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The nature of the polysulfide anion

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THE NATURE OF THE POLYSULFIDE ANION.**

**Iowa State University of Science and Technology, Ph.D., 1967
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THE NATURE OF THE POLYSULFIDE ANION

by

David Lee Pringle

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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Signature was redacted for privacy.

In Charge of Major Work

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Iowa State University
Of Science and Technology
Ames, Iowa

1967

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INTRODUCTION

The Chemistry of the Polysulfides

The bond energies of sulfur-sulfur bonds in elemental sulfur, S_8 , and of carbon-carbon bonds in hydrocarbon chains (1) are very similar, and it is not surprising that a fair number of compounds exist containing sulfur-sulfur bonds. Oxygenated species, such as thiosulfate and tetrathionate, are well known and sulfur-sulfur bonds are also present in the so-called polysulfides with which this thesis is concerned. In the older literature these polysulfides are sometimes referred to as persulfides.

Solutions of polysulfides are very simply prepared, by dissolving sulfur in an aqueous solution of sodium sulfide. The synthesis may also be carried out in alcohol. In water the dissolution of the elemental sulfur proceeds rapidly and continues until the mole ratio of sodium sulfide to dissolved sulfur is 1:4, corresponding to the formation of the pentasulfide, Na_2S_5 .

A good deal of the literature pertaining to polysulfides is devoted to the synthesis of the polysulfides of sodium and potassium in solid form. One of the earliest attempts at such syntheses is that of Böttger (2), who claimed the preparation of sodium disulfide pentahydrate ($Na_2S_2 \cdot 5H_2O$), sodium trisulfide trihydrate ($Na_2S_3 \cdot 3H_2O$), sodium tetrasulfide octahydrate ($Na_2S_4 \cdot 8H_2O$), and sodium pentasulfide octahydrate ($Na_2S_5 \cdot 8H_2O$). The method of preparation was simply to dissolve the appropriate amounts of sulfur and sodium sulfide in a water-alcohol mixture and to evaporate away the solvent. This procedure was criticized by Bloxam (3), who indicated that oxidation occurred unless care was taken to exclude oxygen.

In 1914 Rule and Thomas (4) prepared anhydrous sodium disulfide and sodium tetrasulfide by employing absolute alcohol as a solvent. Although this method was apparently successful for the di- and tetrasulfides, it failed to yield the tri- and pentasulfides. Draves and Tartar (5) claimed the preparation of sodium trisulfide by the action of metallic sodium on sulfur which had been dissolved in toluene. It was later shown (6), however, that the product was a mixture of the di- and tetrasulfides.

A review of the methods for the preparation of polysulfides is found in the 1930 paper by Pearson and Robinson (7). More recently three other authors (8, 9, and 10) have worked on the problem of synthesizing polysulfides employing different solvents such as liquid nitrogen.

The characterization of these polysulfides has generally involved simply the elemental analysis for sulfur and the alkali metal present. Melting point determination was reported in some cases. Neither of these methods distinguishes well between mixtures and pure compounds. In the majority of the syntheses the amounts of sulfide and sulfur are fixed at the ratios desired in the product and the solutions then evaporated to dryness; it is not surprising then that the elemental analyses appear to confirm the existence of the desired product. In the major part of this synthetic work, then, there is great doubt that a definite compound was obtained.

In solution, the polysulfides, or perhaps more accurately, the compound or compounds present in a solution of sodium sulfide carrying dissolved sulfur, are not very stable. Contact with oxygen results in the rapid oxidation to thiosulfate. Addition of acid causes decomposition with

the evolution of hydrogen sulfide gas and the precipitation of sulfur. If the acidification is brought about at low temperature, an oily liquid is obtained which contains the hydrogen derivatives of the polysulfides; these are known as sulfanes. In solution the polysulfides exist as divalent anions because the hydrolysis of sodium sulfide, which occurs in solution because hydrogen sulfide is a very weak acid, is inhibited by dissolved sulfur.

The nature of the polysulfides is of importance in geochemistry in understanding the transport of metals and the formation of the deposits of the metal sulfides such as pyrite, marcasite, and chalcopyrite. Earlier work by the writer (11) was concerned with this problem and, in particular, with the nature of the species produced when pyrite (FeS_2), a naturally occurring disulfide, is dissolved in the absence of oxygen. It was found that the iron was present in the plus two oxidation state. However, it could never be stated with any certainty what happened to the sulfur. Electrode potentials of pyrite dipping into solutions of sodium sulfide were equally inexplicable. During the course of this earlier work, too, sulfide was determined by titration with potassium ferricyanide and the potentiometric titration curves obtained were characterized by two breaks. The position of the first of these breaks was indeed puzzling; elemental sulfur is generated in this titration and a polysulfide is undoubtedly formed in the early stages of the titration and is somewhat involved. For several reasons then it became of interest to determine the nature of the compounds present in an aqueous solution of sodium sulfide into which elemental sulfur has been dissolved.

Literature Search

The problem of the nature of polysulfide solutions has been investigated by EMF, dialysis, and neutralization studies on solutions of sodium sulfide containing dissolved sulfur. The method which has been most frequently applied to the problem of the nature of the anionic species in solutions of sodium sulfide bearing dissolved sulfur has been the measurement of the potential of a platinum electrode dipping into the solution. Electrochemical work on a polysulfide system was first carried out by Peschanski and Valensi (12), who measured the potentials of a platinum electrode dipping into solutions of sodium sulfide containing varying amounts of dissolved sulfur, the reference electrode being a platinum electrode dipped into a solution of sodium sulfide saturated with sulfur. In addition to the potentials, they measured the pH values of the solutions. On the assumption that there was present in the solution disulfide, trisulfide, tetrasulfide, and pentasulfide, but no higher sulfides, they calculated the relative amounts of each species and showed them to be dependent upon the pH and the amount of dissolved sulfur.

Maronny (13) used essentially the same method but adjusted some of the data and estimated the free energy of the various polysulfide anions. He assumed also that all species up to the pentasulfide were present. His results differ from those of Peschanski and Valensi only in the relative amounts of each species present at various ratios of sodium sulfide to sulfur.

The latest person to attack the problem of using the electrochemical method was Cloke (14). The method employed was essentially the same as that of Maronny. Cloke assumed that the energy of formation of the disulfide

and trisulfide were so low as to preclude the existence of these species. He further assumed that the presence of a hexasulfide was probable. Based on his own measurements, Cloke then calculated the relative amounts of tetra-, penta-, and hexasulfides present as a function of the sulfide: sulfur ratio.

In the course of some dialysis experiments Schulek and co-workers (15) investigated a solution which contained sodium sulfide and sulfur in the mole ratio of 1:2, presuming at the beginning of the work that the solution contained simply sodium trisulfide. The results of the dialysis experiments, however, suggested that the species present was most likely a pentasulfide. Schulek even postulated that the pentasulfide was a quite stable species and that the stability resulted from a ring structure of the sulfur atoms.

The latest investigation into the nature of the polysulfides was that of Schwarzenbach and Fischer (16), who began with solid polysulfides of sodium and potassium, presumed to be pure and definite compounds. By means of a special stirring apparatus by means of which they were able to mix the polysulfide with acid before decomposition into hydrogen sulfide and sulfur could occur, they carried out neutralization titrations. From the neutralization curves obtained, Schwarzenbach and Fischer concluded that the di- and trisulfide ions were not present in solution. They reported that when the salts of the di- or trisulfides were dissolved in water a disproportionation to the hydrogen sulfide anion and tetrasulfide took place. They found also that the tetrasulfide disproportionated by a reversible reaction to the hydrogen sulfide anion and pentasulfide. They concluded that irrespective of the concentration of dissolved sulfur, the

hydrogen sulfide anion, the tetrasulfide, and the pentasulfide were always present except when sufficient sulfur was available to convert all the sulfide to pentasulfide.

As can be seen from the above review of the literature, the nature of polysulfide species present in solutions of sodium sulfide containing sulfur is far from settled. In this thesis the problem was attacked by several different methods: polarography, spectrophotometry in the ultraviolet and infrared, and potentiometric titration with ferricyanide. Work was done also on the related problem of the nature of the compound formed when ferrous iron is added to a solution of polysulfide.

THE POLAROGRAPHY OF SOLUTIONS OF SODIUM SULFIDE
CARRYING DISSOLVED SULFUR

Introduction

Inasmuch as polysulfides can be reduced to monosulfide, such reduction could possibly be brought about at a dropping mercury electrode and the polysulfides thus studied with the polarograph. Each species reducible in the range of the polarograph exhibits a characteristic half-wave potential and in the water-sodium sulfide-sulfur system, it would be expected that each polysulfide present would display a characteristic reduction wave.

Some polarographic studies on solutions have already been made. Werner, in a series of papers (17, 18, and 19), described work with solutions corresponding to sodium disulfide and sodium tetrasulfide. He found that there was a reducible species in these solutions; but that the polarograms for the two solutions were identical, the polarograms consisting of one anodic and one cathodic wave. Werner postulated that the anodic wave was caused by the dissolution of mercury forming a sulfide in equilibrium with the polysulfide and that the cathodic wave was caused by the reduction of sulfur to sulfide, the sulfur resulting from a slight dissociation of the polysulfide.

Although the outlook for identifying the various polysulfides was not good in view of the results of Werner, it was decided to repeat the work and extend the study over the entire range of dissolved sulfur, from zero to saturation.

Experimental Work

Preparation of solutions

The solution of sodium sulfide was prepared approximately 1.0 M and not standardized as only the trends of the polarographic waves were of concern. To prepare this solution 240.2 g. of analytical reagent sodium sulfide nonahydrate was weighed out and dissolved in 1 l. of deionized and deaerated water. While not in use, this solution was kept under nitrogen. Solutions containing dissolved sulfur were prepared by pipetting 5.00 ml. of the 1.0 M sodium sulfide solution into a 100-ml. volumetric flask and then adding the required amounts of sulfur, 0.16 g., 0.32 g., 0.48 g., and 0.64 g. respectively. The solutions were thus 0.05 M in sodium sulfide, and the ratio of sulfide to sulfur was 1:1, 1:2, 1:3, and 1:4 respectively. Nitrogen was passed through the flasks to remove air, and the flasks were sealed and shaken until all the sulfur had dissolved. The solutions were then diluted to 100 ml. with deaerated water.

Procedure for obtaining polarograms

The polarograms were obtained by further diluting the solutions, prepared as just described, by pipetting 0.5 ml. of the solution into 50 ml. of a 0.1 M potassium chloride solution, previously deaerated. The supporting electrolyte was thus essentially 0.1 M potassium chloride. The solutions were mixed by passage of a stream of nitrogen and the polarograms then obtained in as little time as possible to prevent or minimize side reactions. The polarograms were obtained using a Leeds and Northrup Electrochemograph Type E polarograph.

Results and Discussion

The polarogram of a solution of sodium sulfide containing no dissolved sulfur showed no reduction wave. This was expected because the sulfide anion is already in the lowest oxidation state possible. The polarograms obtained on sodium sulfide solutions bearing dissolved sulfur, Figure 1, were very similar to those obtained by Werner. A polarographic maximum was present, the height of which increased with increasing amount of dissolved sulfur. The half-wave potential of the reduction wave that follows was almost exactly the same for each of the four waves, -1.65 volts. The diffusion current, height of the polarographic wave measured at -1.80 volts, increased in a nearly linear fashion with increasing content of dissolved sulfur, Table 1.

Table 1. Polarography of solutions of sodium sulfide carrying dissolved sulfur

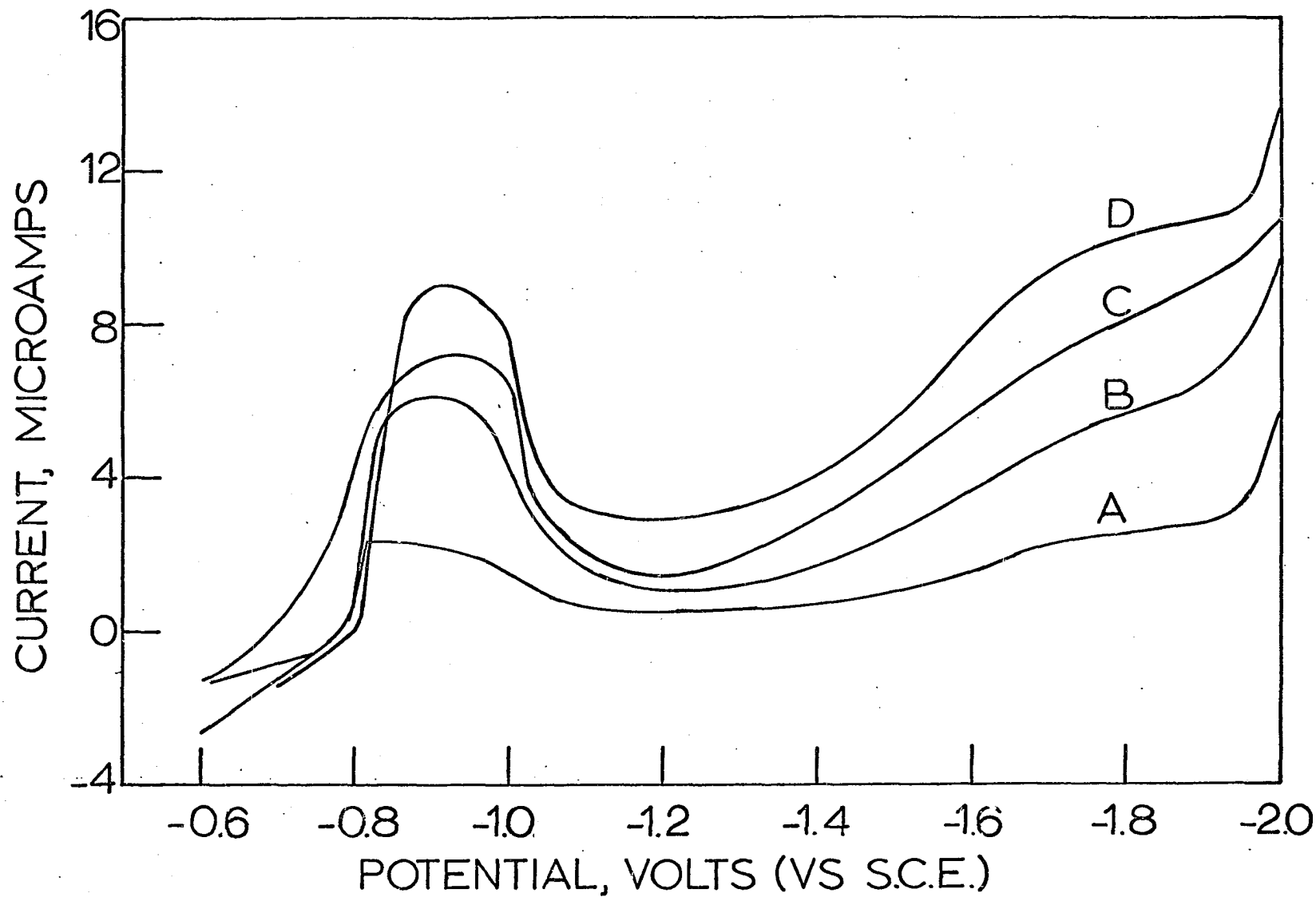
Composition Na ₂ S:S	Half-wave Potential (vs. s.c.e.)	Diffusion Current milliamp
1:1	-1.65	1.62
1:2	-1.66	3.27
1:3	-1.65	5.13
1:4	-1.65	6.54

In view of these results the explanation of Werner that the reduction wave is caused by the reduction of elemental sulfur is hardly tenable for this would imply that the amount of sulfur available for reduction increased linearly on passing progressively from the disulfide, to the trisulfide, to

Figure 1. Polarographic curves of solutions of sodium sulfide containing dissolved sulfur. Each solution 5×10^{-4} M in sodium sulfide.

Mole ratio of sodium sulfide to sulfur:

- A. 1:1
- B. 1:2
- C. 1:3
- D. 1:4



the tetrasulfide and to the pentasulfide. A far simpler explanation is that the reduction wave is caused by only one species, the pentasulfide, and that the amount of pentasulfide increases progressively with increasing content of dissolved sulfur.

The exact nature of the polarographic maximum at -0.8 volts is not known. Werner explained this maximum as a nonuniform adsorption of sulfur on the surface of the mercury drop. Inasmuch as the maximum increases with increasing sulfur, it appears more likely that the adsorption of the pentasulfide is involved.

THE ULTRAVIOLET SPECTROPHOTOMETRY OF SOLUTIONS OF
SODIUM SULFIDE CARRYING DISSOLVED SULFUR

Introduction

The color of a sodium sulfide solution varies markedly with the amount of sulfur dissolved in it, the solution of sodium sulfide being colorless and becoming pale yellow on the addition of a small amount of elemental sulfur. As more sulfur is added, the solution becomes progressively darker and becomes reddish orange by the time saturation is reached at the mole ratio of sulfide to sulfur of 1:4. It would seem that the spectra of such solutions would provide an insight to the nature of the chemical changes occurring.

The absorption spectra of solutions of polysulfides had been considered briefly earlier by Cloke, supplementary to his electrochemical studies. Cloke obtained the absorption spectra of solutions in which the sulfide to sulfur ratio was 1:1, 1:2, and 1:3 and found them very similar with broad absorption bands with maxima at 310 μ and at 365 μ . Cloke reported that rapid oxidation occurred at high dilution but did not give the experimental details as to how the dilutions were made and how oxygen was excluded. Raman spectra of the sulfanes has also been reported, Feher (20).

It was hoped that by careful exclusion of oxygen it would be possible to identify the different polysulfides by their absorption spectra and to determine the relative amounts of each.

Experimental Work

Preparation and standardization of 0.1 M sodium sulfide

The water used for the preparation of the sodium sulfide solution

was deionized by passage through a column of Amberlite MBI ion exchange resin. This water was then deaerated by bubbling a stream of oxygen-free nitrogen through it. In 1 l. of water was then dissolved 24.0 g. of fresh, analytical reagent grade sodium sulfide nonahydrate. During storage a stream of nitrogen was passed continuously over the surface.

The standardization was carried out iodometrically according to the directions outlined in Vogel (21). A volume of 50 ml. of sodium arsenite solution of known concentration was pipetted into a 250 ml. volumetric flask. Then a 20.0 ml. portion of sodium sulfide solution was added and the resulting solution was acidified, causing the precipitation of arsenious sulfide. The solution was then diluted to volume, mixed, and filtered through a dry paper and funnel into a dry beaker. A 100-ml. aliquot of this solution was titrated with a standardized iodine solution, approximately 0.1 M to the starch iodine end-point. From this titration the remaining arsenite and then the concentration of the sodium sulfide solution were calculated; the sulfide solution was 0.09517 M.

