2. When phosphoric acid is neutralized with sodium hydroxide and the solution tested with sodium cobaltic nitrite, a misleading precipitate is secured unless a considerable excess of acetic acid is added.
3. Zirconium can be removed by ammonium hydroxide and potassium detected in the filtrate by sodium cobaltic nitrite, after eliminating the ammonium.
4. The best and shortest way of eliminating zirconium prior to testing for potassium by sodium cobaltic nitrite is by throwing the zirconium into a complex ion with tartaric acid and controlling the acidity with sodium hydroxide and acetic acid.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED VERDE COPPER COMPANY]

THE SYSTEM SODIUM SULFIDE-FERROUS SULFIDE[1]

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This investigation deals with the composition diagram of the system Na_2S–FeS obtained from cooling curves on melts of several compositions and by microscopic examination of polished surfaces of frozen samples of the melts. The principal interest from an industrial standpoint was in the liquidus curves and no great effort was made completely to determine the nature of the phases or phase changes at temperatures beneath the liquidus. Therefore the phase diagram as presented is incomplete but contains the reasonable conclusions and certain inferences that seem to be justified by the data.

Preparation of Sodium Sulfide.—Several methods for preparing pure sodium sulfide were considered: reduction of sodium sulfate with carbon; the Hugot[2] method of reacting with sulfur on a solution of sodium in liquid ammonia with subsequent evaporation of excess ammonia; the Hugot method of reacting on molten sodium with hydrogen sulfide; the Sabatier[3] method of dehydrating the hydrated salt, $Na_2S \cdot 9H_2O$; and the reaction[4] obtained by heating sodium carbonate in sulfur vapor. All of these methods were tested by Friedrich,[5] who found that a reasonably pure product could be obtained by heating the hydrated salt in a rapid stream of hydrogen. The hydrated salt first melts in its water of crystallization, solidifying when the mass has reached about 70% of sodium sulfide by weight and leaving a porous mass from which the remainder of the

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[1] The preparation of materials and cooling curves was carried on in the Pacific Experiment Station of the U. S. Bureau of Mines, at Berkeley, California.

[2] Hugot, *Compt. rend.*, **129**, 388 (1899).

[3] Sabatier, *Ann. chim. phys.*, [5] **22**, 66 (1881).

[4] Vauquelin, *ibid.*, [2] **6**, 32 (1817).

[5] Friedrich, *Metall und Erz*, **11**, 79 (1914).

water evaporates. The solid material loses part of its sulfur by hydrolysis so that the final product contains sodium hydroxide. Friedrich's preparation melted at 920°.

This latter method was used in the present investigation because it was the only convenient one by which large quantities could be prepared. The first stage of evaporation was done in a large vacuum desiccator with a small electric heater, whose temperature never exceeded 50°, leaving a product with about 80% of Na_2S. When heated to 150° the final product in the desiccator, when using phosphorus pentoxide as desiccant, contained about 95% of sodium sulfide. This material when melted in a graphite crucible under nitrogen (losing more water during the heating) and cooled slowly indicated by its cooling curve that it froze at 970°. The melting point of the pure material is probably slightly above this temperature.

Preparation of Pure Iron Sulfide.—Two methods were tested: the thermal decomposition of pure pyrite, FeS_2, and the synthesis from iron and sulfur by absorbing sulfur vapor in fused pure iron.

The first method was used by Mostovitsch[6] in preparing iron sulfide analyzing 63.67% of iron and 36.33% of sulfur; the theoretical analysis is 63.52% of iron and 36.48% of sulfur.

In this research some 200 g. of iron sulfide, analyzing 63.5% of iron and 36.4% of sulfur, was made by the following method. A large specimen of very pure Chinese pyrite was ground through 65 mesh, packed in a graphite crucible under charcoal and covered with a graphite cover. It was heated in an electric resistance furnace to 1000°, cooled, reground, repacked in the crucible, heated just above the melting point and cooled in the furnace. A small amount of siliceous slag that had floated to the top was broken off and discarded. The balance had a rainbow luster and could be broken with the fingers into eighth-inch pieces.

