Of the iron in the filtrate 24 per cent was in the ferric condition. The experiments with ferrous salts were all made in a special precipitating flask in an atmosphere of hydrogen, so that oxidation by air was sufficiently avoided.

SUMMARY OF RESULTS OF EXPERIMENTS WITH CARBONATES.

1. Calcite introduced into a dilute solution of zinc sulphate precipitates the zinc slowly, requiring two or three weeks to precipitate most of the zinc.

2. Freshly precipitated calcium carbonate acts more rapidly in precipitating metallic salts than any other form, and aragonite and calcite follow in the order named.

3. The precipitating action of calcite on manganese, nickel, and silver salts is less marked than on zinc, cadmium, copper, lead, and mercury salts.

4. When a mixture containing two equivalents of two metallic salts, one equivalent of each, is precipitated by one equivalent of a soluble carbonate, a fractionation occurs, and the extent of this fractionation has been determined approximately for a large number of substances.

5. The series obtained, beginning with the metals precipitated to the greatest extent, with sodium carbonate at ordinary temperature is mercury, lead, copper, cadmium, zinc, ferrous iron, nickel, manganese, silver, calcium, magnesium.

6. The series obtained with sodium bicarbonate at ordinary temperature is mercury, lead, copper, cadmium, manganese, silver, ferrous iron, zinc, calcium, magnesium.

7. The series obtained in warm solutions with sodium carbonate is mercury, lead, copper, zinc, cadmium, nickel, iron, calcium, silver, magnesium.

8. Silver salts are partly reduced by ferrous and manganous salts; possibly also by nickelous salts, this effect becoming more marked as the alkalinity increases.

9. In the presence of bicarbonates zinc shows relatively greater solubility than cadmium, and nickel is likewise relatively more soluble than when precipitated with normal carbonate.

10. With rising temperature the precipitates from cadmium, iron, and silver salts appear to increase in solubility relatively faster than the others.

11. The presence of cupric sulphate greatly intensifies the tendency of ferrous salts to oxidize.

SILICATES.

PREVIOUS WORK.

Since many of the natural silicates have been formed under the condition of equilibrium with a magma it is obvious that they will not be in equilibrium with aqueous solutions. In order to complete the study of fractional precipitation, however, it appeared desirable to see if there would be any selective action when solutions containing more than one metallic salt were precipitated by a soluble silicate. Jordis has already studied the precipitation of single metallic silicates from soluble salts[1] with reference to their composition. His experiments with ferric salts,[2] however, are probably complicated by the phenomena of hydrolysis, but he suggests that the behavior of colloids must be considered.

EXPERIMENTS WITH SILICATES AT ORDINARY TEMPERATURE.

My own experiments have consisted of attempts at fractional precipitations of metallic salt solutions by amounts of soluble silicates insufficient for both the metallic constituents. Although it was expected that the sodium silicate, being hydrolyzed, would behave like

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[1] Jordis, Eduard, Zur Chemie der Silikate: Zeitschr. angew. Chemie, vol. 19, p. 1697, 1906; Jour. prakt. Chemie, vol. 77, pp. 226-261, 1906; idem, vol. 81, p. 303, 1910.

[2] Jordis, Eduard, and Lincke, P., Beiträge zur Kenntnis der Metall-Silicate: Jour. prakt. Chemie, vol. 81, p. 289, 1910.

caustic soda, it seemed desirable to determine whether the silicic acid would participate in the reaction. After the results with the hydroxides, it was not surprising to find that in general one metal was precipitated to a greater extent than the other. Moreover, most of the silica was carried down with the precipitate. The results are shown in the following table, where the concentrations are expressed in millimoles per liter, one millimole being a thousandth of the molecular weight taken in grams. A diluted water-glass solution was used as the soluble silicate. The ratio of SiO_2 to Na_2O in it was 3.09 to 1.00. It was free from other metals except for a trace of iron and alumina. After precipitation the solutions stood at about 30° C. for the periods noted in the table. The last column in the table shows the silica not precipitated by the metallic salts present. Sulphates were used except with lead and calcium salts, where nitrates were employed.

Results of the fractional precipitation of silicates, arranged in the order of the solubility deduced from the experiments.

