adsorbed.[9] It should be noted that water having reacted with calcium carbide and combined as calcium hydroxide cannot be driven out and made to react with uncombined calcium carbide. When vessel C was heated with stopcocks closed, a pressure of 12 cm. was built up and a brown product (probably due to polymerization) condensed on the cooler portions of the apparatus. When, however, the water was allowed to distil out into D it came over very quickly and quantitatively.

Results.—The average values of the ratio $-M/N$ from three preliminary experiments are given.

	Vol. bulb, cc.	Diam., cm.	Millicuries Radon	$-M/N$
Expt. 1	4.746	2.085	22.24	22.0
Expt. 2	11.331	2.787	27.91	20.2
Expt. 3	11.370	2.790	2.632	20.0

The average value reported by Lind, Bardwell and Perry,[6] using the same method of calculation (average path method) and the same constants, was 19.8.

In Table I are given the results of three of the differential comparisons.

Conclusion

We conclude that the two rates are equal within the limits of experimental error. Since the chemical action under alpha-radiation is proportional to the ionization, several other factors may be assumed to be equal within these same limits: namely, the probability of ionization of the light and heavy acetylene molecules (which we may term their relative molecular ionization), their stopping power and probably their total ionization by a stream of electrons may also be assumed equal, which is of importance in the positive ray method of analysis of heavy hydrogen and its compounds.

MINNEAPOLIS, MINN. RECEIVED APRIL 15, 1935

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[9] Only a negligible quantity of gas could be produced in that way, confirming the purity of calcium carbide.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

Polymorphism in the FeS–S Solid Solutions. I. Thermal Study

BY HOWARD S. ROBERTS

The FeS–S solid solutions form a small portion of the system Cu–Fe–S investigated at the Geophysical Laboratory by Lombard and Merwin. Their work,[1] which was confined chiefly to the difficult problem of determining the compositions and fields of stability of the solid phases, raised several collateral questions of considerable interest.

In the case of solid solutions of S in FeS several kinds of evidence indicate that these solutions may exist in different polymorphic forms. Lombard and Merwin point out that a sharp break in magnetic properties of the series appears about midway of the sulfur content.

Thermal studies[2] by Rinne and Boeke show a thermal change in the compound FeS at 144°. Allen, Crenshaw, Johnston and Larsen[3] were able to crystallize pyrrhotite from solutions and obtained hexagonal crystals at 80° and orthorhombic crystals above 200°.

Ziegler,[4] in an investigation of the magnetic properties of pyrrhotite, found that its saturation magnetization decreased steadily as the temperature was raised, until 320° was reached, where it dropped suddenly to zero. He attributed this break in the curve to an allotropic transformation. At the same temperature Chevenard[5] observed a discontinuity in the coefficient of expansion; while in magnetite he found that the coefficient of expansion passed through a maximum near the Curie point but showed no discontinuity.

x-Ray powder spectra[6] of these solid solutions at room temperature are reported to form a continuous series from FeS to the sulfur-rich limit, giving no evidence of any abrupt change in structure.

At the beginning of this investigation a few x-ray powder photographs were made with the sul-

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[1] Summarized in Carnegie Institution of Washington Year Book, **25**, 62–69 (1926), and **30**, 82–84 (1931).

[2] Rinne and Boeke, *Z. anorg. allgem. Chem.*, **53**, 338 (1907).

[3] Allen, Crenshaw, Johnston and Larsen, *Am. J. Sci.*, **33**, 169 (1912).

[4] Ziegler, *Mitt. Phys. Ges. Zürich*, **17**, 1 (1915); abstracted in *Beiblätter Ann. Physik*, **40**, 61 (1916).

[5] Chevenard, *Compt. rend.*, **172**, 320 (1921).

[6] (a) Alsen, *Geol. För. Stockholm Förh.*, **47**, 19 (1925); (b) Hägg and Sucksdorff, *Z. physik. Chem.*, **B22**, 444 (1933); (c) Juza, Biltz and Meisel, *Z. anorg. allgem. Chem.*, **205**, 273 (1932).

fide at elevated temperatures. These indicated that some very slow transformation was taking place in the sulfide. Therefore the thermal study reported in this paper was undertaken to locate, for each composition, temperature intervals within which a change of phase appears and to determine how the products of these transformations might be obtained relatively free from metastable forms.