When larger quantities of the iron sulfide were required the limitations of the supply of pure pyrite necessitated the use of some other method of preparation. Approximately a hundred grams of Armco iron turnings was mixed with distilled sulfur and placed in a graphite crucible in an Ajax Northrup Induction Furnace. As the furnace heated, the iron and sulfur united and formed a molten pool into which Armco iron strips and sulfur were alternately fed until there was approximately 1500 g. of material in the crucible. Sulfur was then dropped on the molten material until no more was taken up by the melt, which could be determined by observation. The melt was cooled, ground through 65 mesh, mixed with sulfur and remelted. It was kept in the molten condition for ten minutes, the furnace action providing very efficient stirring. The current was shut off and the temperature was taken every thirty seconds, using the thermocouple arrangement described later. While a very sharp freezing point was not obtained (see Fig. 1), the iron sulfide solidified within a few degrees of 1174°. Check analyses gave the composition as 62.84% of iron and 36.92% of sulfur; 99.95% total. Analysis for carbon and oxygen may show the remainder.

Carbon in varying amounts was known to be present in all the melts, coming from the Acheson graphite crucible in which the work was done. The theoretical analysis of pure iron sulfide calls for 63.52% of iron and 36.48% of sulfur. Our preparation therefore consisted apparently of 98.9% of iron sulfide with the remainder excess sulfur and a small amount of carbon. The excess sulfur is probably present as pyrrhotite,

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[6] Mostovitsch, *Ann. First Tomsk Siberian Technological Inst.*, [47] **1**, 1–74 (1925).

Fe_xS_{x+1}, where the subscript x is likely to have a high value. In the amounts of material with which we worked we did not arrive at a product which was slightly deficient in sulfur and which is reported by Allen and co-workers.[7] According to their experience ferrous sulfide dissociates slightly in the vicinity of its melting point, losing sulfur by volatilization and leaving a material with a slight excess of free iron. They located the melting point of pure ferrous sulfide at 1170 ± 5°. Our slightly impure product gave an arrest in its cooling curve at 1174°, showing thereby very good agreement in thermometry with their work.

Apparatus.—Our mixtures of iron sulfide and sodium sulfide were melted in Acheson graphite crucibles with graphite lids in a high frequency induction furnace, the heat being generated by induced currents in the graphite crucibles. Crucibles of about 3 inches outside diameter and containing from 500 to 1000 g. of melt were used. They were placed in the center space of the induction furnace, which consisted of a vertical cylindrical tube of vitreosil around which was packed finely powdered electrically fused magnesia as an insulator. The bottom of the furnace was also of powdered magnesia. The thickness of this thermal insulation was about 3 inches and outside of everything were the copper tubing coils which constituted the inductors of the high frequency furnace. Sufficient electrical capacity was available to start cold and bring a melt to the desired temperature within five minutes, although the usual practice was to use three or four times as long an interval in order to establish a thermal diffusion gradient.

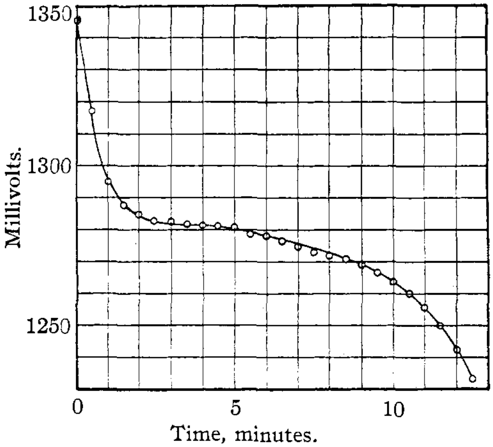

Fig. 1.—Cooling curve of FeS.