Preparation of the sodium sulfide-sulfur solutions

The amount of elemental sulfur needed to react with 50.00 ml. of the 0.09517 M sodium sulfide to form solutions having various mole ratios of sulfide to sulfur was weighed out and placed into 125-ml. Erlenmeyer flasks fitted with ground glass stoppers; the amounts of sulfur weighed out were 0.1526 g., 0.3052 g., 0.4578 g., 0.6104 g., and 0.7630 g., respectively for the 1:1, 1:2, 1:3, 1:4, and 1:5 solutions. Fifty ml. of the 0.09517 M sodium sulfide solution was added to each flask and a stream of nitrogen was passed over the surface of the solution for 60 seconds and the flasks

were then tightly sealed. The flasks were placed on a Burrell shaker and agitated for 48 hours. At this time the solution in each flask was a clear yellow except for that which contained sulfur in the ratio of 1:5, undissolved sulfur being present. The solutions were examined immediately and were opened to the air only for sampling.

Preparation of pH 10 buffer

All buffers used in this work were prepared from the tables given by Bates (22). The pH 10 buffer was prepared by mixing 500 ml. of 0.05 M sodium bicarbonate with 107 ml. of 0.1 M sodium hydroxide and diluting to 1 l. with deionized water. The sodium bicarbonate and sodium hydroxide solutions were also prepared using deionized water. Before using the buffer, it was thoroughly deaerated by passing a stream of nitrogen through it for 30 minutes.

Procedure for obtaining spectra

Before the spectra could be measured, the polysulfide solutions were diluted to a convenient concentration. Because the concentration was in the range of 10^{-4} M and a rapid decomposition by hydrolysis of the polysulfide was possible at this concentration, the spectra were obtained immediately after the dilution, the elapsed time being only that needed to fill the cuvet and place it in the spectrophotometer. The solutions were first diluted 1:1 with deionized and deaerated water and then further diluted by taking 0.25 ml. of the 1:1 solution and diluting to 100 ml. with the buffer described above. The final concentration was 1.19×10^{-4} M in sodium sulfide.

The spectra were obtained using 1 cm. quartz cells. The reference

cell was filled with the buffer as it has an appreciable absorption in the 200 mu to 250 mu range. A Cary Model XV recording spectrophotometer was used to obtain the spectra between 210 mu and 700 mu.

Results and Discussion

The spectra obtained, shown in Figures 2 and 3, can be considered in three parts. The first part, 450 to 750 mu, is featureless. The second part, 285 to 450 mu, shows two shoulders, one at 365 mu and one at 295 mu, for those solutions containing some dissolved sulfur. However, there is no absorption in this region by the solution containing sodium sulfide with no dissolved sulfur. The third region shows an absorption maximum of high intensity between 220 and 230 mu for all of the sulfur-bearing solutions and also for the sodium sulfide solution. In all of the spectra the position of the absorption maxima are identical. The intensity of the absorption increases nearly linearly with the amount of dissolved sulfur.

The molar extinction coefficients of the various solutions at the three different wavelengths are given in Table 2.

Table 2. Molar extinction coefficients of solutions of sodium sulfide containing dissolved sulfur

Na ₂ S:S Ratio	ϵ at 465 mu	ϵ at 295 mu	ϵ at 225 mu
1:0	0.00	0.00	7,500
1:1	300	1,000	9,500
1:2	650	2,300	10,700
1:3	1,000	3,400	12,600
1:4	1,300	4,700	15,500

Figure 2. Absorption spectra of solutions of sodium sulfide containing dissolved sulfur over the wavelength range 200 to 300 m μ . Each solution 1.19×10^{-4} M in sodium sulfide.

Mole ratio of sodium sulfide to sulfur:

- A. No dissolved sulfur
- B. 1:1
- C. 1:2
- D. 1:3
- E. 1:4

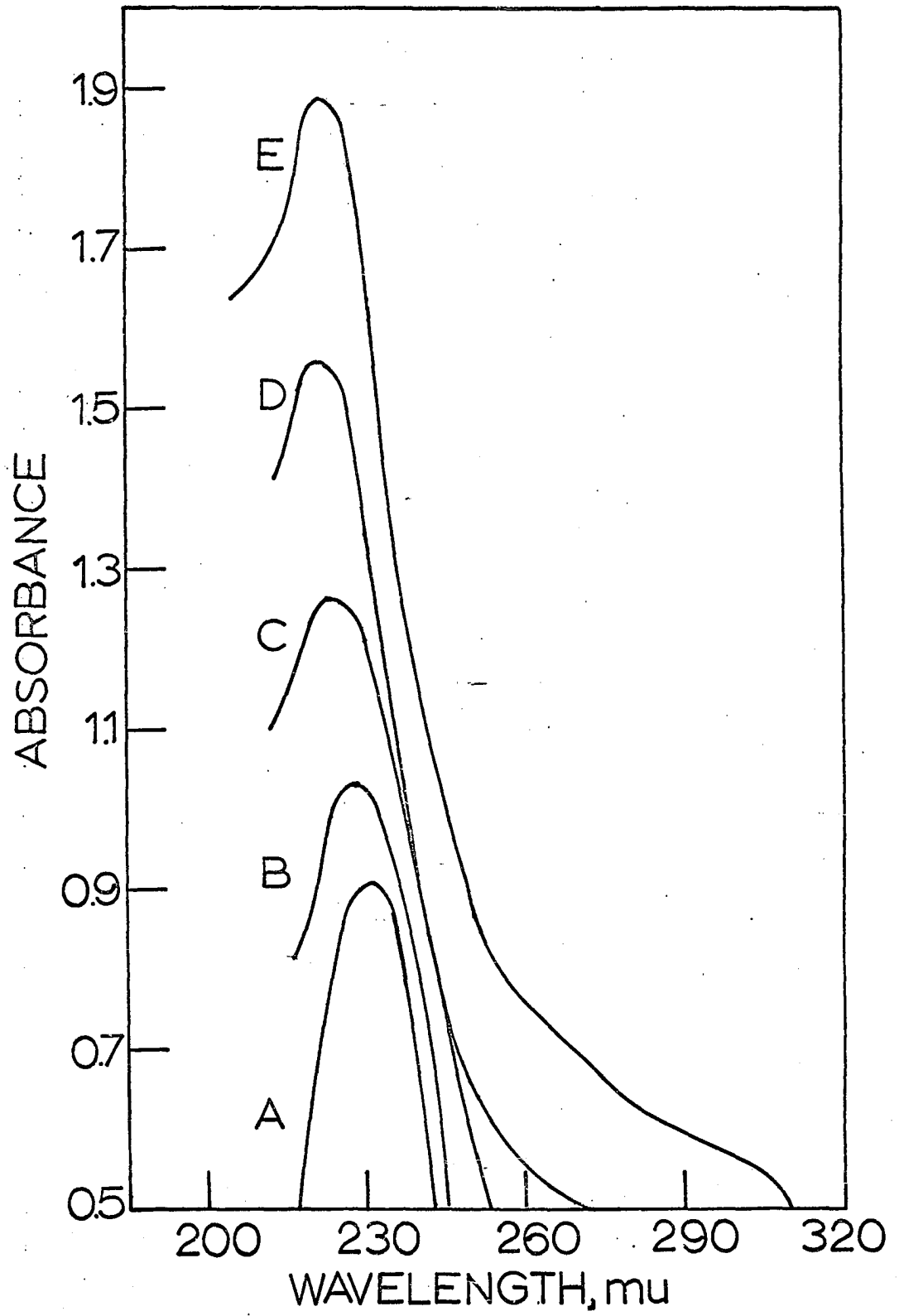
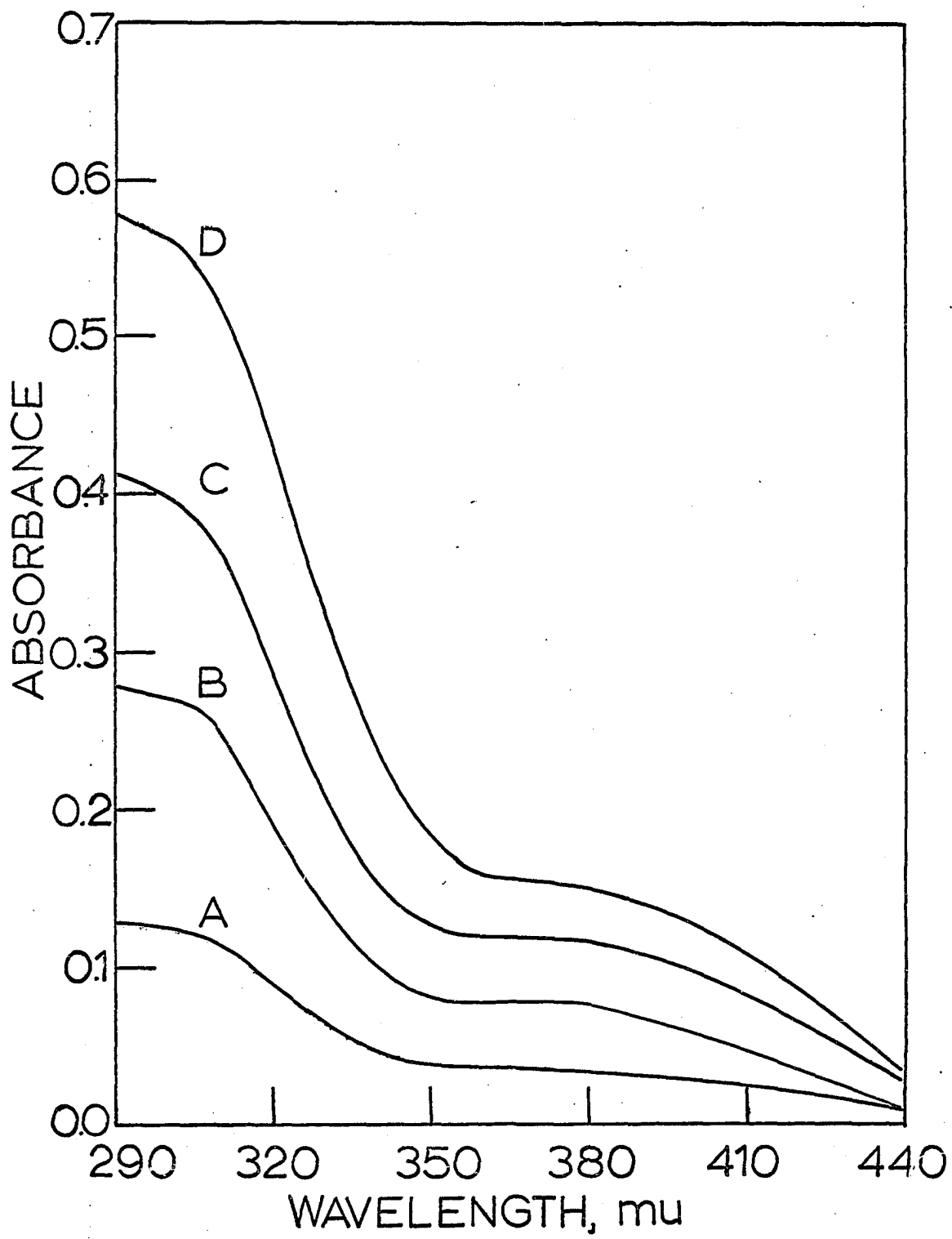


Figure 3. Absorption spectra of solutions of sodium sulfide containing dissolved sulfur over the wavelength range 290 to 440 m μ . Each solution 1.19×10^{-4} M in sodium sulfide.

Mole ratio of sodium sulfide to sulfur:

- A. 1:1
- B. 1:2
- C. 1:3
- D. 1:4



The spectrum of the 1:5 sodium sulfide-sulfur solution was the same as that of the 1:4 solution.

Inasmuch as the spectra of the sulfur-bearing solutions are identical with respect to the position of absorption bands, it is impossible to distinguish individual polysulfides. The results are most easily explained on the basis that only one polysulfide is formed, the pentasulfide, S_5^{-2} . Certainly any polysulfide higher than the pentasulfide is eliminated by the facts that only four moles of sulfur can be dissolved and that no change in absorbance is produced by equilibration with larger amounts of sulfur.

Were several polysulfides present, it would follow that the same chromophore was present in each and that it was not affected by the successive addition of sulfur atoms, a most unlikely phenomenon.

Spectrophotometric Titration

More precise data on the absorbance of solutions of sodium sulfide bearing dissolved sulfur were obtained by increasing the number of solutions examined and refining the technique of handling these solutions without contact with oxygen. Essentially, this is the method spoken of as a spectrophotometric titration.

Experimental work

Preparation and standardization of 0.1 M sodium sulfide Solutions of sodium sulfide were prepared, standardized, and stored as described above.

Preparation of sodium sulfide-sulfur solutions Solutions of sodium sulfide containing sulfur were prepared as described previously

using 50.00 ml. of 0.1 M sodium sulfide and the appropriate amount of sulfur. Because the molarity of the sodium sulfide varied from experiment to experiment, the exact concentration of the sodium sulfide and the exact amount of sulfur weighed out is given below for each set of measurements.

Preparation of buffers The pH 10 buffer was a sodium bicarbonate-sodium hydroxide buffer prepared as described above.

A buffer of pH 11 was prepared by mixing 227 ml. of 0.1 M sodium hydroxide with 500 ml. of 0.05 M sodium bicarbonate and diluting to 1 l. with deionized water.

A buffer with a pH value of 12 was prepared by adding 60 ml. of 0.2 M sodium hydroxide with 250 ml. of 0.2 M potassium chloride and diluting to 1 l. with deionized water.

The actual pH value of the buffers was measured using a Corning Model 10 pH meter.

Measurement of absorbance In order to dilute the samples to a concentration convenient for appropriate absorbance readings, 0.10 ml. or 0.20 ml. of the solutions was diluted to 100 ml. with buffer solution which had previously been deaerated. Each solution was prepared and measured immediately so that not more than a minute or two elapsed between the sampling and the measurement.

The absorbance was measured using a Beckman Model DU spectrophotometer and 1-cm. quartz cells. Although the cells were matched, it was necessary to employ a cell correction of 0.003 absorbance units at 295 m μ and 0.025 absorbance units at 217 m μ . The reference cell for each trial was filled with the buffer used at that particular pH.

Results and discussion

The results of several spectrophotometric titrations measured at different pH values, wavelengths, and concentrations of sodium sulfide are shown below in Table 3 and Figures 4, 5, 6, and 7.

Table 3. Absorbance of solutions of sodium sulfide containing varying amounts of sulfur as a function of pH

Sulfur Present grams	Absorbance, Corrected	$\frac{[S]}{[Na_2S]}$
pH = 10.0 $\lambda = 212 \text{ m}\mu$ $Na_2S = 0.1074 \text{ M}$		
0.0000	0.638	0.00
0.0430	0.668	0.25
0.0860	0.710	0.50
0.1720	0.793	1.00
0.2580	0.872	1.50
0.3440	1.030	2.00
0.4300	1.181	2.50
0.5160	1.351	3.00
0.6020	1.523	3.50
0.6880	1.740	4.00
0.8600	1.750	5.00
ca. 1.5	1.753	ca. 9
pH = 11.8 $\lambda = 217 \text{ m}\mu$ $Na_2S = 0.0921 \text{ M}$		
0.0000	0.450	0.00
0.0487	0.510	0.33
0.0989	0.586	0.67
0.1476	0.697	1.00
0.1963	0.765	1.33
0.2465	0.866	1.67
0.2952	0.947	2.00
0.3439	1.058	2.33
0.3941	1.139	2.67
0.4428	1.240	3.00
0.4915	1.347	3.33

Table 3 (continued)

Sulfur Present grams	Absorbance, Corrected	$\frac{[S]}{[Na_2S]}$
0.5417	1.427	3.67
0.5904	1.591	4.00
0.7380	1.660	5.00
ca. 1.5	1.665	ca. 10
pH = 11.0 $\lambda = 295 \text{ mu}$ $Na_2S = 0.1019 \text{ M}$		
0.0000	0.000	0.00
0.0495	0.072	0.33
0.1120	0.164	0.67
0.1640	0.239	1.00
0.2182	0.329	1.33
0.2721	0.419	1.67
0.3237	0.499	2.00
0.3797	0.589	2.33
0.4351	0.682	2.67
0.4901	0.789	3.00
0.5433	0.882	3.33
0.5998	0.964	3.67
0.6560	1.087	4.00
0.7380	1.210	4.50
0.8200	1.215	5.00
ca. 1.4	1.211	ca. 8.5
pH = 9.90 $\lambda = 295 \text{ mu}$ $Na_2S = 0.0921 \text{ M}$		
0.0000	0.000	0.00
0.0487	0.050	0.33
0.0989	0.144	0.67
0.1476	0.225	1.00
0.1963	0.300	1.33
0.2465	0.384	1.67
0.2952	0.463	2.00
0.3439	0.542	2.33
0.3941	0.635	2.67
0.4428	0.721	3.00
0.4915	0.794	3.33

Table 3 (continued)

Sulfur Present grams	Absorbance, Corrected	$\frac{[S]}{[Na_2S]}$
0.5417	0.884	3.67
0.5758	0.943	3.90
0.6051	0.996	4.10
0.6642	1.040	4.50
0.7380	1.043	5.00
ca. 1.5	1.045	ca. 10

Examination of this data reveals that the absorbance increases in a nearly linear fashion with the increasing mole ratio of sulfur to sodium sulfide. This linear increase is probably distorted at the lower wavelengths, 210 μ and 217 μ , Figures 4 and 5, because in this region the absorption band of the polysulfide overlaps the absorption band of the bisulfide anion (23). At 295 μ , Figures 6 and 7, the absorbance is quite linear up to slightly beyond the ratio of one to four. Beyond this point no further increase in absorbance occurs. As noted earlier, the dissolution of sulfur stops at this point.

