IONIC EQUILIBRIUM IN
POLYSULFIDE SOLUTIONS

by

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Submitted to the Department of Chemical Engineering on August 25, 1958, in partial fulfillment of the requirements for the degree of Doctor of Science.

ABSTRACT

A method for predicting the ionic distributions in aqueous alkali polysulfide (Na_2S_x) solutions was required in order that the existing data on the production of hydrogen persulfides (H_2S_n) by the acidification of such polysulfide solutions might be better interpreted. The major work of the present thesis was a study of equilibrium in the system Na_2S-S-H_2S-H_2O. The independent variables in this study were the temperature, the hydrogen sulfide partial pressure, the sodium ion (Na^+) molality, and the ratio S/Na_2S in the aqueous phase. From the stoichiometric measurements plus direct determinations of elemental sulfur (S_8) activity by extraction with o-xylene simultaneous equations could be written for the desired polysulfide equilibrium constants.

The results of experiments employing two opposite reaction directions indicated that true equilibrium could not be attained at room temperature. On the other hand, the ionic reactions apparently are mobile at 75°C. Unfortunately, it was not possible to obtain data over a sufficiently wide range of sulfur activities to determine the polysulfide equilibrium constants uniquely. Of the several possible sets of constants which could be generated by graphical techniques, the best fit with the experimental data was realized with a distribution including the ions $S_3^=$, $S_4^=$, $S_5^=$, and $S_6^=$. From these "recommended" equilibrium constants the proposed compositions of sodium polysulfide solutions at 75°C. could be computed.

Even though polysulfide ionic distributions apparently do change somewhat with temperature, the proposed ionic compositions at 75°C. were compared with previous data on the production of hydrogen persulfide (raw oil) at room temperature

and below. It was found that at a given mixing rate the fraction of initial polysulfide ions ($S_x^=$) yielding hydrogen persulfides varied but little with ionic distribution. The lack of the disulfide and trisulfide species in raw hydrogen persulfide thus had to be attributed either to their relative absence in the initial polysulfide or to their greater reactivity with the nascent sulfur released by decomposition during acidification. The apparent instability of the acid polysulfide ions (HS_x^-), suggested as the intermediates in the raw oil synthesis, was indicated independently by the results of pH determinations in the equilibrium experiments of the present thesis.

The ionic distributions in aqueous polysulfide solutions might be defined more closely than was possible in the present thesis only if a direct analysis for one or more of the individual polysulfide ions can be developed.

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Professor L. F. Hamilton
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Dear Sir:

The thesis entitled "Ionic Equilibrium in Polysulfide Solutions" is hereby submitted in partial fulfillment of the requirements for the degree of Doctor of Science.

Respectfully submitted,

Donald L. Peters

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SUMMARY

A. Introduction

In the literature are reported considerable data on the production and properties of the hydrogen persulfides, a series of unstable yellow oils having the general formula H_2S_n. Studies have indicated that both the starting material composition and the rate of mixing strongly affect yield and product composition in the usual synthesis of "raw oil", or mixed hydrogen persulfides, by the acidification of an aqueous solution of an alkali polysulfide (normally Na_2S_x). Further research has been extended to the preparation of the individual hydrogen persulfides from raw oil and the possible commercial application of these persulfides in organic syntheses.

Although a qualitative spectroscopic analysis for some of the species present in raw oil has been developed, the lack of any knowledge of the individual ionic constituents of aqueous polysulfide solutions has proven a barrier to the complete interpretation of the persulfide synthesis mechanism. It has not been established, for example, whether the absence of the disulfide and trisulfide species in raw hydrogen persulfide is due to the lack of the corresponding polysulfide ions in the starting material or to the decomposition of these components during acidification. The determination of the ionic compositions of aqueous alkali polysulfide solutions therefore is the object of the present thesis. The distributions to be derived herein, while specifically to be compared to the results of raw oil syntheses, should be equally applicable to any situation in which aqueous solutions of the polysulfides of sodium or of any other metal are to be employed.

The lack of an analysis for any one of the individual polysulfide ($S_x^=$) ions leaves only overall properties available for use in attempting to predict the actual ionic compositions. The data reported in the literature show the hydrolysis of polysulfide solutions to diminish rapidly as "x" in the average formula Na_2S_x increases; the hydrogen persulfides thus are stronger acids than hydrogen sulfide. Values of "x" as high as 5.24 in aqueous solution at room temperature have been obtained by the sulfur saturation of initial sodium monosulfide. Unfortunately, these results in large part were not measured under equilibrium conditions. Various individual polysulfides have been isolated by fractional crystallization from mixed solvent systems, but the preparation of solid sodium disulfide, for instance, cannot be construed as evidence that the disulfide ion is present in stoichiometrically significant proportions in ordinary aqueous polysulfide solutions.

The program of the present thesis was set up to accomplish the following:

1. Determine the conditions under which the ionic equilibria are mobile.
2. Under equilibrium conditions perform measurements from which the polysulfide ionic distributions can be derived.
3. Interpret the existing raw oil synthesis data in view of these findings.

Even though the objective was to study the ionic equilibria in ordinary sodium polysulfide solutions (the system Na_2S-S-H_2O), it was found more fruitful to work experimentally with the general system Na_2S-S-H_2S-H_2O. Besides the over-all or stoichiometric measurements it was possible to determine in this situation the partial pressures or the activities of the following:

Hydrogen sulfide (H_2S)
Elemental sulfur (S_8)
Hydrogen ion (H^+)

From these numbers simultaneous equations could be set up and solved for the polysulfide equilibrium constants, and hence the ionic distributions.

B. Procedure

All experiments were performed in a 1000-ml vessel maintained at the desired temperature and at essentially atmospheric pressure. The ratios H_2O/Na_2S (in effect, sodium ion molality) and H_2S/Na_2S were determined from two iodimetric titrations, while the ratio S/Na_2S was fixed by the weight of "polysulfide sulfur" (PSS) placed in solution. The hydrogen sulfide partial pressure was assumed equal to the total pressure minus the partial pressures of water vapor and any other inert components. The elemental sulfur activity was taken to be unity if solid sulfur remained in equilibrium with the aqueous phase at the completion of the experiment. For those cases in which sulfur saturation was not present, sulfur activities were measured by the sulfur concentrations developed in o-xylene layers in contact with the equilibrium aqueous solutions. Hydrogen ion activities, or pH values, were determined using the glass electrode.

Equilibrium was approached from two directions: (1) sodium hydrosulfide plus sulfur, and (2) sodium polysulfide plus hydrogen sulfide. In the former case the hydrogen sulfide evolved upon the addition of a given amount of sulfur could be measured independent of the final solution analysis, as was done by Rule and Thomas (<u>56</u>) in their study of the sodium hydrosulfide-sulfur reaction in absolute ethanol; a material balance thus could be calculated. The time periods allowed for reaching equilibrium ranged from 0.75 to 10.0 hours, depending on conditions.

Experiments were carried out at 25°C. and at 75°C. At room temperature all operations were at 4.0 sodium ion molality under 1.0 atm hydrogen sulfide partial pressure. At the higher temperature sulfur activity traverses at about 0.6 atm hydrogen sulfide partial pressure were performed at sodium molalities of 1.0 and 4.0. Sulfur saturation experiments at 75°C. also were made at molalities ranging from 0.1 up to 8.0. Some of these latter involved nitrogen dilution to produce hydrogen sulfide partial pressures as low as 0.02 atm.

C. Results

The raw data from the $Na_2S-S-H_2S-H_2O$ equilibrium experiments were converted into the over-all ionic concentrations of sodium (Na^+), polysulfide ($S_x^=$, sum of $[S_2^=] + [S_3^=] + [S_4^=] + \ldots$), and hydrosulfide ($HS^-$). The polysulfide sulfur (PSS) then could be set equal to ($[S_2^=] + 2[S_3^=] + 3[S_4^=] + \ldots$). From various considerations it was shown that in solutions saturated with hydrogen sulfide other possible ionic species, in particular the acid polysulfides (HS_x^-), could be neglected in material balances.

1. The System $Na_2S-S-H_2S-H_2O$ at 25°C.

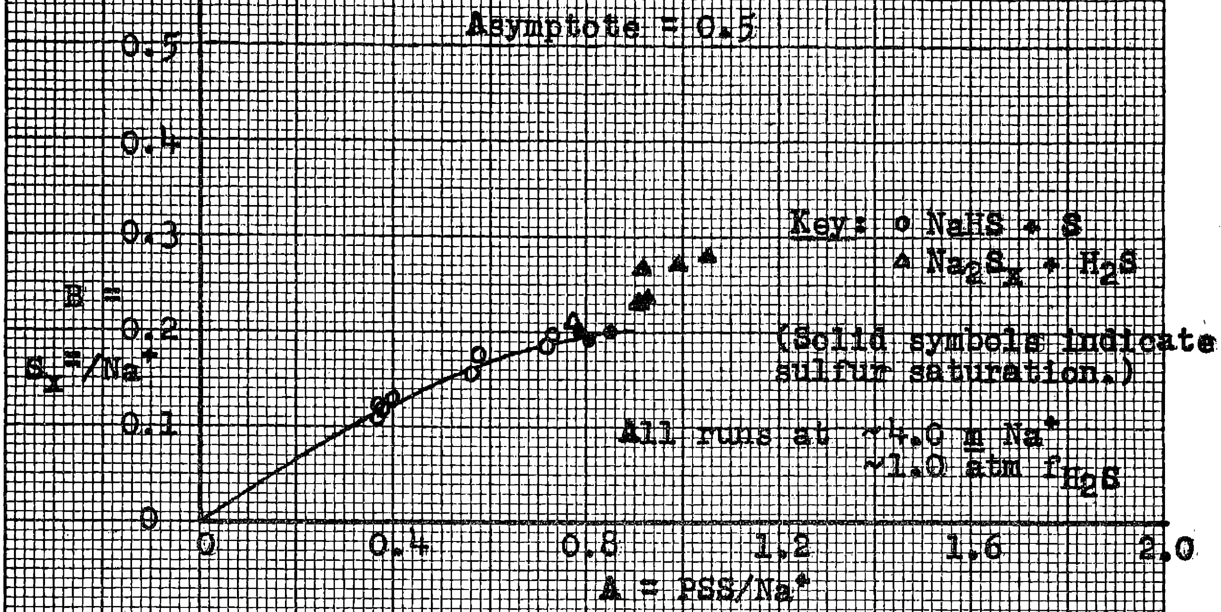
The results of the experiments at 25°C., 4.0 m sodium ion, and 1.0 atm hydrogen sulfide partial pressure are plotted in Figure 12 as the ratio $S_x^=/Na^+$ (or "B") versus the ratio PSS/Na^+ (or "A"). In the sodium hydrosulfide-sulfur reaction "B" and "A" thus should refer to the hydrogen sulfide evolved and the sulfur added, respectively. Examination indicates that the average sulfur subscript of the polysulfides present at equilibrium could be written as $(A/B)+1$. The actual hydrogen sulfide balances ranged from 96 to 100 per cent.

Since the points at sulfur saturation approaching equilibrium from the two directions failed to agree, it was concluded that certain reactions are not mobile at room temperature.

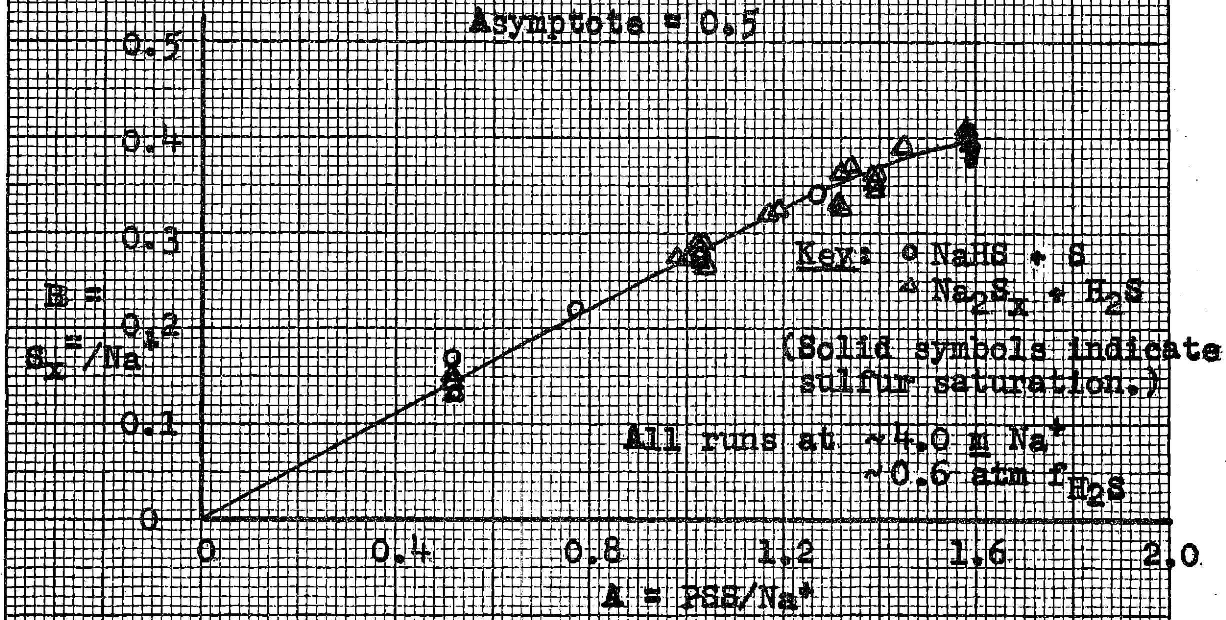
2. The System Na_2S-S-H_2S-H_2O at 75°C.

The data at 75°C., 4.0 m sodium ion, and about 0.6 atm hydrogen sulfide partial pressure similarly are shown in Figure 14. The results obtained using the two reaction directions essentially confirmed the attainment of equilibrium at this higher temperature. A certain amount of scatter, greater than that preducted from the expected measurement errors, nevertheless is evident. A similar traverse at sulfur activities less than unity performed at 1.0 m sodium ion is not shown in the accompanying plot.

Derivations indicated that the functions "X" and "Y" (defined as $\frac{[S_x^=]f_{H_2S}}{[HS^-]^2}$ and $\frac{[PSS]f_{H_2S}}{[HS^-]^2}$, respectively), as calculated for the experiments at sulfur saturation and varying molalities and hydrogen sulfide partial pressures, should not vary except for a factor proportional to an "average" ionic activity coefficient γ_{avg}. The ratio Y/X or $PSS/S_x^=$ at any given sulfur activity thus would be expected to be constant. The 75°C. data at sulfur saturation, which are not shown here, verified this relationship within a rather wide scatter and made possible the estimation of the rough curve of γ_{avg} versus molality shown in Figure 33.



from FIGURE 12
Equilibrium Results at 25°C
(Based on Final Solutions)



from FIGURE 14
Equilibrium Results at 75°C

The pH data at 75°C. were utilized in demonstrating that certain ionic species were unimportant, but owing to their low precision could not be used in the final equilibrium calculations. Since attempted determinations of sulfur activities in o-xylene solutions from vapor pressure measurements proved unsuccessful, the xylene data at 75°C. could be used only as a relative indication of sulfur activity. The activities employed in the final equilibrium calculations were derived mathematically by an integration involving the X and Y quantities.

D. Interpretation of Results

1. Polysulfide Equilibrium Constants

Assuming equilibrium at 75°C. and using the sulfur activities obtained by integration, but compatible with the xylene sulfur data, the two material balances:

$$[S_x^=] = [S_2^=] + [S_3^=] + [S_4^=] + \dots \qquad (43)$$

and

$$[PSS] = [S_2^=] + 2[S_3^=] + 3[S_4^=] + \dots \qquad (44)$$

could be converted into polynomial expressions in $a_{S_8}^{1/8}$:

$$X = r_1 a_{S_8}^{1/8} + r_2 a_{S_8}^{2/8} + r_3 a_{S_8}^{3/8} + \dots \qquad (54)$$

$$Y = r_1 a_{S_8}^{1/8} + 2r_2 a_{S_8}^{2/8} + 3r_3 a_{S_8}^{3/8} + \dots \qquad (55)$$

The relative polysulfide equilibrium constants then could be calculated by solving for the polynomial coefficients, or r's.

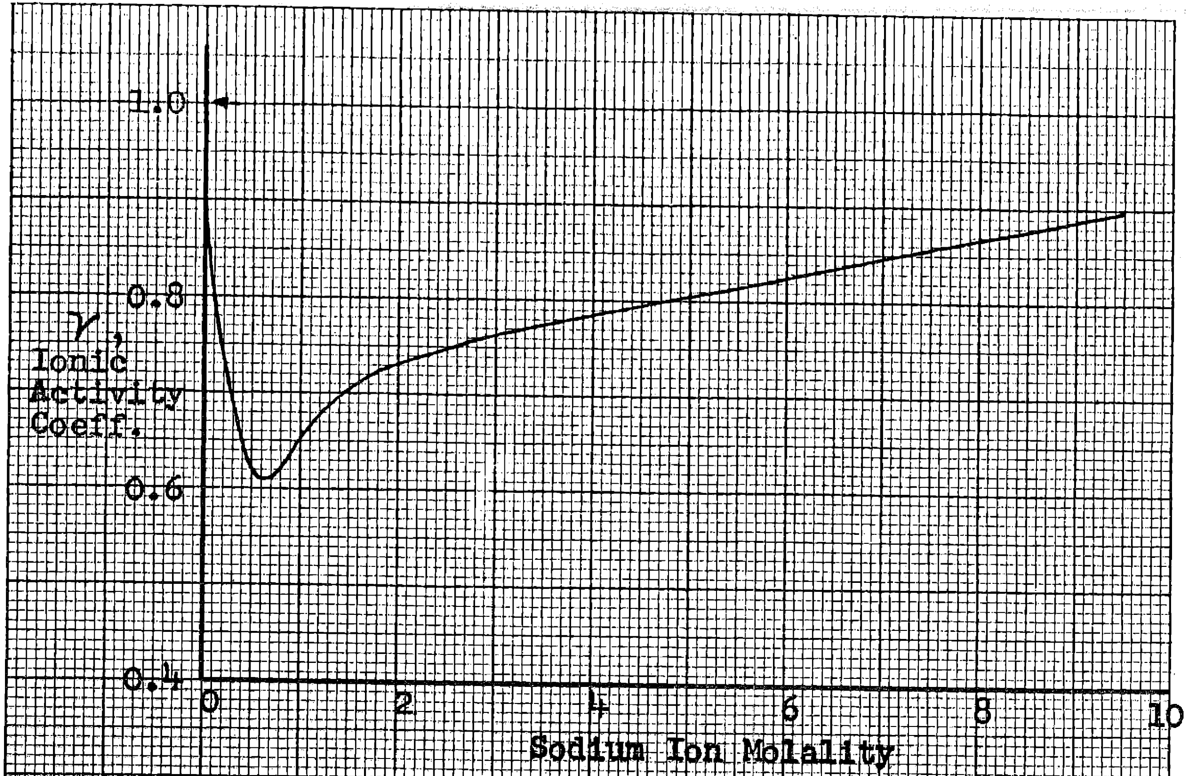
The data available did not extend over a sufficiently wide range of sulfur activities to determine a unique set of equilibrium constants. By graphical techniques a "best fit" solution was obtained which included the ions $S_3^=$, $S_4^=$, $S_5^=$, and $S_6^=$:

$S^= + 2/8\ S_8 = S_3^=$ $k_2 \cong$ 1760 at 75°C.
$S^= + 3/8\ S_8 = S_4^=$ $k_3 \cong$ 33,700 at 75°C.
$S^= + 4/8\ S_8 = S_5^=$ $k_4 \cong$ 68,400 at 75°C.
$S^= + 5/8\ S_8 = S_6^=$ $k_5 \cong$ 21,040 at 75°C.

Unfortunately, the data also could be reproduced within the limits of experimental error by several alternate sets of equilibrium constants, some of which included as few as two polysulfide ions present. The best indications were that while small amounts of at least one ion below $S_4^=$ were present, the ions higher than $S_6^=$ could be neglected in most instances.

2. Ionic Distributions in Polysulfide Solutions

From the "recommended" polysulfide equilibrium constants and the best estimates of the monosulfide hydrolysis, the ionic compositions of sodium polysulfide solutions at 75°C. were calculated. As an example of the distributions obtained, the ionic molalities versus "x" in the average formula Na_2S_x are shown in Figure 73 for 0.5 m polysulfide solutions (1.0 m sodium ion). It may be seen that any given polysulfide ion could be maximized by setting "x" equal to or slightly below the sulfur subscript of that ion. Unfortunately, since the



from FIGURE 33

"Average" Ionic Activity Coefficients at 75°C

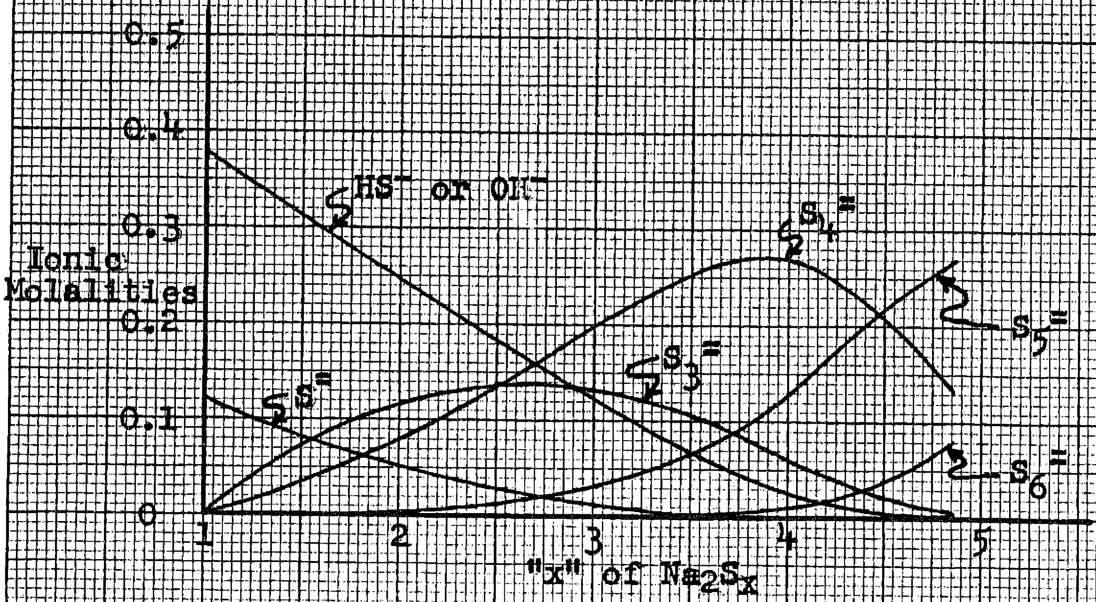


FIGURE 73

Polysulfide Ionic Distributions at 75°C

$Na^+ = 1.0$ m

trisulfide equilibrium constant could not be determined with any reliability, the distribution profiles given must be considered increasingly dubious at "x" values much below 4.0.

Similar profiles calculated for sodium ion molalities from 0.1 to 8.0 showed that the percentage hydrolysis drops and the ratio of actual polysulfide ($S_x^=$) to nominal sodium polysulfide rises as molality is increased at a given "x". The value of "x" at sulfur saturation at 75°C. was predicted to be nearly constant (at 4.86) above 1.0 m sodium ion concentration and to diminish at lower molalities, approaching unity at infinite dilution. The elemental sulfur activities as calculated dropped rapidly as "x" was lowered; at 1.0 m sodium ion concentration, for example, a_{S_8} was predicted to be only 8.7×10^{-6} at "x" = 4.0 and only 2.8×10^{-12} at "x" = 2.0.

The non-equilibrium 25°C. Na_2S-S-H_2S-H_2O data of the present thesis, employing two reaction directions, did permit limits to be placed on the hypothetical equilibrium situation at that emperature, but no set of constants within these limits could be found which were simultaneously compatible with the heats of formation of polysulfide solutions reported in the literature. Nevertheless, the maximum equilibrium "x" in polysulfide solutions at 25°C. apparently is higher than at 75°C., even though owing to slow rates experimentally it might seem lower. An examination of the qualitative rate data obtained from the results at room temperature indicated that reactions involving either solid sulfur or certain of the lower polysulfides (possibly $S_4^=$) are sluggish at the lower temperatures.

3. Application to the Synthesis of Hydrogen Persulfide

For lack of any reliable polysulfide compositions at room temperature or below, the 75°C. ionic distributions were compared to the raw oil synthesis results of Conway (15)(48), who studied the effects of polysulfide molarity and polysulfide "x" at reaction temperatures generally at or below 0°C. Conway found that the mol yield of hydrogen persulfide increased rapidly with "x", but was only slightly affected by molarity. Making use of the findings of the present thesis, however, it was established that the relative mol yields, defined as actual yield divided by theoretical yield ($S_x^=/Na_2S_x$ ratio), increased only slightly with "x" at a given mixing condition. The mol yields, on the other hand, could be drastically improved by the use of higher mixing rates.

Conway found that the sulfur yield based on "polysulfide sulfur" in the starting material varied but little with either mixing rate or "x". Making use of the results of the present thesis, accordingly it was shown that much of the sulfur released by decomposition during the acidification step apparently still appears in the raw oil product in the form of higher sulfur homologues.

The raw oil synthesis mechanism is pictured as follows:

1. Upon acidification the individual polysulfide ions first are converted to the corresponding HS_x^- species, which are unstable.
2. The yield of hydrogen persulfides is determined by the rate at which the second hydrogen ion can be brought to the scene of reaction versus the rates at which the acid polysulfides decompose to HS^- ion and nascent sulfur.
3. Much of the nascent sulfur released by decomposition reacts with the persulfides which are formed, creating higher hydrogen persulfides which do not correspond to polysulfide ions present in the starting material.
4. Under unfavorable mixing conditions raw oil already formed may be brought in contact with fresh polysulfide solution, causing extensive decomposition of both.
5. The hydrogen persulfides which are formed may undergo some homogeneous decomposition before they can be separated from the aqueous phase.
6. Any disulfide and trisulfide in the initial polysulfide are lost during acidification, probably owing either to the greater instability of the lower HS_x^-

species or to their higher reactivity with nascent sulfur.

D. Conclusions

1. At elevated temperatures the ions $S_3^=$, $S_4^=$, $S_5^=$, and $S_6^=$ apparently obey equilibrium relationships and essentially comprise the polysulfide species present in ordinary aqueous polysulfide solutions.
2. Some of the polysulfide ions are slow to react at room temperature and below, but under certain conditions a quasi-equilibrium may be set up.
3. A direct analysis for one or more of the individual polysulfide ions will be required if the ionic distributions are to be defined more closely than was possible in the present thesis.

INTRODUCTION

A. Preface

By the acidification of aqueous polysulfide solutions under the proper conditions, hydrogen persulfides are obtained. These persulfides have the general formula H_2S_n, where "n" may range from 2 up to at least 8 or 9, and are unstable yellow oils immiscible with water. Although the hydrogen persulfides are not in commercial use at the present time, various potential applications exist in the production of organic thio derivatives. Owing to difficulties in preparing, handling, and storing the persulfides, these possibilities have not been investigated extensively.

The so-called "raw oil" formed by the reaction between an alkali metal polysulfide and a strong acid is in fact a mixture of several hydrogen persulfides; the individual pure species can only be obtained either by the cracking or by the high-vacuum distillation of this initial product. The strong dependence of the raw oil yield and composition upon both the rate of mixing and the sulfur content of the polysulfide used ("x" in Na_2S_x) has indicated an urgent need to know the true composition of the starting material before the acidification reaction mechanism can be fully interpreted.

Aqueous polysulfide solutions are considered to be made up of a number of individual polysulfide ions, such as $S_2^=$, $S_3^=$, $S_4^=$, etc. Under certain conditions the distribution of these components at a given polysulfide "x" may be dictated by equilibrium considerations. Upon acidification these ions might be converted to the corresponding hydrogen persulfides:

$$S_x^= + 2\ H^+ = H_2S_x \quad (\text{"x"} = 2, 3, 4, \text{etc.}) \qquad (1)$$

An understanding of the ionic compositions of aqueous polysulfide solutions, while thus of obvious importance in the prediction of raw oil synthesis results, might be equally helpful in other situations in which polysulfides are used.

The determination of ionic distributions in aqueous sodium polysulfide solutions is the object of the present thesis.

B. Properties of Hydrogen Persulfides

1. Physical Properties

Raw oil and each of the pure hydrogen persulfides are transparent yellow liquids having much the appearance of olive oil. The persulfides at room temperature possess pungent, irritating odors combining that of hydrogen sulfide with that of hot molten sulfur. These persulfides comprise a typical homologous series in that their properties vary gradually and consistently with molecular weight; raw oil exhibits properties roughly the same as those of the pure persulfide of corresponding molecular weight. From combined measurements of electron diffraction pattern (62), dipole moment (61), and infra-red (70) and Raman (22)(24) spectra it has been deduced that the persulfides probably have the chain structure H-S-S-S-H.

The physical properties of raw oil and the five hydrogen persulfides isolated in a pure state up to the present time are presented in Table 1.

TABLE I

Physical Properties of Hydrogen Persulfides

(8) (13) (24) (25) (26) (66)

Persulfide	Mol. Wt.	Density gm/ml	Color	Viscosity	Freezing Pt., °C	Boiling Pt., °C
H_2S_2	66.1	1.341	almost colorless	like water	-89	70.7
H_2S_3	98.2	1.495	pale yellow	greater than water	-53?	decomp.
H_2S_4	130.3	1.588	bright yellow	like olive oil	forms glass	decomp.
H_2S_5	162.3	1.660	strong yellow	greater than olive oil	forms glass	decomp.
H_2S_6	194.4	1.699	deep yellow	like glycerine	forms glass	decomp.
Raw Oil	146 to 323?	1.62 to 1.77?	deep yellow	like glycerine	forms glass	decomp.

2. Chemical Properties

a. Instability

The hydrogen persulfides are all unstable. Their decomposition to hydrogen sulfide and sulfur is greatly accelerated by basic media, polar organic solvents, oxidizing agents, and substances with high active surface area (15)(48). In some cases explosive decomposition may result. No inhibitors are known for making the persulfides completely stable, but proper experimental technique can hold decomposition to a negligible amount during the time of a few hours.

In the course of their Raman spectroscopic work Feher and Baudler (24)(25) found that the pure persulfides not only undergo ordinary decomposition, but also disproportionate slowly upon standing to give mixtures of higher and lower persulfides.

b. Reaction as Hydrogen Sulfide or Sulfur

The hydrogen persulfides exhibit the combined chemical behavior of hydrogen sulfide and elemental sulfur. Ignited in air, they burn to sulfur dioxide and water vapor with a pale blue flame (8). The persulfides reduce ordinary oxidizing agents and form sulfide precipitates with metal ions (30)(66); the reactive agent in such cases is the hydrogen sulfide released by decomposition of the persulfide.

c. Reaction with Organic Compounds

Raw oil and especially hydrogen di- and trisulfides react with certain organic compounds to yield strongly sulfided derivatives. With aromatic aldehydes the persulfides react by condensation (12); the intermediate formed from hydrogen disulfide and benzaldehyde can be decomposed to provide an alternate route to dithiobenzoic acid (47). With olefinic compounds such as styrene or amylene the reaction product is a thio-epoxide or perthio-epoxide (38).

C. Production of Hydrogen Persulfides

1. Various Routes to the Persulfides

a. Acidification of Aqueous Polysulfide

Raw oil ordinarily is prepared by the slow addition of polysulfide solution to an excess of stirred, cooled acid. Although quite a few workers have studied this synthesis, most of the early results must be considered unreliable owing to the absence of controlled conditions. The conditions and the results for the published research to date are presented in Table II.

The results of preliminary studies of the production of raw oil in a continuous system (in connection with the thesis of Laplane (42))are reported in detail in the Appendix.

b. Other Syntheses of Raw Oil

Alternate syntheses for hydrogen persulfide have been proposed, but these in general have given lower mol yields than the aqueous acid-polysulfide reaction. The mol yield is considered a more meaningful quantity than the sulfur yield

TABLE II

Studies of the Aqueous Acid-Polysulfide Reaction

Worker	Polysulfide Composition	Acid Composition	Temp. °C	Stir. Sp. rpm	Mol % Yield	"n" of H_2S_n
Scheele (58) (1777)	?	?	?	?	?	?
Thenard (63) (1831)	CaS_x	HCl	?	?	?	7-9
Ramsay (54) (1874)	CaS_x	HCl	?	?	?	7-10
Sabatier (57) (1885)	CaS_x	conc'd HCl	+10°C	?	?	?
Rebs (55) (1888)	1.5 $\underline{M}$ Na_2S_4	29% HCl	0°C ?	?	8	5.5
	BaS_x	HCl	0°C ?	?	15 ?	5
	K_2S_x	HCl	0°C ?	?	15	5
Bloch and Hohn (8) (1908)	Na_2S_2 to Na_2S_5	HCl 15%-30%	-10°C to 0°C	?	22-39	4.7 to 6.2
Schenck and Falcke (59) (1908)	1 $\underline{M}$ $K_2S_{3.35}$	Conc'd HCl	?	?	38 ?	?
Walton and Parsons (66) (1921)	Na_2S_x	HCl + ice	-10°C to -4°C	?	?	?
Butler and Maass (13) (1930)	1.5 to 2 $\underline{M}$ Na_2S_2 to Na_2S_4	HCl 20%-37%	-15°C to -10°C	?	20-48 ?	4.8 to 6.6 ?
Feher and Baudler (25) (26) (1949)	2 $\underline{M}$ $Na_2S_{1.5}$ to $Na_2S_{4.5}$	HCl 11%-30%	-20°C to -15°C	?	7-66	4.5 to 6.0
Becker (3) (1949)	0.45 to 1.3 $\underline{M}$ Na_2S_2 to Na_2S_4	HCl 7%-37%	-14°C to 0°C	?	23-39	4.5 to 12.3

TABLE II (Continued)

Worker	Polysulfide Composition	Acid Composition	Temp. °C	Stir. Sp. rpm	Mol % Yield	"n" of H_2S_n
Ishikawa and Krumrei (37) (1950)	3.3 M $Na_2S_{2.5}$ (also "pure" Na_2S_3)	HCl 16%–33%	−35°C to +30°C (CHCl₃ extraction)	?	12–30	5.0 to 6.8
Chin and Gruwell (14) (1951)	2 M Na_2S_3 to Na_2S_4	HCl 15%–37% H_2SO_4 5%–75%	−10°C to +50°C	?	13–55	6.2 to 9.2
Conway (15) (1952) (48)	0.3 to 4 M $Na_2S_{1.6}$ to $Na_2S_{4.9}$	HCl 10%–37% H_2SO_4 5%–75% H_3PO_4 37%–60%	−35°C to 0°C	"slow" to "very rapid"	0–75	4.2 to 10.2
Haritatos (34) (1952)	2 M $Na_2S_{4.3}$	HCl 10%–35%	about 0°C	780 to 950	65–73	5.3 to 5.7
Laplane (42) (1956)	2 M $Na_2S_{4.5}$	H_2SO_4 25%	0°C	300 to 1200	48–68	5.6 to 6.8

TABLE III

Alternate Syntheses of Hydrogen Persulfide

Worker	Route	Yield	"n" of H_2S_n
Deines (16) (1924)	SO_2 + 50% H_3PO_2, 25-60°C	?	?
Mills and Robinson (49) (1928)	Dry $(NH_4)_2S_5$ + anhyd. formic acid, room temperature	?	5.0 ?
	Vacuum cracking of H_2CS_4	"low"	2.0 ?
Deines (17) (1928)	$Na_2S_2O_3$ soln. + HCl, room temp.	30%-40% S yield	6.0
Deines (18) (1929)	$Na_2S_2O_4$ soln. + HCl	?	?
Bacon and Fanelli (1) (1943)	Exposure of molten sulfur to H_2S	trace ? indicated	?
Feher and Heuer (29) (1947)	Electrolysis of SO_2 soln.	35%-47% S yield	8.7 ?
	H_2S + H_2O_2	?	?
Ishikawa and Krumrei (37) (1950)	Anhyd. Na_2S_2, Na_2S_3, Na_2S_4, + HCl in MeOH, n-PrOH, BzOH; -45 to +20°C	0% - 8% mol yield	6.7-12.3
	Dry Na_2S_2, Na_2S_3, Na_2S_4 + HCl in CS_2, toluene, pyrd., $PhNO_2$, liq. SO_2, -55 to + 110°C	trace ?	?
Black (7) (1950)	Dry Na_2S_3 + HCl gas, -20°C to room temp.	none	-
Bruce and Mattana (11) (1951)	H_2S gas + S, pressures up to 20 atm, temps. up to 500°C	none	-
Madrulli (45) (1951)	$Na_2S_2O_3$ soln.+HCl, -15°C to +27°C	0%-8% S yield	11-20
	$Na_2S_2O_4$ soln.+HCl, +10°C to +33°C	0%-50%? S yield	10 ?
	SO_2 + H_3PO_2, -25°C to +75°C	0%-24%? S yield	6 ?

TABLE III (Continued)

Worker	Route	Yield	"n" of H_2S_n
Baker and Pitcock (2) (1951)	$H_2S + H_2O_2$	none	–
	Reduction of SO_2 by H_2, Zn	trace ?	?
	Electrolysis of SO_2 soln., -15°C to + 35°C	trace	?
Feher, Schliep, and Weber (32) (1953)	Electrolysis of SO_2 soln.	40%-50% S yield	7.8-12.8

because it dictates the amount of hydrogen disulfide which can be obtained from the raw oil; the results of oxidation-reduction syntheses, however, may be calculated only as sulfur yields. The published work to date is summarized in Table III.

Preliminary studies of the production of hydrogen disulfide by the selective decomposition of perthiocarbonic acid (H_2CS_4) were carried out during the course of the present thesis. Although overall disulfide yields of no more than 10 mol per cent (based on the sodium sulfide from which the perthiocarbonic acid was prepared) were obtained, there remains the possibility that the acid itself can be substituted for hydrogen disulfide in its organic reactions. These studies are described in detail in the Appendix.

c. Individual Persulfides from Raw Oil

Pure hydrogen persulfides have been produced from raw oil by high-vacuum distillation, or, in the case of the disulfide and trisulfide, by the actual cracking of the higher persulfides in the oil. The yields of the two lower persulfides can be improved by the use of raw oil having as low a value of "n" as possible. The reported results to date are listed in Table IV.

During the course of the present thesis preliminary work was carried out on the preparation of hydrogen disulfide and hydrogen trisulfide as standards for Raman analysis. The details are reported in the Appendix.

TABLE IV

Preparation of Pure Hydrogen Persulfides from Raw Oil

Worker	Avg. n of Oil	Temp. °C	Press. mm Hg	Mol % Yields				
				H_2S_2	H_2S_3	H_2S_4	H_2S_5	H_2S_6
Ramsay (54) (1874)	?	?	?	none	none	-	-	-
Sabatier (57) (1885)	?	60-85	40-100	?	?	-	-	-
Bloch and Hohn (8) (1908)	5.5?	60	2-30	30?	50?	-	-	-
Schneck and Falcke (59) (1908)	?	43-50	4-5	-	?	-	-	-
Walton and Parsons (66) (1921)	5.0 ?	?	3-25	34?	50?	-	-	-
Walton and Whitford (67) (1923)	?	?	6	?	?	-	-	-
Butler and Maass (13) (1930)	4.8 to 6.6	about 120	10	18-35?	41-55?	-	-	-
Feher and Baudler (22) (1941)	?	120	15	?	-	-	-	-
Feher and Baudler (23) (1947)	5?	150	20-30	62	-	-	-	-
Feher and Baudler (24) (1947)	5	150?	20-30?	13	65	-	-	-
Feher and Baudler (25) (1947)	5	75	10^{-5}	-	-	42	-	-

TABLE IV (Continued)

Worker	Avg. n of oil	Temp. °C	Press. mm Hg	Mol % Yields				
				H_2S_2	H_2S_3	H_2S_4	H_2S_5	H_2S_6
Feher and Baudler (26) (1949)	5.0 to 5.5	100	10^{-4}	-	-	?	8	?
	6.2	100	10^{-4}	-	-	?	?	21
Becker (3) (1949)	4.5 to 5.6	150-170	2-13	50-79	-	-	-	-
Conway (15) (1952)	6.1 to 9.3	150	3-25	38-62	-	-	-	-

2. Variables Influencing Acid-Polysulfide Reaction

a. Polysulfide Variables

Owing to the cheapness and availability of sodium and its salts, the polysulfides of other metals only seldom have been used. The nature of the metal cation ordinarily would not be expected to affect the reaction significantly.

One of the most important variables influencing both yield and raw oil composition is the ratio of total sulfur in the polysulfide to mols of polysulfide ("x" in Na_2S_x). The results of Conway (15)(48) in particular point out that as "x" increases, the mol yield Y_m rises rapidly (Figure 1). Simultaneous with this increase in yield is a less-pronounced rise in "n", the average sulfur subscript of the persulfide (Figure 2). The yield based on polysulfide sulfur rather than mols, however, remains essentially constant as "x" is varied. The average "n" of the raw oil is always greater than the polysulfide "x"; hydrogen persulfide with an average sulfur subscript less than 4.2 never has been obtained, even when feeding polysulfide with "x" only slightly greater than unity. It must be concluded that polysulfides with lower sulfur contents have, on a mol basis, smaller proportions of those constituents which go to form raw oil.

The molar concentration of the polysulfide solution used has a relatively weaker effect. Conway found (Figures 1 and 2) that the mol yield dropped and the value of "n"

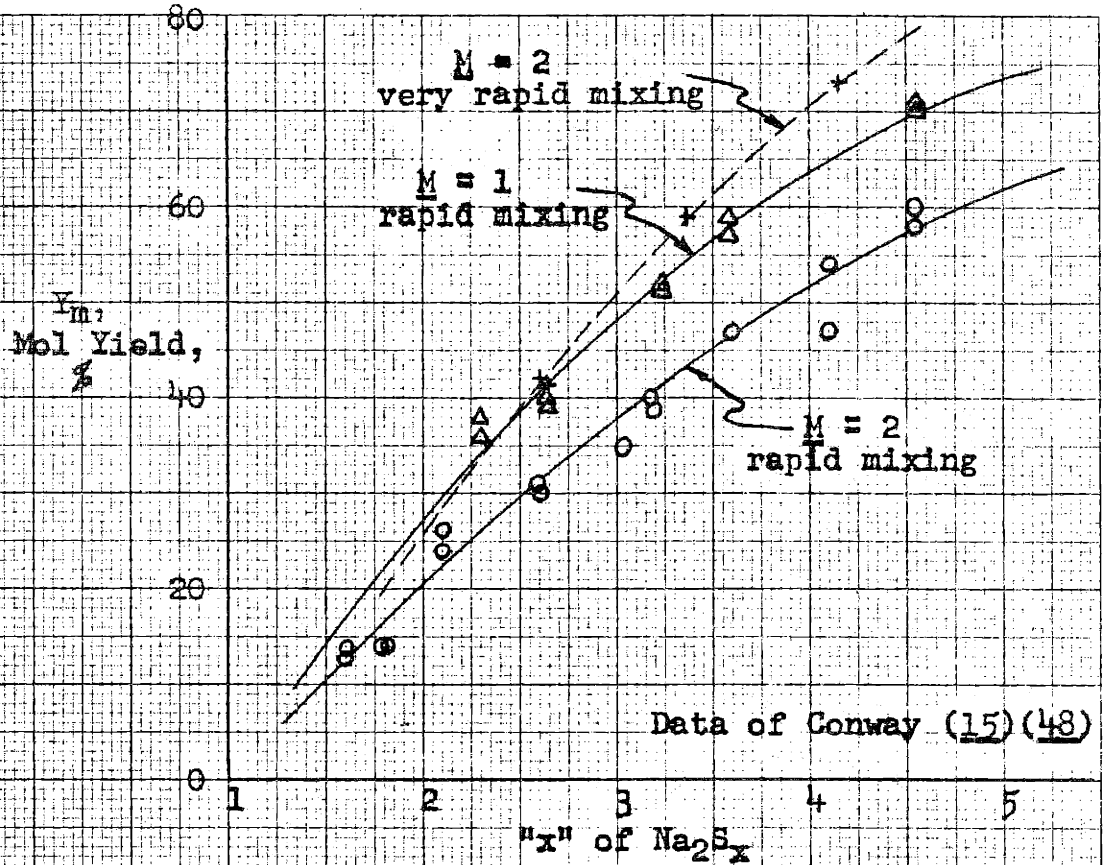


FIGURE 1

Mol Yields for Na_2S_x-HCl Reaction at 0°C

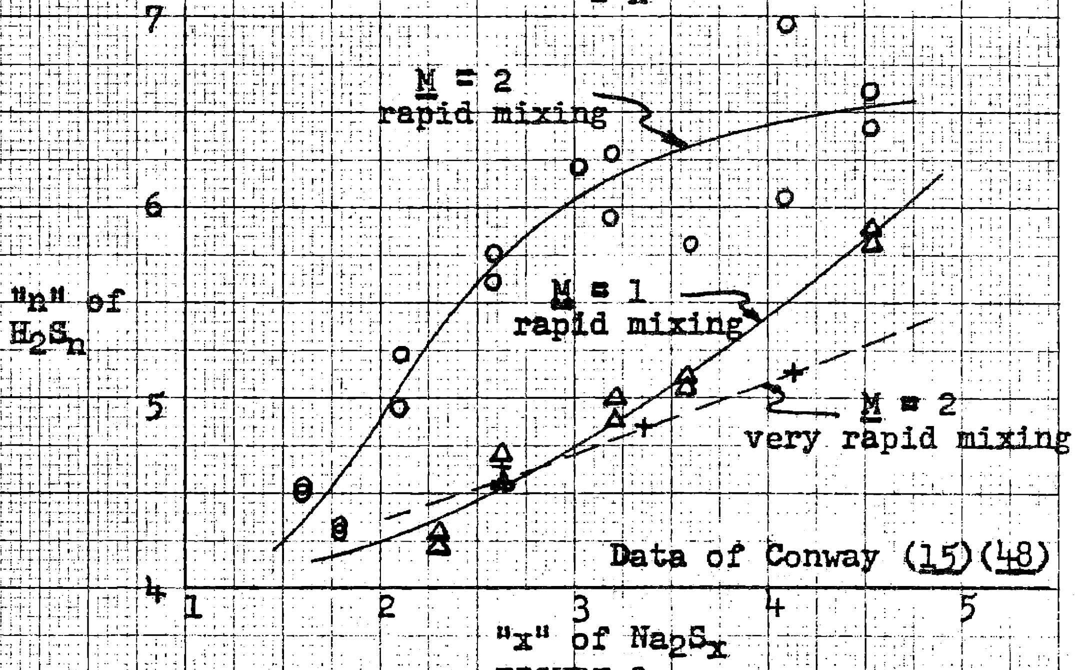


FIGURE 2

Raw Oil Compositions for Na_2S_x-HCl Reaction at 0°C rose in going from 1 M polysulfide to 2 M. At high polysulfide molarities poorer mixing may lead to lower yields; at very low concentrations, on the other hand, uneconomically large excesses of acid are required, and coagulation of raw oil droplets in addition may be hindered.

b. Acid Variables

Up until relatively recently hydrochloric acid always had been employed in the production of hydrogen persulfide. Conway (15) (48) and Chin and Gruwell (14) studied the reaction between sodium polysulfide and sulfuric acid and found, in general, mol yields from 5 to 10 per cent lower than when using hydrochloric acid. The continuous synthesis work of Laplane (42) and the present thesis also was carried out with sulfuric acid. Conway moreover investigated the use of phosphoric acid and obtained an even smaller yield than with sulfuric acid. The poorer results with sulfuric and phosphoric acids may be attributed to higher viscosity, lower percentage ionization, and greater tendency to decompose raw oil already formed.

The acid concentration might be expected to affect the reaction. Conway (15)(48) and Becker (3), however, both found little variation in mol yield between hydrochloric acid concentrations of 7 and 37 per cent. In the case of sulfuric acid Conway and also Chin and Gruwell (14) observed yield at first to increase and then to pass through a maximum at about 35 per cent acid; apparently at higher concentrations greater viscosity and increased oxidizing action give rise to poorer results. At concentrations much lower than normally employed mol yield is believed to be influenced strongly by hydrogen ion concentration regardless of which acid is used.

c. Reaction Variables

Low temperatures usually have been assumed necessary in order to minimize the decomposition of raw oil already formed. Conway (15)(48), however, found no variation in yield in the sodium polysulfide-hydrochloric acid reaction in the temperature range -35°C to 0°C. When working with sulfuric acid both Conway and also Chin and Gruwell (14) obtained lower yields as the temperature was raised from 0°C to 50°C.

The necessity for rapid mixing to ensure high mol yields and low values of "n" only recently has been appreciated fully; much of the unexplained scatter in the data of earlier workers doubtless was due to the lack of control of this variable. Conway (15)(48) first demonstrated a qualitative correlation between output quantities and mixing rate for the sodium polysulfide-hydrochloric acid reaction (Figures 1 and 2), employing impellers and air jets as mixing devices in his unbaffled reaction vessel.

The first quantitative study of the effect of mixing rate was the work of Haritatos (34)(48). He used a cylindrical vessel fitted with four vertical baffles and equipped with a single-blade impeller, and observed the changes in mol yield and "n" as the stirring speed was increased. An unexpected maximum in yield was found at a stirring rate of about 920 rpm (Figure 3); Haritatos explained this phenomenon on the basis of visually observed decomposition at higher stirring speeds upon the mixing of raw oil already formed with the incoming polysulfide feed. It must be remembered that Haritatos worked with a batch system from which no oil was withdrawn until the completion of a run; ample opportunity thus was created for back-mixing. Since the polysulfide was introduced as a jet which impinged on the liquid surface and since the liquid level rose as the run progressed, the true mixing rate doubtless also varied with time.

In order to overcome these drawbacks the continuous synthesis study of Laplane (42) and the present thesis was set up. Although the mixing system chosen was similar to that of Haritatos, provisions were made for holding all reaction conditions, including concentrations and liquid level, constant with time. It indeed was shown that the introduction of the polysulfide feed below the liquid surface and the continuous removal of the raw oil product

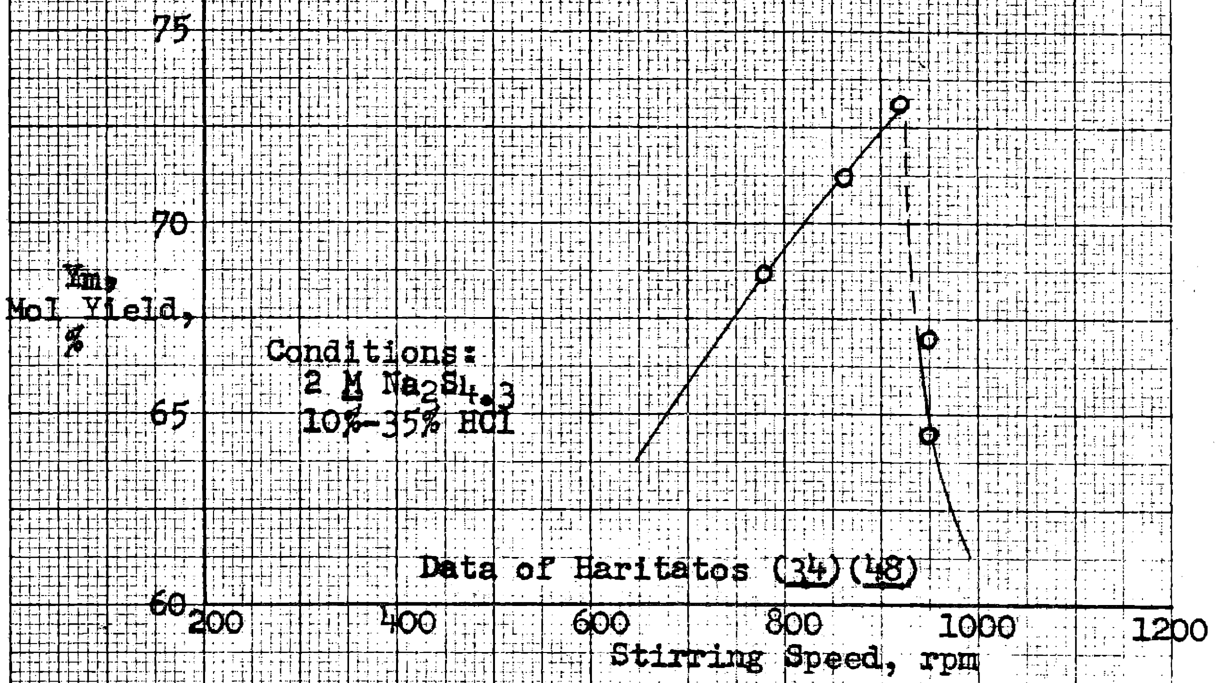


FIGURE 3

Mol Yields for Na_2S_x-HCl Reaction at 0°C

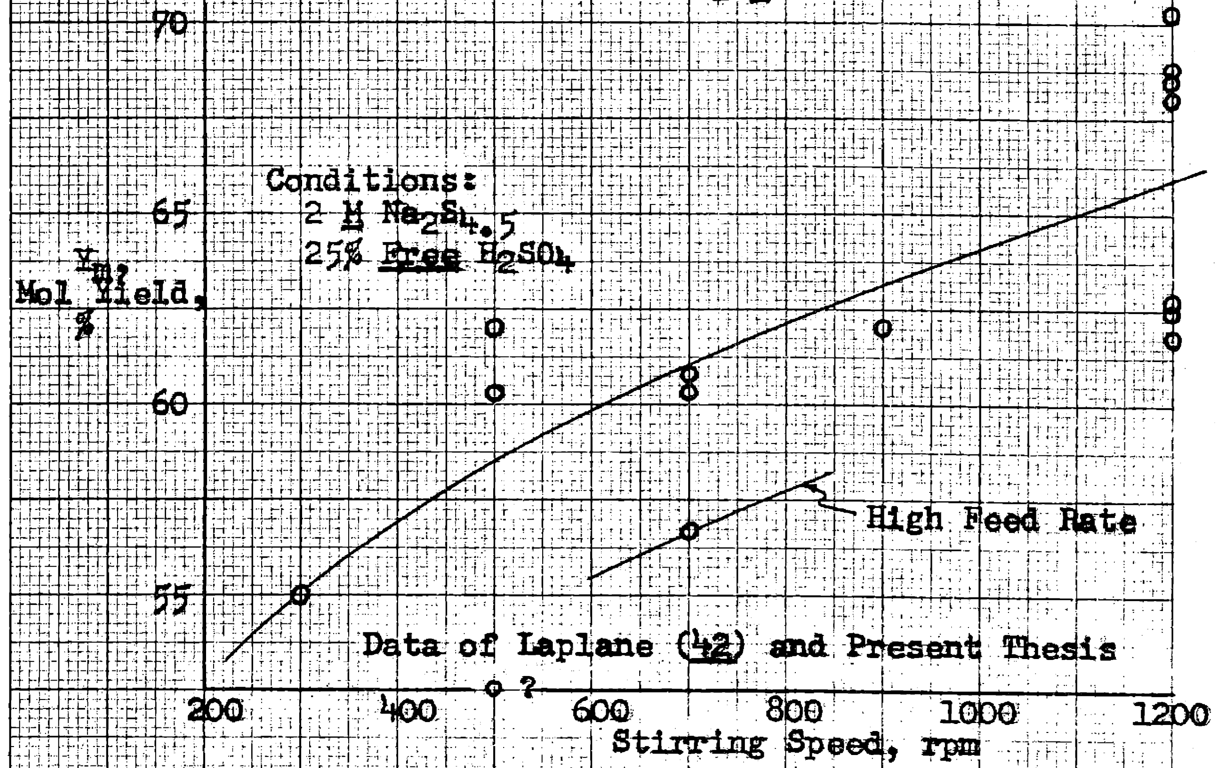


FIGURE 4

Mol Yields for Na_2S_x-H_2SO_4 Reaction at 0°C
(Continuous Synthesis)

from the scene of reaction resulted in essentially no adverse effect due to back-mixing. The mol yields for the continuous synthesis versus stirring speed in rpm are shown in Figure 4. The limitations of the apparatus prevented any increase in stirring speed to a region where yield might approach asymptotically its maximum possible value. The mol yields obtained at 1200 rpm, the highest stirring rate tested, averaged about 65 per cent, compared to a maximum of 55 per cent for the best previous batchwise results using sulfuric acid. (See Appendix for more detailed data.)

3. Constituents of Raw Oil from Acid-Polysulfide Reaction

a. Overall Analysis

The analysis of raw oil either by a volumetric technique or by a gravimetric technique yields the total hydrogen sulfide content of the oil. Other than defining the average value of "n" this approach provides no information as to what individual components may be present.

b. Physically-Dissolved Hydrogen Sulfide

Since hydrogen sulfide is formed both as a by-product in the acid-polysulfide reaction and by the gradual decomposition of hydrogen persulfides, it is reasonable to assume that dissolved hydrogen sulfide normally is a constituent of raw oil. Sabatier (57) first demonstrated that hydrogen sulfide gas is quite soluble in raw oil, yet is removed easily by degassing under vacuum. Conway (15) attempted to develop a quantitative analysis employing this technique; his method is somewhat dubious owing to the simultaneous formation of hydrogen sulfide by the decomposition of the persulfides while under vacuum.

c. Physically-Dissolved Sulfur

Free sulfur likewise is produced both as a by-product in the raw oil synthesis and by the decomposition of the oil. Since, as several workers have shown, raw oil can be a fairly good solvent for sulfur, the presence of some uncombined sulfur in the oil as it normally is prepared might be considered likely. Feher and Baudler (26), on the other hand, found that freshly prepared raw oil dissolved very little sulfur; they further reported that the Raman spectrum of ordinary raw oil did not exhibit lines which were manifested using oil with dissolved sulfur added artificially. It thus would appear that uncombined sulfur is an important constituent only in certain cases, when yields are low or when values of "n" are high. Feher and Rempe (31), indeed, did find by cryoscopic analysis from 5 to 17 mol per cent free sulfur in raw oil produced electrolytically (32), where n averaged about 10.

d. Individual Persulfides Present

The only promising technique to date for the determination of the individual persulfides in raw oil has been Raman spectroscopy. Feher and Baudler (21)(24)(25)(26) obtained Raman spectra of raw oil and the five known pure persulfides (Table V), and concluded that the di- and trisulfides were not present in their raw oil.

TABLE V

Raman Spectra of Hydrogen Persulfides (21) (24) (25) (26)
(frequencies in cm^{-1}, qualitative relative intensities)

H_2S_2*	H_2S_3*	H_2S_4#	H_2S_5#	H_2S_6#	Raw Oil#	Sulfur + Raw Oil #
2513 (5)	2513 (4)	2513 (2)	2513 (2)	2513 (2)	2513 (2)	2513 (2)
882 (3)	882 (2)	882 (1)	882 (0)	882 (0)	882 (1)	882 (1)
-	-	-	-	-	-	520 (0)
508 (9)	-	-	-	-	-	-
-	484 (8)	484 (7)	485 (7)	485 (7)	485 (7)	485 (7)
-	-	-	-	-	-	473 (8)
-	-	-	-	467 (6)	466 (7)	466 (7)
-	-	-	-	-	-	434 (2)
-	-	-	-	246 (0)	242 (0)	245 (3)
-	-	-	-	215 (1)	215 (2)	217 (10)
-	207 (5)	-	-	-	-	-
-	-	183 (4)	182 (00)	183 (2)	183 (2)	184 (3)
-	-	-	-	148 (1)	148 (2)	152 (10)

* Recorded spectra using blue 4358 Å excitation

\# Photographic spectra using green 5460 Å excitation

Inspection of Table V indicates that the same lines were obtained for the pentasulfide as for the tetrasulfide. In addition, the plurality of new lines suddenly appearing when switching to the hexasulfide certainly implies that this distillate was not a pure compound. In view of these uncertainties no definite conclusions regarding any persulfides (other than hydrogen disulfide and hydrogen trisulfide) possibly present in raw oil can be drawn from these qualitative data.

During the course of the present thesis an attempt was made to develop a quantitative analysis for the individual persulfides present in raw oil. The recorded spectra for hydrogen di- and trisulfides were obtained, essentially repeating the work of Feher and Baudler. This portion of the program, unfortunately, had to be abandoned because no suitable instrument could be obtained for measuring the spectra of the higher persulfides or of raw oil; owing to absorption by the yellow persulfides, blue excitation cannot be employed for higher than the trisulfide. This work is described in detail in the Appendix.

D. Information on Alkali Polysulfide Solutions

1. Preparation of Polysulfide Solutions

a. Procedure

Polysulfide solutions normally are prepared by dissolving sulfur in an aqueous solution of the monosulfide. Although sodium sulfide is available commercially as the crystalline hydrate $Na_2S \cdot 9H_2O$, some workers instead have formed their own monosulfide solutions by reacting caustic and hydrogen sulfide. In the polysulfide preparation the sulfur reacts slowly with the monosulfide to form a clear solution which appears deep red in color, but which in thin layers is seen to be essentially yellow. Solution of the sulfur is facilitated both by warming to temperatures in the range 60°C - 100°C and by providing rapid stirring. An inert atmosphere commonly is employed in order to prevent oxidation during polysulfide preparation.

b. Rate of Reaction

Apparently the rate of reaction of solid lumps of sulfur normally is limited by diffusion. Gerischer (33), however, found by turbidimetric measurements that the rate of solution of very finely suspended sulfur varied with polysulfide "x"; a maximum was observed at an average solution composition Na_2S_2. Even when corrected for variation in monosulfide ($S^=$) plus polysulfide ($S_x^=$) concentration due to hydrolysis, his data indicated that some of the polysulfide ions react with sulfur faster than does the monosulfide. Gerischer explained these findings on the basis of lower hydration of the higher polysulfide ions.

c. Equilibrium at Saturation

The extent of solution of sulfur in polysulfide solutions ultimately is limited by equilibrium considerations. The values of "x" in Na_2S_x at saturation have been determined by several investigators. Kuster and Heberlein

(41) have presented data on the variation of the saturation "x" at room temperature with the polysulfide molarity. Inspection of Figure 5 shows that "x" passes through a maximum (5.24) at a molarity of about 0.03. More recent measurements by Peschanski (52) do not confirm exactly the results of Kuster and Heberlein. The sulfur saturation limits at elevated temperature (above 50°C) may range higher than at room temperature, but no reliable quantitative data are reported.

d. Heat of Reaction

The reaction between sulfur and an alkali monosulfide is exothermic, corresponding to an observable temperature rise under adiabatic conditions. Bichowsky and Rossini (6) report the following heats of formation in aqueous solution:

$S^{=}$	+ 10.0 KCal
$S_2^{=}$	+ 9.3 KCal
$S_3^{=}$	+ 7.8 KCal
$S_4^{=}$	+ 5.3 KCal

Slightly different values can be derived from data in Handbook of Chemistry and Physics (36). It must be remembered that all these numbers were obtained by calorimetry in actual polysulfide solutions and thus represent only averages for the distributions of ions really present at the given nominal sulfur subscripts. In any event further

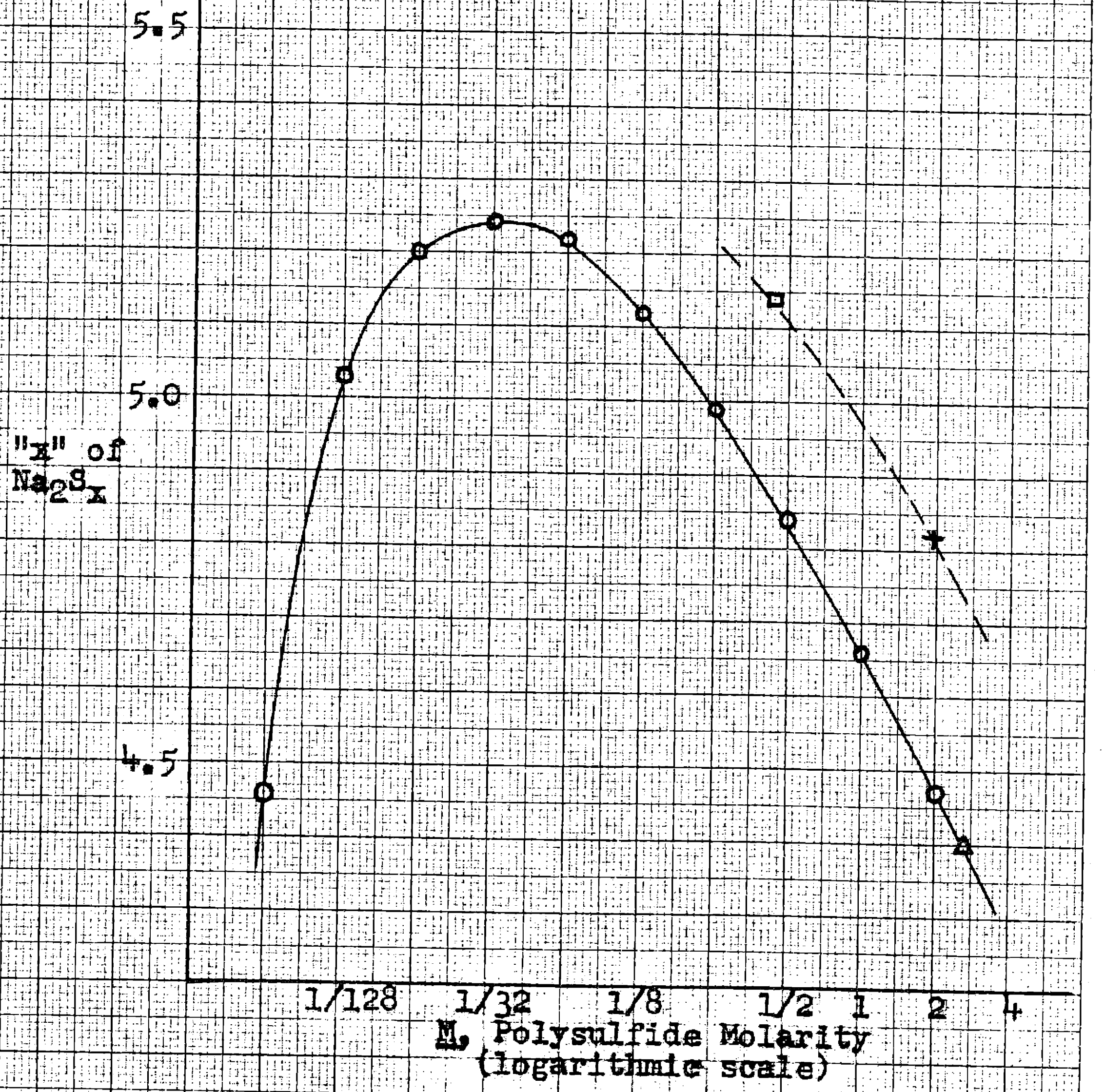


FIGURE 5

Sulfur Saturation Compositions of Sodium Polysulfide Solutions at Room Temperature

- ○ Data of Kuster and Heberlein (41)
- △ Data of Bloxam (9)
- □ Data of Peschanski (52)
- + Data of Present Thesis

attention certainly should be given to the apparent anomaly between the exothermic heats of reaction and the increase in sulfur solubility with increase in temperature.

e. Side Reactions

Monosulfide and polysulfide solutions are susceptible to oxidation by the air; impurities such as thiosulfate, sulfite, and possibly sulfate are formed. If precautions are taken, the extent of oxidation usually can be held to less than 1-2 per cent of the initial total sulfide. Some impurities, however, may be present in the original sodium sulfide used, even with the best grades commercially available. Moreover, the stoichiometric possibility must be considered of reactions such as

$$4S_x^{=} + 6(x-1)OH^{-} = (x-1)S_2O_3^{=} + 2(x+1)S^{=} + 3(x-1)H_2O \qquad (2)$$

which may proceed even in the absence of air. Conway (15)(48) reported slow deterioration of polysulfide solutions during storage, presumably by reactions similar to the preceding.

f. Preparation in Presence of Hydrogen Sulfide

If polysulfide solutions are prepared in the presence of hydrogen sulfide, the reaction tends to be driven back to hydrosulfide and elemental sulfur; an equilibrium may be set up. Bloxam (9) prepared 2.5 M sodium polysulfide with an "x" of 4.4 by the reaction between sulfur and sodium hydrosulfide solution at an elevated temperature; since the final hydrogen sulfide partial pressure was not specified, his results are of no value in equilibrium calculations. Rule and Thomas (56) also carried out the sodium hydrosulfide-sulfur reaction, but in absolute ethanol at the reflux point; they measured hydrogen sulfide evolved versus incremental sulfur added. Their results are shown in Figure 6. Since Rule and Thomas employed a purge of hydrogen to sweep out the hydrogen sulfide as rapidly as it was released, the final partial pressure of that component again was unknown.

A reverse reaction was studied by Kuster and Heberlein (41), who saturated 0.2 M solutions of sodium polysulfide at room temperature with hydrogen sulfide. They reported that one mol of hydrogen sulfide was absorbed per mol of initial polysulfide regardless of "x", but that sulfur was precipitated if the initial polysulfide "x" was much greater than 2. Their results in part are not confirmed by the findings of the present thesis.

2. Nature of Polysulfide Solutions

a. Ionization and Hydrolysis

As polysulfides are formed by the reaction of sulfur with monosulfide solution, the ionization and the hydrolysis

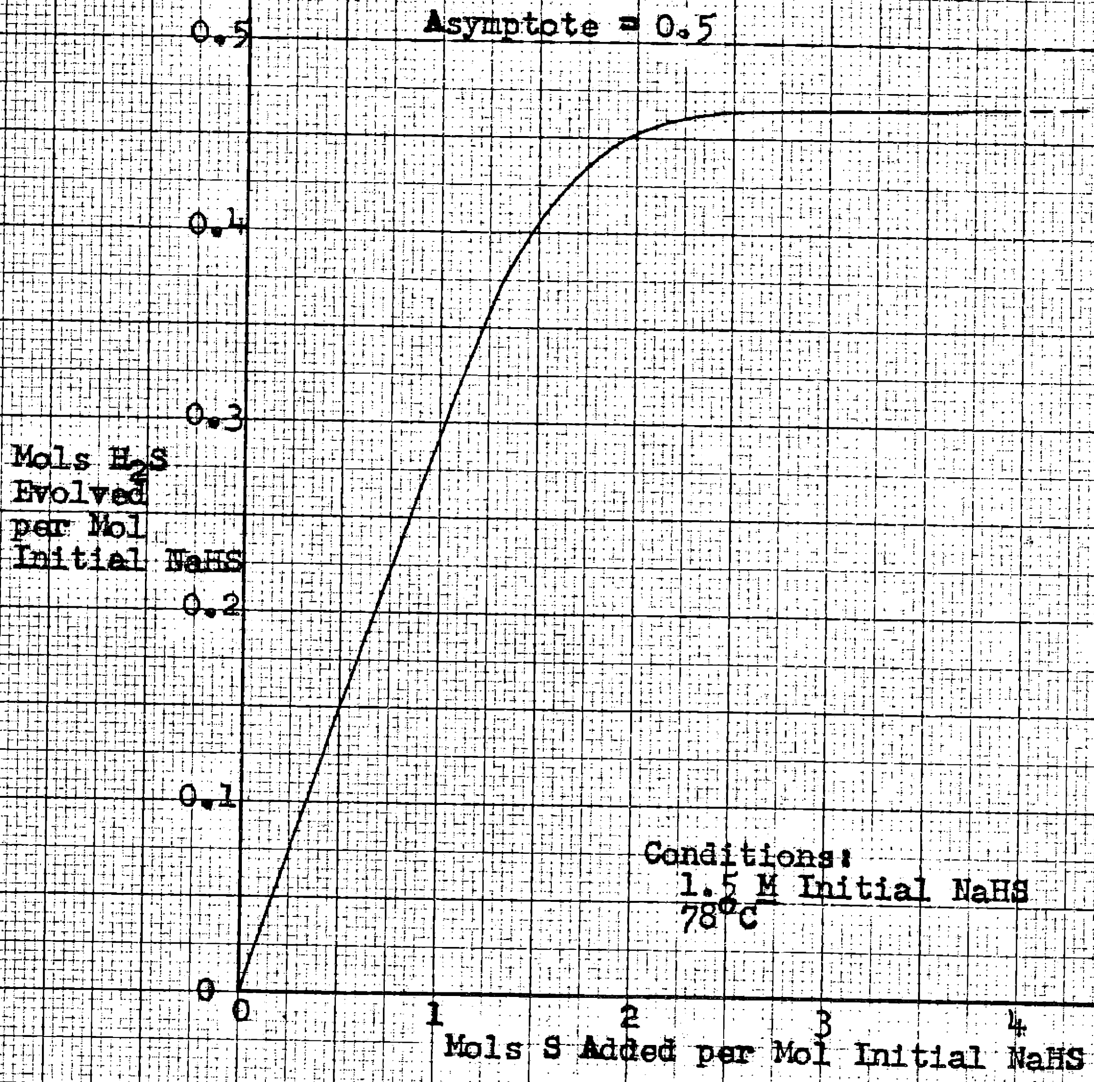


FIGURE 6

Sodium Hydrosulfide-Sulfur Reaction in Absolute Ethanol

Data of Rule and Thomas (56)

apparently both decrease. Kuster and Heberlein (41) determined, in sodium polysulfide solutions at room temperature, particle concentrations by freezing point lowering and hydroxyl concentrations by the rate of decomposition of diacetone alcohol. Peschanski (52) obtained hydrogen ion activities in polysulfide solutions by the use of the glass electrode. Martin (46) and Knox (39) calculated concentrations of $S^{=}$ ion in monosulfide and polysulfide solutions from the solubilities of mercuric sulfide in these solutions. These data are summarized in Table VI.

Examination of Table VI yields several interesting observations. The freezing point data of Kuster and Heberlein imply appreciable association at high polysulfide "x"; for ideal behavior particle concentration in a 0.5 M solution cannot be less than 1.5 M. The pH data of Peschanski indicate much lower hydrolysis of polysulfide solutions than do the reaction rate results of Kuster and Heberlein. Conway (15) assumed what amounted to a constant error in the pH readings and recalculated Peschanski's values so as to fall more in line with those of other workers. The hydrolyses reported by Martin and by Knox for monosulfide solutions agree neither with those of Kuster and Heberlein nor with those calculated using the equilibrium constants taken from the literature, but the finding of

TABLE VI

Ionization and Hydrolysis of Monosulfide and Polysulfide Solutions

A. Data of Kuster and Heberlein (41)

1. Freezing Point Lowering (M = 0.5, temps. -2.4 to -3.6°C)

x	Particle Conc., Mols/Liter
1	1.93
2	1.62
3	1.43
4	1.28

2. Rate of Reaction (M = 0.05, temp. 25.0°C)

x	Percentage Hydrolysis
1	86.4
2	64.6
3	37.6
4	11.8
5.22	5.7

B. Data of Peschanski (52) (M = 0.410-0.788, temps. 17 to 20°C)

x	Percentage Hydrolysis*
1.45	15.6
1.96	12.1
2.71	8.5
3.33	8.5
3.75	8.2
4.22	3.5
4.46	2.0
4.67	1.4
4.83	0.4

* Calculated taking K_w as 6.0×10^{-15}, value at 18.5°C; assuming average molarity = 0.6.

C. Data of Martin (46) and Knox (39) (M = 0.15-0.35, temp. 25°C)

x	M	Percentage Hydrolysis
1	0.15	92.7
1	0.25	91.9
1	0.35	83.8

The result of Knox for an Na_2S_2 solution shows the $S^=$ concentration to be roughly half that for a comparable Na_2S solution.