Temperatures were read with a platinum–platinum-rhodium couple, frequently calibrated against a similar standard couple which had been standardized by the Bureau of Standards. The Leeds and Northrup Type K potentiometer was used for e.m.f. measurements except where specified. The couple was protected by thin-walled chemical porcelain tubes manufactured especially for this work by Coors, the tubes having an outside diameter of 0.25 inch and being introduced into the melt through a small hole in the graphite cover of the crucible. Melts were not allowed to cool to the 298° polymorphic transition of iron sulfide because at this point the volume change was sufficient to crush the porcelain protecting tube. Therefore, after a cooling curve had been followed to about 400° the crucible was reheated until the protection tube could be withdrawn through remelting of the charge. A new porcelain tube was used with each melt, thereby maintaining adequate protection of the couple. The sodium sulfide was kept under nitrogen and the furnace was swept with nitrogen during melting and cooling. Sodium sulfide was weighed under nitrogen only after cooling with an ice-bath.

Results

In all, eleven cooling curves were obtained which could be used for preparing the phase diagram. The curve for pure iron sulfide, as shown in Fig. 1, has already been mentioned. The arrests in the other cooling

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[7] Allen and co-workers, *Am. J. Sci.*, [4] **33**, 169 (1912).

curves have been tabulated in Table I. Four of them were made with mixtures of iron sulfide and sodium sulfide and the remainder, which were higher in sodium sulfide content, were made by adding more sodium sulfide to the product of a previous melt which was merely reheated in the same crucible, to which was added the new sodium sulfide and a sufficient sample withdrawn for analysis.

TABLE I

EXPERIMENTAL DATA

Run	FeS, %	Arrests, Primary	Eutectic	Materials	Remarks
7	98.6	1174		FeS	....
10	93.5	1088	703–688	FeS + Na_2S	Used portable potentiometer. Eutectic crystals in center
11	86.4	....	694–674	FeS + Na_2S	Used portable potentiometer. Granular crystals in bottom of melt. Diff. structure above
18	86.0	907	699–668	FeS + Na_2S	Large crystals in center and on top of melt
12	81.6	850	699–673	FeS + Na_2S	Used portable potentiometer. Similar structure to top of 11. Crystals in center
13	70.3	701	660–647	Run 12 melt + Na_2S	Top of melt cracked and showing long narrow crystals perhaps 1″ by $^1/_{16}$″
17	64.9	696	665–656	Run 16 melt + FeS	Few crystals
14	60.7	695	638–613	Run 13 melt + Na_2S	....
15	50.6	...	625–549	Run 14 melt + Na_2S	Greenish with crystals in center
16	40.7	653	588–560	Run 15 melt + Na_2S	Greenish black with well formed needles in top centers
19	None	970	.....	Na_2S	....

In addition to our own work, three other points in this system have been reported by F. Thomas,[8] but he has placed an erroneous interpretation on his meager data. His points are shown by crosses in circles in our phase diagram, Fig. 2.

In all cases the mixtures wetted the graphite crucibles and the greater the percentage of sodium sulfide the greater the apparent wetting. The only ocular evidences of segregation in the melts are mentioned in the column of "Remarks" in Table I.

The analyses of the samples from the various melts are indicated in Table II. No difficulty was encountered in analysis of the pure iron sulfide samples, but in all cases where sodium sulfide was present more or less graphite was present from the walls of the crucibles and it was not evenly distributed. Even quadruplicate determinations did not check well until chunks of the melts were rapidly pulverized in a porcelain mortar and screened through a 10-mesh sieve to remove coarse pieces of graphite. There are considerable differences between the analyses expected and those

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[8] Thomas, *Metallurgie*, **7**, 706 (1910).

TABLE II

ANALYSES OF SAMPLES

	Theoretical analysis					Analysis found				
Run	FeS, %	Na_2S, %	Fe, %	Na, %	S, %	Fe, %	S, %	Na, %	Total	
9	100	..	63.54	..	36.46	62.60	37.44	..	100.04	
7	100	..	63.54	..	36.46	62.84	36.92	..	99.95	(Insol. = 0.19)
10	93.5	6.5	59.4	3.8	36.8	56.3	37.1	5.1	98.5	
11	86.4	13.6	54.9	8.0	37.1	55.6	38.4	5.2	99.2	
18	86.0	14.0	54.6	8.2	37.2	49.7	37.7	13.1	100.5	
12	81.6	18.4	51.8	10.8	37.4	48.5	37.5	14.4	100.4	
17	64.9	35.1	41.2	20.7	38.1	39.8	38.2	22.0	100.0	
15	50.6	49.4	32.1	29.1	38.8	31.6	39.0	29.6	100.2	
16	40.7	59.3	25.9	34.9	39.2	23.8	38.5	36.8	99.1	