The method employed (differential heating and cooling curves) gives an indication when a transformation of some sort is taking place, provided the latter is not too sluggish. It seldom gives direct information about the nature of the transformation—whether, for instance, this is simply the polymorphic inversion of a single phase or is a chemical reaction involving more than one solid phase—and its interpretation is complicated by the slowness with which solid transformations usually proceed.

All of the measurements were made on synthetic materials prepared from reagent iron wire (supposed to contain 99.5% Fe) and sulfur which had been distilled *in vacuo*. The synthesis was carried out in two steps: first a stock of the compound FeS was prepared and the solid solutions made from this by adding the appropriate amount of sulfur.

To prepare the stock FeS about 50 g. of the iron wire was placed in a Pyrex glass capsule with about 0.1% more sulfur than was needed for the gross composition FeS. It was then evacuated to about 0.5 mm., the sulfur boiled to drive out air and the capsule sealed. Ten days of heating at 550 to 575° sufficed in most cases to convert all of the iron to a brittle mass of sulfide which was very easily crushed to a fine powder. This powder was then heated *in vacuo* with fresh iron wire to combine with the original excess of sulfur; as a check on the completeness of the reaction a third or a fourth heating was made with fresh iron wire until no more sulfide formed on the wire. In this way it was assured that the composition of the final product was at or very close to the iron-rich limit of solid solution, which was believed by Lombard and Merwin[7] to be the compound FeS itself.

Fortunately there was available a quantity of FeS made by Lombard at this Laboratory and found by him to have the composition $FeS_{0.999}$. This material exhibited a transformation at 144.6° on heating, while a sample prepared by the method just described gave 144.2°.

Combination of the stock FeS with additional sulfur to form the final preparations was also carried out at 550 to 575° in evacuated Pyrex capsules. Since it is difficult to determine whether or not an opaque solid solution is homogeneous, each preparation was heated for three periods of at least ten days each, crushing to a fine powder and mixing between heatings. To minimize the extent to which sulfur might become concentrated in the cooler portions of the charge the capsules were enclosed, for their final heating, in copper tubes to equalize temperature.

Each preparation was then sealed up in an evacuated Pyrex capsule containing a Pt-PtRh thermocouple. This type of enclosure was necessary to prevent oxidation. For thermal analysis the capsule, and a similar one containing a mixture of coarse and fine Al_2O_3, occupied adjacent wells drilled in a massive copper cylinder, Fig. 1. A single layer of nichrome wire was wound over asbestos paper on the outside of the cylinder for electric heating. The space between the cylinder and the alundum jacket was left empty and for work at the lower temperatures the jacket was raised a few millimeters above the base to increase the cooling rate.

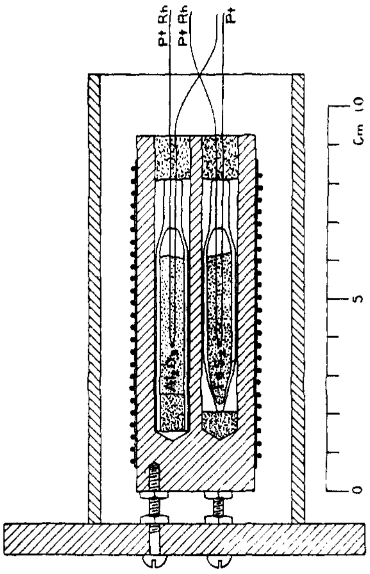

Fig. 1.—Arrangement of sulfide sample and powdered Al_2O_3 neutral body within an electrically heated copper cylinder.

Readings of the changing sulfide temperature were made every minute; of the differential temperature 15, and when desirable 30 and 45 seconds later. In Fig. 2 these differential temperatures are plotted against the corresponding interpolated sulfide temperatures for a few typical runs.

The presence of the Pt-PtRh thermocouple in contact with the sulfide limits this arrangement to temperatures below about 350°. At higher temperatures selective solution in the Pt or PtRh wires tends to change the composition of the charge. For example, holding a preparation of $FeS_{1.01}$ for thirty minutes near 550° caused its heating curve maximum to shift to 120°, corresponding to a change in composition to approximately $FeS_{1.03}$. With the more sensitive PtRh-AuPd couple solution becomes important at even lower temperatures.

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[7] *Op. cit.*, **25**, p. 66.