Knox for a solution having the average composition Na_2S_2 does correspond roughly to the hydrolysis determined by Kuster and Heberlein at that "x".

b. Mobility of Ionic Equilibria

The question arises as to whether the equilibria between the various polysulfide species are mobile. Most available evidence suggests that this is not the case at room temperature. The failure of the sulfur saturation data of Kuster and Heberlein (41) to agree with those of Peschanski (52) (and of the present thesis) may imply that the reaction between the solution and solid sulfur is slow. On the other hand, the discrepancies between the hydrolysis measurements reported by different investigators indicates that one or more homogeneous ionic reactions may not go to equilibrium. This viewpoint is substantiated by the experimental observation that sulfur is precipitated from certain freshly-prepared hot polysulfide solutions upon rapid cooling, but not upon slow cooling. Under certain conditions, however, a quasi-equilibrium may be reached at room temperature; Werner and Konopik (40)(69), for example, obtained the same polarigraphic waves, using the dropping-mercury electrode, for both sodium disulfide and sodium tetrasulfide in aqueous solution. Feher (20), on the other hand, reported "pure" hydrogen tetra- and pentasulfides to be formed by the acidification of the corresponding pure sodium polysulfides, whereas pure sodium disulfide yielded only a mixture of hydrogen persulfides. In view of the uncertainties in his Raman spectroscopic analysis, the purity of Feher's tetra- and pentasulfides must be considered doubtful.

c. Polysulfide Ions Present

Since no analysis techniques have been developed for the individual polysulfide ions in solution, equilibrium must be assumed in order to attempt to solve for the actual ionic distributions. Peschanski and Valensi (53) derived equilibrium constants and ionic concentrations from their measurements of pH and oxidation-reduction potentials in aqueous polysulfide solutions. The molarities of the various ionic species in a 0.5 M sodium polysulfide solution at 20°C, interpolated from their results, are plotted versus polysulfide "x" in Figure 7. It may be seen that their equilibrium constants predict hydrolyses greater than those previously calculated from their pH data alone, and more in line with the findings of other investigators. Since Peschanski and Valensi assumed present only the ions up through the pentasulfide and in addition were forced to guess dubious values of the unknown standard potentials, their findings are of doubtful value and certainly are not applicable to polysulfide solutions with "x" greater than 5.

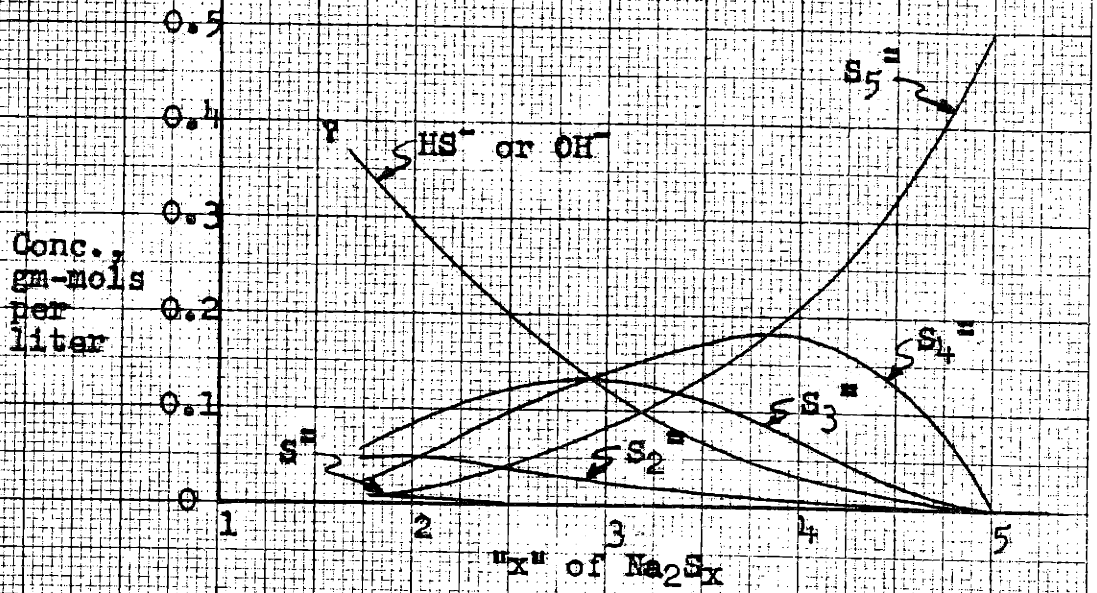


FIGURE 7

Ionic Concentrations in a 0.5 M Polysulfide Solution
(interpolated from results of Peschanski and Valensi (53))

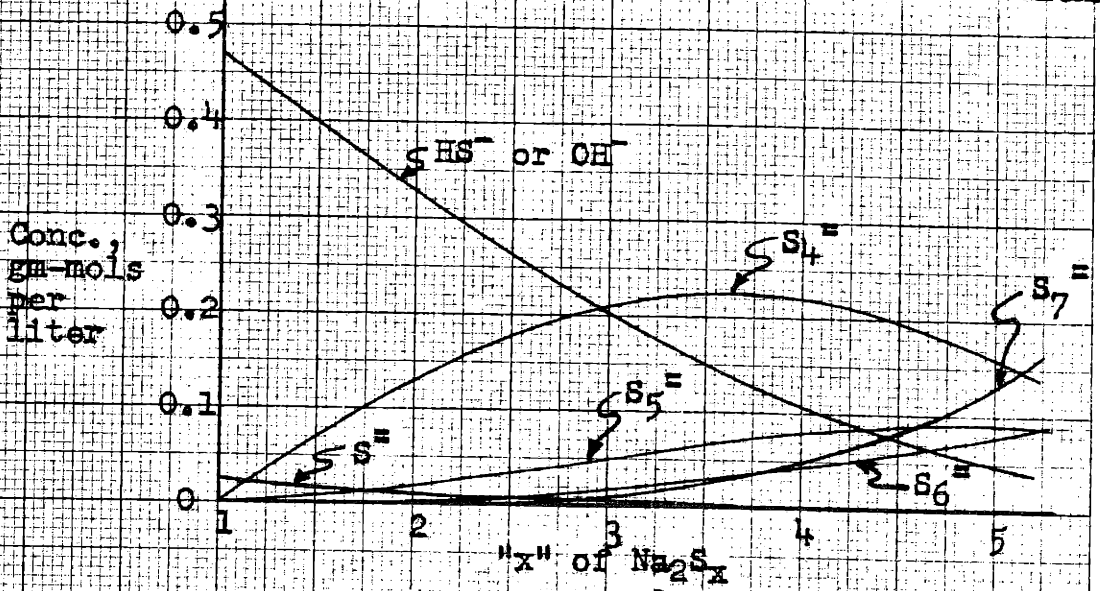


FIGURE 8

Ionic Concentrations in a 0.5 M Polysulfide Solution
(proposed by Conway (15))

Equilibrium constants for the formation of the polysulfide ions may be calculated from the free energies of formation reported by Latimer (43). Since he based his free energies on the literature heats of formation and on assumed entropies of formation, Latimer's numbers are considered doubtful. In any event possible ionic distributions cannot be derived, since only the ions up through the tetrasulfide were considered.

Conway (15) also proposed equilibrium constants and ionic distributions in polysulfide solutions. He based his calculations on the results of Rule and Thomas (56) in absolute ethanol, assuming a final hydrogen sulfide partial pressure. Conway's ionic compositions, also for a 0.5 M solution, are shown as functions of "x" in Figure 8. For several reasons these results cannot be considered valid. First, Conway assumed only the ions from the tetrasulfide through the heptasulfide present, basing this hypothesis on the known lack of the di- and trisulfides in raw oil, plus the fact that the composition Na_2S_4 was indicated for the first polysulfide formed in the Rule and Thomas reaction. (The findings of the present thesis indicate that these phenomena may be explained otherwise.) Second, the results of Rule and Thomas in an organic medium at high temperature should not be considered valid for aqueous solutions at room temperature. Third, in their experiments the final partial pressure of hydrogen sulfide was in fact neither known nor constant from one run to the next. In any event Conway's results for high values of "x" indicate an obvious need to consider ions higher than the heptasulfide in order to obtain more reasonable distributions.

3. Preparation or Identification of Pure Polysulfides

a. Crystallization from Aqueous Solution

Most attempts to produce pure polysulfides by crystallization from aqueous solution have resulted in the formation of mixtures. Kuster and Heberlein (41), however, claim to have prepared pure sodium tetra- and pentasulfides by crystallization from solutions having the initial composition Na_2S_5. Employing potassium instead of sodium, only the tetrasulfide was precipitated. Mills and Robinson (49) prepared pure ammonium pentasulfide by reacting hydrogen sulfide and sulfur with aqueous ammonia.

b. Crystallization from Mixed Ethanol-Water

The conditions in mixed solvents apparently are more favorable for the preparation of the pure polysulfides. Bottger (10) first reported that pure crystalline hydrates could be formed, starting with sulfur, hydrated sodium sulfide crystals, and absolute ethanol. Pearson and Robinson (50) carried out a study of crystallization in 1.5 M polysulfide solutions at temperatures as low as -18°C, with ethanol concentrations ranging from 7 to 100 per cent. Their results are presented in Table VII.

TABLE VII

Preparation of Polysulfides from Ethanol-Water (50)

Range of x	Compound Precipitated
2.0 to 3.2	$Na_2S_2 \cdot 6H_2O$
3.2 to 3.45	$Na_2S_3 \cdot 8H_2O$
3.45 to 5.65	$Na_2S_4 \cdot xH_2O$ (x = 7?, 9, 11)
5.65 to 6.5	$Na_2S_5 \cdot 6H_2O$

If crystallization was not stopped after only small amounts of solids had formed, mixtures of polysulfides resulted. This finding further supports the suspicion that the equilibria between the ions are not mobile at low temperatures. Working with potassium instead of sodium, Pearson and Robinson obtained only the di-, tri-, and tetrasulfides.

c. Preparation in Absolute Ethanol

Rule and Thomas (56) prepared sodium di- and tetrasulfides in the course of their work with the sodium hydrosulfide-sulfur reaction in absolute ethanol. The tetrasulfide was formed directly, whereas the disulfide was produced only by the further reaction of elemental sodium with the tetrasulfide. In the case of the potassium hydrosulfide-sulfur reaction the primary product, in contrast to the sodium experiments, proved to be the pentasulfide. Pearson and Robinson (51) and Feher and Berthold (28), on the other hand, were able to prepare potassium trisulfide as well as the pentasulfide by crystallization from ethanol solution. Working with lithium, Thomas and Jones (64) obtained only the disulfide as a pure compound. By microscopic examination and X-ray diffraction measurements both Rule and Thomas and also Feher and Berthold concluded that their solid polysulfides were pure compounds.

d. Preparation by Direct Combination

Pure polysulfides such as sodium trisulfide, potassium tetrasulfide, and potassium pentasulfide reportedly were prepared by Pearson and Robinson (50)(51) and Draves and Tartar (19), by the direct reaction of sulfur with elemental sodium in a refluxing hydrocarbon (toluene). Feher and Berthold (27), on the other hand, claim that no pure compounds are thus formed. Apparently discounting the results of Pearson and Robinson (50) in mixed ethanol-water, they hence assert that no solid trisulfide of sodium can be prepared. It is interesting to note, in view of their conclusions, that Feher and Berthold at the same time claim to have produced pure sodium pentasulfide and potassium hexasulfide by direct vacuum fusion of lower polysulfides with sulfur under conditions markedly similar to those reported for the direct synthesis of sodium trisulfide.

e. Formation in Liquid Ammonia

Individual polysulfides have been identified by the deflections observed in potentiometric titrations of sulfur with sodium in liquid ammonia; certain of the polysulfides also have been obtained as pure solids. Zintl, Goubeau, and Dullenkopf (72) and also Watt and Otto (68) identified by potentiometric titrations the following polysulfides:

Sodium (68)(72):	Na_2S_2 (?) Na_2S_3 (?) Na_2S_4 Na_2S_5 (?) Na_2S_6 Na_2S_7 (?)
Potassium (68):	K_2S_2 K_2S_4
Rubidium (68):	Rb_2S_2 Rb_2S_4
Cesium (68):	Cs_2S_2 Cs_2S_4

From the work of Bergstrom (4)(5) and Feher and Berthold (28) the following solid polysulfides are reported from liquid ammonia:

Sodium :	Na_2S_2 Na_2S_4
Potassium:	K_2S_2 K_2S_3 K_2S_4
Lithium:	Li_2S_2 Li_2S_4

E. Scope of Thesis

1. Motivation for Research

An acceptable hypothesis for the mechanism of the acid-polysulfide reaction must take into consideration the dependence of the mol yield upon both the mixing rate and the maintenance of an acidic environment. Conway (15) proposed such a mechanism, basing his reaction scheme on the formation of intermediate species such as HS_x^- , which were assumed to be highly unstable:

$$S_x^= + H^+ = HS_x^- \qquad (3)$$

$$HS_x^- + H^+ = H_2S_x \qquad (4)$$

but

$$HS_x^- = (x-1)S + HS^- \qquad (5)$$

$$HS^- + H^+ = H_2S \qquad (6)$$

Thus the formation of persulfides rather than hydrogen sulfide would depend on the rate at which the second hydrogen is brought to the scene of reaction. Conway explained the variation with mixing of the average sulfur subscript of the raw oil by postulating that the rate constants for reaction 5 are greater for the lower polysulfides.

It must be remembered that other factors such as the back-mixing of raw oil with incoming polysulfide and also the spontaneous decomposition of persulfides already formed may serve to decrease the mol yield. In addition the maximum possible yields automatically are reduced by the amount of monosulfide ($S^=$) plus hydrosulfide (HS^-) actually present in nominally sodium polysulfide solution.

If it is assumed that raw oil first must be cracked to the disulfide before use in organic syntheses, then the overall yield of final product is influenced directly by the proportion of lower persulfides in the oil. In particular, the apparent absence of any disulfide or trisulfide in raw oil, as indicated by the Raman spectroscopic work of Feher and Baudler (26), never has been explained fully. Special conditions under which hydrogen disulfide could be produced from an alkali polysulfide in a single step would be highly desirable.

Three possible reasons for the absence of the two lower persulfides in raw oil might be:

1. The ionic equilibria in aqueous polysulfide solutions are such that the disulfide and trisulfide ions are present only in very small amounts.
2. The intermediate ions HS_2^- and HS_3^- are more unstable by order of magnitude than the higher HS_x^- species.
3. Hydrogen disulfide and hydrogen trisulfide actually are formed, but decompose rapidly owing to their extreme instability in contact with even strongly acidic aqueous media.

The finding of Rule and Thomas (<u>56</u>) that polysulfides below the tetrasulfide are not formed in the alcoholic sodium hydrosulfide-sulfur reaction would seem to substantiate the first explanation. On the other hand, solid sodium disulfide and sodium trisulfide are reported accessible under other conditions. The third hypothesis is supported by the finding of Feher and Baudler (<u>23</u>)(<u>24</u>) that an instantaneous precipitated sulfur turbidity forms when either hydrogen disulfide or hydrogen trisulfide is placed in contact with an aqueous solution. Preliminary results in the present thesis, however, have demonstrated that even this decomposition is not complete within a short time. If the decomposition is visualized as taking place via solution and ionization of the persulfide, then the second and third explanations become much the same.

In a more recent paper Feher (<u>20</u>) has proposed that the lower HS_x^- species react with nascent sulfur chains during acidification to yield higher sulfur homologues. This hypothesis merely modifies the preceding second explanation, prescribing the ultimate fate of the sulfur released by decomposition.

In any event it would appear that the determination of the ionic constituents in aqueous polysulfide solutions would constitute a large step forward in trying to establish which processes are important in the acid-polysulfide reaction.

2. Objectives of Research

With the preceding considerations in mind the following thesis goals were set up:

1. Determine the conditions under which the ionic equilibria in aqueous polysulfide solutions are mobile.
2. Under conditions where mobility is ensured, conduct equilibrium measurements from which the actual distributions of polysulfide ions can be calculated.
3. Interpret the existing data on the acid-polysulfide reaction in view of these findings.

3. Method of Approach

a. The System Na_2S-S-H_2O

It might appear that the equilibrium behavior in polysulfide solutions can be predicted from the results of measurements on the system Na_2S-S-H_2O, from which such polysulfide solutions can be made up. Restricting consideration to the liquid phase, we find four degrees of freedom which must be fixed in order to define the system:

1. Temperature
2. Total pressure
3. H_2O/Na_2S
4. S/Na_2S

If the pertinent ionic equilibrium constants were known, then the complete composition of the system could be derived if these four quantities were determined. If, on the other hand, the equilibrium constants were not known, then additional information concerning one or more of the individual species present would be required in order to calculate the unknown constants and thus the ionic distribution.

The following additional measurements on this system were contemplated:

1. Hydrogen ion activity by the glass electrode (c.f. Peschanski (52)).
2. Hydroxyl activity by rate of reaction (c.f. Kuster and Heberlein (41)).
3. Monosulfide ion activity by solubility of mercuric sulfide (c.f. Martin (46)).
4. Water activity by vapor pressure or freezing point (c.f. Kuster and Heberlein (41)).
5. Hydrogen sulfide activity from partial pressure.
6. Sulfur activity by concentration in an organic solvent.

The first four techniques, which had been employed by previous workers, were deemed unsuitable owing to the lack of both precision and reproducibility. The fifth was discarded since, upon reflection, it was seen that if the hydrosulfide and hydroxyl concentrations were assumed equal (no hydrolysis of the polysulfide ions), then the hydrogen sulfide partial pressure was fixed, independent either of molarity or of "x". (The measurement of very small hydrogen sulfide partial pressures moreover would be very difficult.) The sixth possibility was explored in some preliminary experiments; it was found that sulfur activities were too low to be determined conveniently except over a narrow range of "x" adjacent to sulfur saturation. At saturation, of course, solid rhombic sulfur would be present at equilibrium, in which case the activity of S_8 would be unity.

In view of these considerations it was decided to study a more general system in which experimental methods might prove more fruitful.

b. The System Na_2S-S-H_2S-H_2O

In this case, from phase rule considerations, five degrees of freedom must be fixed in order to determine the liquid phase system:

1. Temperature
2. Total pressure
3. H_2O/Na_2S
4. S/Na_2S
5. H_2S/Na_2S

In addition to these five quantities the following three numbers could be measured:

1. Hydrogen sulfide partial pressure
2. Sulfur concentration in organic solvent
3. pH

It indeed was found that if hydrogen sulfide partial pressures large enough to be known accurately were employed, the sulfur activities likewise were high enough to be determined with reliability over a much wider range of ratios of S/Na_2S than possible in the previous case. The investigations of pH, while not sufficiently precise for use in the final equilibrium calculations, nevertheless could be of value in establishing which species were present in stoichiometrically significant amounts.

The equilibrium constants for the various polysulfide ions, obtained via measurements on the system $Na_2S-S-H_2S-H_2O$, would be equally valid for the prediction of the ionic distributions in ordinary alkali polysulfide solutions.

c. Program of Research

The following experimental attack was adopted: Equilibrium measurements would be performed on the system $Na_2S-S-H_2S-H_2O$. For convenience the following independent variables would be predetermined for each experiment:

1. Temperature
2. Total pressure (weak effect in liquid system)
3. Hydrogen sulfide partial pressure
4. Ratio H_2O/Na_2S
5. Ratio S/Na_2S

The dependent variables then would be:

1. Ratio H_2S/Na_2S
2. Sulfur concentration in solvent
3. pH

For cases in which solid sulfur would be present at equilibrium, the sulfur activity would be fixed at unity and the ratio S/Na_2S in the aqueous phase then would become a dependent variable.

Equilibrium in this system would be approached from two convenient directions:

1. Reaction between sulfur and sodium hydrosulfide.

$$2NaHS + (x-1)S = Na_2S_x + H_2S \qquad (7)$$

2. Reaction between hydrogen sulfide and sodium polysulfide.

$$Na_2S_x + H_2S = 2NaHS + (x-1)S \qquad (8)$$

Although reaction 7 had been studied previously by Bloxam (9) and Rule and Thomas (56), and reaction 8 by Kuster and Heberlein (41), their results, as was mentioned earlier, were judged to be of little value to the present thesis.

It was recognized that any single equilibrium experiment in the system Na_2S-S-H_2S-H_2O would not provide sufficient information to permit solution for the unknown equilibrium constants; data from a series of such runs at varying conditions would be required. Material balances could be written for each experimental point, expressing the unknown ionic concentrations in terms of measured quantities and the unknown equilibrium constants; the resulting set of simultaneous equations then could be solved for the desired constants.

PROCEDURE

A. Outline of Experimental Work

1. Runs at Room Temperature

The initial study of equilibrium behavior in the system $Na_2S-S-H_2S-H_2O$ was carried out at room temperature (25.7°C). This temperature was chosen because raw oil normally is produced from polysulfide stored and fed at room conditions. In this preliminary series only the ratio S/Na^+ in the aqueous phase was varied (from 0.38 to 1.05); the sodium ion concentration and the hydrogen sulfide partial pressure were constant at about 3.5 M and about 1.0 atm, respectively.

Equilibrium was approached from both directions. The sodium hydrosulfide-sulfur reaction (equation 7) was employed in 11 runs, whereas the sodium polysulfide-hydrogen sulfide reaction (equation 8) was utilized in 6 runs. No attempts were made to measure solvent sulfur concentration or pH in any of these initial experiments. In 8 out of the 17 runs carried out at room temperature considerable solid sulfur was present in the reaction mixture at completion of the experiment.

The failure of the results of runs from one direction to agree with the results of corresponding runs employing the reverse reaction indicated that true equilibrium was not reached at room temperature. The experiments at 25.7°C therefore were curtailed; elevated temperatures were employed in all subsequent work.

2. Runs at Elevated Temperature

By far the majority of equilibrium experiments in the system $Na_2S-S-H_2S-H_2O$ were carried out at 75°C, a temperature chosen somewhat arbitrarily, but one at which equilibrium was attained. It is of some pertinence to note that polysulfide solutions normally are prepared at elevated temperatures in this neighborhood. In this series of runs the following were varied:

Ratio S/Na^+ in aqueous phase:	0.5 to 1.6
Sodium ion molarity:	0.1 M to 6.2 M
Hydrogen sulfide partial pressure:	0.02 atm to 0.7 atm

Equilibrium at 75°C was verified by runs from both directions. The sodium hydrosulfide-sulfur reaction (eq. 7) was used in 8 experiments; the sodium polysulfide-hydrogen sulfide reaction (equation 8) was employed in 45 runs. Of the latter, 18 runs involved determination of sulfur concentration in a solvent layer; 8 runs included measurement of pH; in 2 runs sodium chloride was added as an inert electrolyte. In 21 out of the 53 experiments carried out at 75°C solid sulfur was present at equilibrium.

B. Experimental Technique

1. Apparatus

All the equilibrium experiments at room temperature and the first 22 runs at 75°C were performed in a stoppered 1000-ml wide-mouth Erlenmeyer flask with no provision for mixing other than by swirling (Figure 9). The reaction vessel for the later 31 runs at elevated temperature was a 1000-ml standard-taper three-neck flask fitted with a jacketed mechanical stirrer (Figure 10). The volumes of aqueous solution averaged 500-600 ml in most runs. A condenser in the gas outlet line was employed in all the experiments at 75°C.

In all cases the reaction vessel was immersed in a water or oil bath which was held at a constant temperature ± 0.2°C. A separate thermometer indicated the actual temperature of the equilibrium solution. All runs were carried out at essentially atmospheric total pressure. The system pressure, equal to the ambient pressure plus the small drop through the outlet gas system, was measured by a dibutyl phthalate manometer.

2. The Sodium Hydrosulfide-Sulfur Reaction

The initial solutions of sodium hydrosulfide for use in the runs employing reaction 7 were prepared by first dissolving sodium sulfide crystals in water. The analyses of the resulting solutions either were found by iodimetric titration or were assumed from the predetermined assay of the sodium sulfide. The monosulfide solutions then were converted to hydrosulfide by saturation with hydrogen sulfide while in the reaction vessel at the temperature chosen for the experiment.

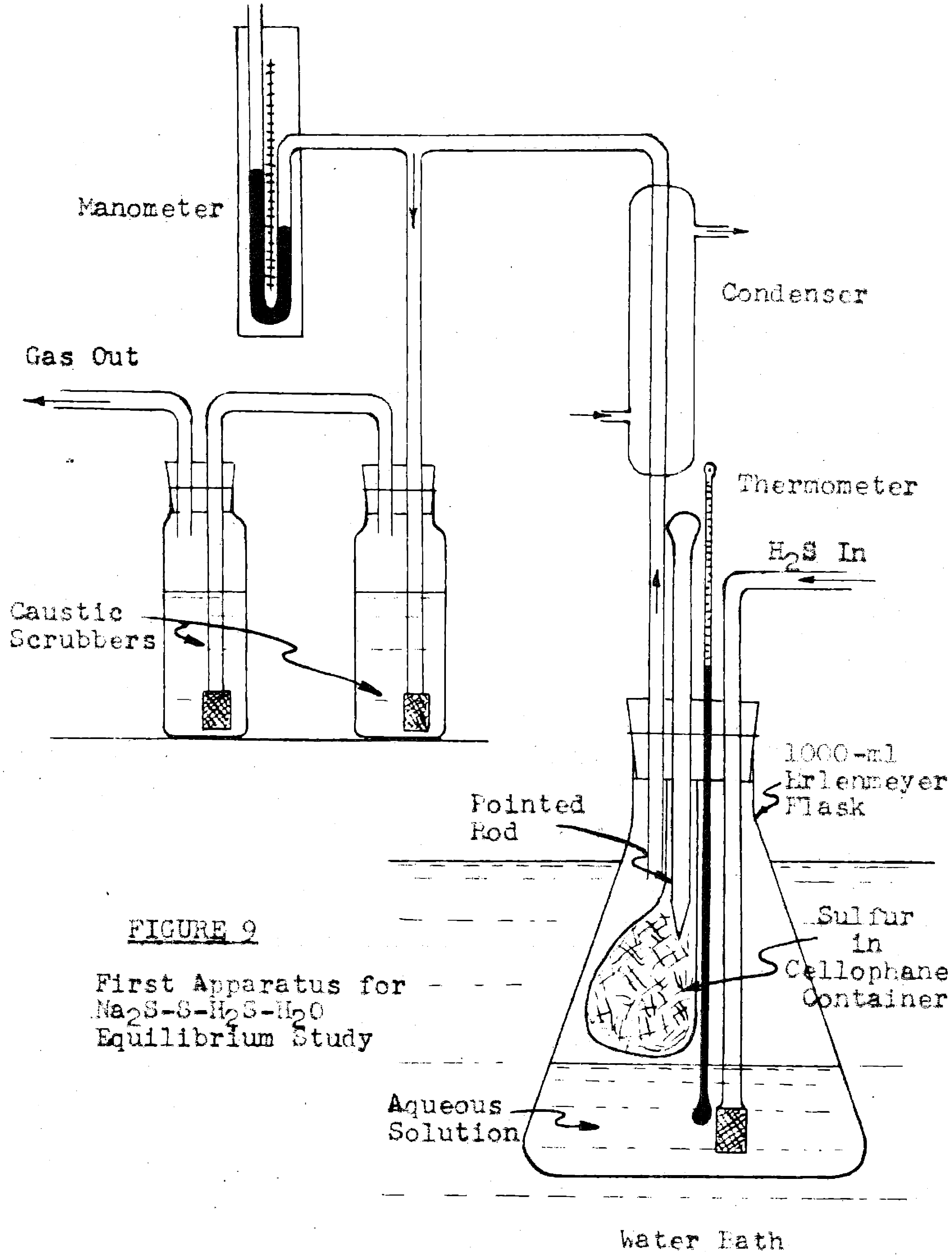


FIGURE 9

First Apparatus for Na_2S-S-H_2S-H_2O Equilibrium Study

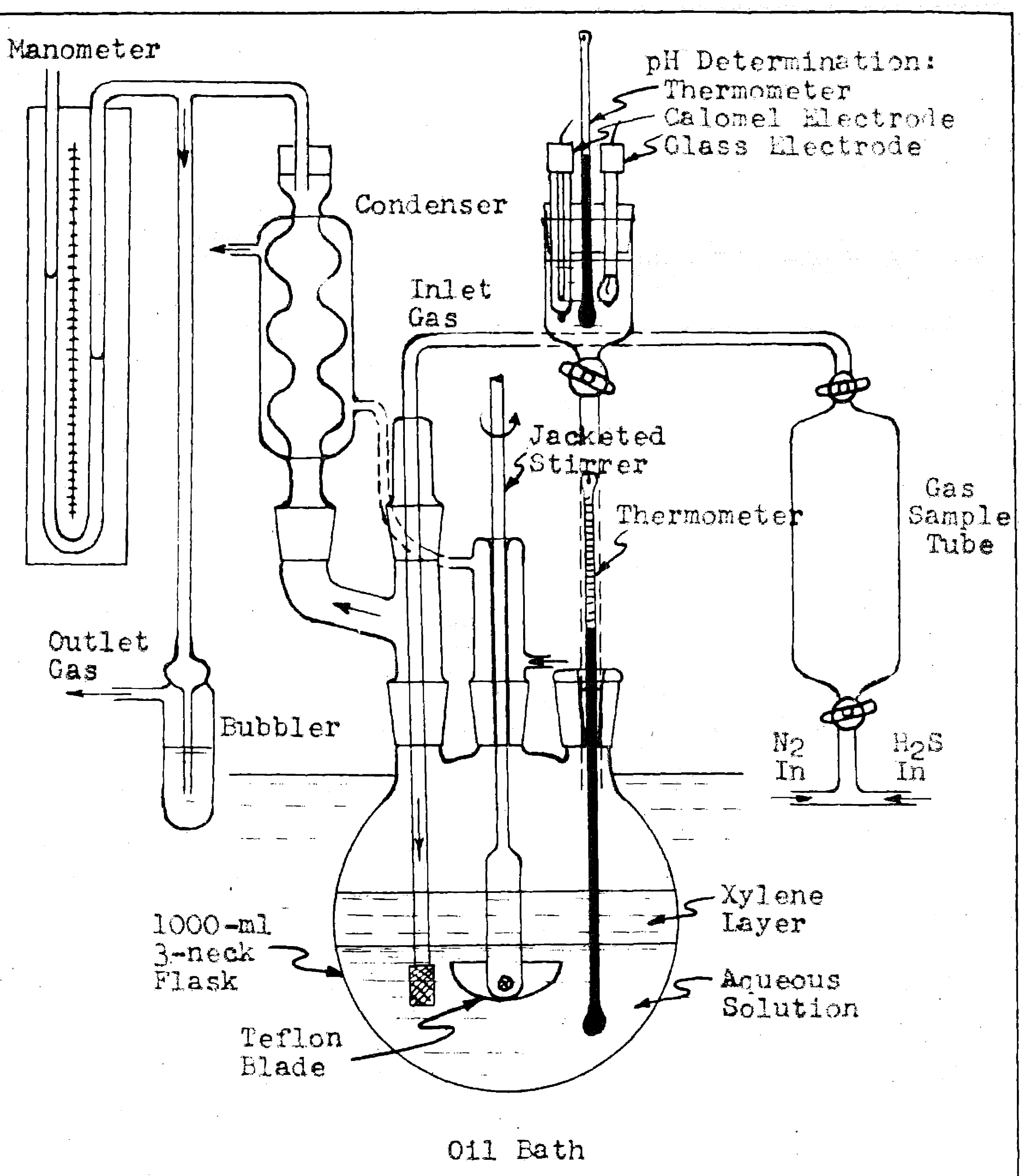


FIGURE 10

Second Apparatus for
Na_2S-S-H_2S-H_2O
Equilibrium Study

In all except two runs the evolutions of hydrogen sulfide upon additions of sulfur were measured and material balances were calculated. The charges of sulfur were enclosed in cellophane and were positioned over the solutions during the initial hydrogen sulfide saturations. Without allowing air to enter the reaction vessel, the cellophane containers then were broken so that the charges of sulfur dropped into the solutions and began to react. The hydrogen sulfide released was absorbed into caustic by means of scrubbers in the exit gas line. In runs E-58 and E-59 the sulfur was added without any precautions to maintain a hydrogen sulfide atmosphere; no material balances were attempted.

The runs were continued until hydrogen sulfide evolution had ceased; this time ranged from 5 to 10 hours at room temperature to only 1 1/2 to 5 hours at elevated temperature. At the conclusion of a run the final aqueous solution and the caustic in the scrubbers were sampled and titrated iodimetrically for total sulfides. Any unreacted sulfur also was collected, washed, dried, and weighed.

3. The Sodium Polysulfide-Hydrogen Sulfide Reaction

The initial polysulfide solutions for experiments involving reaction 8 were prepared by reacting together sodium sulfide, sulfur, and water, in the reaction flask at about the temperature later to be used during the run. The resulting solutions were sampled and titrated for total sulfides. In any case where a significant quantity of unreacted sulfur remained, this sulfur was collected and weighed. In most instances, however, the amounts of such sulfur merely were estimated, no separations being attempted.

Since large excesses of hydrogen sulfide were required in order to sweep out the gas phase and ensure saturation, no material balances were possible in runs approaching equilibrium from this direction. A porous glass sparger was employed to introduce hydrogen sulfide into the polysulfide solutions. The rates of purge initially were high, but were cut back after about 1/2 hour in order to permit the equilibrium partial pressures of water vapor to develop. The experiments were adjudged complete when no further gas absorption could be noted; the run times averaged generally shorter than for the sodium hydrosulfide-sulfur reaction. The volumetric analyses of final aqueous solutions and the gravimetric determinations of any precipitated sulfur were similar to those in the preceding case.

4. Special Cases

a. Runs with Xylene

In order to arrive at an indication of elemental sulfur activity in cases where sulfur saturation did not exist, experiments were required involving the measurement of sulfur concentration in a solvent layer present at equilibrium. Many good sulfur solvents (carbon disulfide, for example) were found not to be chemically inert to polysulfide solutions; finally selected for use, owing to suitable volatility and solubility characteristics, was *o*-xylene. The following properties of *o*-xylene are reported (36)(65):

Molecular weight:	106.16
Density at 20°C:	0.8745 gm/cc
Boiling point:	144°C
Vapor pressure at 75°C:	79 mm Hg
Sulfur solubility at 75°C:	9.8 wt. %

In a typical experiment in which *o*-xylene was used, approximately 100 ml xylene was added to the reaction vessel immediately preparatory to beginning the run. In all except the first 4 of the 18 xylene runs the mixing of the two phases during equilibration was ensured by rapid stirring. At the completion of a xylene experiment the organic layer was sampled and the weight per cent sulfur was determined gravimetrically by evaporation to dryness.

In certain instances a slight chemical reaction between sulfur and xylene was evidenced by a darkening in color and a sharpening in odor. It was demonstrated, however, that this reaction was not sufficient to affect the sulfur solubility properties of the xylene.

b. Runs with pH Determination

A Beckman Model M direct-reading pH meter was employed to measure hydrogen ion activities in certain runs at sodium ion molarities of 1.0 and below. For this purpose the apparatus shown in Figure 10 was modified by the attachment of a pH sampling cell which permitted determination at the equilibrium hydrogen sulfide partial pressure for the run.

In performing a pH measurement the instrument first was standardized against one or more known buffer solutions immersed in the bath at the reaction temperature. The electrode assembly immediately was transferred to the sampling cell and equilibrium gas from the reaction vessel was purged through; aqueous solution then was forced up by the application of slight pressure. Since the sampling cell was not jacketed, cooling proceeded as the pH was read. Two such pH versus temperature traverses were obtained for each unknown; the correct pH value at 75°C then was determined by extrapolation.

c. Runs with Reduced Hydrogen Sulfide Partial Pressure

Operation at lowered partial pressures of hydrogen sulfide was required at low sodium ion molarities in order that uncertainties in the estimation of physically-dissolved hydrogen sulfide in the aqueous phase did not jeopardize the results. Variations in hydrogen sulfide partial pressure also were desirable in order to verify the attainment of equilibrium between that component and the remaining constituents of the system.

Rather than work at total pressures different from 1.0 atm it was decided to achieve low hydrogen sulfide partial pressures through the use of nitrogen as a diluent. Whereas a mix tank might have been employed for this purpose, gas of desired composition instead was prepared by flow mixing of the two pure components. The rates of flow were controlled by needle valves; the mixed gas was routed through a sample tube located upstream from the reaction vessel. This technique was, of course, applicable only to experiments involving the sodium polysulfide hydrogen sulfide reaction.

In performing a run at lowered hydrogen sulfide partial pressure the two flow rates were set initially to give the desired mixture and were not changed thereafter. Gas samples were taken periodically throughout the run and were analyzed for hydrogen sulfide content by iodimetric titration.

5. Improvements in Technique

a. Purity of Reagents

During the course of the experimental program it was found that in certain instances the results were being influenced by impurities present in the initial sodium sulfide. Although the best grade sodium sulfide commercially available (Mallinckrodt AR crystals) was used, tests of sulfur precipitation upon acidification nevertheless disclosed higher proportions of thiosulfate ($S_2O_3^{=}$) and sulfite ($SO_3^{=}$) than called for by the reagent specification (0.10% as SO_2). It was found, however, that essentially all these oxidation impurities could be eliminated by washing the crystals to dissolve the outer layer, followed by storage under nitrogen.

This procedure was adopted in the last 14 runs made. Further details concerning this problem are given in the Appendix.

In all runs USP precipitated sulfur was used. No analyses were available for this material, but indications were that it was quite pure. Even though tests showed negligible moisture content, the sulfur for the last 31 runs was dried overnight at 80-90°C in order to be certain that no water remained which would appear as false weight.

Distilled water from laboratory lines was employed in making up all solutions. In the last 31 runs the water was boiled before being used in order to remove air and carbon dioxide which might react with the polysulfide.

Whereas "technical grade" hydrogen sulfide had been used in some earlier runs, the last 24 experiments were carried out with "purified grade" gas. The specifications and analyses indicated that this hydrogen sulfide as discharged from the cylinder was essentially pure.

The first 4 sulfur activity runs were performed using reagent grade mixed xylene consisting of roughly 60 per cent m-xylene and 20 per cent each of o-xylene and p-xylene. In the remaining 14 xylene experiments "pure" o-xylene (Eastman) was employed. Even though no analysis was available for this latter material, it was assumed to be free of non-hydrocarbon impurities.

b. Experimental

Because polysulfide solutions are susceptible to oxidation, the exposure to air was minimized during polysulfide preparation and handling. In all later runs the initial solutions were made up under nitrogen. Although some chance still existed for deterioration during the various necessary manipulations, tests in which air actually was bubbled into hot polysulfide solutions indicated that even then oxidation was not nearly so extensive as had been supposed.

Another problem which could lead to error was possible loss of hydrogen sulfide from solutions being transferred for analysis. Gas evolution was noted visually, in fact, in final solutions from earlier sodium hydrosulfide-sulfur experiments in which hydrogen sulfide supersaturation was suspected. Even though tests demonstrated that such errors normally were negligible, the final solution samples in the remaining runs carried out at 75° C were pipetted under the equilibrium hydrogen sulfide partial pressure, employing a technique similar to that utilized in the pH measurements.

In the xylene runs made in the Figure 10 apparatus errors in xylene sulfur concentration were possible owing to nonvolatile stopcock lubricant dissolving in the organic layer. After 3 such runs had been performed this difficulty was eliminated; no grease was employed in the last 11 experiments.

Comparisons between otherwise duplicate runs indicated, however, only negligible differences.

C. Quantities Measured

1. Direct Readings

The temperatures of the equilibrium solutions were indicated to ± 0.1°C by a thermometer immersed directly in the reaction mixtures. The system absolute pressures were measured, accurate to 0.5 mm Hg, by a combination of differential manometer and atmospheric barometer. Although the pH instrument could be read to the nearest 0.01 pH unit, the values obtained probably were not reliable to closer than 0.05 pH unit.

2. Weights

The initial sulfur charged in each run was weighed out to the nearest 0.1 gm on a laboratory balance (to the nearest 0.0001 gm on an analytical balance if less than 50 gm). Any final free sulfur was treated similarily. In certain runs the final aqueous solution was weighed, accurate to 0.1 gm. Duplicate xylene samples in runs to determine sulfur activity were weighed to ± 0.0001 gm on the analytical balance; the samples were evaporated to dryness and the residues again were weighed.

3. Volumes

The volumes of initial and final solutions were determined using a graduate cylinder accurate to ± 1 ml. These volumes were measured at or near the reaction temperature. In the case of final solutions corrections were applied for the volumes of any solid sulfur present during measurement; such sulfur could not be separated readily without entraining some aqueous phase. The organic layer volumes were determined in xylene runs.

4. Titrations

The samples of both initial and final aqueous solutions were titrated iodimetrically for total reducing equivalents. The caustic scrubbers for hydrogen sulfide in the sodium hydrosulfide-sulfur runs were similarily titrated. In the experiments at lowered hydrogen sulfide partial pressures gas samples also were analyzed titrimetrically. In all cases the titrations could be assumed accurate to ± 0.5 per cent.

RESULTS

A. Calculation of Results

1. Chemical Species Present

In order to convert the experimental measurements taken on the system $Na_2S-S-H_2S-H_2O$ into a form suitable for the determination of ionic equilibrium constants, it was necessary to assume only certain chemical species present in stoichiometrically significant amounts. The aqueous solutions in all cases were considered to be comprised of essentially the following components:

a. Polysulfide ($S_x^=$) ions, such as $S_2^=$, $S_3^=$, $S_4^=$, etc.
b. Hydrosulfide (HS^-) ion
c. Sodium (Na^+) ion
d. Dissolved hydrogen sulfide (H_2S)
e. Water (H_2O)

Other possible ions or compounds might be imagined. Since the justification for neglecting these is based in part upon the experimental findings of the present thesis, any examination of the evidence underlying this justification is deferred until section B under Discussion of Results.

2. Assumed Physical Properties

Further assumptions were required in order to calculate hydrogen sulfide partial pressures, concentrations of physically-dissolved hydrogen sulfide, and in some cases conversions of molarity to molality.

a. "Total Ionic Concentration"

The water vapor pressures over and the gas solubilities in aqueous solutions of electrolytes normally are reduced from the values in pure water by amounts dependent on the ionic strength, which is defined as follows:

$$\mu = 1/2 \sum m_i z_i^2 \qquad (9)$$

in which μ is ionic strength

m_i is molality of ionic component "i"

z_i is charge on ionic component "i".

Since quantitative data on these corrections are lacking for the ionic systems under consideration, more approximate relations were assumed, based instead on the "total ionic concentration", which could be estimated from the experimental equilibrium measurements:

$$\mu' = [Na^+] + ([S_x^=] + [HS^-]) \cong \frac{n_1 + (0.5n_2)}{V} \qquad (10)$$

in which μ' is "total ionic concentration" (molarity)

n_1 is initial (Na_2S or Na_2S_x) titration, gm-eqs.

n_2 is final (equilibrium) titration, gm-eqs.

V is final solution volume, liters.

b. Water Partial Pressure

The partial pressures of water vapor were estimated assuming the following relation:

$$p_{H_2O} \cong P_{H_2O} - \alpha \, \mu' \qquad (11)$$

in which p_{H_2O} is water partial pressure, mm Hg
P_{H_2O} is vapor pressure of pure water, mm Hg
α is a constant, mm Hg-liters/gm-mol.

At 25°C, $P_{H_2O} = 25$
$\alpha \cong 0.3$ (assumed)

At 75°C, $P_{H_2O} = 289$
$\alpha \cong 3.6$ (assumed)

e. Xylene Partial Pressure

In those experiments at 75°C in which xylene was employed to indicate sulfur activities, the partial pressures of xylene vapor were estimated as follows:

$$p_{Xyl} \cong P_{Xyl} - 0.3 \, (\%S) \qquad (12)$$

in which p_{Xyl} is xylene partial pressure, mm Hg
P_{Xyl} is vapor pressure of pure xylene, mm Hg
%S is weight per cent sulfur dissolved in the xylene.

For mixed xylenes, P_{Xyl} was taken as 93 mm Hg at 75°C.

For pure o-xylene, P_{Xyl} was taken as 79 mm Hg at 75°C.

This relation was based on experimental determinations (60) of the vapor pressure lowering over solutions saturated with sulfur.

d. Dissolved Hydrogen Sulfide Concentration

Hydrogen sulfide in solution was assumed to obey the relation for dissolved gases proposed by Harned and Owen (35):

$$[H_2S] \cong H\, f_{H_2S}\, e^{-\beta\mu'} \qquad (13)$$

in which $[H_2S]$ is concentration of hydrogen sulfide, gm-mols/liter

H is the Henry's law constant, gm-mols/liter-atm.

f_{H_2S} is the hydrogen sulfide partial pressure, atm, = $p_{H_2S}/760$.

β is a constant, liters/gm-mol

(μ' has been substituted for the rigorously correct μ)

From the literature (36), H = 0.10 at 25°C
= 0.04 at 75°C

On the basis of both the apparent solubilities of hydrogen sulfide in sodium hydrosulfide solutions determined in the present thesis and also the salting-out coefficients for other electrolyte systems reported by Harned and Owen, β was assumed constant at 0.07.

e. Aqueous Solution Density

In order to convert the ionic molarities into molalities for use in correlations of activity coefficients and in the determination of equilibrium constants, it was necessary to know the densities of the final aqueous phases, and thus the weights of water per given volumes of solution. For those experiments in which only the volumes were measured these quantities were estimated from graphical correlations of density versus sodium ion molarity with the total ratio $S:Na_2S$ as a parameter. These relationships at the temperatures 25°C and 75°C are shown in Figure 11. The curves at 25°C have been adapted from the densities reported by Conway (15); those at the higher temperature are based mainly on the findings of the present thesis. In both cases it was assumed that the densities did not change significantly upon the addition of hydrogen sulfide to the polysulfide solutions.

3. Manipulation of the Data

a. Hydrogen Sulfide Partial Pressure

The partial pressures of hydrogen sulfide at equilibrium were calculated by difference:

$$p_{H_2S} = \pi - p_{H_2O} - p_{Xyl} \qquad (14)$$

in which p_{H_2S} is hydrogen sulfide partial pressure, mm Hg

π is total pressure, mm Hg

p_{H_2O} and p_{Xyl} are computed by equations 11 and 12, respectively.

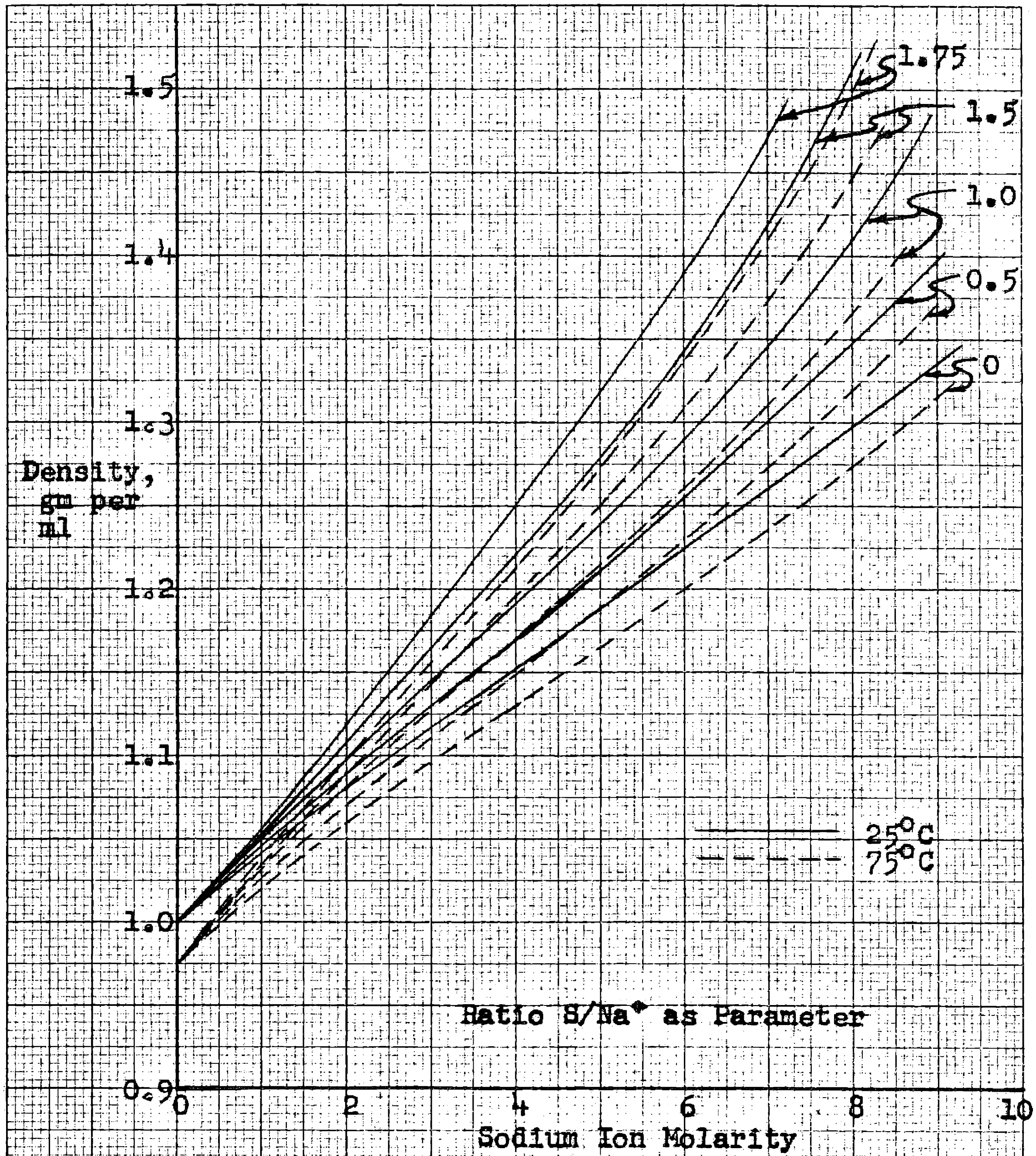


FIGURE 11

Densities of Aqueous Sodium Polysulfide Solutions

In those experiments carried out at reduced hydrogen sulfide partial pressures, of course, the numbers obtained from equation 14 were multiplied by the percentages of hydrogen sulfide in the nitrogen diluent mixtures fed.

It might be questioned whether the partial pressures calculated for the various components represent the equilibrium values "seen" by the ionic constituents of the aqueous phase. Regardless of the composition of the vapor in the reaction vessel the water partial pressure within the aqueous solution should be that predicted. In view of the rapid mixing imposed in all the later runs, moreover, the gas phase and liquid phase partial pressures of xylene vapor, nitrogen, and hence of hydrogen sulfide also shall be assumed to coincide with the values calculated for those runs.

b. Hydrogen Sulfide Balance

The determination of hydrogen sulfide evolved in the runs employing the sodium hydrosulfide - sulfur reaction (equation 7) made possible the calculation of sulfide material balances for those runs. The values of hydrogen sulfide released first were corrected for the changes in mols of dissolved and vapor space hydrogen sulfide during the reaction owing to (1) the volumes occupied by the initial sulfur charges, and (2) any differences between the initial and the final system pressures. Having taken these small adjustments into account, it then was assumed that the dissolved hydrogen sulfide concentration in any initial sodium hydrosulfide solution was the same as that calculated by equation 13 for the corresponding final equilibrium solution. The total reducing equivalents in the sodium hydrosulfide solution thus could be set equal to $2n_1 + 2V[H_2S]$, whereas the reducing equivalents in solution at equilibrium could be set equal to n_2. The total sulfides material balance then became:

$$\text{Per Cent Material Balance} = \frac{n_2 + 2(H_2S\ \text{off})}{2n_1 + 2V[H_2S]} \times 100 \qquad (15)$$

in which (H_2S off) is expressed in gm-mols.

c. Equilibrium Gross Ionic Composition

The calculated final ionic compositions in all experiments were based upon combinations of the initial and final titrimetric analyses. The final reducing equivalents corresponding only to polysulfide ($S_x^=$) plus hydrosulfide (HS^-) differed from the total by the equivalents of physically-dissolved hydrogen sulfide:

$$n_{2_c} = n_2 - 2V[H_2S] \qquad (16)$$

in which n_{2_c} is "corrected" final titration, gm-eqs. By virtue of the electrical neutrality requirement the sodium ion could be set equal to the initial (Na_2S or Na_2S_x) titration:

$$Na^+ = n_1 \qquad (17)$$

in which Na^+ is gm-mols sodium ion.

The polysulfide and hydrosulfide ions then were determined as follows,

$$S_x^= = n_1 - 0.5\, n_{2_c} \qquad (18)$$

$$HS^- = n_{2_c} - n_1 \qquad (19)$$

in which $S^=$ is gm-mols polysulfide ions

HS^- is gm-mols hydrosulfide ion,

such that twice their sum equaled the corrected final titration and such that electrical neutrality was complied with.

These mol quantities were converted to molarities merely by dividing by the final aqueous solution volumes. The weights of water in solution were calculated by subtracting the weights of the other components from the measured or estimated final solution weights. The ionic molalities then were determined by divisions analagous to those for molarities.

d. Polysulfide Sulfur in Solution at Equilibrium

"Polysulfide sulfur" (PSS) was defined as the total "S" required to make up the Na_2S-S-H_2S-H_2O system under consideration. If only the assumed chemical species were present, this quantity also could be written as $S_2^= + 2S_3^= + 3S_4^= + \ldots.$ Experimentally, the polysulfide sulfur in a final aqueous solution was determined by subtracting from the gm-atoms sulfur initially charged as such the sulfur removed during the course of the run by (1) the initial polysulfide (Na_2S_x) samples withdrawn for analysis, (2) any precipitated or unreacted sulfur present at equilibrium, and (3) extraction by a xylene layer, if used:

$$\text{PSS} = (\text{Initial S Charged}) - (Na_2S_x \text{ Sample S}) - (\text{Solid S}) - (\text{Xylene S}) \qquad (20)$$

The gm-atoms polysulfide sulfur removed by a polysulfide sample was calculated as follows:

$$(Na_2S_x \text{ Sample S}) = \left(\frac{\text{Vol. Samples}}{\text{Total Vol.}}\right) (\text{Initial S Charged}) - (\text{Unreacted S}) \qquad (21)$$

Thus relatively large errors could be tolerated in estimating any small amount of unreacted sulfur remaining after polysulfide preparation. The solid sulfur at equilibrium was weighed directly. The sulfur in a xylene layer was determined from the xylene analysis:

$$(\text{Xylene S}) = \left(\frac{\text{Total Xylene Vol.}}{\text{Sample Vol.}}\right) (\text{S in Sample}) \qquad (22)$$

B. Presentation of Results

1. The System Na_2S-S-H_2S-H_2O: Equilibrium Studies at 25°C

a. Tabulation of Results

The conditions and the results for the 17 equilibrium experiments performed at room temperature are given in

TABLE VIII-a

System Na_2S-S-H_2S-H_2O: Equilibrium Results at 25°C

1. Run Number	E-1	E-2	E-3	E-4	E-5
Run Conditions					
2. Temperature °C	25.7	25.7	25.7	25.7	25.7
3. Total Pressure, mm Hg	793	815	811	815	817
4. H_2S Partial Press., atm	1.013	1.043	1.038	1.043	1.045
5. Solution Volume, ml	555	546	546	545	550
6. Solution Weight, gm	(636)	(628)	(628)	(634)	(639)
7. H_2O in Solution, gm	509	501	501	490	495
8. H_2S in Solution, gm-mols	0.035	0.035	0.035	0.036	0.036
9. Final Solid S, gm	0.6	0.6	0.2	2.2	2.8
10. Run Time, hrs.	5.0	5.0	5.0	5.0	5.0
Measured Results					
11. Initial Titr., gm-eqs	(1.966)	(1.966)	(1.966)	(1.966)	(1.966)
12. Final Titr., gm-eqs	(3.522)	3.570	3.530	3.232	3.270
13. Corr. Final Titr., gm-eqs	3.452	3.499	3.460	3.160	3.197
14. H_2S Evolved, gm-mols	0.205	0.180	0.183	0.330	0.325
15. Total H_2S Balance, %	??	98.5	97.7	97.6	98.2
16. PSS in Soln., gm-atoms	0.730	0.730	0.742	1.430	1.410
Concentrations					
17. Na^+ Molarity	3.54	3.60	3.60	3.61	3.57
18. $S_x^=$ Molarity	0.432	0.395	0.432	0.708	0.667
19. HS^- Molarity	2.678	2.806	2.737	2.191	2.239
20. PSS Molarity	1.316	1.337	1.360	2.623	2.562
21. Na^+ Molality	3.86	3.92	3.92	4.01	3.97
22. $S_x^=$ Molality	0.471	0.431	0.471	0.787	0.741
23. HS^- Molality	2.920	3.060	2.982	2.438	2.486
24. PSS Molality	1.435	1.458	1.482	2.918	2.847
Derived Numbers					
25. "A" = PSS/Na^+	0.371	0.371	0.377	0.727	0.717
26. "B" = $S_x^=/Na^+$	0.122	0.110	0.120	0.196	0.187
27. A/B = PSS/$S_x^=$	3.04	3.38	3.15	3.70	3.84
28. "X" = $\frac{[S_x^=]\ f_{H_2S}}{[HS^-]^2}$	0.0559	0.0480	0.0549	0.1382	0.1251
29. "Y" = $\frac{[PSS]\ f_{H_2S}}{[HS^-]^2}$	0.1705	0.1624	0.1727	0.512	0.481
(X and Y based on molalities)					
Notes					
30. Reaction Direction	a	a	a	a	a
31. Sulfur Activity	-	-	-	-	-
32. Miscellaneous	H_2S leak?	-	-	-	-

TABLE VIII-b

System $Na_2S-S-H_2S-H_2O$: Equilibrium Results at 25°C

1.	E-6	E-7	E-8	E-9	E-10	E-11	E-12
2.	25.7	25.7	25.7	25.7	25.7	25.7	25.7
3.	811	801	810	764	829	824	756
4.	1.038	1.024	1.037	0.975	1.061	1.055	0.964
5.	(548)	(548)	(548)	(464)	547	552	476
6.	(639)	(638)	(638)	(554)	(628)	(638)	(565)
7.	487	491	488	405	500	502	419
8.	0.036	0.036	0.036	0.028	0.036	0.037	0.029
9.	42.5	14.6	21.1	44.0	22.5	0.6	17.5
10.	5.0	10.0	5.0	??	0.83	5.0	0.75
11.	(1.966)	(1.966)	(1.966)	1.842	(1.966)	(1.966)	1.846
12.	3.220	3.208	3.240	2.714	3.492	3.390	2.754
13.	3.148	3.137	3.168	2.658	3.420	3.317	2.697
14.	0.336	0.336	0.342	-	0.175	0.269	-
15.	97.7	97.3	98.5	-	96.4	98.5	-
16.	1.670	1.540	1.590	1.940	0.795	1.104	1.825
17.	3.59	3.59	3.59	3.97	3.59	3.56	3.88
18.	0.715	0.725	0.697	1.106	0.467	0.556	1.045
19.	2.160	2.139	2.197	1.760	2.658	2.446	1.789
20.	3.048	2.810	2.901	4.18	1.453	2.000	3.83
21.	4.04	4.00	4.03	4.55	3.93	3.92	4.41
22.	0.805	0.808	0.783	1.268	0.512	0.611	1.189
23.	2.429	2.383	2.465	2.017	2.908	2.693	2.034
24.	3.430	3.137	3.260	4.79	1.590	2.200	4.36
25.	0.850	0.783	0.809	1.053	0.404	0.562	0.989
26.	0.199	0.202	0.194	0.278	0.130	0.156	0.269
27.	4.26	3.88	4.16	3.78	3.11	3.60	3.67
28.	0.1414	0.1456	0.1332	0.3045	0.0642	0.0890	0.2776
29.	0.602	0.565	0.555	1.128	0.1992	0.320	1.019
30.	a	a	a	b	a	a	b
31.	1.0	1.0	1.0	1.0	-	-	1.0
32.	-	-	-	-	short run	-	-

TABLE VIII-c

System $Na_2S-S-H_2S-H_2O$: Equilibrium Results at 25°C

1.	E-13	E-14	E-15	E-16	E-20
2.	25.7	25.7	25.7	25.7	25.7
3.	831	763	765	766	763
4.	1.064	0.974	0.977	0.978	0.974
5.	545	(464)	497	(464)	470
6.	(631)	(550)	(581)	(551)	(556)
7.	495	406	445	407	415
8.	0.036	0.028	0.031	0.028	0.028
9.	11.8	52.0	0	51.2	22.1
10.	0.83	1.0	1.0	1.0	1.5
11.	(1.966)	1.844	1.836	1.838	1.830
12.	3.316	2.888	2.956	2.868	2.740
13.	3.243	2.833	2.895	2.813	2.683
14.	0.267	-	-	-	-
15.	96.6	-	-	-	-
16.	1.130	1.690	1.425	1.716	1.680
17.	3.61	3.97	3.69	3.96	3.89
18.	0.631	0.920	0.780	0.929	1.038
19.	2.341	2.131	2.130	2.103	1.816
20.	2.073	3.64	2.864	3.70	3.57
21.	397	4.54	4.12	4.51	4.41
22.	0.695	1.052	0.871	1.060	1.176
23.	2.580	2.437	2.379	2.397	2.057
24.	2.282	4.16	3.20	4.21	4.05
25.	0.575	0.916	0.776	0.934	0.918
26.	0.175	0.232	0.211	0.235	0.266
27.	3.28	3.96	3.67	3.98	3.44
28.	0.1155	0.1730	0.1507	0.1807	0.2712
29.	0.379	0.684	0.553	0.718	0.934
30.	a	b	b	b	b
31.	-	1.0	-	1.0	1.0
32.	short run	-	-	-	-

TABLE VIII-d

System $Na_2S-S_2H_2S-H_2O$: Equilibrium Results at 25°C

Explanation of Notes

Quantities in Parentheses indicate values estimated, but not measured.

Reaction Direction: Approach to equilibrium by the NaHS+S reaction is denoted by "a"; approach by the $Na_2S_x+H_2S$ reaction is denoted by "b".

Sulfur Activity: For those runs in which sulfur saturation is believed to have been reached, a sulfur (S_8) activity of unity is indicated.

Improvements in Technique: All the runs at 25°C were carried out in the Figure 9 apparatus. None of these experiments involved lowered hydrogen sulfide partial pressures or determinations of sulfur activity by xylene extraction. In all the runs at room temperature reagent grade sodium sulfide, USP sulfur, "technical" grade hydrogen sulfide, and laboratory distilled water were used without further attempts at purification. No nitrogen purges were employed in making up solutions; any samples for analysis were withdrawn by ordinary pipetting.

Table VIII. In this table the ionic concentrations are expressed both as molarities and as molalities. The quantities "A" and "B" were found useful in preliminary graphical examination of the data; the functions "X" and "Y", as will be shown later, are significant in the interpretation of results and in the derivation of ionic equilibrium constants.

b. Examination of Results

The results of the equilibrium experiments at 25°C are shown as "B" plotted versus "A" in Figure 12. In the sodium hydrosulfide-sulfur reaction (Equation 7) "A" represents the gm-atoms sulfur added per mol initial sodium hydrosulfide and "B" should equal the mols hydrogen sulfide evolved on that basis. The actual values of hydrogen sulfide released in the sodium hydrosulfide - sulfur runs are plotted versus "A" in Figure 13. As may be noted both by inspection of Table VIII and by comparison of the two graphs, the hydrogen sulfide material balances were consistently low. This discrepancy might be due either to a lack of hydrogen sulfide saturation in the initial sodium hydrosulfide solutions or else to supersaturation in the final solutions.

If the values calculated from the final solution analyses are assumed to be the more reliable, the points (as shown in Figure 12) then fall roughly on the curve determined by Rule and Thomas (56). In view of the differences in

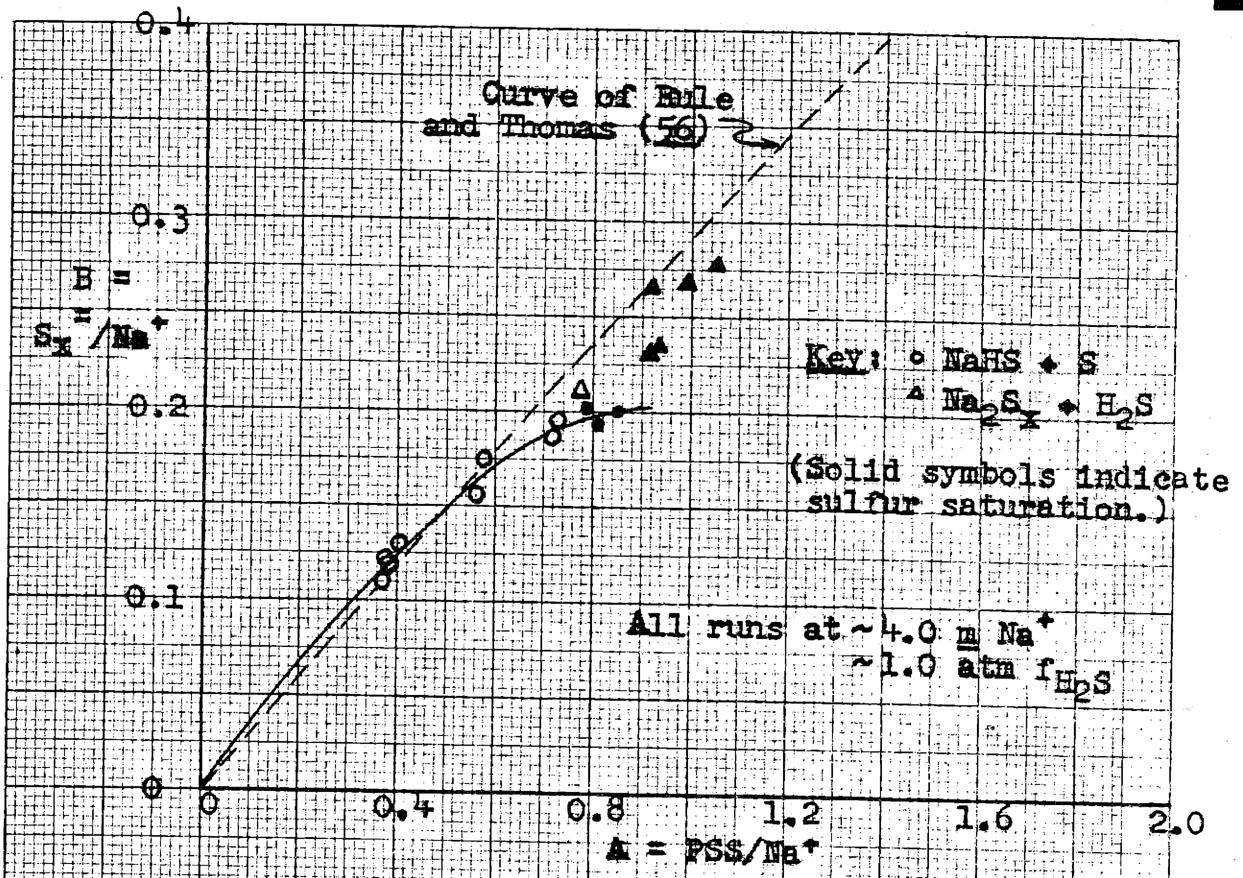


FIGURE 12
Equilibrium Results at 25°C, Based on Final Solutions

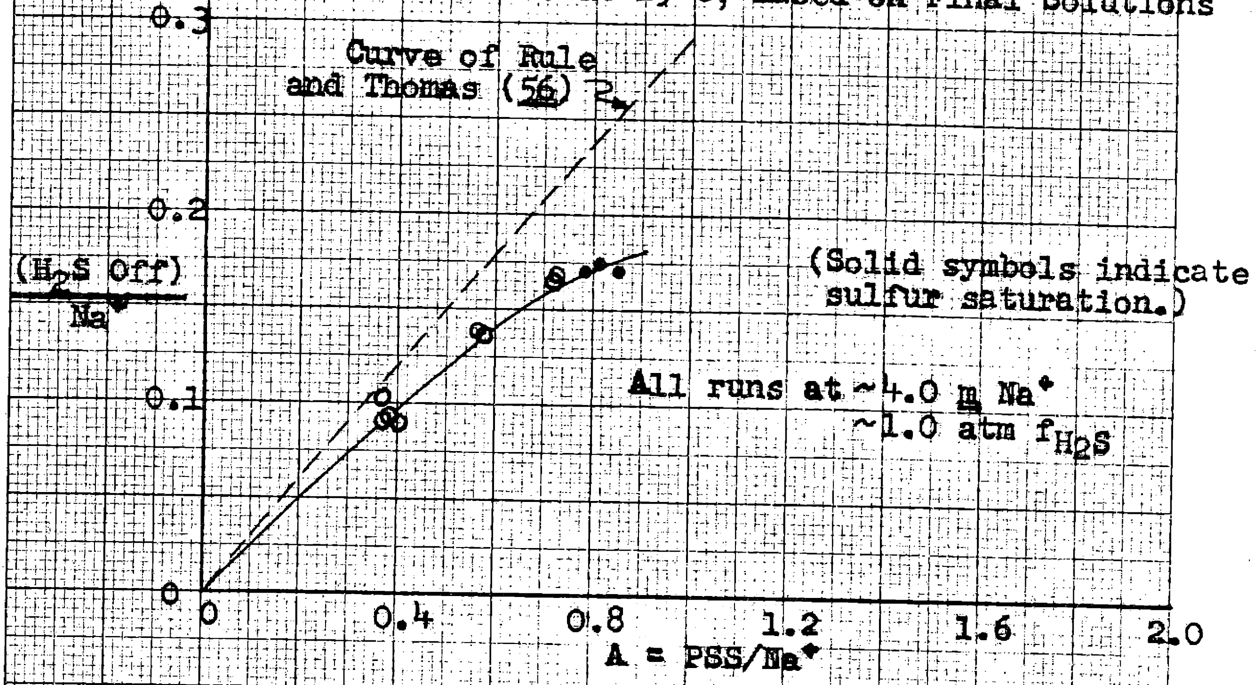


FIGURE 13
Equilibrium Results at 25°C, Based on H_2S Evolved

solvent, temperature, and hydrogen sulfide partial pressure, no significant interpretation may be placed on this finding.

Examination of Figures 12 and 13 indicates that even though the results of the runs at lower sulfur activities were moderately reproducible, the data from the sulfur saturation experiments carried out using the sodium polysulfide-hydrogen sulfide reaction both scattered widely and failed to approach the results of the experiments involving the opposite reaction. It was concluded that equilibrium was not being attained in some, and possibly all the Na_2S-S-H_2S-H_2O runs at room temperature.

2. The System Na_2S-S-H_2S-H_2O: Equilibrium Studies at 75°C.

a. Tabulation of Results

Complete data for the 53 equilibrium experiments performed at 75°C are listed in Table IX. In addition to those quantities listed in Table VIII, hydrogen sulfide in nitrogen analyses, pH determinations, and sulfur in xylene analyses also are reported for applicable runs.

b. Examination of Results

The stoichiometric ("B" versus "A") equilibrium results at 75°C are shown in Figures 14 and 15. These data essentially may be grouped as follows: (1) two traverses of polysulfide in solution versus sulfur in solution (Figure 14) at a constant hydrogen sulfide partial pressure and at sodium

TABLE IX-a

System Na_2S-S-H_2S-H_2O: Equilibrium Results at 75°C

1. Run Number	E-17	E-18	E-19	E-21	E-22
Run Conditions:					
2. Temperature °C	75.0	75.0	75.0	75.0	75.0
3. Total Press., mm Hg	813	809	762	819	808
4. H_2S% in N_2 Mixture	-	-	-	-	-
5. H_2S Partial Press., atm	0.717	0.712	0.650	0.725	0.713
6. Soln. Volume, ml	565	562	544	540	552
7. Soln. Weight, gm	(648)	(645)	(623)	(619)	(625)
8. H_2O in Soln., gm	493	491	476	472	495
9. H_2S in Soln., gm-mols	0.011	0.010	0.009	0.010	0.010
10. Final Solid S, gm	0	0	0	0	0
11. Run Time, hrs	4.0	4.0	1.0	1.0	2.0
Measured Results					
12. Initial Titr., gm-eqs	(1.936)	(1.936)	1.848	1.850	(1.936)
13. Final Titr., gm-eqs	2.820	2.806	2.640	2.646	3.244
14. Corr. Final Titr., gm-eqs	2.799	2.785	2.622	2.626	3.224
15. H_2S Evolved, gm-mols	0.524	0.522	-	-	0.269
16. Total H_2S Balance, %	99.7	99.1	-	-	97.4
17. PSS in Soln., gm-mols	1.997	1.997	1.903	1.902	0.998
18. Xylene Weight % S	-	-	-	-	-
19. pH	-	-	-	-	-
Concentrations					
20. Na^+ Molarity	3.42	3.44	3.40	3.42	3.50
21. $S_x^=$ Molarity	0.949	0.965	0.988	0.994	0.586
22. HS^- Molarity	1.530	1.511	1.425	1.440	2.330
23. PSS Molarity	3.53	3.55	3.50	3.52	1.809
24. Na^+ Molality	3.92	3.94	3.87	3.92	3.91
25. $S_x^=$ Molality	1.089	1.105	1.128	1.139	0.654
26. HS^- Molality	1.752	1.729	1.624	1.645	2.600
27. PSS Molality	4.05	4.06	3.99	4.03	2.018
Derived Numbers					
28. "A" = PSS/Na^+	1.032	1.032	1.030	1.029	0.515
29. "B" = $S_x^=/Na^+$	0.278	0.281	0.291	0.290	0.167
30. A/B = PSS/$S_x^=$	3.71	3.68	3.54	3.55	3.08
31. "X" = $\frac{[S_x^=]\, f_{H_2S}}{[HS^-]^2}$	0.2541	0.2637	0.2779	0.305	0.0689
32. "Y" = $\frac{[PSS]\, f_{H_2S}}{[HS^-]^2}$	0.945	0.969	0.983	1.081	0.2128
(X and Y based on molalities)					
Notes					
33. Reaction Direction	a	a	b	b	a
34. Sulfur Activity	-	-	-	-	-
35. Miscellaneous	-	-	-	-	-

TABLE IX-b

System $Na_2S-S-H_2S-H_2O$: Equilibrium Results at 75°C

1.	E-23	E-24	E-25	E-26	E-27	E-28	E-29	E-30
2.	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
3.	835	(832)	(832)	(835)	(834)	(810)	(834)	(830)
4.	-	-	-	-	-	-	-	-
5.	0.748	0.745	0.745	0.744	0.744	0.715	0.744	0.739
6.	533	535	477	491	550	558	545	546
7.	(602)	(605)	(538)	(572)	(643)	(636)	(630)	(630)
8.	477	480	428	420	469	494	472	472
9.	0.010	0.010	0.009	0.010	0.011	0.010	0.011	0.011
10.	0	0	0	12.4	12.9	0	0	0
11.	1.0	1.0	1.0	1.3	1.25	2.0	1.25	1.25
12.	1.826	1.834	1.620	1.646	1.870	(1.936)	1.822	1.794
13.	3.188	3.154	2.780	1.992	2.268	3.038	2.454	2.444
14.	3.168	3.134	2.762	1.972	2.246	3.018	2.433	2.422
15.	-	-	-	-	-	0.402	-	-
16.	-	-	-	-	-	98.9	-	-
17.	0.952	0.954	0.851	2.565	2.940	1.498	2.381	2.381
18.	-	-	-	-	-	-	-	-
19.	-	-	-	-	-	-	-	-
20.	3.42	3.43	3.39	3.35	3.40	3.47	3.34	3.28
21.	0.454	0.499	0.501	1.343	1.360	0.765	1.110	1.068
22.	2.520	2.428	2.395	0.663	0.683	1.940	1.122	1.150
23.	1.788	1.784	1.785	5.22	5.35	2.682	4.37	4.36
24.	3.82	3.82	3.78	3.92	3.99	3.92	3.86	3.80
25.	0.507	0.556	0.558	1.572	1.595	0.865	1.282	1.235
26.	2.812	2.708	2.670	0.776	0.820	2.193	1.295	1.330
27.	1.996	1.989	1.990	6.11	6.27	3.03	5.04	5.04
28.	0.521	0.520	0.526	1.560	1.572	0.773	1.310	1.329
29.	0.133	0.145	0.148	0.401	0.400	0.220	0.332	0.325
30.	3.92	3.59	3.56	3.88	3.93	3.52	3.94	4.09
31.	0.0480	0.0565	0.0583	1.940	1.844	0.1289	0.569	0.516
32.	0.1890	0.2020	0.2080	7.54	7.25	0.451	2.236	2.102
33.	b	b	b	b	b	a	b	b
34.	-	-	-	1.0	1.0	-	-	-
35.	-	-	-	-	-	-	-	-

TABLE IX-c

System Na_2S-S-H_2S-H_2O: Equilibrium Results at 75°C

1.	E-31	E-32	E-33	E-34	E-35	E-36	E-37	E-38
2.	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
3.	(804)	(836)	(835)	(830)	(815)	(825)	(825)	(826)
4.	-	-	-	-	-	-	-	-
5.	0.705	0.747	0.746	0.739	0.719	0.608	0.608	0.608
6.	565	542	(542)	549	(547)	(548)	548	549
7.	(656)	(621)	(621)	(640)	(638)	(633)	(634)	(634)
8.	488	475	474	467	466	473	471	472
9.	0.010	0.011	0.011	0.011	0.011	0.009	0.009	0.009
10.	0	0	0	13.3	28.4	0	0	0
11.	4.0	1.5	1.5	1.5	5.0	1.5	1.5	1.5
12.	1.960	1.814	1.830	1.850	1.832	1.802	1.828	1.828
13.	2.588	2.668	2.682	2.258	2.304	2.336	2.404	2.390
14.	2.567	2.647	2.661	2.236	2.283*	2.318	2.386	2.372
15.	0.630	-	-	-	0.188	-	-	-
16.	97.9	-	-	-	??	-	-	-
17.	2.497	1.903	1.903	2.925	2.892	2.507	2.546	2.535
18.	-	-	-	-	-	2.94	1.91	2.19
19.	-	-	-	-	-	-	-	-
20.	3.47	3.34	3.38	3.37	3.35	3.29	3.34	3.33
21.	1.199	0.903	0.920	1.337	1.261	1.175	1.160	1.171
22.	1.075	1.538	1.534	0.704	0.825	0.942	1.020	0.990
23.	4.41	3.51	3.51	5.34	5.28	4.58	4.65	4.61
24.	4.01	3.82	3.86	3.96	3.93	3.81	3.88	3.87
25.	1.388	1.032	1.053	1.569	1.480	1.360	1.349	1.360
26.	1.245	1.755	1.757	0.825	0.967	1.092	1.184	1.152
27.	5.11	4.01	4.02	6.26	6.20	5.30	5.40	5.36
28.	1.273	1.051	1.039	1.582	1.579	1.392	1.392	1.386
29.	0.345	0.270	0.272	0.396	0.377	0.357	0.358	0.352
30.	3.69	3.89	3.82	3.99	4.18	3.90	3.89	3.94
31.	0.630	0.2507	0.2550	1.704	1.138	0.692	0.584	0.621
32.	2.327	0.975	0.973	6.80	4.76	2.699	2.341	2.456
33.	a	b	b	b	a	b	b	b
34.	-	-	-	1.0	1.0	-	-	-
35.	-	-	-	-	*	-	-	-

TABLE IX-d

System Na_2S-S-H_2S-H_2O: Equilibrium Results at 75°C

1.	E-39	E-43	E-44	E-45	E-46	E-47	E-48	E-49
2.	75.0	73.7	74.0	73.0	73.0	73.5	74.0	73.5
3.	(823)	767	767	762	764	764	762	762
4.	-	-	-	-	-	-	-	-
5.	0.608	0.655	0.675	0.636	0.633	0.654	0.668	0.636
6.	548	547	619	482	489	522	623	485
7.	(633)	(642)	(825)	(523)	(505)	(574)	(829)	(526)
8.	471	464	469	442	463	464	473	444
9.	0.009	0.010	0.008	0.010	0.011	0.009	0.008	0.010
10.	0	10.8	18.7	9.9	7.21	8.41	18.8	9.3
11.	1.5	3.08	2.0	2.0	2.0	2.0	2.5	2.0
12.	1.820	1.908	3.848	0.904	0.484	0.486	3.842	0.906
13.	2.398	2.297	4.400	1.168	0.688	0.698	4.385	1.175
14.	2.380	2.278	4.383	1.149	0.666	0.681	4.368	1.155
15.	-	-	-	-	-	-	-	-
16.	-	-	-	-	-	-	-	-
17.	2.535	3.020	6.140	1.295	0.615	0.579	6.145	1.300
18.	2.13	-	-	-	-	-	-	-
19.	-	-	-	-	-	-	-	-
20.	3.32	3.48	6.22	1.875	0.990	0.930#	6.16	1.870
21.	1.150	1.406	2.677	0.682	0.309	0.278	2.660	0.676
22.	1.022	0.676	0.865	0.508	0.372	0.373	0.845	0.513
23.	4.62	5.52	9.92	2.683	1.260	1.110	9.85	2.680
24.	3.86	4.11	8.20	2.043	1.045	1.050#	8.12	2.043
25.	1.338	1.660	3.53	0.744	0.326	0.312	3.50	0.739
26.	1.189	0.798	1.142	0.554	0.393	0.421	1.113	0.561
27.	5.37	6.51	13.10	2.927	1.330	1.250	13.00	2.928
28.	1.392	1.584	1.596	1.434	1.272	1.191#	1.600	1.434
29.	0.346	0.404	0.430	0.364	0.312	0.299#	0.432	0.362
30.	4.02	3.92	3.71	3.94	4.08	4.00	3.71	3.96
31.	0.575	1.710	1.825	1.545	1.338	1.150	1.887	1.492
32.	2.313	6.70	6.76	6.08	5.45	4.60	7.00	5.91
33.	b	b	b	b	b	b	b	b
34.	-	1.0	1.0	1.0	1.0	1.0	1.0	1.0
35.	-	-	-	-	-	#69.1 gm NaCl in soln.		