These findings, that the absorbance of the solution increases linearly as the mole ratio of sulfur to sodium sulfide is increased and that the absorption changes very little after a mole ratio of one to four has been reached, lead to the conclusion that only one polysulfide species is present and that it is the pentasulfide ion. The slight increase in absorbance beyond the ratio of one to four indicates that the pentasulfide ion is slightly dissociated. The extent of the dissociation was calculated from the absorption data. The difference between the absorbance at the

Figure 4. Combining ratio of sodium sulfide and sulfur.
pH = 10.0
wavelength = 212 mμ

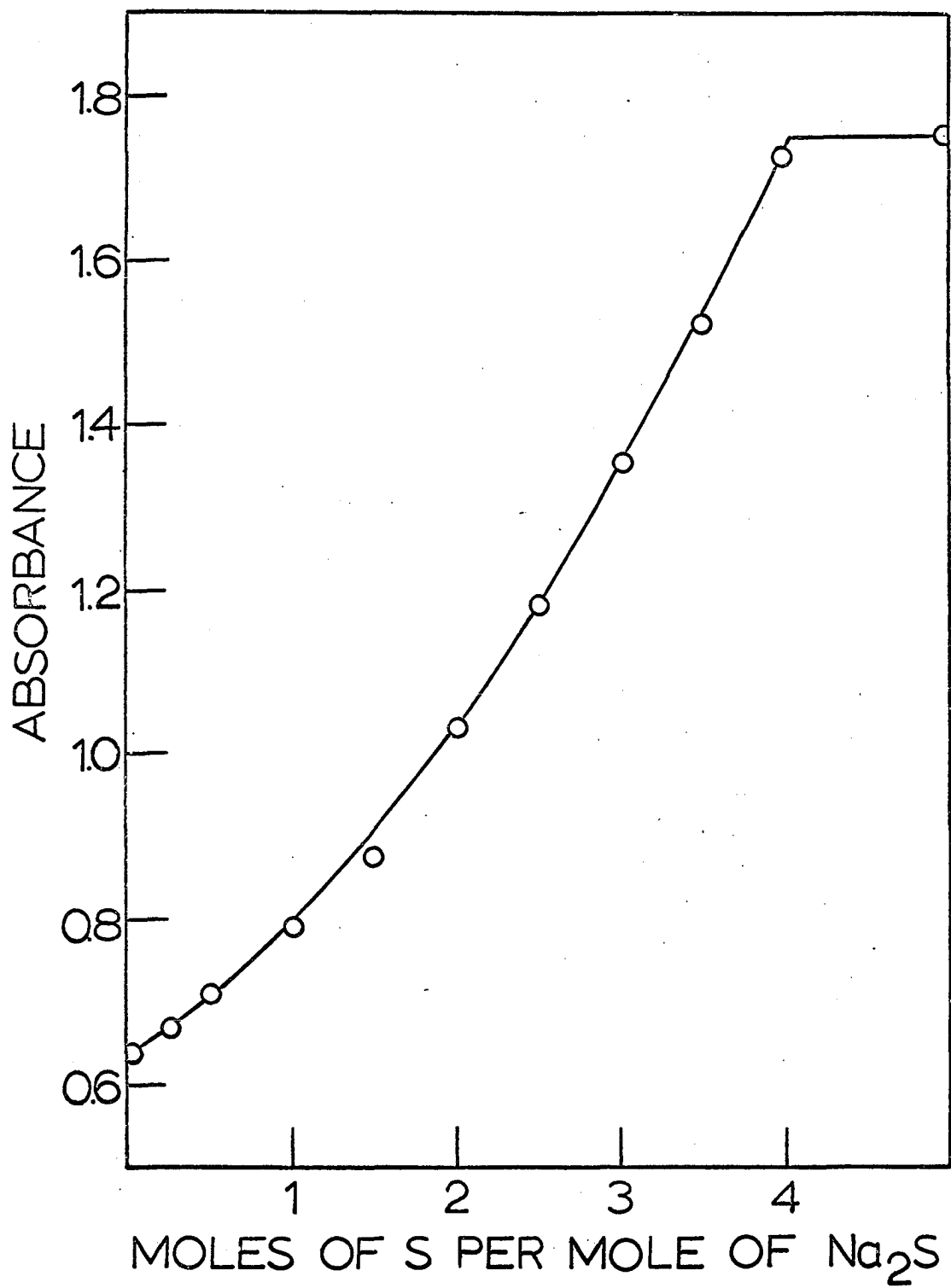


Figure 5. Combining ratio of sodium sulfide and sulfur.
pH = 11.8
wavelength = 217 mu

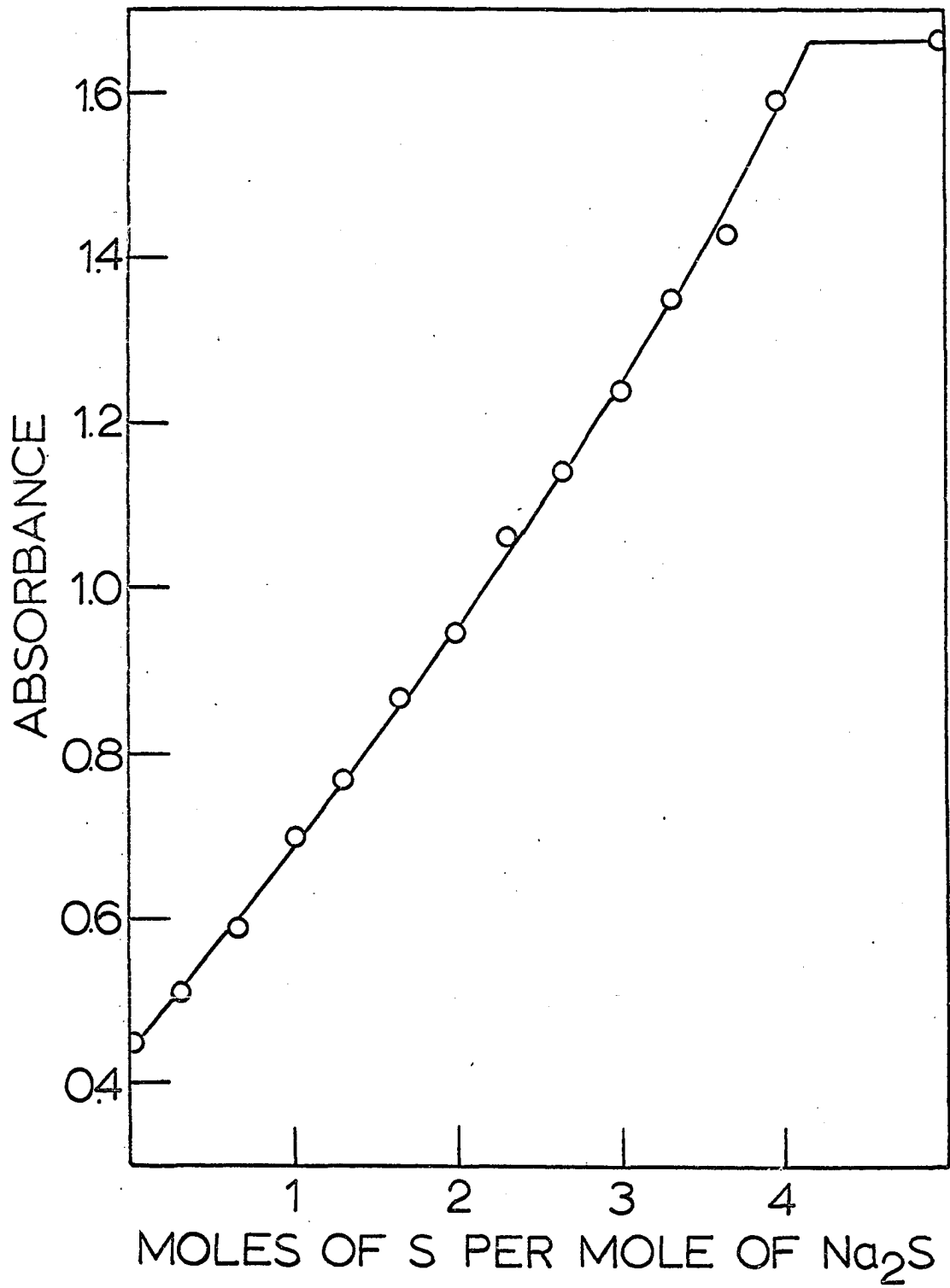


Figure 6. Combining ratio of sodium sulfide and sulfur.
pH = 11.0
wavelength = 295 mu

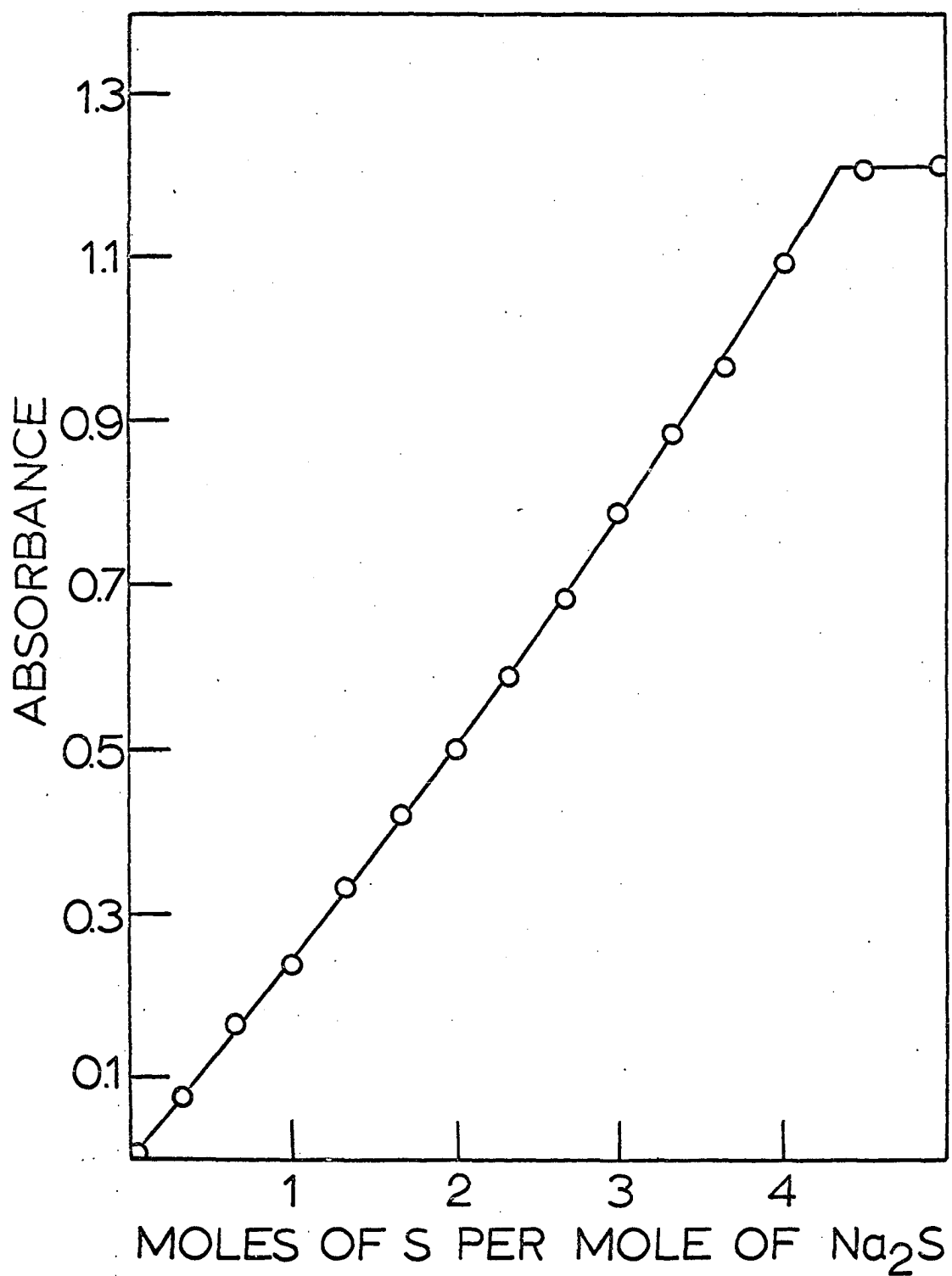
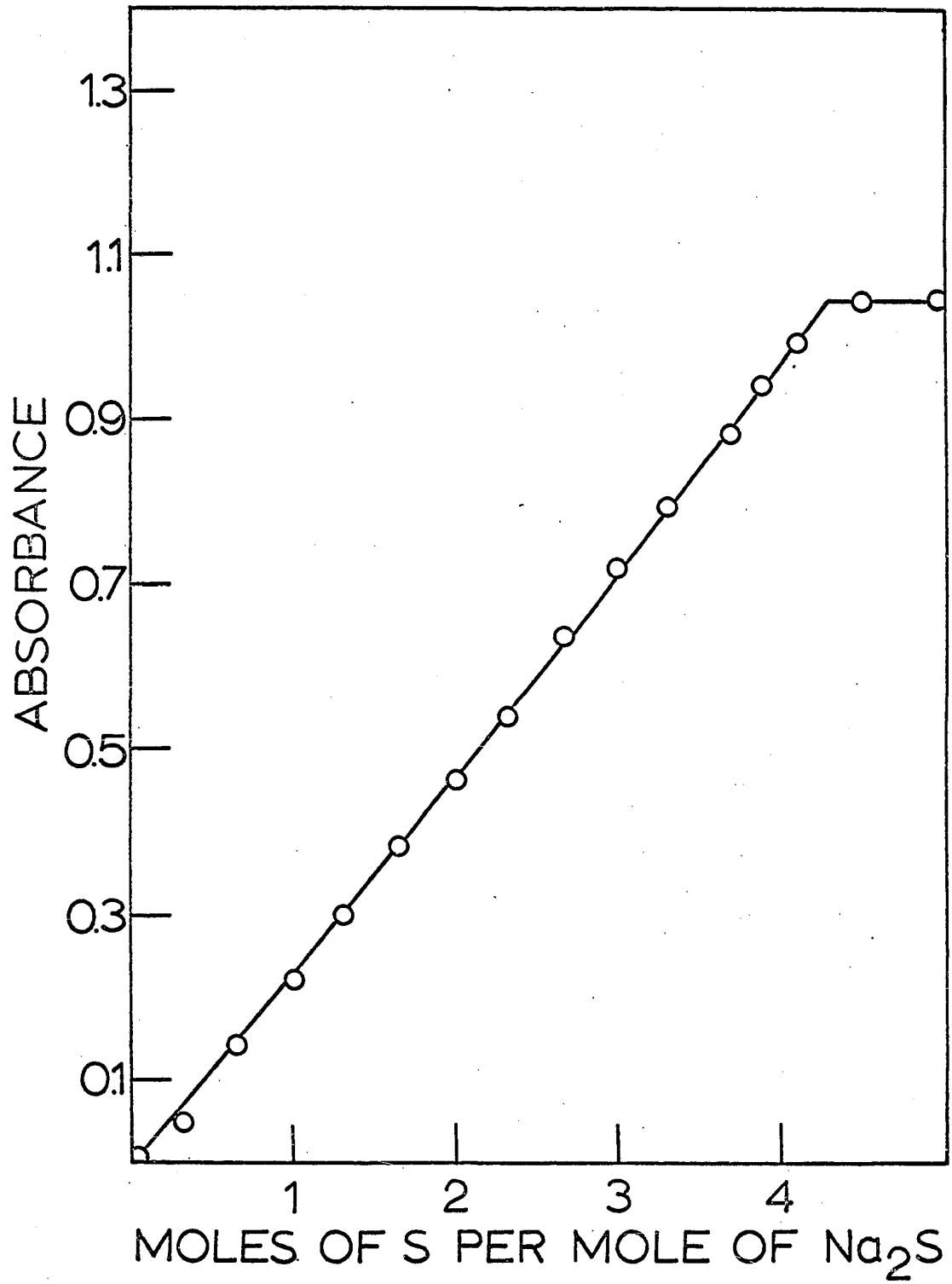


Figure 7. Combining ratio of sodium sulfide and sulfur.
pH = 9.90
wavelength = 295 mμ



ratio of 1:4 and the maximum absorbance attained was assumed to be indicative of the dissociated pentasulfide. The maximum absorbance was then assumed to be a measure of the total pentasulfide. The ratio of the dissociated pentasulfide to the total pentasulfide multiplied by 100 gave rise to the per cent of dissociation. For the four spectrophotometric titrations the dissociation was calculated and found to be 1.6 per cent, 5.9 per cent, 7.7 per cent, and 9.9 per cent. The value of 1.6 per cent was not used to obtain an average value for the dissociation inasmuch as the data at 212 μ seemed greatly distorted and unreliable. The value for the extent of the dissociation is calculated to be 8 per cent.

THE INFRARED SPECTROPHOTOMETRY OF SOLUTIONS OF SODIUM
SULFIDE CARRYING DISSOLVED SULFUR

Introduction

Examination of the infrared absorption characteristics of water and of sulfur indicated that some information about the polysulfides might well be obtained from the infrared spectrum of solutions of sodium sulfide carrying dissolved sulfur. It has been reported (24) that water exhibits two absorption bands in the infrared, a broad band which covers the range 3000 to 3600 cm^{-1} and a less intense, sharp band at about 1600 cm^{-1} . The infrared spectra of sulfur, S_8 , in carbon disulfide show absorption at 1050 cm^{-1} , 1300 cm^{-1} , and 1500 cm^{-1} and at numerous other absorptions below 900 cm^{-1} (25).

The literature indicates that organic disulfides absorb below 800 cm^{-1} . However, it was found (26) that some inorganic compounds containing sulfur-sulfur bonds, such as the thiosulfate, absorb in the region between 900 and 1500 cm^{-1} . Inasmuch as this region is relatively free from absorption by water and sulfur and is within the useful range of Irtran cells, it was thought that an examination of the spectrum in the infrared might prove fruitful.

Experimental Work

Cells

A set of Irtran cells was obtained from the Barnes Engineering Company. The windows of these cells are made from pressed zinc sulfide. They are transparent in the infrared from 4000 to 700 cm^{-1} , stable toward mild oxidizing and reducing agents, and most importantly, they are not

attacked by water.

The path length of the cells, as received, was 10 mm., much too long in view of the fact that the samples were to be aqueous solutions. By altering the construction of the cells, cells of several shorter path lengths were obtained. The best results were obtained by simply placing a drop of the sulfide-sulfur solution on one window and placing the other window directly on this. Because there was no shim or spacer between the plates, the sample examined was simply in the form of a thin film. Several samples were prepared in this fashion and found to give reasonably reproducible results. The results, of course, were only qualitative.

Preparation of solutions

Because it had been found that sodium thiosulfate absorbs in the infrared region to be investigated and because commercial sodium sulfide often contains the thiosulfate as an impurity, the sodium sulfide used to make up the solutions was purified by repeated recrystallization from water.

The solutions of sodium sulfide carrying dissolved sulfur were made up as concentrated as possible by starting with a saturated solution of sodium sulfide. At the temperature at which the solution was prepared, the final concentration of sodium sulfide was 3.2 M. The polysulfide solutions were prepared by dissolving the requisite amount of sulfur in the sodium sulfide solution.

All handling operations were carried out as rapidly as possible and under nitrogen when feasible. All solutions were prepared using deionized and deaerated water and were stored under nitrogen.

Procedure for obtaining spectra

The spectra were obtained using a Beckman IR8 infrared spectrophotometer. The samples were prepared as described above and the spectra obtained with the greatest possible haste to prevent oxidation by oxygen.