Experiment.	Time (days).	Quantities precipitated (millimoles).	SiO_2 not precipitated (millimoles).
114	97	4.8 copper, 0.2 lead, 11.2 SiO_2	4.0
115	91	6.7 copper, 0.7 zinc, 12.8 SiO_2	2.4
116	91	6.6 copper, no cadmium, 12.2 SiO_2	3.0
117	107	8.1 zinc, 5.6 manganese, 13.0 SiO_2	3.2
118	97	5.1 zinc, 0.1 silver, 11.9 SiO_2	3.3
119	31	5.1 zinc, 2.6 nickel, 10.5 SiO_2	4.7
120	102	5.9 manganese, 4.2 cadmium, 12.9 SiO_2	2.3
121	31	Very little cadmium and zinc, 12.5 SiO^2	2.7
122	95	5.13 nickel, no calcium, 12.9 SiO_2	2.3
123	97	4.8 magnesium, 0.2 calcium, 13.0 SiO_2	2.2
[a] 124	95	13.0 nickel, 0.8 calcium, 28.1 SiO_2	2.3
[a] 125	95	10.7 magnesium, 2.9 calcium, 27.6 SiO_2	2.8

[a] Double quantities taken.

Quantities taken in each experiment:
9.10 millimoles M_1SO_4 per liter of the mixture.
9.10 millimoles M_2SO_4 per liter of the mixture.
4.95 millimoles Na_2O, 15.2 millimoles SiO_2 per liter of the mixture.

SUMMARY OF RESULTS OF EXPERIMENTS WITH SILICATES.

From the above results it appears that:

1. The order of precipitability of the metals by soluble silicate solutions is roughly as follows, beginning with the most precipitable: Copper, zinc, manganese, cadmium, lead, nickel, silver, magnesium, calcium.
2. The metals are precipitated almost as they would be by solutions of caustic soda, so that no marked specific effect appears to be due to the presence of the silicate.
3. Most of the silica is precipitated.
4. Some silica remains in solution, even with an excess of the metallic salt, and the quantity that remains appears to be independent of the nature of the metallic salt.

GENERAL VIEW OF THE RESULTS OF THE INVESTIGATION.

For comparison the several series obtained in the study of fractional precipitation in aqueous solution have been brought together in the following table:

Order of solubility for each class of compounds deduced from these experiments on fractional precipitation.

Sulphides.	Carbonates.	Bicarbonates.	Hydroxides.	Silicates.
Palladium			Ferric	
Mercury	Mercury	Mercury	Aluminum	
Silver	Lead	Lead		
Copper	Copper	Copper	Copper	Copper.
Bismuth				
Cadmium	Cadmium	Cadmium		
Antimony				
Tin	Zinc		Zinc	Zinc.
Lead			Lead	Manganese.
Zinc				Cadmium.
Nickel	Iron			Lead.
Cobalt				
Ferrous	Nickel		Nickel	Nickel.
Arsenic				
Thallium	Manganese	Manganese		
Manganese	Silver	Silver	Silver	Silver.
		Ferrous	Ferrous	
		Zinc	Manganese	
	Calcium	Calcium	Magnesium	Magnesium.
	Magnesium	Magnesium	Calcium	

It would be possible to work out still other series by fractional precipitation. For example, the series of chlorides would be relatively short, whereas that of the phosphates would be longer, for most phosphates are insoluble. The compounds studied, however, cover the ordinary geologic transformations and the studies show the general relations. Furthermore, in the tabulation of the results no attempt has been made to do more than arrange the several series in parallel columns. By a scheme that would exhibit cross relations all possible compounds might be arranged in a single series that would show the order of precipitation under like conditions. Such a series, however, would have little practical application, for several reasons. A comparison of two compounds with no common radicle would really imply the possible existence of at least four compounds, a degree of complexity greater than that considered in the present study of fractional precipitation. Furthermore, the effects of mass action are always conjoined with the solubility requirements, a fact illustrated by the relations of certain silver haloids at Tonopah, Nev.[1] In this locality silver chloride, cerargyrite, was deposited before the chlorobromide, embolite, and the

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[1] Burgess, J. A., The halogen salts of silver and associated minerals at Tonopah, Nev.: Econ. Geology, vol. 6, p. 13, 1911.

iodide, iodyrite, which is more insoluble than the cerargyrite, probably because of the great excess of chlorides in the original solution. This series well illustrates the application of the mass law. Silver iodide is more insoluble in water than silver chloride, but if a solution of a silver salt meets a solution containing a great deal of chloride and very little iodide, after mixing (it being assumed for argument that precipitation does not occur instantaneously) the silver ion concentration will have a fixed value, the chloride ion concentration will be very large, and the iodide ion concentration very small. Hence the solubility product of silver chloride will be exceeded and that of silver iodide not be exceeded, although the solubility product of silver chloride is larger than that of silver iodide. Silver chloride may therefore be deposited before silver iodide, in apparent contradiction to the stated solubilities of the two compounds in water. On the other hand, the solubility of a compound in water is one of its most important properties, and it was to determine the order of these solubilities that these experiments on fractional precipitation were made.

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