The very small heat effects obtained with some compositions, $FeS_{1.06}$ for instance in Fig. 2, made it necessary to minimize external influences on the differential readings. These came chiefly from irregularities in heating or cooling rate and from parasitic voltages in the measuring circuits. The effect of the former was made insignificant by employing a very steady rate and making the neutral body of such proportions of coarse and fine Al_2O_3 that the lag of its thermocouple was nearly the same as that of the couple in the sulfide. The effect of parasitics within the potentiometer system was taken care of by very frequent use of an eliminating switch;[8] then by careful annealing of the Pt–PtRh leads the total irregularity superposed on the differential readings could be made less than 0.1 μ v., about 0.12°.

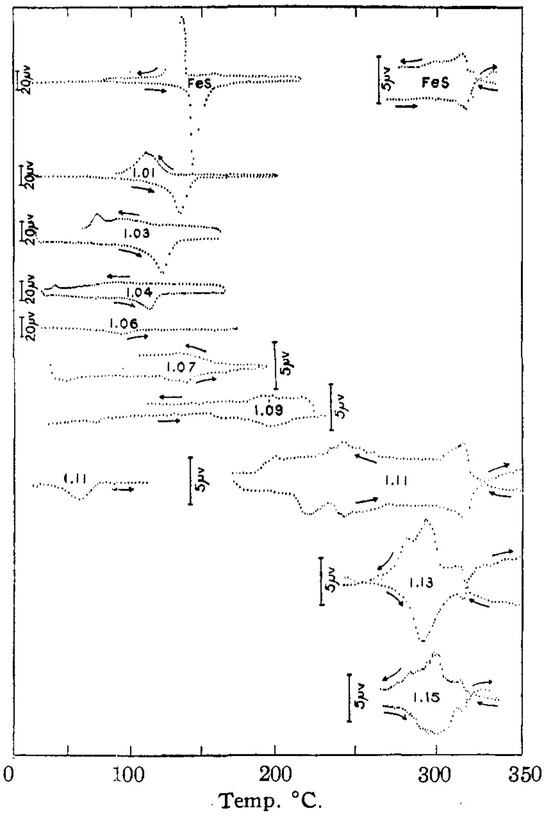

Fig. 2.—Representative differential heating and cooling curves.

The apparatus was calibrated occasionally at the melting point[9] of $K_2Cr_2O_7$ with the dichromate taking the place of the sulfide. Since the same neutral body couple was used with all of the preparations and this couple was not subject to contamination, it was used as a secondary standard for routine calibration of the working couple.

In Fig. 3 temperatures at which maxima were observed on the heating curves are plotted against composition. It is evident from the curves of Fig. 2 that each of these temperatures stands for an interval of considerable extent within which some sort of transformation takes place as the temperature is raised or lowered. Thus the curves of Fig. 3 are to be thought of as lanes dividing the diagram into five regions, *b* to *f*, where no transformation was detected. The existence of a sixth region, *a*, at the higher temperatures is indicated by the fact that the first heating curve made with preparations $FeS_{1.10}$ and $FeS_{1.12}$ showed no transformations at all; a second heating curve exhibited a slight break about 318° which developed in subsequent heatings to the form of curve shown in Fig. 2. These two preparations had been cooled rapidly to room temperature when they were taken out of the furnace in which they were made. The original stock of $FeS_{1.11}$ and of $FeS_{1.13}$ was therefore reheated to 550° and cooled in the furnace over a period of eight hours, to 200°. With these the usual maxima appeared on the first heating curve.

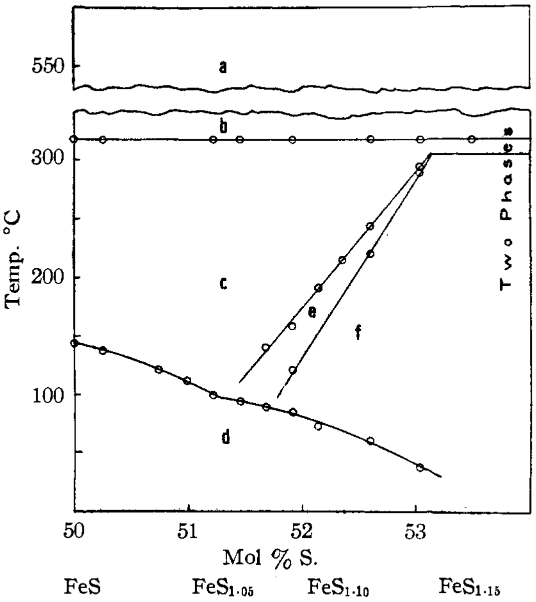

Fig. 3.—Temperatures at which maxima were obtained on the *heating* curves. These curves do not represent temperatures at which two phases are in equilibrium.