actually found in several of the samples. In addition to the difficulty due to suspended graphite, there was probably also inhomogeneity due to segregation during cooling and a certain amount of unavoidable oxidation of sodium sulfide to sulfate. Calculating the iron and sodium to sulfide in these analyses, there is a slight excess of sulfur remaining in all cases, reaching a maximum of 2.8% in Run 11, but usually much less than this. Due to all these possible sources of error, the "observed" analyses were not used in preparing the phase diagram.

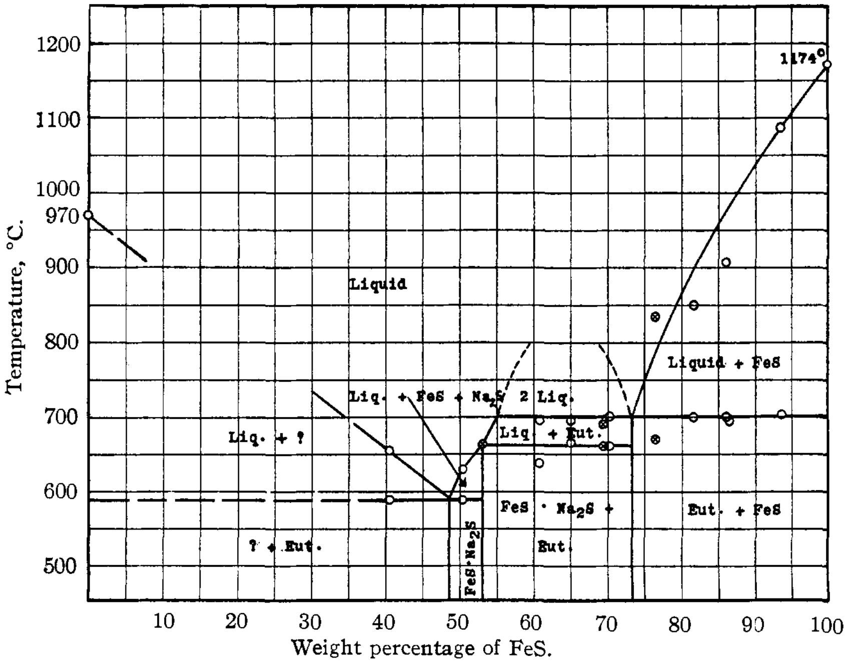

Fig. 2.—The system FeS–Na_2S. ⊗, Thomas; ○, Authors.

Every melt containing sodium sulfide oxidized rapidly if left in air and an odor of hydrogen sulfide arose from the action of moisture. They would crumble to a powder in a short time if left in the open air. All samples were therefore preserved in sealed containers. Contrary to expectation, the melts which reacted with air most quickly were those containing the higher percentages of iron sulfide.

Phase Diagram.—Based largely on the cooling curves and the ratios of iron sulfide and sodium sulfide used, the phase diagram of Fig. 2 was sketched, giving the temperature–composition relationships as far as it was possible to judge them from the few data. To a certain extent this diagram is supported by the metallographic examination of polished sections which is described below. The liquidus of this diagram is fairly well determined, although melts between pure sodium sulfide and 38% iron sulfide were not prepared and the vacant part of the diagram may be more complex than that sketched. The research was financed mainly to determine the liquidus and much work beyond this objective was not justified.

The secondary arrests in the cooling curves were somewhat difficult of interpretation but it is believed the diagram satisfactorily accounts for them. A separation into two conjugate liquids in the region between 55 and 73% of iron sulfide is necessary, although no direct evidence of this was obtained. Furthermore, the formation of a transitory double compound, $Na_2S \cdot FeS$, is assumed in this area of the diagram. The physical evidence supporting this latter conclusion is the presence of a white constituent in the polished surfaces under the microscope, whereas pure iron sulfide is yellowish and is found in the specimens with greater than 73% of iron sulfide. The composition of the white constituent was not determined but is assumed to be a double compound, probably $Na_2S \cdot FeS$, which seems to fit the cooling curves best.