TABLE IX-e

System $Na_2S-S-H_2S-H_2O$: Equilibrium Results at 75°C

1.	E-50	E-51	E-52	E-53	E-54	E-55	E-56	E-57
2.	73.0	(75.0)	(75.0)	(75.0)	(75.0)	(75.0)	(75.0)	(75.0)
3.	770	769	755	763	761	771	765	780
4.	3.54	-	8.86	-	16.4	4.36	16.0	6.69
5.	0.0224	0.640	0.0547	0.626	0.1023	0.0277	0.1010	0.0438
6.	493	584	605	568	566	492	607	578
7.	485	604	628	564	564	(484)	629	588
8.	480	554	571	550	549	479	573	550
9.	0.00043	0.013	0.0011	0.0135	0.0022	0.00053	0.0022	0.0009
10.	0	8.73	0.25	7.28	4.16	2.73	5.19	4.96
11.	2.5	4.0	2.5	2.0	3.5	3.5	3.5	3.42
12.	0.0562	0.580	0.598	0.1756	0.1714	0.0521	0.585	0.1672
13.	0.0703	0.830	0.686	0.3055	0.2237	0.0670	0.688	0.2017
14.	0.0694	0.804	0.684	0.2785	0.2193	0.0659	0.684	0.1999
15.	-	-	-	- ?	-	-	-	-
16.	-	-	-	-	-	-	-	-
17.	0.0774	0.726	0.998	0.143	0.234	0.0790	0.961	0.262
18.	-	-	-	-	-	-	-	-
19.	8.8 ??	7.55	8.23	7.22	7.74	7.87	7.99	7.89
20.	0.1140	0.994	0.988	0.309	0.302	0.1060	0.963	0.289#
21.	0.0436	0.305	0.423	0.0639	0.1090	0.0390	0.400	0.1164
22.	0.0268	0.384	0.142	0.1810	0.0845	0.0280	0.163	0.0565
23.	0.1570	1.245	1.651	0.2519	0.413	0.1607	1.585	0.453
24.	0.1172	1.049	1.048	0.319	0.312	0.1090	1.021	0.304#
25.	0.0448	0.322	0.448	0.0660	0.1126	0.0399	0.424	0.1223
26.	0.0275	0.405	0.151	0.1870	0.0872	0.0288	0.173	0.0595
27.	0.1612	1.314	1.748	0.260	0.427	0.1651	1.680	0.476
28.	1.378	1.250	1.670	0.815	1.365	1.515	1.645	1.565#
29.	0.382	0.307	0.428	0.207	0.361	0.368	0.415	0.402#
30.	3.60	4.08	3.90	3.94	3.78	4.14	3.96	3.89
31.	1.328	1.258	1.075	1.183	1.515	1.332	1.430	1.515
32.	4.77	5.13	4.19	4.66	5.74	5.51	5.66	5.90
33.	b	b	b	b	b	b	b	b
34.	??	1.0	1.0 ?	1.0	1.0	1.0	1.0	1.0
35.	-	-	-	-	-	-	-	

#22.8 gm NaCl in soln.

TABLE IX-f

System Na_2S-S-H_2S-H_2O: Equilibrium Results at 75°C

1.	E-58	E-59	E-60	E-61	E-62	E-63	E-64	E-65
2.	74.3	74.5	74.5	74.5	74.3	75.0	75.0	74.7
3.	764	746	750	753	754	754	761	745
4.	-	-	-	-	-	-	-	-
5.	0.651	0.628	0.530	0.534	0.535	0.538	0.545	0.524
6.	653	627	667	667	659	673	677	666
7.	766	735	(778)	(770)	(759)	(789)	(789)	(771)
8.	554	533	575	578	577	572	583	577
9.	0.011	0.011	0.009	0.009	0.009	0.010	0.010	0.009
10.	29.9	31.8	0	0	0	4.3	0	0
11.	2.5	2.5**	2.0	2.5	2.5	2.5	2.5	2.5
12.	2.264	2.152	2.334	2.314	2.324	2.356	2.382	2.358
13.	2.763	2.643	2.970	3.137	3.373	2.801	3.051	3.218
14.	2.740	2.622	2.952	3.119	3.355	2.782	3.032	3.200
15.	??	??	-	-	-	-	-	-
16.	??	??	-	-	-	-	-	-
17.	3.592	3.407	3.140	2.736	2.281	3.666	3.159	2.735
18.	-	-	2.20	0.612	0.230	9.69 ?	1.53	0.449
19.	-	-	-	-	-	-	-	-
20.	3.47	3.43	3.50	3.46	3.53	3.50	3.52	3.54
21.	1.370	1.342	1.287	1.131	0.981	1.435	1.280	1.139
22.	0.730	0.749	0.926	1.208	1.565	0.634	0.960	1.265
23.	5.50	5.43	4.70	4.10	3.46	5.45	4.66	4.10
24.	4.09	4.04	4.06	4.00	4.03	4.11	4.09	4.08
25.	1.616	1.580	1.492	1.305	1.120	1.688	1.488	1.314
26.	0.860	0.882	1.075	1.394	1.787	0.745	1.116	1.460
27.	6.49	6.39	5.46	4.73	3.95	6.40	5.41	4.74
28.	1.586	1.585	1.344	1.185	0.980	1.559	1.325	1.160
29.	0.395	0.391	0.367	0.327	0.278	0.410	0.364	0.322
30.	4.01	4.05	3.66	3.62	3.53	3.80	3.64	3.60
31.	1.424	1.277	0.685	0.358	0.1879	1.638	0.650	0.323
32.	5.71	5.15	2.507	1.299	0.662	6.20	2.370	1.164
33.	a	a,b**	b	b	b	b	b	b
34.	1.0	1.0	-	-	-	1.0	-	-
35.	-	**	-	-	-	-	-	-

TABLE IX-g

System Na_2S-S-H_2S-H_2O: Equilibrium Results at 75°C

1.	E-66	E-67	E-68	E-69	E-70	E-71	E-72	E-73
2.	74.9	74.4	74.8	74.7	74.6	74.7	74.7	74.5
3.	749	753	766	764	756	764	765	765
4.	-	-	-	-	-	-	-	-
5.	0.530	0.535	0.533	0.530	0.519	0.530	0.531	0.530
6.	664	670	578	578	576	578	580	579
7.	(762)	(782)	(596)	(595)	(591)	(596)	(596)	(594)
8.	581	571	551	551	550	551	552	552
9.	0.009	0.010	0.011	0.011	0.010	0.011	0.011	0.011
10.	0	0	0	0	0	0	0	0
11.	2.5	2.67	2.5	2.5	2.5	2.58	2.5	2.5
12.	2.302	2.354	0.554	0.548	0.548	0.556	0.550	0.548
13.	3.340	2.883	0.816	0.852	0.888	0.818	0.859	0.895
14.	3.322	2.864	0.794	0.813	0.867	0.797	0.838	0.874
15.	-	-	-	-	-	-	-	-
16.	-	-	-	-	-	-	-	-
17.	2.280	3.418	0.595	0.526	0.440	0.596	0.526	0.439
18.	0.155	4.54	3.39	1.75	0.714	3.34	1.74	0.750
19.	-	-	-	-	-	-	-	-
20.	3.47	3.51	0.958	0.948	0.950	0.962	0.948	0.946
21.	0.966	1.377	0.272	0.228	0.198	0.272	0.226	0.192
22.	1.537	0.761	0.415	0.490	0.553	0.417	0.496	0.563
23.	3.44	5.10	1.030	0.910	0.763	1.032	0.907	0.758
24.	3.96	4.11	1.004	0.993	0.996	1.010	0.995	0.992
25.	1.105	1.614	0.284	0.239	0.207	0.285	0.237	0.201
26.	1.754	0.892	0.435	0.513	0.580	0.437	0.522	0.590
27.	3.92	5.97	1.080	0.955	0.800	1.082	0.953	0.794
28.	0.990	1.454	1.075	0.960	0.803	1.072	0.956	0.800
29.	0.278	0.392	0.284	0.240	0.208	0.282	0.238	0.202
30.	3.56	3.71	3.78	4.00	3.86	3.80	4.02	3.96
31.	0.1905	1.086	0.800	0.481	0.319	0.790	0.461	0.306
32.	0.675	4.01	3.041	1.924	1.234	3.003	1.857	1.210
33.	b	b	b	b	b	b	b	b
34.	-	-	-	-	-	-	-	-
35.	-	-	-	-	-	-	-	-

TABLE IX-h

System Na_2S-S-H_2S-H_2O: Equilibrium Results at 75°C

Explanation of Notes

Quantities in Parentheses indicate values estimated, but not measured.

Reaction Direction: Approach to equilibrium by the NaHS + S reaction is denoted by "a"; approach by the Na_2S_x + H_2S reaction is denoted by "b".

Sulfur Activity: For those runs in which sulfur saturation was present, a sulfur (S_8) activity of unity is indicated.

Improvements in Technique: The experiments beginning with run E-43 employed dried sulfur and boiled distilled water, and were carried out in the Figure 10 apparatus, with nitrogen purges during initial solution preparations. The use of "purified" grade hydrogen sulfide and pipetting under equilibrium hydrogen sulfide partial pressure both were instituted after run E-49. The initial sodium sulfide was purified by washing starting with run E-58. Pure o-xylene rather than mixed xylenes was used in xylene runs starting with run E-60; stopcock grease was excluded from the system beginning with experiment E-63.

NaHS + S Runs:

*Equilibrium in run E-35 was approached by reacting sulfur with a polysulfide (Na_2S_3) solution initially presaturated with hydrogen sulfide.

**Equilibrium in run E-59 was verified from both directions. After completion of the sodium hydrosulfide-sulfur reaction the solution was partially degassed under vacuum and then again saturated with hydrogen sulfide for 2 hours. The second final titration (the one recorded in the table) checked within 0.010 gm-eqs of the first.

NaCl Addition:

#Sodium chloride as an inert electrolyte was added in two runs, E-47 and E-57, with amounts present as indicated. The sodium ion concentrations reported in the table do not include sodium ion from this source.

Preliminary Xylene Runs: The duplicate runs E-36 through E-39 were performed using mixed xylenes in order to study the effects of reagent impurities, oxidation, and run time on the xylene sulfur concentration. In addition, three further tests at this same condition were carried out, but without quantitative measurements except for xylene sulfur concentrations. The findings were as follows:

Run	E-36	E-37	E-38	E-39	E-40	E-41	E-42
Run time, hrs	1.5	1.5	1.5	1.5/5.0	1.5	1.5	1.5
Na_2S Used	old	new	new	new	new	new	new
Na_2S_x Prep'n	-	-	-	-	- /2 hrs 100°C	N_2 /air purges	N_2 purge
Xylene % S	2.94	1.91	2.19	2.13/2.21	2.31/2.22	1.89/2.07	1.94

ion molalities of 1.0 and 4.0, respectively, and (2) experiments at sulfur saturation (Figure 15), but with both molality and hydrogen sulfide partial pressure varying. The values of hydrogen sulfide evolved in the sodium hydrosulfide-sulfur runs are not shown graphically, but examination of Table IX indicates that the material balances at 75°C again averaged consistently less than 100 per cent.

Inspection of Figure 14 shows that both the sulfur saturation limit and the polysulfide formed per polysulfide sulfur added are higher for the 4.0 m curve. Both curves, however, lie below the one determined by Rule and Thomas (56) at about 1.5 m sodium ion and roughly the same temperature, but in absolute ethanol and at a much smaller and unknown hydrogen sulfide partial pressure. Even though equilibrium appears to have been achieved in the experiments at 75°C, the data nevertheless exhibit considerably more scatter than the 0.3 per cent error in "A" and 0.003 absolute error in "B" predicted by the Error Analysis (see Appendix). Some possible reasons for this lack of reproducibility will be dealt with in later discussion.

It will be shown that regardless of the ionic molality or the hydrogen sulfide partial pressure the "B" versus "A" points at sulfur saturation should lie on a straight line passing through the origin. The data thus plotted in Figure 15 for the most part appear to follow this relation.

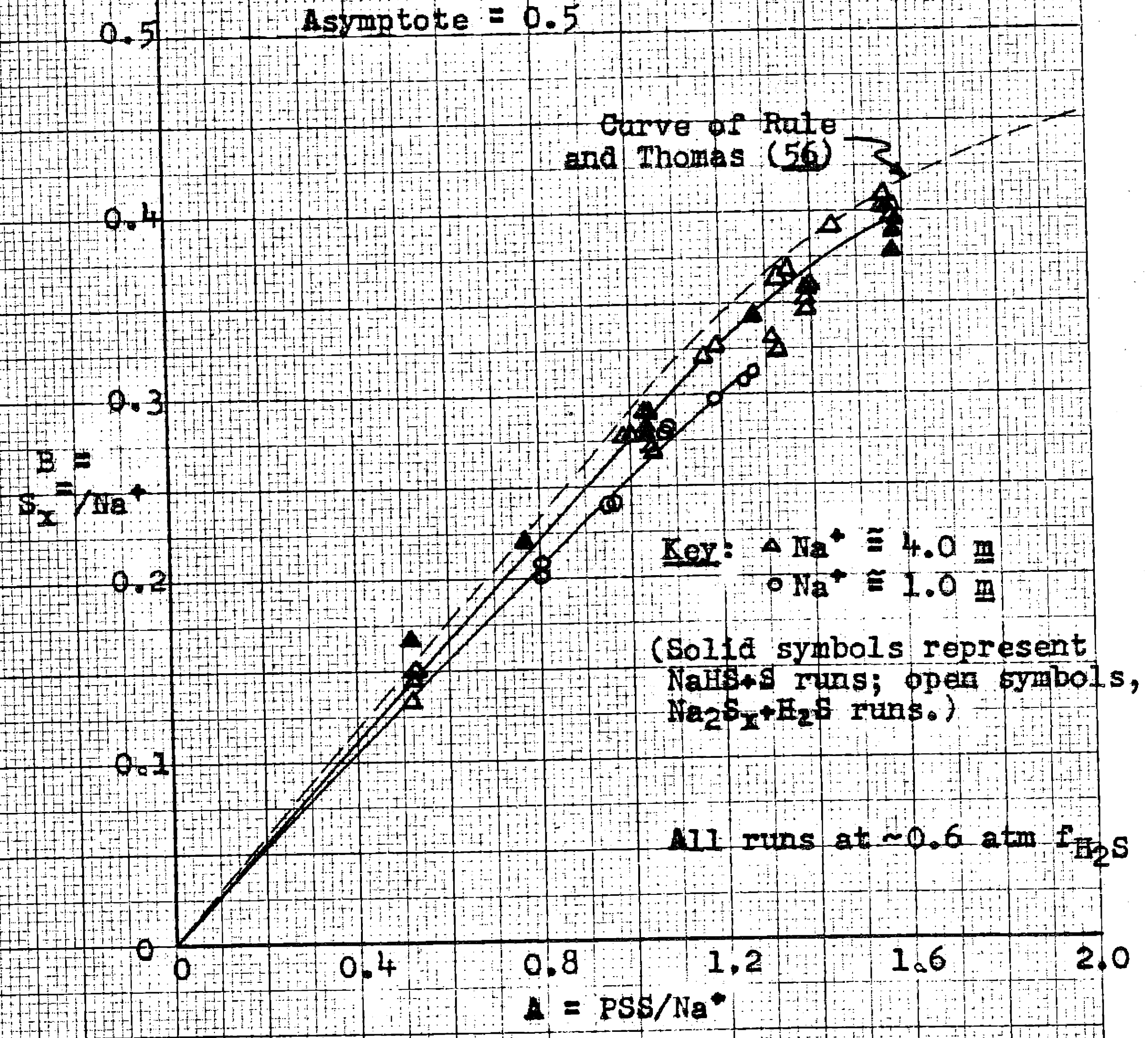
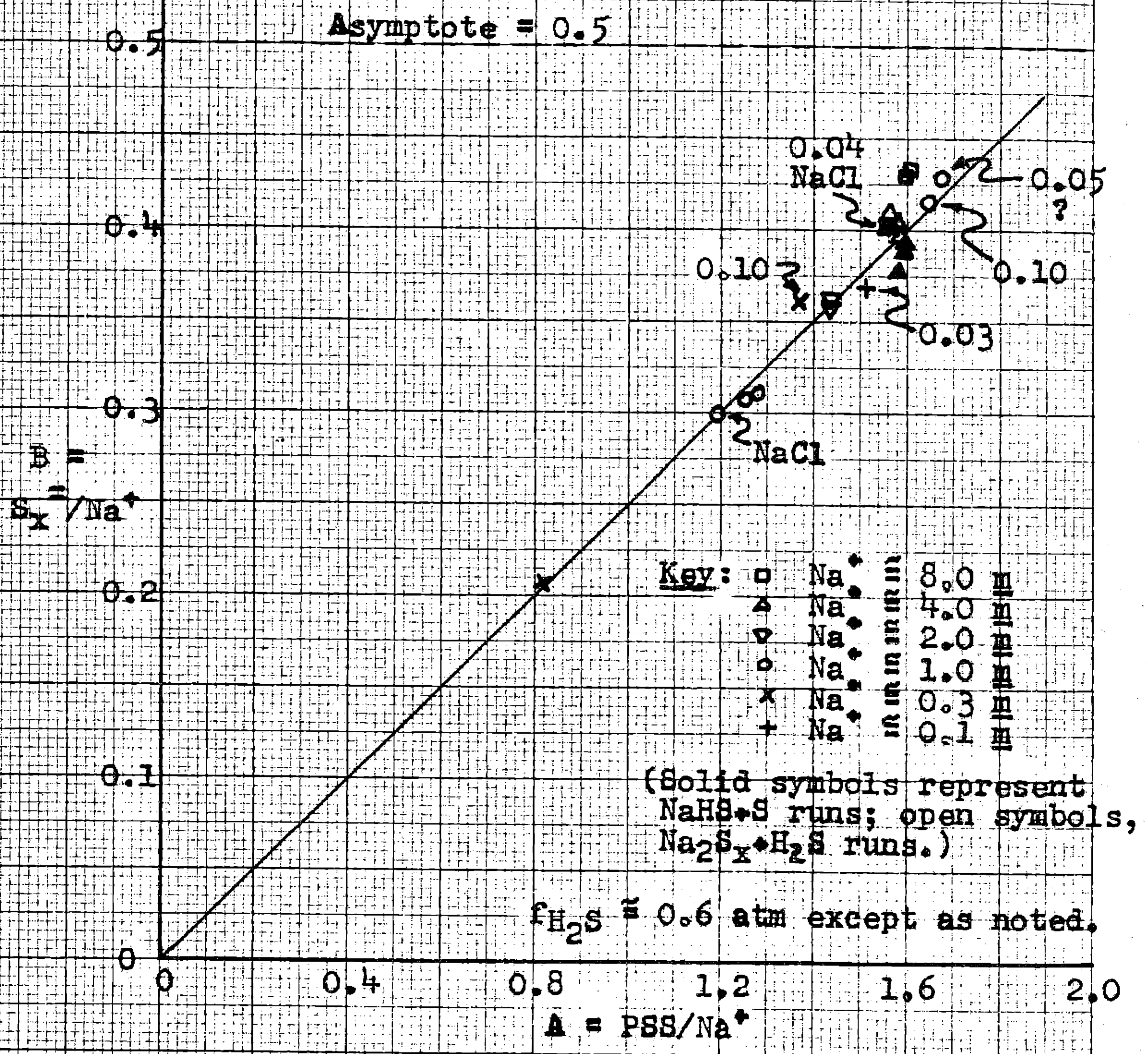


FIGURE 14

Equilibrium Results at 75°C



(Solid symbols represent $NaHS+S$ runs; open symbols, $Na_2S_x+H_2S$ runs.)

$f_{H_2S} \cong 0.6$ atm except as noted.

FIGURE 15

Sulfur Saturation Equilibrium Results at 75°C

The deviations which are exhibited, however, will be discussed in succeeding portions of this thesis.

In Figure 16 the xylene sulfur concentrations obtained in the xylene runs are plotted versus "A", the gm-atoms sulfur added per mol sodium ion. By inspection it is evident that the steep rise in sulfur activity as sulfur saturation is approached limits somewhat the range of "A" values over which solvent sulfur concentrations can be measured accurately. It was found (Table IX) that the scatter among the four mixed xylene points at 4.0 m sodium ion was caused mainly by variations in the oxidation impurities in the initial sodium sulfide.

From inspection of Figure 17 it is seen that the pH values at sulfur saturation could be correlated versus molality with hydrogen sulfide partial pressure as a parameter. Owing to the increasing unreliability of the glass electrode in concentrated solutions this correlation, however, could not be tested at sodium ion molalities higher than 1.0. Even though no duplicate pH experiments were made, the results of run E-51 at 1.05 m sodium ion and 0.640 atm hydrogen sulfide partial pressure did check closely with the stoichiometric values obtained in similar runs without pH determination. These pH data will be analyzed in detail in later portions of this thesis.

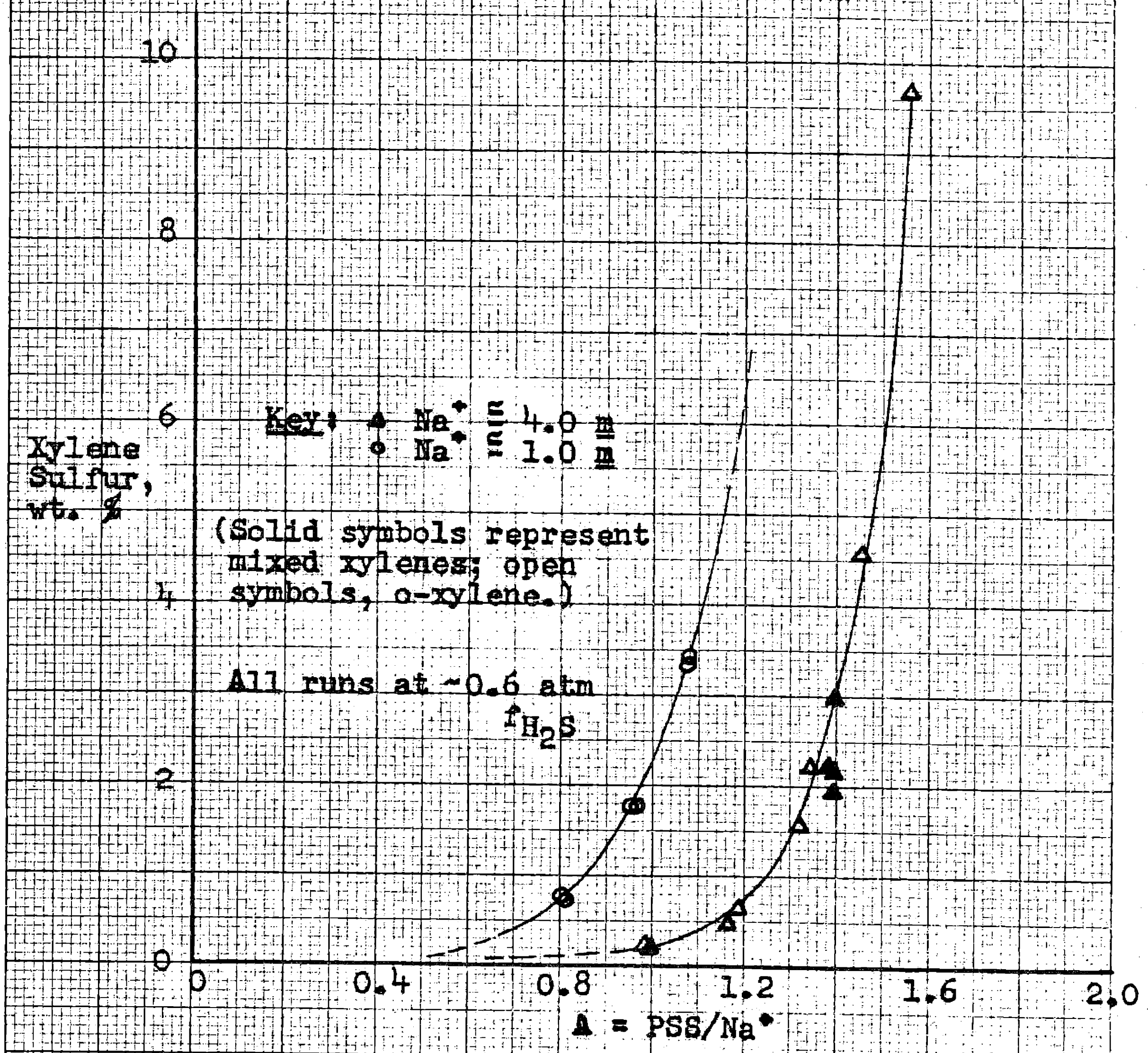


FIGURE 16

Xylene Sulfur Equilibrium Results at 75°C

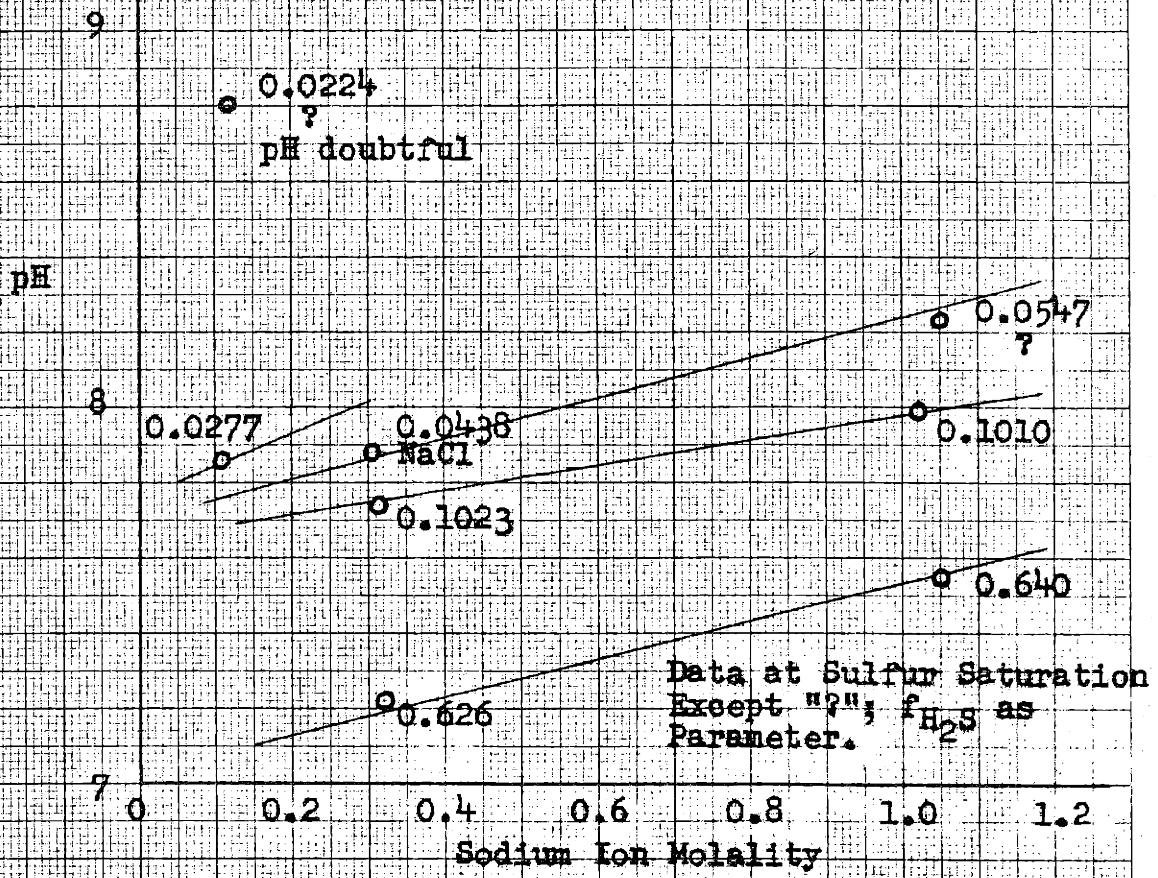


FIGURE 17

pH Equilibrium Results at 75°C

From the results of runs E-47 and E-57 (Table IX and Figures 14, 15, and 17) it might be concluded that the addition of sodium chloride as an inert electrolyte has little or no effect on the equilibrium. This finding will be re-examined in subsequent discussion.

3. Other Results

a. The System Na_2S-S-H_2O

Some preliminary studies were carried out with ordinary sodium polysulfide solutions. The apparent maximum value of "x" in Na_2S_x after 24 hours sulfur saturation at 25°C was found to be 4.82 for a 1.94 M solution, compared to the value 4.46 taken from the curve (Figure 5) of Kuster and Heberlein (41). Some possible reasons for this difference will be discussed later. Some semi-quantitative estimations of saturation "x" in less concentrated polysulfide solutions at room temperature moreover were obtained by diluting with distilled water a polysulfide having the initial composition 0.5 M $Na_2S_{4.25}$, and by then observing the appearance of turbidity. The results are summarized in Table X:

TABLE X

Dilution of 0.5 M Sodium Polysulfide ($Na_2S_{4.25}$) at 25°C

Molarity	Instantaneous	After 1 Min	After 12 Hrs
0.05	orange soln.	orange soln.	orange soln.
0.005	yellow soln.	yellow soln.	turbid yellow
0.0005	pale yellow soln.	turbid yellow	turbid white
0.00005	turbid white	turbid white	turbid white

If the sulfur precipitation in the 0.005 M solution after 12 hours is assumed due only to a reaction with carbon dioxide or oxygen from the air, then the molarity at which the sulfur saturation "x" drops to 4.25 is placed somewhere between 0.0005 and 0.005. This result does agree qualitatively with the curve of Kuster and Heberlein (Figure 5).

Attempts were made to determine sulfur activities in aqueous sodium polysulfide solutions at 75°C by measuring the solvent sulfur concentrations in equilibrium with the polysulfides. These experiments were carried out using toluene and mixed xylenes. In one pair of tests it was shown that the same xylene sulfur concentration was reached for a given final polysulfide "x" regardless of whether the net sulfur transfer was from the aqueous phase into the xylene or vice versa. The results are listed in Table XI:

TABLE XI

Sulfur Activities in Sodium Polysulfide Solutions at 75°C

Final M	Final "x"	Initial Solvent	Run Time, hrs	Weight %S
1.9 (?)	4.6 (?)	toluene	2.0	0.194
1.9 (?)	4.6 (?)	xylenes	2.0	0.127
2.0	4.50	xylenes	2.0	0.081
2.0	4.50	xylenes + S	2.0	0.082
2.0	4.50	xylenes + S	4.0	0.074

These solvent sulfur concentrations, even though too small to be precise, later will be compared to the calculated elemental sulfur activities in polysulfide solutions to be derived in a subsequent portion of this thesis.

b. pH of Sodium Hydrosulfide Solutions

In order to check the approximate magnitudes of the pH values found in the $Na_2S-S-H_2S-H_2O$ equilibrium experiments at 75°C and to obtain rough estimations of the ionic activity coefficients at known hydrosulfide (HS^-) ion concentrations, pH values were determined in sodium hydrosulfide solutions at 25°C and 75°C under controlled partial pressures of hydrogen sulfide. These data follow:

TABLE XII

pH of Sodium Hydrosulfide Solutions

Temp., °C	Molarity	H_2S Partial Press., atm	pH
25.0	1.002	0.979	7.70
75.0	0.995	0.642	7.84

c. Activity of Sulfur in Xylene Solutions

The conversion of the measured xylene sulfur concentrations to elemental sulfur activities demands knowledge of the relation between concentration and activity at the particular temperature involved. One point on the desired curve could be fixed, of course, by the sulfur solubility, since at equilibrium with solid rhombic sulfur the activity of S_8

has been defined as unity. Sulfur solubilities in xylenes are reported in the literature (65), and in addition have been measured both by Simmons (60) and in the course of the present thesis. The data from these two latter sources are listed in Table XIII:

TABLE XIII

Solubility of Sulfur in Xylenes

Solvent	Temp., °C	S Soly., Wt.%	Source
toluene, dry	75.0	8.55	present thesis
xylenes, dry	75.0	8.25	present thesis
o-xylene, dry*	75.0	9.8	present thesis
o-xylene, sat'd. H_2S, H_2O	75.0	9.8	present thesis
o-xylene, sat'd. E-63 soln.	75.0	9.4(?), 10.0(?)	present thesis
o-xylene, dry	74.2	9.14	Simmons (60)

*darkening, evidence of chemical reaction.

The value 9.8 weight per cent for the solubility of sulfur in o-xylene at 75°C appears to be the best of the tabulated numbers. The points taken from Table XIII are plotted in Figure 18 along with sulfur solubility versus temperature data reported in the literature (65) for various aromatics.

In order to determine sulfur activities in unsaturated o-xylene solutions attempts were made by Simmons (60) to measure the vapor pressure lowering over such solutions. The apparatus employed by Simmons (Figure 19) was a closed system

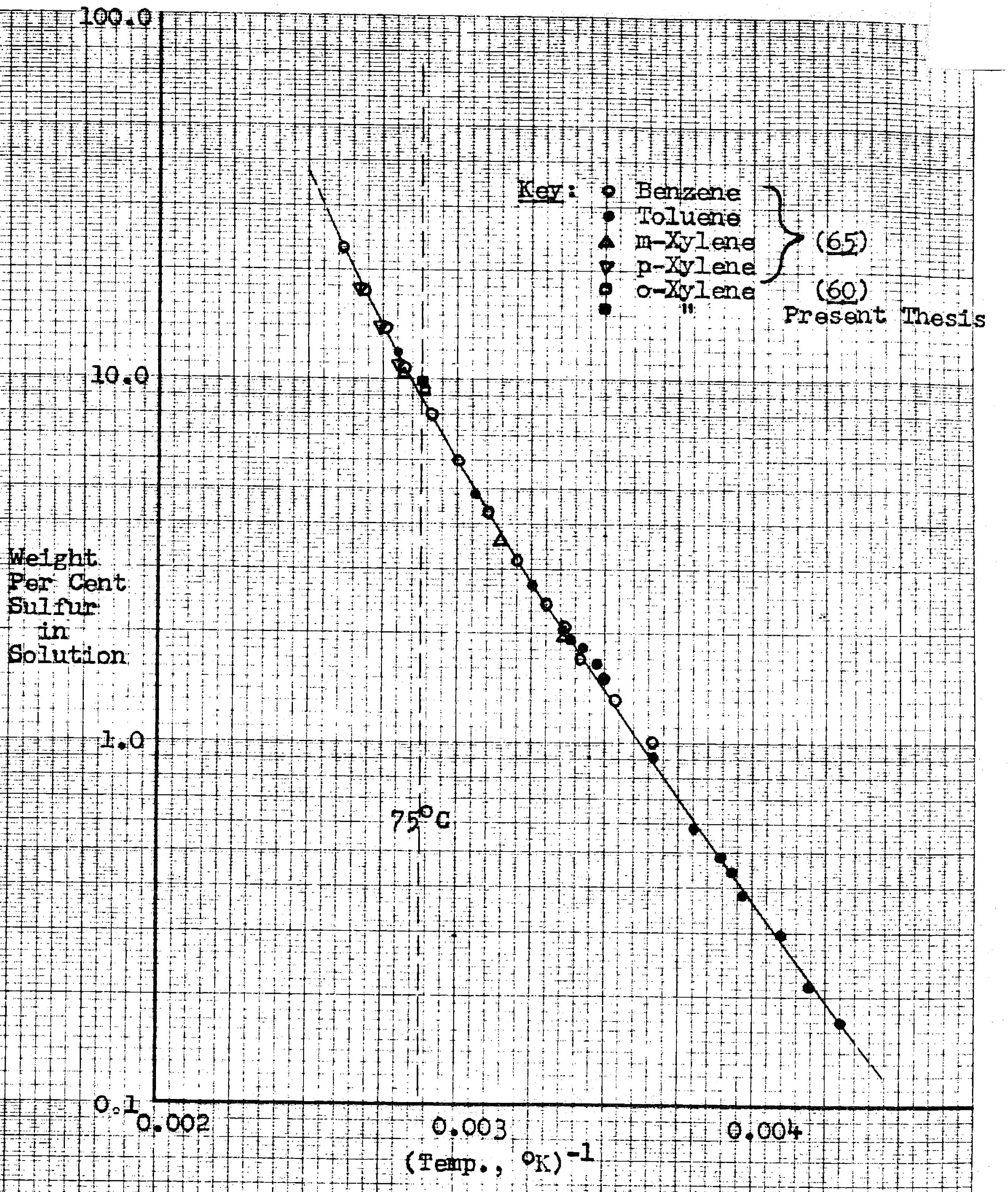


FIGURE 18

Sulfur Solubility in Aromatic Hydrocarbons

consisting of two 100-ml standard-taper round-bottom flasks connected by a glycerine manometer. The system was operated at the vapor pressure of xylene and was so immersed in an oil bath to maintain the flasks at the desired constant temperature and the manometer lines at a temperature sufficiently higher that condensation would not occur. The hot stopcocks were lubricated with a grease designed especially for that purpose, compounded from starch, glycerine, polyvinyl alcohol, and Volclay.

In performing a vapor pressure determination the right-hand flask was filled with pure o-xylene and the left-hand flask with a solution of sulfur in the xylene. The entire system first was subjected to a vacuum of about 30 mm Hg in order to degass the xylene solutions and sweep out non-condensables; during this initial degassing any xylene which previously had condensed in the manometer and about two-thirds of the xylene in the two flasks was boiled away. At the completion of this step the system was isolated, the stopcock connecting the two sides was closed, and the pressure difference as indicated by the manometer was allowed to reach equilibrium. The attainment of true equilibrium could be checked by momentarily equalizing the two pressures, again closing the connection, and noting the new reading on the differential manometer. This equilibration after an equalization required up to 30 minutes. At the completion of a satisfactory determination the xylene in the solution-side flask was sampled

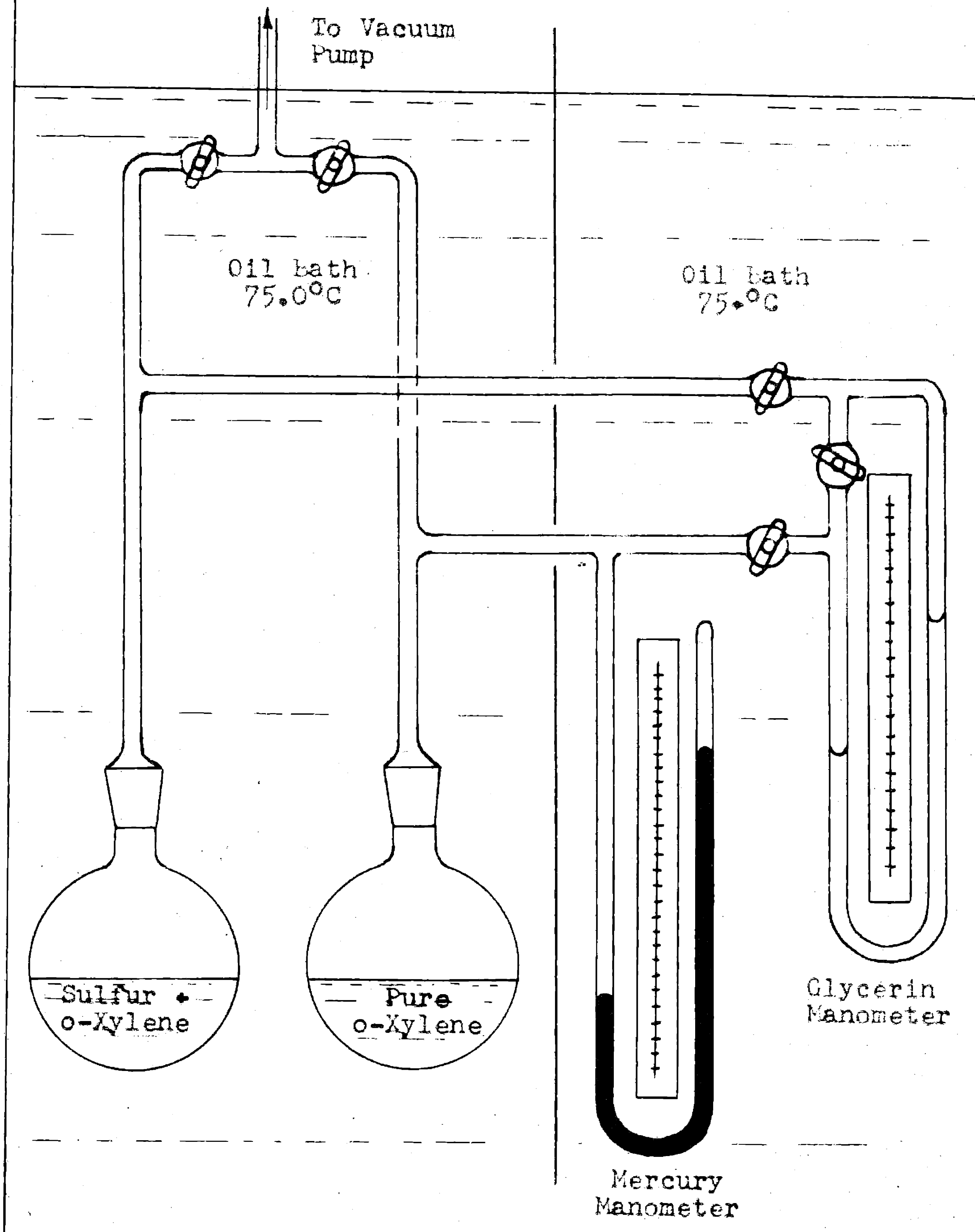


FIGURE 19

Apparatus for Xylene Vapor Pressure Measurements and analyzed gravimetrically. Only in the runs made at sulfur saturation could a further check be obtained by degassing under vacuum a second time, followed by a repeat of the preceding procedure.

Owing to difficulties including leaks, the presence of non-condensables, surface tension effects in the glycerine manometer, and the inhibition of equilibrium evaporation from the surfaces of the solutions, no completely satisfactory results were obtained. At a temperature of 74.2°C and a vapor pressure of pure o-xylene of about 76.5 mm Hg two possible values were found for the vapor pressure lowering over a solution saturated with sulfur: (1) 31.5 mm glycerine, and (2) 29.4 mm glycerine. Simmons attempted to correlate these numbers with the measured sulfur solubility assuming that a simplified Margules relation for "regular solutions" was valid, but was unable to verify this assumption. Within the limits of experimental error, however, the second value given agreed with that predicted from solubility considerations.

The results of Simmons later will be subjected to further scrutiny in connection with the findings of the present thesis.

DISCUSSION OF RESULTS

A. Equilibrium Relationships

1. Ionization Constants of Hydrogen Sulfide

The equilibria between the non-polysulfide ionic species in aqueous polysulfide solutions are governed by the two ionization constants of hydrogen sulfide. The first ionization constant at room temperature is given in the literature (43)(44); the computed values at 75°C are based on reported heats of formation (36):

For the reaction $H_2S\ (aq) = H^+ + HS^-$ (23)

$$K_1 = \frac{a_{H^+}\ a_{HS^-}}{\gamma_{H_2S}\ [H_2S]} \begin{array}{l} = 1.15 \times 10^{-7} \text{ at } 25°C \\ \cong 4.07 \times 10^{-7} \text{ at } 75°C \end{array} \qquad (24)$$

in which K_1 is the first ionization constant of H_2S

a is activity

γ is activity coefficient.

Since the partial pressure of hydrogen sulfide rather than its aqueous phase concentration was controlled during the present series of experiments, the following alternate formulation will be employed:

For the reaction $H_2S(g) = H^+ + HS^-$ (25)

$$K_1' = \frac{a_{H^+}\ a_{HS^-}}{f_{H_2S}} \begin{array}{l} = 1.17 \times 10^{-8} \text{ at } 25°C \\ \cong 1.79 \times 10^{-8} \text{ at } 75°C \end{array} \qquad (26)$$

in which K_1' is the "modified" first ionization constant of H_2S.

The numerical value of the second ionization constant of hydrogen sulfide is in doubt, since determinations of the monosulfide hydrolysis yield only this constant multiplied by a factor involving unknown ionic activity coefficients. By combining the results of recent hydrolysis studies by Martin (<u>46</u>) with the known (<u>36</u>) ionization constant of water:

$$H_2O = H^+ + OH^- \qquad (27)$$

$$K_w' = a_{H^+}a_{OH^-} = 1.01 \times 10^{-14} \text{ at } 25°C$$
$$= 2.21 \times 10^{-13} \text{ at } 75°C \qquad (28)$$

in which K_w' is the "modified" ionization constant of water, the following approximate values were obtained for use in the present thesis:

$$HS^- = H^+ + S^= \qquad (29)$$

$$K_2 = \frac{a_{H^+} \; a_{S^=}}{a_{HS^-}} \cong 1.3 \times 10^{-14} \text{ at } 25°C$$
$$\cong 2.9 \times 10^{-13} \text{ at } 75°C \qquad (30)$$

in which K_2 is the second ionization constant of H_2S. These numbers are considered somewhat better than any previous estimates (1.2×10^{-15} at 25°C) reported in the literature (<u>36</u>). It fortunately was not necessary to separate the numerical value of K_2 from the equally unknown ionic activity coefficients in order to predict the ionic distributions in <u>most</u> aqueous polysulfide solutions.

From equations 26 and 30 the following useful relation can be derived:

$$a_{S^=} = (\gamma_{HS^-})^2 \left(\frac{K_2}{K_1'}\right) \left(\frac{[HS^-]^2}{f_{H_2S}}\right) \tag{31}$$

2. Polysulfide Equilibria

If the various polysulfide species do conform to equilibrium requirements, the following relations then must hold:

$$S^= + 1/8\ S_8\ (rh) = S_2^= \tag{32}$$

$$k_1 = \frac{a_{S_2^=}}{a_{S^=}\, a_{S_8}^{1/8}} \tag{33}$$

$$S^= + 2/8\ S_8\ (rh) = S_3^= \tag{34}$$

$$k_2 = \frac{a_{S_3^=}}{a_{S^=}\, a_{S_8}^{2/8}} \tag{35}$$

$$S^= + 3/8\ S_8\ (rh) = S_4^= \tag{36}$$

$$k_3 = \frac{a_{S_4^=}}{a_{S^=}\, a_{S_8}^{3/8}} \tag{37}$$

etc.

in which k_1, k_2, k_3, etc. are the polysulfide equilibrium constants.

It should be recognized that no independent equations would result from any different formulation such as:

$$S_2^{=} + S_4^{=} = 2S_3^{=} \tag{38}$$

since the equilibrium constant for the preceding reaction, for example, merely would be:

$$\frac{a_{S_3^{=}}^{\,2}}{a_{S_2^{=}}\, a_{S_4^{=}}} = \frac{k_2^{\,2}}{k_1\, k_3} \tag{39}$$

Equations 33, 35, 37, and the like can be solved for the concentrations of the polysulfide ionic species in terms of the monosulfide activity and the activity of elemental sulfur:

$$[S_2^{=}] = \frac{k_1}{\gamma_{S_2^{=}}} \left(\frac{a_{S_8}^{\,1/8}}{S^{=}}\right)(a_{S^{=}}) \tag{40}$$

$$[S_3^{=}] = \frac{k_2}{\gamma S_3^{=}} \left(\frac{a_{S_8}^{\,2/8}}{S^{=}}\right)(a_{S^{=}}) \tag{41}$$

$$[S_4^{=}] = \frac{k_3}{\gamma S_4^{=}} \left(\frac{a_{S_8}^{\,3/8}}{S^{=}}\right)(a_{S^{=}}) \tag{42}$$

etc.

3. Polysulfide Material Balances

The total polysulfide ion concentration $[S_x^{=}]$ obviously may be written as the sum of its components:

$$[S_x^{=}] = [S_2^{=}] + [S_3^{=}] + [S_4^{=}] + \ldots \tag{43}$$

The concentration of polysulfide sulfur may be expressed as follows, if the assumptions limiting the chemical species present are valid:

$$[\mathrm{PSS}] = [S_2^=] + 2\,[S_3^=] + 3\,[S_4^=] + \ldots \qquad (44)$$

By substitution of the expressions from equations 40, 41, 42, and the like into the two preceding relations, the following are obtained:

$$\frac{[S_x^=]}{a_{S^=}} = \frac{k_1 a_{S_8}^{1/8}}{\gamma_{S_2^=}} + \frac{k_2 a_{S_8}^{2/8}}{\gamma_{S_3^=}} + \frac{k_3 a_{S_8}^{3/8}}{\gamma_{S_4^=}} + \ldots \qquad (45)$$

$$\frac{[\mathrm{PSS}]}{a_{S^=}} = \frac{k_1 a_{S_8}^{1/8}}{\gamma_{S_2^=}} + \frac{2k_2 a_{S_8}^{2/8}}{\gamma_{S_3^=}} + \frac{3k_3 a_{S_8}^{3/8}}{\gamma_{S_4^=}} + \ldots \qquad (46)$$

The monosulfide ion activity then may be eliminated using equation 31; rearrangement yields the following final expressions:

$$\frac{[S_x^=]\,f_{H_2S}}{[HS^-]^2} = X = (\gamma_{HS^-})^2 \left(\frac{K_2}{K_1{}'}\right) \left[\frac{k_1 a_{S_8}^{1/8}}{\gamma_{S_2^=}} + \frac{k_2 a_{S_8}^{2/8}}{\gamma_{S_3^=}} + \frac{k_3 a_{S_8}^{3/8}}{\gamma_{S_4^=}} + \ldots\right] \qquad (47)$$

$$\frac{[\mathrm{PSS}]\,f_{H_2S}}{[HS^-]^2} = Y = (\gamma_{HS^-})^2 \left(\frac{K_2}{K_1{}'}\right) \left[\frac{k_1 a_{S_8}^{1/8}}{\gamma_{S_2^=}} + \frac{2k_2 a_{S_8}^{2/8}}{\gamma_{S_3^=}} + \frac{3k_3 a_{S_8}^{3/8}}{\gamma_{S_4^=}} + \ldots\right] \qquad (48)$$

Thus the quantities X and Y obtained from the experimental data of the present thesis can be equated to expressions involving only the unknown polysulfide equilibrium constants, powers of elemental sulfur activity, ionic activity coefficients, and the "known" dissociation constants of hydrogen sulfide. Equations 47 and 48 may be simplified further if it is assumed that the activity coefficients of the individual polysulfide ions are all equal to an average $\gamma_{S_x^=}$:

$$\frac{[S_x^=]\, f_{H_2S}}{[HS^-]^2} = X \cong \frac{(\gamma_{HS^-})^2}{\gamma_{S_x^=}} \left(\frac{K_2}{K_1'}\right) \left[k_1 a_{S_8}^{1/8} + k_2 a_{S_8}^{2/8} + k_3 a_{S_8}^{3/8} + \dots \right] \tag{49}$$

$$\frac{[PSS]\, f_{H_2S}}{[HS^-]^2} = Y \cong \frac{(\gamma_{HS^-})^2}{\gamma_{S_x^=}} \left(\frac{K_2}{K_1'}\right) \left[k_1 a_{S_8}^{1/8} + 2k_2 a_{S_8}^{2/8} + 3k_3 a_{S_8}^{3/8} + \dots \right] \tag{50}$$

The activities of individual ions and thus their individual activity coefficients have been employed in this derivation even though such quantities are difficult of exact thermodynamic definition. The concentrations of these ions certainly must exist; the activities therefore are regarded merely as numbers which satisfy the necessary mass-action equilibrium relationships and which are compatible with the overall mean activity coefficients as conventionally defined. In this connection it will be convenient to consider the ratio $(\gamma_{HS^-})^2/\gamma_{S_x^=}$ as "γ_{avg}" for the anions present, even though this quantity would not be the same as the overall mean activity coefficient.

It might appear that numerical values of both K_2 and γ_{avg} are needed in order to determine the unknown polysulfide equilibrium constants. The relative values of the k's, however, may be found knowing neither of these:

Define: $$r_1 = \left(\gamma_{avg} \frac{K_2}{K_1'}\right) k_1 \qquad (51)$$

$$r_2 = \left(\gamma_{avg} \frac{K_2}{K_1'}\right) k_2 \qquad (52)$$

$$r_3 = \left(\gamma_{avg} \frac{K_2}{K_1'}\right) k_3 \qquad (53)$$

etc.

in which r_1, r_2, r_3, etc. are the relative polysulfide equilibrium constants.

The r's are thus "equilibrium constants" which also include a function of ionic activity coefficients. Equations 49 and 50 then may be written as:

$$\frac{[S_x^=]\, f_{H_2S}}{[HS^-]^2} = X = r_1 a_{S_8}^{1/8} + r_2 a_{S_8}^{2/8} + r_3 a_{S_8}^{3/8} + \ldots \qquad (54)$$

$$\frac{[PSS]\, f_{H_2S}}{[HS^-]^2} = Y = r_1 a_{S_8}^{1/8} + 2r_2 a_{S_8}^{2/8} + 3r_3 a_{S_8}^{3/8} + \ldots \qquad (55)$$

If a constant γ_{avg} could be assumed for a given group of equilibrium data, then the r's could be solved for knowing only the sulfur activities in addition to the information already tabulated.

It must be emphasized that the use of elemental sulfur activities does not imply the existence of stoichiometrically significant concentrations of physically-dissolved sulfur in the aqueous phase. The concept of sulfur activity pertains to equilibrium, and by no means stipulates the mechanism by which the polysulfide ions do equilibrate.

B. Justification of Assumed Species Present

It was assumed previously that only polysulfide ions ($S_x^=$), hydrosulfide ion (HS^-), sodium ion (Na^+), hydrogen sulfide (H_2S), and water (H_2O) were present in stoichiometrically significant amounts in the aqueous solutions of the equilibrium systems studied in the present thesis. The possible existence of other chemical species now will be explored.

1. Dissolved Hydrogen Persulfides (H_2S_n)

Since all the known hydrogen persulfides are reasonably stable only in strongly acidic media, the presence of significant amounts of any persulfide either in highly basic sodium polysulfide solutions or in the equilibrium systems studied (pH ranging between 7 and 9) is considered extremely unlikely.

2. Undissociated Species: NaS_x^-, Na_2S_x, $NaHS_x$

Sodium is not known to form complexes such as the first of the three indicated. Any possible existence of such species moreover would be taken into account in the formulation of ionic activity coefficients, in much the manner that hydration or solvation effects are treated. Consideration of the hypothesized presence of undissociated NaS_x^- would serve to illustrate this fact: Besides the $S_x^=$ concentration as given by equation 45 we would have:

$$\frac{[NaS_x^-]}{a_{NaS^-}} = \frac{c_1 a_{S_8}^{1/8}}{\gamma_{NaS_2^-}} + \frac{c_2 a_{S_8}^{2/8}}{\gamma_{NaS_3^-}} + \frac{c_3 a_{S_8}^{3/8}}{\gamma_{NaS_4^-}} + \ldots \qquad (56)$$

and

$$a_{NaS^-} = C\, a_{S^=}\, a_{Na^+} \qquad (57)$$

in which c_1, c_2, c_3 etc. are the equilibrium constants for polysulfide formation by the complex.

C is the monosulfide complexing constant.

X then would correspond to the apparent $S_x^=$ concentration as determined stoichiometrically:

$$X = \frac{(\,[S_x^=] + [NaS_x^-]\,)\,f_{H_2S}}{[HS^-]^2}$$

$$= (\gamma_{HS^-})^2 \left(\frac{K_2}{K_1'}\right) \left[\frac{k_1(1+C\frac{c_1}{k_1} a_{Na^+})a_{S_8}^{1/8}}{\gamma_{S_2^=}} + \frac{k_2(1+C\frac{c_2}{k_2} a_{Na^+})a_{S_8}^{2/8}}{\gamma_{S_3^=}} + \ldots \right]$$

(if the NaS_x^- activity coefficients are assumed equal to those of the corresponding $S_x^=$ ions.)

$$= (\gamma_{HS^-})^2 \left(\frac{K_2}{K_1'}\right) \left[\frac{k_1 a_{S_8}^{1/8}}{\gamma'_{S_2^=}} + \frac{k_2 a_{S_8}^{2/8}}{\gamma'_{S_3^=}} + \ldots \right]$$

(in which the (γ')'s are the "modified" ionic activity coefficients.)

$$= \frac{(\gamma_{HS^-})^2}{\gamma'_{S_x^=}} \left(\frac{K_2}{K_1'}\right) \left[k_1 a_{S_8}^{1/8} + k_2 a_{S_8}^{2/8} + \ldots \right] \quad (58)$$

(if the (γ')'s are assumed all equal.)

A similar expression would be obtained considering the polysulfide sulfur balance Y.

The same polysulfide equilibrium constants thus would apply whether or not NaS_x^- were present; the apparent activity coefficients, however, would differ. The polysulfide ionic concentrations as calculated from these constants actually would be the sums of the ordinary polysulfides plus the corresponding complexes. These sums indeed would be the quantities which should be correctly compared with the data on the production of raw oil.

Much the same considerations would apply for the formation of undissociated Na_2S_x or $NaHS_x$. In addition, it was found that sodium chloride addition in two equilibrium experiments in the present thesis did not affect the "average" ionic activity coefficients, contrary to what would be predicted by equation 58. For the various preceding reasons undissociated complex formation was neglected in setting up the equilibrium relations in this thesis.

3. Impurities: $S_2O_3^=$, $SO_3^=$, $SO_4^=$, $CO_3^=$

Such foreign ions in the final aqueous solutions of the Na_2S-S-H_2S-H_2O equilibrium experiments might have arisen either from the same impurities in the initial sodium sulfide or else through oxidation or other side-reactions during polysulfide preparation and equilibration. The analyses for impurities in the sodium sulfide crystals used are described in the Appendix. Carbonate ($CO_3^=$) and either excess hydroxide (OH^-) or excess hydrosulfide (HS^-) all were ruled out since the sodium hydrosulfide prepared by the hydrogen sulfide saturation of the initial monosulfide possessed almost exactly twice the initial reducing equivalents plus the small amount assignable to physically-dissolved hydrogen sulfide. Sulfate ($SO_4^=$) as an impurity could be neglected since it would appear inert during all the reactions and titrations.

The major impurities in the sodium sulfide as commercially available were found to be thiosulfate ($S_2O_3^=$) or sulfite ($SO_3^=$) or both, present in total amount up to 2.8 mol per cent, but usually averaging about 1.0-1.5 per cent. Since these two ions both react during the iodimetric titrations for total sulfides, errors in the calculated equilibrium results could well be present. For an impurity content of 1.0 mol per cent the error in the calculated X would be +2.6 per cent or less if the foreign ion were thiosulfate and +5 per cent or less if sulfite. There would be no error in the calculated values of Y. These uncertainties are not large compared with the roughly 3 per cent error predicted by the Error Analysis (see Appendix) and the actual X and Y scatter in excess of 10 per cent. Lower values of X and higher Y/X ratios moreover were not realized in the later runs in which the initial sodium sulfide first had been purified by washing, contrary to what might be expected if the supposed impurity errors had been eliminated:

Foreign ions such as thiosulfate or sulfite also could be formed during polysulfide preparation, either by a reaction with the air or through an internal oxidation-reduction process. Peschanski (52) indeed reported that 3 per cent of an initial sodium sulfide was converted to thiosulfate after 9 hours sulfur saturation at 17°C. The formation of thiosulfate by air oxidation should be accompanied by a drop in reducing equivalents. On the other hand, no such differences were noted in the present thesis between polysulfide preparations carried out in contact with the air and under an inert atmosphere.

The formation of impurities by an internal oxidation-reduction as described by equation 2:

$$4S_x^{=} + 6(x-1)OH^{-} = (x-1)S_2O_3^{=} + 2(x+1)S^{=} + 3(x-1)H_2O \quad (2)$$

or similar reactions would lead to a decided <u>increase</u> in reducing equivalents over and above that of the initial sodium sulfide. For the conversion of $S_5^{=}$ ion to the thiosulfate, for example, the preceding equation states that if 2 per cent of the nominal polysulfide thus reacts, the titrimetric equivalents would be increased by 7 per cent. No such differences in reducing power were evident when polysulfide analyses per unit weights of sodium sulfide were compared to the assays independently determined for the crystals. Owing to the variable water content of the starting material the actual mols of either monosulfide or polysulfide per apparent mol by weight of initial sodium sulfide ranged from 0.97 to 1.02.

For the reasons discussed in the preceding sections thiosulfate and sulfite were assumed absent in making all equilibrium calculations.

4. Physically-Dissolved Sulfur (S_8)

In view of the extremely small solubility of free sulfur in either pure water or aqueous solutions of the usual electrolytes, the presence of appreciable uncombined sulfur in aqueous polysulfide solutions might be considered unlikely. This supposition is supported by the findings of the present thesis. Consider the plot of "B" versus "A" at 75°C for the runs at a sodium molality of 4.0 and a hydrogen sulfide partial pressure of about 0.6 atm (Figure 14). The ratio $PSS/S_x^=$ increases from roughly 3.7 at "A" = 1.33 to about 3.9 at sulfur saturation ("A" = 1.58). If appreciable physically-dissolved sulfur actually were present at sulfur saturation, the true $PSS/S_x^=$ ratio then would have to be less than the calculated value 3.9. Consideration of equations 49 and 50 indicates that the true $PSS/S_x^=$ ratio nevertheless also must increase with sulfur activity, and hence with "A":

$$\frac{PSS}{S_x^=} = \frac{Y}{X} = \frac{k_1 a_{S_8}^{1/8} + 2k_2 a_{S_8}^{2/8} + 3k_3 a_{S_8}^{3/8} + \ldots}{k_1 a_{S_8}^{1/8} + k_2 a_{S_8}^{2/8} + k_3 a_{S_8}^{3/8} + \ldots} \qquad (59)$$

At sulfur saturation ("A" = 1.58) the activity of elemental sulfur was unity. At "A" = 1.33, on the other hand, the xylene measurements yielded a sulfur concentration of about 2.2 weight per cent, compared to the 9.8 per cent sulfur solubility in o-xylene. It will be shown later that this concentration corresponds to a sulfur activity of about 0.16. If physically-dissolved sulfur were present in the aqueous phase, its concentration, to a first approximation, might be assumed proportional to the elemental sulfur activity. Thus the dissolved sulfur concentration at "A" = 1.33 would be only 0.16 of the sulfur concentration at saturation.

Although the increase in the true PSS/$S_x^=$ ratio with sulfur activity cannot be evaluated from equation 59 without some knowledge of the k's, as an extreme case the ratio might be assumed constant at roughly 3.7 in going from a sulfur activity of 0.16 to one of unity. Even though the total increase in all forms of sulfur in solution in going from "A" = 1.33 to "A" = 1.58 is 0.15 gm-atoms per gm-mol sodium ion, the portion of this due to the increase in dissolved sulfur then could be only about 0.0077 gm-atoms per mol Na^+. Thus the total free sulfur in solution at saturation would be only 0.0092 gm-atoms per mol Na^+, or less than 0.6 per cent of the sulfur combined as polysulfides. If an increase in the true PSS/$S_x^=$ ratio with increasing sulfur activity were taken into consideration, the amount of physically-dissolved sulfur would be smaller still.

It therefore shall be assumed that uncombined sulfur is not present in stoichiometrically significant amounts in aqueous polysulfide solutions.

5. Hydrogen from Hydrogen Sulfide Decomposition

For the reaction:

$$H_2S(g) \quad = \quad H_2(g) \quad + \quad 1/8\ S_8\ (rh) \qquad (60)$$

the following values for the equilibrium constant may be obtained from the literature (<u>36</u>):

$$\frac{f_{H_2} a_{S_8}^{1/8}}{f_{H_2S}} \begin{array}{l} = 1.84 \times 10^{-6} \text{ at } 25°C \\ = 5.7 \times 10^{-6} \text{ at } 75°C \end{array} \qquad (61)$$

Examination of equation 61 indicates that even at sulfur activities as low as 10^{-16} the hydrogen partial pressure developed by decomposition is negligible relative to the partial pressure of hydrogen sulfide. The formation of hydrogen thus could be assumed nil in all the Na_2S-S-H_2S-H_2O equilibrium experiments carried out in the present thesis.

6. Hydrogen Ion (H^+), Hydroxyl Ion (OH^-), Monosulfide Ion ($S^=$)

The pH measurements in the Na_2S-S-H_2S-H_2O equilibrium study indicated that the hydrogen ion activity ranged between 10^{-7} and 10^{-9}, depending on conditions. (The final equilibrium solutions essentially were buffers made up of basic sulfides and polysulfides plus hydrogen sulfide.) Accordingly, both hydrogen ion and hydroxyl ion could be considered negligible in material balances. The substitution into equation 31 of some of the data values listed in Table IX moreover indicates that the monosulfide ion concentration also could be neglected, provided that the hydrogen sulfide partial pressure was not too small.

In ordinary sodium polysulfide solutions, of course, both hydroxyl and monosulfide ions can be present in appreciable amounts.

7. Acid Polysulfide Ions (HS_x^-)

The decreasing hydrolysis of polysulfide solutions having higher "x" values indicates that the hydrogen persulfides are stronger acids than hydrogen sulfide. The hypothesized mechanism of raw oil production, involving the HS_x^- species as unstable intermediates, also requires that such ions not be favored by equilibrium. The findings of the present thesis, however, provide the strongest evidence that the acid polysulfides may be neglected in material balances.

If the HS_x^- ions obey equilibrium requirements, their concentrations would have to be governed by relations similar to those already derived for the $S_x^=$ ions:

$$HS^- + 1/8\ S_8\ (rh) = HS_2^- \tag{62}$$

$$h_1 = \frac{a_{HS_2^-}}{a_{HS^-}a_{S_8}^{1/8}} \tag{63}$$

$$HS^- + 2/8\ S_8\ (rh) = HS_3^- \tag{64}$$

$$h_2 = \frac{a_{HS_3^-}}{a_{HS^-}a_{S_8}^{2/8}} \tag{65}$$

etc.

in which h_1, h_2, etc. are the equilibrium constants for the formation of the acid polysulfides.

Since equation 44 then would become:

$$[PSS] = \left\{[S_2^=] + 2\,[S_3^=] + 3\,[S_4^=] + \ldots\right\} + \left\{[HS_2^-] + 2\,[HS_3^-] + 3\,[HS_4^-] + \ldots\right\} \qquad (66)$$

the following relation for the ratio $PSS/S_x^=$ could be derived:

$$\frac{PSS}{S_x^=} = \left\{\frac{k_1 a_{S_8}^{1/8} + 2k_2 a_{S_8}^{2/8} + \ldots}{k_1 a_{S_8}^{1/8} + k_2 a_{S_8}^{2/8} + \ldots}\right\} + \left\{\frac{h_1 a_{S_8}^{1/8} + 2h_2 a_{S_8}^{2/8} + \ldots}{1 + h_1 a_{S_8}^{1/8} + h_2 a_{S_8}^{2/8} + \ldots}\right\}\left(\frac{[HS^-]'}{[S_x^=]}\right) \qquad (67)$$

in which $[HS^-]'$ is the "apparent" hydrosulfide ion concentration as determined stoichiometrically, actually equal to $[HS^-] + [HS_x^-]$.

At a constant sulfur activity equation 67 would take the form:

$$\frac{PSS}{S_x^=} = G_1 + G_2\,\frac{[HS^-]'}{[S_x^=]} \qquad (68)$$

in which G_1 and G_2 are constants which depend only on the sulfur activity.

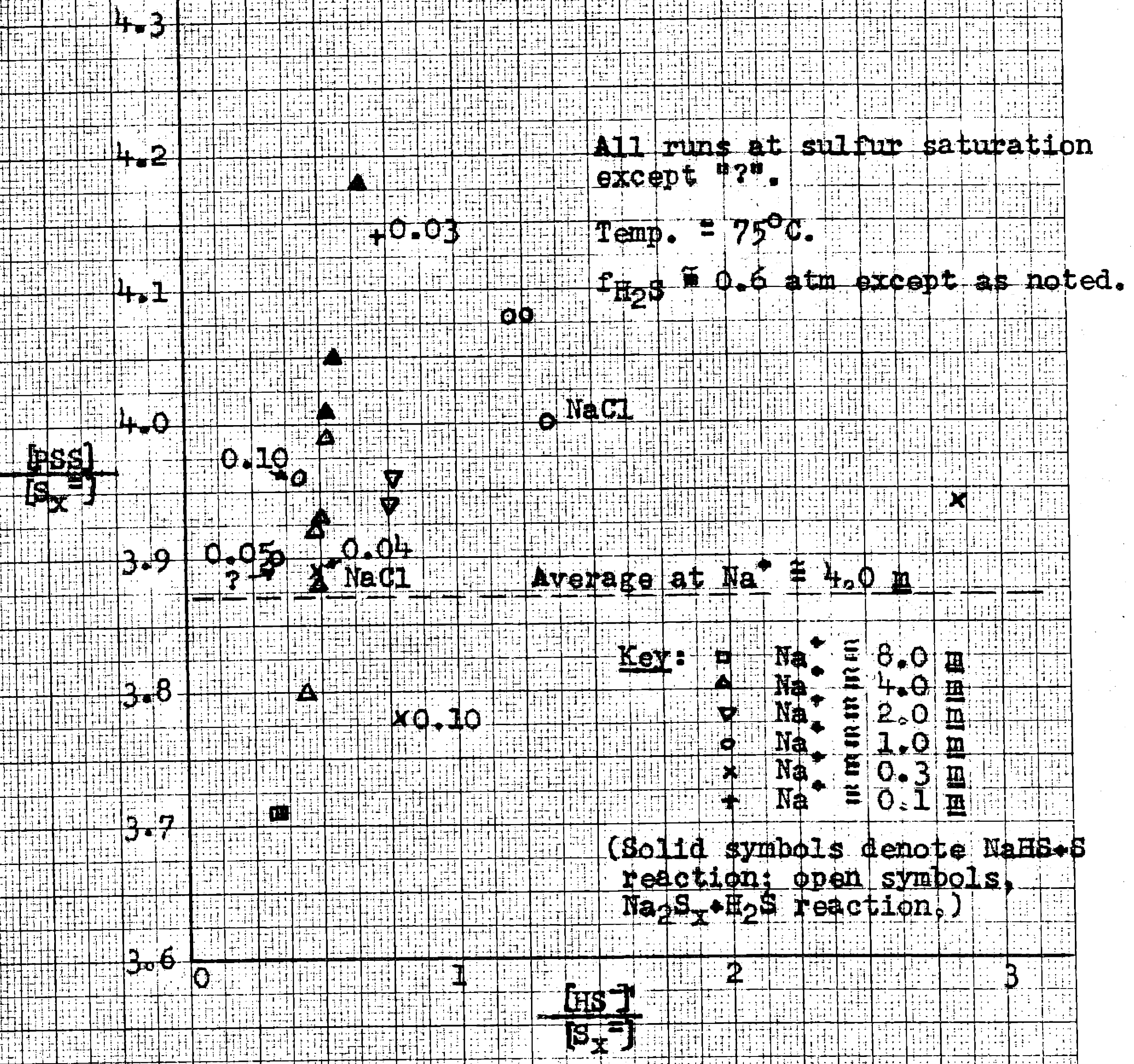
Thus if the ratio $PSS/S_x^=$ at a constant sulfur activity were plotted versus the ratio $[HS^-]'/[S_x^=]$, a straight line should be obtained with intercept G_1 and slope G_2. If the HS_x^- ions were absent, G_2 would have to be zero.

Such a plot for all the sulfur saturation ($a_{S_8} = 1.0$) runs at 75°C is shown in Figure 20. Even though the points scatter considerably, any definite upward trend is lacking. Within the limits of experimental error G_2 thus could be taken as zero.

Since the preceding correlation was somewhat inconclusive, the results of the pH experiments were examined for more direct evidence that the HS_x^- species indeed could be neglected. Based on the pH measurements, hydrosulfide ion activities were calculated with the aid of equation 26:

$$a_{HS^-} = \frac{K_1' \, f_{H_2S}}{a_{H^+}} \qquad (69)$$

in which a_{H^+} was computed as $10^{-(pH)}$. The calculated hydrosulfide activities then were compared to the total apparent hydrosulfide concentrations $[HS^-]'$ as determined by stoichiometry. If the true hydrosulfide made up only a part of the apparent hydrosulfide, its activity as measured by pH then should be low relative to its apparent concentration as derived from the titrimetric results. The numbers actually obtained are given in Table XIV:



All runs at sulfur saturation except "?".

