THE THEORY OF THE FORMATION OF NICKEL SUL-PHIDE.

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NICKEL sulphide is precipitated from alkaline solutions by hydrogen sulphide gas, and when once formed is insoluble in dilute acids. Notwithstanding this insolubility, however, the precipitate is not formed when the gas is passed through a solution containing this strength of acid. By following out the general laws as to the formation of the metallic sulphides it is possible to explain this anomalous behavior in quite a simple way, and the object of this paper is to present and prove this theory as applied to nickel sulphide. Since cobalt sulphide behaves in the same manner, it is not necessary to go into details regarding it. As yet it is not known whether ions of sulphur exist in the free state, $\overset{=}{S}$, or are always combined with hydrogen in the form $\overset{-}{HS}$. *In this paper we shall consider that free ions of sulphur, $\overset{=}{S}$, do exist, but it is only for the sake of simplicity.* If hydrogen sulphide ionizes according to the scheme,

$$H_2S = \overset{+}{H} + \overset{-}{HS},$$

then all sulphides will do the same ; *viz.*,

$$MS + H_2O = \overset{+}{M} + \overset{-}{HS} + \overset{-}{OH},$$
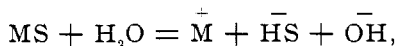
so that the relation of the concentrations of $\overset{-}{HS}$ ions in the two sulphides will be the same as would that of the $\overset{=}{S}$ ions, if they were formed. Since the sulphide is formed, it is simpler to consider $\overset{=}{S}$ ions to be present, for then the sulphide is formed directly. When $\overset{-}{HS}$ ions are present the reaction would be

$$\overset{++}{M} + 2\overset{-}{Cl} + 2\overset{-}{HS} + 2\overset{+}{H} = MS + H_2S + 2\overset{+}{H} + 2\overset{-}{Cl},$$
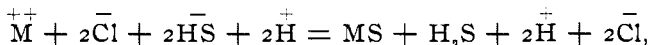
the result being the same, but reached in a more complicated

way. It is to be remembered then that, although we speak of $\overset{-}{S}$ ions, it is not necessary that they exist, for all conclusions will still hold with $\overset{-}{HS}$ ions, providing only that the metallic sulphides dissociate in the same way as hydrogen sulphide does, a fact which is well known.

All substances are soluble to a certain extent, the term insoluble being only a relative one. Nickel sulphide in water, then, goes into solution to a certain extent, as undissociated nickel sulphide and as ions of $\overset{++}{Ni}$ and $\overset{-\,-}{S}$. The equation of equilibrium which regulates the amount of each of these products is

$$\overset{++}{Ni} \times \overset{-\,-}{S} = K_o \times NiS ;$$
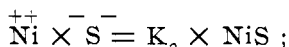
i. e., the product of the concentrations of the ions is equal to the concentration of the undissociated portion multiplied by the ionization constant, the concentrations being expressed in gram-molecules per liter. According to Nernst in a saturated solution, the undissociated portion always remains constant. If by any means, then, the dissociation is driven back, a certain amount of undissociated nickel sulphide will be formed, which will separate out as a solid, since the solution is already saturated with it. In the equation of equilibrium we have, then, two constant terms upon the right side, hence the left side must also remain constant ; *i. e.*,

$$\overset{++}{Ni} \times \overset{-\,-}{S} = K.$$
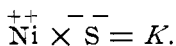
This term K is called the *solubility product* of the nickel sulphide. The meaning of K in words is as follows: If $\overset{++}{Ni}$ and $\overset{-\,-}{S}$ ions are present together in a liquid, no undissociated nickel sulphide will be formed until this product is exceeded, in which case enough undissociated nickel sulphide will be formed to cause the product of the concentrations of the ions still free to just reach this value, K. The undissociated NiS will first saturate the solution, the remainder separating out as a solid. The amount of $\overset{++}{Ni}$ ions will be the smaller the greater the amount of $\overset{-\,-}{S}$ ions, for the product must remain constant. If in a solution we have a small number of metal ions, it is necessary to