Results and Conclusions

Spectra were obtained of the solutions of sodium sulfide alone and with dissolved sulfur in the ratios 1:1, 1:2, 1:3, and 1:4. The infrared spectrum of sodium sulfide in the range 900 to 1700 cm^{-1} (6 to 11 μ) is shown in Figure 8; no absorption band appears except for that at 1600 cm^{-1} (6.2 μ) which is an absorption band of water. The spectra of 1:3 and 1:4 solutions of sodium sulfide and sulfur are shown in Figure 9. In addition to the absorption band of water, two smaller absorption bands are present. These bands appear in the same position in both spectra, a broad absorption band centered at 1100 cm^{-1} (9 μ) and a narrow band located at 980 cm^{-1} (10.2 μ). The spectrum of the 1:3 mixture is rather poor but the absorption bands are unmistakable. These absorption bands were not discernible in the spectra of the solutions lower in sulfur although some minor fluctuations in the base line were evident.

Because infrared absorption spectra, arising as they do from the modes of vibration of the absorbing molecule, are so sensitive to the structural features of the absorbing molecule, it is highly probable that the bands observed in the spectra of the 1:3 and 1:4 solutions arise from a single species. Because the absorbance at both wavelengths is greater in the 1:4 solution, the absorbing species must be the pentasulfide. It is unfortunate that the nature of the system makes the infrared method so insensitive.

Figure 8. Infrared spectrum of an aqueous solution of 3.2 M sodium sulfide.

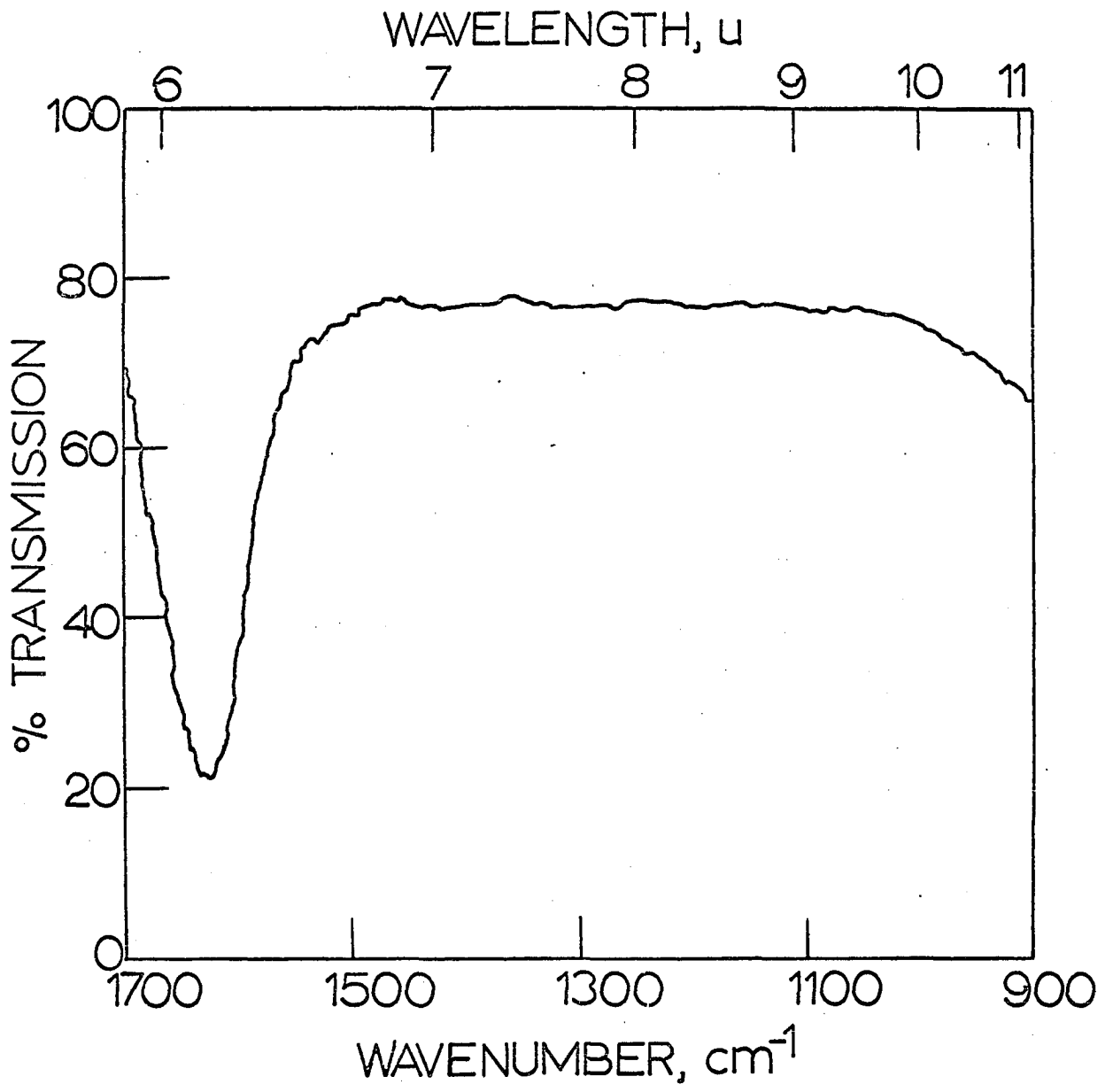
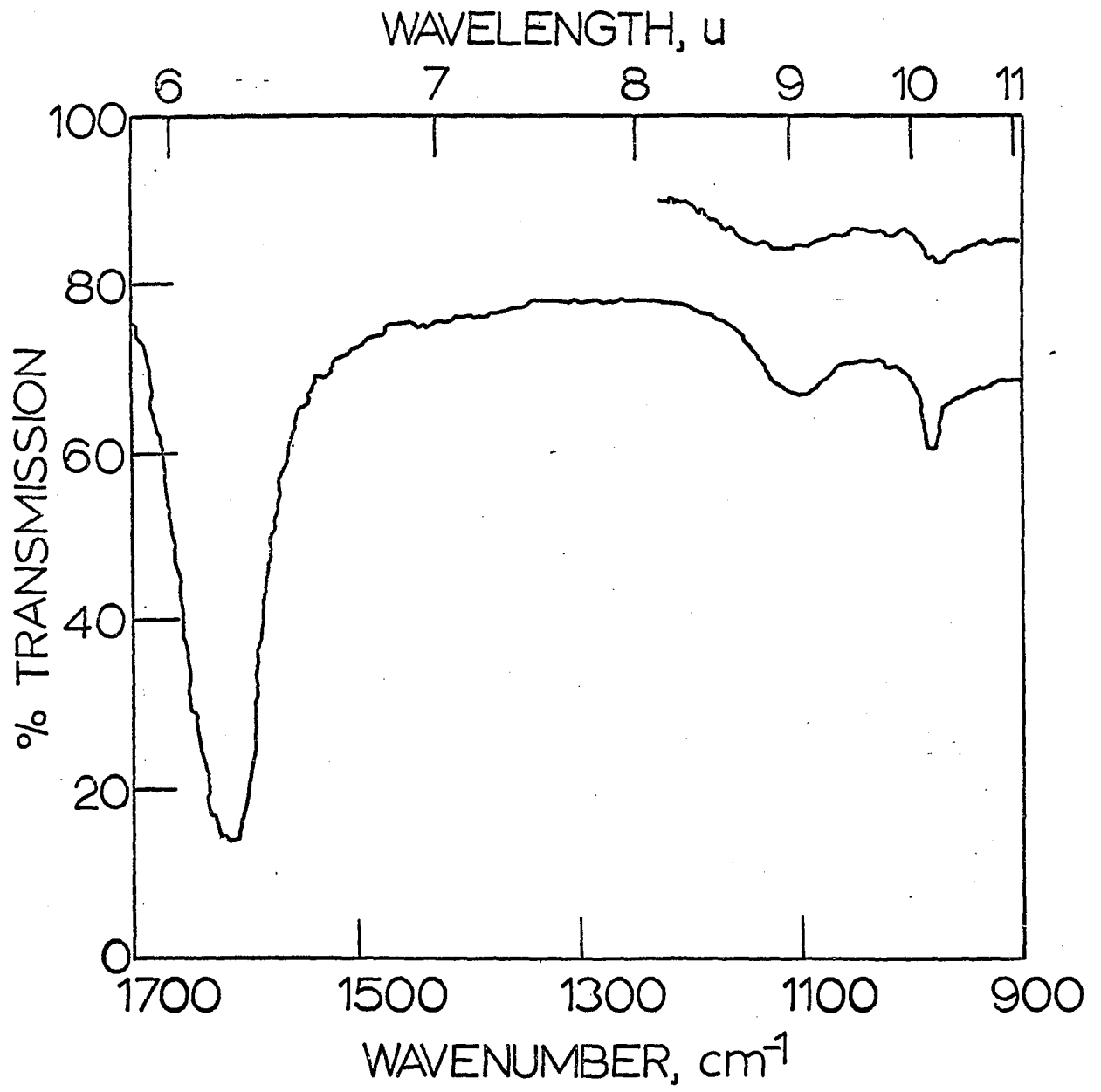


Figure 9. Infrared spectra of solutions of sodium sulfide carrying dissolved sulfur. Solution 3.2 M in sodium sulfide.

Upper curve: Sodium sulfide-sulfur ratio 1:3
Lower curve: Sodium sulfide-sulfur ratio 1:4



THE POTENTIOMETRIC TITRATION WITH FERRICYANIDE OF SOLUTIONS
OF SODIUM SULFIDE CARRYING DISSOLVED SULFUR

Introduction

The titration of sodium sulfide with potassium ferricyanide was employed as far back as 1892 by Hempel (27) for completing the determination of sulfur in organic sulfides. More recently the method was recommended by Clark (28), who used sodium nitroprusside and iron(II) dimethylglyoxime as indicators for the titration.

The writer had previously carried out the titration of solutions of sodium sulfide containing dissolved sulfur with ferricyanide using a platinum electrode and a saturated calomel electrode to follow the titration (11). The solutions titrated contained sodium sulfide and dissolved sulfur in the ratios 1:0, 1:1, and 1:2. The titration curves showed two breaks. The position of the first break depended on the amount of dissolved sulfur; the second was dependent only on the amount of sodium sulfide being titrated.

A more detailed study of the ferricyanide titration was undertaken to learn the nature of these phenomena, closer attention being paid to the experimental factors such as the purity of the sodium sulfide, the exclusion of air, and the control of the pH.

Inasmuch as the platinum electrode does not respond to a single species in solution but to the potential set up by an oxidation-reduction couple, the shape of the curve should give information concerning the sulfur species present, the oxidation number of the total sulfur present being different for each of the possible polysulfides.

Experimental Work

The sodium sulfide employed in these titrations was a commercial, analytical reagent grade material; it was used as received and also after being purified by recrystallization from water, as described above in the section dealing with spectrophotometry in the infrared.

The titrations were made using a Leeds and Northrup 7401 pH meter. The calomel electrode used was a commercial model; the platinum electrode used was bright platinum foil 1 cm. square. The titration vessel was fitted with a rubber stopper pierced with an inlet for nitrogen gas. Nitrogen was passed over the solution throughout the entire titration.

During the titration of solutions containing sodium sulfide only, or sodium sulfide and small amounts of sulfur, the response of the platinum electrode was slow. The shape of the titration curves thus depended somewhat on the speed with which the titration was carried out. Consistent results were obtained by adopting a uniform procedure for reading the potential. In general, measurements were taken four minutes after the sulfur, which precipitates upon each addition of the potassium ferricyanide, had redissolved.

Results and Conclusions

The results of these titrations are shown in Figures 10, 11, and 12. The titration curves show two breaks, a small one which varies with the amount of sulfur added and a large break which occurs when all of the sulfide has been converted to sulfur and which is independent of the amount of sulfur initially in the solution.

Figure 10. Titration of solutions of sodium sulfide carrying dissolved sulfur with potassium ferricyanide at pH = 10.0. Curves shown from left to right are for solutions having the mole ratio of sulfide to sulfur of 1:4, 1:3, 1:2, 1:1, and 1:0 respectively.

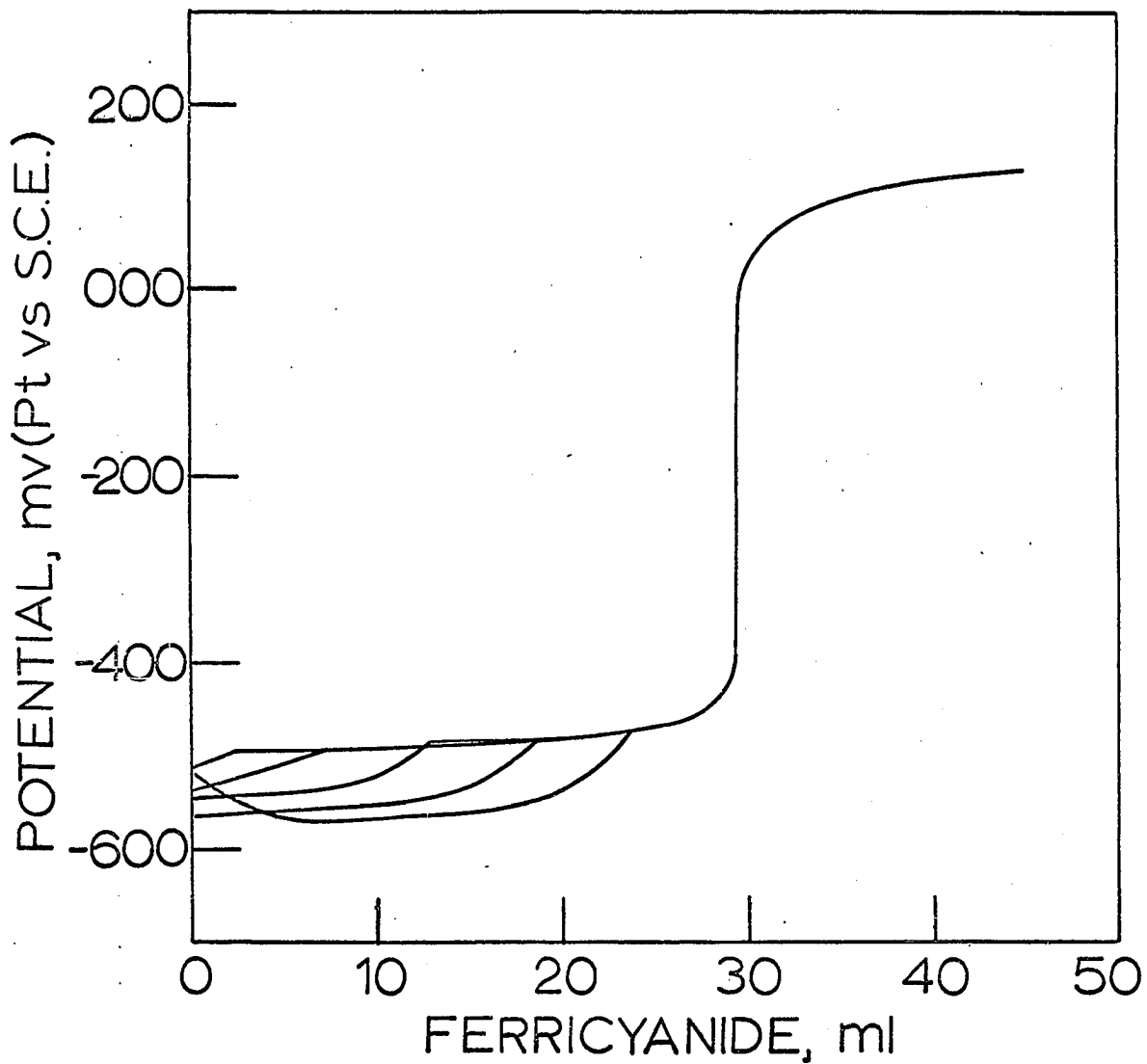


Figure 11. Titration of sodium sulfide with potassium ferricyanide at pH value of 12.6. Curves shown are for two trials; the potentials of one were measured immediately after the introduction of the electrodes (upper curve) and the potentials of the other were measured after the electrodes were allowed to equilibrate with the solution for two hours before titrating (lower curve).

