[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF IDAHO]

A Study of the Anomalous Behavior of Nickel Sulfide

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Attempts to explain the extremely slow dissolution of nickel sulfide in hydrochloric acid on the basis of a polymeric change were made by Herz.[1] Thiel and Ohl[2] and later Thiel and Gessner[3] extended this idea and postulated the existence of three isomers; however, they reported an inability to obtain anything more than a rough separation of the surmised alpha, beta and gamma forms. From an analysis of the mixtures they concluded that each had the formula NiS.

The rather arbitrary nature of these results and the doubts expressed by some writers[4] were the reasons for beginning a series of studies on the behavior of nickel sulfide. While a theory involving adsorption has been a guide in this work, a discussion of this theory will be reserved for a future paper.

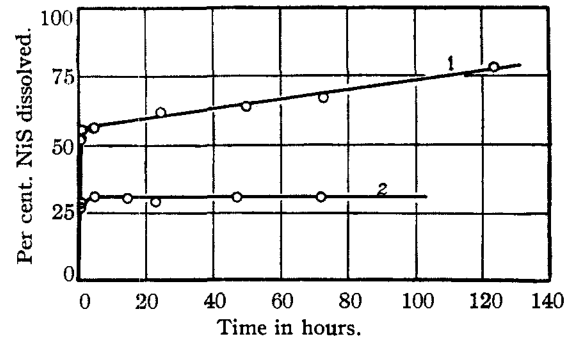

Fig. 1.—Rate of dissolution of NiS in 2 normal HCl: Curve 1, washed sample; Curve 2, saturated with H_2S.

Experimental

Rate of Dissolution in Hydrochloric Acid.—Nickel sulfide samples were prepared by precipitating with hydrogen sulfide an ammoniacal solution of nickel chloride containing 5 g. of nickel chloride per liter. After settling, the precipitate was washed by decantation until the washings gave no test for chlorides, and the sulfide was diluted to the original volume.

Tartar, Bryan and Shinn[5] have shown that the addition of polyvalent anions to a positively charged aluminum hydroxide sol caused a greatly increased rate of dissolution of that sol in hydrochloric acid. It was thought that the addition of polyvalent cations to the negatively charged nickel sulfide might likewise increase its rate of dissolution in hydrochloric acid. Aluminum chloride, chromium chloride, zinc chloride, ferrous chloride and thorium chloride were added to nickel sulfide in 2 *N* hydrochloric acid with little if any effect.

In determining the effect of hydrogen sulfide on the rate of dissolution, the mixture was agitated with a motor stirrer while samples were pipetted out. These samples were placed in 120 cc. bottles, and sufficient hydrochloric acid was added to make the acid concentration 2 *N*.

The bottles were closed with stoppers containing capillary tubes to allow the escape of any hydrogen sulfide evolved and were agitated in a thermostat at 25°. Another set of samples was treated in the same manner except that the mixture was previously saturated with hydrogen sulfide. The addition of the hydrogen sulfide had the effect of peptizing the mixture and of producing a stable nickel sulfide sol. At varying time intervals bottles were removed from the thermostat and the supernatant liquids were analyzed for nickel content. The addition of the hydrogen sulfide decreased the rate of dissolution as shown in Fig. 1.

Influence of Nascent Hydrogen.—Equivalent amounts of various metals were added to nickel sulfide–hydrochloric acid mixtures, and the supernatant liquids were pipetted off after forty-five minutes and analyzed. The results are shown in Table I.

TABLE I

INFLUENCE OF NASCENT HYDROGEN ON THE RATE OF DISSOLUTION

Metal	NiS dissolved, %
None	33.68
Iron	82.22
Manganese	86.95
Chromium	87.30
Aluminum	89.26
Tin	82.05

It is to be noted that all of the metals increased the rate of dissolution of the nickel sulfide. The slight variations are due perhaps to differences in the rate at which hydrogen is evolved by the several metals. Since it was shown that the salts of the metals had no effect, this increased rate could be due only to evolved hydrogen.

Electrolytic hydrogen produced within the system from a platinum electrode, care being taken to avoid diffusion of oxygen into the system, brought about a 60% dissolution in one hour, while a control dissolved to the extent of 30%. Violent agitation with hydrogen and nitrogen from cylinders and carbon monoxide from a formic acid–sulfuric acid generator was without effect.