Transformation $b \rightleftharpoons c$ is evidently the one observed by Ziegler. Essentially similar curves were obtained for all of the compositions studied

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(8) W. P. White, THIS JOURNAL, **36**, 1859 (1914).

(9) "International Critical Tables," Vol. 1, p. 54.

except that the transformation temperature was about 1° higher for compositions near FeS.

Transformation $c \rightleftharpoons d$ in the compound FeS is well defined and with very slow heating and cooling the maxima appear at 144 and 139°, respectively. With increasing sulfur content the transformation temperature is lowered, the maxima on heating and cooling lie farther apart and become increasingly broad, particularly on cooling. Experiments in which a halt of an hour or so was made near the cooling maximum indicate that the increase in breadth is due in part to a greatly decreased time rate of transformation.

Rinne and Boeke[2] obtained essentially the same relation between transformation temperature and composition except that their curve is displaced toward Fe. They report that preparations richer in *iron* than 7% Fe, 93% FeS by weight exhibited the transformation at 139° on heating. As the excess of iron was decreased the temperature and sharpness of transformation decreased until at 4% Fe it could no longer be observed. It seems certain that the sulfide phase in their preparations, which were partly oxidized, contained about 7% less iron than they believed.

With the compound FeS the present work showed low maxima at about 160° on cooling as well as on heating curves. They are easily reproducible with FeS but could not be obtained with $FeS_{1.01}$. On cooling curves of $FeS_{1.03}$ and $FeS_{1.04}$, however, a second evolution of heat appears at a low temperature (see Fig. 2). This is easily reproducible after cooling as slowly as 1° per minute through the higher maximum but was absent after the preparation had been held for two hours at the higher maximum. The behavior of these compositions raises the question of a narrow region near FeS between *c* and *d*, with the further possibility that the region may be metastable beyond $FeS_{1.01}$.

Beyond about $FeS_{1.05}$ in Fig. 3 an intermediate region, *e*, lies between *d* and *c*; and beyond $FeS_{1.07}$ a second intermediate region, *f*, between *d* and *e*. From these two regions transformation to the low temperature condition proceeds very slowly and cooling curves give no indication of it. With $FeS_{1.06}$ it was not complete in six weeks at room temperature nor in three weeks at 55°. With compositions of higher sulfur content definite low maxima were obtained on heating (see $FeS_{1.11}$ in Fig. 2) but only after the preparations had been kept at room temperature for several months.

Transformation $c \rightleftharpoons e$ takes place promptly in either direction. Although the heat effect extends over a considerable temperature interval this interval is nearly the same on cooling as on heating and the two maxima are only a few degrees apart.

Transformation $e \rightleftharpoons f$ is characterized by a considerable difference between the temperatures of the maxima on heating and on cooling. In $FeS_{1.11}$ and $FeS_{1.13}$ it takes place promptly enough to permit the $e \longrightarrow c$ maximum to be obtained on the same heating curve. With less sulfur, $FeS_{1.07}$ and $FeS_{1.08}$, the low-temperature state persists and the temperature must be raised very slowly or oscillated for many hours through its transformation range before enough of *e* is obtained to exhibit the $e \longrightarrow c$ transformation. In this region the change $e \longrightarrow f$ (cooling) takes place at a much lower temperature than $f \longrightarrow e$ (heating). It should consequently be possible to obtain either *e* or *f* free from the other by oscillating the temperature through the appropriate interval for a sufficient time.

With increasing sulfur content the temperature interval between transformations $c \rightleftharpoons e$ and $e \rightleftharpoons f$ becomes smaller and with $FeS_{1.13}$ the two maxima on heating appear as one, although two may be obtained on the cooling curve.

Limit of Solid Solution

With freshly prepared material of still higher sulfur content than $FeS_{1.13}$ only one maximum appeared on each curve. On successive heating and cooling curves these maxima came at successively lower temperatures which seemed to be approaching 300°. A heating curve using a fresh sample of gross composition $FeS_{1.15}$ exhibited its single maximum at 322°. After several days in the neighborhood of 300° two successive heating curves gave maxima at 304 and 306° with the usual $b \rightleftharpoons c$ break at 318°. Similar results were obtained with $FeS_{1.18}$ and $FeS_{1.20}$; but with $FeS_{1.13}$ no such lowering of the transformation temperature occurred.