Temp. = 75°C.

f_{H_2S} ≅ 0.6 atm except as noted.

(Solid symbols denote NaHS+S reaction; open symbols, Na_2S_x+H_2S reaction.)

FIGURE 20

Possible Presence of HS_x^- from Stoichiometric Equilibrium Results

TABLE XIV

Hydrosulfide Ion Activities by pH Measurements

Run	E-51	E-52	E-53	E-54	E-55	E-56	E-57 +NaCl	NaHS (75°C)	NaHS (25°C)
f_{H_2S}	0.640	0.0547	0.626	0.1023	0.0277	0.101	0.0438	0.642	0.979
pH	7.55	8.23	7.22	7.74	7.87	7.99	7.89	7.84	7.70
$a_{H^+} \times 10^8$	2.8	0.59	6.0	1.82	1.35	1.02	1.29	1.45	1.99
a_{HS^-}	0.41	0.166	0.186	0.101	0.037	0.177	0.061	0.79	0.58
$[HS^-]'$	0.405	0.151	0.187	0.0872	0.0288	0.173	0.0595	1.02	1.00
$\left(\frac{a_{HS^-}}{[HS^-]}\right)'$	1.01	1.10	1.00	1.16	1.28	1.02	1.02	0.77	0.58

Note: All the equilibrium runs were performed at 75°C and unity sulfur activity with the sodium ion molality ranging from 0.1 to 1.0. The two sodium hydrosulfide pH experiments were carried out using 1.0 m NaHS solutions.

The two latter experiments listed in Table XIV indicated in 1.0 m sodium hydrosulfide solution apparent HS^- ionic activity coefficients of 0.58 and 0.77 at 25°C and 75°C, respectively. If the HS_x^- ions were present in the Na_2S-S-H_2S-H_2O equilibrium solutions, then the ratios $a_{HS^-} / [HS^-]'$ as calculated would have to be less than the true hydrosulfide activity coefficients in these same solutions. The fact that these ratios in fact are higher than in the corresponding sodium hydrosulfide tests indicates that the activity coefficients are higher in polysulfide solutions, but in addition certainly implies that the acid polysulfides make up little if any of the apparent hydrosulfide concentration $[HS^-]'$.

Further correlation of these pH results will be attempted in the following section of this thesis.

C. Correlation of Ionic Activity Coefficients

1. Activity Coefficients from Stoichiometric Results

Some information on ionic activity coefficients can be gained by an examination of the stoichiometric equilibrium data for the system Na_2S-S-H_2S-H_2O. Inspection of equations 49 and 50 indicates that at a constant sulfur activity the functions X and Y both are proportional to the "average" ionic activity coefficient (defined as $(\gamma_{HS^-})^2/\gamma_{S_x^=}$). A correlation of the data at sulfur saturation, where the sulfur activity was unity, thus might well yield values of γ_{avg}.

The quantities X calculated for the runs at sulfur saturation at 75°C are plotted versus ionic strength (defined by equation 9) in Figure 21; the values of Y for these same experiments similarly are shown in Figure 22. These two graphs exhibit a scatter of more than 10 per cent between duplicate runs approaching equilibrium from the one direction, and in addition show a consistent discrepancy between the two reaction directions at a sodium molality of 4.0. Even though any errors in the original titrimetric and gravimetric data

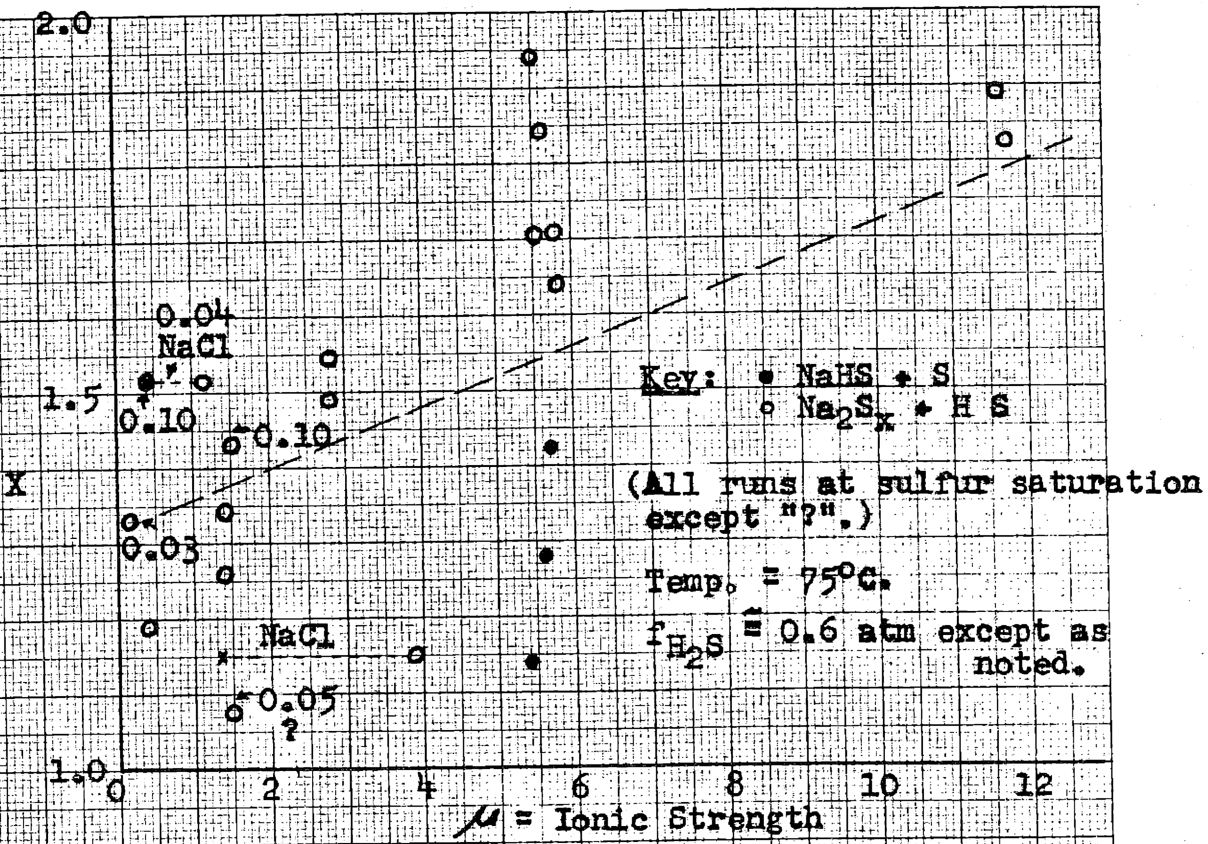


FIGURE 21

Activity Coefficients from "X" versus Ionic Strength

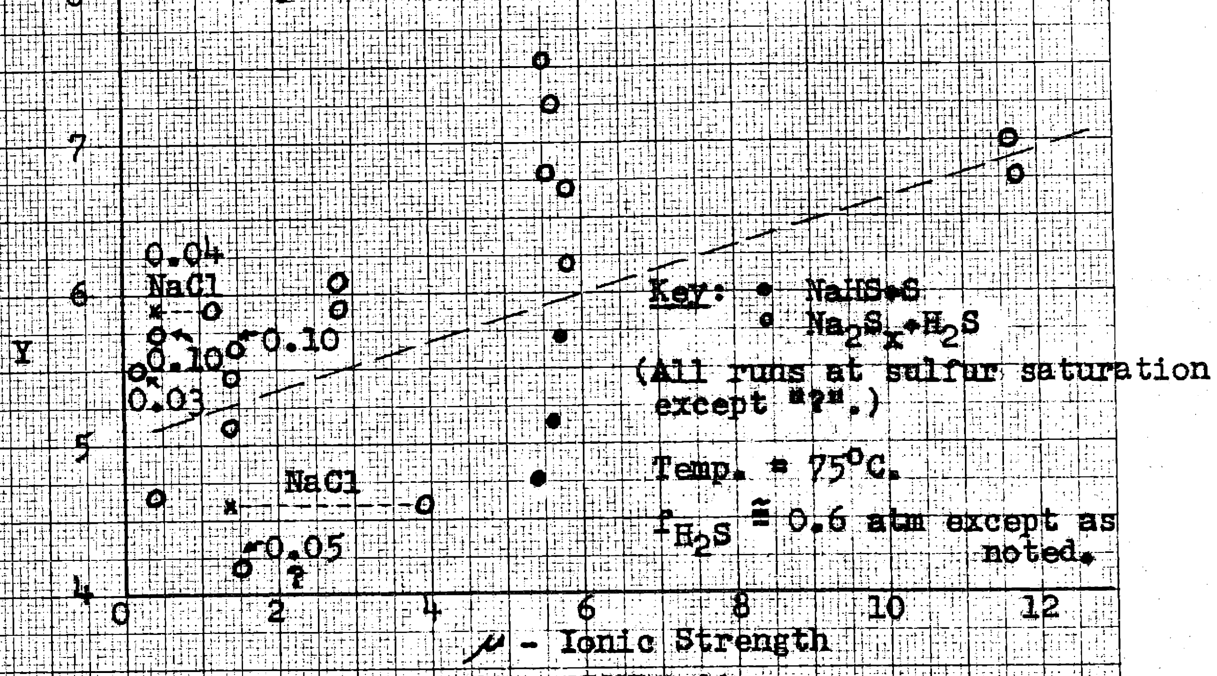


FIGURE 22

Activity Coefficients from "Y" versus Ionic Strength are greatly magnified in the X and Y functions, this lack of reproducibility far exceeds the 2.4 to 3.3 per cent error in X and the 1.1 to 2.3 per cent error in Y predicted by the Error Analysis (see Appendix), and reflects, of course, the unexplained scatter of the raw data.

In spite of these uncertainties the two figures indicate that the average ionic activity coefficient apparently increases with ionic strength, at least above 1.0 sodium ion molality. A minimum in γ_{avg} might exist in the low concentration region. Owing to the scatter it was possible neither to extrapolate to zero concentration (thus obtaining numerical values of the activity coefficients) nor to determine the relative activity coefficients at two different ionic strengths with a precision closer than about 10 per cent. The results of the sodium chloride runs, calculated in two ways: (a) ignoring, and (b) taking into account the sodium chloride added, indicate that within the limits of experimental error the addition of this salt does not affect γ_{avg}, even though the ionic strength is increased (Figures 21 and 22). Some possible reasons for this phenomenon will be considered shortly.

It was found more convenient in the solution of simultaneous equations for the polysulfide equilibrium constants and in the calculation of ionic compositions of aqueous polysulfide solutions to assume that the "average" ionic activity coefficient could be correlated versus the sodium ion molality rather than the ionic strength. The points shown in Figures 21 and 22 therefore are replotted versus sodium (Na^+) molality in Figures 23 and 24, respectively. Considering the scatter of the data these correlations are no worse than the previous ones versus ionic strength. Correlations versus $S_x^=$ ion molality and HS^- ion molality also were attempted; these in general did not fit the experimental points any better.

The indicated curves in Figures 23 and 24 were assumed in all future calculations in this thesis. Besides depending on the actual points shown, the two curves were chosen to be compatible, as will be explained later, with the measured xylene sulfur concentrations in the non-saturated systems at the sodium ion molalities of 1.0 and 4.0. The numerical values of γ_{avg} and hence the intercepts at zero concentration were estimated, as will be shown, from comparisons with the pH measurements and with literature data on the ionic activity coefficients in other electrolytes. Knowing the intercepts, the curves below 0.1 m sodium ion then were calculated assuming the simple form of the Debye-Huckel equation to apply:

$$-\ln \gamma \cong a\sqrt{\mu} \qquad (70)$$

in which γ is ionic activity coefficient

μ is ionic strength

a is a constant

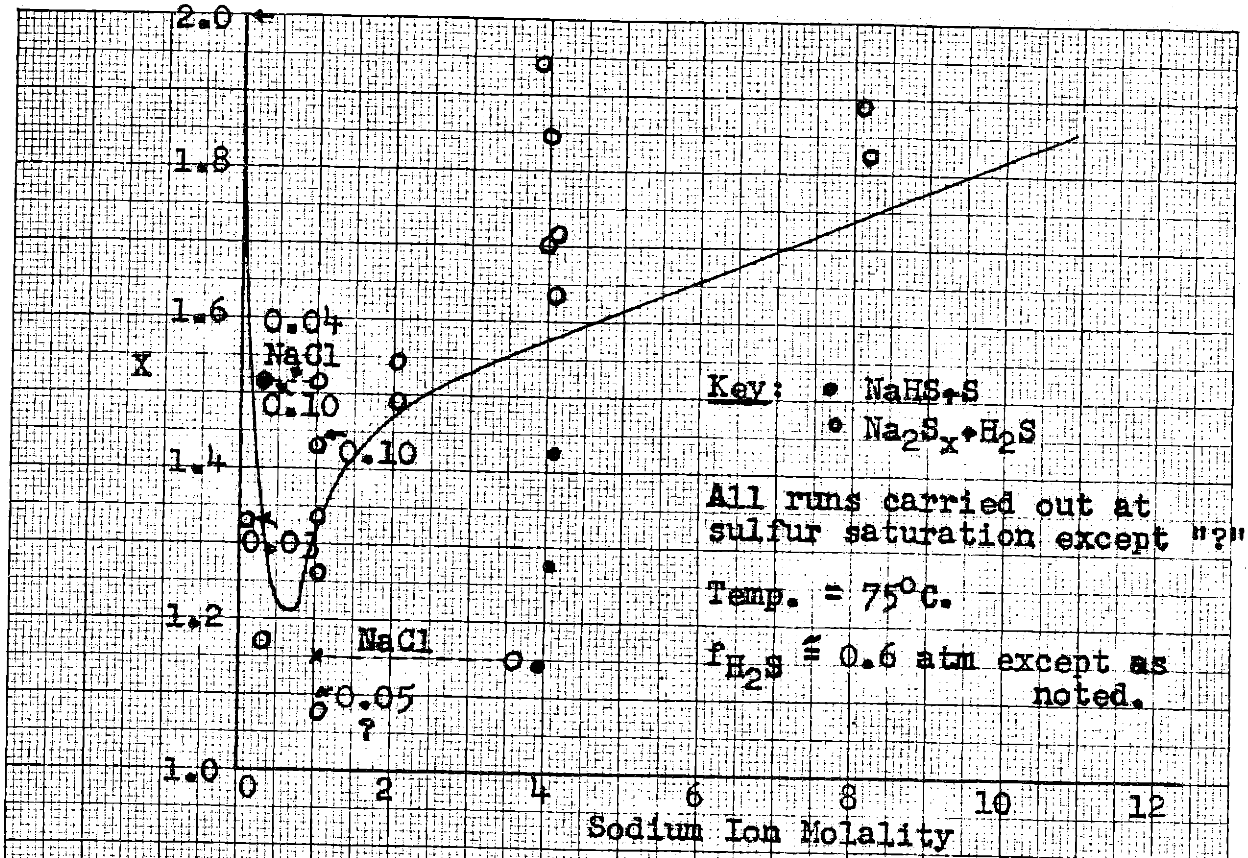


FIGURE 23

Activity Coefficients from "X" versus Sodium Molality

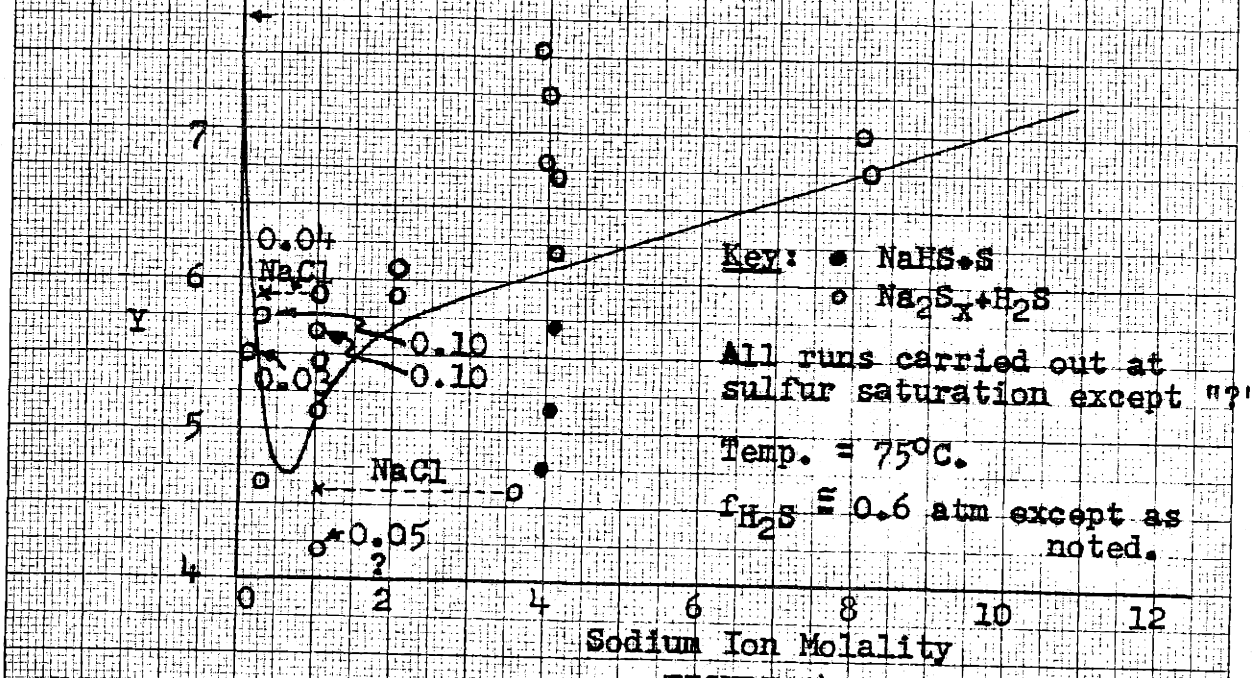


FIGURE 24

Activity Coefficients from "Y" versus Sodium Molality

In practice the sodium ion molality rather than the ionic strength was employed in equation 70, in line with the approximations already made. Since the ratio Y/X or $PSS/S_x^=$ at a given sulfur activity had to be fixed at a constant value (taken as 3.87 at 75°C) if the γ_{avg} simplifications (equations 49 and 50) were assumed valid, the Y curve in Figure 24 thus was drawn proportional to the X curve in Figure 23 by that constant factor.

Even though the average ionic activity coefficients have been correlated versus sodium ion molality, it nevertheless should be understood that, in view of the sodium chloride results, sodium ion as such evidently is not the primary controller of ionic activity coefficients.

2. Activity Coefficients from pH Data

Quantities supposedly equal to or proportional to <u>individual</u> ionic activity coefficients could be derived from the pH results obtained at 75°C and sulfur saturation. Since the HS_x^- species were assumed absent, the numbers already calculated using equation 69 and presented in Table XIV could be taken as the hydrosulfide ionic activity coefficients:

$$\gamma_{HS^-} = \frac{a_{HS^-}}{[HS^-]} \qquad (71)$$

(at <u>any</u> sulfur activity)

Owing to the uncertainty in K_2, neither the activity nor the concentration of the monosulfide ($S^=$) ion itself could be determined with any precision from the data available. If all the individual polysulfide ionic activity coefficients were assumed equal to $\gamma_{S_x^=}$, however, a function proportional to the polysulfide activity coefficient then could be derived from simultaneous consideration of equation 30 and equation 45 (or equation 46):

$$\gamma_{S_x^=} \text{ is proportional to } \frac{a_{HS^-}}{a_{H^+}\;[S_x^=]} \tag{72}$$

or

$$\gamma_{S_x^=} \text{ is proportional to } \frac{a_{HS^-}}{a_{H^+}\;[PSS]} \tag{73}$$

(at a constant sulfur activity)

Quantities proportional to the ratios of the two individual activity coefficients also could be computed:

$$\frac{\gamma_{HS^-}}{\gamma_{S_x^=}} \text{ is proportional to } \frac{a_{H^+}\,[S_x^=]}{[HS^-]} \tag{74}$$

or

$$\frac{\gamma_{HS^-}}{\gamma_{S_x^=}} \text{ is proportional to } \frac{a_{H^+}\;[PSS]}{[HS^-]} \tag{75}$$

(at a constant sulfur activity)

If the two γ's were always equal or varied in a constant ratio, then the expressions in equation 74 and 75 would have to be constant.

The functions of the pH and stoichiometric data defined by equations 71-75 are given for the seven valid pH runs in Table XV:

TABLE XV

Analysis of pH Measurements in Na_2S-S-H_2S-H_2O System at 75°C

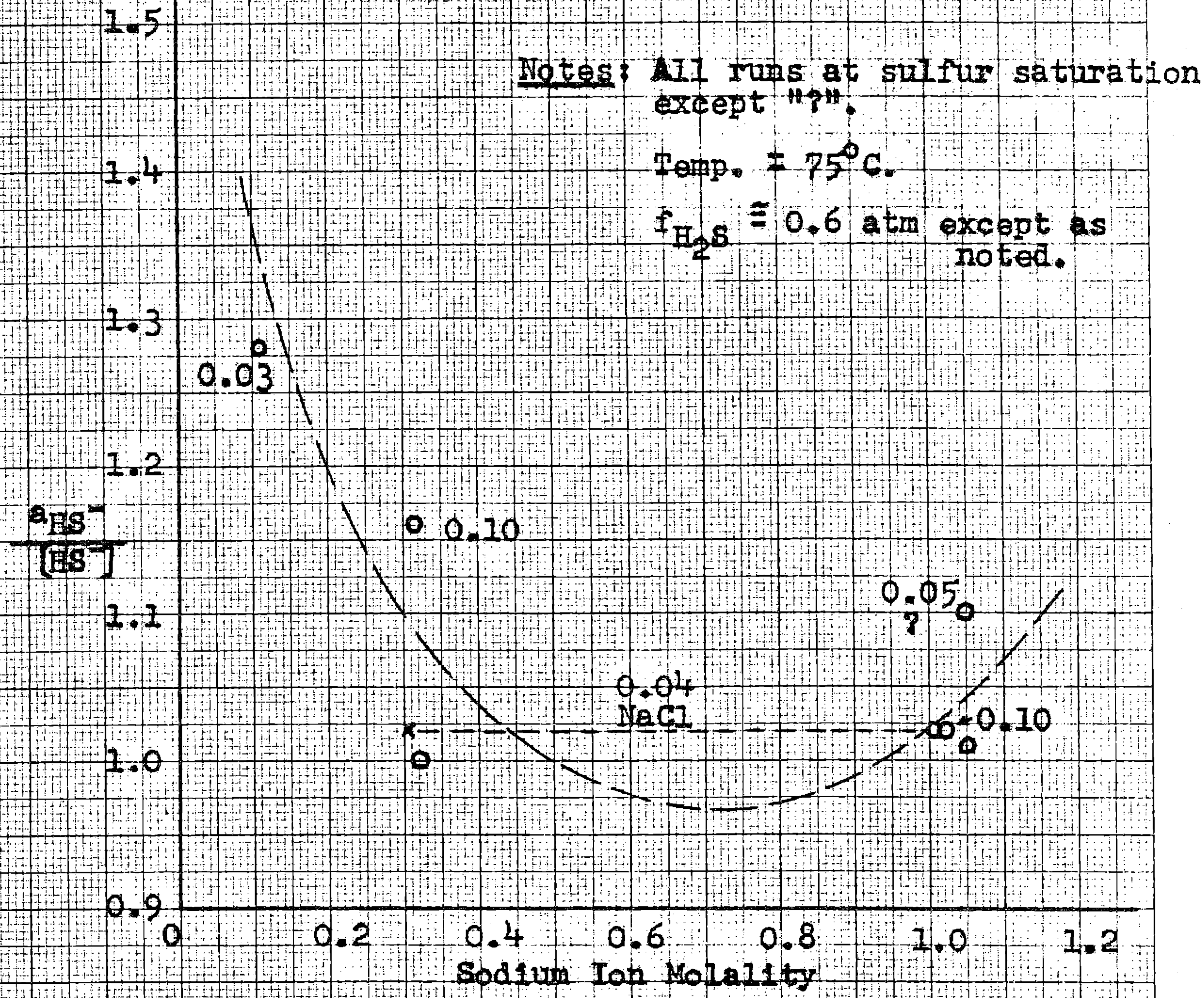
Run	E-51	E-52*	E-53	E-54	E-55	E-56	E-57
f_{H_2S}	0.640	0.0547	0.626	0.1023	0.0277	0.1010	0.0438
Molalities							
Na^+	1.049	1.048	0.319	0.312	0.1090	1.021	1.013 (0.304)
$S_x^=$	0.322	0.448	0.0660	0.1126	0.0399	0.424	0.1223
HS^-	0.405	0.151	0.187	0.0872	0.0288	0.173	0.0595
PSS	1.314	1.748	0.260	0.427	0.1651	1.680	0.476
pH	7.55	8.23	7.22	7.74	7.87	7.99	7.89
$a_{H^+} \times 10^8$	2.8	0.59	6.0	1.82	1.35	1.02	1.29
a_{HS^-}	0.41	0.166	0.186	0.101	0.037	0.177	0.061
$\left(\frac{a_{HS^-}}{[HS^-]}\right)$	1.01	1.10	1.00	1.16	1.28	1.02	1.02
$\left(\frac{a_{HS^-}}{a_{H^+}[S_x^=]}\right) \times 10^{-7}$	4.6	6.3	4.7	4.9	6.9	4.1	3.9
$\left(\frac{a_{HS^-}}{a_{H^+}[PSS]}\right) \times 10^{-7}$	1.13	1.62	1.19	1.30	1.67	1.04	1.00
$\left(\frac{a_{H^+}[S_x^=]}{[HS^-]}\right) \times 10^8$	2.2	1.8	2.1	2.3	1.9	2.5	2.7
$\left(\frac{a_{H^+}[PSS]}{[HS^-]}\right) \times 10^8$	8.9	6.8	8.4	8.9	7.7	9.8	10.2

Notes: Parentheses () indicates value calculated neglecting sodium chloride added.

* Sulfur saturation doubtful in run E-52.

The apparent hydrosulfide ionic activity coefficient $a_{HS^-}/[HS^-]$ is plotted versus sodium ion molality in Figure 25. The functions from equations 72 and 73, supposedly both proportional to the polysulfide ionic activity coefficient, similarly are plotted in Figures 26 and 27, respectively. In Figures 28 and 29 the numbers proportional to the activity coefficient ratios (equations 74 and 75, respectively) also are shown as functions of the sodium ion molality. Although considerable scatter is evident in all five graphs, Figures 25, 26, and 27 at least are not <u>incompatible</u> with the assumed average activity coefficient correlation below 1.0 sodium ion molality (Figures 23 and 24). Little or no trend in activity coefficient ratios may be observed in Figures 28 and 29. The plots of the preceding functions versus the ionic strength rather than the sodium molality were found to yield much the same information, and hence are not shown.

Even in dilute polysulfide solutions at elevated temperature the pH readings as given by the glass electrode could well be considered dubious. Some evidence of a systematic error in hydrogen ion activity, in addition to the more than 10 per cent possible random error, is seen in Figure 25; the numerical ratio $a_{HS^-}/[HS^-]$ actually should approach unity as the concentration approaches zero. Nevertheless it is felt that the changes in indicated pH should reflect, at least to some degree, the actual changes in hydrogen



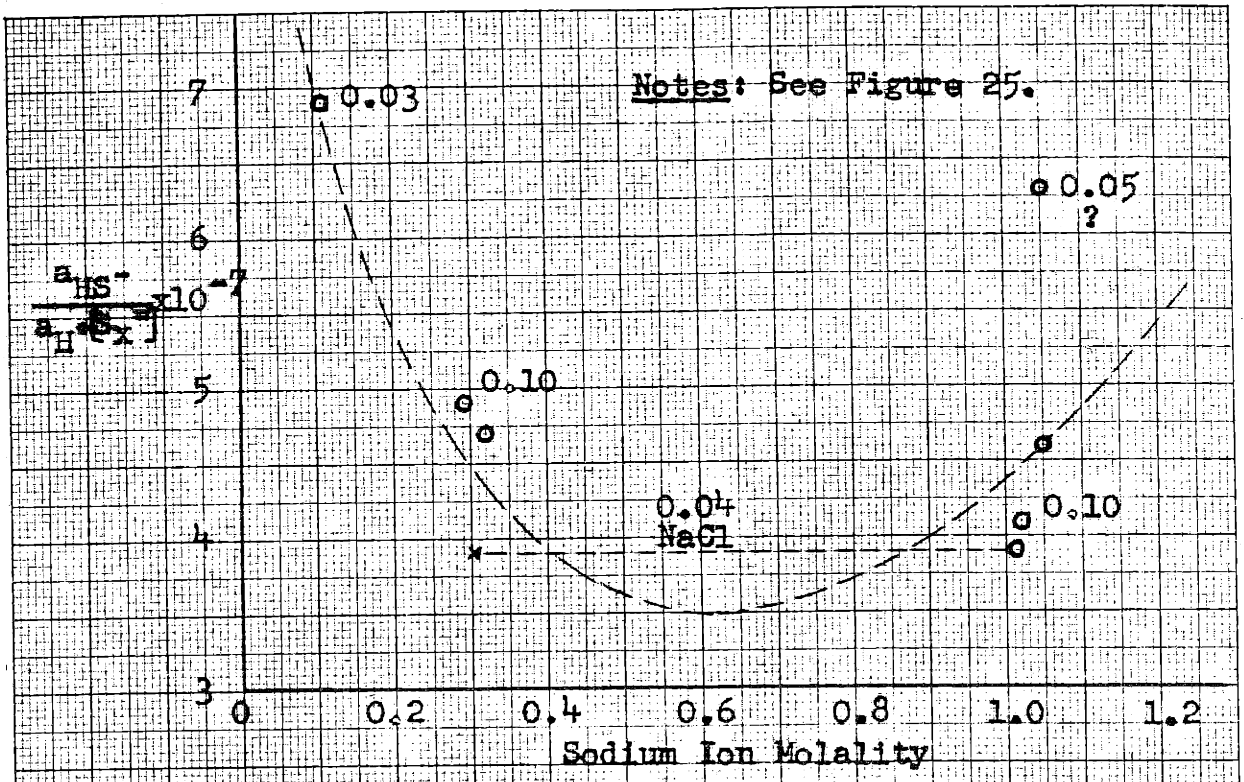
Notes: All runs at sulfur saturation except "?".

Temp. ± 75°C.

$f_{H_2S} \cong 0.6$ atm except as noted.

FIGURE 25

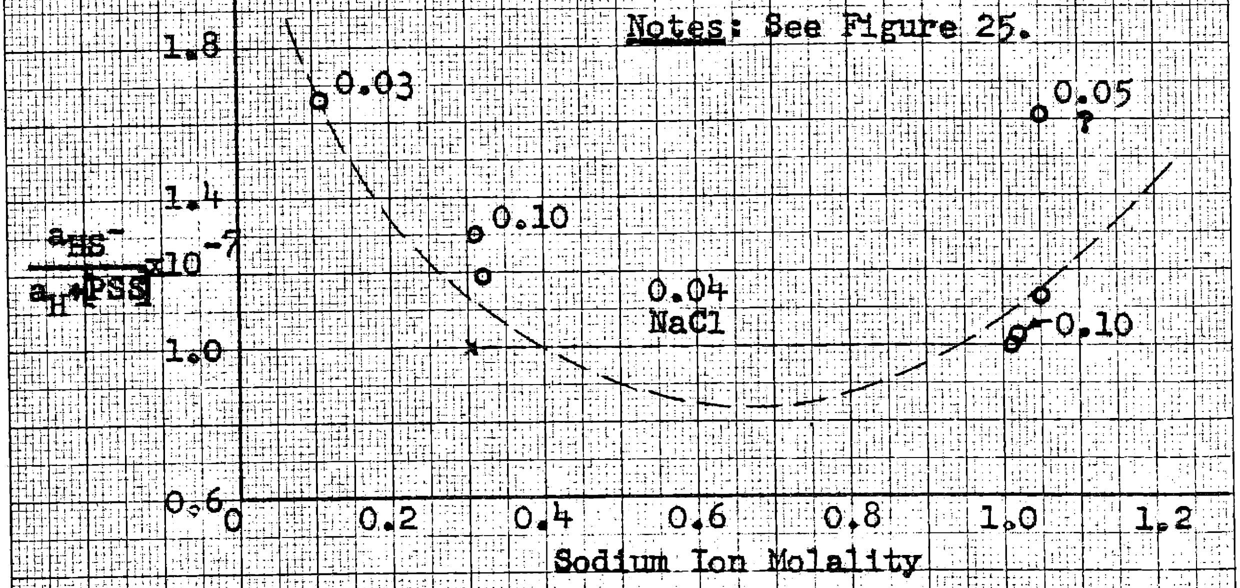
Hydrosulfide Ionic Activity Coefficients by pH



Notes: See Figure 25.

FIGURE 26

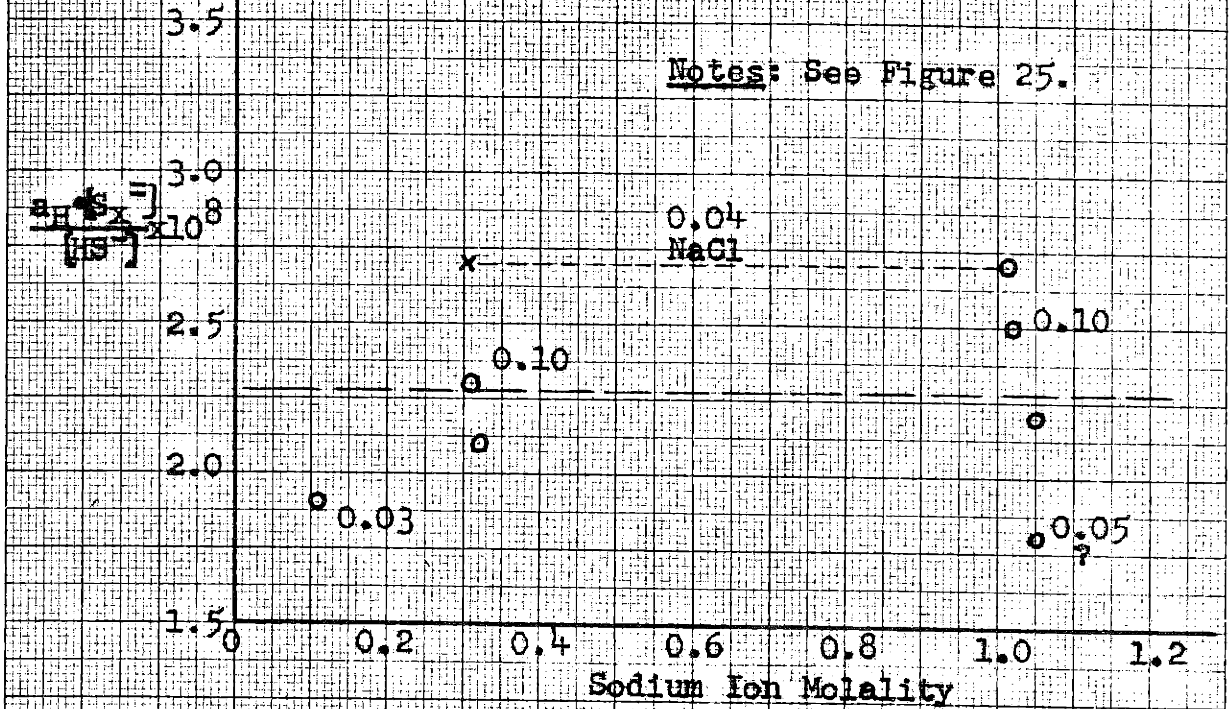
Polysulfide Ionic Activity Coefficients by pH
(Based on Polysulfide Ion)



Notes: See Figure 25.

FIGURE 27

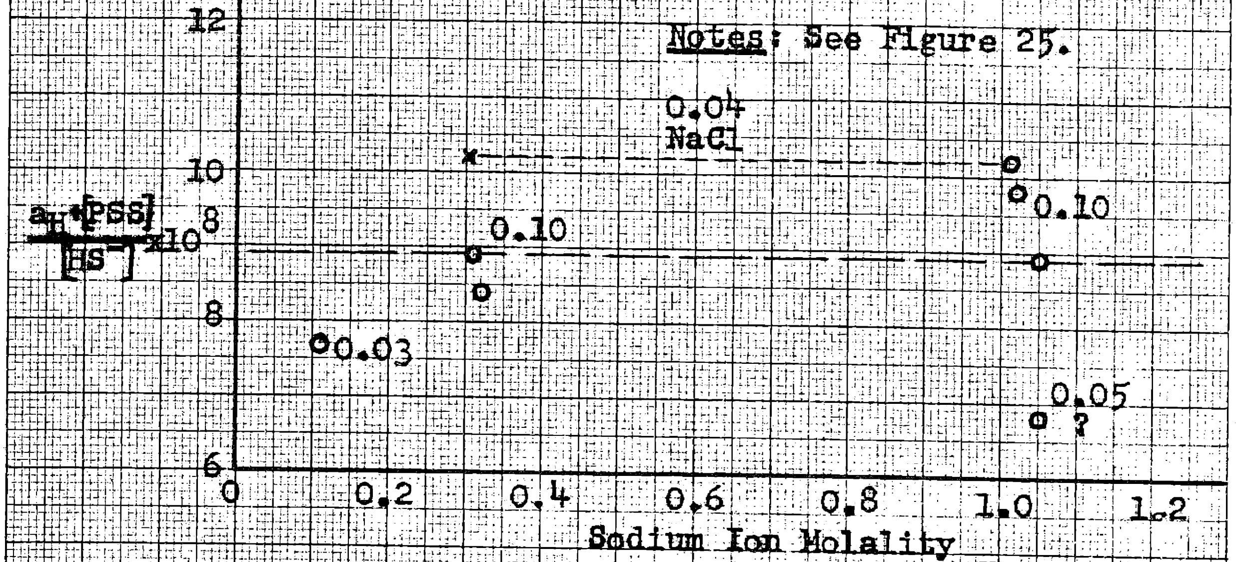
Polysulfide Ionic Activity Coefficients by pH
(Based on Polysulfide Sulfur)



Notes: See Figure 25.

FIGURE 28

Ionic Activity Coefficient Ratios by pH
(Based on Polysulfide Ion)



Notes: See Figure 25.

FIGURE 29

Ionic Activity Coefficient Ratios by pH
(Based on Polysulfide Sulfur)

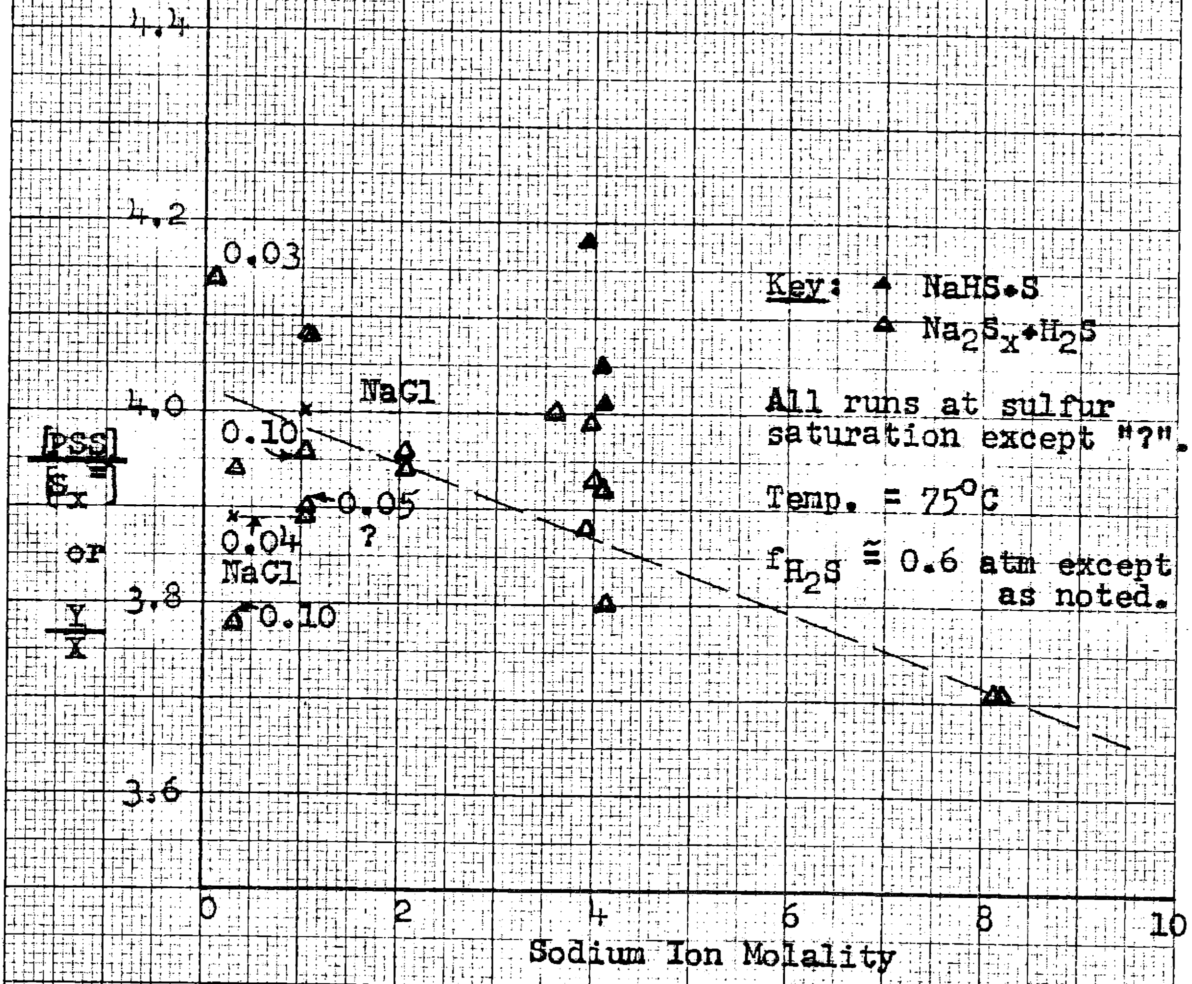
ion activities.

3. Effects of Individual Ionic Activity Coefficients

Since the apparent individual ionic activity coefficients indicated by the glass electrode measurements were under suspicion, the stoichiometric equilibrium data again were examined to discover if the effects of individual activity coefficients could be analyzed without recourse to the pH data. From equations 47 and 48 it is evident that if the activity coefficients of all the polysulfide ions were equal (or even in a constant ratio), the ratio Y/X or $PSS/S_x^=$ also should be constant at a given sulfur activity:

$$\frac{Y}{X} = \frac{PSS}{S_x^=} = \frac{\dfrac{k_1 a_{S_8}^{1/8}}{\gamma_{S_2^=}} + \dfrac{2k_2 a_{S_8}^{2/8}}{\gamma_{S_3^=}} + \dfrac{3k_3 a_{S_8}^{3/8}}{\gamma_{S_4^=}} + \ldots}{\dfrac{k_1 a_{S_8}^{1/8}}{\gamma_{S_2^=}} + \dfrac{k_2 a_{S_8}^{2/8}}{\gamma_{S_3^=}} + \dfrac{k_3 a_{S_8}^{3/8}}{\gamma_{S_4^=}} + \ldots} \qquad (76)$$

The ratios Y/X for the sulfur saturation experiments at 75°C are plotted against sodium ion molality in Figure 30. A downward trend with concentration is particularly marked from 4.0 m to 8.0 m sodium ion. Inspection of equation 76 shows that such would be the case if some of the higher polysulfide activity coefficients increased more rapidly with concentration than did the coefficients of the lower ions. Since any really quantitative correlation could not be made, however, the ratio $PSS/S_x^=$ at any given temperature



All runs at sulfur saturation except "?".

Temp. = 75°C

$f_{H_2S} \cong 0.6$ atm except as noted.

FIGURE 30

Effect of Individual Ionic Activity Coefficient Variation on Y/X and any given sulfur activity will be assumed constant throughout the remainder of this thesis.

As has been shown, the pH results were not sufficiently precise for separating the quantity γ_{avg} into its components $(\gamma_{avg} = (\gamma_{HS^-})^2/\gamma_{S_x^=})$. Harned and Owen (35), however, propose a rule by which the individual ionic activity coefficients can be characterized in mixtures of concentrated electrolytes:

$$\ln \gamma_{S_1} \text{ in } S_1\text{-}S_2 \text{ mixture (at constant total ionic strength) is linear in the ionic strength of } S_1. \tag{77}$$

in which S_1 and S_2 are the two salts used in making up the electrolyte.

Harned and Owen qualify their rule by adding that equation 77 is only approximate and that higher powers of the ionic strength may be required. Since the final equilibrium solutions in the Na_2S-S-H_2S-H_2O system nevertheless could be considered as mixtures of sodium polysulfide and sodium hydrosulfide, some of the observed scatter in the "average" activity coefficient thus might be caused by variations the relative proportions of the two salts.

To test this possibility, the ratios of HS^- ion concentration to sodium ion molality were computed for the sulfur saturation runs at 75°C. Using these numbers as guides, contours of constant ratio then were drawn on the plots of X and Y versus ionic strength (Figures 21 and 22). The results are shown in Figures 31 and 32, respectively. In spite of the scatter of the points some correlation between γ_{avg} and $[HS^-] / [Na^+]$ is evident. The indicated curves, however, were sufficiently dubious that equation 77 could not be employed to calculate the separate values of γ_{HS^-} and $\gamma_{S_x^=}$. Since the use of these individual ionic activity coefficients moreover would require unwarranted trial-and-error procedures in the calculation of equilibrium constants and polysulfide compositions, only the activity coefficient γ_{avg} will be employed in the remaining portions of this thesis.

4. Estimation of Numerical Activity Coefficient Values

While the shape of the "recommended" ionic activity coefficient correlation (Figure 23 or Figure 24) was chosen considering only the results of the present thesis, reference to activity coefficient relations given in the literature was required in order that numerical values of γ_{avg} could be obtained. In Figure 33 the recommended average activity coefficient correlation versus sodium ion molality is shown, derived from either Figure 23 or Figure 24. For comparison purposes the mean activity coefficient curve for sodium chloride at 25°C (taken from the literature (35)), and the two dubious hydrosulfide ion activity coefficient points obtained by pH measurements

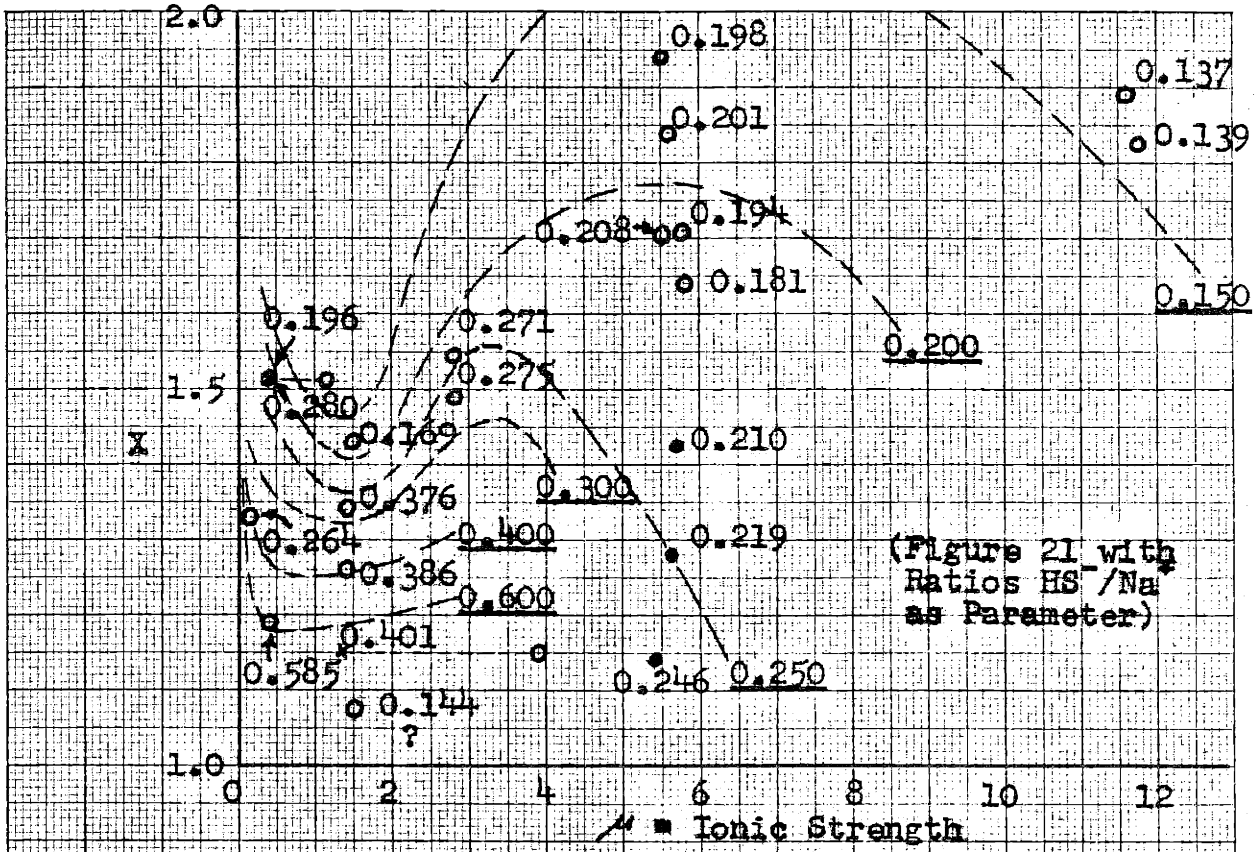


FIGURE 31

Effect of Individual Ionic Activity Coefficient Variation on X

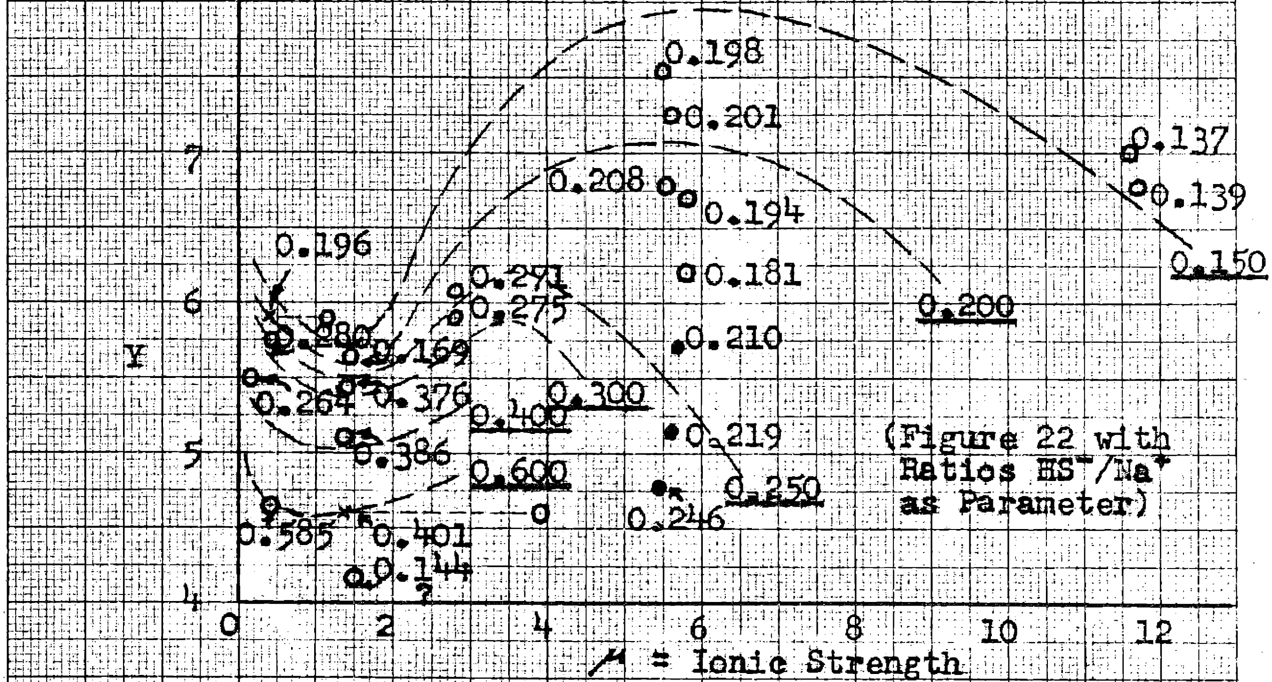


FIGURE 32

Effect of Individual Ionic Activity Coefficient Variation on Y (in the present thesis) also are plotted in Figure 33. As has been noted, the addition of sodium chloride at 1.0 initial sodium ion molality did not affect γ_{avg} within the scatter of the data. This circumstance was considered reasonable only if the average ionic activity coefficient γ_{avg} at this molality was nearly the same as that of the sodium chloride at the same concentration. The intercepts indicated in Figures 23 and 24 and thus the absolute values of γ_{avg} shown in Figure 33 accordingly were chosen so that these two activity coefficient curves coincided at 1.0 sodium ion molality. (In view of the lack of information to the contrary the change in sodium chloride activity coefficient with temperature was assumed to be nil.)

For purposes of further comparison the activity coefficients (35) of four other electrolytes besides sodium chloride are plotted against ionic strength in Figure 34. Simultaneous examination of the two graphs is facilitated if it is remembered that for 1-1 sodium cation electrolytes the sodium molality and the ionic strength are identical. Even though the γ_{avg} activity coefficient correlation shown in Figure 33 does not quite resemble any of the curves for the other salts, it need not necessarily be wrong, since the polysulfide system admittedly is more complex.

Considering that the "recommended" ionic activity coefficient correlation is none too reliable, it is

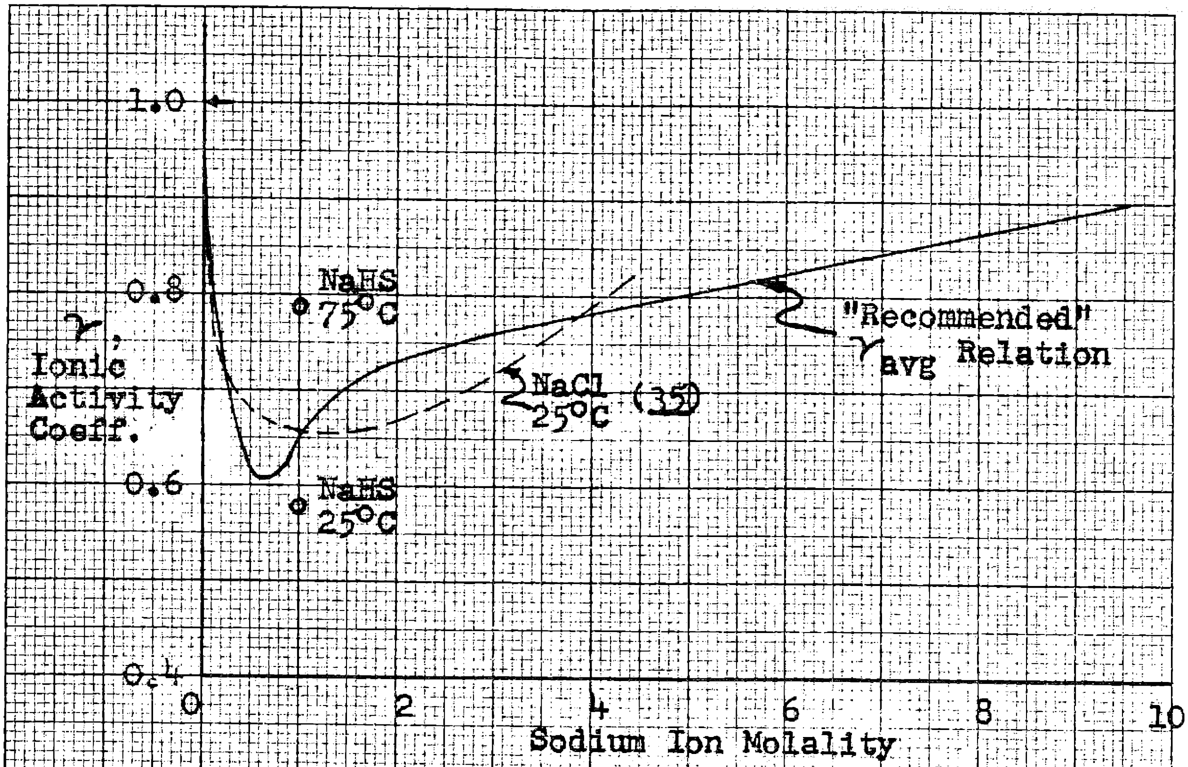


FIGURE 33

"Average" Ionic Activity Coefficients at 75°C

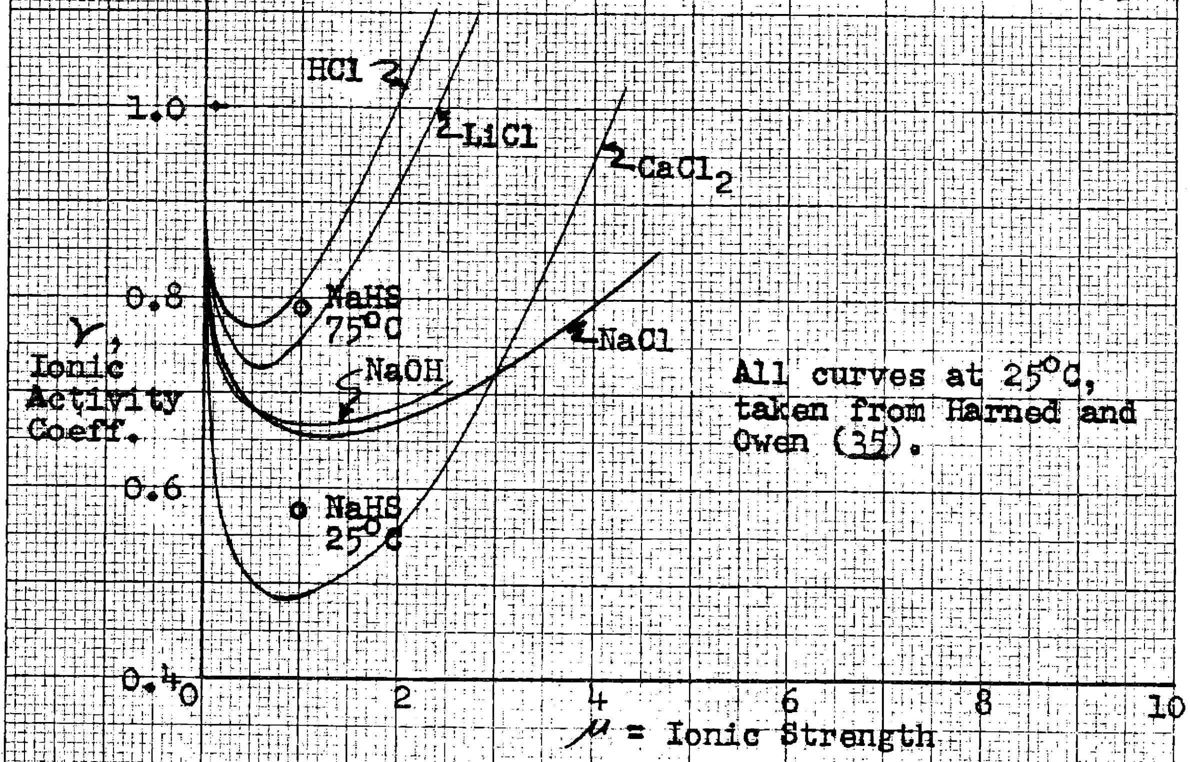


FIGURE 34

Ionic Activity Coefficients for Various Electrolytes important to note that activity coefficient values were not required for the determination of the relative polysulfide equilibrium constants. Only the relative γ_{avg} relation moreover was needed for the calculation of absolute equilibrium constant values and for the computation of ionic distributions in most polysulfide solutions.

D. Determination of Sulfur Activities

1. Sulfur Activities by Integration of Stoichiometric Data

In order to solve relations such as equations 49 and 50 (or equations 54 and 55) for the unknown polysulfide equilibrium constants it was necessary to have, in addition to the tabulated quantities X and Y, the values of elemental sulfur activity at conditions where sulfur saturation was not present. These sulfur activities indeed could be measured experimentally (and independently) by the xylene extraction technique, but also could be derived, as now will be shown, by a simple graphical integration of the X and Y data. Consider equations 49 and 50:

$$X = \gamma_{avg}\left(\frac{K_2}{K_1}\right)\left[k_1 a_{S_8}^{1/8} + k_2 a_{S_8}^{2/8} + k_3 a_{S_8}^{3/8} + \dots\right] \tag{49}$$

$$Y = \gamma_{avg}\left(\frac{K_2}{K_1}\right)\left[k_1 a_{S_8}^{1/8} + 2k_2 a_{S_8}^{2/8} + 3k_3 a_{S_8}^{3/8} + \dots\right] \tag{50}$$

If γ_{avg} is assumed constant, differentiation of equation 49 with respect to $a_{S_8}^{1/8}$ yields:

$$\frac{d\ X}{d\ a_{S_8}{}^{1/8}} = \gamma_{avg} \left(\frac{K_2}{K_1{}'}\right) \left[k_1 + 2k_2 a_{S_8}{}^{1/8} + 3k_3 a_{S_8}{}^{2/8} + \dots \right] \tag{78}$$

From equation 78 and equation 50 the following must be true:

$$a_{S_8}{}^{1/8} \frac{d\ X}{d\ a_{S_8}{}^{1/8}} = \underline{Y} \tag{79}$$

Equation 79 may be rearranged to give:

$$\frac{d\ a_{S_8}{}^{1/8}}{a_{S_8}{}^{1/8}} = \frac{1}{Y}\, d\ X \tag{80}$$

The preceding equation now may be integrated between limits to yield the elemental sulfur activity values for all conditions at which X and Y are known:

$$-\ln\ a_{S_8}{}^{1/8} = \int_{X}^{X sat.} \frac{1}{Y}\ d\ X \tag{81}$$

$$\left(\text{since } \ln\ a_{S_8}{}^{1/8} = 0 \text{ at } X = X_{sat.}\right)$$

This integration has been performed on the 75°C equilibrium data at the two sodium ion molalities (4.0 m and 1.0 m) at which traverses at sulfur activities less than unity were carried out. In both these cases it was necessary to assume, of course, that γ_{avg} was constant at a given sodium molality. The integration curves as drawn through the data points are shown for the 4.0 m and 1.0 m traverses in Figures 35 and 36, respectively. Although the X and Y values scatter considerably,

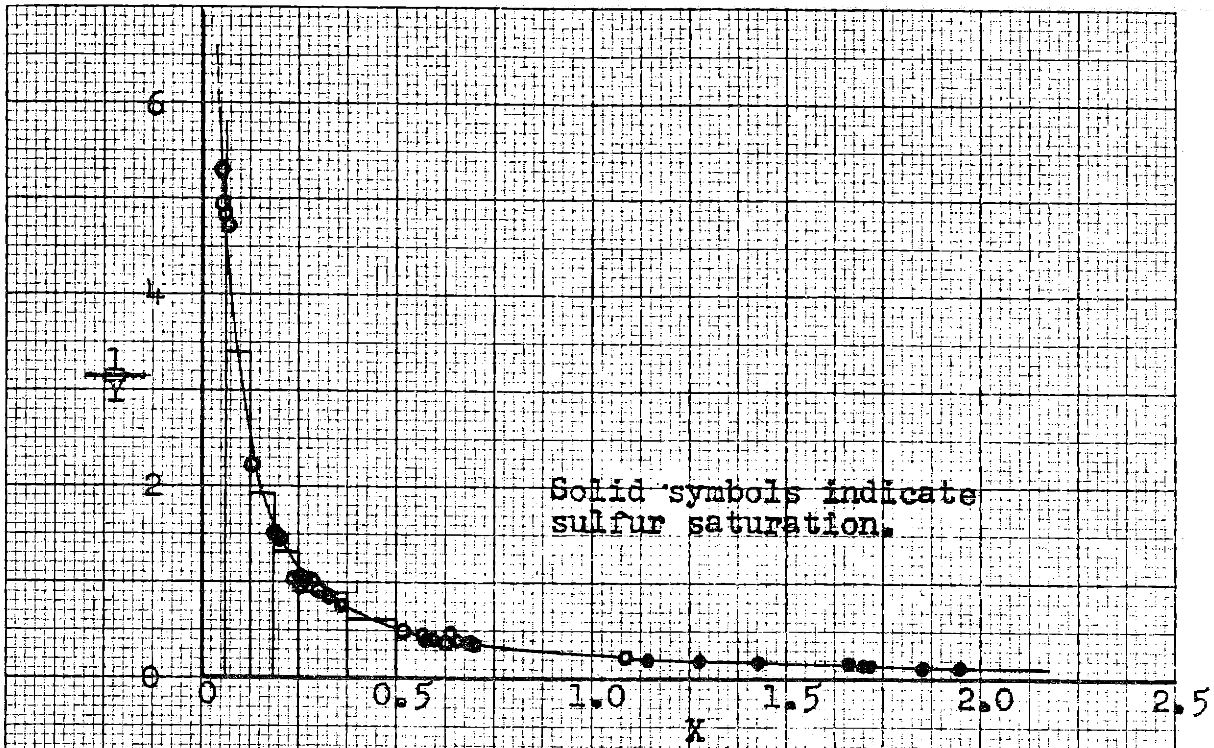
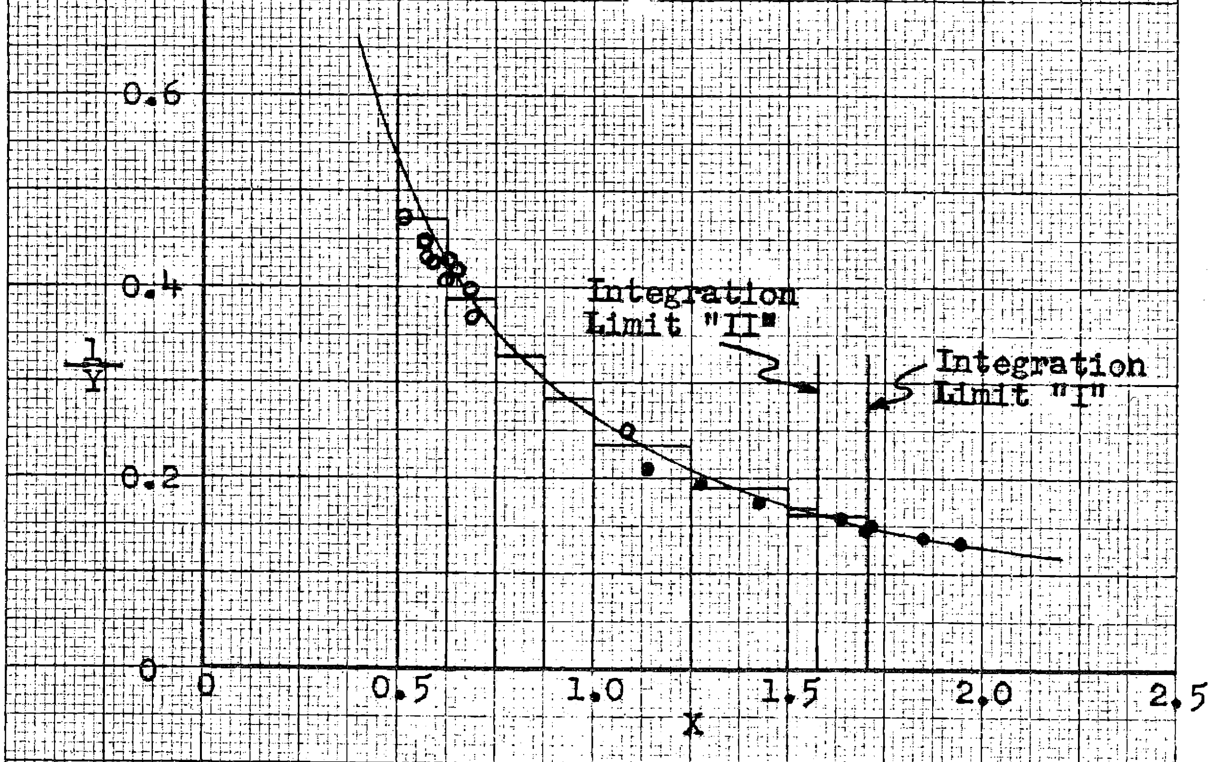


FIGURE 35

Graphical Integration at Na$^+$ = 4.0 m



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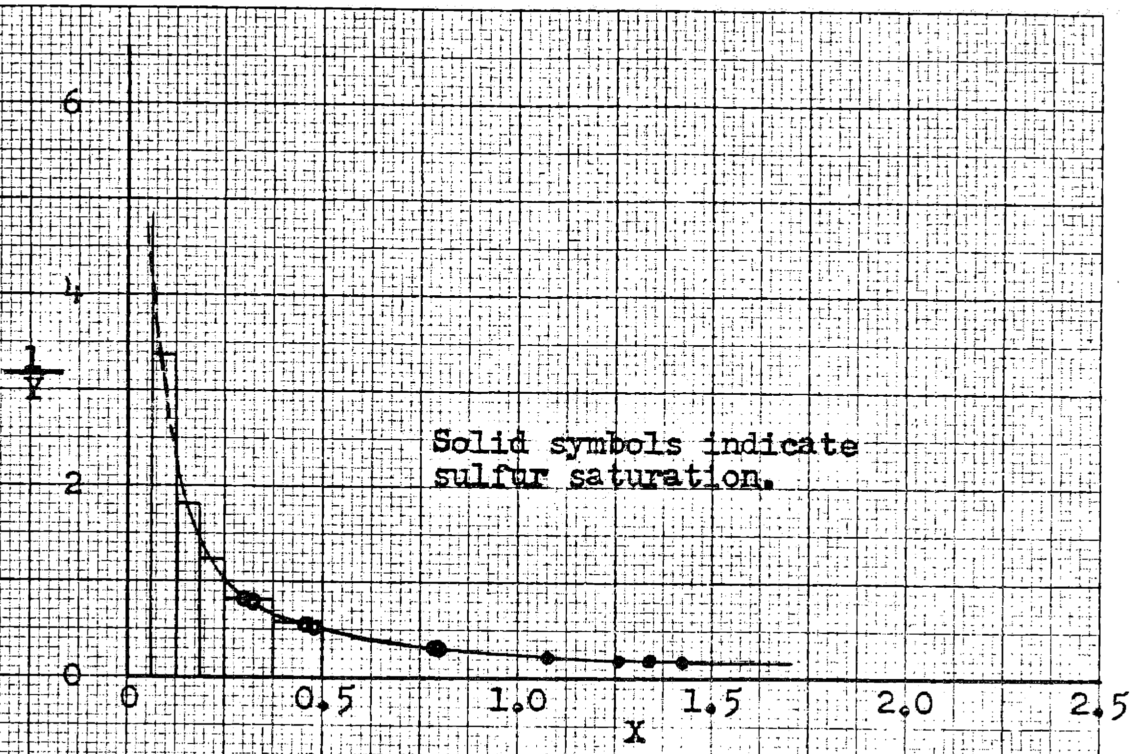
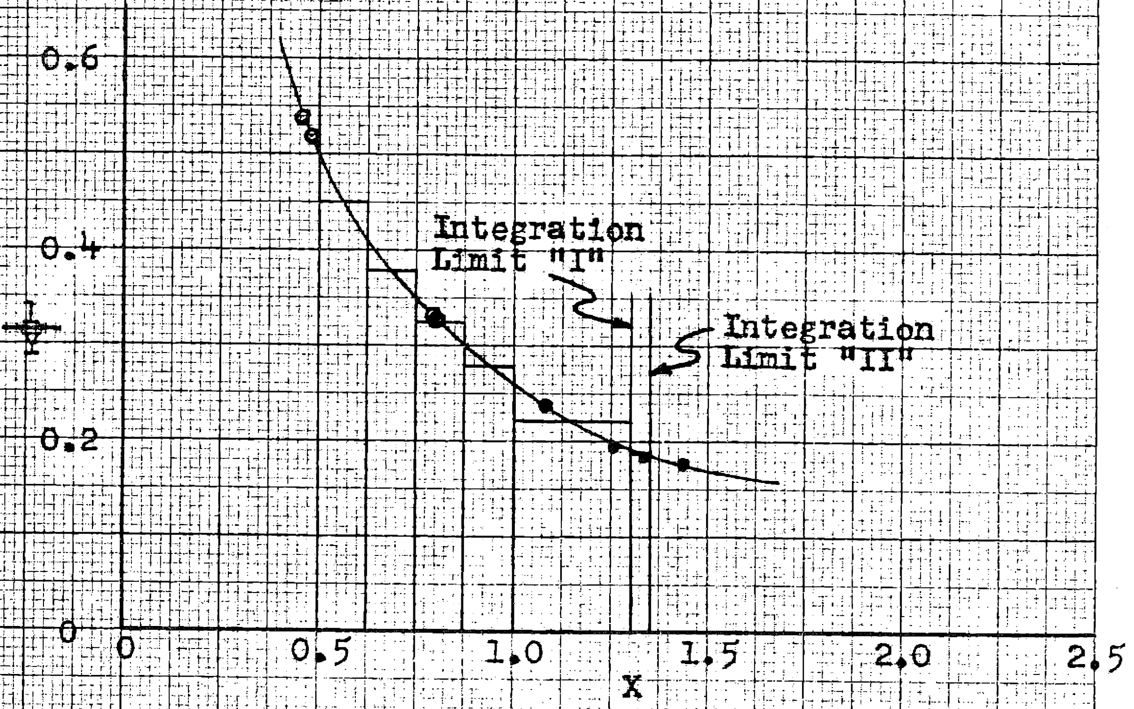


Solid symbols indicate sulfur saturation.

FIGURE 36

Graphical Integration at $\text{Na}^+ = 1.0$ m



(Enlarged Section)

the ratio Y/X was somewhat more reproducible; hence the integration curves are fairly well defined. Thus the relative values of sulfur activity could be obtained to a reasonably good precision. The absolute sulfur activity values, on the other hand, were more in doubt, owing to the 10-20 per cent scatter in X and Y at sulfur saturation and hence this uncertainty in the upper limit to the integration. As will be shown, however, this apparent lack of precision in sulfur activity could be considered in effect merely an uncertainty in the value of γ_{avg}, the ionic activity coefficient.

Indicated in Figures 35 and 36 are two sets of possible integration limits. The "I" limits were estimated by preliminary visual inspection, whereas the "II" limits were chosen, as will be shown, to make the calculated sulfur activities at the two molalities compatible with measured xylene sulfur concentrations. The "II" integration limits and their corresponding curves of X and Y versus sulfur activity therefore are believed to be the more nearly correct of the two. In Figures 37 and 38 the functions X and Y, respectively, are plotted against the sulfur activities derived by the integration at 4.0 sodium ion molality; the X and Y relations at 1.0 m similarly are shown in Figures 39 and 40, respectively.