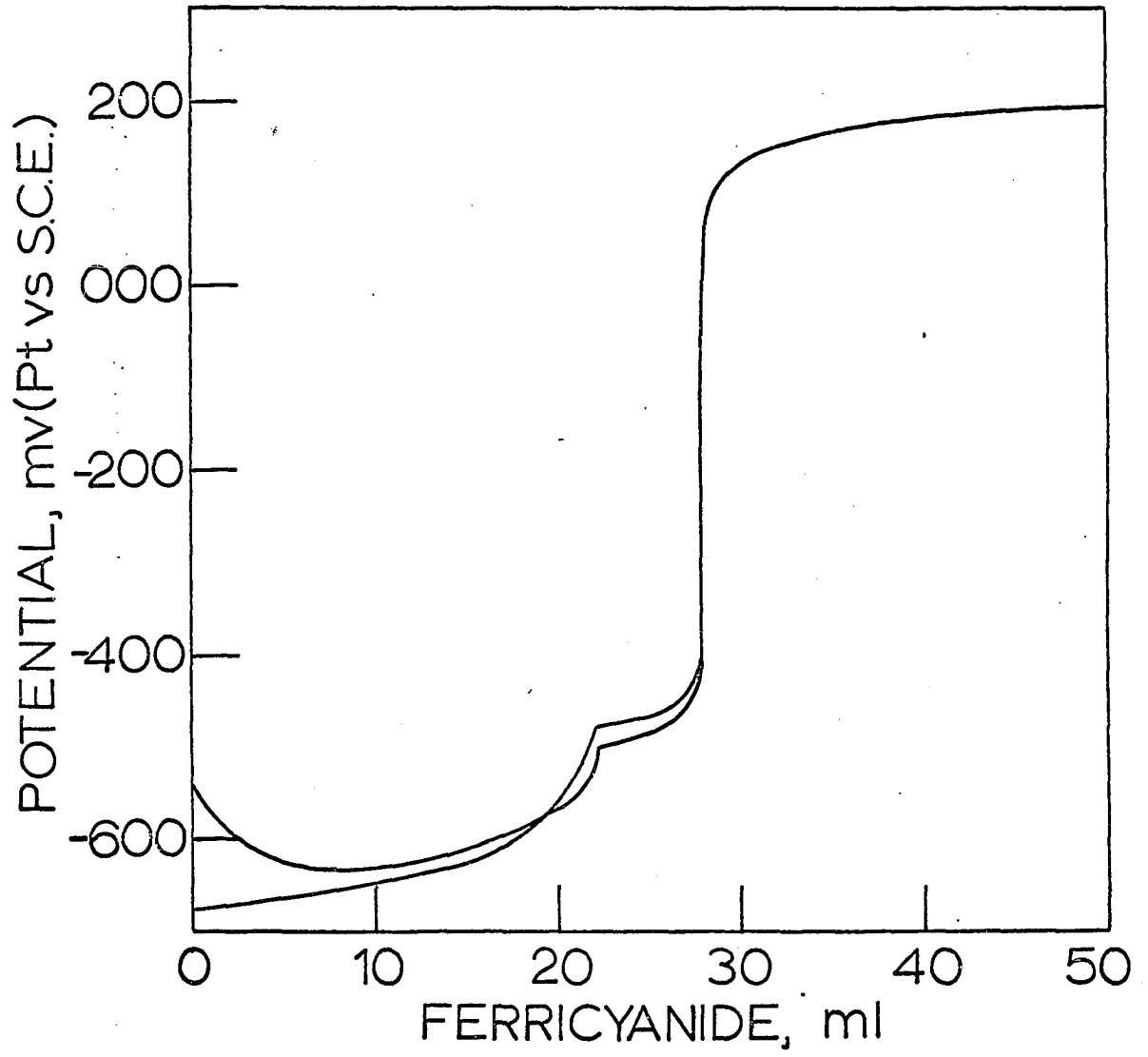
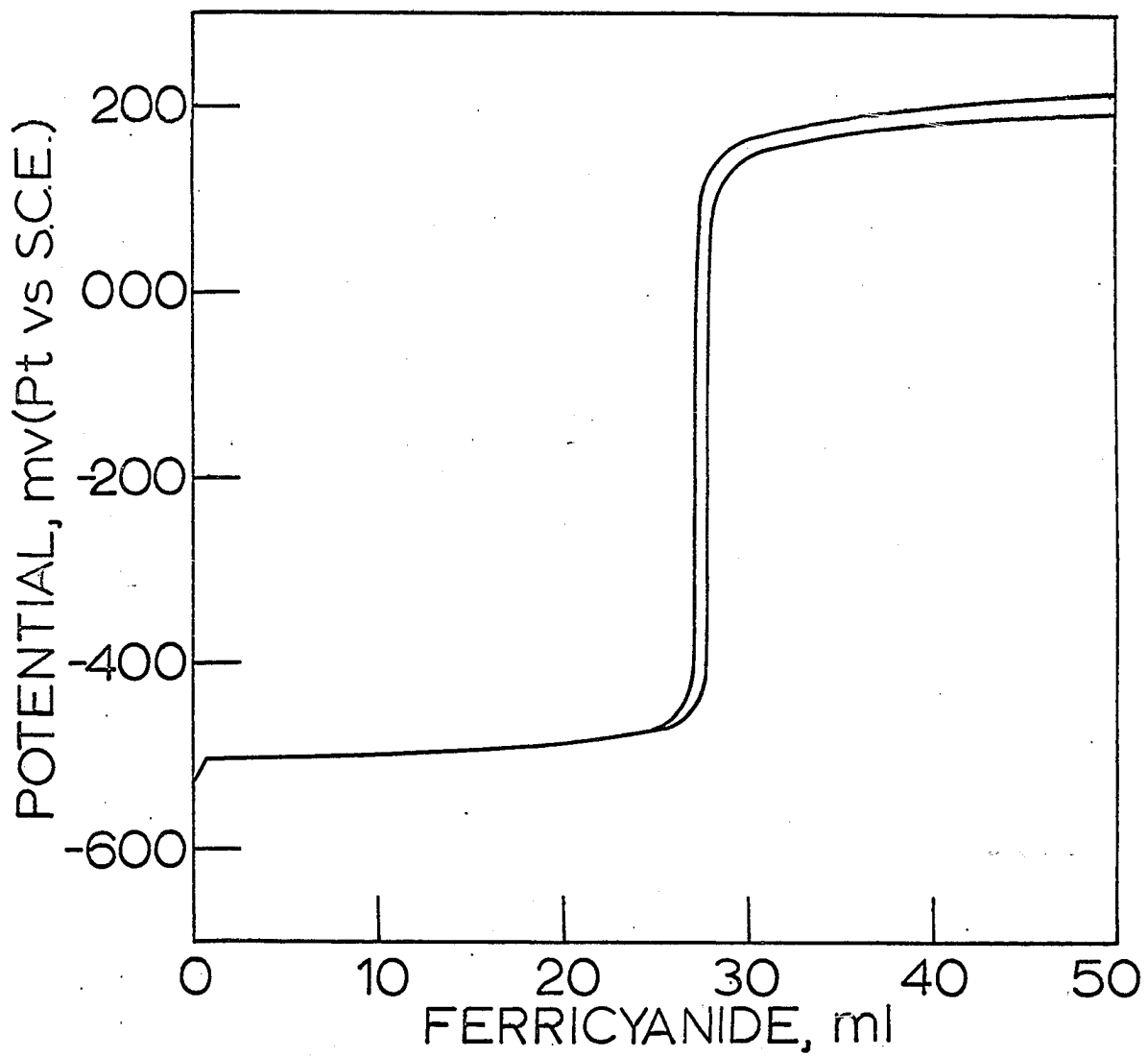


Figure 12. Titration of solutions of sodium sulfide carrying dissolved sulfur with potassium ferricyanide at pH 12.6. Curves shown are for two different trials on a solution having the mole ratio of sulfide to sulfur of 1:4. The curves show the variance in end-points for two typical titrations.



It was found that the potentials measured up to the first break in solutions of commercial sodium sulfide were anywhere from 20 to 50 mv. higher than in solutions of sodium sulfide which had been recrystallized. This was probably the result of the presence of some impurity, possibly thiosulfate, in the sodium sulfide. Even though the potentials were somewhat higher, the general shape of the curve was not altered and the presence of the oxygenated species did not interfere with the titration.

The titrations were made at two different values of pH. At pH 10 some loss of hydrogen sulfide occurred if long periods of time were allowed between successive additions of the potassium ferricyanide. The loss of hydrogen sulfide was detected by the clouding of the drop of ferricyanide which remained on the tip of the buret. If the titration was carried out rapidly, however, the loss was not serious. At pH 12.6 there was no problem with escape of hydrogen sulfide; solutions which required three hours for titrations gave results identical with those which were titrated in forty-five minutes.

The effect of time on the titration is shown in Figure 11. The upper curve with the peculiar downward slope at the beginning was the result of a titration which was started within ten minutes after the addition of the sample to the titration vessel. The lower curve was the result of a titration which was started approximately two hours after the addition of the sample. It appears that it takes a great deal of time for equilibrium to be established at the platinum electrode in solutions containing only sulfide. When there is a great deal of sulfur present, however, equilibrium is established very rapidly.

As mentioned above, the large potential break is indicative of the total sulfide concentration in the sample. The point of discontinuity on the curve occurs when the sulfur, which is being produced during the titration, no longer redissolves. Calculation showed that the relative amounts of sulfide and sulfur at this discontinuous point, for any initial amount of added sulfur, is very close to 1:4. This ratio, of course, corresponds to the pentasulfide. Up to this point on the curve the potential being measured must be that set up by the pentasulfide-sulfide couple. After the discontinuous point, the couple responsible for the potential must be the sulfur-pentasulfide couple. If other polysulfide species were present before the first break, the titration curve would be more complex.

Finally, from an examination of Figures 10 and 12, it will be seen that the first break present in the solutions containing a 1:4 sulfide to sulfur ratio comes at 8 per cent titrated on the titration curve shown in Figure 10 and at 3 per cent on the titration curve shown in Figure 12. There should be no break for a solution with a 1:4 sulfide to sulfur ratio because all the sulfide should be converted to polysulfide. Therefore, the first drop of ferricyanide should cause precipitation of sulfur and a gradual rise in the potential. The fact that there is a small initial break supports the dissociation of the pentasulfide noted in the spectrophotometric study. Even the values of 8 and 3 per cent agree reasonably well with the values of 9.9, 7.7, and 5.9 per cent obtained in the spectrophotometric study.

THE NATURE OF THE FERROUS COMPOUND FORMED IN SOLUTIONS
OF SODIUM SULFIDE CARRYING DISSOLVED SULFUR

Introduction

In the course of earlier work dealing with the solubility of pyrite, it was noticed that iron(II) formed an intensely green solution in the presence of a great excess of sodium sulfide. An investigation of this non-dissociated compound of iron and sulfide was undertaken for two reasons.

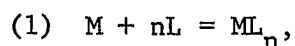
First, that iron forms a soluble species in the presence of sulfide is of great importance to the geochemist trying to explain the transport of iron in waters bearing sulfide. Some literature has already appeared on the chemistry of highly alkaline solutions containing iron and sulfide, the work dealing principally with the uses of such solutions in industry and with the products which may be isolated from such solutions. No work was found reporting a study of the combining ratio or stability constants of iron and sulfide in aqueous solution.

Secondly, it had been noted in a qualitative fashion that the presence of sulfur dissolved in the sodium sulfide changed the intensity of the color of the iron compound. Although the color of the solution did not change, it was apparent that the presence of sulfur in the system did affect the amount of the iron-sulfide derivative formed.

To make the study of the iron-sulfide derivative complete, the effects of pH and sulfide concentrations were studied. The stability of the compound formed was determined as well as the combining ratio of the iron(II) and sulfide.

Preliminary investigations indicated that the stability of the compound was not very great. The method chosen for handling the data, therefore, was the log-ratio method, a spectrophotometric method previously employed by Diehl (29) in the study of the reaction of vitamin B₁₂ with cyanide.

As generally used, this method is applied to the reaction between a metal and a combining ligand as in the reaction,



where L is the total ligand concentration. For this reaction the formation constant is defined by

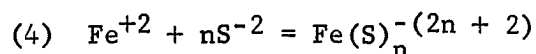
$$(2) \quad K = \frac{[ML_n]}{[M][L]^n}$$

By taking the logarithms of both sides of this equation and rearranging, the equation

$$(3) \quad \log \frac{[ML_n]}{[M]} = n \log [L] + \log K$$

is obtained. By plotting $\log [L]$ versus $\log [ML_n]/[M]$ a straight line is obtained, the slope being equal to n and the intercept equal to $\log K$. The concentration of L is assumed to be that of the total ligand added and the ratio $[ML_n]/[M]$ is obtained from spectrophotometric data. The method yields satisfactory results provided the amount of ligand tied up by the metal does not appreciably alter the total concentration of the ligand.

In the case at hand iron(II) is the metal and sulfide is the ligand according to the following equation:



Equation (3) then becomes

$$(5) \quad \log \frac{[\text{Fe}(\text{S})_n^{-(2n+2)}]}{[\text{Fe}^{+2}]} = n \log [\text{S}^{-2}] + \log K$$

Experimentally, a log-ratio plot is obtained by first preparing solutions containing a constant concentration of metal and varying known concentrations of ligand and then measuring the absorbance of the solutions. The absorbance of the solutions indicates the amount of metal that has reacted with the ligand. The unreacted metal is found by difference and the term $\log \frac{[\text{ML}_n]}{[\text{M}]}$ is then calculated. The term $\log [\text{L}]$ is known from the total ligand added. The data is then plotted and the values of n and $\log K$ are calculated by means of a least squares treatment.

Experimental Work

Iron(II)-sodium monosulfide derivative

To study the effect of pH, buffers of varying pH values were made up between pH 9.6 and 13.0. It had been noticed that little or no reaction took place to form the green compound below a pH of 9.6 and that the solutions turned a brownish color. Above pH 13 the solution became turbid very rapidly, presumably owing to the precipitation of the iron as the hydrated oxide.

Buffers were prepared as indicated in the previous section using

analytical grade reagents and deionized water.

The iron(II) solution was prepared by weighing out 0.1911 g. of ferrous ethylenediammonium sulfate and diluting to 1 l. with deionized and deaerated water. The final concentration of the solution was 5.0×10^{-4} M in iron. This solution was used immediately and never kept for more than one day to eliminate possible interference by iron(III) produced by oxidation by air.

A solution 5.0×10^{-2} M in sodium sulfide was prepared by weight using analytical reagent grade sodium sulfide nonahydrate, which had been recrystallized. The water used was both deionized and deaerated and the solution used was filtered after preparation to remove any heavy metal sulfides.

The solutions used for absorption measurements were prepared by mixing 15 ml. of the 5.0×10^{-4} M iron and 10 ml. of the 5.0×10^{-2} M sodium sulfide and diluting to 100 ml. with the appropriate buffer. While mixing the solutions, it was noted that a much more intense color was produced when the iron solution was added to the sulfide solution before the buffer. Therefore, this order of addition was followed throughout the investigation.

The pH of the final solution was measured using a Leeds and Northrup pH meter. The spectra were obtained using a Cary XV recording spectrophotometer and matched 1 cm. silica cells. Water was used as a blank inasmuch as none of the buffers employed exhibited absorption bands in the wavelength region of interest.

The dependence of the absorption of the non-dissociated iron(II)-

monosulfide system on pH is shown in Figure 13. These data indicate that the maximum color is obtained over the pH range 10.7 to 12.2. However, on standing, the solutions below pH 12 and above pH 12.5 deteriorated rapidly. The solution at pH 12.2 proved quite stable, lasting without change for about 12 hours if care was taken to exclude oxygen.

The spectrum of the iron(II)-monosulfide compound at pH 12.2 is shown in Figure 14. The spectrum shows an absorption maximum centered at 636 m μ and several lesser absorption bands at lower wavelengths. The absorbance of 0.720 at 636 m μ corresponds to a molar extinction coefficient, ϵ , of 9800 cm⁻¹M⁻¹.

The spectrophotometric measurements to determine the combining ratio of sulfide to iron(II) and the value of the formation constant were carried out at a wavelength of 636 m μ , where the derivative showed its maximum absorbance, and at pH 12.2. All solutions were deaerated before the preparation of the final solutions. Measurements of each solution were taken periodically until maximum absorbance values were obtained; this took approximately one hour for the solution less concentrated in sulfide.

Slope and intercept were calculated from the spectrophotometric data using the method of least squares (Table 4, Figure 15). The combining ratio was found to be 1.60, which would indicate that a non-dissociated compound containing two irons and three sulfides is formed. The log K for this compound at a pH 12.2 is 4.90.

Figure 13. The absorbance of the iron(II)-sodium sulfide system as a function of pH.

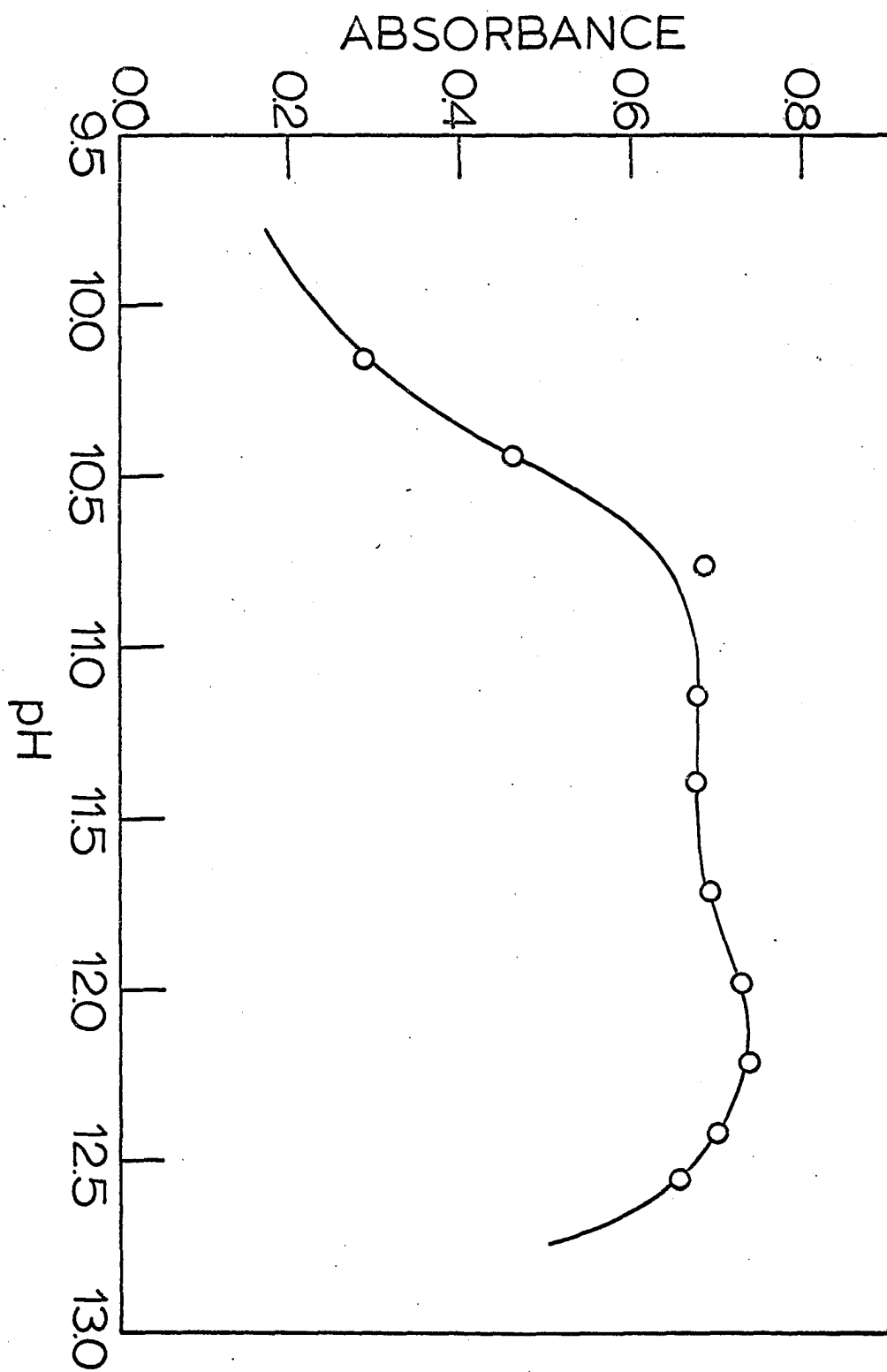


Figure 14. Absorption spectrum of the iron(II)-sodium sulfide system. pH 12.2. Solution 7.75×10^{-5} M in iron(II) and 5.0×10^{-3} M in sulfide.