If this behavior of $FeS_{1.15}$ was the result of gradual unmixing of a solid solution formed at 550°, we may place the high sulfur limit of solid solution at about $FeS_{1.14}$ (53.2 mol per cent. sulfur) for temperatures near 300°. Allen, Crenshaw, Johnston and Larsen[10] obtained the value 54.5 mol per cent. of sulfur at 565° and Hägg and Sucksdorff[11] 55.5 mol per cent. at 650°.

(10) Ref. 3, p. 201.

(11) Ref. 6b, p. 448.

I wish to express my thanks to Dr. H. E. Merwin of the Geophysical Laboratory for his invaluable help in the interpretation of these results and in their presentation.

Summary

The series of solid solutions that includes the minerals troilite and pyrrhotite extends from the compound FeS to approximately the composition $FeS_{1.14}$ at 300°. Thermal analyses of synthetic materials indicate that these solid solutions appear in six different forms between room temperature and 575°. However, thermal data alone are inadequate to preclude the possibility that one or more of these "forms" may in reality be a mixture of two distinct solid phases in equilibrium. A prompt, reversible transformation takes place in all of these compositions between 315 and 318° and there is strong evidence that the form *b*, stable just above 318°, is not the form *a* which is synthesized at 550–575°. In the compound FeS the form *c*, stable just below 315°, transforms reversibly between 144 and 139° to a new form *d* which appears to be the stable form of all these solid solutions at room temperature. With increasing sulfur content the temperature of this transformation is lowered and it becomes very sluggish. From FeS to about the composition $FeS_{1.05}$ the transformation is between forms *d* and *c;* at the latter point an intermediate form *e* appears and beyond about $FeS_{1.07}$ the transformation is between form *d* and an additional intermediate form *f*. Temperatures of transformations $c \rightleftharpoons e$ and $e \rightleftharpoons f$ are raised by increasing sulfur content, reaching the limit of solid solution very close together a few degrees below the $b \rightleftharpoons c$ transformation.

WASHINGTON, D. C. RECEIVED APRIL 17, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Ternary Systems: Water, Allyl Alcohol and Salts at 25°

BY P. M. GINNINGS AND MARY DEES

Previous investigations[1–4] have revealed some interesting relationships in this class of systems. Consider the systems of the saturated, water soluble, aliphatic alcohols with various inorganic salts and water. It is not surprising to find that methanol is by far the most difficult to salt out, followed by ethanol and then by *n*-propanol. Also, rearrangement of the straight chain to the branched types which are present in the iso, secondary and tertiary compounds results in alcohols more difficult to salt out. This is entirely in accord with the theory, particularly if the solubilities of the four butanols in water are considered. If an arbitrary salting out scale is arranged with all of these alcohols placed thereon, the differentials between methanol and ethanol and between ethanol and *n*-propanol are large enough to more than nullify any preferential characteristics of the inorganic salt used. Any salt that will salt out (produce two liquid phases) with methanol will invariably do the same to ethanol. Similarly, *n*-propanol will always be salted out by any salt that salts out ethanol. However, three of these saturated alcohols—isopropanol, *n*-propanol and *t*-butanol—are so similar in their solubility behavior that the preferential action of some salts in a few cases becomes sufficiently dominant that the usual order of these three alcohols on the salting out scale is changed. The reason for this unexpected change is not evident at present. However, with a few exceptions isopropanol is more difficult to salt out than *n*-propanol and the latter slightly more so than *t*-butanol.

The main object in the present work was to study the effect of the change from a saturated to an unsaturated group in the alcohol molecule upon the salting out characteristics and to compare this with the effect that occurs when the straight molecular chain is rearranged to a branched configuration. The mathematical aspects were also investigated in connection with the quantitative data. Search of the literature revealed only one pertinent paper on this particular subject[5] in which data on the systems of allyl alcohol with four salts were reported. Since reliable comparisons with such limited data are difficult, qualitative tests with allyl alcohol,

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(1) Ginnings and Robbins, THIS JOURNAL, **52**, 2282–2286 (1930).

(2) Ginnings and Chen, *ibid.*, **53**, 3765–3769 (1931).

(3) Ginnings, Herring and Webb, *ibid.*, **55**, 875–878 (1933).

(4) Ginnings, Webb and Hinohara, *ibid.*, **55**, 4898–4899 (1933).

(5) Frankforter and Temple, *ibid.*, **37**, 2709–2715 (1915).