The exact composition of the transitory double compound, while we believe it to be $Na_2S \cdot FeS$, is insufficiently determined. Stromeyer[9] once prepared what he thought to be $Na_2S \cdot 2FeS$ and it is this double compound which Thorpe[10] assumes caused difficulty in the Blythe and Kopp process of making soda. One of Thomas' points is at the composition $Na_2S \cdot FeS$ and shows only one arrest. He may or may not have missed the eutectic arrest at 585°. Therefore further work in the "two liquids" region of the diagram is urgently needed.

Our interpretation of these meager data is somewhat influenced by the work of F. Friedrich[11] on the system $Na_2S{:}Ni_3S_2$, which is very similar as far as the form of the phase diagram is concerned.

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[9] Stromeyer, *Ann.*, **107,** 233 (1858).

[10] Thorpe, "Dictionary of Applied Chemistry," **1926,** Vol. 6, p. 179.

[11] F. Friedrich, *Metall und Erz,* **11,** 197 (1914).

Metallographic Examination.—Lumps of about one inch diameter were used for preparation of polished surfaces. To protect them from attack by the atmosphere they were soaked in molten paraffin wax, which was adequate for the period of time necessary in polishing a surface, examining it under the microscope and photographing it. In place of water, kerosene was used on the polishing wheels. The polished surfaces, on account of difficulty of manipulation, are far from perfect, so caution must be used in implying inconsistences between the phase diagram and the micro-structure.

In general the melts high in iron sulfide showed the characteristic yellow iron sulfide dendrites. As melts lower in iron sulfide were approached, the yellow color diminished and in the two-liquid region the crystals seemed to be white. While magnifications up to 1000 diameters were used, a definite eutectic structure was usually difficult to find and especially the temporary eutectic (B) was disappointing from this standpoint.

The notes on the polished sections prepared are given herewith and also four photomicrographs to accompany them.

Examination of Polished Sections

Melt No. 10 (91.1% of FeS) (Plate 1).—Structure consists of rounded grains of yellow iron sulfide in transparent matrix which appears dark under the microscope.

Melt No. 11 (90% of FeS).—The iron sulfide is in the form of long dendrites in the transparent matrix. The dendrites can be seen with the naked eye.

Melt No. 18 (78.3% of FeS).—Similar to No. 10. Irregular patches of yellow iron sulfide, although some are white.

Melt No. 12 (76.4% of FeS) (Plate 2).—Dendrites of iron sulfide in dark matrix. The iron sulfide is much lighter in color than in previous specimens. The iron sulfide areas are much smaller and are very irregular.

Melt No. 17 (62.7% of FeS) (Plate 3).—Small white crystals in the form of squares and triangles in a brown colored matrix which shows no sign of a eutectic structure.

Melt No. 15 (50% of FeS) (Plate 4).—Tiny specks of the white constituent of previous specimen in groundmass of very coarse eutectic. The groundmass, as can be seen from the photograph, is entirely different from that of the previous specimen.

Melt No. 16 (37.5% of FeS).—Two constituents are present; both are dark by reflected light so that structure cannot be distinguished. Under the binocular microscope it is barely possible to distinguish between them on account of a slight relief due to difference in hardness. One constituent is more sectile than the other and shows a slightly metallic streak when scratched. The absence of eutectic may be due to smearing of the soft constituent when polishing.

Polished sections of Melts 10 and 17 were examined at the highest magnification of which our apparatus is capable (1000 diameters). Both appear to have the same groundmass, which may be a very fine-grained eutectic, but the structure is beyond the resolving power of the apparatus, so that a definite conclusion is impossible. No light colored constituent could be distinguished in the groundmass of either constituent.