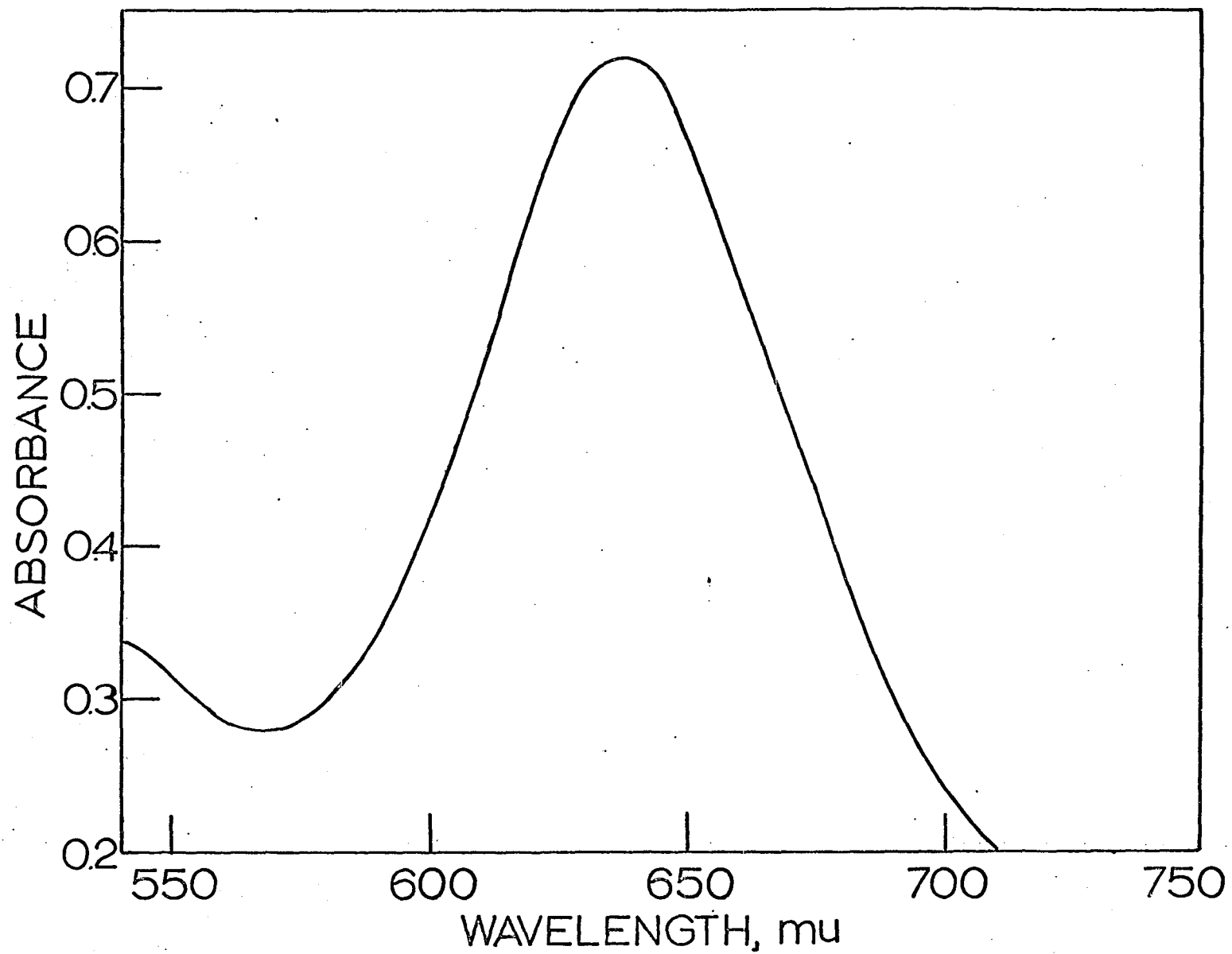


Figure 15. Log-ratio plot of spectrophotometric data
obtained on the iron(II)-sodium sulfide system.
Data of Table 4.

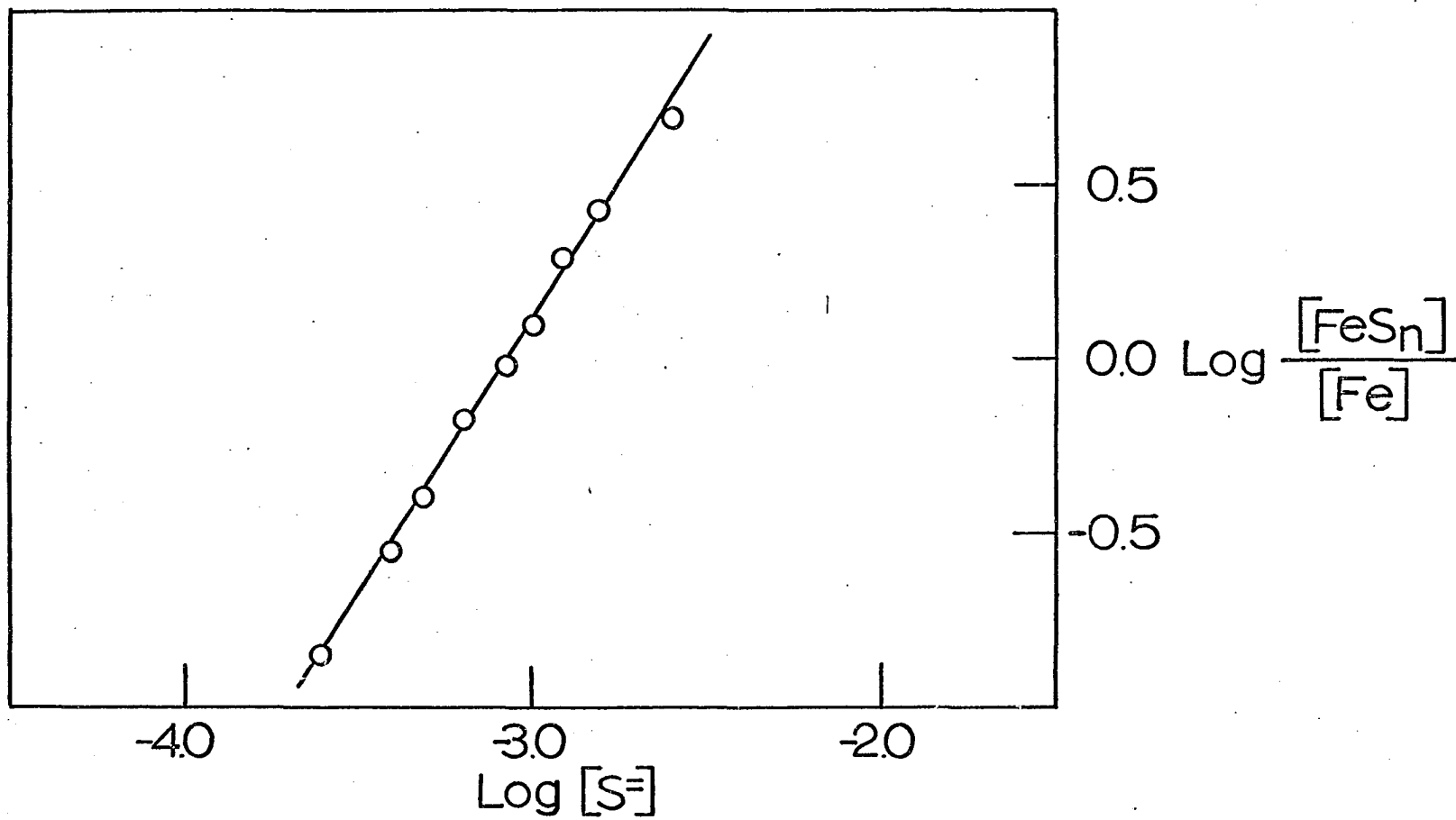


Table 4. Spectrophotometric determination of combining ratio of iron(II)-sulfide system. pH 12.2. Measurements at 636 mu.

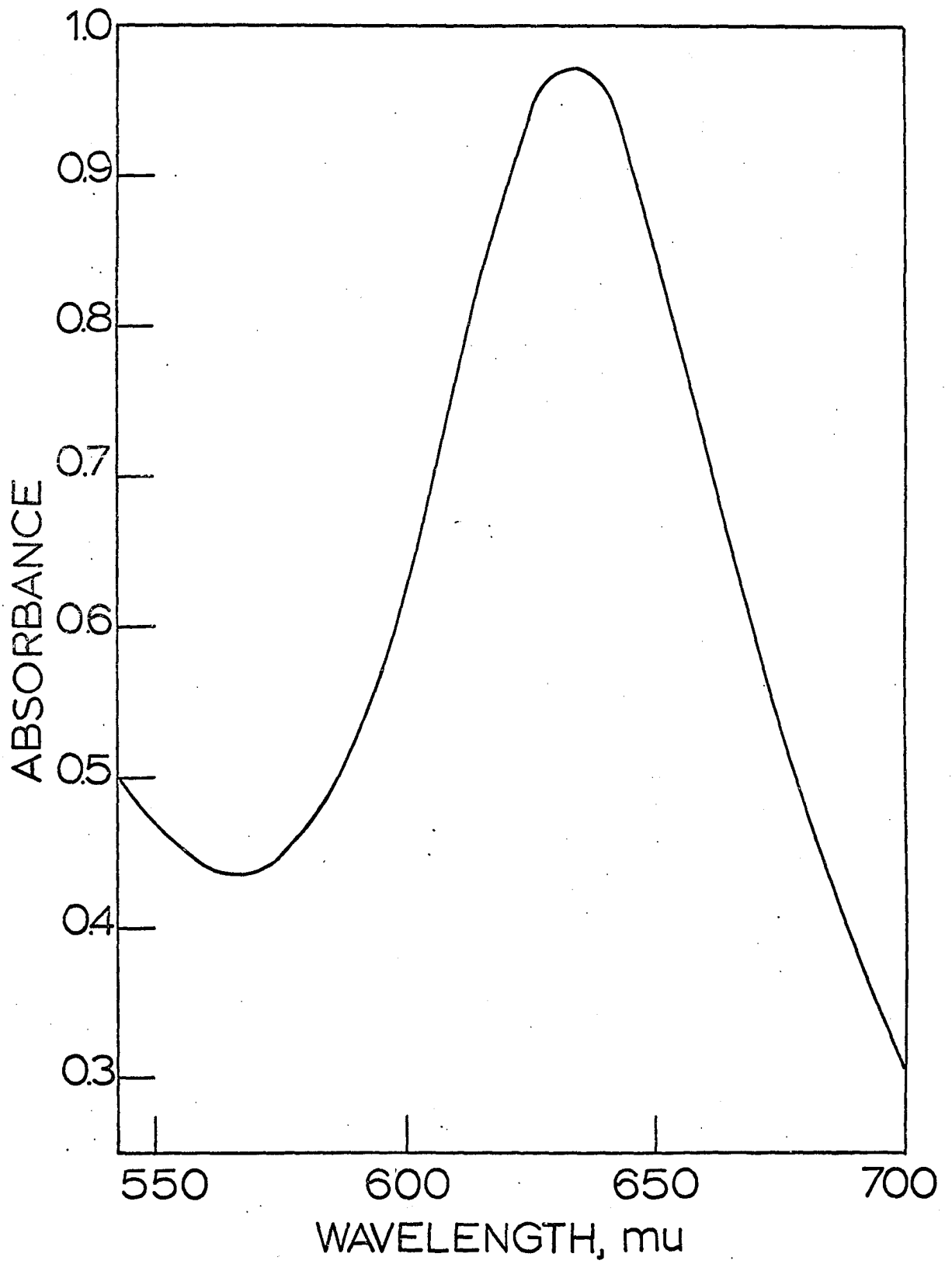
Log $[S^{-2}]$	A	$[Fe(S)_n]$ per cent	$[Fe^{+2}]$ per cent	Log $\frac{[Fe(S)_n]}{[Fe^{+2}]}$
-2.301	0.734	100.0	00.0	---
-2.602	0.610	83.1	16.9	0.692
-2.824	0.536	73.0	27.0	0.431
-2.903	0.482	65.7	34.3	0.283
-3.000	0.408	55.6	44.4	0.097
-3.071	0.357	48.6	51.4	-0.024
-3.187	0.294	40.1	59.9	-0.175
-3.301	0.212	28.9	71.1	-0.391
-3.398	0.160	21.8	78.2	-0.554
-3.602	0.090	12.3	87.7	-0.854
---	0.000	00.0	100.0	---

Iron(II)-1:1 sodium sulfide-sulfur system

It was found that the absorption spectrum of a solution 1:1 in sodium sulfide and sulfur to which iron(II) was added was very similar to that of the iron(II)-monosulfide solution described above. At pH 12.3 and with sufficient sulfide present the molar extinction coefficient was $9900 \text{ cm}^{-1}\text{M}^{-1}$ at 635 mu, the wavelength of maximum absorption. The absorption spectrum of a solution $1.25 \times 10^{-4} \text{ M}$ in iron(II) is shown in Figure 16.

The spectrophotometric method was employed to determine the combining ratio of disulfide to iron(II) and an apparent formation constant on the basis that a disulfide, S_2^{-2} , was present. The measurements were made at a wavelength of 635 mu, wavelength of maximum absorbance, and pH 12.3. The solution of 1:1 sodium sulfide-sulfur was prepared by weighing out 0.8896 g. of sulfur and dissolving it in 100 ml. of 0.278 M sodium sulfide. All solutions were deaerated before the preparation of the final solutions, which were buffered at pH 12.3. Absorbance was measured periodically and

Figure 16. Absorption spectrum of the iron(II) compound present in a solution 1:1 in sodium sulfide and sulfur. pH 12.3. Solutions 1.25×10^{-4} M in iron(II) and 2.50×10^{-2} M in sulfide.



the highest values obtained were used in the calculations. The solutions of high concentrations of sulfide were stable for at least 12 hours; other solutions decomposed after only a short time.

Slope and intercept were calculated from the spectrophotometric data using the method of least squares (Table 5, Figure 17). The combining ratio was found to be 1.44, indicating that a non-dissociated compound containing two atoms of iron and three sulfide radicals is formed. The value found for an apparent formation compound was $\log K = 4.13$.

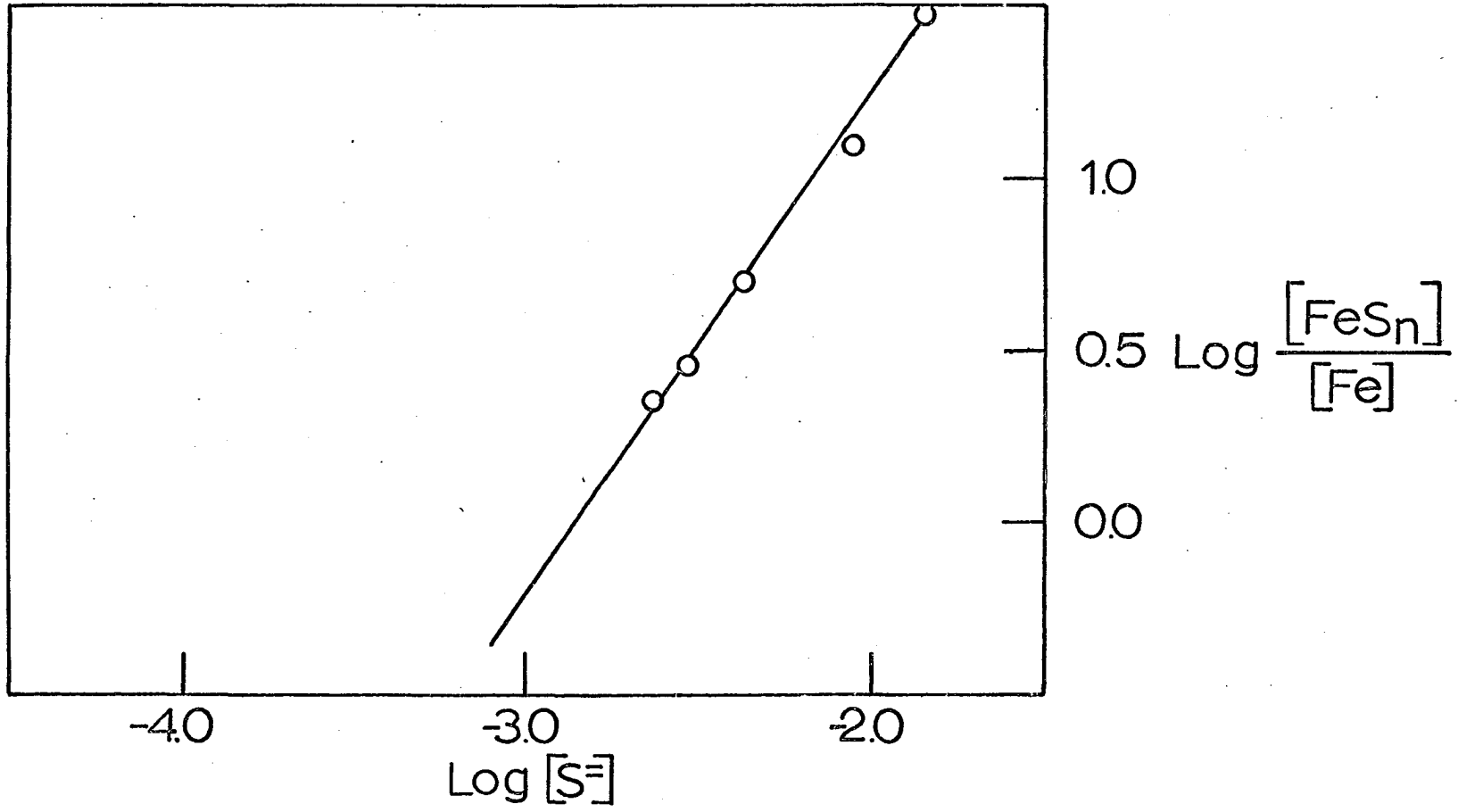
Table 5. Spectrophotometric determination of combining ratio of iron(II)-1:1 sodium sulfide-sulfur system. pH 12.3. Measurements at 636 mu.

Log $[S^{-2}]$	A	$[\text{Fe}(\text{S})_n]$ per cent	$[\text{Fe}^{+2}]$ per cent	Log $\frac{[\text{Fe}(\text{S})_n]}{[\text{Fe}^{+2}]}$
-1.556	0.745	100.0	0.0	---
-1.857	0.722	96.9	3.1	1.496
-2.078	0.690	92.6	7.4	1.097
-2.380	0.622	83.5	16.5	0.704
-2.556	0.549	73.7	26.3	0.447
-2.652	0.512	68.8	31.2	0.344
---	0.000	00.0	100.0	---

Iron(II)-1:2 sodium sulfide-sulfur solutions

The absorption spectrum of a solution bearing sodium sulfide and sulfur in the mole ratio of 1:2 and containing iron(II) was identical with that of sodium sulfide solutions containing iron. At pH 12.2 and with sufficient 1:2 sodium sulfide-sulfur solution to react with all of the iron(II) present, a value of $10,300 \text{ cm}^{-1}\text{M}^{-1}$ was found for the molar extinction coefficient at 635 mu. The spectrum of a solution $4.50 \times 10^{-5} \text{ M}$

Figure 17. Log-ratio plot of the spectrophotometric data obtained on the iron(II)-1:1 sodium sulfide-sulfur system. Data of Table 5.



in iron(II) and 1.50×10^{-2} M in sulfide is shown in Figure 18.