have an excess of $\overset{-}{\overset{-}{S}}$ ions in order that the solubility product may be exceeded, and undissociated sulphide formed. The smaller the solubility product the smaller will be the number of $\overset{-}{\overset{-}{S}}$ ions necessary for precipitation. Upon the size of the solubility product depends, then, the behavior of the salt solutions of a metal toward hydrogen sulphide gas. If the product is small enough to be exceeded by the aid of the ions of $\overset{-}{S}$ contained in a solution of hydrogen sulphide gas, the metal will belong to one of the higher analytical groups. If the product is large, then it will only be reached by an alkaline sulphide, for that contains more ions of $\overset{-}{\overset{-}{S}}$ than a saturated solution of hydrogen sulphide gas. We can divide the metals, then, into two groups, those which have products which can be exceeded by the $\overset{-}{\overset{-}{S}}$ ions in hydrogen sulphide solution, and those whose products can only be exceeded by a greater number of $\overset{-}{\overset{-}{S}}$ ions. Metals of the former class will be precipitated by hydrogen sulphide in neutral or acid solutions, those of the latter only in alkaline solutions. Some metals are partly precipitated in neutral solutions. This is due to the fact that the solubility product is at first exceeded by the simple hydrogen sulphide solution. Later, since acid is formed by the reaction, the $\overset{-}{H}$ ions increase and cause the $\overset{-}{\overset{-}{S}}$ ions of the hydrogen sulphide to decrease to such an extent that the product is no longer exceeded. The amount of the sulphide precipitated from the neutral salt depends, then, upon the strength of the acid formed, for the greater its dissociation constant the more the dissociation of the hydrogen sulphide will be affected. Since nickel, cobalt, and zinc are precipitated by hydrogen sulphide in presence of weak acids, their sulphides partake of the characteristics of the higher as well as of the lower group of metals. The solubility products must therefore be smaller than those of the others of the iron group and greater than those of the copper group. We see, then, that the division between the two general groups is not sharply defined, and so we should expect to find an anomalous action of some kind in connection with the metals of the middle group. In the case with zinc this is not observed because it partakes more

of the characteristics of the upper than the lower group, but with nickel and cobalt it is marked. When nickel sulphide is brought in contact with strong hydrochloric acid, hydrogen sulphide gas and nickel chloride are formed. Hydrogen sulphide, however, can only be formed when the product of the concentration of $\overset{+}{H}$ ions multiplied by that of the $\overset{-}{S}\overset{-}{}$ ($\overset{-}{HS}$) ions exceeds the solubility product. Then the gas formed saturates the solution and is given off in the gaseous state. A sulphide which in a water solution has a larger concentration of $\overset{-}{S}\overset{-}{}$ ions than exists in a saturated solution of pure hydrogen sulphide, must be soluble in acid, for the product $\overset{+}{H} \times \overset{-}{S}\overset{-}{}$ ($\overset{-}{HS}$) will be greater than the solubility product of hydrogen sulphide. Such a sulphide could also only be formed in an alkaline solution; *i. e.*, one in which there is a greater number of $\overset{-}{S}\overset{-}{}$ ions than in hydrogen sulphide. The process of solution is quite simple, ions of $\overset{+}{H}$ and $\overset{-}{S}\overset{-}{}$ ($\overset{-}{HS}$) are together in large numbers and so unite to form undissociated hydrogen sulphide. This leaves the solution unsaturated with the ions, hence more of the sulphide dissolves and dissociates, the process continuing until all the sulphide is dissolved or all the acid used up.

A sulphide which contains a smaller number of $\overset{-}{S}\overset{-}{}$ ($\overset{-}{HS}$) ions in a saturated solution than exists in a solution of hydrogen sulphide, will be insoluble in acid, since the solubility product of hydrogen sulphide cannot be exceeded, and the salts will be precipitated by hydrogen sulphide even in the presence of acid.

The smaller the solubility-product of the sulphide the more rapidly will the sulphide be formed by hydrogen sulphide. The greater the solubility-product of a sulphide the more rapidly it will dissolve in acid. Nickel sulphide has a solubility-product which lies between these two extremes, and must contain in a saturated solution a slightly smaller concentration of $\overset{-}{S}\overset{-}{}$ ($\overset{-}{HS}$) ions than hydrogen sulphide (otherwise nickel sulphide would not be formed in presence of acid). The difference in concentration of $\overset{-}{S}\overset{-}{}$ ions must be small, for a little acid prevents

the precipitation by decreasing the difference.   The anomalous behavior of the sulphide is due to this small difference. To cause the sulphide to dissolve it is necessary to have $\overset{\mathbf{--}}{\mathrm{H}}$ ions present to such an extent that the $\overset{=}{\mathrm{S}}$ $(\overset{-}{\mathrm{HS}})$ ions in the hydrogen sulphide formed may be smaller in number than those of the sulphide.   If the acid is of such a strength that hydrogen sulphide in it would have the same, or nearly the same, concentration of $\overset{=}{\mathrm{S}}$ ions as the sulphide, the speed of solution will be almost infinitely slow ; $i.\ e.$, practically no solution will take place during any short period of time.   The sulphide will then remain in its original state.   As the amount of acid is increased, its H ions decrease the number of $\overset{=}{\mathrm{S}}$ $(\overset{-}{\mathrm{HS}})$ ions which are necessary to exceed the solubility-product of the hydrogen sulphide gas, and finally it is formed.   The velocity of the change will increase slowly with the concentration of acid, but no sharp distinction can be made.