The errors carrying through the integration process should be smaller, if anything, than the errors in the ratio Y/X,

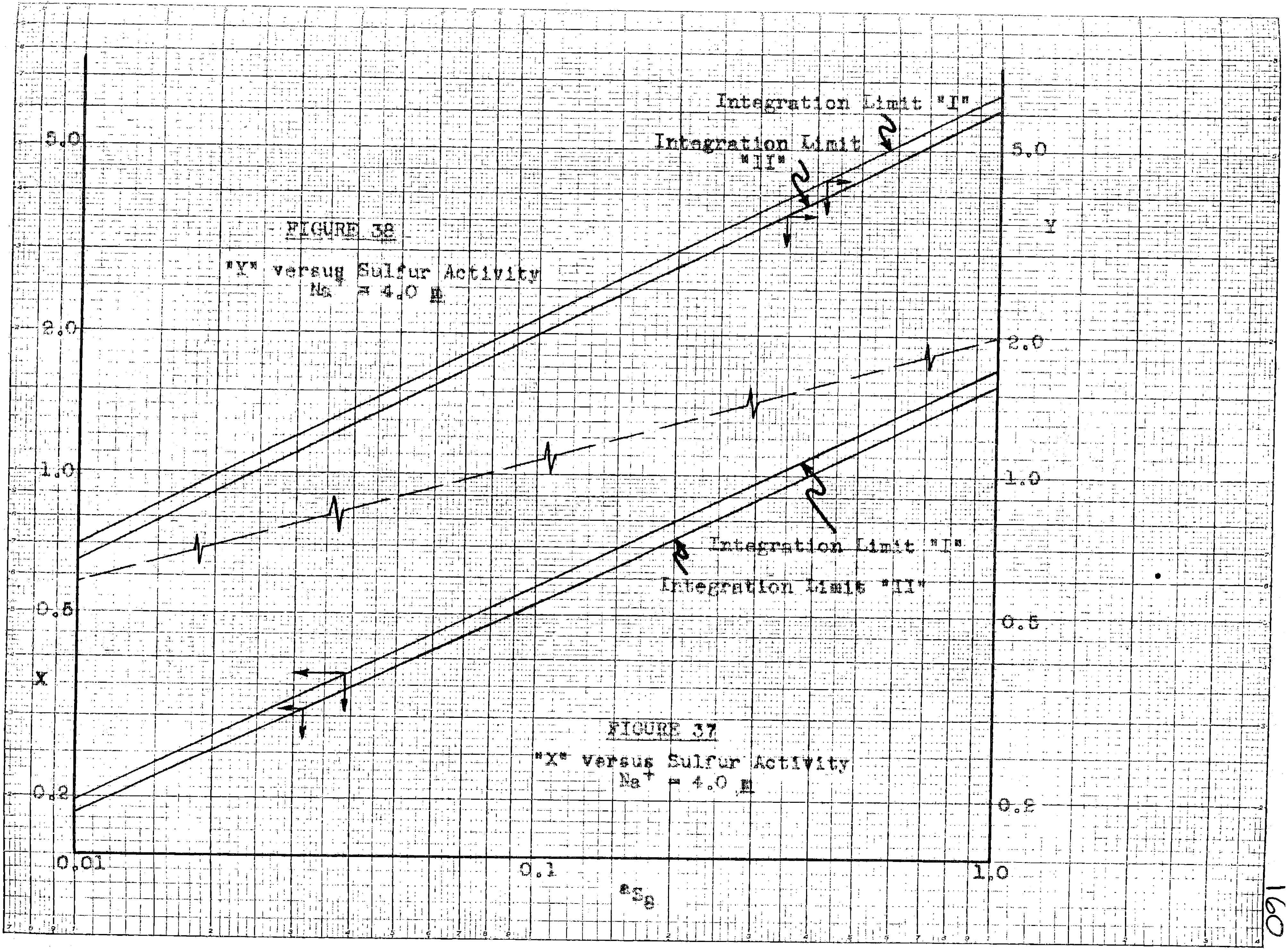


FIGURE 38

"Y" versus Sulfur Activity
Na^+ = 4.0 m

FIGURE 37

"X" versus Sulfur Activity
Na^+ = 4.0 m

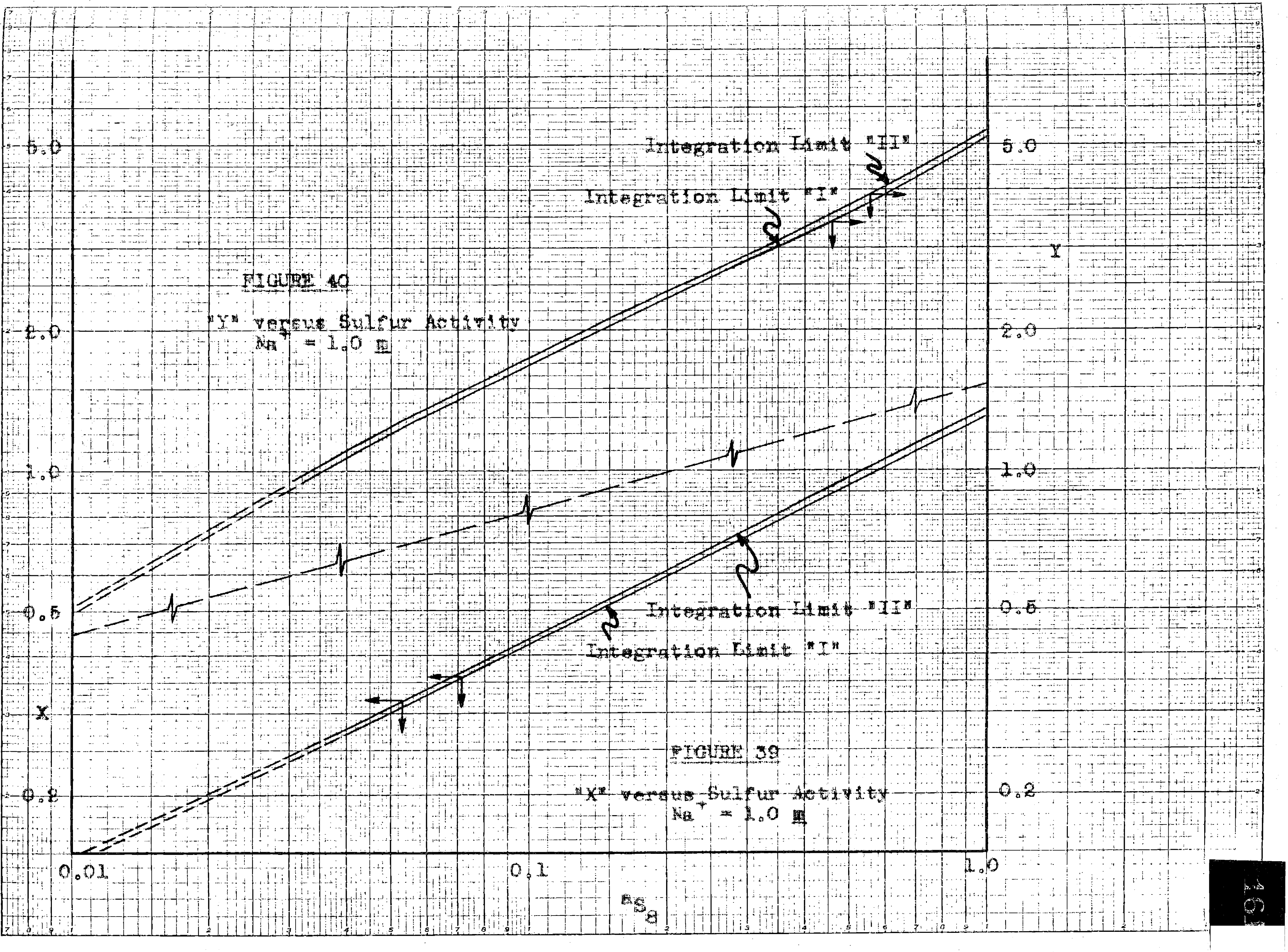


FIGURE 40

"Y" versus Sulfur Activity
$Na^+ = 1.0$ m

FIGURE 39

"X" versus Sulfur Activity
$Na^+ = 1.0$ m

on which the integration is based. If a 3 per cent error in the actual integration summation were assumed, the error in the <u>relative</u> sulfur activity would be about 6.6 per cent at $a_{S_8} = 0.1$. Since this uncertainty becomes proportionately larger further away from sulfur saturation, the integration curves below a sulfur activity of 0.01 in general were not considered accurate for the determination of polysulfide equilibrium constants.

2. Comparison with Xylene Data

Had the vapor pressure measurements of Simmons (60) yielded a valid relation between xylene sulfur concentration and sulfur activity, the xylene determinations of the present thesis then might have provided an independent check on the sulfur activities derived by integration. Even without this vapor pressure information, however, it was possible to check the calculated sulfur activities at 1.0 sodium ion molality against those derived at 4.0 *m*, using the indisputable rule that the sulfur activities, even if numerically unknown, still must be the same in two experiments with equal xylene sulfur concentrations. For each xylene run a value of a_{S_8} could be obtained from the calculated X, using Figure 37 or Figure 39; a second sulfur activity value then could be found from the quantity Y with the aid of either Figure 38 or Figure 40. The average of these two numbers was taken as the elemental sulfur activity corresponding to the measured xylene sulfur concentration.

The sulfur activities thus determined using the "I" correlations are plotted against xylene sulfur concentration in Figure 41. Inspection shows that the 1.0 m points do not agree with those determined using the data at 4.0 sodium ion molality. Far from indicating a possible flaw in assumptions or experimental technique, this discrepancy merely signifies that the "I" sulfur saturation limits as estimated in Figures 35 and 36 are not compatible with each other.

The "II" sulfur saturation limits accordingly were chosen so as to yield essentially the same activity versus xylene sulfur concentration relation for both molalities, and still to be roughly centered within the scatter of the sulfur saturation X and Y data. The sulfur activities thus derived are shown versus xylene sulfur concentration in Figure 42. In this case examination indeed verifies that the points for the most part could be fitted by a single curve, as would have to be true if the sulfur activities were correct. The possible significance of this curve compared to the findings of Simmons (60) will be discussed later.

Reference to the integration procedure (equation 81) indicates that a shift in the sulfur saturation limit changes the sulfur activity at a given X (or Y) only by a constant factor. Thus any number of other possible pairs of inte-

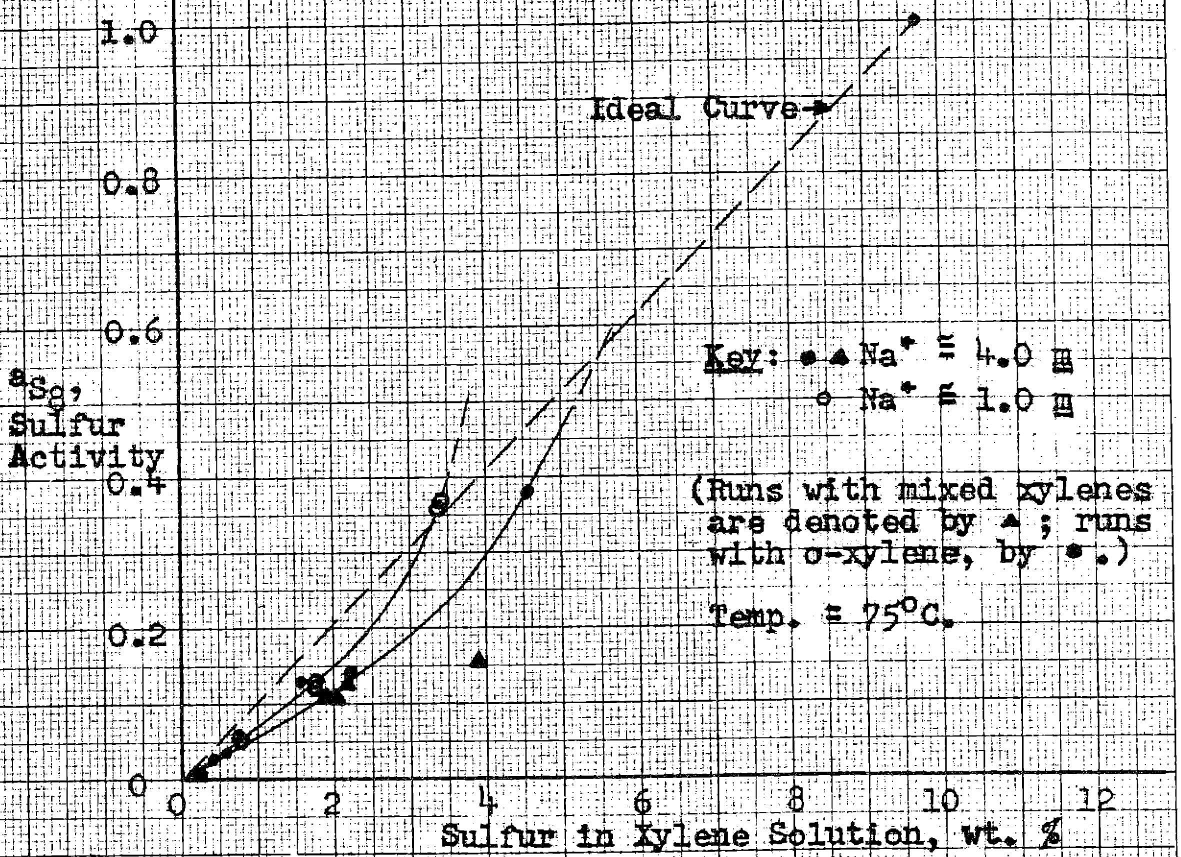
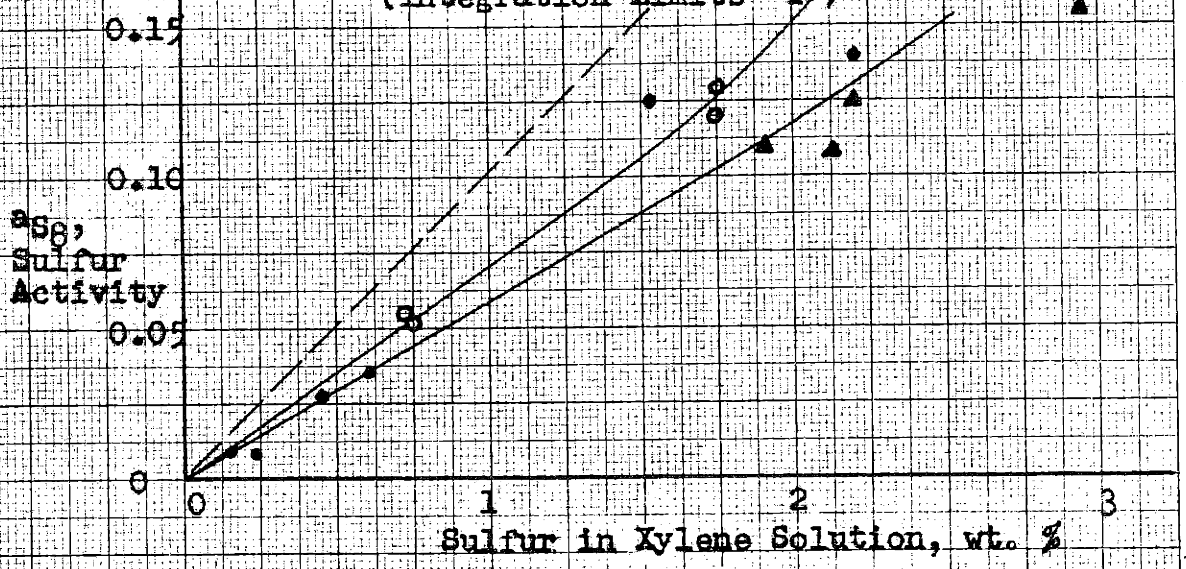


FIGURE 41

Activity versus Concentration, Sulfur in o-Xylene
(Integration Limits "I")



(Enlarged Section)

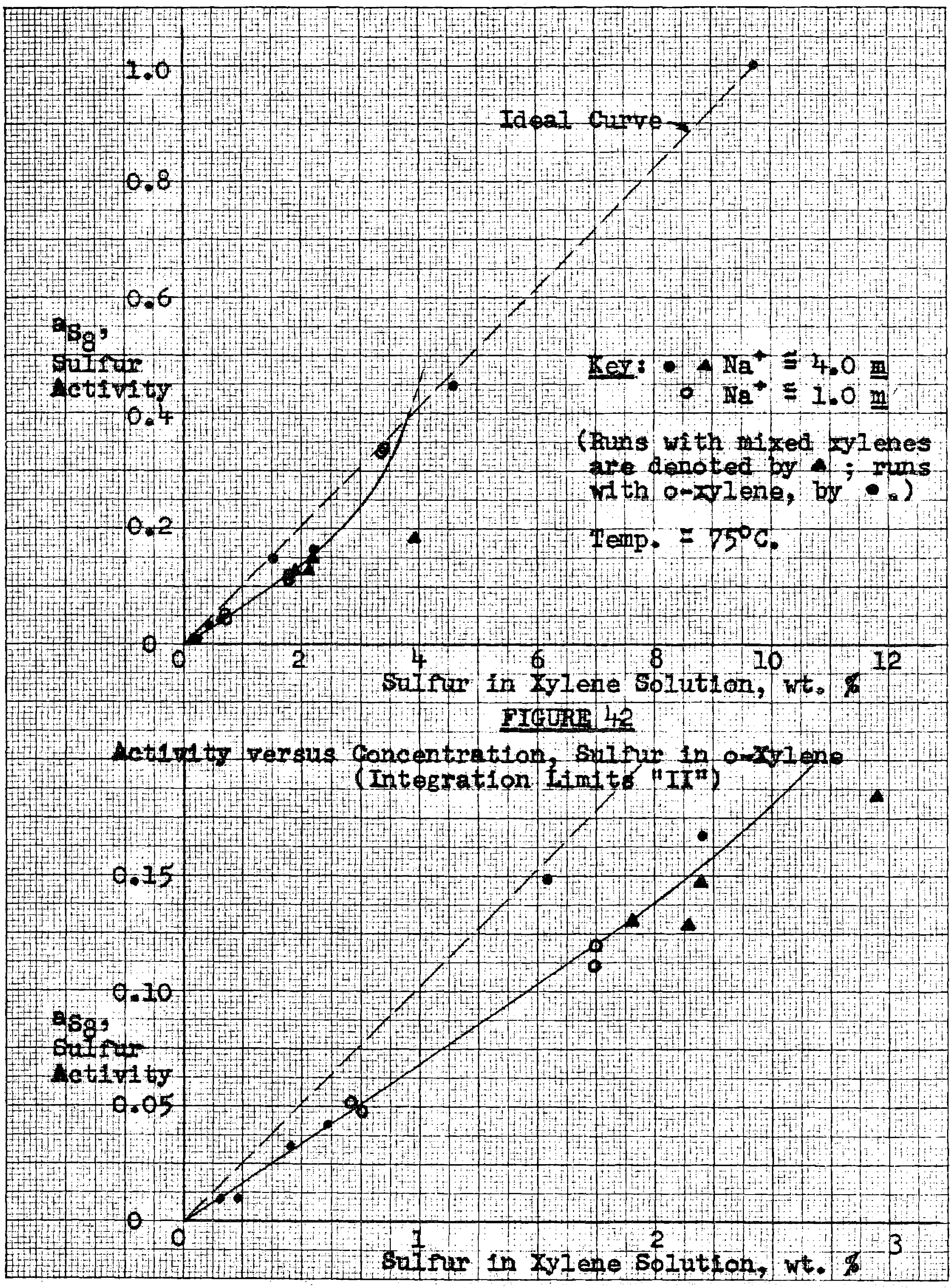


FIGURE 42

Activity versus Concentration, Sulfur in o-Xylene (Integration Limits "II")

(Enlarged Section)

gration limits similar to the "II" correlations might be found which would be equally compatible with the measured xylene sulfur concentrations, though perhaps not as well centered within the scatter of the X and Y data. It might be expected that the polysulfide equilibrium constants to be derived would differ depending on this choice of integration limits. Although the change in either X or Y <u>at a given sulfur activity</u> upon shifting the sulfur saturation limit cannot be expressed by a simple relation, examination of Figures 37-40 indicates that to a good approximation X and Y themselves are changed only by a constant factor. Inspection of equations 49 and 50 then leads to the conclusion that a change in the integration limit in effect multiplies only γ_{avg} by a factor, and thus does not alter the unknown k's.

If the average ionic activity coefficient truly is a function only of sodium ion molality, then the X versus a_{S_8} curve in Figure 39 must lie in a constant ratio to the corresponding curve in Figure 37; similar considerations also should apply to the Y correlations in Figures 38 and 40. The actual ratios between the 1.0 $\underline{m}$ sodium ion curves and the 4.0 $\underline{m}$ curves are shown for the X and Y relations in Figures 43 and 44, respectively. Considering the scatter and the relative paucity of the data at the lower ionic concentration, the activity coefficient ratio indeed appears not to be too far from constant. Since the "II"correlations were considered the more nearly correct, the ratio of γ_{avg} at 1.0 $\underline{m}$ to

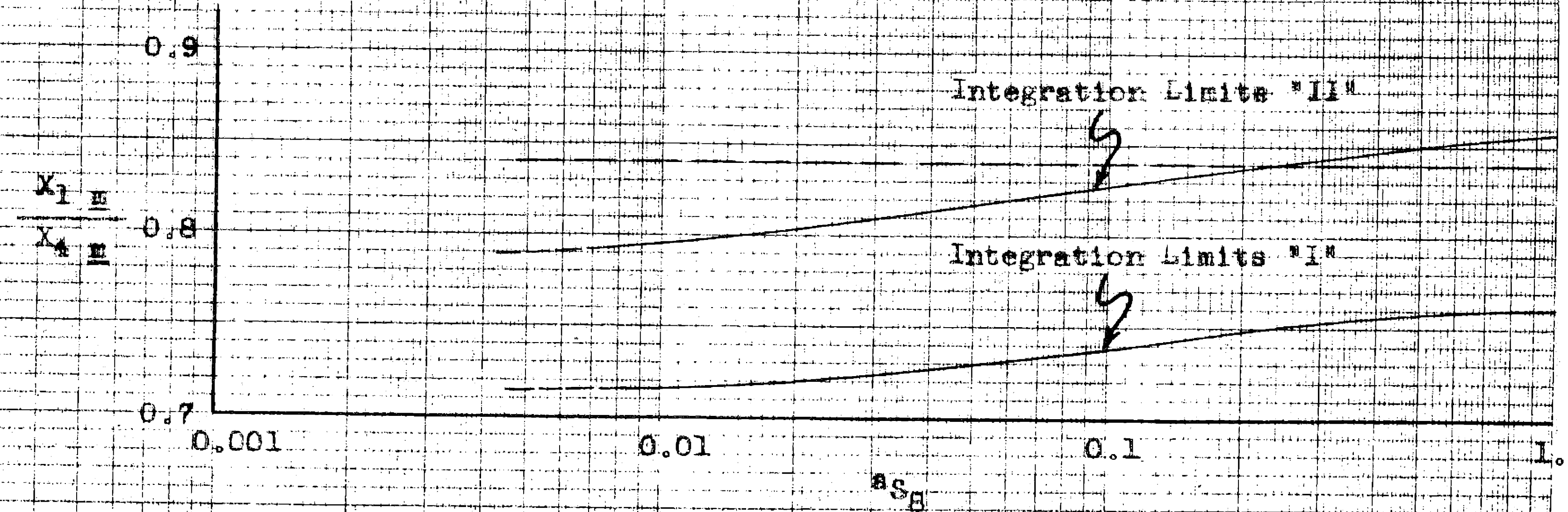


FIGURE 43

"X" Ratios, 1.0 m to 4.0 m

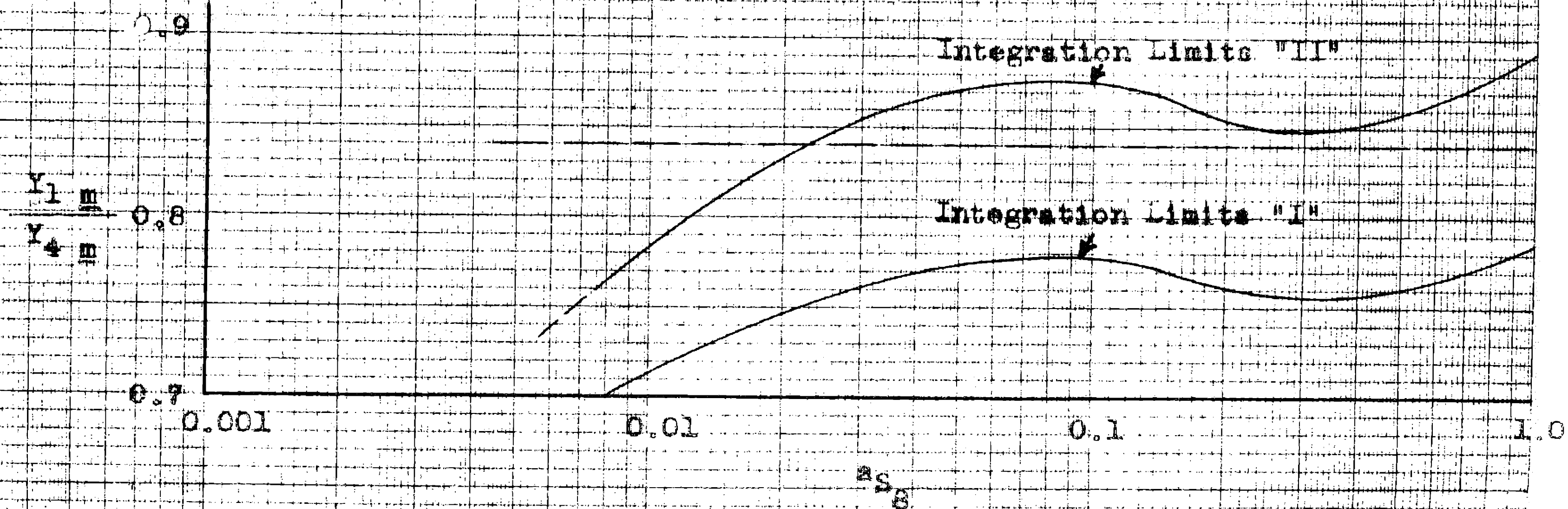


FIGURE 44

"Y" Ratios, 1.0 m to 4.0 m

γ_{avg} at 4.0 m was taken to be 0.841 in drawing the activity coefficient correlation curves in Figures 23, 24, and 33.

In conclusion, owing to the scatter in the sulfur saturation data the measured xylene sulfur concentrations at the two molalities had to be employed in fixing the best limits for integration. Thus these xylene data did in effect, determine the ionic activity coefficient ratio between the two sodium ion molalities, but at the same time no longer could be used as a completely independent check on the sulfur activities derived by integration. Had the xylene experiments been carried out at varying hydrogen sulfide partial pressures as well as at varying molalities, the constancy of γ_{avg} at a given sodium ion concentration might have been checked more conclusively than was possible in the present thesis.

3. Activity vs Concentration, Sulfur in o-Xyelene

The sulfur activities derived in the preceding section can be compared to the vapor pressure measurements of Simmons (60). These differential pressure data indicated, at 74.2°C and 0.03999 mol fraction S_8 at saturation, an o-xylene activity of either 0.9654 or 0.9629, depending on which of the two experimental values was assumed correct. Thus Simmons concluded that the sulfur-xylene system exhibits a positive deviation from ideality.

In Figure 45 the results of Simmons are compared to the xylene activities calculated assuming (a) ideality, and (b) the "symmetrical relations". The former, of course, gives a linear relation between activity and concentration. The latter, valid for so-called "regular solutions", are defined as follows:

$$\ln \frac{a_{S_8}}{y_{S_8}} = \Gamma\, (y_{Xyl})^2 \qquad (82)$$

$$\ln \frac{a_{Xyl}}{y_{Xyl}} = \Gamma\, (y_{S_8})^2 \qquad (83)$$

in which y is mol fraction in solution.

Γ is a constant.

Thus the value of Γ and hence the xylene activity curve for the symmetrical (simplified Margules) relations could be derived knowing only the sulfur solubility. The curves shown in Figure 45 were calculated for 75°C (sulfur solubility = 0.0430 mol fraction) rather than 74.2°C, so that they might be directly comparable with the xylene data of the present thesis. As may be seen from the graph, the upper of the two experimental points at 0.03999 mol fraction S_8 coincides almost exactly with the curve based on the simplified Margules relations. Since the shift in vapor pressure lowering in going from 74.2°C to 75°C is difficult to assess, no valid conclusions may be drawn without better xylene activity data.

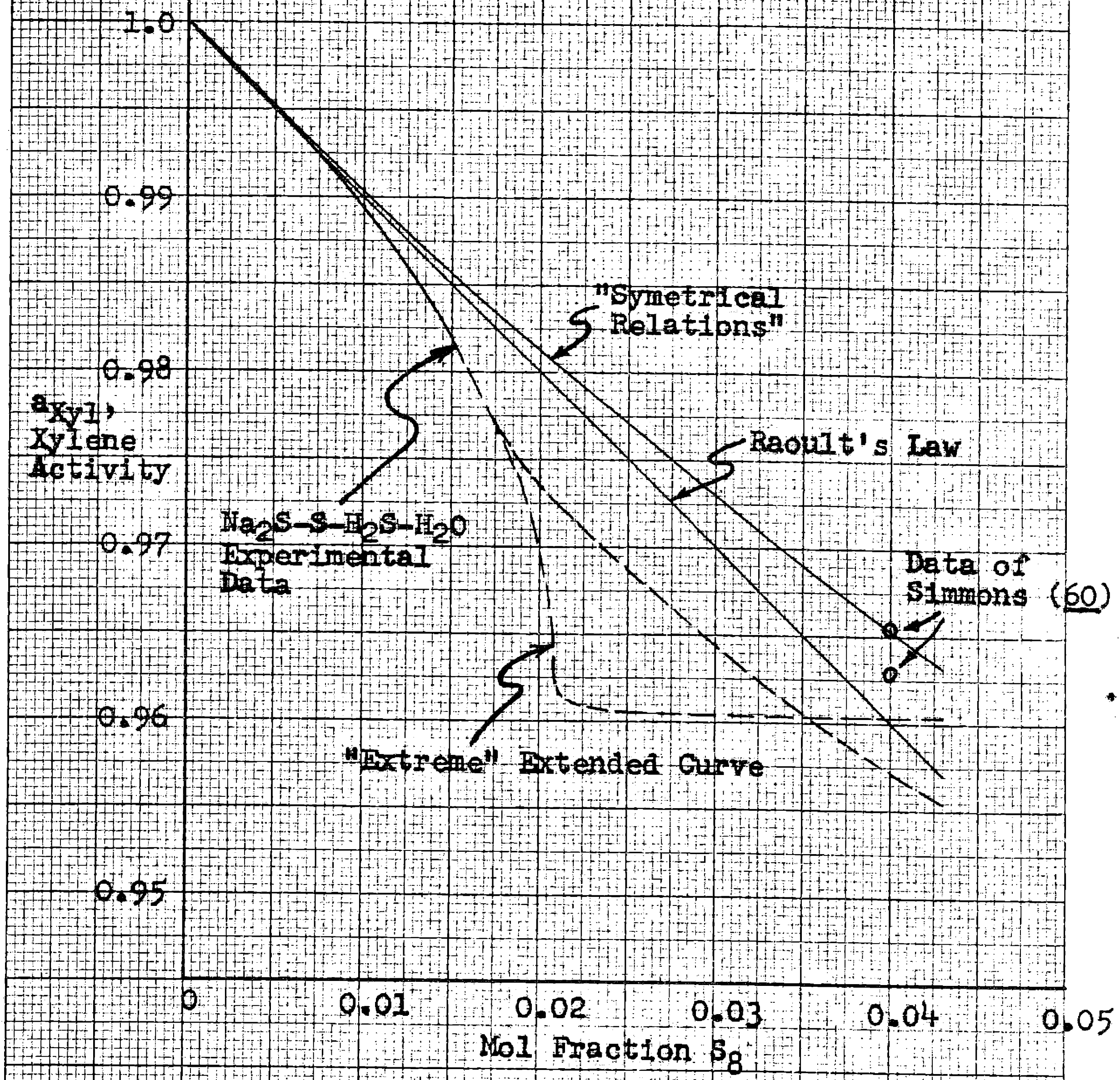


FIGURE 45

Activity of o-Xylene in o-Xylene-Sulfur Solutions at 75°C

The sulfur activity versus concentration relations obtained assuming (a) ideality, and (b) the "symmetrical relations" are compared in Figure 46 to the sulfur activities calculated by integration using the "II" sulfur saturation limits (Figure 42). Inspection indicates that the Na_2S-S-H_2S-H_2O equilibrium data of the present thesis dictate sulfur activities below ideality, at least in the low concentration region. Two possible extensions of the experimental curve are shown in Figure 46. Based on these two curves, xylene activity relations were computed using the integrated form of the Duhem equation:

$$\ln a_{Xyl} = -\int_0^{a_{S_8}} \left(\frac{y_{S_8}}{1-y_{S_8}}\right) \left(\frac{1}{a_{S_8}}\right) d\, a_{S_8} \qquad (84)$$

These xylene activity curves are shown in Figure 45. Even using the "extreme" extended curve in Figure 46 the predicted xylene activity at sulfur saturation still falls below either of the two values found by Simmons. In order to be compatible with the vapor pressure measurements, the sulfur activity curve of the present thesis in Figure 46 would have to be brought closer to or even above ideality in the low concentration region. To accomplish this, however, the sulfur activity integration limits would have to be taken outside the scatter of the X and Y data at sulfur saturation.

Since the vapor pressure data of Simmons are not

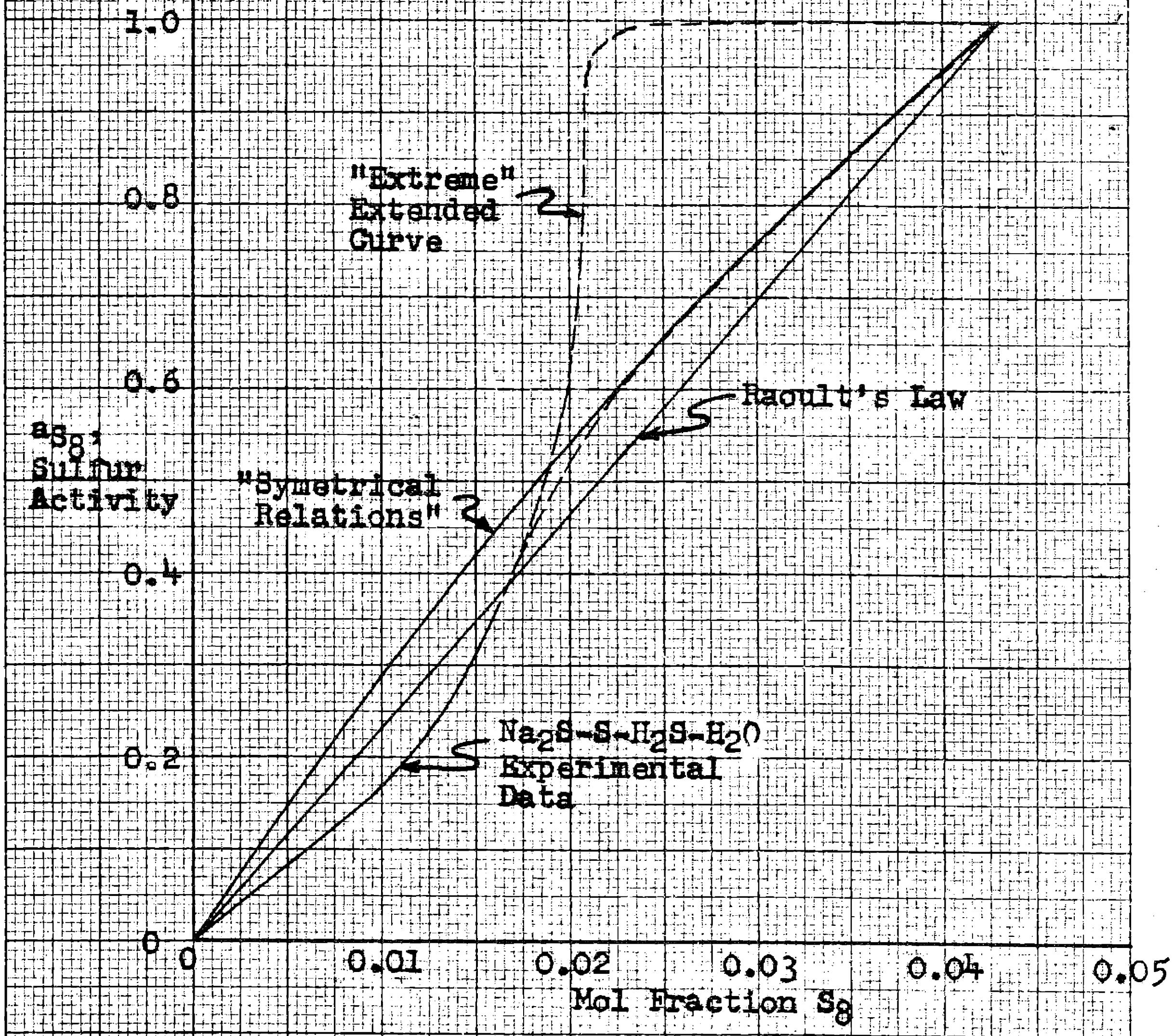


FIGURE 46

Activity of Sulfur in o-Xylene-Sulfur Solutions at 75°C considered reliable, the sulfur activity versus concentration curve in Figure 46, derived from the Na_2S-S-H_2S-H_2O equilibrium results, therefore is recommended in the lower sulfur in o-xylene concentration region at 75°C. No recommendation is made for sulfur activities above 0.4.

E. Derivation of Polysulfide Equilibrium Constants

Since the functions X and Y may be regarded as polynomials in $a_{S_8}{}^{1/8}$, the problem of solving for the polysulfide equilibrium constants could be considered that of determining the unknown polynomial coefficients. In order to obtain equilibrium constants which would not be jeopardized if the assumed numerical values of γ_{avg} and K_2 were wrong, it was decided first to derive the relative equilibrium constants as defined by equations 54 and 55:

$$X = r_1 a_{S_8}{}^{1/8} + r_2 a_{S_8}{}^{2/8} + r_3 a_{S_8}{}^{3/8} + \ldots \qquad (54)$$

$$Y = r_1 a_{S_8}{}^{1/8} + 2r_2 a_{S_8}{}^{2/8} + 3r_3 a_{S_8}{}^{3/8} + \ldots \qquad (55)$$

It was recognized, of course, that X and Y at a given sulfur activity, and hence these r's, should all change proportionally as γ_{avg} varied with concentration. The experimental results (Figures 43 and 44) indeed verify that this rule roughly holds true between sodium ion molalities of 1.0 and 4.0.

In the preceding portion of the thesis it was shown that the X and Y values, at given sulfur activities, also varied in constant ratios between the "I" and the "II" curves (Figures 37-40). Even though the "II" integration limits are considered more nearly correct, much of the attempted determination of polysulfide equilibrium constants was carried out using values taken from the "I" curves; the constants thus obtained differed only by a factor from the ones which would have been generated from the "II" correlations.

1. Formal Solution of Simultaneous Equations

The obvious technique for determining the unknown polysulfide equilibrium constants at first appeared to be the algebraic solution of simultaneous linear equations. These equations could be written once the number of polysulfide ions present in significant quantities had been assumed and sufficient points from the curves in Figures 37-40 had been selected so that the required number of relations were obtained. This procedure was carried out using values taken from the "I" lines at 4.0 sodium ion molality (Figures 37 and 38). Polysulfide ions from $S_2^=$ through $S_9^=$, inclusive, were assumed to be present. Four sulfur activity points accordingly were required in order that eight simultaneous equations in the eight unknown equilibrium constants could be written. The sulfur activities chosen and the relations thus obtained by substitution in equation 54 and 55 are given in Table XVI:

TABLE XVI

Simultaneous Equations for Polysulfide Equilibrium Constants

a_{S_8}	Equations
1.0	$r_1 + r_2 + \dots + r_8 = 1.707$
	$r_1 + 2r_2 + \dots + 8r_8 = 6.60$
0.4	$(0.4)^{1/8} r_1 + (0.4)^{2/8} r_2 + \dots + (0.4)^{8/8} r_8 = 1.100$
	$(0.4)^{1/8} r_1 + 2(0.4)^{2/8} r_2 + \dots + 8(0.4)^{8/8} r_8 = 4.18$
0.1	$(0.1)^{1/8} r_1 + (0.1)^{2/8} r_2 + \dots + (0.1)^{8/8} r_8 = 0.572$
	$(0.1)^{1/8} r_1 + 2(0.1)^{2/8} r_2 + \dots + 8(0.1)^{8/8} r_8 = 2.17$
0.01	$(0.01)^{1/8} r_1 + (0.01)^{2/8} r_2 + \dots + (0.01)^{8/8} r_8 = 0.198$
	$(0.01)^{1/8} r_1 + 2(0.01)^{2/8} r_2 + \dots + 8(0.01)^{8/8} r_8 = 0.700$

The solution of this 8 x 8 matrix of linear equations proved to be more difficult than anticipated. Ten significant figures had to be carried through the numerical inversion of the coefficient matrix in order that sufficient accuracy be maintained. Even with this precaution the equations still were found to be unstable relative to the precision of the experimental data. No significant figures were retained in the answers if these data were considered correct only to the indicated number of digits. If the X and Y values in Table XVI were assumed to be exact, an impossible solution was obtained:

$r_1 = -132$

$r_2 = +1197$

$r_3 = -4600$

$r_4 = +9714$

$r_5 = -12,174$

$r_6 = +9064$

$r_7 = -3714$

$r_8 = +647$

Within the limits of significant figures, however, these r's were shown to satisfy the original eight equations.

No single equation could be recognized whose coefficients either were nearly in a constant ratio to or were nearly a linear combination of the coefficients of one or more of the remaining equations. To approach instability this circumstance nevertheless must be present. The failure of the equations to define reasonable values of the polysulfide equilibrium constants is ascribed to the relatively narrow range of sulfur activities over which accurate data could be taken, rather than to any unfortunate choice of points from the curves in Figures 37 and 38.

Since as many as eight different polysulfide ions could not be treated with the information at hand, a second attempt was made to determine equilibrium constants, this time assuming only the ions $S_4^=$ through $S_7^=$ present, as did Conway (15) in his derivation of equilibrium constants. The equations thus written were:

TABLE XVII

Simultaneous Equations Assuming Only Four Polysulfide Ions

a_{S_8}	Equations			
1.0	$r_3 +$	$r_4 +$	$r_5 +$	$r_6 = 1.707$
	$3r_3 +$	$4r_4 +$	$5r_5 +$	$6r_6 = 6.600$
0.1	$(0.1)^{3/8} r_3 +$	$(0.1)^{4/8} r_4 +$	$(0.1)^{5/8} r_5 +$	$(0.1)^{6/8} r_6 = 0.572$
	$3(0.1)^{3/8} r_3 +$	$4(0.1)^{4/8} r_4 +$	$5(0.1)^{5/8} r_5 +$	$6(0.1)^{6/8} r_6 = 2.170$

Even in this simplified case a reasonable result was not obtained. The solution to the equations in Table XVII was found to be:

$$r_3 = -0.793$$
$$r_4 = +5.294$$
$$r_5 = -4.567$$
$$r_6 = +1.773$$

with only two digits really significant in view of the precision of the data. The instability of even this 4 x 4 system of equations relative to the input quantities further was demonstrated by the formal inversion of the coefficient matrix, as is indicated in Table XVIII:

TABLE XVIII

Formal Inversion of 4 x 4 Matrix of Equations (Table XVII)

$$r_3 = +107.856(1.707) - 8.990(6.60) - 75.700(0.572) - 37.910(2.17)$$

$$r_4 = -386.520(1.707) + 32.968(6.60) + 302.902(0.572) + 126.376(2.17)$$

$$r_5 = +455.472(1.707) - 39.965(6.60) - 378.703(0.572) - 139.020(2.17)$$

$$r_6 = -175.808(1.707) + 15.987(6.60) + 151.502(0.572) + 50.554(2.17)$$

Conway was able to obtain a solution in his case because the Rule and Thomas (56) data which he used extended over a wider range of variables than possible in aqueous solutions.

Since the formal substitution of the Na_2S-S-H_2S-H_2O equilibrium data into simultaneous algebraic equations failed to yield values of the polysulfide equilibrium constants, other techniques had to be employed in order to place limits on the unknown constants.

2. Information by Graphical Techniques

Upper and lower limits on the unknown equilibrium constants could be established by estimating intercepts and slopes from the plots of certain functions of the data, derived as follows from the original equations 54 and 55:

$$\frac{X}{a_{S_8}^{1/8}} = X_1 = r_1 + r_2 a_{S_8}^{1/8} + r_3 a_{S_8}^{2/8} + \ldots \qquad (85)$$

$$\frac{Y}{a_{S_8}^{1/8}} = Y_1 = r_1 + 2r_2a_{S_8}^{1/8} + 3r_3a_{S_8}^{2/8} + \dots \tag{86}$$

$$\frac{Y-X}{a_{S_8}^{2/8}} = \Delta_1 = r_2 + 2r_3a_{S_8}^{1/8} + 3r_4a_{S_8}^{2/8} + \dots \tag{87}$$

The relative equilibrium constant for $S_2^=$ formation (r_1) therefore must equal the limit of either X_1 or Y_1 as sulfur activity approaches zero. The value of r_2 furthermore may be obtained from the limit of equation 87 as a_{S_8} approaches zero.

If it should be true that the disulfide ion is absent, that is, <u>if r_1 is zero</u>, then the additional following relations must be valid:

$$\frac{X}{a_{S_8}^{2/8}} = X_2 = r_2 + r_3a_{S_8}^{1/8} + r_4a_{S_8}^{2/8} + \dots \tag{88}$$

$$\frac{Y}{a_{S_8}^{2/8}} = Y_2 = 2r_2 + 3r_3a_{S_8}^{1/8} + 4r_4a_{S_8}^{2/8} + \dots \tag{89}$$

$$\frac{Y-2X}{a_{S_8}^{3/8}} = \Delta_2 = r_3 + 2r_4a_{S_8}^{1/8} + 3r_5a_{S_8}^{2/8} + \dots \tag{90}$$

Thus if the assumption underlying these three preceding equations is correct, additional estimations of r_2 and also an indication of the value of r_3 may be obtained by considering the limits at zero sulfur activity.

If the equilibria should be such that the $S_2^=$ and $S_3^=$ ions both are negligible stoichiometrically (both r_1 and r_2 equal to zero), as was assumed by Conway (15), based on the absence of the hydrogen di-and trisulfides in raw oil (26), then information on the equilibrium constants of even higher polysulfide ions may be derived from equations 54 and 55:

$$\frac{X}{a_{S_8}^{3/8}} = X_3 = r_3 + r_4 a_{S_8}^{1/8} + r_5 a_{S_8}^{2/8} + \ldots \tag{91}$$

$$\frac{Y}{a_{S_8}^{3/8}} = Y_3 = 3r_3 + 4r_4 a_{S_8}^{1/8} + 5r_5 a_{S_8}^{2/8} + \ldots \tag{92}$$

$$\frac{Y-3X}{a_{S_8}^{4/8}} = \Delta_3 = r_4 + 2r_5 a_{S_8}^{1/8} + 3r_6 a_{S_8}^{2/8} + \ldots \tag{93}$$

Equations 91 and 92 thus would yield values of r_3 as sulfur activity approaches zero, whereas equation 93 would give, in the limit, r_4.

Even though precision is lost in taking slopes graphically, some additional information still might be forthcoming from a consideration of the first derivatives of the preceding equations with respect to $a_{S_8}^{1/8}$:

From equation 54:

$$\frac{d\,X}{d\,a_{S_8}^{1/8}} = X' = r_1 + 2r_2 a_{S_8}^{1/8} + 3r_3 a_{S_8}^{2/8} + \ldots \tag{94}$$

$$= Y_1 = r_1 \text{ at zero sulfur activity.}$$

From equation 55:

$$\frac{d\,Y}{d\,a_{S_8}^{1/8}} = Y' = r_1 + 4r_2 a_{S_8}^{1/8} + 9r_3 a_{S_8}^{2/8} + \ldots \tag{95}$$

$$= r_1 \text{ at zero sulfur activity.}$$

From equation 85:

$$\frac{d\,X_1}{d\,a_{S_8}^{1/8}} = X_1' = r_2 + 2r_3 a_{S_8}^{1/8} + 3r_4 a_{S_8}^{2/8} + \ldots \tag{96}$$

$$= \Delta_1 = r_2 \text{ at zero sulfur activity.}$$

From equation 86:

$$\frac{d\,Y_1}{d\,a_{S_8}^{1/8}} = Y_1' = 2r_2 + 6r_3 a_{S_8}^{1/8} + 12r_4 a_{S_8}^{2/8} + \ldots \tag{97}$$

$$= \frac{Y' - r_1}{a_{S_8}^{1/8}} = Y_2 = 2r_2 \text{ at zero sulfur activity.}$$

From equation 87:

$$\frac{d\,\Delta_1}{d\,a_{S_8}^{1/8}} = \Delta_1' = 2r_3 + 6r_4 a_{S_8}^{1/8} + 12r_5 a_{S_8}^{2/8} + \ldots \tag{98}$$

$$= \frac{Y' - r_1}{a_{S_8}^{2/8}} - \frac{Y_2 + 2\Delta_1}{a_{S_8}^{1/8}} = 2r_3 \text{ at zero sulfur activity.}$$

If r_1 is zero:

From equation 88:

$$\frac{d\,X_2}{d\,a_{S_8}^{1/8}} = X_2' = r_3 + 2r_4 a_{S_8}^{1/8} + 3r_5 a_{S_8}^{2/8} + \ldots \tag{99}$$

$$= \Delta_2 = r_3 \text{ at zero sulfur activity.}$$

From equation 89:

$$\frac{d\,Y_2}{d\,a_{S_8}^{1/8}} = Y_2' = 3r_3 + 8r_4 a_{S_8}^{1/8} + 15r_5 a_{S_8}^{2/8} + \ldots \qquad (100)$$

$$= \frac{Y'}{a_{S_8}^{2/8}} - \frac{Y_2 + 2\Delta_1}{a_{S_8}^{1/8}} + \Delta_2 = 3r_3 \text{ at zero sulfur activity.}$$

From equation 90:

$$\frac{d\,\Delta_2}{d\,a_{S_8}^{1/8}} = \Delta_2' = 2r_4 + 6r_5 a_{S_8}^{1/8} + 12r_6 a_{S_8}^{2/8} + \ldots \qquad (101)$$

$$= \frac{Y'}{a_{S_8}^{3/8}} - \frac{Y_2 + 2\Delta_1}{a_{S_8}^{2/8}} - \frac{2\Delta_2}{a_{S_8}^{1/8}} = 2r_4 \text{ at zero sulfur activity.}$$

If both r_1 and r_2 are zero:

From equation 91:

$$\frac{d\,X_3}{d\,a_{S_8}^{1/8}} = X_3' = r_4 + 2r_5 a_{S_8}^{1/8} + 3r_6 a_{S_8}^{2/8} + \ldots \qquad (102)$$

$$= \Delta_3 = r_4 \text{ at zero sulfur activity.}$$

From equation 92:

$$\frac{d\,Y_3}{d\,a_{S_8}^{1/8}} = Y_3' = 4r_4 + 10r_5 a_{S_8}^{1/8} + 18r_6 a_{S_8}^{2/8} + \ldots \qquad (103)$$

$$= \frac{Y'}{a_{S_8}^{3/8}} - \frac{Y_2 + 2\Delta_1}{a_{S_8}^{2/8}} - \frac{2\Delta_2}{a_{S_8}^{1/8}} + 2\Delta_3 = 4r_4 \text{ at zero sulfur activity.}$$

From equation 93:

$$\frac{d\,\Delta_3}{d\,a_{S_8}^{1/8}} = \Delta_3' = 2r_5 + 6r_6 a_{S_8}^{1/8} + 12r_7 a_{S_8}^{2/8} + \ldots$$

$$= \frac{Y'}{a_{S_8}^{4/8}} - \frac{Y_2 + 2\Delta_1}{a_{S_8}^{3/8}} - \frac{2\Delta_2}{a_{S_8}^{2/8}} - \frac{2\Delta_3}{a_{S_8}^{1/8}} = 2r_5 \text{ at zero sulfur activity} \qquad (104)$$

Graphical evaluation of the expressions defined by equations 85-104 was attempted. In Figures 47, 48, and 49 the functions X_1 (equation 85), Y_1 (equation 86), and Δ_1 (equation 87), respectively, are plotted against $a_{S_8}^{1/8}$, using values taken from the "I" X and Y versus sulfur activity relations at 4.0 m sodium ion concentration. Making the provisional assumption that the disulfide ion could be neglected, the functions X_2 (equation 88), Y_2 (equation 89), and Δ_2 (equation 90) likewise are shown graphically in Figures 50, 51, and 52, respectively. In order to investigate the proportions of higher polysulfide ions if both $S_2^=$ and $S_3^=$ could be assumed absent, the functions X_3 (equation 91), Y_3 (equation 92), and Δ_3 (equation 93) similarly have been plotted in Figures 53, 54, and 55, respectively. These graphical correlations also were attempted for the "II" sulfur activity relations at 4.0 m and for both the "I" and the "II" curves at 1.0 m sodium ion; the resulting plots, which are not included in this thesis, appeared much the same as Figures 47-55 except for the factors of proportionality.

In each of the graphs the estimated upper and lower limits on the intercepts at zero sulfur activity are indicated. Summarizing this information as obtained from the "I" X and Y versus sulfur activity relations, the following initial conclusions were drawn:

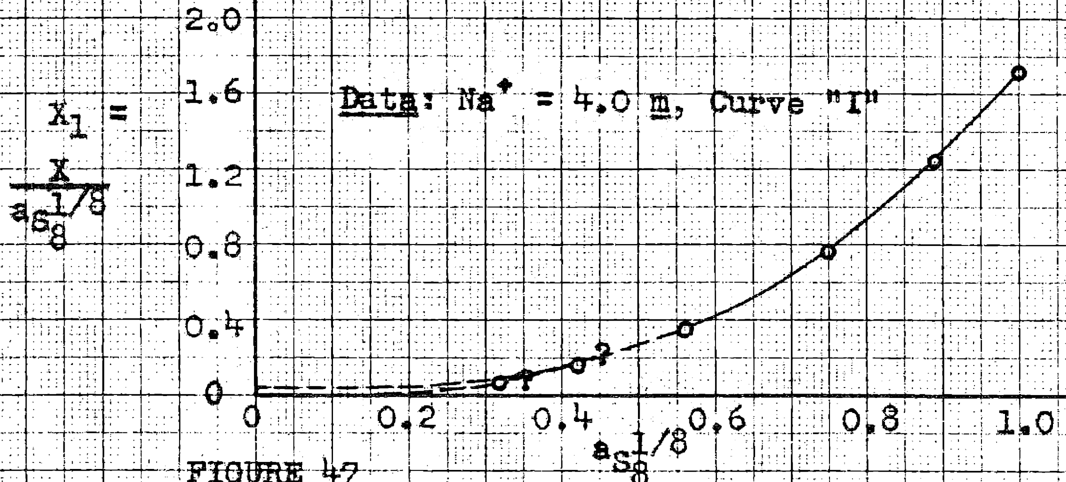


FIGURE 47
Equilibrium Constant of $S_2^=$ Ion from X_1 Intercept

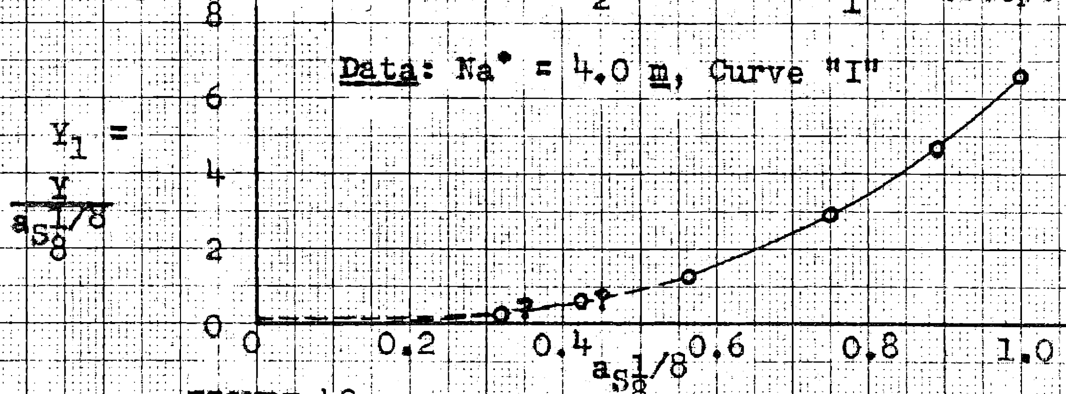


FIGURE 48
Equilibrium Constant of $S_2^=$ Ion from Y_1 Intercept

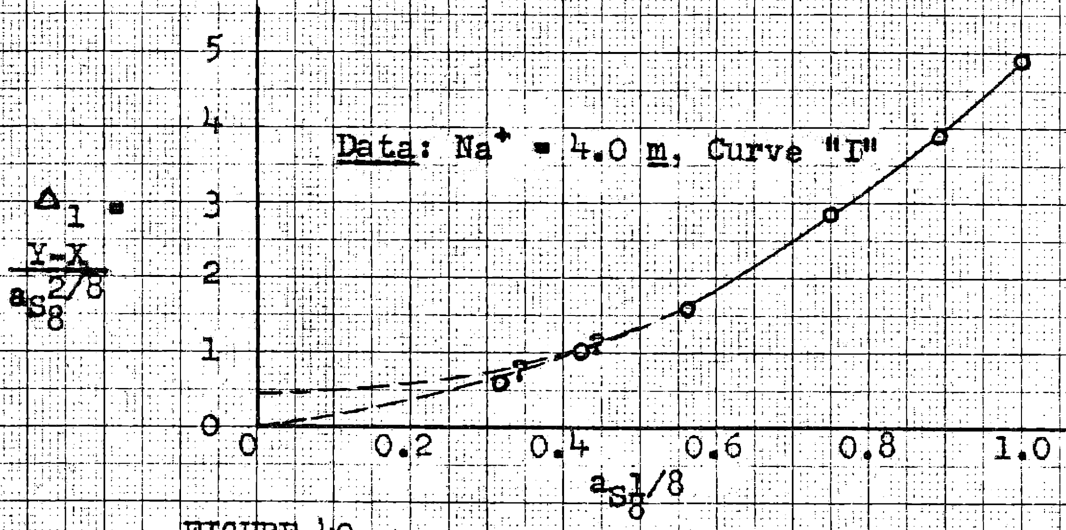


FIGURE 49
Equilibrium Constant of $S_3^=$ Ion from Δ_1 Intercept

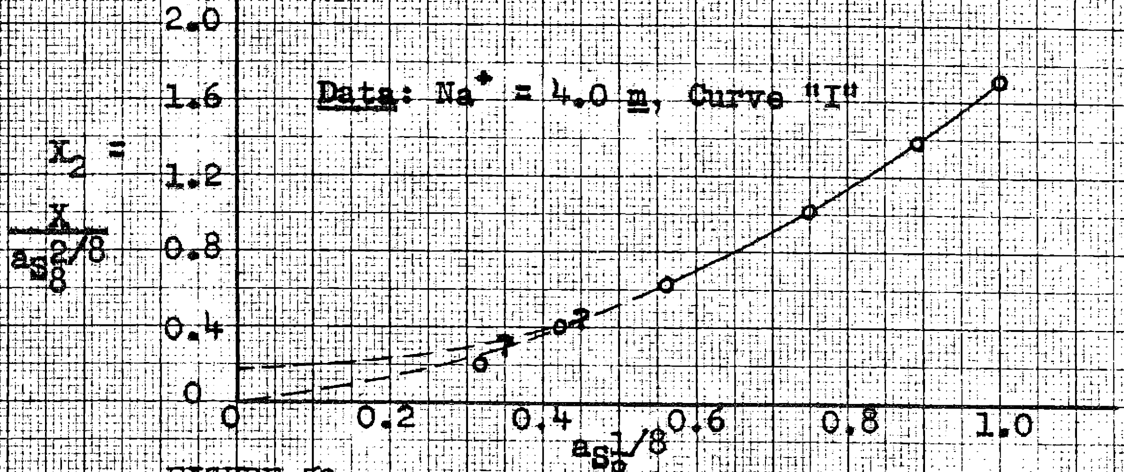


FIGURE 50

Equilibrium Constant of $S_3^=$ Ion from X_2 Intercept

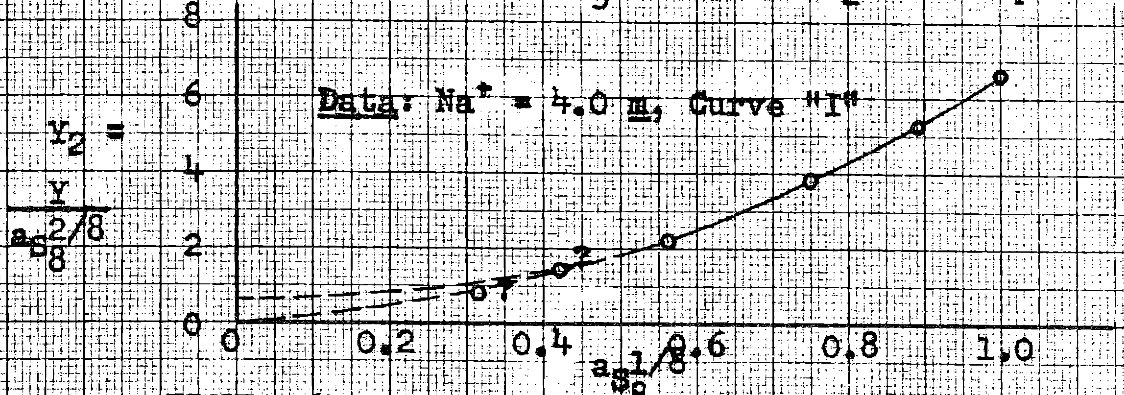


FIGURE 51

Equilibrium Constant of $S_3^=$ Ion from Y_2 Intercept

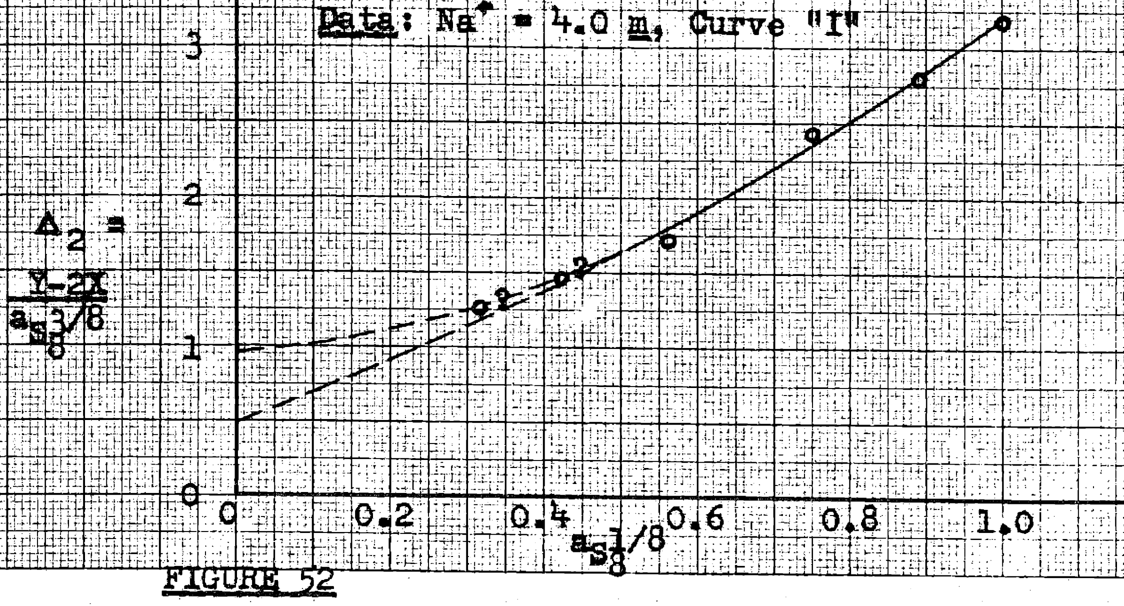


FIGURE 52

Equilibrium Constant of $S_4^=$ Ion from Δ_2 Intercept

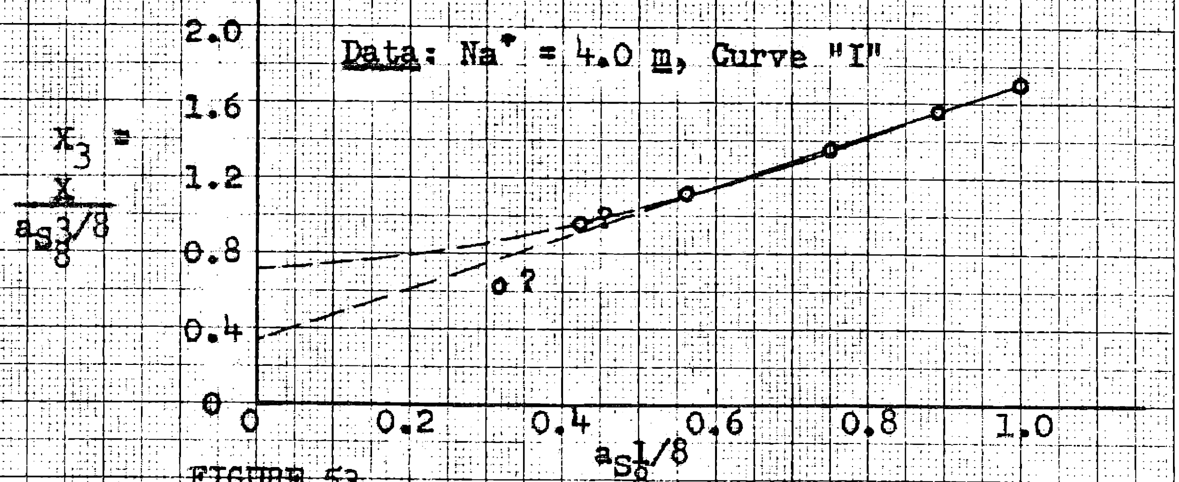


FIGURE 53
Equilibrium Constant of $S_4^=$ Ion from X_3 Intercept

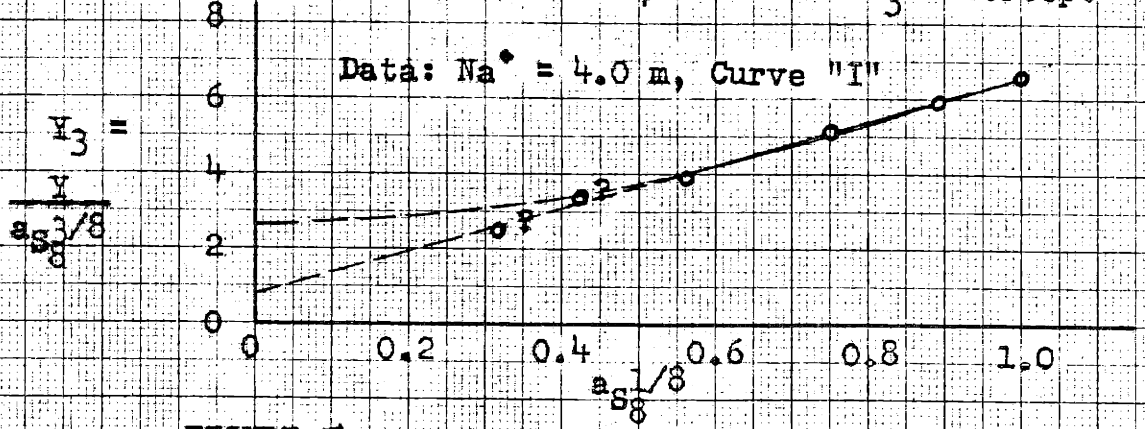


FIGURE 54
Equilibrium Constant of $S_4^=$ Ion from Y_3 Intercept

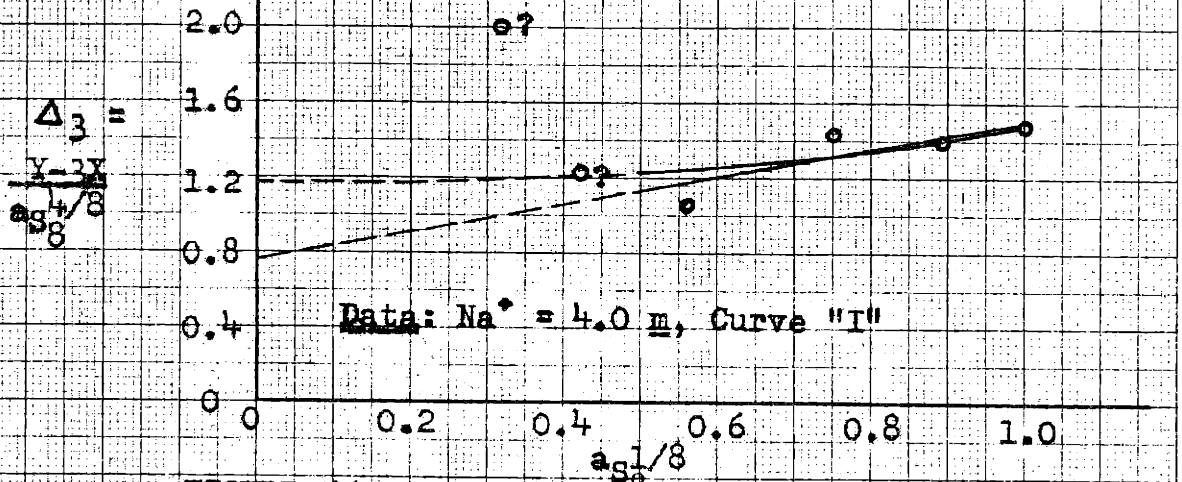


FIGURE 55
Equilibrium Constant of $S_5^=$ Ion from Δ_3 Intercept

1. r_1 is probably zero, and is certainly less than 0.03.
2. r_2 is probably <u>not</u> zero, but is not greater than 0.18.
3. r_3 is almost certainly not zero, and probably lies between the limits 0.27 to 0.72.
4. r_4 likewise almost certainly is not zero, and may lie between the limits 0.76 to 1.18.

Since the points below ${a_{S_8}}^{1/8} = 0.562$ ($a_{S_8} = 0.01$) are subject to increasingly serious errors, these conclusions cannot be considered unequivocal. In view of such uncertainties the conclusions derived from Figures 53, 54, and 55 were taken to be approximately valid even though a small but non-zero value for r_2 was indicated.

Considering the further inaccuracies involved in estimating derivatives graphically, only a small amount of additional information was obtained by taking slopes in Figures 47-55. These slopes, of course, were especially doubtful at zero sulfur activity. From Figures 47 and 48, however, it was deduced that at least one of the two relative equilibrium constants r_1 and r_2 had to be negligible in order that the indicated curves could be fitted. The estimation of apparent initial slopes in Figures 49, 50, and 51 yielded, using equations 98, 99, and 100, respectively, limits on r_3 essentially the same as those already stated.

A similar inspection of Figures 52, 53, and 54 also confirmed the limits established for r_4 using initial intercepts. The use of equation 104 in conjunction with Figure 55 indicated that r_5 was not greater than 0.38.

If the polysulfide ionic distributions could be assumed "normal", that it, if the equilibrium constant for any ion could not be less than both that of the ion immediately above it and that of the ion immediately below it in sulfur subscript, somewhat closer limits then could be placed on the relative equilibrium constants by considering simultaneously the initial intercepts and the initial slopes. The conclusions dependent on this assumption were:

1. r_1 is zero
2. r_2 is between zero and 0.17
3. r_3 is between 0.35 and 0.59
4. r_4 is between 0.72 and 1.03
5. r_5 is less than 0.38.

The slopes at unity sulfur activity also were examined for possible information. Those from Figures 47, 48, and 49 yielded expressions involving too many unknown equilibrium constants to be useful, whereas those from Figures 53, 54, and 55 could not be read with sufficient precision. For use with the remaining three graphs the following expressions were derived:

From equations 99-101:

$$Y_2' - 3X_2' = \Delta_2' \, a_{S_8}^{1/8} = 2r_4 a_{S_8}^{1/8} + 6r_5 a_{S_8}^{2/8} + 12r_6 a_{S_8}^{3/8} + \dots \qquad (105)$$

$$= 2r_4 + 6r_5 + 12r_6 + \dots \quad \text{at } a_{S_8} = 1.0.$$

$$Y_2' - 4X_2' = -r_3 + 3r_5 a_{S_8}^{2/8} + 8r_6 a_{S_8}^{3/8} + \dots \qquad (106)$$

$$= -r_3 + 3r_5 + 8r_6 + \dots \quad \text{at } a_{S_8} = 1.0.$$

Evaluations from Figures 50, 51, and 52 yielded, for equation 105, an approximate numerical value of 4.0 ± 0.5, and for equation 106, an estimated value of 0.9 ± 0.5. Use will be made of these relations later.

Clarification of which, if either, of the two lower polysulfide ions really are present in significant quantities was attempted by considering the limit of the ratio Y/X or $PSS/S_x^=$ as sulfur activity approaches zero. From equation 59:

$$\frac{Y}{X} = \frac{k_1 a_{S_8}^{1/8} + 2k_2 a_{S_8}^{2/8} + 3k_3 a_{S_8}^{3/8} + \dots}{k_1 a_{S_8}^{1/8} + k_2 a_{S_8}^{2/8} + k_3 a_{S_8}^{3/8} + \dots} \qquad (59)$$

it is seen that this ratio approaches unity if the disulfide ion is present. If k_1 (or r_1) is zero, this ratio approaches 2 at zero sulfur activity, whereas if both k_1 and k_2 are zero, the limit is then 3. The values of Y/X obtained from the Na_2S-S-H_2S-H_2O equilibrium data at 4.0 sodium ion molality, assuming sulfur activity relation "I", are plotted versus $a_{S_8}^{1/8}$ in Figure 56. Essentially the same points would be obtained if the "II" correlations or the data at 1.0 m sodium ion were used.

Since the experimental results of the present thesis did not extend to sufficiently low sulfur activities to make possible an estimation of the intercept at zero sulfur activity, points also were derived from measurements by Peschanski (52) and by Kuster and Heberlein (41) of the hydrolysis of ordinary sodium polysulfide solutions at room temperature. This calculation involved an assumption of the monosulfide hydrolysis equilibrium relation, followed by sulfur activity graphical integrations similar to those already described. These hydrolysis data also are shown in Figure 56. Even though at least the curve of Peschanski is highly doubtful owing to the method (glass electrode) employed, both correlations do indicate the presence of something below $S_4^=$ in the polysulfide system at room temperature. The apparent "breaks" in both curves (at a polysulfide composition of about Na_2S_4) have not been explained, but are believed to be related to rate rather than equilibrium considerations. It has been shown that

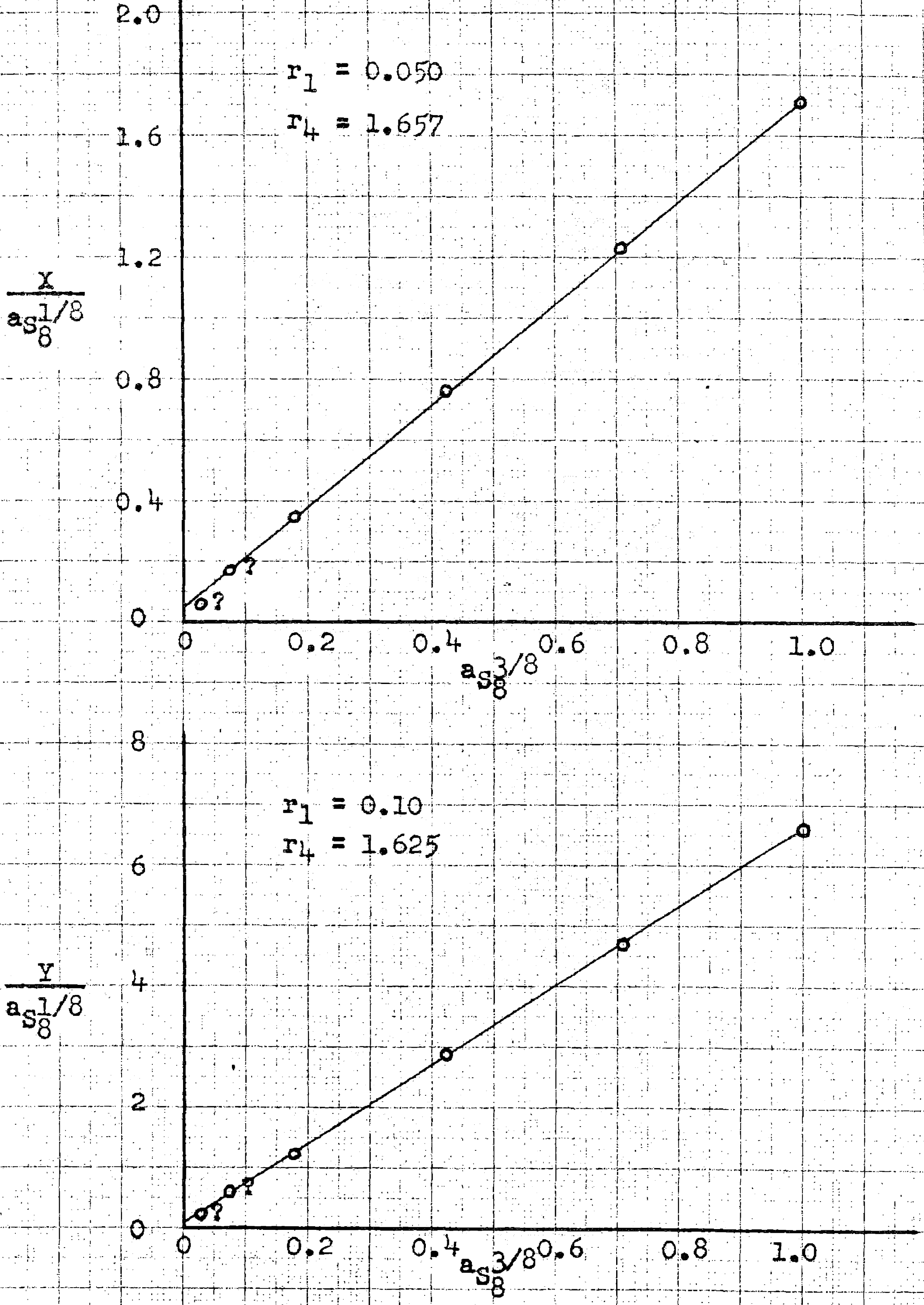


FIGURE 57

Graphical Solution for Assumption 1

Data: Na^+ = 4.0 m, Curve "I"

certain of the polysulfide equilibria are not mobile at room temperature; for this reason no attempts were made to subject the curves in Figure 56 to further analysis.