While no explanation of this phenomenon is offered at this time, it appears doubtful that the hydrogen could bring about a change of polymeric forms.

Adsorption of Hydrogen Sulfide.—During the course of solubility measurements it was noted that very little hy-

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(1) Herz, *Z. anorg. Chem.*, **27**, 390 (1901).

(2) Thiel and Ohl, *ibid.*, **61**, 396 (1909).

(3) Thiel and Gessner, *ibid.*, **86**, 1 (1914).

(4) Weiser, "The Colloidal Salts," McGraw-Hill Book Co., New York City, 1928, pp. 101–104.

(5) Tartar, Bryan and Shinn, THIS JOURNAL, **55**, 2266 (1933).

drogen sulfide gas was evolved. Calculations based on amounts of nickel sulfide dissolved indicated that there should be more than enough to saturate the solvent medium. Accordingly adsorption experiments were carried out by means of the apparatus illustrated in Fig. 2. Since nickel sulfide showed considerable adsorption, measurements were made on other metallic sulfides.

The operation of the apparatus was as follows. Hydrogen sulfide gas was passed through the apparatus to sweep out air. The stopcocks were closed, and the system was allowed to stand for twenty-four hours in order that any remaining trace of oxygen might react with the hydrogen sulfide. The pressure inside the apparatus was then equalized to atmospheric pressure by means of the adjustable leveling tube. The level of the meniscus on the buret was noted. Ten cc. of the substance whose sorption was to be measured was next run into the flask through the separatory funnel. Atmospheric pressure was maintained in the apparatus until equilibrium was attained. This usually required about twenty-four hours. The change in volume of the hydrogen sulfide represented the combined absorption and adsorption. To find the adsorption separate determinations were made on an equal volume of the absorbing liquid. The sorption apparatus was maintained at a temperature of 25°, and all volumes were calculated to 760 mm. pressure.

TABLE II

ADSORPTION OF HYDROGEN SULFIDE BY 0.000415 MOLE OF METALLIC SULFIDES

Medium	Adsorption on sulfide, cc. NiS	PbS	CdS	FeS
Neutral	15.1	5.9	0.9	5.1
0.03 *N* HCl	16.6	4.9	.9	...
.06 *N* HCl	17.4	1.4	.9	...
.08 *N* HCl	18.5	0.0	.9	...
.11 *N* HCl	21.0	.0	.9	...
1.00 *N* HCl	20.7	.0	..	...
2.00 *N* HCl	21.0	.0	..	...

It is to be noted from Table II that the adsorption on nickel sulfide increases with increase in acid concentration until a normality of 0.11 is reached. It seems possible that this may have some bearing on its rate of dissolution. The adsorption on lead sulfide is less than on nickel sulfide and decreases with increase in acid concentration. Adsorption on cadmium sulfide is small but remains constant over a considerable range of acid concentrations. The adsorption behavior parallels qualitatively the solubility behavior of these sulfides.

Composition of Nickel Sulfide.—In order to measure analytically the amount of adsorbed hydrogen sulfide on nickel sulfide particles, it was necessary to prepare, wash and sample in an oxygen-free atmosphere in order to prevent the formation of free sulfur. Nickel chloride was dissolved in freshly boiled water which had been cooled in an atmosphere of nitrogen. The solution was made ammoniacal and hydrogen sulfide was bubbled through until complete precipitation had taken place. The precipitate was allowed to settle, and the ammonium chloride was washed out by allowing a slow stream of oxygen-free water to flow in through an inlet tube and the washings to escape through a trapped outlet tube.

Analyses were made for nickel, total sulfur and sulfur in the supernatant liquid or ultrafiltrate. Sampling was accomplished by forcing the mixture from the flask into a pipet by means of nitrogen from a cylinder. Nickel was determined by titration with potassium cyanide, and the sulfide was oxidized to sulfate with aqua regia and weighed as barium sulfate.