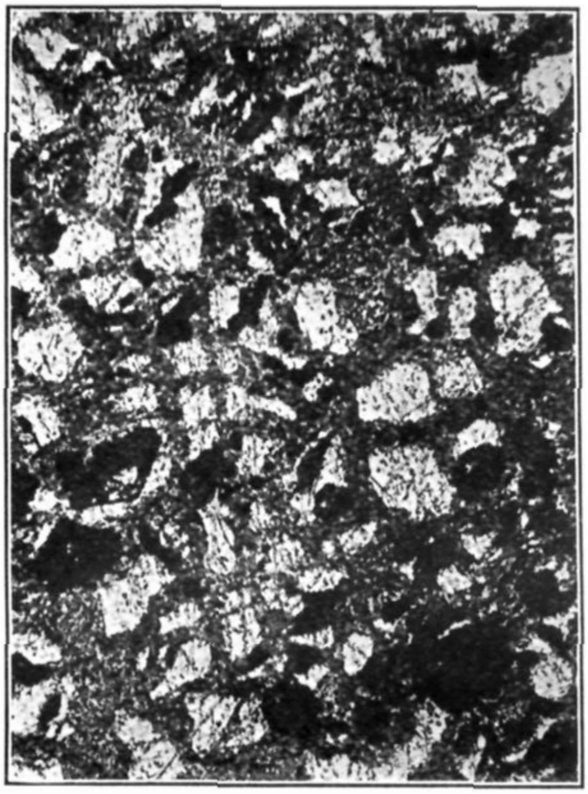

Plate 1.—91.1% of FeS. Mag. × 85.

Plate 2.—76.4% of FeS. Mag. × 35.

Plate 3.—62.7% of FeS. Mag. × 170.

Plate 4.—49.8% of FeS. Mag. × 35.

Summary

Eleven melts and cooling curves have been prepared in the system Na_2S–FeS which have allowed preparation of a satisfactory liquidus in the temperature–composition phase diagram but insufficient points were taken to determine fully the solidus and a complete outline of the phase diagram. Such points as have been obtained indicate a region between 53 and 73% iron sulfide in which two liquid phases can form, one being a double compound, probably $FeS \cdot Na_2S$, saturated with iron sulfide, and the other being iron sulfide saturated with double compound, or something similar to it. One true eutectic is found at 46% of iron sulfide and 585°. The melting point of sodium sulfide has been determined as 970°, although its purity was such that the melting point of pure sodium sulfide can be expected to be slightly higher. No mixture containing less than 37% of iron sulfide was investigated.

CLARKDALE, ARIZONA

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIUM IN THE SYSTEM $Co-H_2O-CoO-H_2$. FREE ENERGY CHANGES FOR THE REACTION $CoO + H_2 = Co + H_2O$ AND THE REACTION $Co + {}^1/_2O_2 = CoO$

BY P. H. EMMETT AND J. F. SHULTZ

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Introduction

In the course of some experiments with cobalt catalysts, we desired to know the ratio of steam to hydrogen above which cobalt is oxidized to cobaltous oxide. The only determinations in the literature seemed to be those of Chaudron[1] and of Wöhler and Balz.[2] The former obtained a value of 20 at 1000°. The latter workers obtained a value of 14 at 450° and 19 at 750°. The apparatus and method of procedure used in both of these researches, however, were those used by Deville[3] in the study of iron oxide equilibria. Such a procedure is not well adapted to the determination of the equilibrium constant in the case of cobalt, since the partial pressure of hydrogen in equilibrium with 25 mm. of water vapor will be a millimeter or less. Any occluded gases in the solid material would cause one to obtain too low a value for the steam–hydrogen ratio. It was, therefore, probable that one or both of the above experiments might be in error, especially since preliminary observations indicated that the equilibrium ratio of steam to hydrogen was 50 or greater at 450°.

[1] Chaudron, *Ann. chim.*, **16**, 243 (1921).

[2] Wöhler and Balz, *Z. Elektrochem.*, **27**, 406 (1921).

[3] Sainte-Claire Deville, *Compt. rend.*, **70**, 834 (1870).