The spectrophotometric method was again employed to determine combining ratio and apparent formation constant. The spectrophotometric work was carried out at a wavelength of 635 mu, and all solutions were buffered at a pH of 12.2. The solution of 1:2 sodium sulfide-sulfur was prepared by weighing out 1.7792 g. of sulfur and equilibrating it with 100 ml. of 0.278 M sodium sulfide. Absorbance was measured periodically and the highest value obtained used in the calculations. All solutions were deaerated and kept under nitrogen during the course of the experiment.

The slope and intercept of the resulting log-ratio plot were calculated using the method of least squares (Table 6, Figure 19). The combining ratio was found to be 1.48 and the log K was found to be 4.00. The combining ratio was similar to the first two derivatives investigated indicating again a 3:2 compound.

Table 6. Spectrophotometric determination of combining ratio of iron(II)-1:2 sodium sulfide-sulfur system. pH 12.3. Measurements at 636 mu.

Log $[S^{-2}]$	A	$[\text{Fe}(\text{S})_n]$ per cent	$[\text{Fe}^{+2}]$ per cent	Log $\frac{[\text{Fe}(\text{S})_n]}{[\text{Fe}^{+2}]}$
-1.380	0.771	100.0	0.0	---
-1.556	0.757	98.2	1.8	1.737
-1.857	0.725	94.0	6.0	1.196
-2.078	0.678	87.9	12.1	0.861
-2.380	0.570	73.9	26.1	0.452
-2.556	0.490	63.6	36.4	0.243
---	0.000	00.0	100.0	---

Figure 18. Absorption spectrum of the iron(II) compound present in a solution 1:1 in sodium sulfide and sulfur. pH 12.2. Solutions 4.50×10^{-5} M in iron(II) and 1.50×10^{-2} M in sulfide.

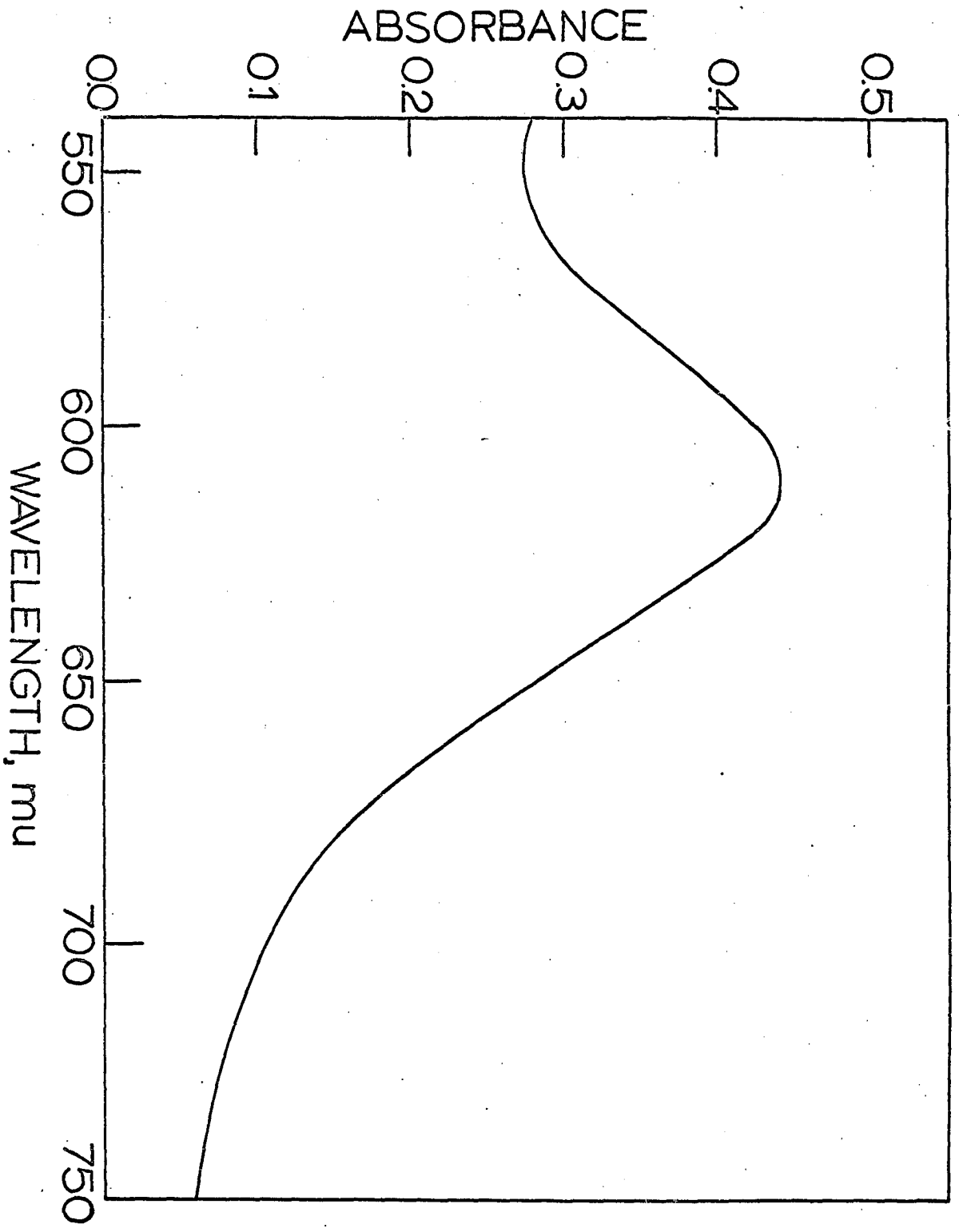
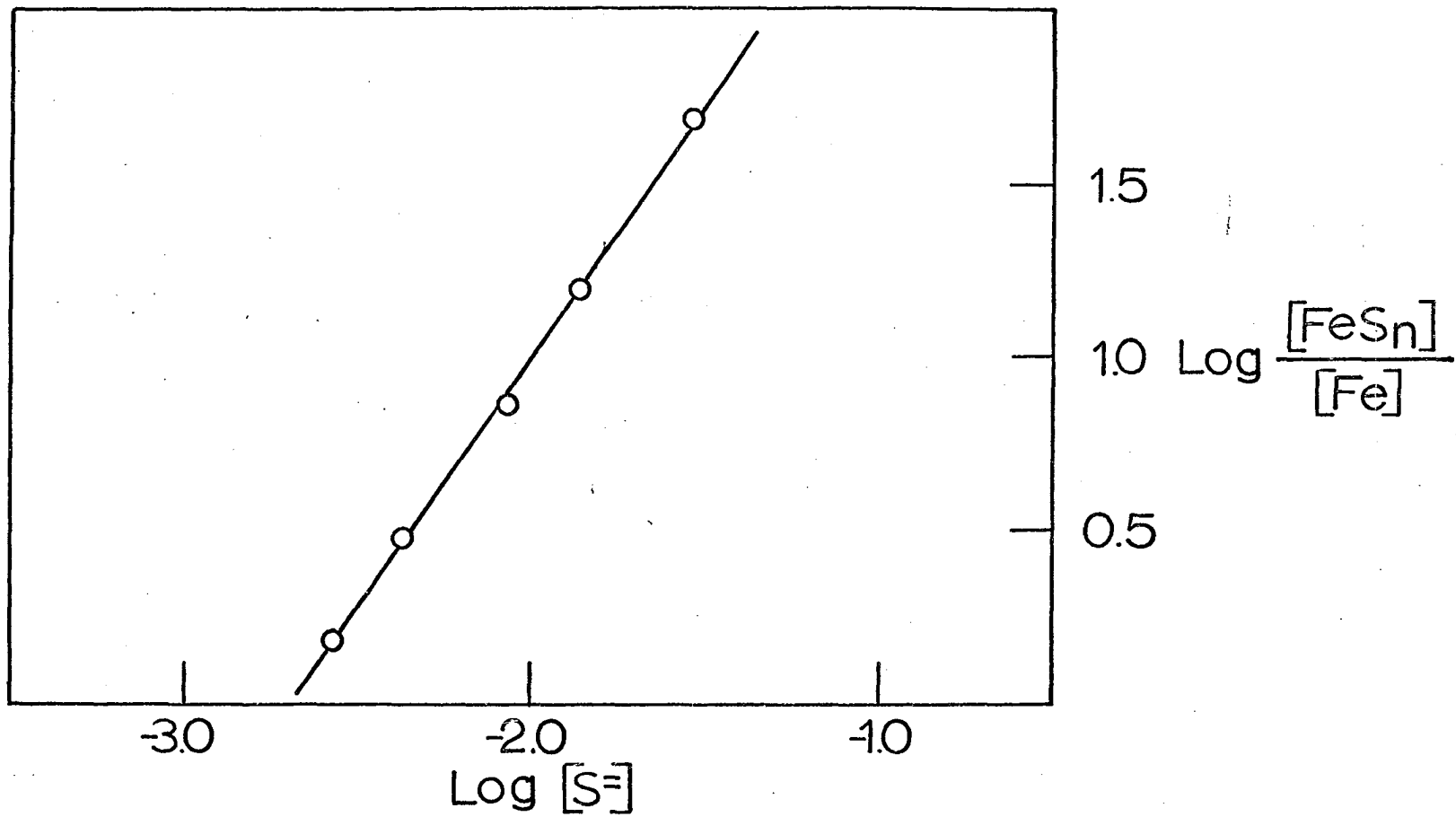


Figure 19. Log-ratio plot of the spectrophotometric data obtained on the iron(II)-1:2 sodium sulfide-sulfur system. Data of Table 6.



Iron(II)-1:4 sodium sulfide-sulfur solutions

The absorption spectra of a solution 1:4 in sodium sulfide and sulfur to which iron(II) was added was very similar to that of the iron(II)-sulfide solution. The spectrum of this solution is shown in Figure 20, the solution being 7.50×10^{-5} M in iron(II) and 2.96×10^{-1} M in sulfide. At this concentration of iron the molar extinction coefficient was about $10,200 \text{ cm}^{-1}\text{M}^{-1}$ at 637 mu, the wavelength of maximum absorbance.

To find the combining ratio and apparent formation constant, a solution 1.033 M in sodium sulfide was prepared. This solution was saturated with sulfur and the excess sulfur removed by filtration. Solutions containing 3 ml. of 2.50×10^{-3} M in iron(II) and varying amounts of the sodium sulfide-sulfur solution were then prepared and buffered at a pH of 11.1. The absorbance of each solution was measured periodically and the highest values were used in subsequent calculations.

The slope and intercept of the resulting log-ratio plot (Table 7, Figure 21) were calculated using the method of least squares. The combining ratio was found to be 1.54 and the log of the apparent formation was found to be 3.08. The combining ratio of 3:2 was the same as obtained in the solutions previously investigated.

Figure 20. Absorption spectrum of the iron(II) compound present in a solution 1:4 in sodium sulfide and sulfur. pH 12.2. Solution 7.50×10^{-5} M in iron(II) and 2.96×10^{-1} M in sulfide.

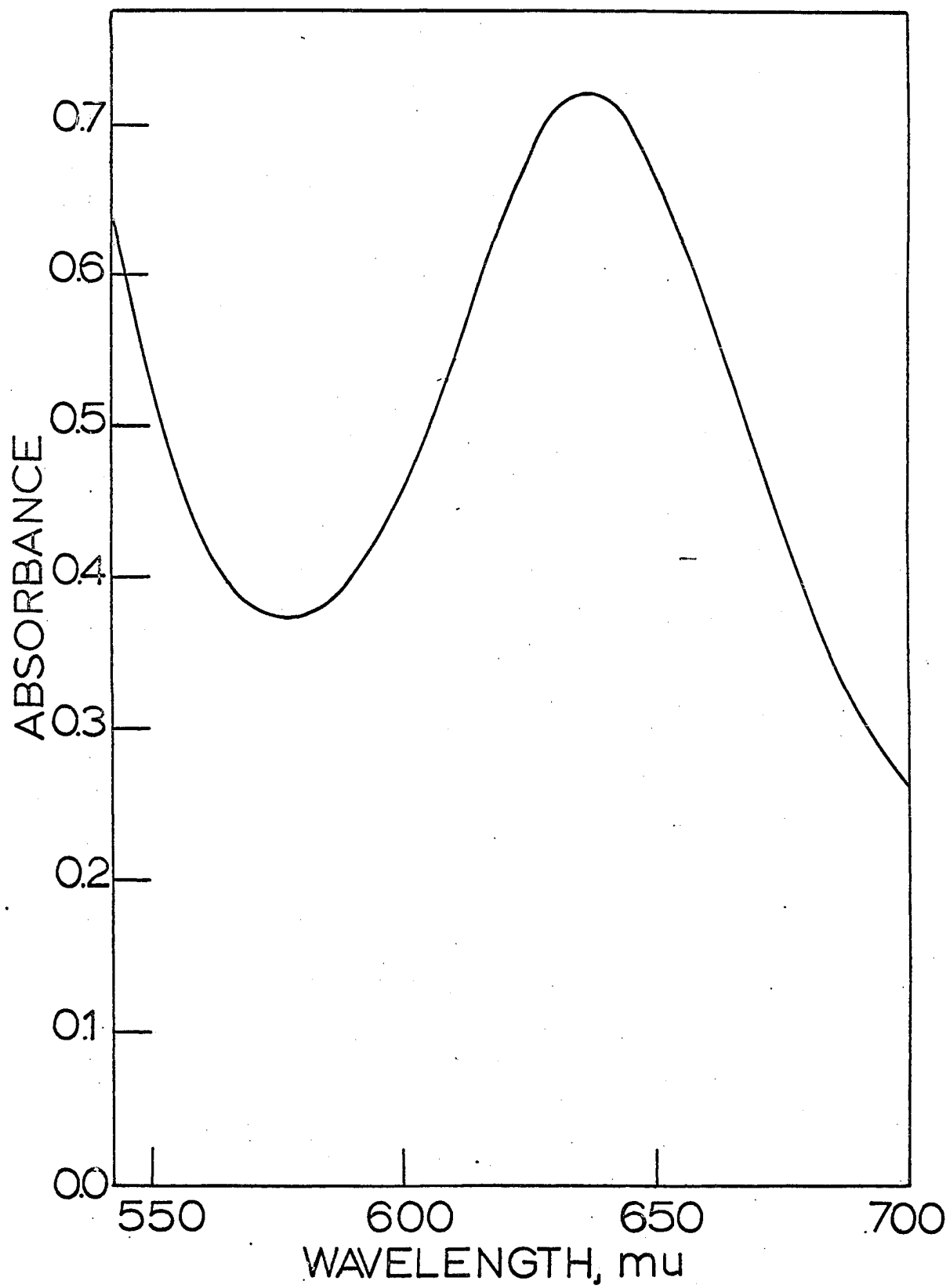


Figure 21. Log-ratio plot of the spectrophotometric data obtained on the iron(II)-1:4 sodium sulfide-sulfur system. Data of Table 7.

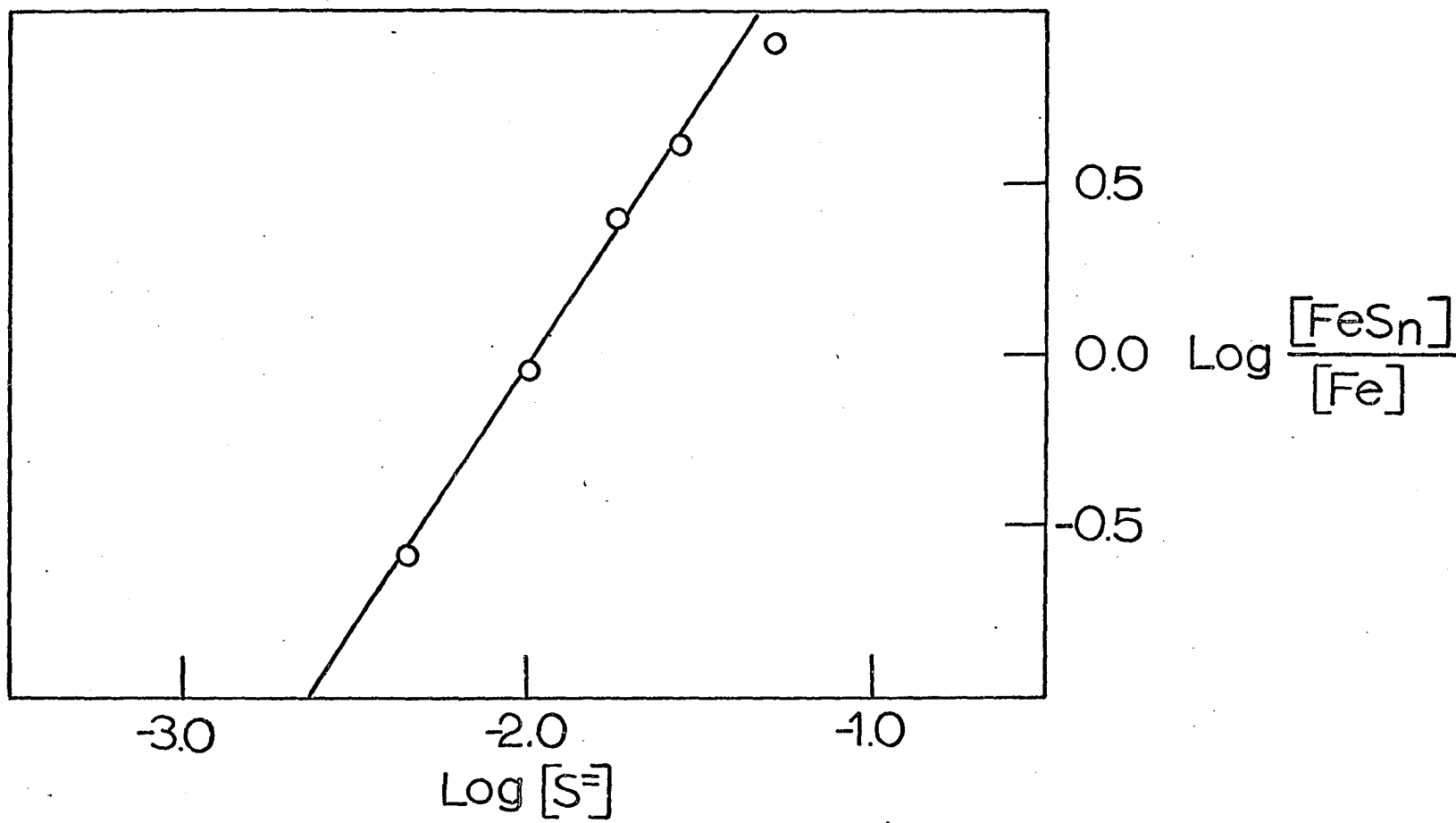


Table 7. Spectrophotometric determination of combining ratio of iron(II)-1:4 sodium sulfide-sulfur system. pH 11.1. Measurements at 637 mu.