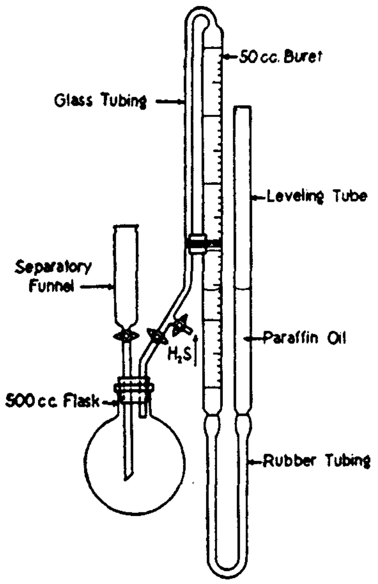

Fig. 2.—Sorption apparatus.

It was found that the addition of hydrogen sulfide to these well washed nickel sulfide–water mixtures accompanied with vigorous shaking produced a rather stable nickel sulfide sol. In analyzing for sulfide in the dispersion medium, it was necessary to prepare an ultrafilter of collodion which was connected directly to the sampling arrangement, thus preventing the occurrence of any oxidation.

The results of these determinations are given in Table III.

TABLE III

S/Ni RATIO OF NICKEL SULFIDE SOLS

	Moles/50 cc. × 10^4				
Sample	Total S	Ultrafilt. S	Diff. S	Ni	Ratio S/Ni
1 (a)	3.90	0.12	3.78	3.72	1.02
(b)	22.20	20.00	2.20	1.17	1.88
2 (a)	3.09	0.12	2.97	2.76	1.08
(b)	24.60	20.30	4.30	1.80	2.38

The (a) samples were taken from the thoroughly washed, unpeptized sulfide suspensions. Fairly homogeneous samples were obtained by constant agitation of the system during withdrawal.

Vigorous shaking for several one-hour periods with the intermittent addition of hydrogen sulfide into the closed system peptized these sols. Samples (b) were withdrawn from a constant level five hours after the last shaking.

The S/Ni ratios of the peptized nickel sulfide sols agree very well with those calculated from the adsorption data.

Summary

1. The initial rate of dissolution of nickel sulfide is dependent upon the concentration of hydrogen sulfide in the system.

2. Nascent hydrogen increases the rate of dissolution.

3. Hydrogen sulfide is more strongly adsorbed on nickel sulfide than on other sulfides investigated, and this adsorption increases with acid concentration.

4. Analysis shows the nickel sulfide to have the composition NiS_x, where x is equal to or greater than one and increases with increase in the hydrogen sulfide concentration in the system.

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[Contribution from the Chemical Laboratory of the University of California]

Racemization in the Preparation of the Grignard Reagent

By C. W. Porter

In the hope of synthesizing an optically active compound with one atom of hydrogen and one of deuterium attached to the asymmetric carbon atom, the Grignard reaction was applied to two optically active alkyl bromides and one active alkylaryl bromide.

Methyl-*n*-hexylcarbinol was resolved into active components by the method of Kenyon[1] and from these the corresponding bromides were obtained by treatment with phosphorus tribromide. No attempt was made to secure optically pure compounds. The bromides obtained had rotations of +22.7 and −20.4° when read in 10-cm. tubes with a sodium arc as the source of light. No racemization occurred under the influence of phosphorus tribromide and good yields of the alkyl bromides were obtained.

In a typical experiment the Grignard reagent was made by mixing 40 g. of active octyl bromide, 120 g. of dry ether, 8 g. of magnesium and a crystal of iodine. The mixture was protected from air and moisture by an atmosphere of dry nitrogen until the reaction, which proceeds spontaneously, was completed. The ether solution of $C_8H_{17}MgBr$ displayed slight optical activity, but this was due to unchanged octyl bromide. When a portion of the Grignard reagent was condensed with acetone and the resulting carbinol was purified by vacuum distillation, the condensation product was found to be optically inactive. An aliquot part of the ether solution of the Grignard reagent was decomposed by water and when the unchanged octyl bromide in this sample was recovered, it was found to be adequate to account for the activity observed in the ether solution of the Grignard reagent.

A series of similar experiments in which optically active methylphenylbromomethanes were substituted for active octyl bromides gave rise to racemic Grignard reagents in the same way.

Conclusion

It is evident that complete racemization occurs when an optically active halide reacts with magnesium in the formation of a Grignard reagent.

Berkeley, California Received April 23, 1935

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[1] Jos. Kenyon, *J. Chem. Soc.*, **121**, 2540 (1922).