If we attempt to precipitate nickel sulphide from a nickel salt in the presence of acid of such strength that hydrogen sulphide has nearly the same concentration of $\overset{=}{\mathrm{S}}$ ions as the nickel sulphide would have if it were formed, no sulphide will be formed for the velocity of formation will be almost infinitely slow.

In short, if two substances have the same concentration of one kind of ion, the one will not be transformed into the other.   If there is but a slight difference between the concentrations, the reaction will take place, but so slowly that it will not be observed until the concentration difference is marked. The substance which is present will always remain unaltered until the difference becomes great enough to cause a certain speed of reaction. This is the proposed theory for the explanation of the behavior of nickel and cobalt sulphides.   In a few words it may be summed up as follows :

The concentration of $\overset{=}{\mathrm{S}}$ $(\overset{-}{\mathrm{HS}})$ ions in a saturated solution of nickel sulphide or cobalt sulphide is so little less than that in a saturated solution of hydrogen sulphide gas, that addition of a small amount of acid causes the latter to decrease to nearly the

value of the former, so that the substance which is already present (hydrogen sulphide or nickel sulphide) remains unchanged, owing to the slight velocity of the change which is proportional to the difference in concentration of the two with respect to the $\overline{S}$ $(\overline{HS})$ ions.[1]

As to the proof for this, the fact that the sulphide is formed in the presence of a large amount of acetic acid and also in that of a small amount of hydrochloric acid shows that the formation is simply a question of the concentration of sulphur ions. Neutral solutions, as the dichloracetate, allow a certain amount of precipitate to be formed ; $i.\ e.$, until the concentration of the $\overset{+}{H}$ ions of the acid formed causes the two concentrations of $\overline{S}$ $(\overline{HS})$ ions to become equalized. The clearest proof would be to compare the solubility-products of the nickel sulphide and hydrogen sulphide,[2] but, unfortunately, this is impossible, for neither is known. It seems, however, hardly necessary to go to such an extent as this to prove the correctness of the theory, for it is thought that the results which have been given already and those that follow are conclusive, although such a final comparison would be of interest.

The results of the analyses given below show quantitatively just what effect an acid has upon the amount of nickel sulphide formed. The amount precipitated in nickel dichloracetate is too small, for the latter was found afterward to contain free acid, the amount of which could not be determined. Nickel acetate is almost completely precipitated in a neutral solution, which was partly prevented by the addition of varying amounts of hydrochloric acid, and the amount of nickel sulphide determined.

[1] Since writing the above, mention of an experiment has been found which is perhaps the best proof of the theory advanced. Baubigny (*Compt. rend.*, 94, 961, 1183, 1251, 1417, 1473, 1595, 1715 ; 95, 34) found that neutral solutions of the salts of nickel are completely precipitated by hydrogen sulphide in one month's time. This shows that the formation of the sulphide takes time and that its non-formation is due to the fact that the process is too slow to be observed during an ordinary analytical precipitation. In the same way it is probable that acid would dissolve the sulphide in the course of time, even when it has no effect as ordinarily attempted.

[2] A method for the determination of S ions in general is the subject of an investigation in the laboratory now, and if results are obtained this comparison will be made.

Mols. per liter.

Nickel dichloracetate, concentration············· 0.253
Dichloracetic acid ······························· 0.1424
Nickel salt precipitated as nickel sulphide······· 0.00722
Dichloracetic acid formed ························· 0.0144
Nickel salt remaining in solution ··········· ··· 0.24

Mols. per liter.

Nickel acetate, concentration ···················· 0.071
Hydrochloric acid ······························· 0.78
Nickel salt as nickel sulphide···················· 0.019
Nickel salt left in solution······················· 0.052

The acetic acid formed in these cases was neglected on account of its slight dissociation.

Mols. per liter.

Nickel acetate, concentration ···················· 0.0624
Hydrochloric acid ······························· 0.083
Nickel salt as nickel sulphide···················· 0.003
Nickel salt left in solution ······················ 0.0594

Mols. per liter.

Nickel acetate, concentration···················· 0.0788
Hydrochloric acid ······························· 0.0807
Nickel salt as nickel sulphide ··················· 0.0139
Nickel salt left in solution······················· 0.0649

Mols. per liter.