Log $[S^{-2}]$	A	$[\text{Fe(S)}_n]$ per cent	$[\text{Fe}^{+2}]$ per cent	Log $\frac{[\text{Fe(S)}_n]}{[\text{Fe}^{+2}]}$
-0.810	0.762	100.0	00.0	---
-0.987	0.750	98.4	1.6	1.790
-1.286	0.680	89.2	10.8	0.917
-1.588	0.615	80.7	19.3	0.621
-1.745	0.549	72.0	28.0	0.410
-1.987	0.360	47.2	52.8	-0.049
-2.286	0.155	20.3	79.7	-0.594
-2.987	0.028	3.7	86.3	-1.367
---	0.000	0.0	100.0	---

Results and Conclusions

The data derived from the experimental work discussed above is summarized in Table 8.

Table 8. Summary of results of determination of combining ratios and apparent formation constants in iron(II)-sulfide-sulfur systems.

$\text{Na}_2\text{S}:\text{S}$ Ratio	Absorption Maximum	ϵ	Combining Ratio Fe:S	Apparent Formation Constant log K
1:0	636 mu	9,800	1.60	4.90
1:1	635 mu	9,900	1.44	4.13
1:2	635 mu	10,300	1.48	4.00
1:4	636 mu	10,200	1.54	3.08

From the results it is apparent that the iron(II)-sulfide species formed is the same irrespective of the amount of sulfur dissolved in the solution; wavelength of the absorption maximum, molar extinction coefficient,

and combining ratios are the same in each solution.

It is evident, however, that the addition of sulfur to the system has a pronounced effect on the apparent formation constant as indicated by the decrease in $\log K$ as the sulfur concentration increases. An obvious explanation is that the iron derivative involves the simple monosulfide anion only and that the addition of the sulfur simply reduces the concentration of the latter by converting some of it to the pentasulfide. This can be easily demonstrated. Assuming that the only anions present are monosulfide and pentasulfide, the concentration of monosulfide in the various solutions studied in the preceding section were recalculated on the basis of complete conversion of the added sulfur to pentasulfide. The concentration of sulfide in the solution 1:1 in sulfide and sulfur is thus only 75 per cent of the original concentration; that of the 1:2 solution only 50 per cent. In the 1:4 mixture all the sulfide should be tied up as a pentasulfide; however, earlier work indicated that some dissociation of the pentasulfide occurs in this solution. On the basis of the spectrophotometric data obtained on the 1:4 sulfide-sulfur system, it was assumed that 8 per cent of the original sulfide concentration is present as the monosulfide. Using these new concentrations of sulfide, the log-ratio data obtained as described above was recalculated and plotted, Figure 22.

As will be seen, the lines now fall very closely together. From the recalculated data the best approximation of the formation constant for the iron(II)-sulfide compound is $\log K = 4.8$.

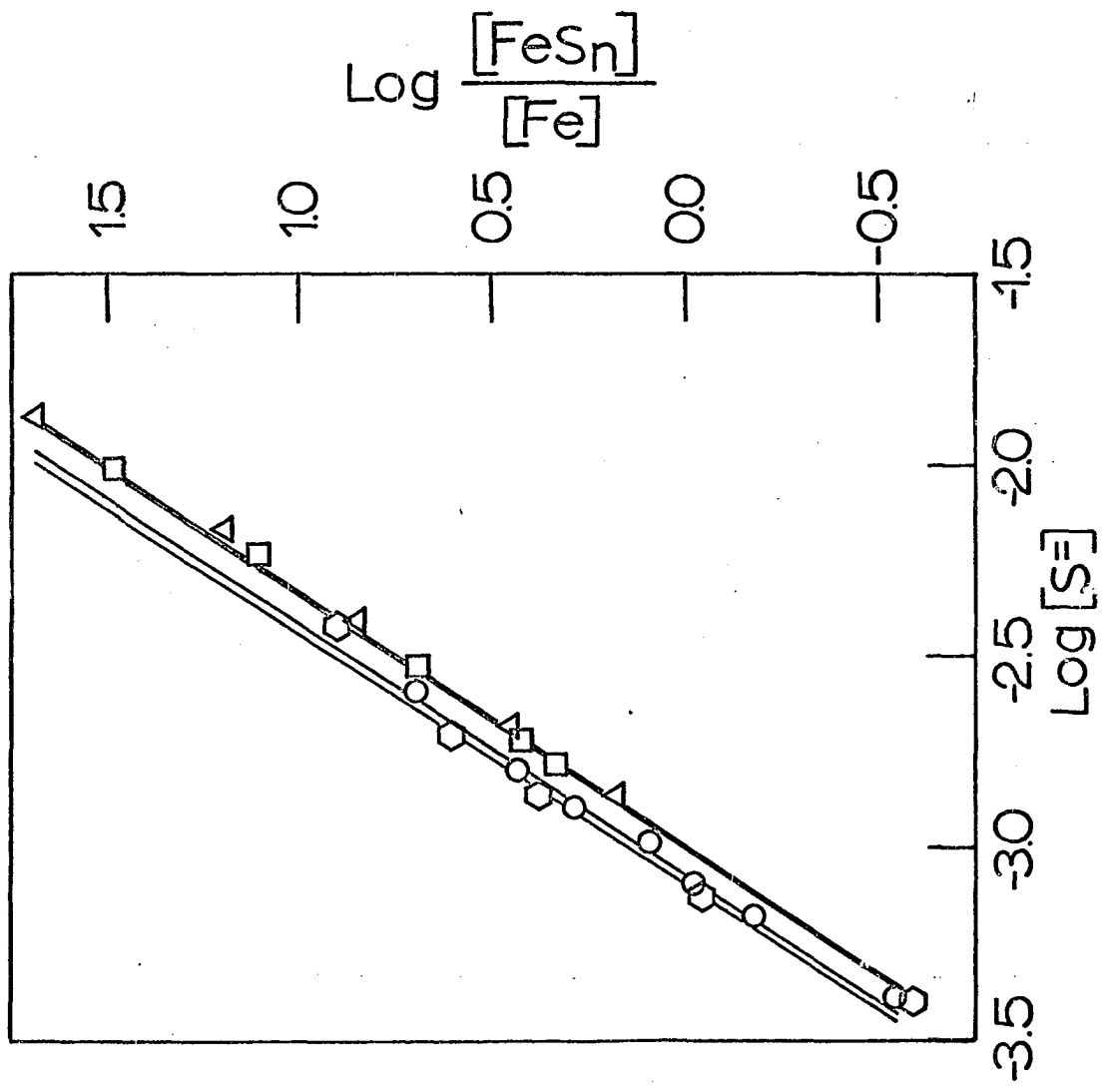
Figure 22. Log-ratio plots for all iron(II)-sodium sulfide-sulfur systems with the concentration of sulfide corrected on the assumption that the sulfide concentration was lowered by conversion to pentasulfide by the sulfur added.

○ sodium sulfide

□ sodium sulfide:sulfur = 1:1

△ sodium sulfide:sulfur = 1:2

◇ sodium sulfide:sulfur = 1:4



DISCUSSION AND CONCLUSIONS

An investigation has been made into the nature of the polysulfide produced when elemental sulfur is dissolved in a solution of sodium sulfide. Polarography and spectrophotometry in the ultraviolet and infrared regions have been used in this investigation. A detailed investigation has been made of the ferricyanide titration of sulfide-sulfur mixtures. The nature of the compound formed when iron(II) is added to a solution of sodium sulfide carrying dissolved sulfur has been investigated.

For the polarographic studies, solutions were prepared by dissolving sulfur in a solution of sodium sulfide in mole ratios of sodium sulfide to sulfur of 1:0, 1:1, 1:2, 1:3, and 1:4. Precautions were taken to exclude oxygen from the solutions. All measurements were carried out as quickly as possible and under nitrogen where feasible. The polarograph of the solution of sodium sulfide with no dissolved sulfur showed no reduction wave, this being expected inasmuch as the sulfur is in the lowest oxidation state possible. The solutions containing dissolved sulfur all showed reduction waves, the half-wave potential of which was the same for every solution, -1.65 volts. The diffusion current, the height of the polarographic wave, increased with increasing amounts of dissolved sulfur up to the ratio of 1:4. These findings are best interpreted on the basis that only one polysulfide species, namely the pentasulfide, S_5^{2-} , is formed.

In the investigation of the ultraviolet absorption spectra, solutions were prepared with ratios of sulfide to dissolved sulfur ranging from 1:0 to 1:4. For all solutions the spectrum was obtained from 210 m μ to 750 m μ . In the spectrum of sodium sulfide a single absorption band was present, at

225 μ . The spectra of the solutions containing dissolved sulfur differed from the spectrum of sodium sulfide in that shoulders were present at 295 μ and at 365 μ and an absorption band was present at 225 μ . Although the absorption bands of the sulfur-bearing solutions were identical in position, the absorbance increased with increasing sulfur.

Spectrophotometric titrations were then made, the wavelengths 225 μ and 295 μ being used for the absorbance measurements. Solutions of sodium sulfide were prepared with the mole ratio of sulfide to sulfur varying from 1:0 to 1:8. The solutions were buffered and the absorbance measured. The spectrophotometric titration curve showed a smooth, nearly linear increase in absorbance up to the sulfide to sulfur ratio of 1:4. The maximum absorbance was reached at a slightly higher ratio, 1:4.2. This evidence is also best interpreted on the basis that only a pentasulfide is formed with some dissociation, about 8 per cent, occurring in solution in which the mole ratio is 1:4.

In the study of the sulfide-sulfur system by infrared spectroscopy, Irtran cells were employed; these cells are made of zinc sulfide and are resistant to attack by aqueous solutions. The cells were used so that the sample was essentially a thin film, prepared by placing a drop or two of solution under study between the cell windows. The solutions were prepared from a saturated solution of sodium sulfide. Spectra over the wavelength range of 6 μ to 11 μ were obtained of solutions bearing dissolved sulfur in the mole ratio of sulfide to sulfur of 1:0, 1:1, 1:2, 1:3, and 1:4. A single, large absorption band, at 6.2 μ , was present in the spectrum of the sodium sulfide solution and present also in the spectra of all the

sulfur-bearing solutions but is an absorption band of water. In the absorption spectra of the 1:3 and 1:4 solutions, absorption bands were present at 9 μ and 10.2 μ ; the absorbance of the 1:3 solution was somewhat less than that of the 1:4 solution. In the spectra of the 1:1 and 1:2 solutions these bands were not present. Because of the large amount of water present, the method is not very sensitive. These results also indicate that only the pentasulfide is formed but the evidence is qualitative only.

All three lines of evidence, polarography, spectrophotometry in the ultraviolet, and spectrophotometry in the infrared, indicate that only one species, namely the pentasulfide, S_5^{-2} , is present. Were several species present concurrently, the polarographic diffusion current and the absorbance in the ultraviolet would not increase linearly with the content of dissolved sulfur as was observed, inasmuch as other polysulfide species, if present, would be expected to have different formation constants and different reduction and light absorption properties.

The oxidimetric titration of solutions of sodium sulfide bearing dissolved sulfur provided further evidence that only the pentasulfide is present. The electrode system employed was a platinum electrode-saturated calomel pair; the oxidizing agent was potassium ferricyanide. Each of the potentiometric titration curves obtained showed two breaks. The first break was dependent upon the amount of sulfur initially dissolved in the sodium sulfide and moved to the left, that is appeared earlier, with increasing amounts of dissolved sulfur. This break occurred when the sulfur, which is a result of the oxidation of sulfide by ferricyanide, was

no longer redissolved by the sodium sulfide still present in solution. At this first break the ratio of sulfide to sulfur was found to be very close to 1:4 in each of the titrations. The second break occurred at the point where all the sulfide had been oxidized to sulfur and was found to be independent of the initial concentration of sulfur.

The character of these titration curves is neatly in accord with the concept that only a single polysulfide, the pentasulfide, is present. If species other than the pentasulfide were present, a more complex titration curve would be expected. The oxidation-reduction couple responsible for the potential up to the first break is the pentasulfide-sulfide couple with an E° value of about -0.61 volts (vs. s.c.e.). Between the first and second breaks the responsible couple is the sulfur-pentasulfide couple with an E° value of approximately -0.51 volts (vs. s.c.e.).

The titration curve of the 1:4 mixture, that is, the sulfide solution initially saturated with sulfur, is of interest in that the first break actually appears at 3 to 8 per cent titrated rather than at zero; this is interpreted as being caused by the slight dissociation of the pentasulfide as found earlier in the ultraviolet spectrophotometric work. The estimates of this dissociation by the two methods are in rough agreement.

Finally, an investigation of the green, water soluble compound formed between iron(II) and large amounts of sodium sulfide was undertaken. The nature of this compound was also studied with respect to the amount of dissolved sulfur in the system. It was found that the absorption spectrum of the iron(II)-sulfide compound was unaltered by the addition of sulfur

except for the absorption of the polysulfide formed. The combining ratio of iron and sulfide was determined using spectrophotometric data. This combining ratio, iron(II) to sulfide, was found to be 2:3 and to be independent of the amount of dissolved sulfur.

As estimated spectrophotometrically, the amount of the iron(II)-sulfide compound formed decreased with increasing amounts of dissolved sulfur. This effect was directly explicable on the basis that the dissolved sulfur simply combined with sulfide to reduce the concentration of the latter. On the basis that only one polysulfide, the pentasulfide, was present, the spectrophotometric data were recalculated and a formation constant obtained for the formation of the iron(II)-sulfide compound. It was necessary to take into account the small dissociation of the pentasulfide, 8 per cent as calculated earlier from the ultraviolet absorption data. The log of the formation constant for the iron(II)-sulfide compound was estimated to be 4.8.

In conclusion, the data obtained by polarography, spectrophotometry in the ultraviolet and infrared, titration with ferricyanide, and the nature of the iron(II)-sulfide-sulfur system all indicate that only a single polysulfide, the pentasulfide, S_5^{-2} , is present in solutions of sulfide containing dissolved sulfur.

This conclusion is not in agreement with the earlier work of Peschanski, Maronny, and Cloke, in which it is assumed that several of the possible polysulfides are present and the amounts of each calculated from electrochemical data. Cloke assumed that no di- and trisulfides were present but included a hexasulfide in his calculations. Peschanski and

Maronny assumed that all polysulfide species up to and including pentasulfide were present. Included in the calculations of these authors is free energy data obtained from measurements on the crystalline compounds, a very questionable practice inasmuch as it is far from established that such materials are true compounds and not mixtures.

The present work is in much better agreement with the work of Schwarzenbach and Fischer who found no evidence for di-, tri-, and hexasulfides but found it necessary to assume the existence of the tetrasulfide as well as the pentasulfide to explain the results of their rapid titration of alkali polysulfides with acid. Schwarzenbach and Fischer do state that the tetrasulfide disproportionates into sulfide and pentasulfide and it may be simply that with a longer period for the establishment of equilibrium their findings would be in agreement with the conclusion of the present work that the only polysulfide present in solution is the pentasulfide, S_5^{2-} .

SUMMARY

The nature of the sodium polysulfide formed when elemental sulfur is dissolved in a solution of sodium sulfide has been investigated by four independent methods: polarography, spectrophotometry in the ultraviolet, spectrophotometry in the infrared, and potentiometric titration. The nature of the compound formed when iron(II) is introduced into a solution of a polysulfide has been established.

Polarograms of solutions of sodium sulfide carrying varying amounts of dissolved sulfur showed only one reduction wave, not present in that of a solution of sodium sulfide alone, appearing at -1.65 volts on the introduction of sulfur, and with increasing sulfur content remaining unchanged in half-wave potential but increasing linearly in height to the point where the mole ratio of sodium sulfide to sulfur was 1:4. The polarography thus indicates that a single polysulfide species is present and that it is the pentasulfide, S_5^{-2} .

The ultraviolet absorption spectra of solutions of sodium sulfide containing dissolved sulfur were identical, with absorption bands at 365 μ , 295 μ , and 225 μ . The absorbance at these wavelengths increased with increasing sulfur concentration. A spectrophotometric titration indicated that the only species present was the pentasulfide. The spectrophotometric data also showed that in the solution in which the mole ratio of sulfide to sulfur is 1:4 the pentasulfide is dissociated to the extent of 8 per cent.

In the infrared spectra of solutions of sodium sulfide bearing dissolved sulfur, bands were found at 9 μ and 10.2 μ in those solutions in which the ratio of sulfide to sulfur was 1:3 and 1:4, the absorbance of the 1:4

solution at each of these wavelengths being greater. These bands were not present in the 1:1 and 1:2 solutions; but because of the experimental difficulties and the insensitivity of the method, they may actually be present and simply lost in the high background. As far as it goes, the infrared spectra are also best interpreted on the basis that only one sulfide, the pentasulfide, is present.

Potentiometric titrations of solutions of sodium sulfide alone and carrying dissolved sulfur with potassium ferricyanide showed two breaks. The first break was dependent upon the total amount of sulfur present, that is, on the sum of the dissolved sulfur initially present and that formed during the oxidation; in every titration this break occurred at the point where the ratio of sulfide to sulfur was 1:4. The second break was independent of the amount of sulfur present and occurred when all the sulfide had been oxidized to sulfur. Thus, the titration curves also indicate that a single polysulfide, the pentasulfide, is present in solutions of sodium sulfide bearing dissolved sulfur. The couple responsible for the potential up to the first break is the pentasulfide-sulfide couple, from the first break to the second, the sulfur-pentasulfide couple. The estimated E° values for these couples are -0.61 volts and -0.51 volts respectively.

The green compound formed on the addition of iron(II) to solutions of sodium sulfide bearing dissolved sulfur has been studied. It was found that the same compound is present irrespective of the amount of dissolved sulfur present and that the combining ratio of iron to sulfide is 2:3. The amount of the ferrous compound formed decreased with increasing amounts

of dissolved sulfur, this effect resulting simply from the decrease in the concentration of the sulfide resulting from the formation of the pentasulfide. The log of the formation constant for the iron(II)-sulfide compound was estimated to be 4.8.

Four independent lines of investigation thus lead to the conclusion that a single species, sodium pentasulfide, Na_2S_5 , is present in solutions of sodium sulfide carrying dissolved sulfur. This pentasulfide is dissociated to the extent of about 8 per cent. Iron(II) reacts with sulfide to form a soluble, green compound, $\text{Fe}_2\text{S}_3^{-2}$, the composition of this compound being independent of any dissolved sulfur.

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