3. Generation of Possible Sets of Equilibrium Constants

Since all attempts to obtain a unique solution for the relative polysulfide equilibrium constants were unsuccessful, an investigation was launched into which possible sets of constants best satisfied the equations derived from the experimental data. If only two or if only three polysulfide ions were assumed present in significant amounts, the "best fit" solutions could be obtained graphically. For more than three ions the possible solutions had to be approximated by trial-and-error procedures.

It was found that the experimental data apparently could be correlated assuming as few as two polysulfide ions present. The equilibrium constants for such cases were generated as follows: Assuming only the ions $S_{u+1}^{=}$ and $S_{v+1}^{=}$ present, equations 54 and 55 then became:

$$X = r_u a_{S_8}^{u/8} + r_v a_{S_8}^{v/8} \qquad (107)$$

$$Y = u r_u a_{S_8}^{u/8} + v r_v a_{S}^{v/8} \qquad (108)$$

(in which $v > u$)

The following equations accordingly could be written:

$$\frac{X}{a_{S_8}^{u/8}} = r_u + r_v a_{S_8}^{(v-u)/8} \qquad (109)$$

$$\frac{Y}{a_{S_8}^{u/8}} = ur_u + vr_v a_{S_8}^{(v-u)/8} \qquad (110)$$

Thus if the quantities $\frac{X}{a_{S_8}^{u/8}}$ and $\frac{Y}{a_{S_8}^{u/8}}$ were plotted versus $a_{S_8}^{(v-u)/8}$, straight lines should be obtained in both instances; the values of r_u and r_v then could be found from the intercepts and the slopes, respectively.

This procedure was carried out for five different assumptions involving in each case only two polysulfide ions present:

Assumption 1: $S_2^=$ and $S_5^=$
Assumption 2: $S_3^=$ and $S_5^=$
Assumption 3: $S_3^=$ and $S_6^=$
Assumption 4: $S_4^=$ and $S_5^=$
Assumption 5: $S_4^=$ and $S_6^=$

The pairs of plots for each of these five assumptions are shown in Figures 57, 58, 59, 60, and 61, respectively. These plots all are based on the "I" sulfur activity relations at 4.0 m sodium ion. With the exception of assumption 3 all the cases are seen to fit reasonably well with the data. The relative equilibrium constants based on these assumptions were obtained in each case by averaging the two values of a given "r" derived from the pair of plots; these constants were further adjusted as required in order

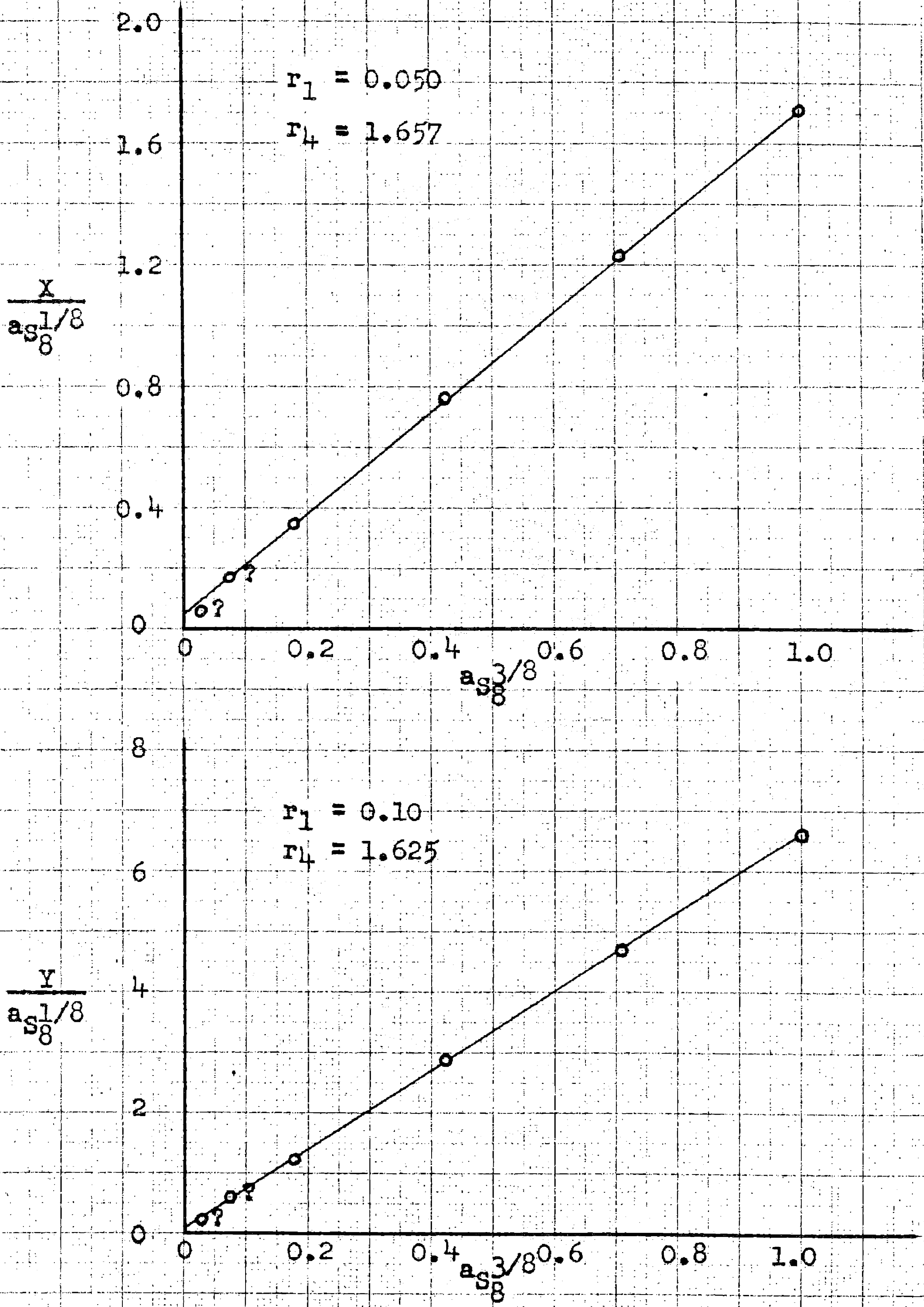


FIGURE 57

Graphical Solution for Assumption 1

Data: Na^+ = 4.0 m, Curve "I"

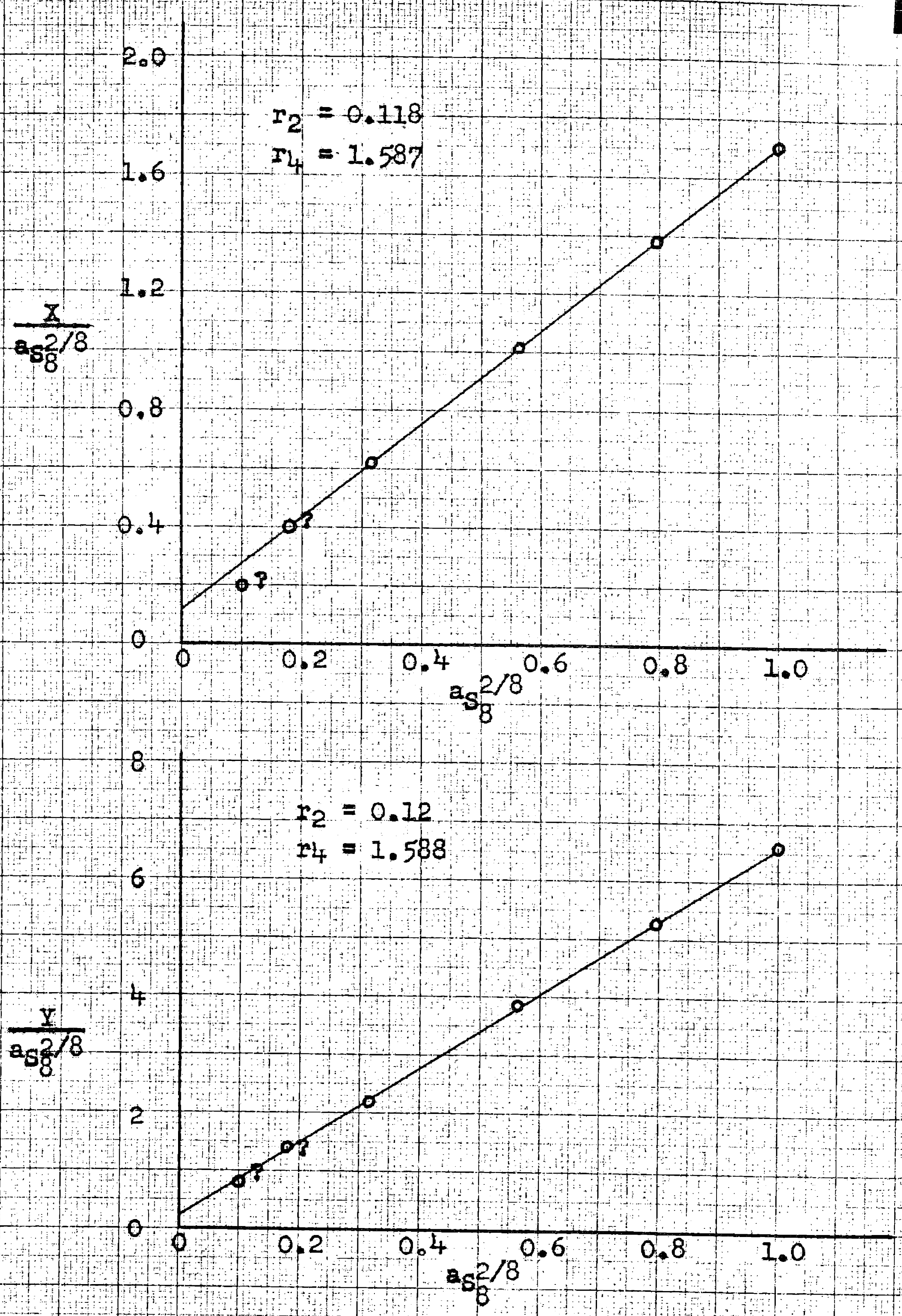


FIGURE 58

Graphical Solution for Assumption 2

Data: Na^+ = 4.0 m, Curve "I"

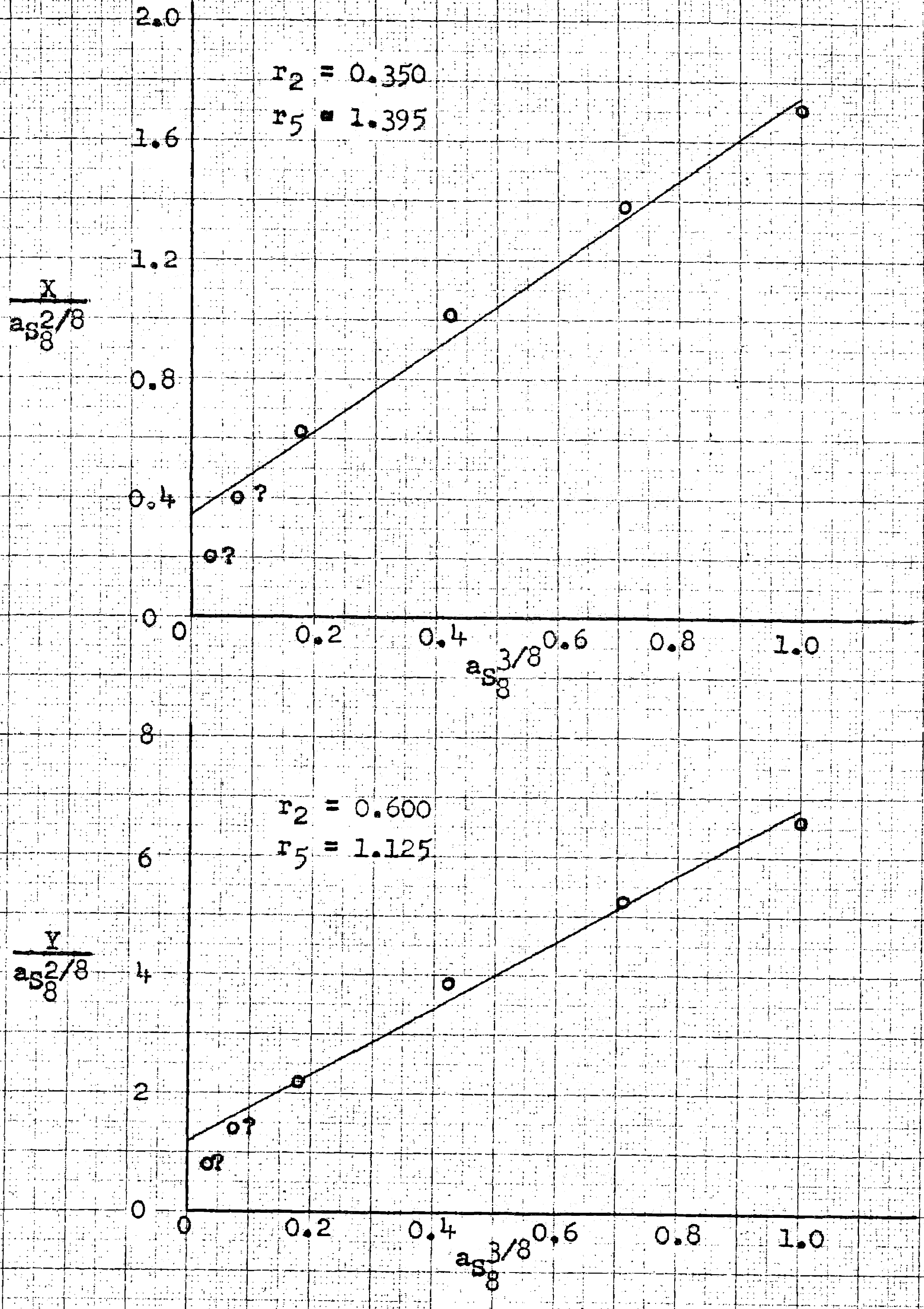


FIGURE 59

Graphical Solution for Assumption 3

Data: Na^+ = 4.0 m, Curve "I"

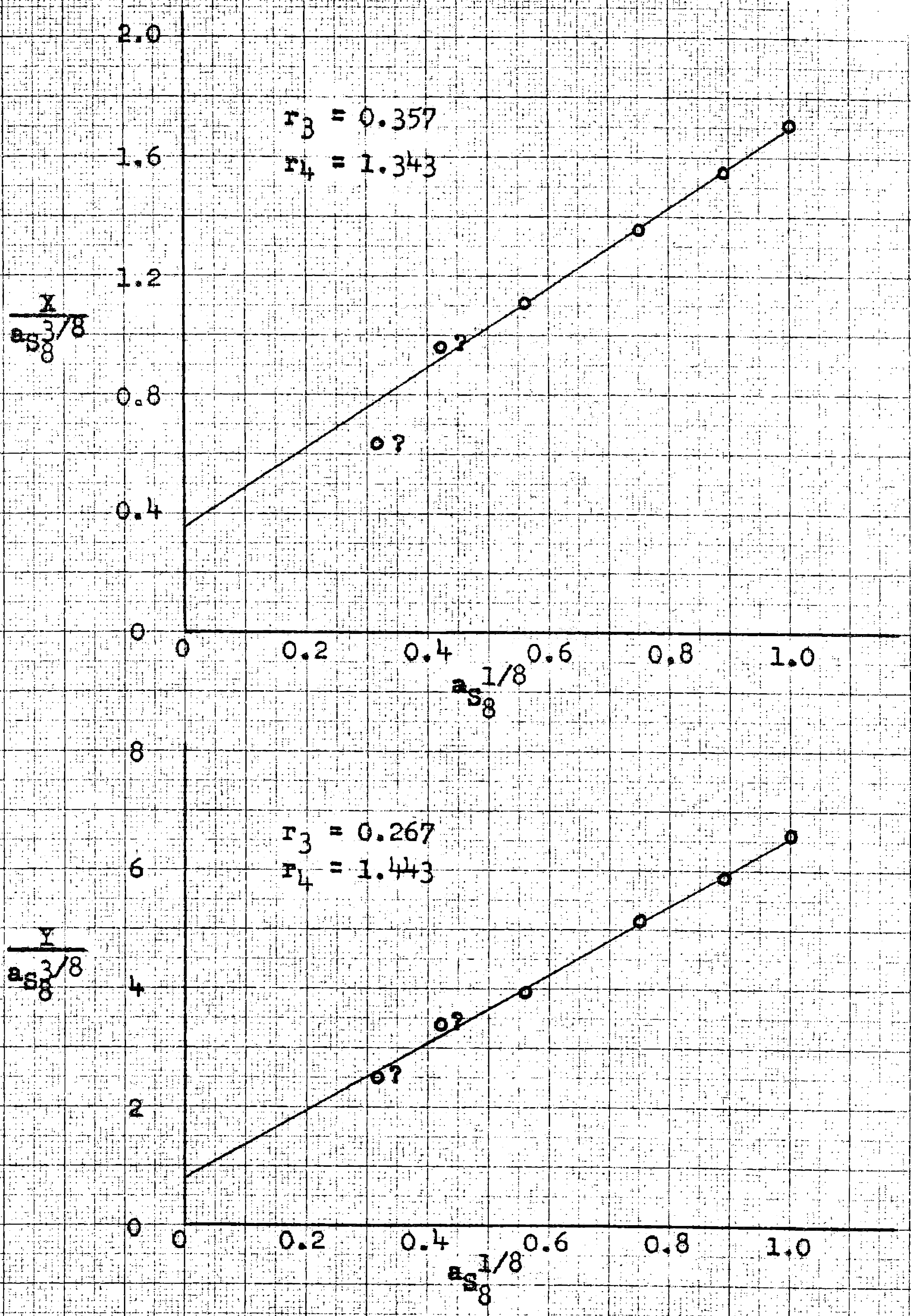


FIGURE 60

Graphical Solution for Assumption 4

Data: $Na^+ = 4.0$ m, Curve "I"

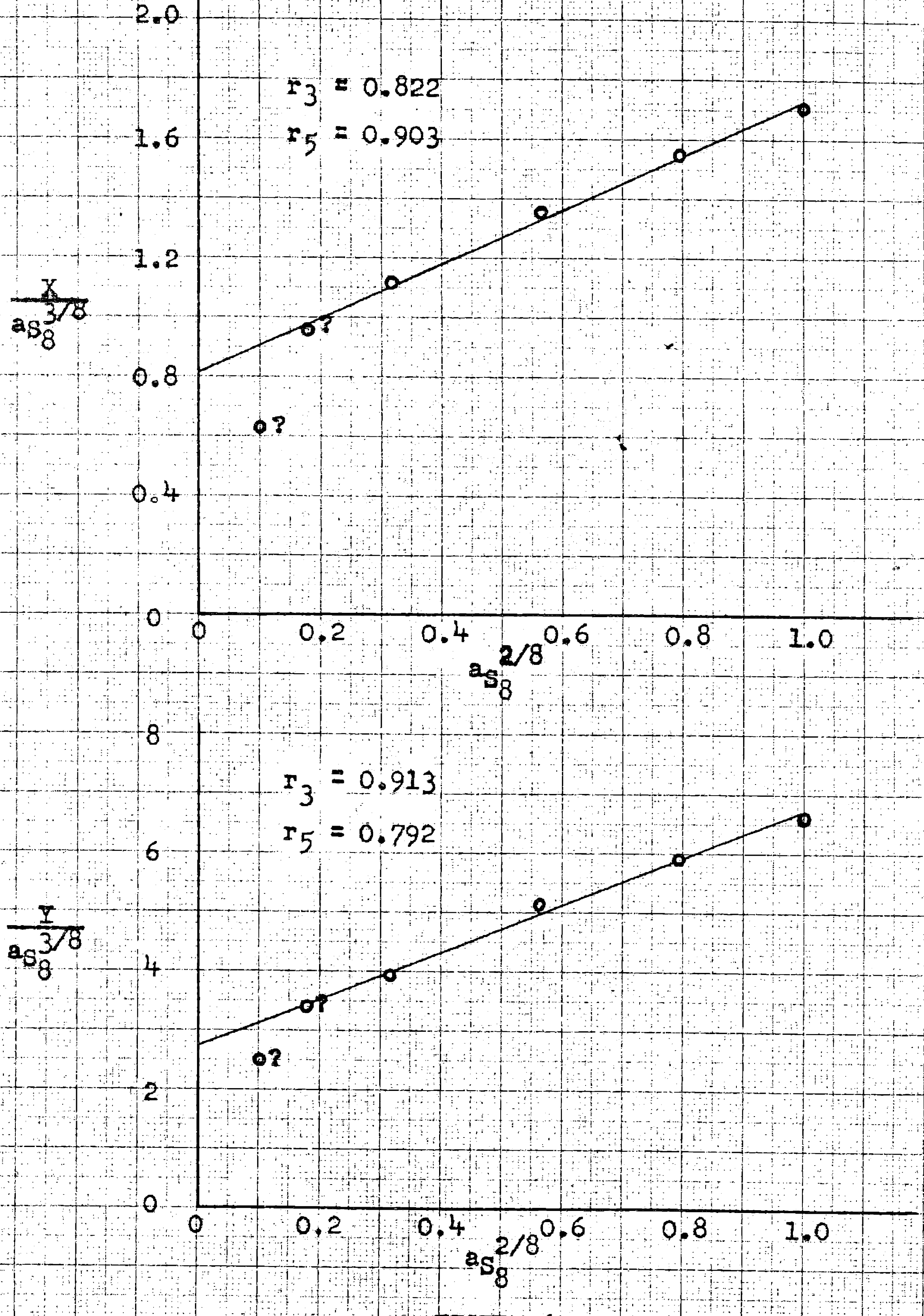


FIGURE 61

Graphical Solution for Assumption 5

Data: Na^+ = 4.0 m, Curve "I"

to correct for any consistent deviation from the data owing to not having drawn the best possible lines. The equilibrium constants thus obtained for these five cases are listed in Table XIX.

If three polysulfide ions were assumed present, the "best fit" relative equilibrium constants still could be obtained graphically, as follows:

From equation 54:

$$X = r_u a_{S_8}^{u/8} + r_v a_{S_8}^{v/8} + r_w a_{S_8}^{w/8} \tag{111}$$

From equation 55:

$$Y = u r_u a_{S_8}^{u/8} + v r_v a_{S_8}^{v/8} + w r_w a_{S_8}^{w/8} \tag{112}$$

(in which $w > v > u$)

From equations 111 and 112 the following may be derived:

$$\frac{Y-uX}{a_{S_8}^{v/8}} = (v-u) r_v + (w-u) r_w a_{S_8}^{(w-v)/8} \tag{113}$$

$$\frac{Y-vX}{a_{S_8}^{u/8}} = -(v-u) r_u + (w-v) r_w a_{S_8}^{(w-u)/8} \tag{114}$$

$$\frac{Y-wX}{a_{S_8}^{u/8}} = -(w-u) r_u - (w-v) r_v a_{S_8}^{(v-u)/8} \tag{115}$$

From these three equations it is seen that if the quantities $\frac{Y-uX}{a_{S_8}^{v/8}}$, $\frac{Y-vX}{a_{S_8}^{u/8}}$, and $\frac{Y-wX}{a_{S_8}^{u/8}}$ are plotted versus $a_{S_8}^{(w-v)/8}$,

$a_{S_8}^{(w-u)/8}$, and $a_{S_8}^{(v-u)/8}$, respectively, three linear graphs should be obtained which would yield, from the intercepts and the slopes, pairs of values for each of the unknown equilibrium constants r_u, r_v, and r_w. The "best fit" values again could be obtained by averaging, followed by any necessary adjustment to relieve systematic departure from the data.

This procedure has been carried out for the following assumed sets of only three ions present:

Assumption 6: $S_3^=$, $S_4^=$, and $S_5^=$
Assumption 7: $S_4^=$, $S_5^=$, and $S_6^=$
Assumption 8: $S_2^=$, $S_4^=$, and $S_6^=$
Assumption 9: $S_3^=$, $S_5^=$, and $S_7^=$

The groups of three plots for each of these four assumptions are shown in Figures 62, 63, 64, and 65, respectively, again all taken from the "I" sulfur activity correlation at a sodium ion molality of 4.0. Considerable precision was lost in going to the functions required for a graphical solution with three ions present; both the intercepts and the slopes of the lines indicated on the plots thus could well be considerably in error. Preliminary inspection does suggest, however, that assumptions 8 and 9 must be discarded, since they apparently lead to negative values for r_1 and r_6, respectively. The equilibrium constants for these four cases also are listed in Table XIX.

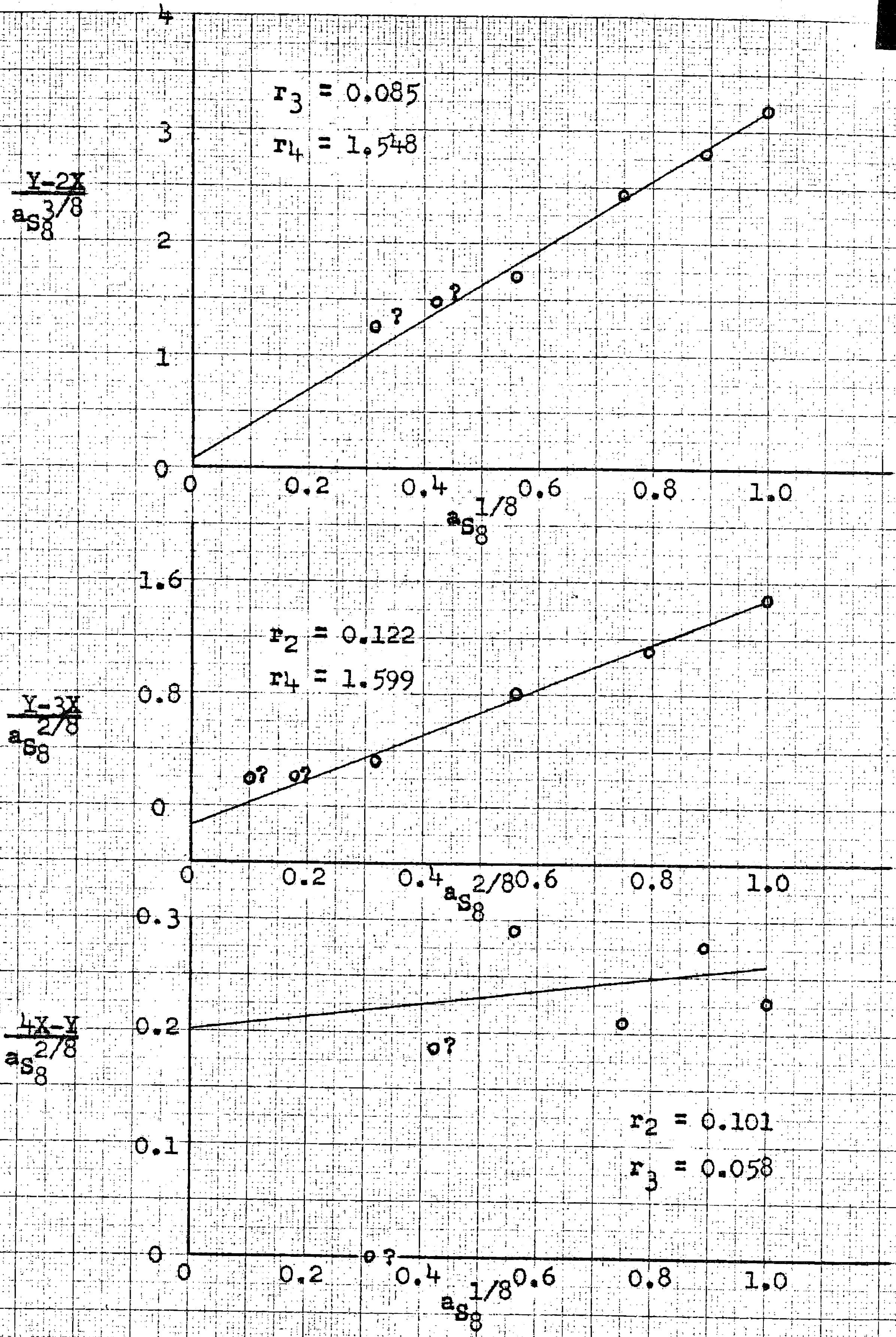


FIGURE 62

Graphical Solution for Assumption 6

Data: Na^+ = 4.0 m, Curve "I"

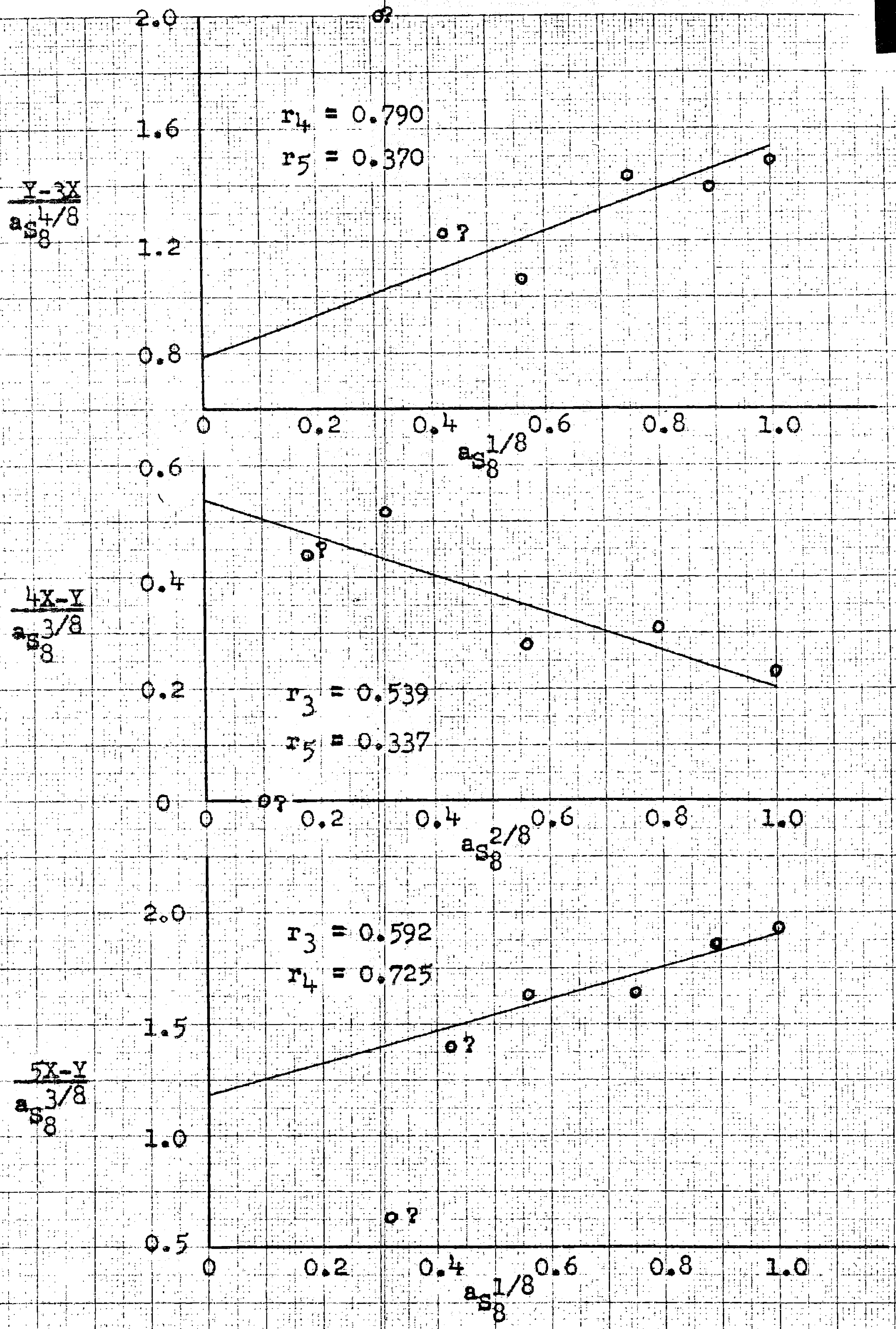
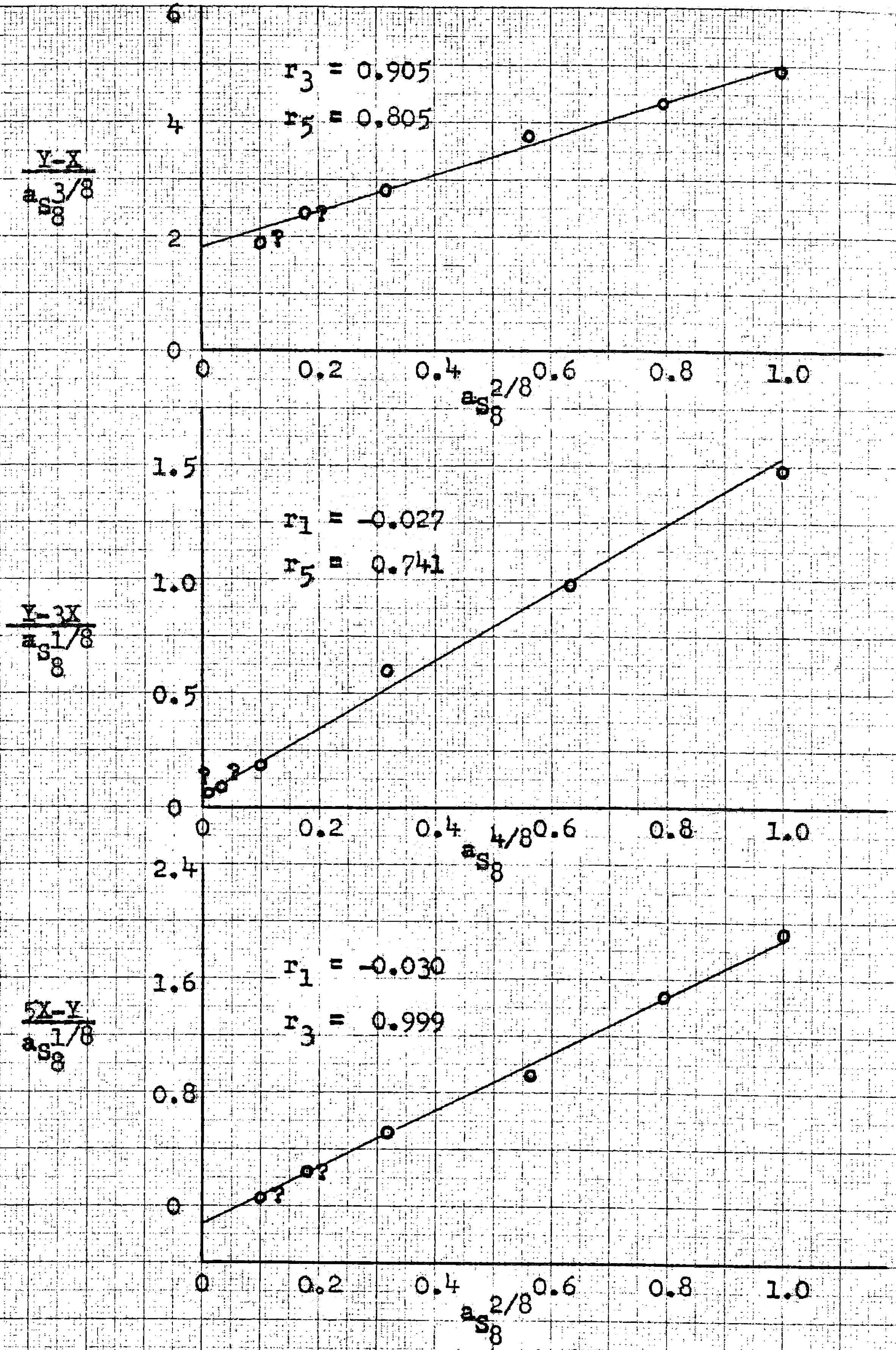


FIGURE 63

Graphical Solution for Assumption 7

Data: Na^{+} = 4.0 m, Curve "I"



<u>FIGURE 64</u>

Graphical Solution for Assumption 8
<u>Data</u>: $Na^+ = 4.0$ m, Curve "I"

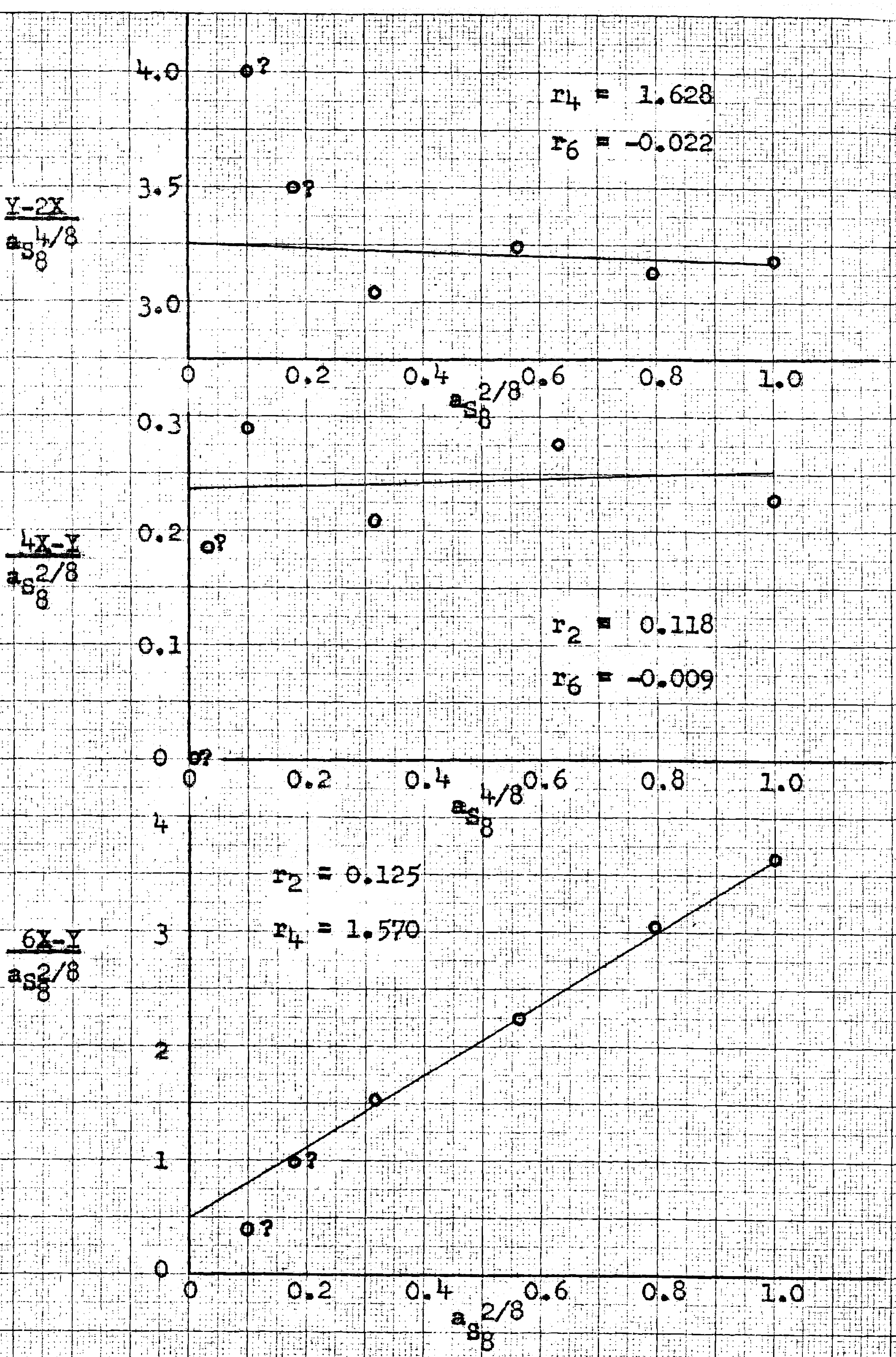


FIGURE 65

Graphical Solution for Assumption 9

Data: Na^{+} = 4.0 m, Curve "I"

Besides the nine assumptions already discussed, the equilibrium constants which were obtained for two additional cases also are presented in Table XIX. These two sets were estimated within the limits already placed on the equilibrium constants assuming a "normal" ionic distribution, and then were adjusted as much as convenient in order best to coincide with the data. Assumption 10 differs from assumption 11 only in that a small amount of $S_2{=}$ ion was assumed to be present in the former. Both these assumptions were formulated taking into account ions as high as $S_8^{=}$.

Maximum and root-mean square errors within which the eleven assumptions match the data for 4.0 m sodium ion, curve "I" also are given in Table XIX. These errors were calculated by comparisons at sulfur activities of 1.0, 0.4, 0.1, and 0.01.

TABLE XIX

Possible Sets of Relative Equilibrium Constants

(75°C, Na^+ = 4.0 m, curve "I")

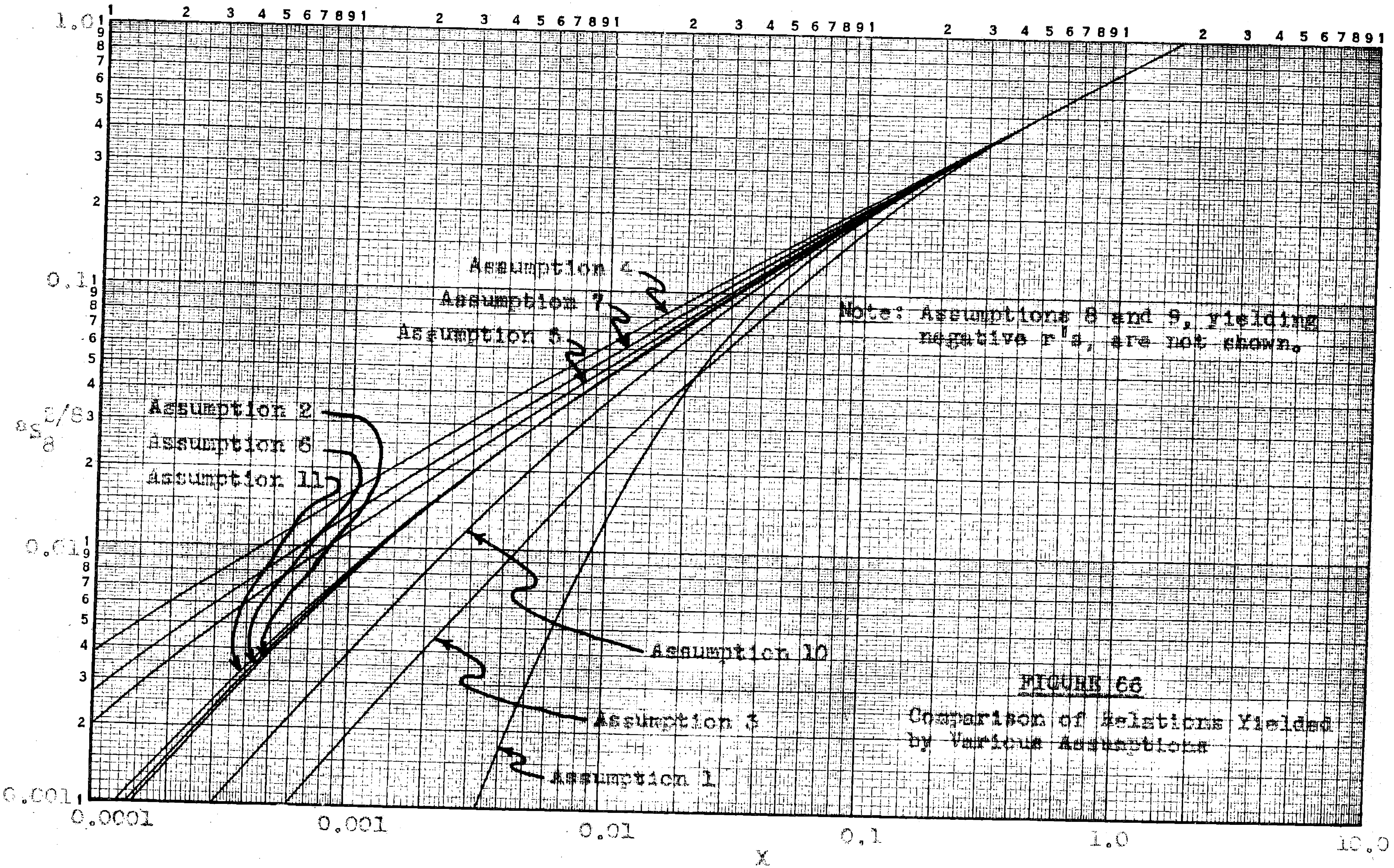
Assumption	$(S_2{=})$ r_1	$(S_3{=})$ r_2	$(S_4{=})$ r_3	$(S_5{=})$ r_4	$(S_6{=})$ r_5	$(S_7{=})$ r_6	$(S_8{=})$ r_7	Max.% Error	Rms% Error
1	0.074			1.630				3.3	1.4
2		0.119		1.590				1.5	0.8
3		0.469			1.242			10.2	6.3
4			0.312	1.394				3.1	1.4
5			0.864		0.845			3.6	1.9
6		0.108	0.070	1.524				2.4	1.1
7			0.575	0.768	0.359			2.1	1.1
8	-0.029		0.957		0.777			2.6	1.5
9		0.122		1.599		-0.016		2.0	0.9
10	0.010	0.079	0.394	0.906	0.246	0.049	0.010	4.6	2.1
11		0.080	0.398	0.915	0.249	0.050	0.010	2.8	1.4

In order to compare these possible sets of equilibrium constants over a wider range of sulfur activities, values of X versus activity were calculated for each set; these curves are shown in Figure 66. It is seen that nearly all the assumptions coincide reasonably well in the region in which experimental data could be obtained, but diverge from each other at lower sulfur activities, again pointing out the need for some sort of information in the low activity region. With the exception of assumption 3, all of the sets of constants listed in Table XIX fitted the data within 5 per cent and thus (with the exception of course of assumptions 8 and 9) might be considered valid solutions within the limits of experimental precision.

To a more limited extent equilibrium constants also were generated graphically using the "II" sulfur activity correlation and the curves at 1.0 sodium ion molality. These constants, in general, differed from the ones already found only by the expected factors of proportionality, and accordingly are not listed here.

4. Formulation of "Recommended" Equilibrium Constants

Since more than one possible set of equilibrium constants were found which fitted the experimental data within the limits of error, additional assumptions were required in order to determine a "recommended" set of



Note: Assumptions 8 and 9, yielding negative r's, are not shown.

FIGURE 66

Comparison of Relations Yielded by Various Assumptions constants and ionic compositions. The polysulfide distributions were assumed, in the first place, to be "normal", i.e., no ion less in concentration than both the ion above it and the ion below it in sulfur subscript. This supposition appeared to some extent to be warranted, since "highly abnormal" distributions such as assumption 3 in Table XIX fitted the data poorest of all. The disulfide ion $S_2^=$ furthermore was assumed to be absent, since any sets of constants which included r_1 in general either violated the "normal distribution" requirement or gave poorer fits than the same assumptions with r_1 taken as zero. Finally, ions higher than $S_6^=$ were neglected. In formulating assumptions 10 and 11 the constants for these higher polysulfide ions had to be set relatively small; their concentrations, as will be shown, moreover must diminish rapidly as sulfur activity decreases from unity at sulfur saturation. Therefore the "recommended" set of ionic equilibrium constants comprises a "normal" distribution made up of the $S_3^=$, $S_4^=$, $S_5^=$, and $S_6^=$ ions.

Consideration of equations 54 and 55 will show that if two sets of possible equilibrium constants satisfy the data within a given error, any linear combination of these two sets must be equally as good a "solution" (even though theoretically only one <u>exact</u> solution may exist). The "recommended" relative equilibrium constants were obtained by use of this rule. Of the five remaining sets of constants in Table XIX which might be employed in making up this combination, assumption 2 and assumption 7 were selected because these two yielded the best agreements with the experimental data. Thus the set of equilibrium constants to be recommended could be expressed as ϵ (assumption 2) + $(1-\epsilon)$ (assumption 7). The r's defined in this manner are shown as functions of the parameter ϵ in Figure 67. Limits then could be placed on ϵ. The requirement that the distribution be "normal" dictated that ϵ be less than 0.82. The limits on r_3 already stated for normal distributions further restricted ϵ to values below 0.39. Finally, ϵ had to be less than 0.32 if the 1.03 upper limit on r_4 were not violated.

Additional restrictions on ϵ were imposed by the graphical slopes at sulfur saturation. As was mentioned previously, equation 105 had an estimated numerical value at unity sulfur activity of 3.5 to 4.5; equation 106 was found to equal 0.4 to 1.4. These specifications on r_3, r_4, and r_5 dictated that from equation 105 ϵ had to be less than 0.37, whereas from equation 106 ϵ had to fall in the range 0.15 to 0.76.

On the basis of all the evidence presented ϵ was assigned the value 0.2 for purposes of generating the recommended equilibrium constants. The numbers thus obtained were

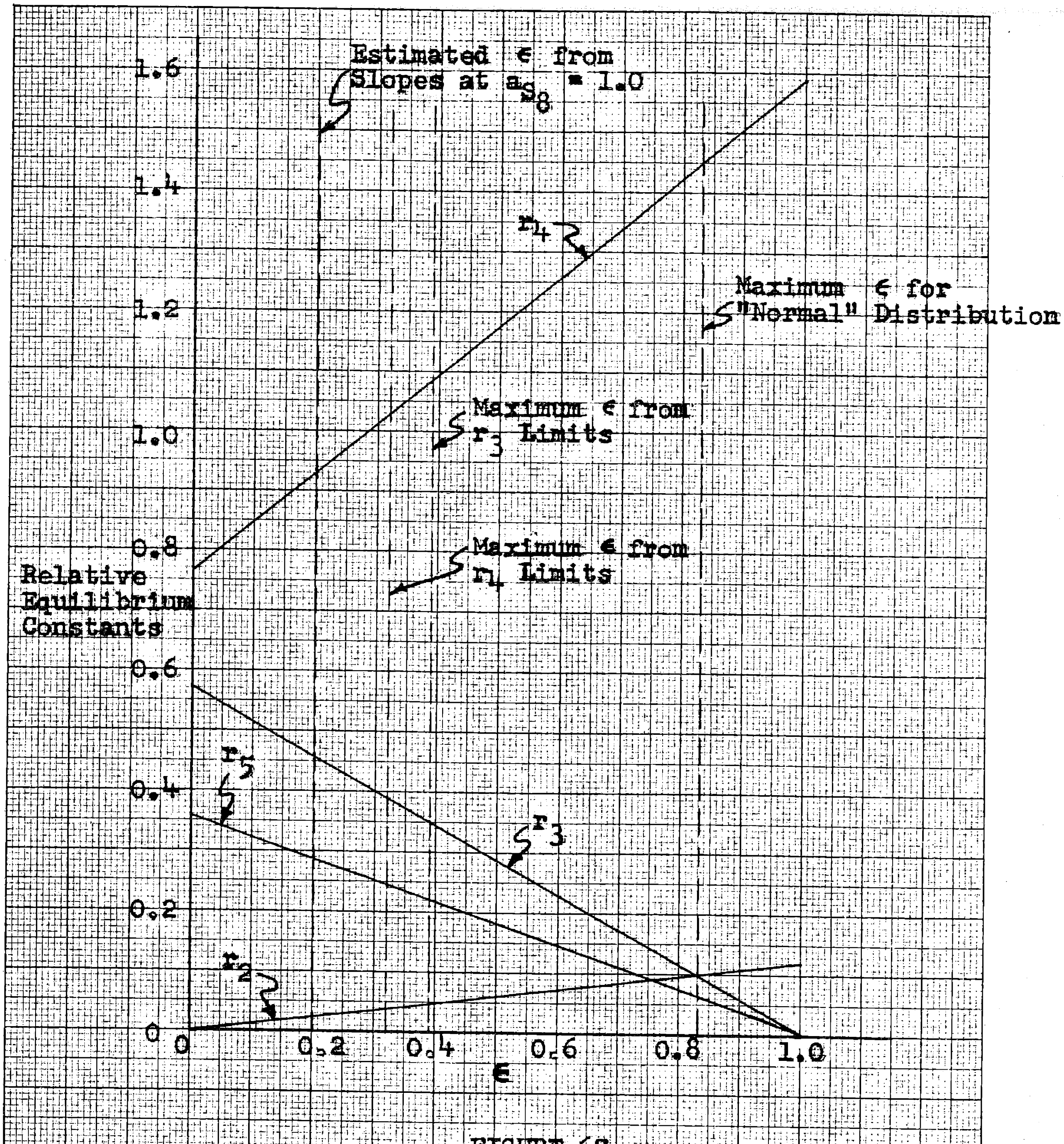


FIGURE 67

"Recommended" Equilibrium Constants by Linear Combination

(Relative Constants for Na^+ = 4.0 m, Curve "I") multiplied by 0.925 to yield relative equilibrium constants satisfying the "II" sulfur activity relations at 4.0 m sodium ion, and by 0.749 and by 0.775 in order to yield constants at 1.0 m for the "I" and "II" correlations, respectively. The "r" values determined by this procedure and the error limits within which the data at sulfur activities from 0.01 to 1.0 were reproduced are given in Table XX:

TABLE XX

"Recommended" Relative Equilibrium Constants at 75°C

Correlation	($S_3^=$) r_2	($S_4^=$) r_3	($S_5^=$) r_4	($S_6^=$) r_5	Max.% Error	RMS % Error
Na^+ = 4.0 m, "I"	0.024	0.460	0.933	0.287	2.1	1.0
Na^+ = 4.0 m, "II"	0.022	0.425	0.863	0.265	2.0	1.0
Na^+ = 1.0 m, "I"	0.018	0.345	0.699	0.216	7.2	4.2
Na^+ = 1.0 m, "II"	0.019	0.357	0.724	0.222	8.8	4.8

The apparently poor fit with the 1.0 m data in part should be disregarded, since both the "I" and the "II" curves at that molality had to be extended by extrapolation to sulfur activities of 0.01 and below, owing to the absence of actual data at such activities. None of the previous assumptions 1 to 11 fitted the 1.0 m sodium ion curves very well below sulfur activities of 0.1; it accordingly is believed that the extrapolated curves were not well-chosen.

F. Ionic Compositions of Polysulfide Solutions

1. Equilibrium Distributions at 75°C

a. Monosulfide Hydrolysis Equilibrium

Knowledge of the equilibrium relating monosulfide ($S^=$), hydrosulfide (HS^-), and hydroxyl (OH^-) ions was required in order that the absolute values of the polysulfide equilibrium constants and also the ionic compositions of ordinary sodium polysulfide solutions could be calculated. The most reliable monosulfide hydrolysis measurements to date appear to be those of Martin (46), who determined $S^=$ ion concentrations in sodium sulfide - sodium hydroxide mixtures by measuring the solubilities of mercuric sulfide. These complete data are presented in Table XXI:

TABLE XXI

Complete Hydrolysis Data of Martin (46)

Temperature °C	Na_2S Molarity	NaOH Molarity	Per Cent Hydrolysis	$Z_1' = [S^=]/[HS^-][OH^-]$
25	0.15	0	92.7	0.569
		0.25	79.7	0.690
		0.50	66.7	0.834
		0.75	56.8	0.909
		1.50	37.8	1.060
	0.25	0	91.9	0.385
		0.25	80.3	0.544
		0.75	58.7	0.784
		1.50	41.0	0.898
	0.35	0	83.8	0.658
		0.25	71.9	0.775
		0.75	55.1	0.862
		1.50	33.1	1.250
110	0.20	0	89.3	0.568
		0.25	79.3	0.636
		0.50	67.1	0.775
		0.75	51.9	1.086
		1.50	43.1	0.832

TABLE XXI (Continued)

Temperature °C	Na_2S Molarity	NaOH Molarity	Per Cent Hydrolysis	$Z_1' = [S^=]/[HS^-][OH^-]$
165	0.20	0	92.0	0.472
		0.25	84.5	0.438
		0.50	72.0	0.604
		0.75	53.5	1.015
		1.50	46.9	0.710

(Z_1' based on molarities)

From equations 28 and 30 the function Z_1' tabulated in Table XXI can be expressed as follows:

$$Z_1' \cong Z_1 = \frac{[S^=]}{[HS^-][OH^-]} = \frac{\gamma_{HS^-}\,\gamma_{OH^-}}{\gamma_{S^=}} \left(\frac{K_2}{K_w'}\right) \qquad (116)$$

(in which Z_1 is based on molalities)

In view of the other approximations which had to be made the interchanging of molalities and molarities in setting up the preceding equation was considered justifiable.

In order to show how the activity coefficient group in equation 116 varies with concentration, the values of Z_1' from Table XXI are plotted versus sodium ion molarity in Figure 68. The relation at 75°C, estimated from the data at the three given temperatures, also is indicated in Figure 68.

Simultaneous consideration of equations 49 and 50 compared to equation 116 shows that the γ_{avg} defined as

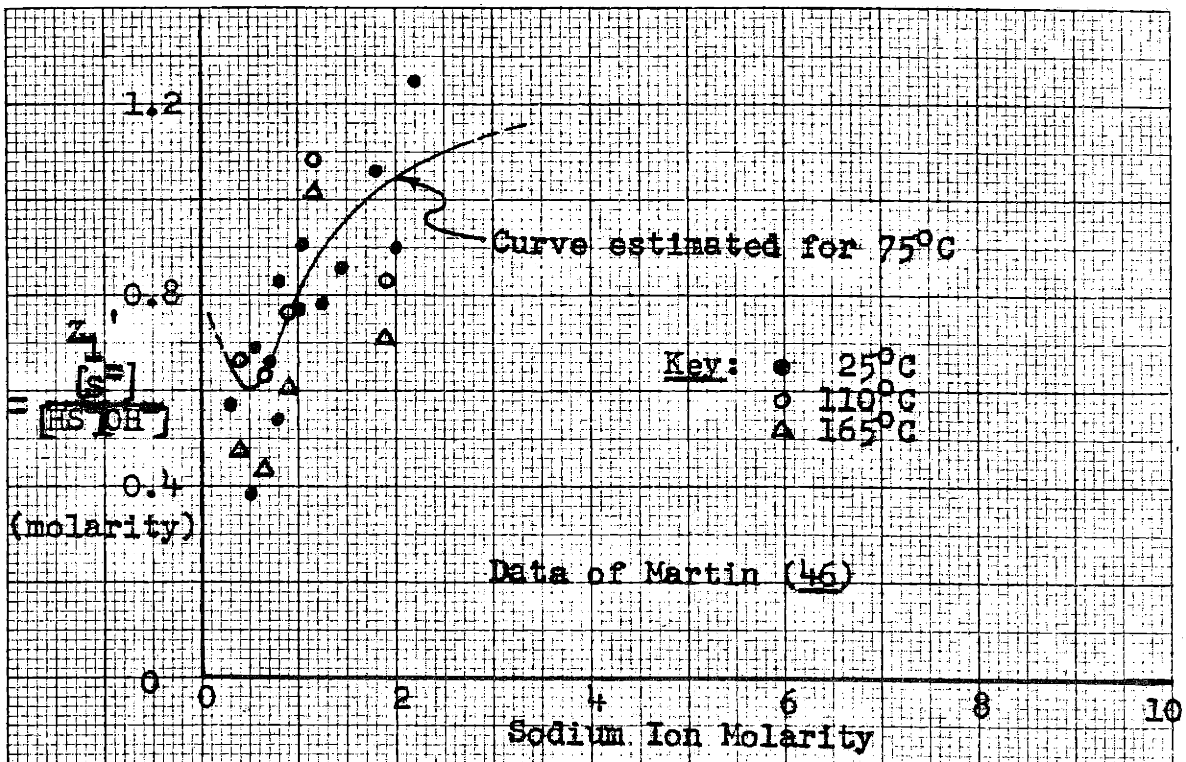


FIGURE 68

Monosulfide Hydrolysis Equilibrium Relation

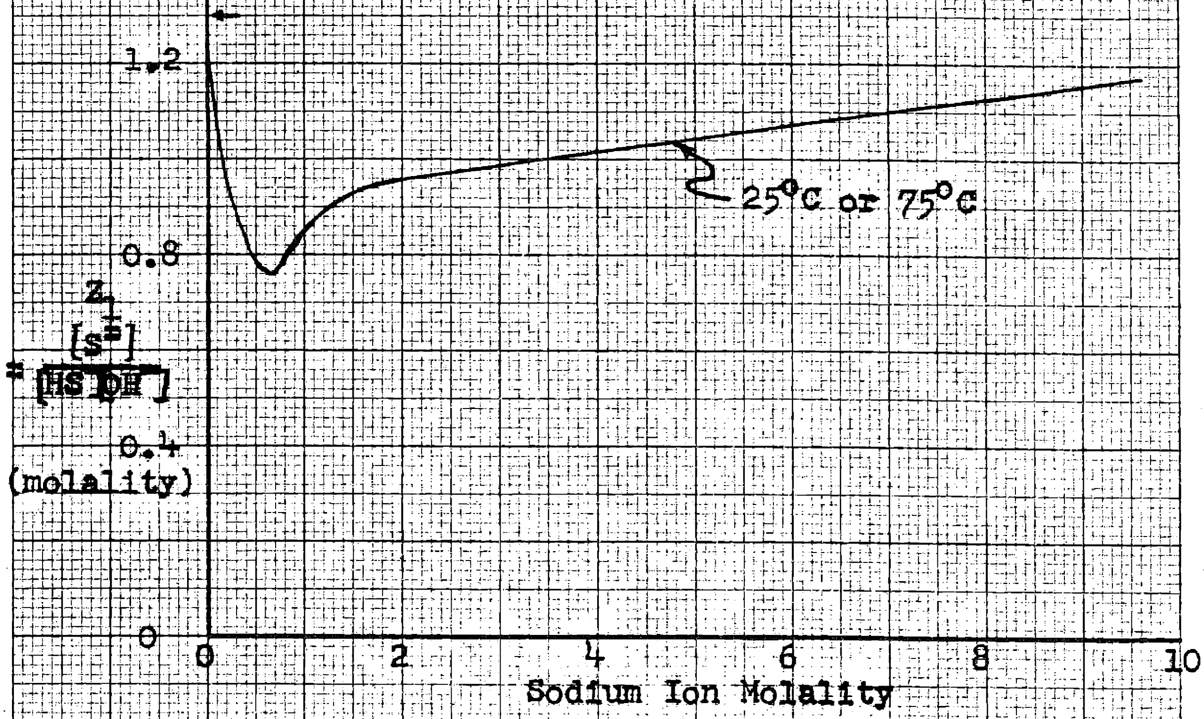


FIGURE 69

Revised Monosulfide Hydrolysis Equilibrium Relation

$(\gamma_{HS^-})^2/\gamma_{S_x^=}$ in the two former relations resembles the $\gamma_{HS^-}\ \gamma_{OH^-}/\ \gamma_{S^=}$ term in the latter. Taking into account the simplifying assumptions already made, it was judged unwarranted to carry two different "average" ionic activity coefficients through the remainder of the calculations. Therefore γ_{OH^-} was assumed equal to γ_{HS^-} and $\gamma_{S^=}$ was taken as equal to $\gamma_{S_x^=}$. Since the two activity coefficient groups then had to be the same, the Z_1 (or Z_1') curve based on the hydrolysis data taken from the literature had to be modified in order to be compatible with the activity coefficient correlations of the present thesis. Since the Z_1' points at 25°C and the curve drawn for 75°C were not too dissimilar, the same revised Z_1 relation was assumed for both temperatures, as is shown in Figure 69. This curve was drawn to approximate the same average Z_1 as the uncorrected data, but to be proportional at all molalities to the X and Y activity coefficient relations already decided on (Figures 23 and 24). The intercept (1.299) indicated in Figure 69 corresponds to the K_2 values ("recommended" in equation 30) of about 1.3×10^{-14} at 25°C and about 2.9×10^{-13} at 75°C.

b. Numerical Values of Polysulfide Equilibrium Constants

In view of the powerful evidence presented by the comparison of xylene sulfur concentrations at the two molalities, the "II" X and Y versus sulfur activity curves and their corresponding relative equilibrium constants (Table XX) were employed in determining the absolute values of the equilibrium constants and in calculating the ionic distributions in polysulfide solutions. As was mentioned earlier, Figures 23 and 24 were drawn based on these "II" relations. The numerical values of the polysulfide equilibrium constants could be obtained from the relative "r's" by the use of the following relation, derived from equations 51, 52, 53 and the like, in conjunction with equation 116:

$$k_{1,2,\text{ etc.}} = \left(\frac{K_1'}{K_W'}\right)\left(\frac{r_{1,2,\text{etc.}}}{Z_1}\right) \qquad (117)$$

Since the activity coefficient terms dropped out in setting up equation 117, it follows that the numerical k's could be found knowing only the Z_1 values from Figure 69 (in effect, the products of γ_{avg} and K_2). It therefore was not necessary that K_2 itself be known in order to proceed with the remainder of the calculations. The polysulfide equilibrium constants at 75°C as obtained in this manner from the "recommended" set of r's are presented in Table XXII.

TABLE XXII

Recommended Polysulfide Equilibrium Constants at 75°C

Reaction	Equilibrium Constant
$S^{=} + 1/8\ S_8 = S_2^{=}$	$k_1 = 0$
$S^{=} + 2/8\ S_8 = S_3^{=}$	$k_2 = 1760$
$S^{=} + 3/8\ S_8 = S_4^{=}$	$k_3 = 33,700$
$S^{=} + 4/8\ S_8 = S_5^{=}$	$k_4 = 68,400$
$S^{=} + 5/8\ S_8 = S_6^{=}$	$k_5 = 21,040$
$S^{=} + 6/8\ S_8 = S_7^{=}$	$k_6 = 0$
etc.	etc.

c. Calculation of Polysulfide Ionic Compositions

In order to avoid lengthy trial-and-error procedures in computing the ionic distributions in sodium polysulfide solutions, all the calculations were carried out for selected values of sulfur activity rather than for selected values of "x", the average sulfur subscript. The compositions at any desired "x" then could be obtained by interpolation.

From the elemental sulfur activity the values of X and Y could be determined using equations 54 and 55, if the relative equilibrium constants (r's) were known:

$$X = r_1 a_{S_8}^{1/8} + r_2 a_{S_8}^{2/8} + r_3 a_{S_8}^{3/8} + \dots \qquad (54)$$

$$Y = r_1 a_{S_8}^{1/8} + 2r_2 a_{S_8}^{2/8} + 3r_3 a_{S_8}^{3/8} + \ldots \qquad (55)$$

The relative proportions of the various polysulfide species moreover would be indicated by the corresponding terms on the right-hand side of equation 54. Although the r's were functions of ionic activity coefficients and hence of molality, it was not necessary to compute X and Y and the individual $r_1 a_{S_8}^{1/8}$ products versus sulfur activities for each polysulfide concentration at which ionic distributions were to be calculated (since the preceding two equations are multiplied only by a constant factor as molality is varied). This tabulation instead could be done for any set of r's which were proportional to the recommended ones (Table XX), and the quantities X and Y at the chosen sulfur activity a_{S_8} then could be determined as follows:

$$X = \left(\frac{X_{sat}}{X_{o,sat}}\right) X_{o,a_{S_8}} \qquad (118)$$

$$Y = \left(\frac{Y_{sat}}{Y_{o,sat}}\right) Y_{o,a_{S_8}} \qquad (119)$$

in which the subscript "o" refers to the quantities tabulated versus that a_{S_8} value, and in which X_{sat} and Y_{sat} for the actual sodium ion molality are obtained using Figure 23 and Figure 24, respectively.

For no reason other than convenience the tabulation of X_o, Y_o, and the various $r_1 a_{S_8}^{1/8}$ products was performed using the first set of "r" values listed in Table XX (those for $Na^+ = 4.0$ m, curve "I"). The quantities thus derived are presented in Table XXIII:

If the HS_x^- species may be assumed absent, then either in sodium monosulfide or in sodium polysulfide solutions the hydroxyl (OH^-) concentration must equal the hydrosulfide (HS^-) concentration. With this rule in mind, simultaneous consideration of equations 26 and 28 shows that the equilibrium hydrogen sulfide partial pressure over such solutions is constant, unaffected either by the molality or by the average sulfur subscript ("x" of Na_2S_x):

$$f_{H_2S} \cong \frac{K_w'}{K_1'} = 8.63 \times 10^{-7} \text{ at } 25°C \qquad (120$$

$$= 1.235 \times 10^{-5} \text{ at } 75°C$$

Since X is defined as $\frac{[S_x^=] \; f_{H_2S}}{[HS^-]^2}$, substitution of equation 120 and rearrangement yields:

$$\frac{K_1'}{K_w'} X = \frac{[S_x^=]}{[HS^-]^2} = Z_2 \qquad (121)$$

Similarly, the expression for Z_1 may be simplified if $[OH^-]$ can be taken equal to $[HS^-]$:

$$Z_1 = \gamma_{avg} \frac{K_2}{K_w'} = \frac{[S^=]}{[HS^-]^2} \qquad (122)$$

TABLE XXIII

Relative Polysulfide Ionic Distributions at 75°C

(based on relative equilibrium constants for Na^+ = 4.0 m, curve "I")

a_{S_8}	1.0	0.4	0.1	0.01	0.001	10^{-4}
$r_2 a_{S_8}^{2/8}$	0.0240	0.0191	0.0135	0.00759	0.00426	0.00240
$r_3 a_{S_8}^{3/8}$	0.460	0.326	0.194	0.0817	0.0345	0.01456
$r_4 a_{S_8}^{4/8}$	0.933	0.590	0.295	0.0933	0.0295	0.00933
$r_5 a_{S_8}^{5/8}$	0.287	0.162	0.0680	0.0161	0.00383	0.00091
X	1.704	1.097	0.571	0.1987	0.0721	0.02720
$2r_2 a_{S_8}^{2/8}$	0.0480	0.0382	0.0270	0.0152	0.00853	0.00480
$3r_3 a_{S_8}^{3/8}$	1.380	0.978	0.582	0.246	0.1035	0.0436
$4r_4 a_{S_8}^{4/8}$	3.732	2.360	1.180	0.373	0.1180	0.0373
$5r_5 a_{S_8}^{5/8}$	1.435	0.809	0.340	0.0806	0.0191	0.00450
Y	6.595	4.185	2.129	0.715	0.2491	0.0902

TABLE XXIII (Continued)

a_{S_8}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}
$r_2 a_{S_8}^{2/8}$	0.00135	0.000759	0.000426	2.40×10^{-4}	1.35×10^{-4}	7.59×10^{-5}
$r_3 a_{S_8}^{3/8}$	0.00613	0.00259	0.001090	4.60×10^{-4}	1.94×10^{-4}	8.17×10^{-5}
$r_4 a_{S_8}^{4/8}$	0.00295	0.000933	0.000295	0.93×10^{-4}	0.30×10^{-4}	0.93×10^{-5}
$r_5 a_{S_8}^{5/8}$	0.00022	0.000051	0.000012	0.03×10^{-4}	0.01×10^{-4}	0.02×10^{-5}
X	0.01065	0.00433	0.001823	7.96×10^{-4}	3.60×10^{-4}	16.71×10^{-5}
$2r_2 a_{S_8}^{2/8}$	0.00270	0.00152	0.000853	4.80×10^{-4}	2.70×10^{-4}	15.2×10^{-5}
$3r_3 a_{S_8}^{3/8}$	0.01840	0.00776	0.00327	13.80×10^{-4}	5.82×10^{-4}	24.6×10^{-5}
$4r_4 a_{S_8}^{4/8}$	0.01180	0.00373	0.00118	3.73×10^{-4}	1.18×10^{-4}	3.73×10^{-5}
$5r_5 a_{S_8}^{5/8}$	0.00108	0.000255	0.000061	0.14×10^{-4}	0.03×10^{-4}	0.08×10^{-5}
Y	0.0340	0.01327	0.00536	22.5×10^{-4}	9.73×10^{-4}	43.6×10^{-5}

TABLE XXIII (Continued)

a_{S_8}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	10^{-15}	10^{-16}
$r_2 a_{S_8}^{2/8}$	4.26×10^{-5}	2.40×10^{-5}	1.35×10^{-5}	7.59×10^{-6}	4.26×10^{-6}	2.40×10^{-6}
$r_3 a_{S_8}^{3/8}$	3.45×10^{-5}	1.46×10^{-5}	0.61×10^{-5}	2.59×10^{-6}	1.09×10^{-6}	0.46×10^{-6}
$r_4 a_{S_8}^{4/8}$	0.30×10^{-5}	0.09×10^{-5}	0.03×10^{-5}	0.09×10^{-6}	0.03×10^{-6}	0.01×10^{-6}
$r_5 a_{S_8}^{5/8}$	0.00×10^{-5}	0.00×10^{-5}	0.00×10^{-5}	0.00×10^{-6}	0.00×10^{-6}	0.00×10^{-6}
X	8.01×10^{-5}	3.95×10^{-5}	1.99×10^{-5}	10.27×10^{-6}	5.38×10^{-6}	2.87×10^{-6}
$2r_2 a_{S_8}^{2/8}$	8.53×10^{-5}	4.80×10^{-5}	2.70×10^{-5}	15.2×10^{-6}	8.53×10^{-6}	4.80×10^{-6}
$3r_3 a_{S_8}^{3/8}$	10.35×10^{-5}	4.36×10^{-5}	1.84×10^{-5}	7.76×10^{-6}	3.27×10^{-6}	1.38×10^{-6}
$4r_4 a_{S_8}^{4/8}$	1.18×10^{-5}	0.37×10^{-5}	0.12×10^{-5}	0.37×10^{-6}	0.12×10^{-6}	0.04×10^{-6}
$5r_5 a_{S_8}^{5/8}$	0.02×10^{-5}	0.00×10^{-5}	0.00×10^{-5}	0.00×10^{-6}	0.00×10^{-6}	0.00×10^{-6}
Y	20.08×10^{-5}	9.53×10^{-5}	4.66×10^{-5}	23.33×10^{-6}	11.92×10^{-6}	6.22×10^{-6}

Finally, the electrical neutrality requirement may be written:

$$[Na^+] = \underline{m} = 2[S_x^=] + 2[S^=] + [HS^-] + [OH^-] \quad (123)$$

(in which $[OH^-]$ is equal to $[HS^-]$.)

Equations 121, 122, and 123 may be considered three simultaneous relations in the three unknowns $[S_x^=]$, $[S^=]$, and $[HS^-]$, dependent only on the three known quantities Z_1, Z_2, and $\underline{m}$. Solving for the hydrosulfide (HS^-) concentration thus yields:

$$[HS^-] \ (= [OH^-]) = \frac{-1 + \sqrt{1 + 2m\ (Z_1 + Z_2)}}{2\ (Z_1 + Z_2)} \quad (124)$$

The monosulfide ($S^=$) and polysulfide ($S_x^=$) concentrations then could be calculated from equations 122 and 121, respectively.

In the calculation of a polysulfide solution composition at $\underline{m}$ sodium ion molality and a_{S_8} sulfur activity, Z_1 was determined from the revised curve in Figure 69 and the values of X_{sat} and Y_{sat} at that same molality were read from Figures 23 and 24, respectively. The actual X and Y quantities at a_{S_8} sulfur activity were obtained from Table XXIII, with the aid of equations 118 and 119, respectively. From the actual X value the function Z_2 as defined in equation 121 was calculated. The hydrosulfide (HS^-)

molality then could be computed by means of equation 124; the $S^=$ and $S_x^=$ ionic molalities thus also could be found. The true polysulfide concentration could be divided up into its constituent ions $S_3^=$, $S_4^=$, $S_5^=$, and $S_6^=$ by pro-rating the "$r_i a_{S_8}^{1/8}$" products listed in Table XXIII. Finally, the gm-atoms polysulfide sulfur on a molality basis could be calculated by multiplying the actual $S_x^=$ concentration by the ratio Y/X. The apparent "x" (or sulfur subscript in the formula Na_2S_x) then could be derived by dividing the polysulfide sulfur molality by one-half the sodium ion molality, and adding one to the quotient.