Nickel acetate, concentration···················· 0.0723
Hydrochloric acid ······························· 0.079
Nickel salt as nickel sulphide ··················· 0.0112
Nickel salt left in solution······················· 0.0601

Although the solubility products of the metallic sulphides are unknown there is one way in which we may get an approximate relation between them. Zengelis[1] has determined the electromotive force of several kinds of metal ions in contact with tenth-normal solutions of potassium sulphide. Neumann[2] has determined the electromotive force of all the metals in their salt solutions. By combining these measurements by the method of Ostwald[3] it is possible to find the ionic concentrations of the metals in contact with the same, but an unknown amount of $\overline{S}$ $(\overline{HS})$ ions. For each metal we have a certain solubility-product; i. e.,

$$M \times S = K,$$

[1] Ztschr. phys. Chem., 12, 311.
[2] Ibid., 14, 215.
[3] Lehrbuch d. allg. chem., III, 881.

where S and K are unknown. S, however, is the same in the case of all metals ; $i.\ e.$, the concentration of $\overline{\overline{S}}$ ions in a tenth-normal solution of potassium sulphide, hence the solubility-products will be proportional to the ionic concentrations of the metals in the potassium sulphide solution. Using this method, a few relative solubility-products have been determined, and they serve to show the great difference between the metals of the iron group and those of the copper group.[1]

Nickel............ 0.0191	⎫	Concentration of metal ions in
Cobalt 0.0034	⎪	mols. per liter in presence of
		$-\ -$
Copper 0.00021	⎬	the S (HS) ions contained
Lead 0.000024	⎪	in a tenth-normal solution of
	⎭	potassium sulphide.

Zinc, which is completely precipitated by hydrogen sulphide in acetic acid, should have a product still smaller than cobalt, which is not. Cobalt and zinc show the disappearance of the anomalous behavior, cobalt having it to a smaller extent than nickel, and zinc not showing it at all. We see from the results that the solubility-product of nickel sulphide is about 100 times greater than that of copper sulphide and 1000 times greater than that of lead sulphide. This means that equal amounts of solution, containing the same ionic concentration of metal ions, will be precipitated when the concentration of $\overline{S}$ ($\overline{HS}$) ions for nickel, copper, and lead are in the ratio

$$1000 : 100 : 1.$$

There is still one point to be considered in the behavior of nickel and cobalt sulphides. When the sulphides of nickel, cobalt, and zinc are treated with dilute hydrochloric acid, the zinc dissolves, leaving the sulphides of cobalt and nickel behind, notwithstanding the fact that in water zinc sulphide is more insoluble than these. This is also quite easily explained and depends simply upon the salt solution which is formed. When a sulphide is dissolved in acid, as has already been mentioned, the ions of $\overset{+}{H}$ and $\overline{S}$ ($\overline{HS}$) unite to form hydrogen sulphide. This

[1] Other determinations of the relative solubility-products are being made, and it is proposed to find also the absolute values by comparison with the value of one of the more soluble salts, determined by the method of the electrical conductivity.

removes the $\overline{S}$ ($\overline{HS}$) ions of the sulphide from the solution so that more salt dissolves and has its ions removed in the same way. Finally, we have a salt of the metal and hydrogen sulphide gas. The salt formed, if largely ionized, will prevent the sulphide from giving off enough $\overline{S}$ ($\overline{HS}$) ions to reach with the $\overset{+}{H}$ of the acid, the solubility-product of hydrogen sulphide; while if but slightly ionized this effect will not be noticed. The whole process is similar to that of the formation of sulphide from a neutral salt, when the acid formed prevents the hydrogen sulphide from dissociating to an extent sufficient to cause the solubility-product of the sulphide to be exceeded. This is the process which takes place when we attempt to dissolve the sulphides of nickel, cobalt, and zinc in dilute hydrochloric acid. The chlorides of nickel and cobalt are nearly completely ionized ; *i. e.*, the conductivity is found to be almost constant for all dilutions. If then a small amount of the chloride of nickel or cobalt is formed it will prevent any more being produced. In the case of zinc sulphide, however, the ionization is not so great, and, in addition, the solution is hydrolytically dissociated to a great extent. Since hydrolytic dissociation removes zinc ions from the solution, less of the depressing effect upon the solubility of the zinc sulphide is observed and it dissolves. In this way nickel and cobalt sulphides do not dissolve in acid in which zinc sulphide is soluble, since the solubility of these is depressed by the small portion which may dissolve; zinc sulphide, on the contrary, retaining its original solubility, dissolves. As a direct consequence of this the nickel and cobalt sulphides should be formed from the chlorides more readily than zinc sulphide. There are undoubtedly a number of examples of this process where the relation of solubility is reversed, but it is believed that this is the first one in the case of a salt to be observed. If it were possible to find a salt of nickel and cobalt which is ionized to a lesser degree than the corresponding one of zinc, then, if the latter were not hydrolytically dissociated, the relation in regard to solubility would be the same in the acid, which would form that salt, as in water.