Based on the recommended set of equilibrium constants at 75°C, complete profiles of polysulfide ionic compositions versus "x" thus were calculated for the following sodium ion molalities: 8.0, 4.0, 2.0, 1.0, 0.5, 0.2, 0.1. In addition, the compositions of polysulfide solutions at sulfur saturation were computed, based on the extrapolated activity coefficient correlation (Figures 23, 24, and 69), at sodium ion molalities of 0.01, 0.001, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7}. These latter did depend, more or less, on the assumed numerical values of γ_{avg} and K_2. All these results are presented in Table XXIV:

TABLE XXIV-a

Compositions of Sodium Polysulfide Solutions at 75°C

Na^+ m	x	$[HS^-]$ or $[OH^-]$	$[S^=]$	$[S_3^=]$	$[S_4^=]$	$[S_5^=]$	$[S_6^=]$	a_{S_8}
8.0	4.86	0.00532	0.0000320	0.0562	1.079	2.187	0.673	1.0
	4.72	0.00918	0.0000952	0.0943	1.358	2.063	0.476	0.1
	4.42	0.02576	0.000748	0.2345	1.901	1.626	0.2109	0.001
	4.14	0.0666	0.00502	0.498	2.262	1.089	0.0793	10^{-5}
	3.97	0.1040	0.01222	0.680	2.322	0.836	0.0458	10^{-6}
	3.80	0.1588	0.02847	0.891	2.281	0.616	0.0253	10^{-7}
	3.62	0.2368	0.0634	1.116	2.137	0.434	0.0133	10^{-8}
	3.38	0.344	0.1338	1.324	1.902	0.2887	0.0067	10^{-9}
	3.12	0.485	0.2657	1.475	1.590	0.1814	0.0031	10^{-10}
	2.79	0.656	0.487	1.521	1.230	0.1052	0.0014	10^{-11}
	2.41	0.847	0.811	1.423	0.863	0.0553	0.0005	10^{-12}
	1.68	1.189	1.605	0.891	0.304	0.0110	0.0001	10^{-14}
	1.25	1.384	2.162	0.380	0.0727	0.0015	0.0000	10^{-16}
	1.00	1.489	2.511	0	0	0	0	0
4.0	4.86	0.00395	0.0000160	0.0281	0.539	1.093	0.336	1.0
	4.80	0.00493	0.0000248	0.0347	0.593	1.073	0.294	0.4
	4.72	0.00682	0.0000475	0.0471	0.677	1.031	0.238	0.1
	4.58	0.01158	0.0001369	0.0759	0.817	0.934	0.161	0.01
	4.42	0.01920	0.000376	0.1170	0.947	0.811	0.1052	0.001
	4.26	0.0311	0.000988	0.1736	1.053	0.675	0.0659	10^{-4}
	4.11	0.0495	0.00250	0.247	1.122	0.540	0.0393	10^{-5}
	3.93	0.0769	0.00604	0.336	1.146	0.412	0.0226	10^{-6}
	3.74	0.1172	0.01402	0.437	1.118	0.302	0.0124	10^{-7}
	3.54	0.1740	0.0309	0.541	1.038	0.2103	0.0065	10^{-8}
	3.28	0.2504	0.0641	0.633	0.911	0.1381	0.0032	10^{-9}
	2.99	0.349	0.1246	0.693	0.747	0.0852	0.0015	10^{-10}
	2.64	0.468	0.2238	0.697	0.563	0.0481	0.0005	10^{-11}
	2.26	0.594	0.360	0.636	0.385	0.0247	0.0002	10^{-12}
	1.89	0.715	0.522	0.516	0.235	0.0113	0.0001	10^{-13}
	1.58	0.815	0.676	0.376	0.1284	0.0046	0.0000	10^{-14}
	1.35	0.885	0.799	0.2497	0.0638	0.0018	0.0000	10^{-15}
	1.20	0.931	0.883	0.1559	0.0298	0.0006	0.0000	10^{-16}
	1.00	0.993	1.007	0	0	0	0	0

TABLE XXIV-a (Continued)

Na^+ m	x	$[HS^-]$ or $[OH^-]$	$[S^=]$	$[S_3^=]$	$[S_4^=]$	$[S_5^=]$	$[S_6^=]$	$^aS_8$
2.0	4.86	0.002887	8.00×10^{-6}	0.01404	0.2689	0.546	0.1679	1.0
	4.71	0.00499	0.0000239	0.02350	0.338	0.515	0.1184	0.1
	4.40	0.01395	0.0001868	0.0583	0.471	0.404	0.0524	0.001
	4.08	0.0359	0.001238	0.1220	0.554	0.2666	0.01945	10^{-5}
	3.88	0.0556	0.002975	0.1649	0.562	0.2028	0.01109	10^{-6}
	3.68	0.0844	0.00683	0.2123	0.544	0.1470	0.00603	10^{-7}
	3.43	0.1242	0.01481	0.2596	0.497	0.1009	0.00310	10^{-8}
	3.14	0.1775	0.0302	0.298	0.428	0.0649	0.00150	10^{-9}
	2.83	0.2442	0.0573	0.317	0.342	0.0390	0.00067	10^{-10}
	2.46	0.321	0.0992	0.309	0.2498	0.02137	0.00028	10^{-11}
	2.08	0.401	0.1544	0.2703	0.1640	0.01051	0.00010	10^{-12}
	1.46	0.529	0.2694	0.1492	0.0510	0.00184	0.00001	10^{-14}
	1.15	0.592	0.337	0.0589	0.01131	0.00023	0.00000	10^{-16}
	1.00	0.625	0.375	0	0	0	0	0

TABLE XXIV-b

Compositions of Sodium Polysulfide Solutions at 75°C

Na^+ m	x	$[HS^-]$ or $[OH^-]$	$[S^=]$	$[S_3^=]$	$[S_4^=]$	$[S_5^=]$	$[S_8^=]$	a_{S_8}
1.0	4.86	0.002160	3.98×10^{-6}	0.00701	0.1344	0.2730	0.0838	1.0
	4.69	0.00373	0.0000120	0.01172	0.1685	0.2562	0.0591	0.1
	4.38	0.01043	0.0000930	0.02895	0.2342	0.2004	0.0260	0.001
	4.02	0.02660	0.000604	0.0599	0.2724	0.1311	0.00955	10^{-5}
	3.80	0.0412	0.001448	0.0801	0.2730	0.0987	0.00539	10^{-6}
	3.56	0.0618	0.00326	0.1017	0.2600	0.0704	0.00289	10^{-7}
	3.28	0.0899	0.00690	0.1215	0.2328	0.0472	0.00145	10^{-8}
	2.94	0.1266	0.01368	0.135	0.194	0.0295	0.00068	10^{-9}
	2.59	0.1714	0.02504	0.1380	0.1488	0.01697	0.00029	10^{-10}
	2.20	0.2188	0.0409	0.1278	0.1033	0.00884	0.00011	10^{-11}
	1.84	0.2656	0.0602	0.1059	0.0642	0.00411	0.00004	10^{-12}
	1.32	0.334	0.0951	0.0528	0.01800	0.00065	0.00000	10^{-14}
	1.10	0.364	0.1125	0.01972	0.00378	0.00008	0.00000	10^{-16}
	1.00	0.378	0.1220	0	0	0	0	0
0.5	4.85	0.001584	1.977×10^{-6}	0.00350	0.0671	0.1359	0.0419	1.0
	4.68	0.00273	5.87×10^{-6}	0.00584	0.0841	0.1280	0.02942	0.1
	4.53	0.00461	0.0000167	0.00937	0.1009	0.1152	0.01989	0.01
	4.35	0.00759	0.0000454	0.01434	0.1160	0.0992	0.01289	0.001
	4.15	0.01225	0.0001182	0.02097	0.1271	0.0815	0.00795	10^{-4}
	3.94	0.01926	0.0002921	0.02920	0.1327	0.0638	0.00465	10^{-5}
	3.68	0.02946	0.000684	0.0383	0.1307	0.0470	0.00258	10^{-6}
	3.40	0.0440	0.001524	0.0478	0.1222	0.0331	0.00136	10^{-7}
	3.08	0.0630	0.00313	0.0554	0.1062	0.02156	0.00066	10^{-8}
	2.71	0.0867	0.00592	0.0592	0.0850	0.01290	0.00030	10^{-9}
	2.31	0.1146	0.01018	0.0569	0.0612	0.00699	0.00012	10^{-10}
	1.93	0.1412	0.01574	0.0496	0.0401	0.00343	0.00004	10^{-11}
	1.61	0.1655	0.02150	0.0383	0.02322	0.00149	0.00001	110^{-12}
	1.21	0.1967	0.0303	0.01696	0.00579	0.00021	0.00000	10^{-14}
	1.00	0.2138	0.0362	0	0	0	0	0

TABLE XXIV-b (Continued)

Na^+ m	x	$[HS^-]$ or $[OH^-]$	$[S^=]$	$[S_3^=]$	$[S_4^=]$	$[S_5^=]$	$[S_6^=]$	a_{S_8}
0.2	4.83	0.000912	7.90×10^{-7}	0.00140	0.02675	0.0542	0.01670	1.0
	4.66	0.001570	2.34×10^{-6}	0.00232	0.0335	0.0509	0.01171	0.1
	4.50	0.002650	6.68×10^{-6}	0.00371	0.0400	0.0457	0.00789	0.01
	4.30	0.00437	0.0000182	0.00565	0.0457	0.0391	0.00508	0.001
	4.09	0.00700	0.0000465	0.00821	0.0498	0.0319	0.00311	10^{-4}
	3.84	0.01092	0.0001135	0.01128	0.0513	0.02462	0.00180	10^{-5}
	3.55	0.01657	0.0002608	0.01456	0.0496	0.01790	0.00098	10^{-6}
	3.21	0.02435	0.000562	0.01758	0.0449	0.01215	0.00050	10^{-7}
	2.83	0.0341	0.001107	0.01952	0.0375	0.00759	0.00023	10^{-8}
	2.41	0.0456	0.001981	0.01965	0.02820	0.00430	0.00010	10^{-9}
	2.02	0.0578	0.00317	0.01770	0.01908	0.00218	0.00004	10^{-10}
	1.67	0.0689	0.00451	0.01414	0.01145	0.00098	0.00001	10^{-11}
	1.40	0.0777	0.00570	0.01009	0.00611	0.00039	0.00000	10^{-12}
	1.12	0.0873	0.00725	0.00405	0.00138	0.00005	0.00000	10^{-14}
	1.0	0.0920	0.00805	0	0	0	0	0

TABLE XXIV-c

Compositions of Sodium Polysulfide Solutions at 75°C

Na^+ m	x	$[HS^-]$ or $[OH^-]$	$[S^=]$	$[S_3^=]$	$[S_4^=]$	$[S_5^=]$	$[S_6^=]$	a_{S_8}
0.1	4.82	0.000607	$3.96x10^{-7}$	0.000695	0.01332	0.02702	0.00831	1.0
	4.65	0.001043	$1.170x10^{-6}$	0.001158	0.01664	0.02529	0.00583	0.1
	4.46	0.001760	$3.32x10^{-6}$	0.001842	0.01985	0.02265	0.00391	0.01
	4.25	0.002880	$8.91x10^{-6}$	0.002780	0.02248	0.01923	0.002497	0.001
	4.01	0.00460	0.0000228	0.00400	0.02428	0.01557	0.001518	10^{-4}
	3.73	0.00715	0.0000549	0.00543	0.02463	0.01187	0.000865	10^{-5}
	3.40	0.01073	0.0001239	0.00687	0.02346	0.00845	0.000462	10^{-6}
	3.02	0.01545	0.0002562	0.00803	0.02050	0.00555	0.000228	10^{-7}
	2.60	0.02125	0.000486	0.00854	0.01636	0.00332	0.000102	10^{-8}
	2.16	0.02763	0.000817	0.00810	0.01164	0.001765	0.000041	10^{-9}
	1.78	0.0338	0.001221	0.00679	0.00731	0.000835	0.000014	10^{-10}
	1.48	0.0389	0.001621	0.00507	0.00410	0.000350	0.000005	10^{-11}
	1.27	0.0425	0.001938	0.00341	0.002065	0.000132	0.000001	10^{-12}
	1.08	0.0457	0.002243	0.001249	0.000426	0.000015	0.000000	10^{-14}
	1.00	0.0476	0.00242	0	0	0	0	0
0.01	4.74	0.0001774	$3.87x10^{-8}$	$6.79x10^{-5}$	0.001302	0.002640	0.000812	1.0
0.001	4.46	0.0000530	$3.58x10^{-9}$	$6.30x10^{-6}$	0.000121	0.000245	0.000075	1.0
10^{-4}	3.72	$1.480x10^{-5}$	$2.83x10^{-10}$	$4.96x10^{-7}$	$9.50x10^{-6}$	$1.93x10^{-5}$	$5.93x10^{-6}$	1.0
10^{-5}	2.34	$3.27x10^{-6}$	$1.39x10^{-11}$	$2.44x10^{-8}$	$4.67x10^{-7}$	$9.46x10^{-7}$	$2.91x10^{-7}$	1.0
10^{-6}	1.27	$4.65x10^{-7}$	$2.78x10^{-13}$	$4.89x10^{-10}$	$9.37x10^{-9}$	$1.90x10^{-8}$	$5.84x10^{-9}$	1.0
10^{-7}	1.03	$4.96x10^{-8}$	$3.17x10^{-15}$	$5.56x10^{-12}$	$1.07x10^{-10}$	$2.16x10^{-10}$	$6.65x10^{-11}$	1.0

d. Examination of "Recommended" Ionic Compositions

The polysulfide concentration profiles presented in Table XXIV are plotted as ionic molalities versus "x", for sodium ion molalities of 8.0, 4.0, 2.0, 1.0, 0.5, 0.2, and 0.1, in Figures 70, 71, 72, 73, 74, 75, and 76, respectively. Both from Table XXIV and from the graphs it is evident that even though the trisulfide ion is low in concentration in the vicinity of sulfur saturation, it becomes an important constituent at smaller "x" values. Since the relative equilibrium constant (r_2) for trisulfide formation obviously was not determined with any precision whatever, the polysulfide compositions as presented must be considered increasingly dubious at "x" values much below 4.0.

The ionic distributions at 1.0 m sodium ion are compared with those at the same concentration proposed by Peschanski and Valensi (53) and by Conway (15) in Figures 77 and 78, respectively. Both these predictions from the literature assumed hydrolyses of the monosulfide ion greater than those selected from the data of Martin (46) and employed in the present thesis. The distributions of Peschanski and Valensi have the obvious flaw that ions higher than $S_5^=$ were neglected. The compositions calculated by Conway from the results of Rule and Thomas (56) do not satisfy the assumed requirement that the ionic distribution be

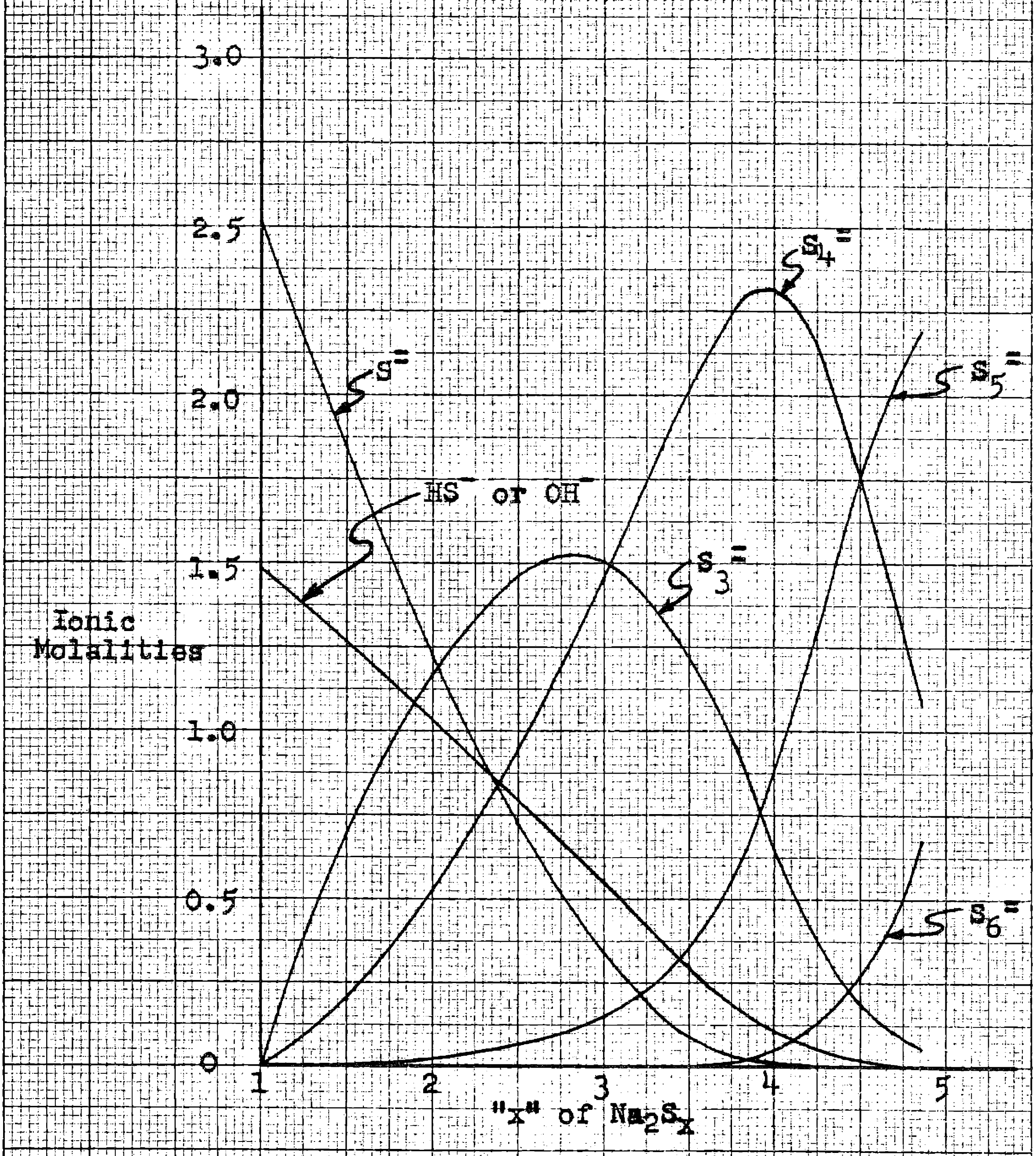


FIGURE 70

Polysulfide Ionic Distributions at 75°C
$Na^+ = 8.0$ m

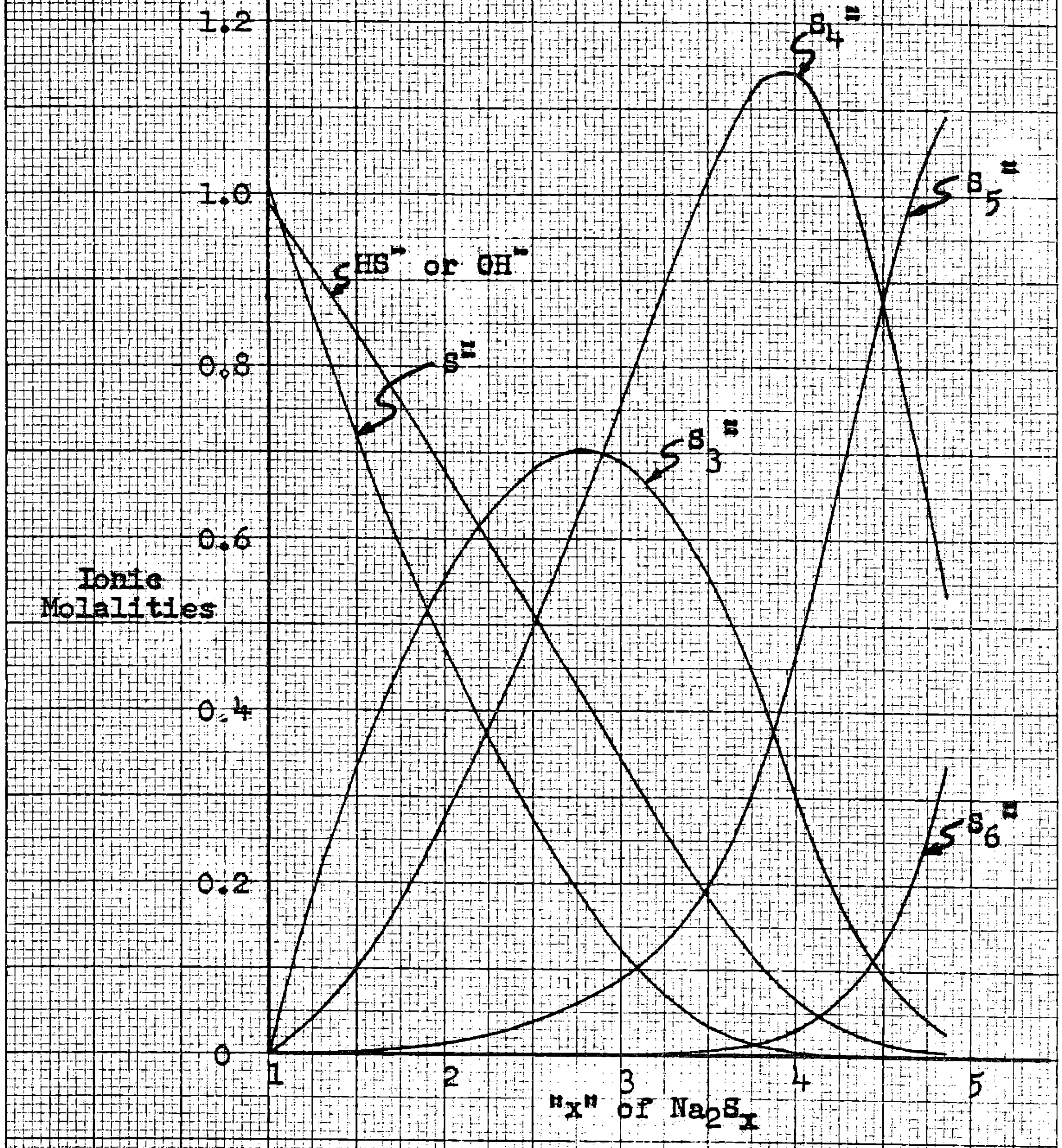


FIGURE 71

Polysulfide Ionic Distributions at 75°C
$Na^+ = 4.0$ m

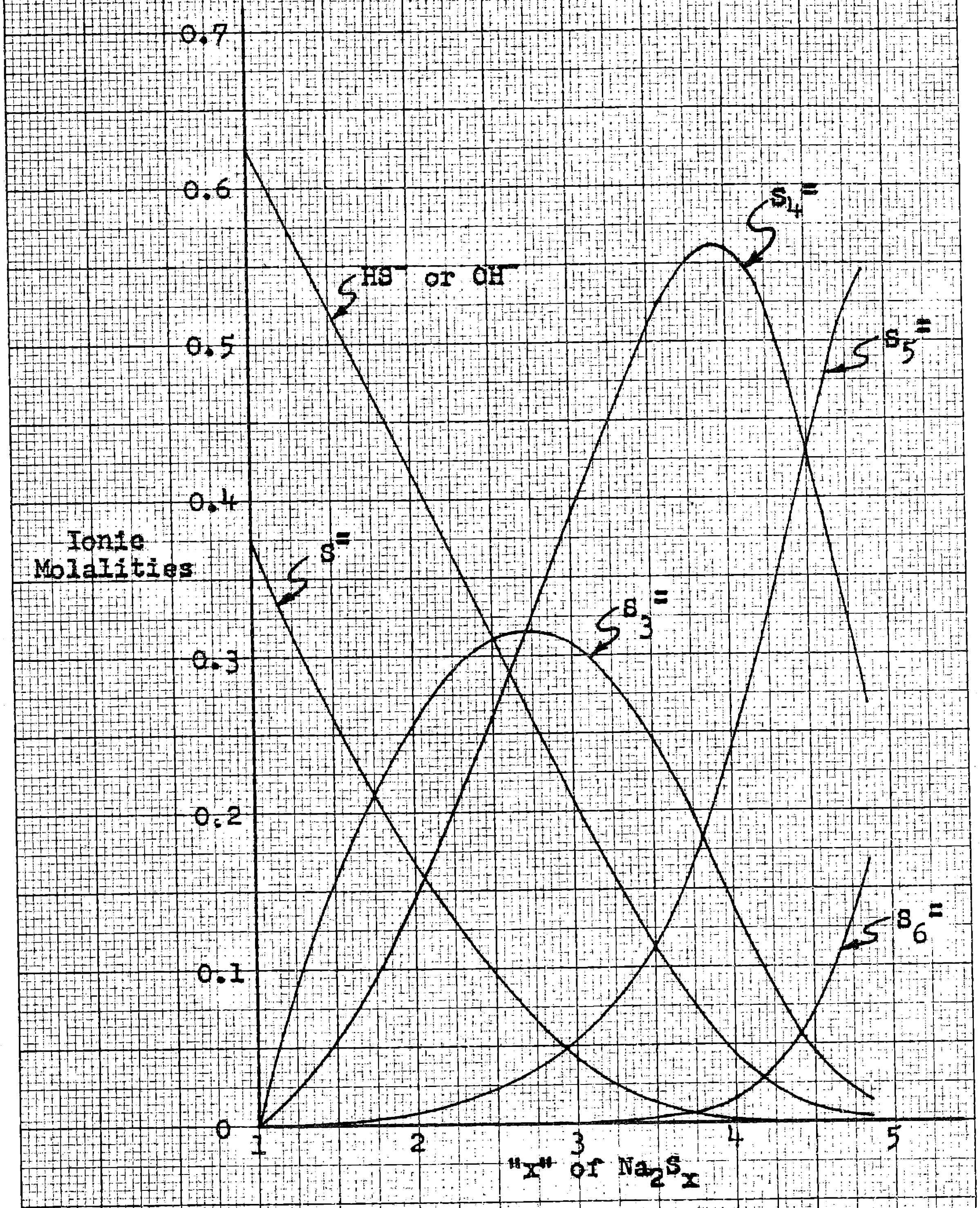


FIGURE 72

Polysulfide Ionic Distributions at 75°C
$Na^+ = 2.0$ m

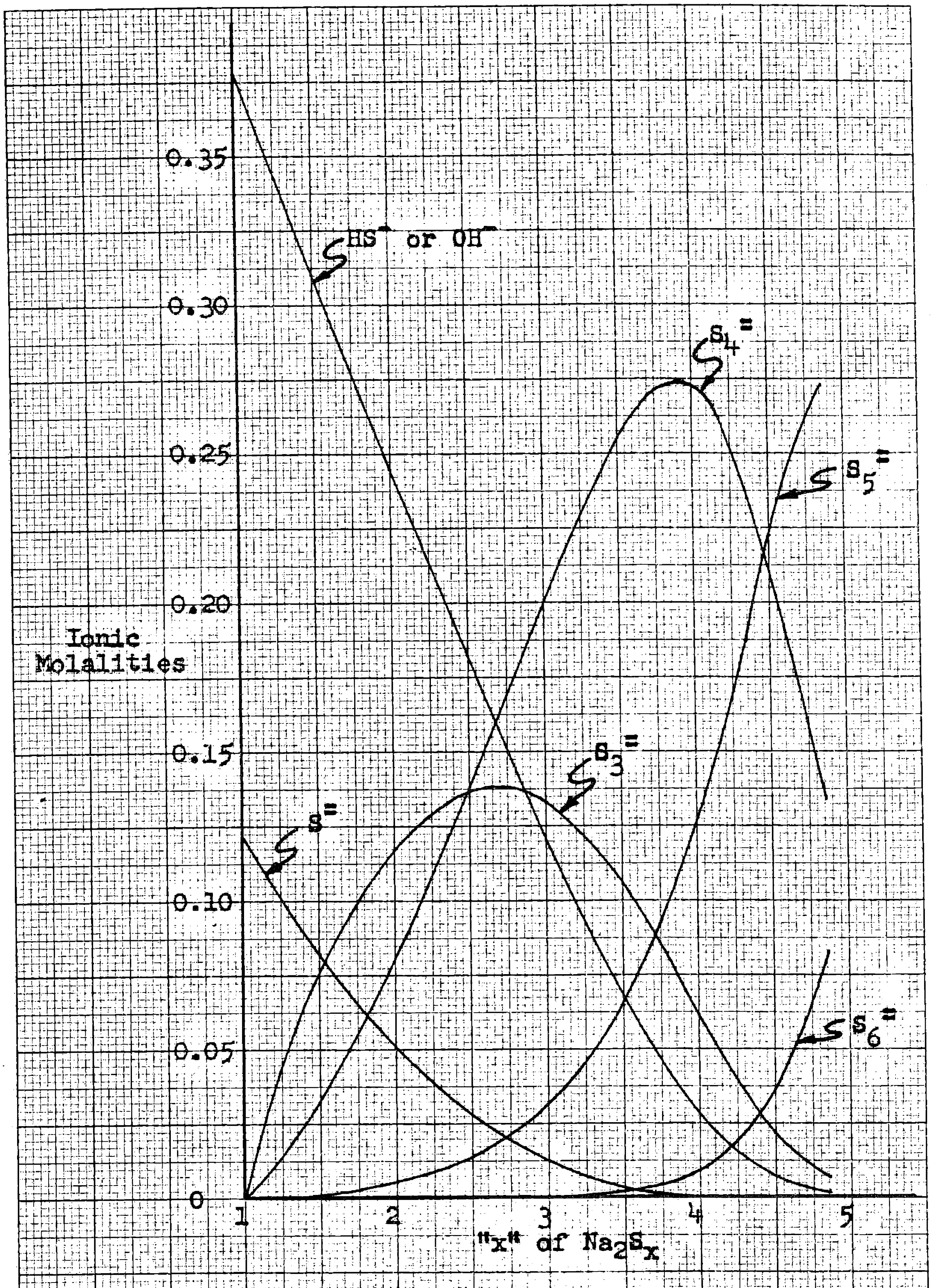


FIGURE 73

Polysulfide Ionic Distributions at 75°C

$Na^+ = 1.0$ m

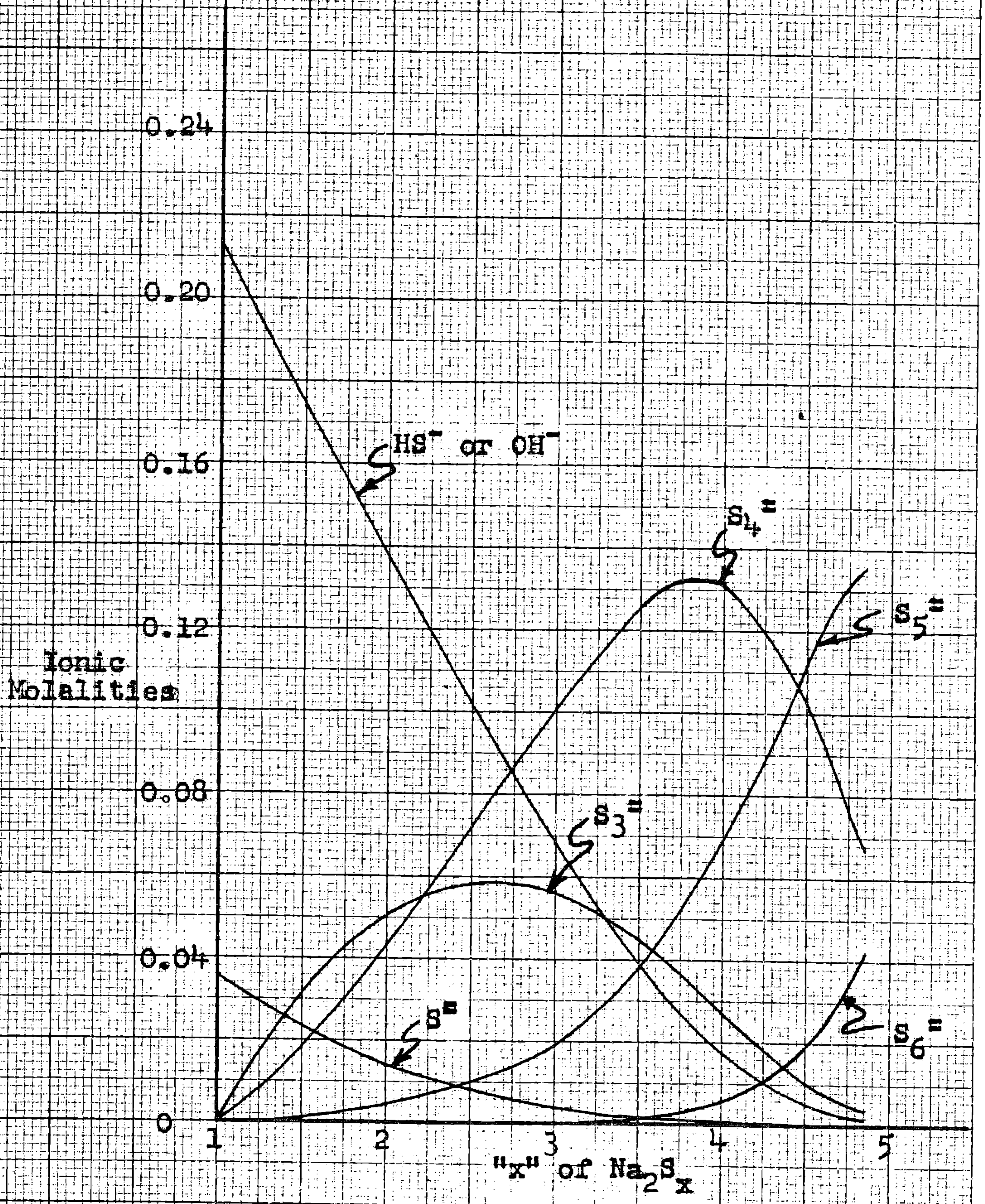


FIGURE 74

Polysulfide Ionic Distributions at 75°C
$Na^+ = 0.5$ m

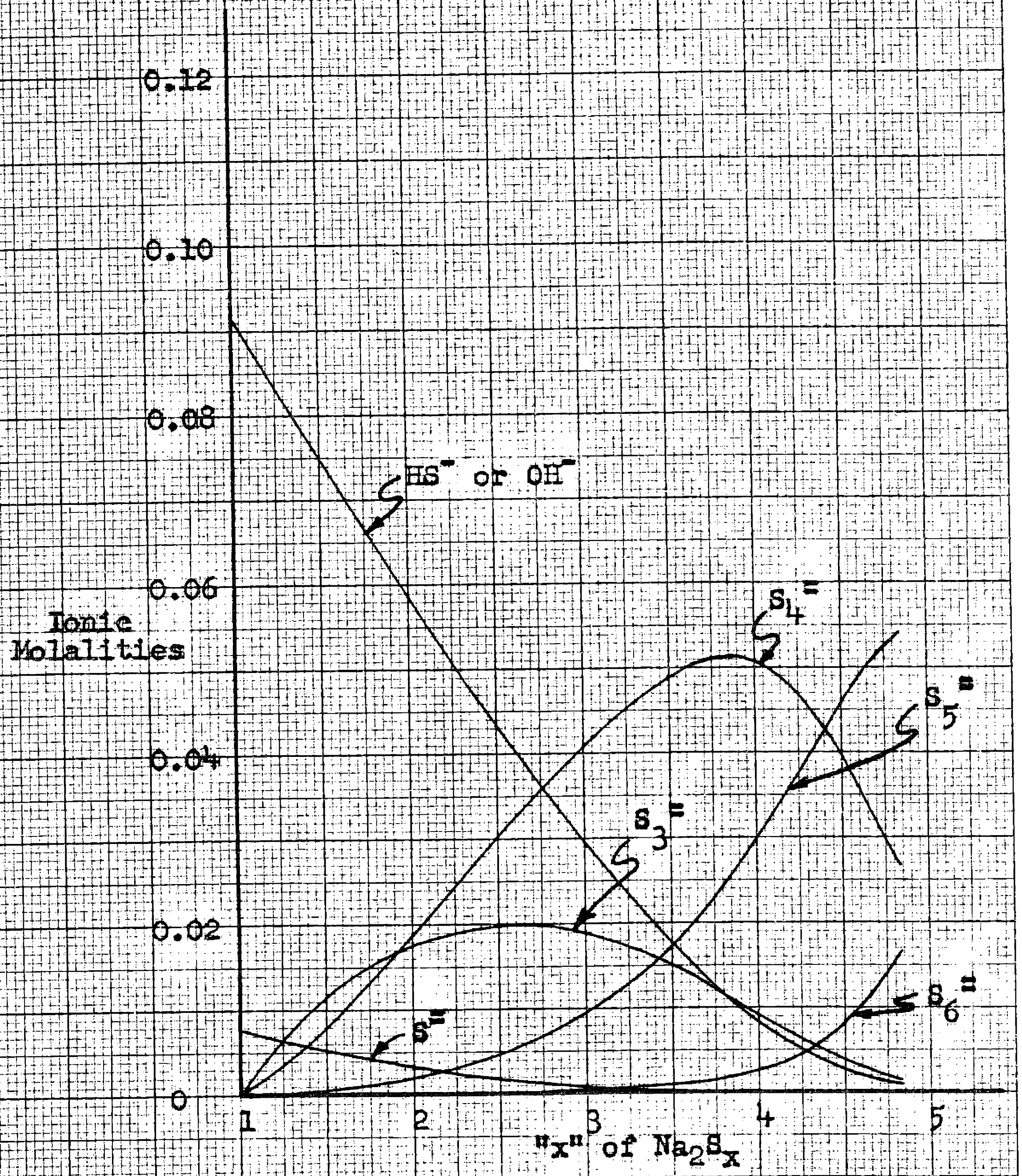


FIGURE 75

Polysulfide Ionic Distributions at 75°C
$Na^+ = 0.2$ m

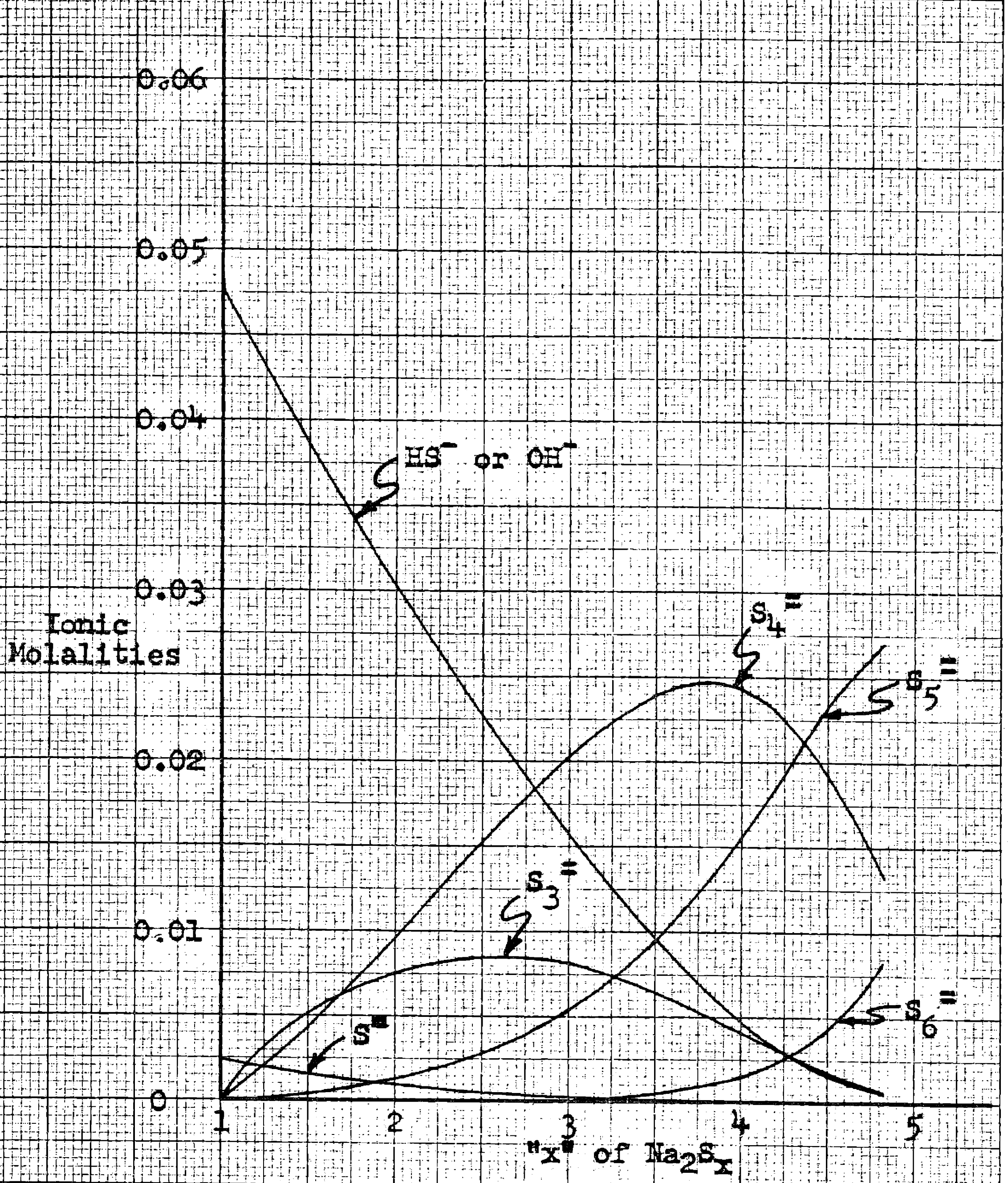


FIGURE 76

Polysulfide Ionic Distributions at 75°C

$Na^+ = 0.1\ \underline{m}$

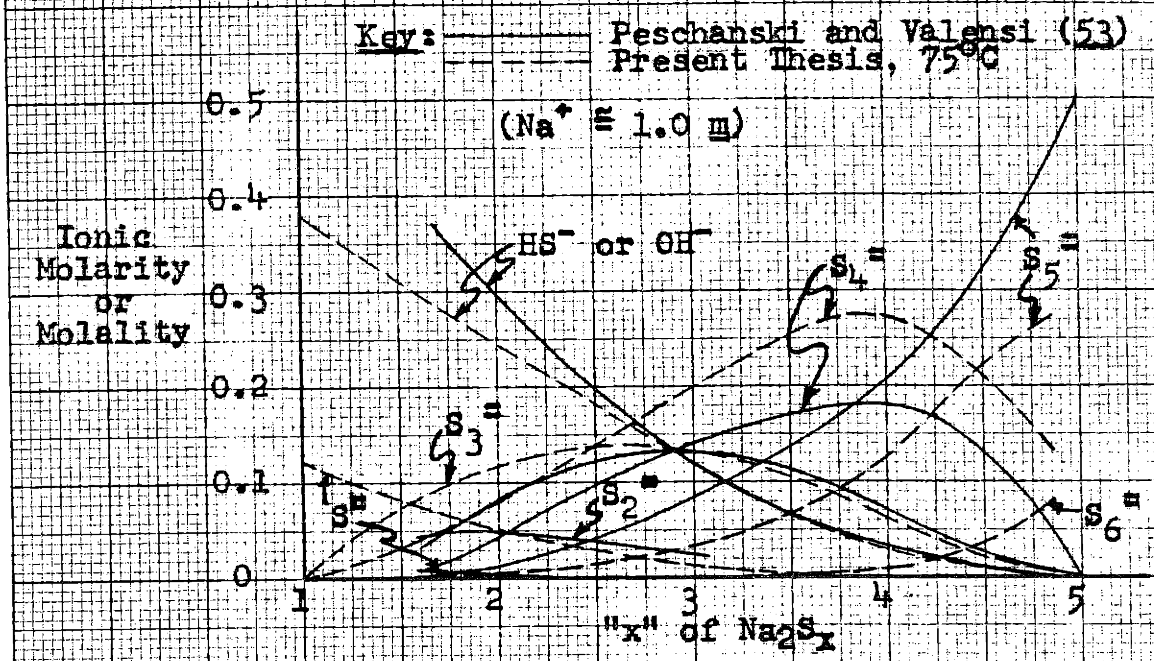


FIGURE 77

Comparison with Ionic Distributions
Proposed by Peschanski and Valensi

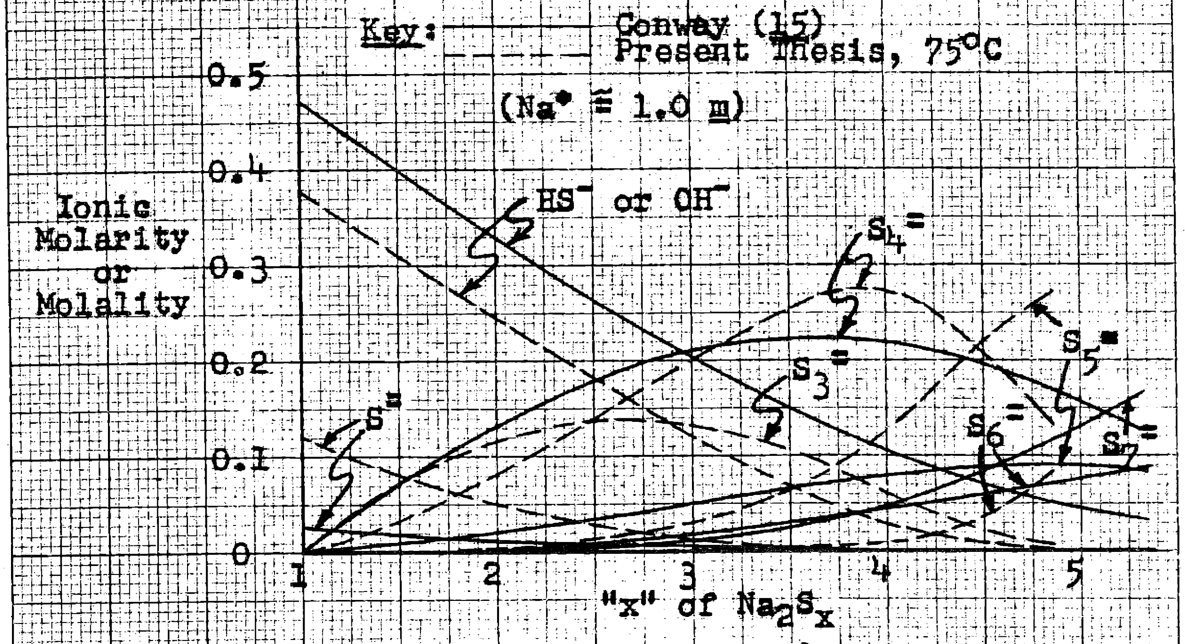


FIGURE 78

Comparison with Ionic Distributions
Proposed by Conway

"normal"; at high "x" values the pentasulfide concentration, on the contrary, is indicated to be less than that of either the tetrasulfide or the two next higher ions. The "recommended" ionic compositions of the present thesis, while obviously not unquestionable, thus are believed to be closer to the true distributions than are either of these two earlier proposals.

In addition to the profiles shown in Figures 70-76, several other correlations may be drawn from the results presented in Table XXIV. In Figure 79 the per cent hydrolyses, based on the calculated HS^- concentrations, are plotted versus polysulfide "x" with molality as a parameter. Inspection indicates that the fractional hydrolysis decreases quite rapidly as "x" increases, but also drops for a given sulfur subscript as the molality increases. At sulfur saturation the hydrolysis is less than 2 per cent even at sodium ion molalities as low as 0.1. Also indicated in Figure 79 are the hydrolyses reported in the literature by Kuster and Heberlein (<u>41</u>) and by Peschanski (<u>52</u>). Even though these data at room temperature correctly should not be compared to the values calculated for 75°C, later analysis will demonstrate that the change in hydrolysis with temperature is probably small. In general, the literature data do follow the trends exhibited by the

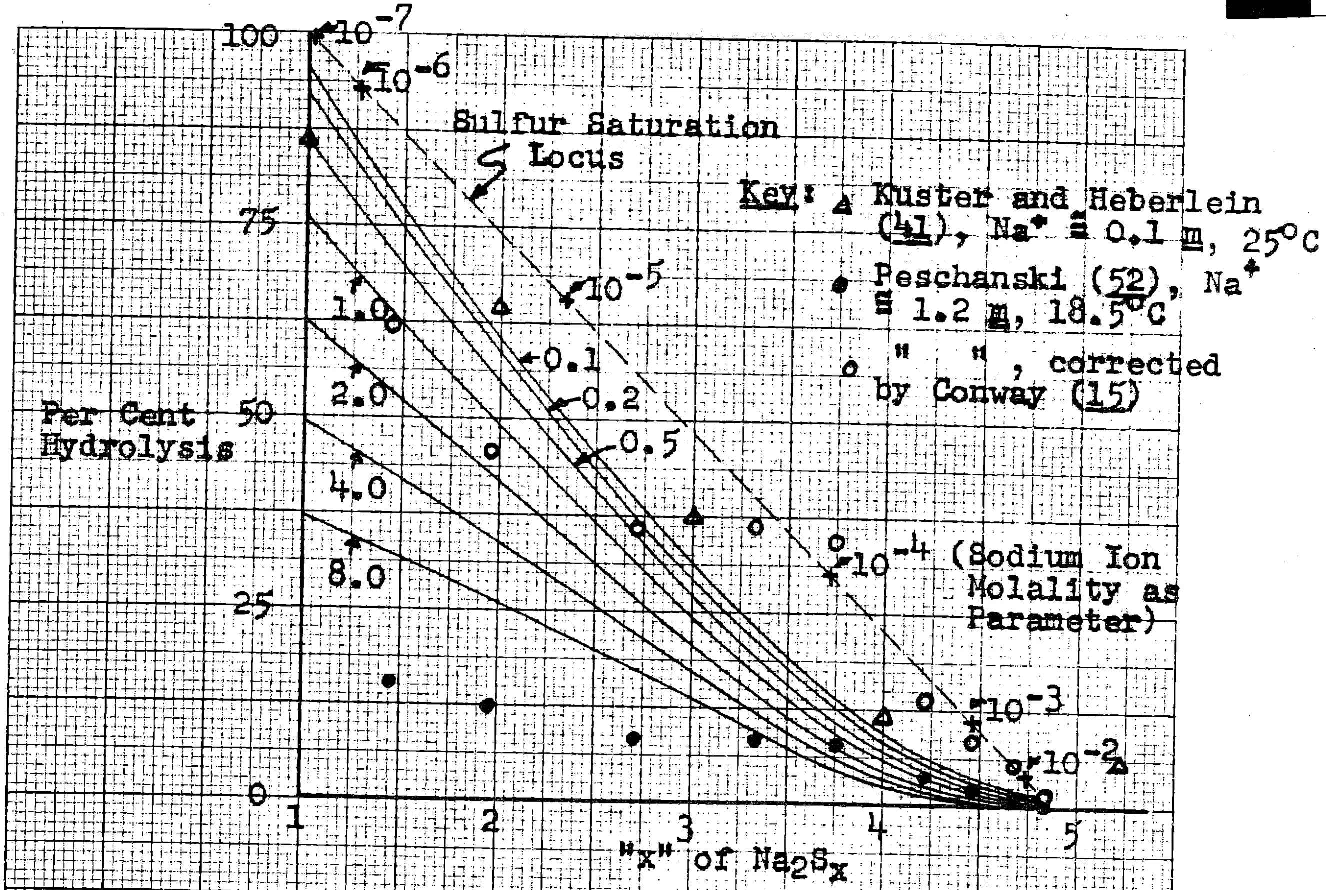


FIGURE 79

Predicted Hydrolyses of Sodium Polysulfide Solutions at 75°C

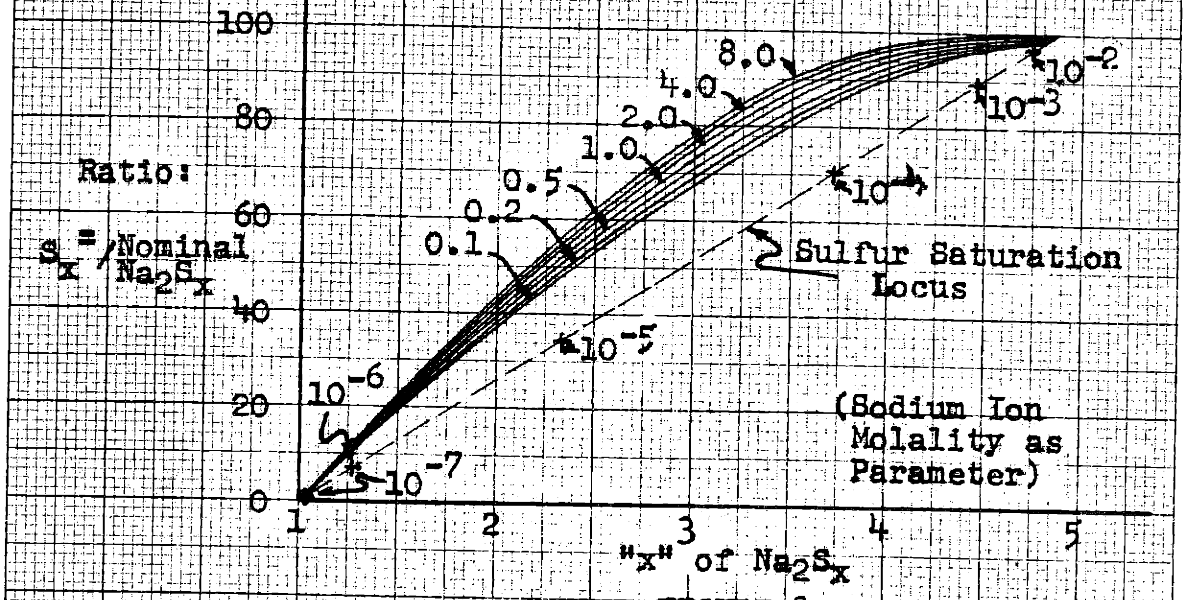


FIGURE 80

Ratio of Actual to Nominal Polysulfide at 75°C calculated points. In view of the scatter of the experimental measurements no further conclusions may be reached.

In Figure 80 the fraction of actual $S_x^=$ ions to nominal or apparent sodium polysulfide likewise is shown as a function of "x" with molality as a parameter. Examination verifies that this ratio rises rapidly as "x" is increased, and also is somewhat larger at the higher molalities. Owing to the rise in monosulfide ($S^=$) ion as concentration increases, however, the molality effect is not as pronounced as in the preceding plot.

In Figures 81, 82, 83, and 84 the ratios to nominal sodium polysulfide of $S_3^=$ ion, $S_4^=$ ion, $S_5^=$ ion, and $S_6^=$ ion, respectively, are plotted against "x" for each of the seven sodium ion molalities at which traverses were calculated. Inspection shows that the fraction of any ion on this basis is approximately maximized when "x" is equal to or slightly below the sulfur subscript of that ion. From the four graphs it is also seen that both the trisulfide and the tetrasulfide are maximized by the use of as high a molality as possible, whereas for a given "x" the proportions of the two higher polysulfide ions are greater in dilute solutions.

Also of interest in the production of raw oil are the fractions of the individual polysulfide ions referred to actual polysulfide ($S_x^=$) rather than nominal polysulfide.

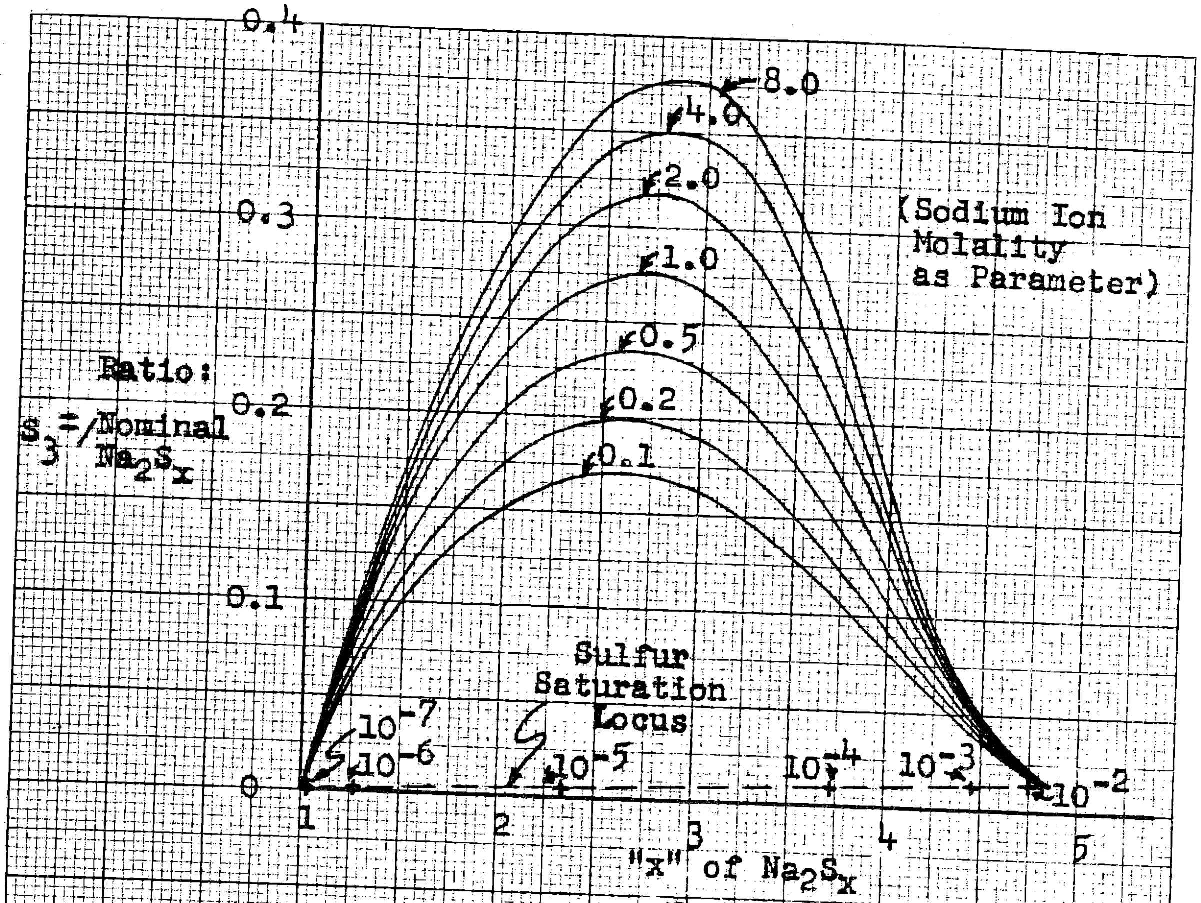


FIGURE 81

Ratio of $S_3^=$ to Nominal Polysulfide at 75°C

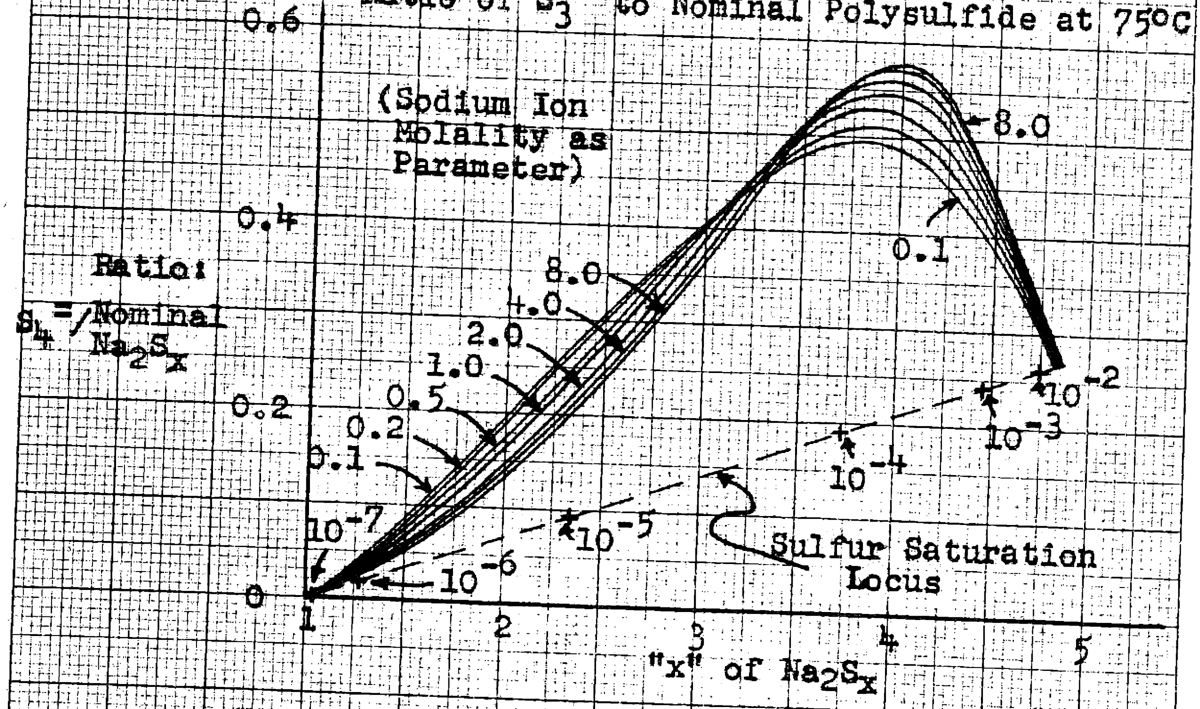


FIGURE 82

Ratio of $S_4^=$ to Nominal Polysulfide at 75°C

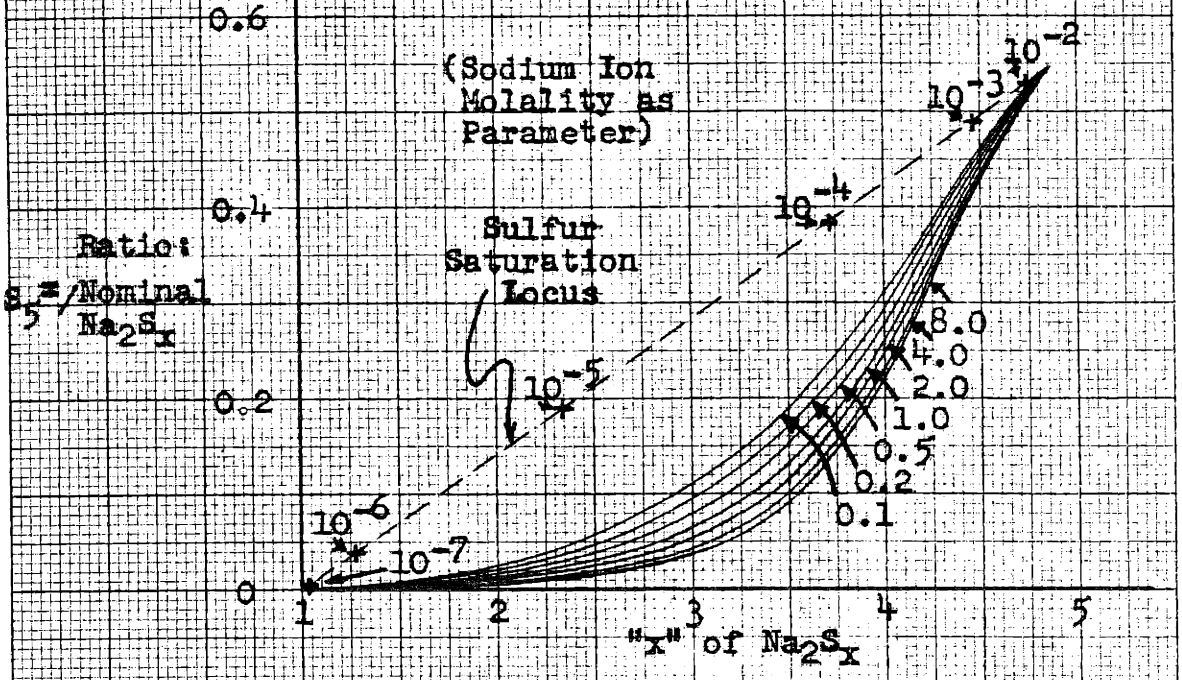


FIGURE 83

Ratios of $S_5^=$ to Nominal Polysulfide at 75°C

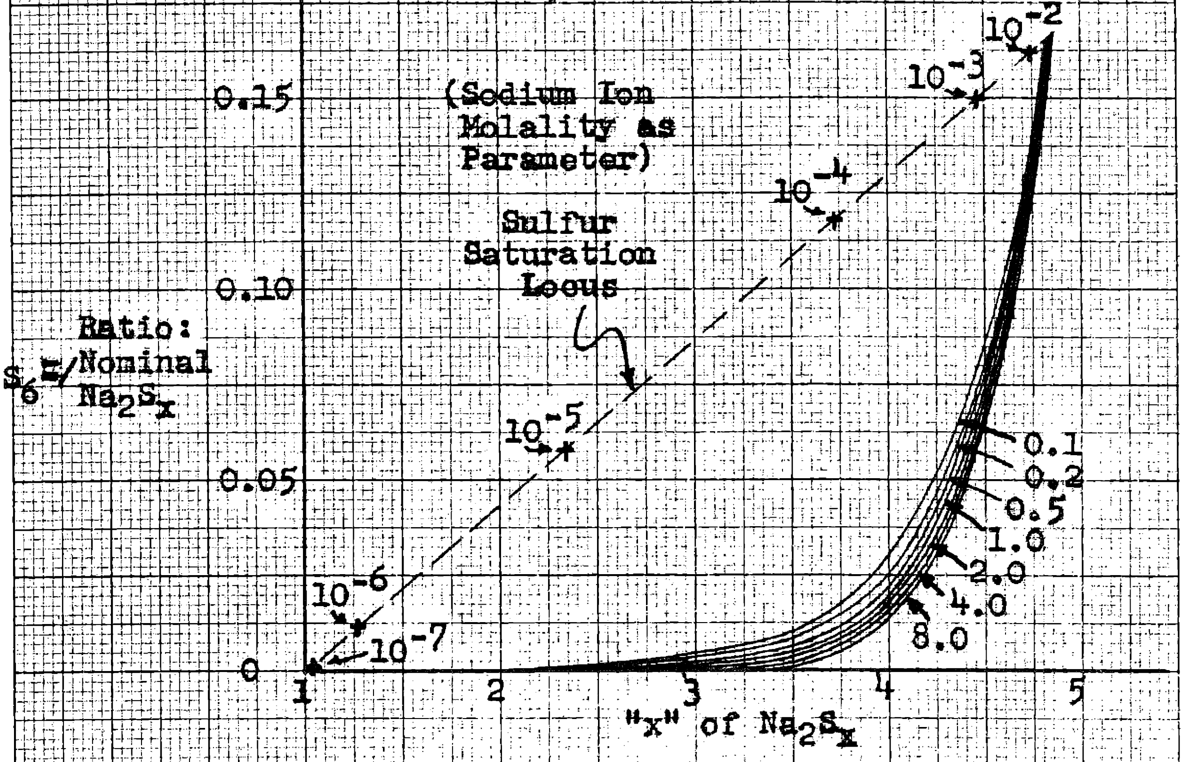


FIGURE 84

Ratios of $S_6^=$ to Nominal Polysulfide at 75°C

Plots of this ratio for $S_3^=$ ion, $S_4^=$ ion, $S_5^=$ ion, and $S_6^=$ ion are shown in the same manner as the preceding correlations in Figures 85, 86, 87, and 88, respectively. In Figure 85 it is seen that if the disulfide ion truly is absent, the ratio of $S_3^=$ to total $S_x^=$ must approach unity as the nominal "x" approaches 1.0. Figure 86 indicates that the fraction of $S_4^=$ based on actual $S_x^=$ is maximized at slightly lower values of "x" than that based on nominal sodium polysulfide (Figure 82). Figures 87 and 88 appear much the same as the corresponding Figures 83 and 84, respectively.

In Figure 89 the ratio $PSS/S_x^=$ is plotted as a function of polysulfide "x" with sodium ion molality as a parameter. As might be expected from an examination of the preceding correlations, this ratio increases as sulfur activity and hence "x" increases. The elemental sulfur activities themselves are of some interest; these activities as listed in Table XXIV are plotted versus "x" in Figure 90. The sulfur activity at a given "x" apparently varies but little with molality in the vicinity of sulfur saturation, but drops by a factor of several thousand at lower "x" values when the concentration is increased from 0.1 m to 8.0 m sodium ion. For comparison, three points taken from Table XI, representing xylene sulfur concentrations measured in hot sodium polysulfide solutions and converted

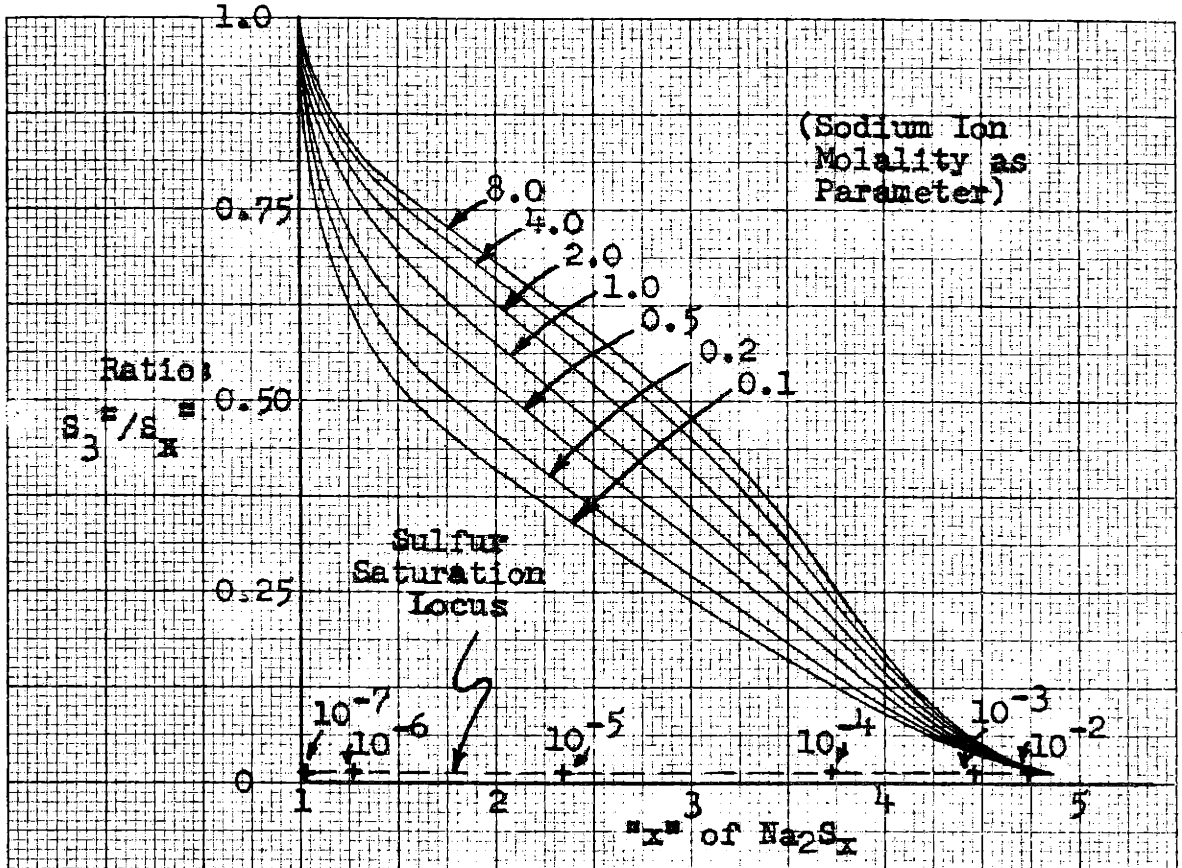


FIGURE 85

Ratios $S_3^=/S_x^=$ in Polysulfide Solutions at 75°C

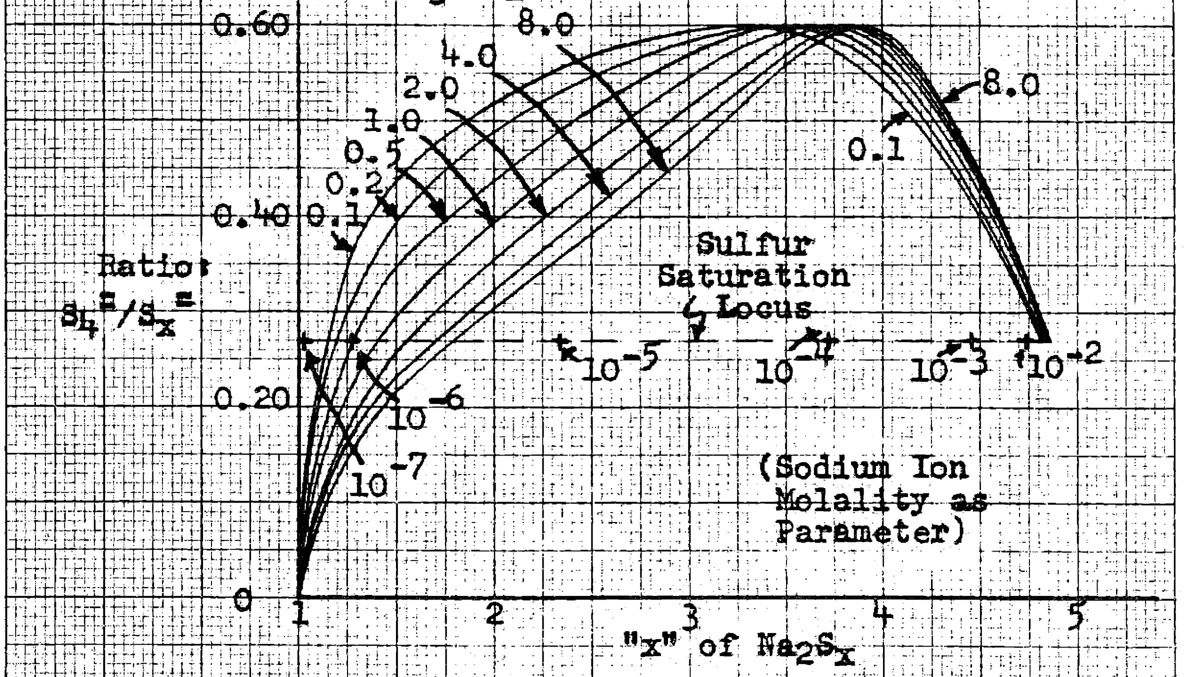


FIGURE 86

Ratios $S_4^=/S_x^=$ in Polysulfide Solutions at 75°C

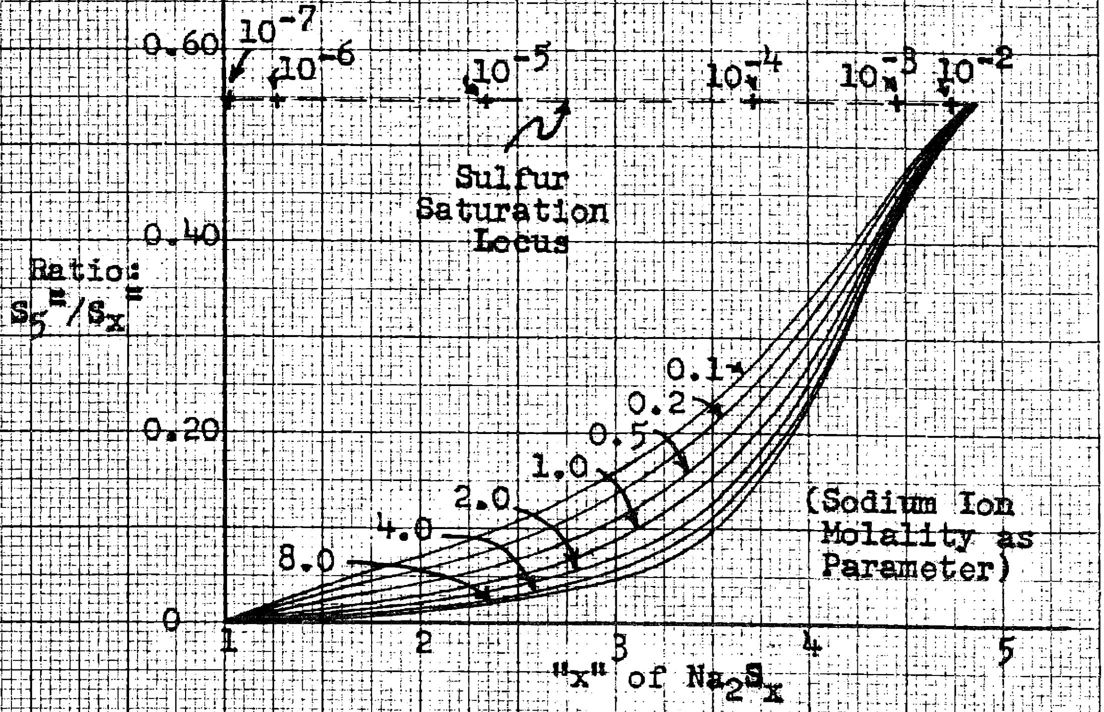


FIGURE 87

Ratios $S_5^=/S_x^=$ in Polysulfide Solutions at 75°C

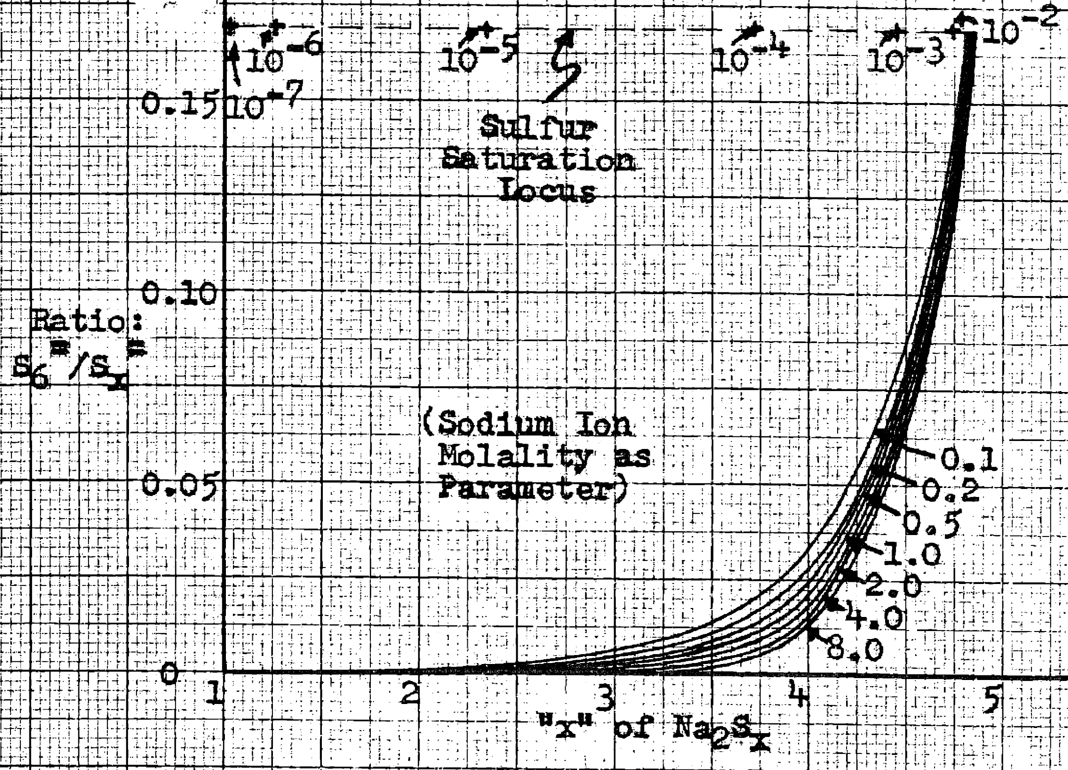
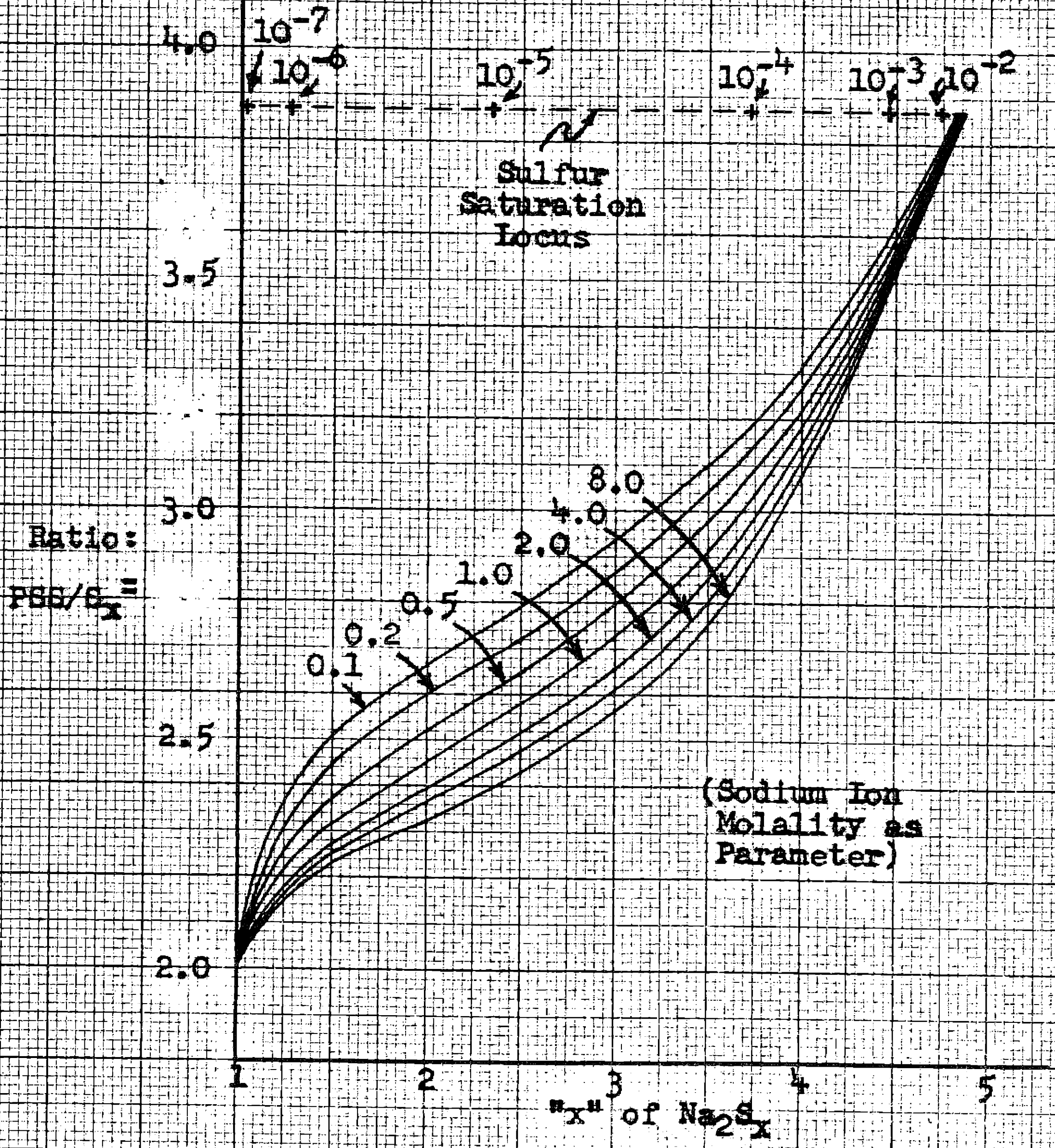


FIGURE 88

Ratios $S_6^=/S_x^=$ in Polysulfide Solutions at 75°C



<u>**FIGURE 89**</u>

Ratios $PSS/S_x^=$ in Polysulfide Solutions at 75°C

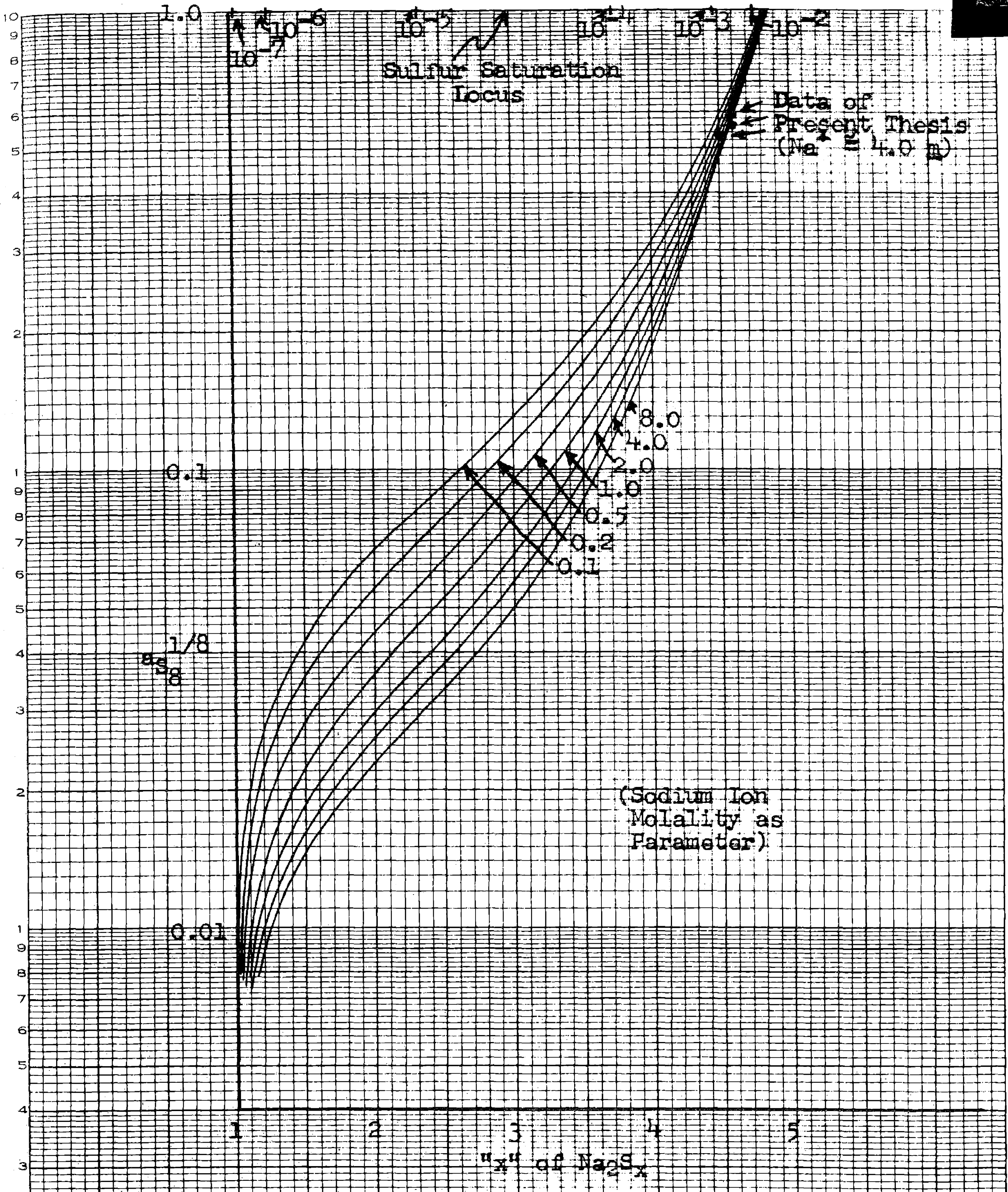


FIGURE 90

Sulfur Activities in Polysulfide Solutions at 75°C to activities using the correlation recommended in Figure 46, also are plotted in Figure 90. These data, obtained at a sodium ion molality of about 4.0, agree with the calculated curve at that molality within the limits of experimental determination of polysulfide "x". As will be shown, however, this finding cannot be construed as evidence that the "recommended" equilibrium constants are more nearly correct than any of the other possible sets listed in Table XIX.

For convenience in using these "recommended" ionic distributions in situations in which the molarity rather than the molality is known, the relations for converting the former into the latter are shown graphically for 25°C and for 75°C in Figure 91. Even though the indicated curves were derived from the density plot in Figure 11, these conversion relations apply only to sodium monosulfide and sodium polysulfide solutions, and not to any aqueous solution made up from the more general system Na_2S-S-H_2S-H_2O.

e. Examination of Alternate Ionic Distributions

As should be obvious from the numerous assumptions which were required, the polysulfide ionic compositions derived from the "recommended" equilibrium constants are considered none too reliable. In order to indicate some possible limits on the ionic distributions in view of the equilibrium data, four "extreme" sets of relative constants

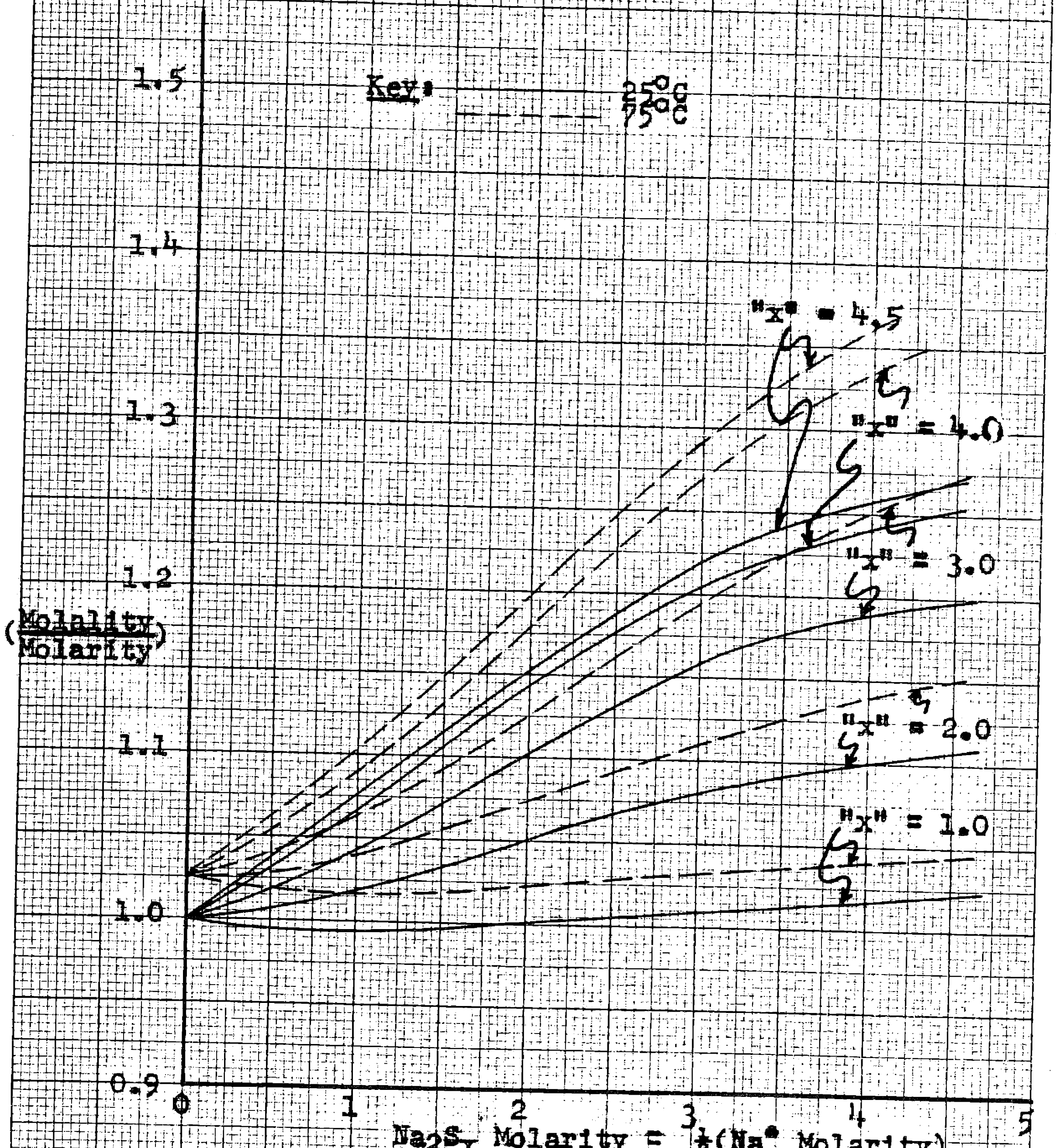


FIGURE 91

Conversion of Molarities to Molalities in Sodium Polysulfide Solutions were derived from the 11 assumptions in Table XIX. The polysulfide composition profiles at 1.0 m sodium ion concentration then were calculated for each of these four cases for comparison with the recommended ionic distributions at that molality. The relative equilibrium constants for the four alternate cases, adjusted to 1.0 m sodium ion (sulfur activity correlation "II"), are listed in Table XXV:

TABLE XXV

Alternate Sets of Relative Equilibrium Constants at 75°C

(Na^+ = 1.0 m, curve "II")

Set No.	r_1	r_2	r_3	r_4	r_5	r_6	r_7
"Recommended"	-	0.019	0.357	0.724	0.222	-	-
#1	0.027	-	0.127	1.161	-	-	-
#2	-	0.092	-	1.225	-	-	-
#3	-	-	0.665	-	0.651	-	-
#4	-	0.062	0.307	0.705	0.192	0.039	0.008

These four "extreme" sets of relative equilibrium constants, being not confined to the assumption that the ionic distributions had to be "normal", were chosen specifically to illustrate the estimated maxima and minima constants for the various ions. Set #1, a linear combination of assumptions 1 and 4 (Table XIX), was selected so that r_1 did not exceed the limits placed upon it by graphical considerations. Sets #2, #3, and #4, on the other hand, were obtained directly from assumptions 2, 5, and 11, respectively. If a "normal" distribution were not necessarily assumed, any one of the polysulfide ions itself could be considered absent, and a reasonably good fit with the experimental data still could be found using only the remaining ions. Thus, as may be seen by inspection of the various possibilities in Table XXV, the lower limit on each of the r's was zero. Set #1 was chosen to yield a maximum value for r_1. Set #2 was selected to provide maximum values for r_2 and r_4. The estimated upper limits on r_3 and r_5 were defined by set #3, whereas set #4 indicated the maximum proportions of the higher ions $S_7^=$ and $S_8^=$. (In order to obtain a good agreement with the data using this last set, a relatively large value of r_2 was required for balance.)

The ionic distributions in 0.5 m polysulfide solutions (1.0 m sodium ion) at 75°C were calculated for these four alternate systems using the method already employed for the "recommended" ionic compositions. The plots of these ionic concentrations versus "x" at this molality are shown for each of the four "extreme" sets of equilibrium constants in Figures 92, 93, 94, and 95, respectively; the "recommended" distribution profiles at 1.0 m also are indicated on each graph for comparison. From an inspection of Figure 95 it

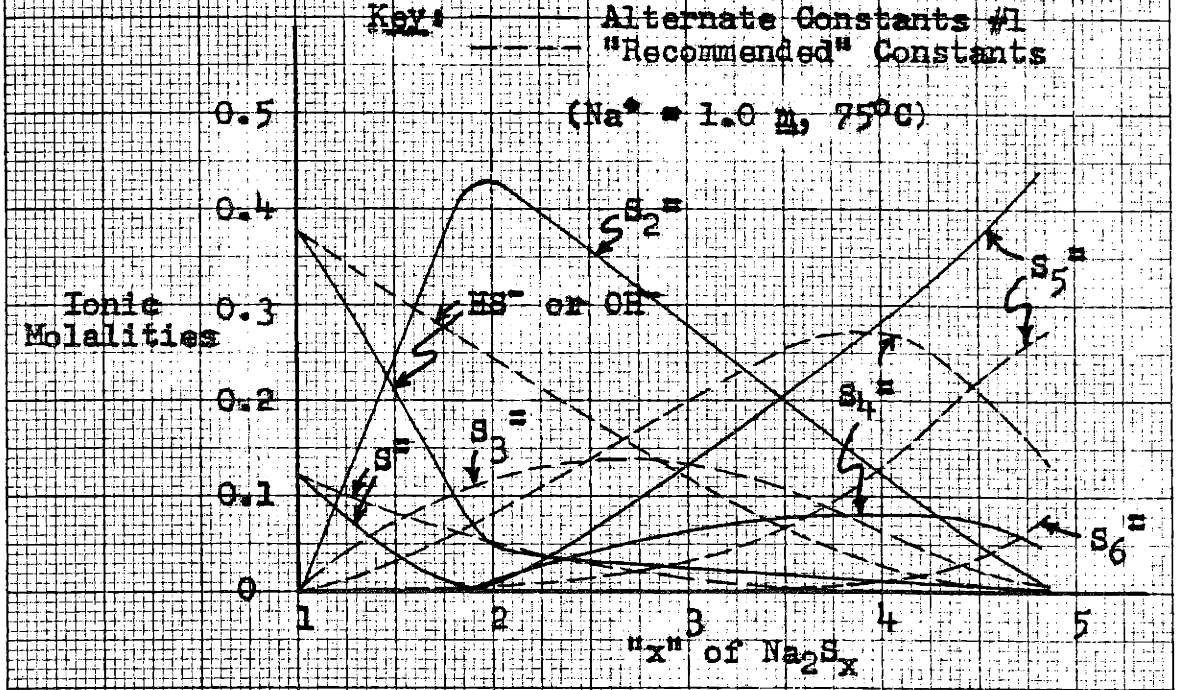


FIGURE 92

Polysulfide Ionic Distributions for Alternate Equilibrium Constants #1

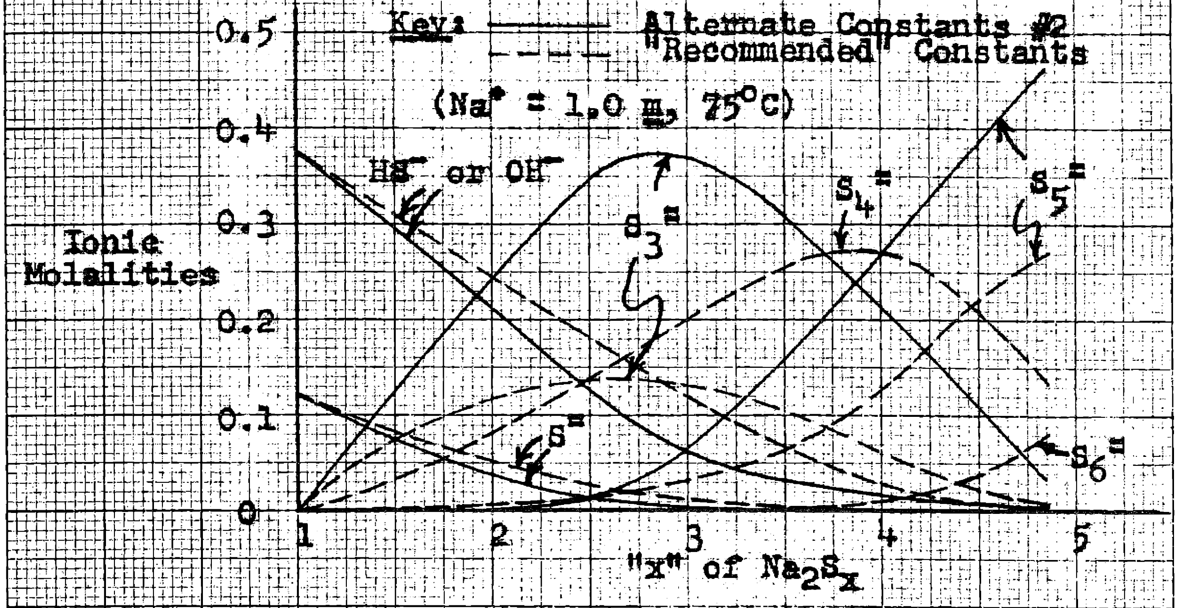


FIGURE 93

Polysulfide Ionic Distributions for Alternate Equilibrium Constants #2

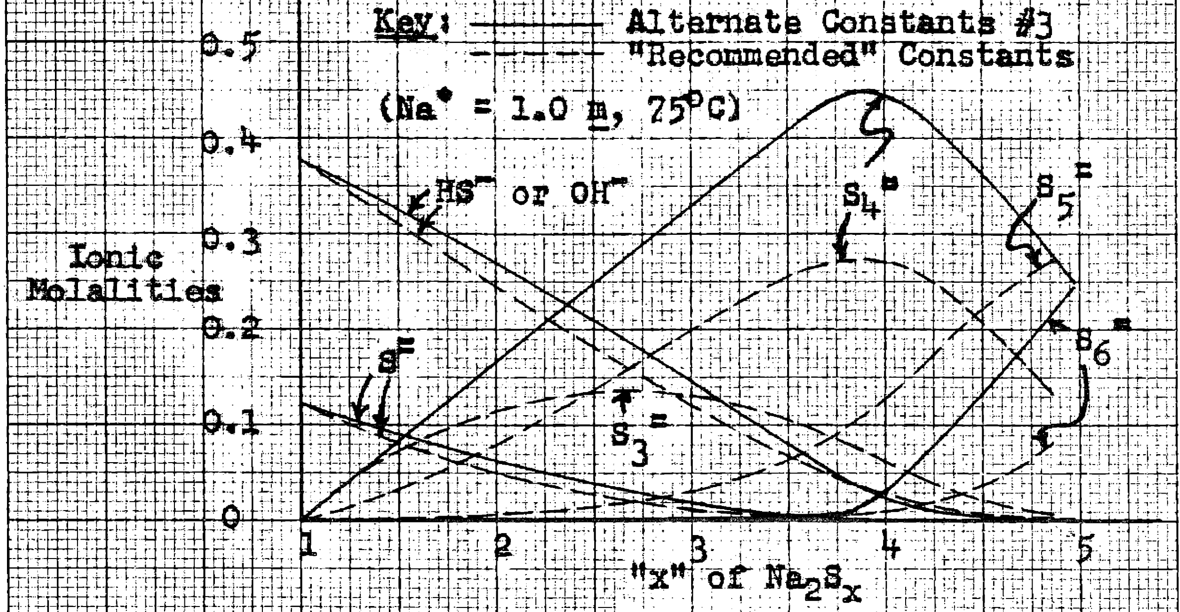


FIGURE 94

Polysulfide Ionic Distributions for Alternate Equilibrium Constants #3

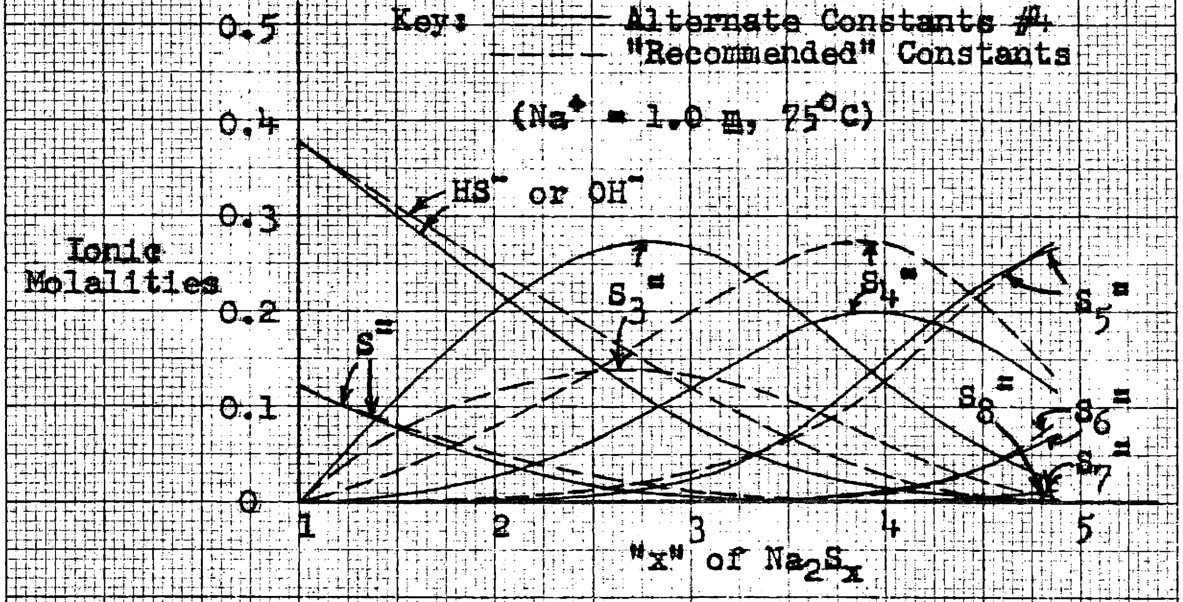


FIGURE 95

Polysulfide Ionic Distributions for Alternate Equilibrium Constants #4 indeed is evident that the ions above $S_6^=$ could well be neglected in formulating the recommended ionic distributions, since the concentrations of such ions fall off rapidly a short distance away from sulfur saturation.

In a further attempt to compare the four alternate sets of equilibrium constants to the "recommended" cconstants, two additional correlations of properties capable of being measured experimentally were made. The per cent hydrolyses for the four cases are compared in Figure 96 to the curve predicted by the recommended compositions. With the exception of set #1, the hydrolyses indicated for the alternate groups of r's are not sufficiently different from the "recommended" curve for the correct set of constants to be established using experimental hydrolysis data of the precision obtainable to date. In Figure 97 the sulfur activities for the four alternate sets of equilibrium constants are compared at 1.0 m sodium ion to those predicted by the recommended constants. It is seen that the five curves are essentially indistinguishable within the limits of experimental error in the range in which xylene sulfur measurements in sodium polysulfide solutions were attempted during the course of the present thesis, whereas at lower values of "x" the sulfur activities predicted by the various relations differ by factors of 10 or 100 or more. Thus some very precise determinations of

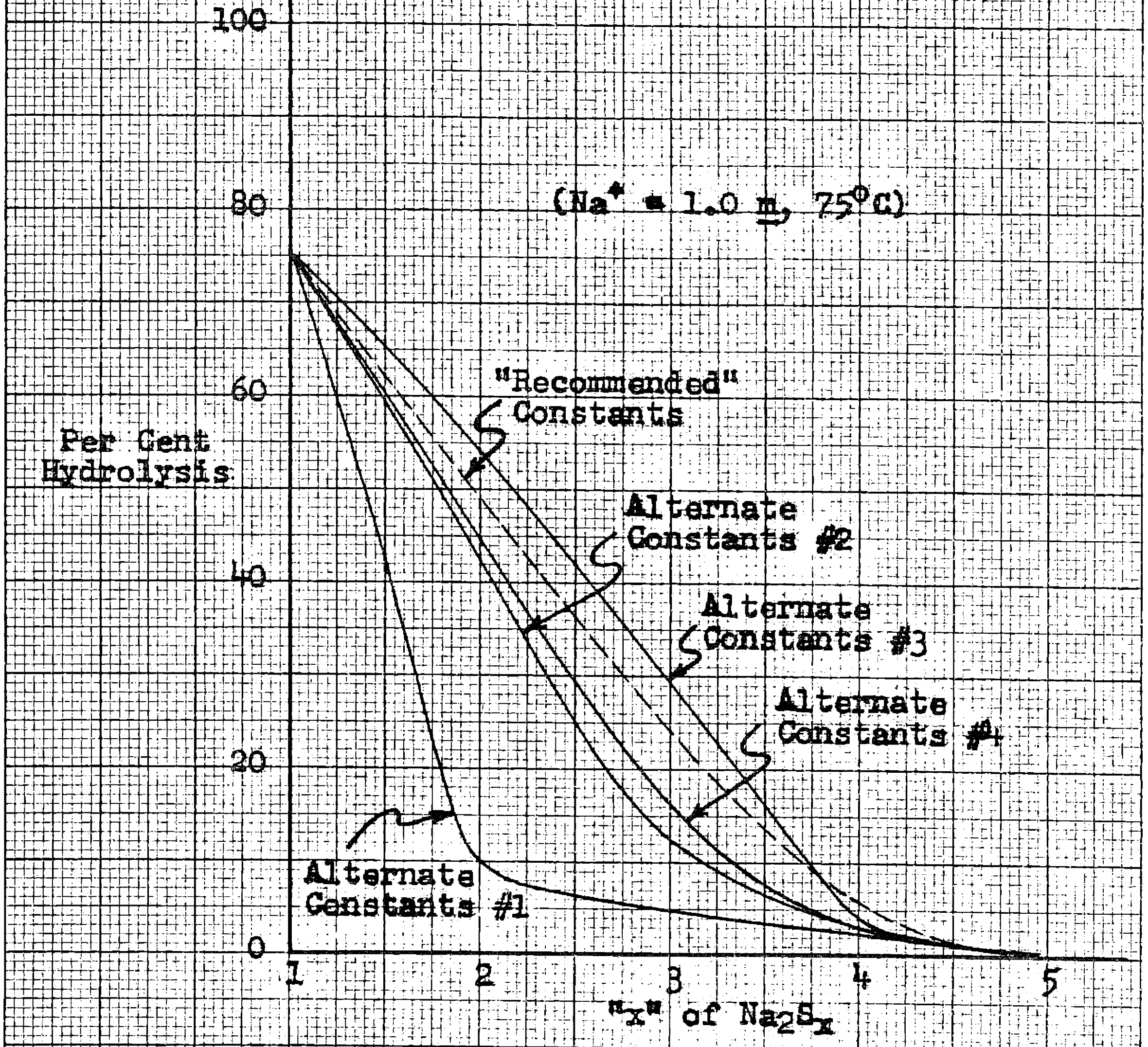


FIGURE 96

Sodium Polysulfide Hydrolyses from Alternate Equilibrium Constants

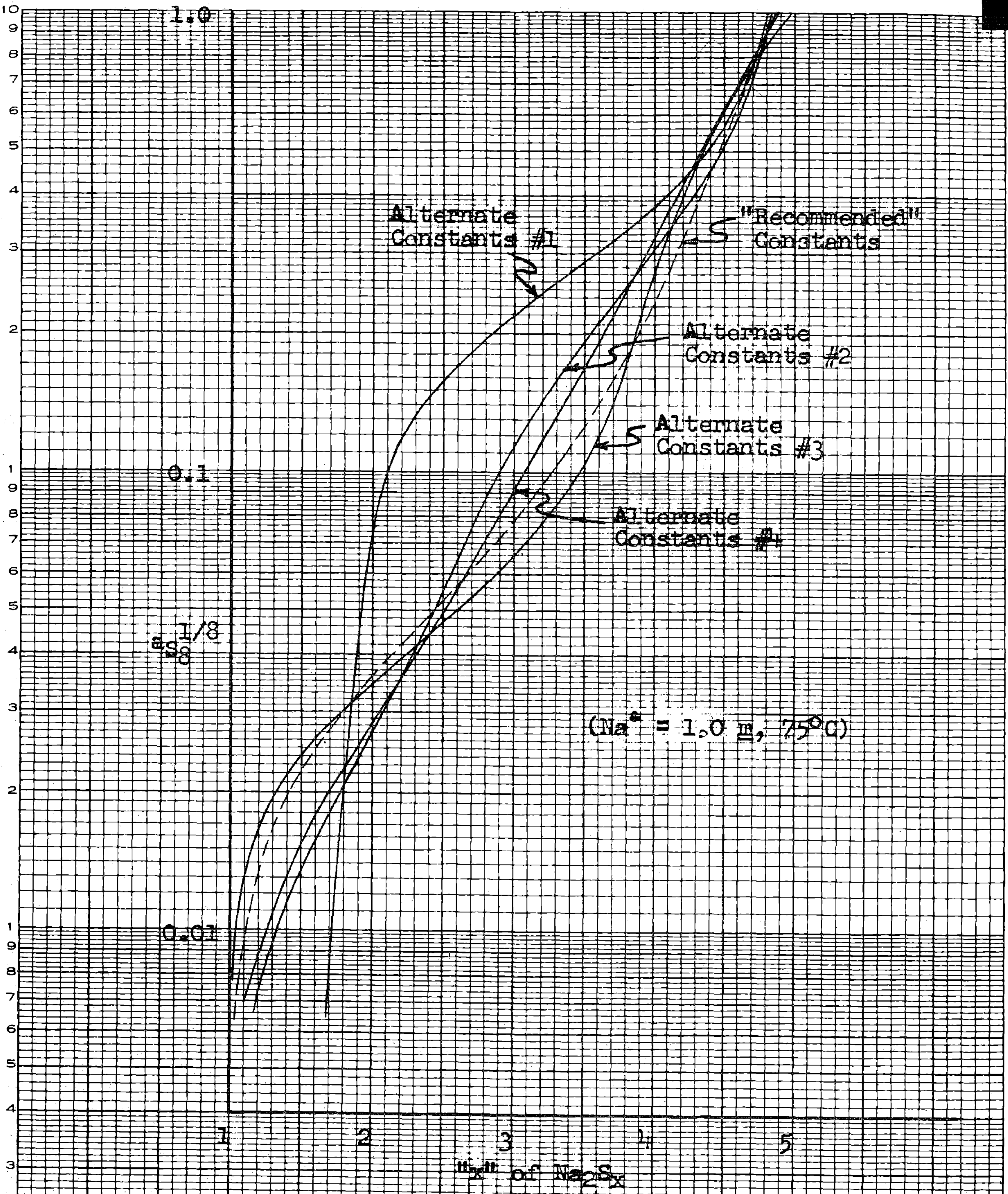


FIGURE 97

Sulfur Activities in Polysulfide Solutions for Alternate Equilibrium Constants the extremely small xylene sulfur concentrations in equilibrium with hot polysulfide solutions having "x" values between 3.0 and 4.0 might narrow down the possible limits on the unknown equilibrium constants. A comparison of Figures 97 and 90 suggests that such experiments be performed using as dilute solutions as possible in order to obtain relatively larger xylene sulfur concentrations at the lower values of "x".

2. Equilibrium Distributions at 25°C

Polysulfide solutions for use in the production of raw oil, while often prepared at elevated temperatures in the neighborhood of 75°C, usually are acidified at room temperature or below. Thus the change in ionic composition with temperature should be evaluated before the results of the present thesis can be applied to the preparation of hydrogen persulfide. Even though certain of the polysulfide equilibria apparently are not mobile at low temperatures, an examination of the hypothetical equilibrium situation would be a first step in attempting to predict the non-equilibrium behavior and the actual ionic compositions. Attempts therefore were made to extrapolate the "recommended" equilibrium constants to 25°C, chosen because considerable data on polysulfide solutions at this temperature are reported in the literature.

a. Information on Equilibrium at 25°C

The Na_2S-S-H_2S-H_2O 25°C data of the present thesis, even though not taken at equilibrium, might be used to place limits on the unknown true equilibrium at this temperature if this true condition could be assumed to lie between the results obtained employing the two reaction directions. Examination of Table VIII indicates that at 25°C and 4.0 m sodium ion the quantity X at sulfur saturation ranged between 0.13 and 0.30, while the ratio Y/X or PSS/$S_x^=$ at saturation ranged from 3.44 up to 4.26. The values of X were lower and more reproducible and the ratios Y/X were higher for the experiments employing the sodium hydrosulfide-sulfur reaction. On the basis of both this better reproducibility and also rate considerations to be dealt with later, the sodium hydrosulfide - sulfur results at 25°C are believed to come closer to the true equilibrium than the results of runs involving the reverse reaction.

The determinations by Kuster and Heberlein (41) of sulfur solubilities in sodium polysulfide solutions also indicate (Figure 5) that PSS/$S_x^=$ ratios as high as 4.24 ("x" values up to 5.24) could be attained at 25°C. Even though these literature data are not considered to represent equilibrium, it is difficult to imagine how the 5.24 number might be any higher than the true equilibrium value if it was reached by reacting initially sodium sulfide and sulfur.

From the findings of the present thesis and the data of Kuster and Heberlein it is concluded that the equilibrium ratio Y/X at unity sulfur activity probably takes on values at room temperature and below somewhat higher than the 3.87 taken as average for sulfur saturation at 75°C. Any apparent rise in sulfur solubility in polysulfide solutions with increasing temperature thus is considered to be the result of rate phenomena.

b. Attempted Extrapolation from 75°C

Independent of any "equilibrium" information at 25°C, the polysulfide equilibrium constants at 75°C might be extrapolated to this lower temperature if the thermodynamic data for the reactions involved were available. Values purported to be the heats of formation of the various polysulfide ions, but actually obtained calorimetrically upon the addition of sulfur to sodium sulfide to yield a solution with "x" corresponding to that of the supposed pure polysulfide, are reported in the literature (6)(36). These literature "heats of reaction" thus require further treatment to be converted into the true enthalpy changes for the formation of the various polysulfide species.

These "apparent heats of formation" are plotted versus "x" in Figure 98. The numbers given by Bichowsky and Rossini (6) average higher than do those reported in Handbook of Chemistry and Physics (36), and, as will be

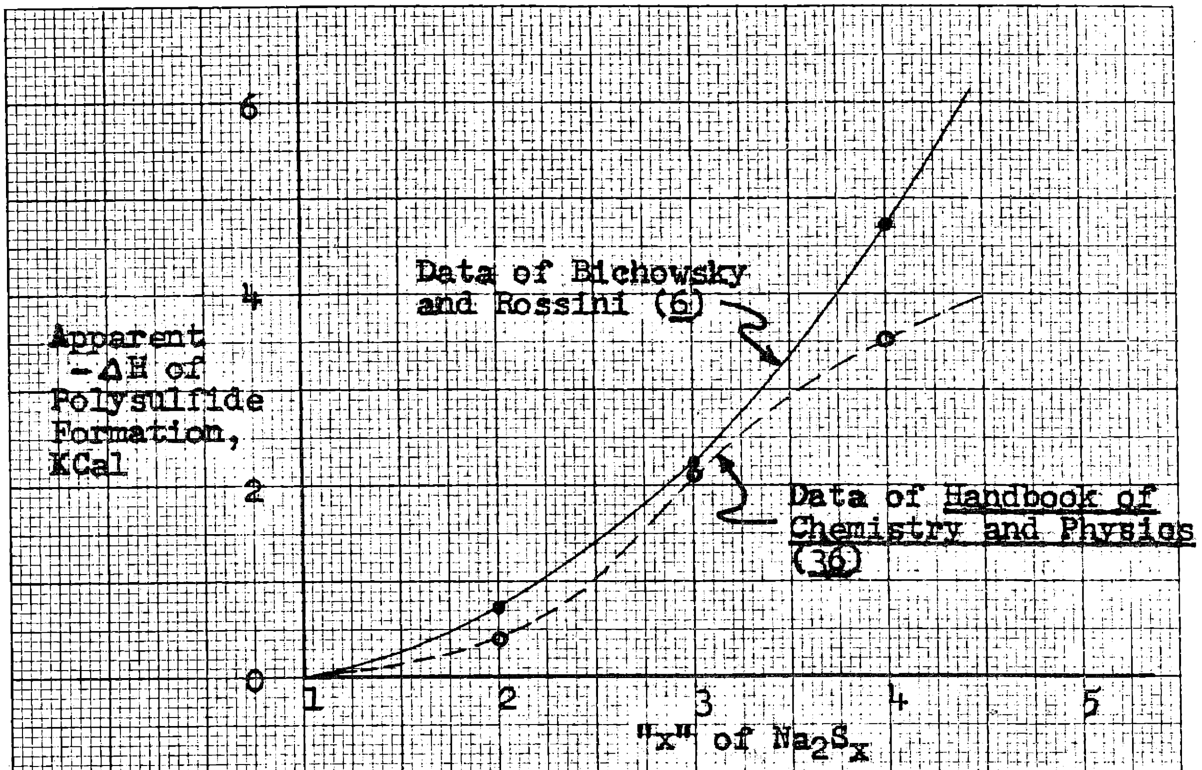


FIGURE 98

Heats of Formation of Polysulfide Solutions at 25°C

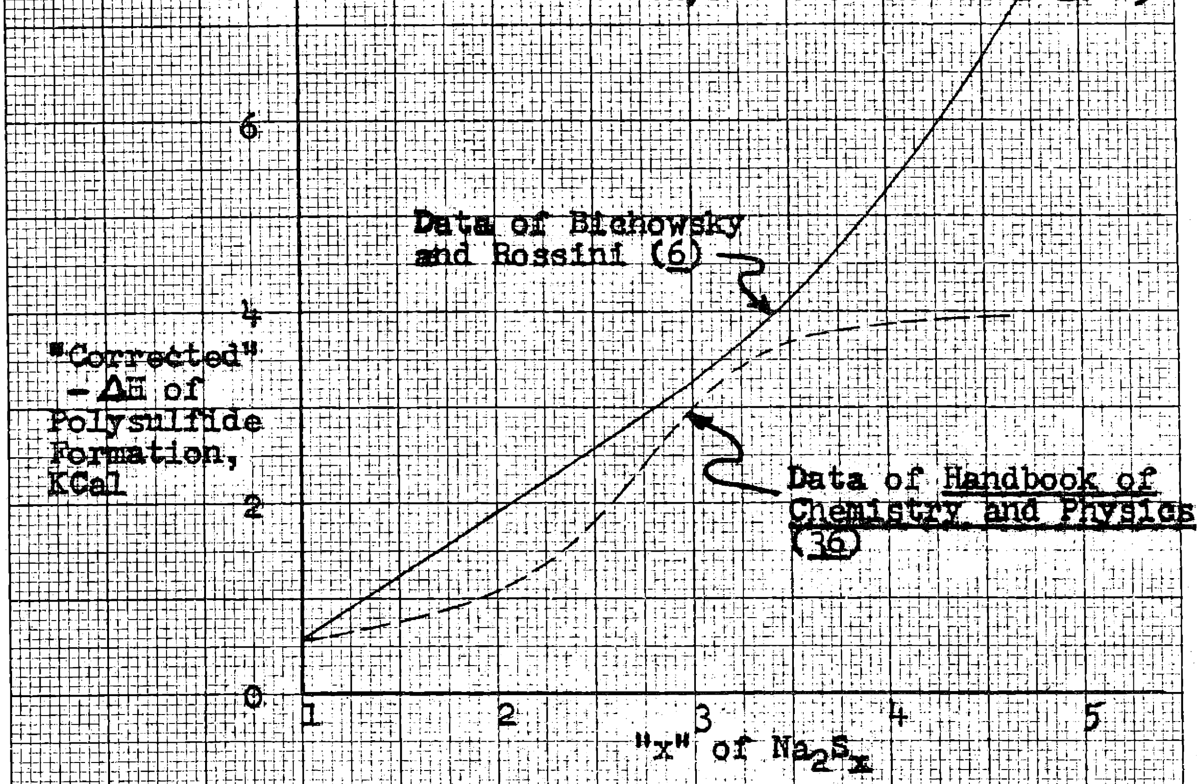


FIGURE 99

Average Heats of Formation of Actual Polysulfide at 25°C shown, are believed to be the more reliable.

Since the hydrolysis reaction of monosulfide ($S^=$) to hydrosulfide (HS^-) and hydroxyl (OH^-) apparently has no heat effect, i.e., its equilibrium constant does not vary with temperature, the values reported in the literature for the heat of formation of monosulfide ion could be assumed correct. The "apparent heats of formation" of the polysulfide species, however, had to be divided by the ratios of actual polysulfide to nominal polysulfide in order to yield the average heats of formation based only on the polysulfide ions present. The findings of the present thesis indicate that these ratios of actual to nominal polysulfide vary but little with molality at a given "x" (Figure 80). Accordingly, the ratios at 0.1 m sodium ion derived using the "recommended" equilibrium constants at 75°C were assumed in making this conversion. The "true" average enthalpies of polysulfide formation thus obtained are plotted against "x" in Figure 99.

The heats of formation of the individual polysulfide ions could be derived from the information in Figure 99 if the ionic distributions for any "x" were known. Since this data was lacking under the conditions at which the calorimetric measurements were made, two different approximations were assumed. As a crude estimate the ΔH's of formation of the individual ions from monosulfide plus sulfur were taken to be the numbers read from Figure 99 at the "x" values one less than the sulfur subscripts of the various ions. Thus the heat of formation of $S_3^=$ ion was taken as the value indicated at "x" = 2, etc. Consideration indeed shows that the intercept determined by extrapolation to "x" = 1 should be the ΔH of formation of the lowest polysulfide ion, i.e., $S_2^=$, even if only present in small amounts at higher "x" values. The enthalpies of formation approximated by this technique, based on the <u>average</u> of the two literature curves in Figure 99, are listed in Table XXVI, along with the "apparent heats of formation" reported directly by these two sources.

As a second and slightly more justifiable assumption the ionic distributions valid for Figure 99 were taken to be those calculated for 0.1 <u>m</u> sodium ion using the "recommended" equilibrium constants at 75°C (Figure 76). Thus the individual enthalpies of reaction could be obtained by the solution of a system of simultaneous linear equations. This procedure was carried out for both the curve of Bichowsky and Rossini (<u>6</u>) and that of <u>Handbook of Chemistry and Physics</u> (<u>36</u>); the resulting sets of heats of formation also are shown in Table XXVI.

TABLE XXVI

Enthalpies of Formation of Polysulfide Ions

(-ΔH's of reaction, KCal)

Reaction	A	B	C	D	E*
$S^= + 1/8\ S_8 = S_2^=$	0.74	0.41	0.58	?	?
$S^= + 2/8\ S_8 = S_3^=$	2.24	2.11	1.50	0.58	0.58
$S^= + 3/8\ S_8 = S_4^=$	4.74	3.52	3.10	2.01	0.26
$S^= + 4/8\ S_8 = S_5^=$	?	?	4.60	12.32	13.25
$S^= + 5/8\ S_8 = S_6^=$	?	?	6.0 ?	2.84	-19.82
$S^= + 6/8\ S_8 = S_7^=$	?	?	7.2 ?	?	?

Key: <u>A</u>: "Apparent ΔH's" from Bichowsky and Rossini (<u>6</u>).

<u>B</u>: "Apparent ΔH's" from <u>Handbook of Chemistry and Physics</u> (<u>36</u>).

<u>C</u>: "Crude approximation", as described.

<u>D</u>: From <u>A</u>, but using ionic distributions for 75°C, 0.1 <u>m</u> Na^+.

<u>E</u>: From <u>B</u>, but using ionic distributions for 75°C, 0.1 <u>m</u> Na^+.

* The <u>E</u> ΔH's could not be made to fit the data well.

Examination of Table XXVI indicates that the E calculated heats of formation neither appear reasonable nor match the curve in Figure 99 very well. The values reported in Handbook of Chemistry and Physics therefore must be considered doubtful.

From the "recommended" ionic equilibrium constants at 75°C and the C and D enthalpies of formation listed in Table XXVI, two corresponding sets of equilibrium constants at 25°C were derived, making the assumption that the enthalpies (ΔH's) and entropies (ΔS's) of reaction did not vary with temperature. Thus the temperature conversion could be effected using the following two equations:

$$\Delta F^\circ = -RT \ln k \qquad (125)$$

$$\Delta H^\circ = \Delta F^\circ - T\,\Delta S^\circ \qquad (126)$$

in which ΔF° is the standard free energy change, KCal/mol.

ΔH° is the standard enthalpy change, KCal/mol.

ΔS° is the standard entropy change, KCal/mol-°K.

T is temperature, °K.

k is polysulfide equilibrium constant.

R is 0.001987 KCal/mol-°K.

The results of this calculation are shown in Table XXVII:

TABLE XXVII

Equilibrium Constants at 25°C from Heats of Formation

	Reaction	k_{348}	$-\Delta F^\circ_{348}$	$-\Delta H^\circ$	$+\Delta S^\circ$	$-\Delta F^\circ_{298}$	k_{298}
Case C:	$S^= + 1/8\ S_8 = S_2^=$	?	?	0.58	?	?	?
	$S^= + 2/8\ S_8 = S_3^=$	1760	5.16	1.50	0.01051	4.63	2460
	$S^= + 3/8\ S_8 = S_4^=$	33,700	7.22	3.10	0.01185	6.63	72,500
	$S^= + 4/8\ S_8 = S_5^=$	68,400	7.70	4.60	0.00890	7.25	207,500
	$S^= + 5/8\ S_8 = S_6^=$	21,040	6.87	6.0 ?	0.00250	6.75	105,800
	$S^= + 6/8\ S_8 = S_7^=$	?	?	7.2 ?	?	?	?
Case D:	$S^= + 1/8\ S_8 = S_2^=$	?	?	?	?	?	?
	$S^= + 2/8\ S_8 = S_3^=$	1760	5.16	0.58	0.01316	4.50	2000
	$S^= + 3/8\ S_8 = S_4^=$	33,700	7.22	2.01	0.01499	6.48	56,600
	$S^= + 4/8\ S_8 = S_5^=$	68,400	7.70	12.32	-0.01329	8.36	1,364,000
	$S^= + 5/8\ S_8 = S_6^=$	21,040	6.87	2.84	0.01158	6.29	41,400
	$S^= + 6/8\ S_8 = S_7^=$	?	?	?	?	?	?

For comparison with the 25°C "equilibrium" results of the present thesis, X, Y, and Y/X values at 4.0 m sodium ion and unity sulfur activity were estimated for the two cases presented in Table XXVII. Since the monosulfide hydrolysis equilibrium apparently changes but little in going from 75°C to 25°C (Figure 68), Z_1 at 25°C was assigned the same value (1.021) as at the higher temperature at this same molality. The k's then could be converted to r's by the use of equation 117, and X and Y could be calculated from equation 54 and equation 55, respectively:

For the C equilibrium constants the values were:

$X = 0.343$

$Y = 1.396$

$Y/X = 4.06$

For the D equilibrium constants the values were:

$X = 1.291$

$Y = 5.145$

$Y/X = 3.98$

Neither of these two cases yielded numbers within the apparent limits indicated by the 25°C sulfur saturation data of the present thesis. Even though the C constants did come closer to fitting the stoichiometric results than did the D constants, no reasonable equilibrium constants at 25°C could be found which were compatible both with the measured heats of formation and with the Na_2S-S-H_2S-H_2O experimental findings of the present thesis.

c. "Suggested" Equilibrium Compositions at 25°C

Since extrapolation by means of enthalpy of reaction data failed to determine satisfactory equilibrium constants at 25°C, a set of "suggested" constants was arbitrarily selected which conformed to the limits indicated by the room temperature measurements of the present thesis and which gave "reasonable" values of the thermodynamic quantities involved, even if not in agreement with the results of calorimetric determinations. These constants are listed in Table XXVIII:

TABLE XXVII

"Suggested" Polysulfide Equilibrium Constants at 25°C

Reaction	k_{348}	$-\Delta F^\circ_{348}$	k_{298}	$-\Delta F^\circ_{298}$	$-\Delta H^\circ$	$+\Delta S^\circ$
$S^= + 1/8\ S_8 = S_2^=$	?	?	?	?	?	?
$S^= + 2/8\ S_8 = S_3^=$	1760	5.16	2270 ?	4.58 ?	1.08 ?	0.0116
$S^= + 3/8\ S_8 = S_4^=$	33,700	7.22	43,100	6.19	0.05	0.0206
$S^= + 4/8\ S_8 = S_5^=$	68,400	7.70	73,800	6.64	0.31	0.0212
$S^= + 5/8\ S_8 = S_6^=$	21,040	6.87	42,000	6.30	2.92	0.0114
$S^= + 6/8\ S_8 = S_7^=$	?	?	18,170	5.80	13.58?	-0.0260?

The conversion of these k's to the X, Y, and Y/X values at 4.0 m sodium ion and sulfur saturation yielded the following:

$X = 0.1500$

$Y = 0.6350$

$Y/X = 4.23$

These numbers thus agree with the fairly reproducible results of the 25°C sodium hydrosulfide - sulfur experiments of the present thesis.

In order to compare these "suggested" equilibrium constants at 25°C with the "recommended" constants at 75°C, a complete ionic distribution profile was calculated for 1.0 m sodium ion (the concentration used for previous comparisons) at 25°C. The compositions of solutions saturated with sulfur at 25°C also were computed at sodium ion molalities of 0.1, 0.01, 0.001, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7}, for comparison with those calculated for the higher temperature. In these calculations the same Z_1 versus molality plot was employed as was used for the "recommended" compositions at 75°C (Figure 69).

The ionic molalities at 25°C thus derived for a sodium ion concentration of 1.0 m are plotted versus "x" in Figure 100, along with the similar profiles calculated from the "recommended" equilibrium constants at 75°C. Except for the inclusion of the $S_7^=$ ion at 25°C the plots for the two temperatures are markedly similar. In neither case, however, can the curves be considered reliable at "x" values much below 4.0.

Because of the close resemblance of the "suggested" ionic distributions at 25°C to the "recommended" compositions at 75°C, comparisons of hydrolyses, $S_x^=/Na_2S_x$ ratios, PSS/$S_x^=$ ratios, sulfur activities, etc. also indicated little or no significant differences between the two temperatures, and hence are not presented here.

The effect of concentration on the maximum "x" in sodium polysulfide at sulfur saturation, as derived both

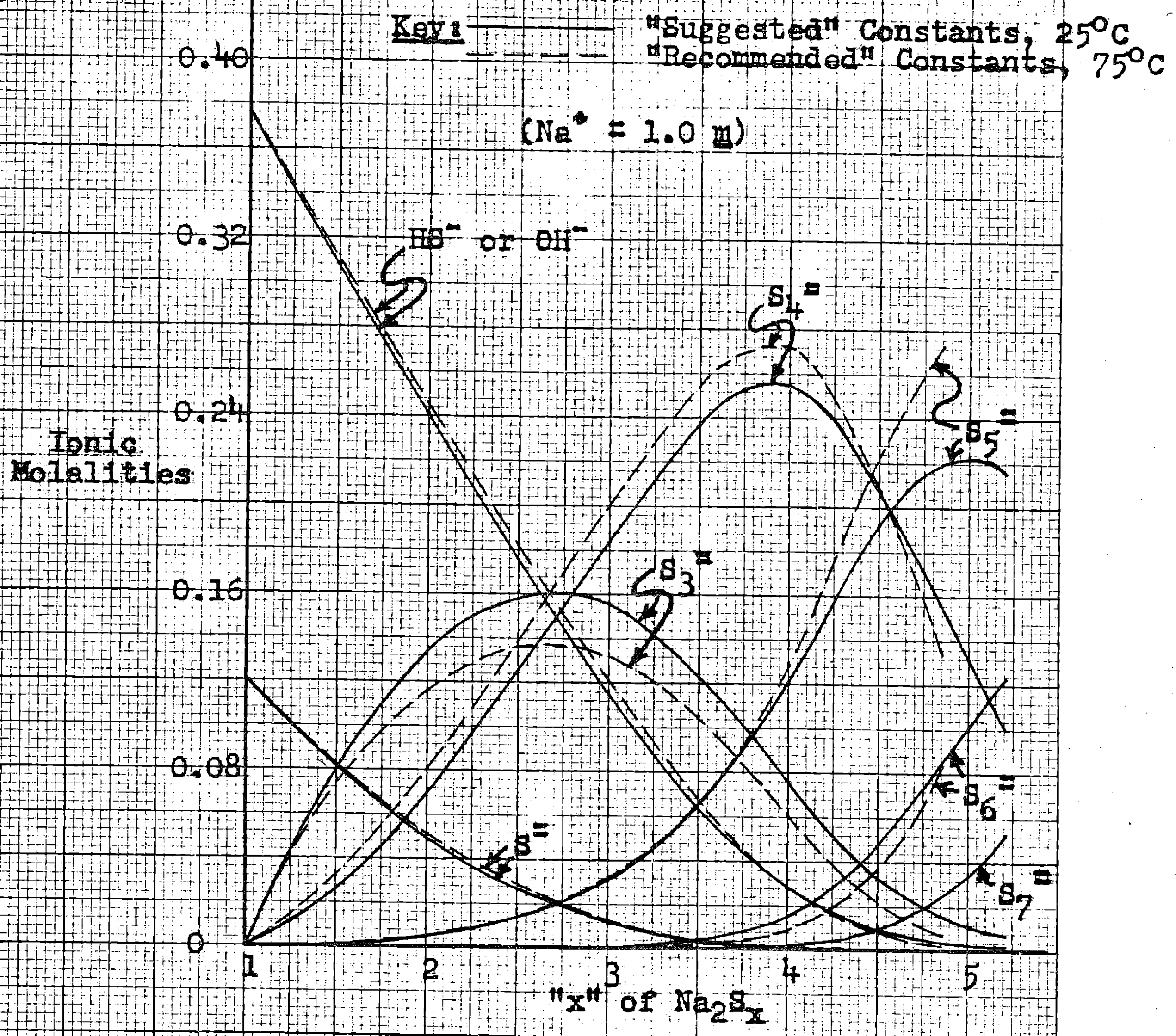


FIGURE 100

"Suggested" Polysulfide Ionic Distributions at 25°C from the "recommended" equilibrium constants at 75°C and from the "suggested" constants at 25°C, is shown in Figure 101. Although the room temperature relation coincides more nearly with the maximum portion of the experimental curve of Kuster and Heberlein (41) (see Figure 5), neither set of constants predicts this curve in its entirety. Accordingly, as suggested by the more recent determinations also plotted in Figure 101, the curve of Kuster and Heberlein must be considered a non-equilibrium one. The apparent rapid drop in saturation "x" below 0.02 m sodium ion thus might be explained on the basis of extremely low rates of sulfur solution or else the relatively increasing effects of side reactions with oxygen and carbon dioxide from the air. Since the semi-quantitative polysulfide dilution tests of the present thesis roughly confirmed that portion of the curve of Kuster and Heberlein, the latter explanation appears more likely.

From the enthalpies of formation listed in Table XXVIII and the "suggested" ionic compositions at 25°C, "apparent" heats of formation of polysulfide solutions at 1.0 m sodium ion concentration were derived. These "predicted calorimetric heat effects" are plotted versus "x" in Figure 102 for comparison with the two experimental curves taken from Figure 98. It is evident that the "suggested" polysulfide equilibrium constants correspond to heats of

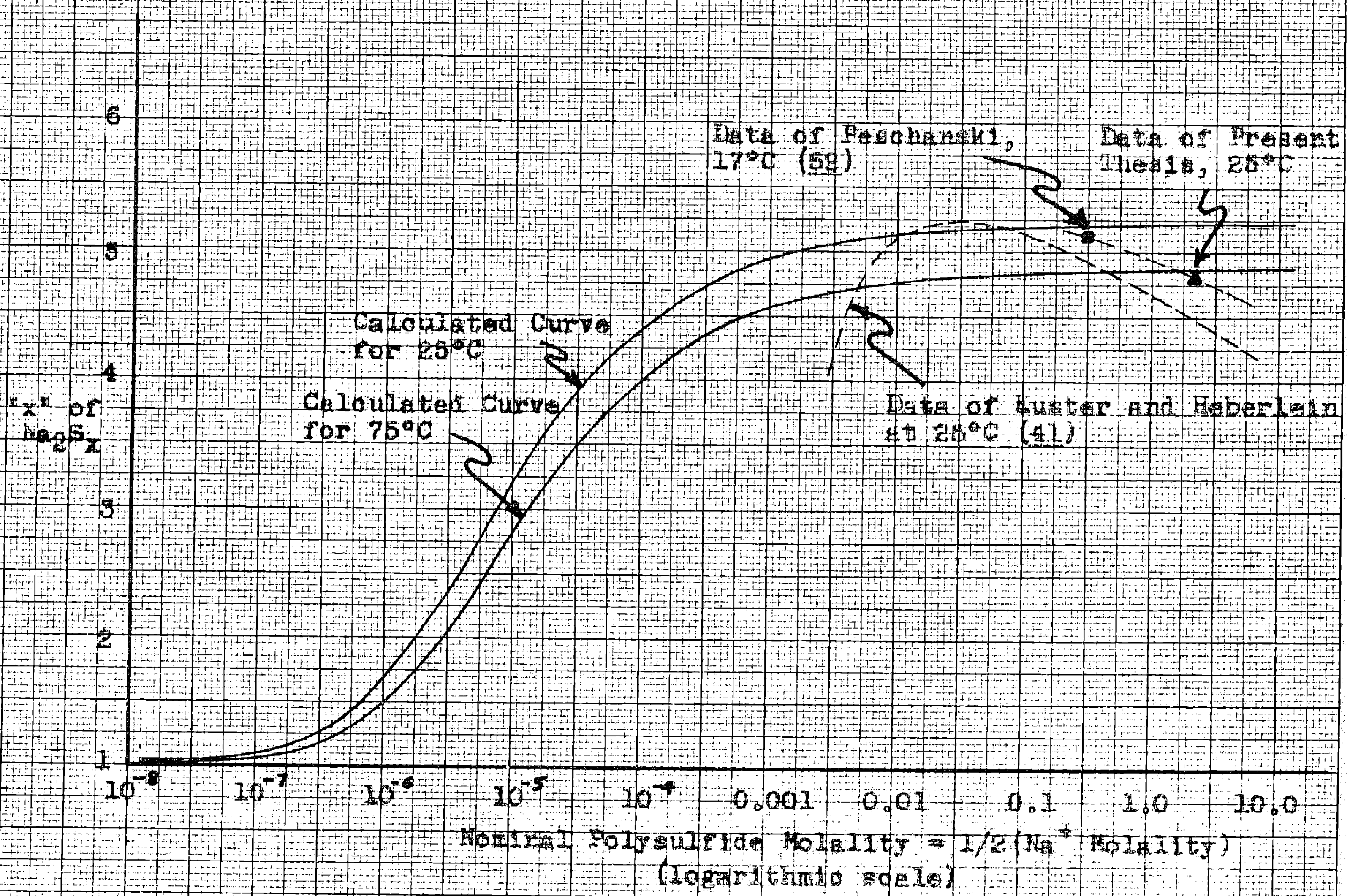


FIGURE 101

Saturation "x" in Sodium Polysulfide Solutions

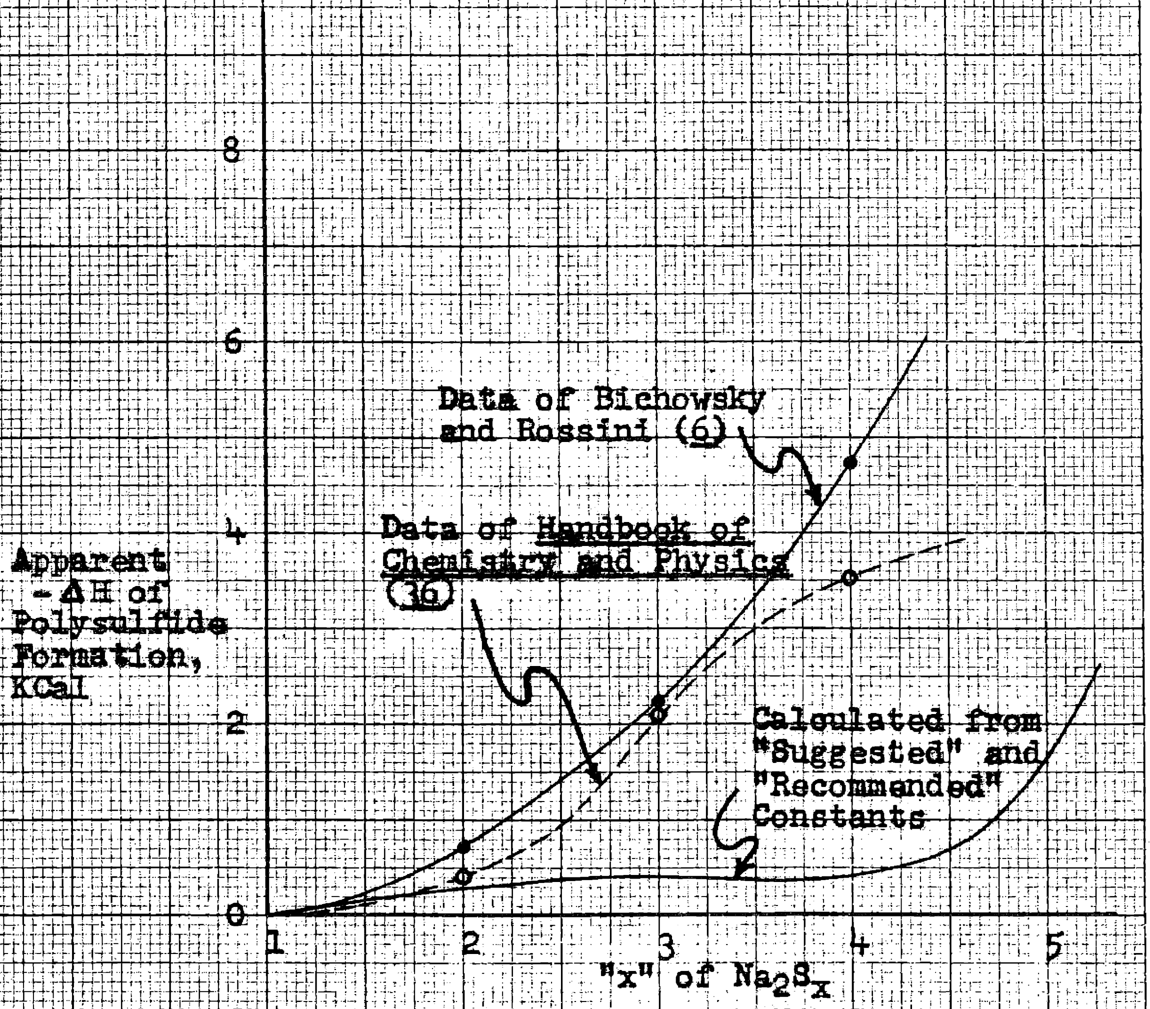


FIGURE 102

"Suggested" Heats of Formation of Polysulfide Solutions formation much smaller than those actually measured. (The discrepancy would have been even slightly more had the calculated curve in Figure 102 been based on the "suggested" ionic distributions which could be calculated for 0.1 m sodium ion.) On the other hand, if the measured enthalpies were assumed correct, the equilibrium conditions thus dictated at 25°C would have to lie outside the apparent boundaries defined by the room temperature Na_2S-S_2H_2S-H_2O experiments of the present thesis.

3. Hypothesized Non-Equilibrium Behavior at 25°C

Since certain of the polysulfide ionic reactions apparently are not mobile at room temperature, the compositions derived from any equilibrium considerations (such as the "suggested" 25°C constants presented in the preceding section) are likely to be in error. Even though equilibrium assumptions may not be valid, the stoichiometric information obtained in the 25°C Na_2S-S-H_2S-H_2O studies of the present thesis does provide clues as to which ions are slow to react. As was mentioned previously, the points obtained using the sodium hydrosulfide - sulfur reaction were more reproducible than those from experiments following the sodium polysulfide - hydrogen sulfide route. The attainment of at least a quasi-equilibrium with the former approach further was indicated by Run E-10 (see Table VIII); even though considerable unreacted sulfur remained after the relatively short 50 minute reaction time, the aqueous phase analysis coincided with those obtained in similar experiments after longer run times and with essentially no solid sulfur remaining at "equilibrium". It was deduced that some of the ionic constituents equilibrate more rapidly than does the reaction between free sulfur and the solution.

Consideration of only those experiments from Table VIII believed to have been performed at "sulfur saturation" provides the best comparison between the two routes. The runs with appreciable solid sulfur present after reasonably long time periods are summarized in Table XXIX:

TABLE XXIX

The System Na_2S-S-H_2S-H_2O: Sulfur Saturation Runs at 25°C

Run	E-6	E-7	E-8	E-9	E-12	E-14	E-15*	E-16	E-20
Direction	a	a	a	b	b	b	b	b	b
Time, hrs	5.0	10.0	5.0	?	0.75#	1.0#	1.0	1.0#	1.0#
Solid S, gm/l	77.6	26.6	38.5	94.9	36.7	112.1	0	110.5	47.0
"x" of Na_2S_x (in "b" runs)	-	-	-	4.5	3.5	4.5	2.5	4.5	3.5
X	0.141	0.146	0.133	0.305	0.278	0.173	0.151	0.181	0.271
Y	0.602	0.565	0.555	1.128	1.019	0.684	0.553	0.718	0.934
Y/X	4.26	3.88	4.16	3.78	3.67	3.96	3.67	3.98	3.44

Notes: "a" indicates use of the NaHS + S reaction; "b" denotes Na_2S_x + H_2S reaction.

* - Since no sulfur was precipitated, run E-15 probably was not carried out at sulfur saturation, but is believed to have been close.

- In the indicated experiments no further sulfur precipitation was evidenced after 1/2 to 1 hrs additional H_2S saturation.

From Table XXIX it is seen that the X and Y values for the three sodium hydrosulfide - sulfur experiments at sulfur saturation are nearly constant. The ratio Y/X or PSS/$S_x^=$, however, was affected somewhat by the reaction conditions. Although the data are really too few to be conclusive, high values of this ratio apparently were favored by large "concentrations" of unreacted sulfur, along with shorter reaction times.

If run E-9 were discarded on the basis of either too short a time or some other reason for a failure to reach equilibrium, the four remaining sodium polysulfide - hydrogen sulfide experiments at sulfur saturation exhibit a trend with the "x" of the initial polysulfide used. Inspection of Table XXIX and Figure 103 indicates that the ratio Y/X at "equilibrium" increases with initial "x". This finding constitutes evidence that certain of the polysulfide ions present in ordinary sodium polysulfide solution are sluggish to react upon hydrogen sulfide saturation. From Figures 104 and 105 it is evident, however, that as "x" is increased, X and Y both drop, possibly approaching at sulfur saturation the numbers obtained employing the sodium hydrosulfide - sulfur reaction. It was concluded that the <u>lower</u> polysulfide ions (present in larger quantities in polysulfides of lower "x") are the ones which are slow to decompose upon hydrogen sulfide addition, since the presence of these non-equilibrium

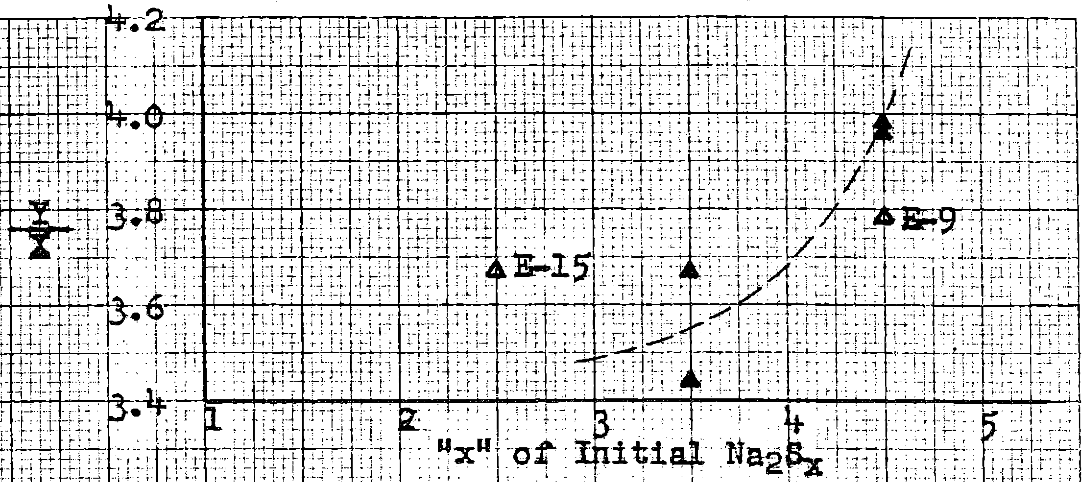


FIGURE 103

Na_2S_x-H_2S Reaction at 25°C:
Effect of Initial "x" on Y/X

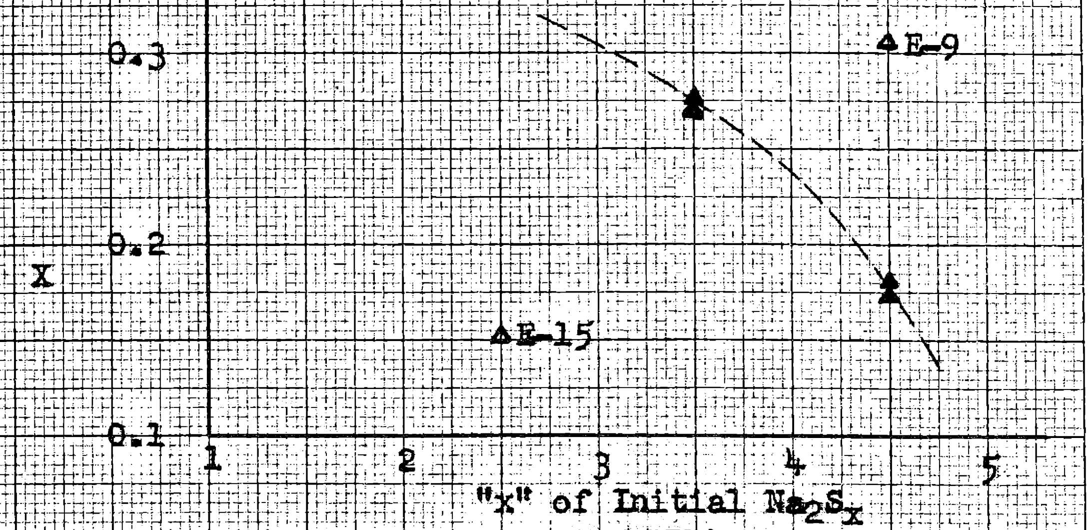


FIGURE 104

Na_2S_x-H_2S Reaction at 25°C:
Effect of Initial "x" on X

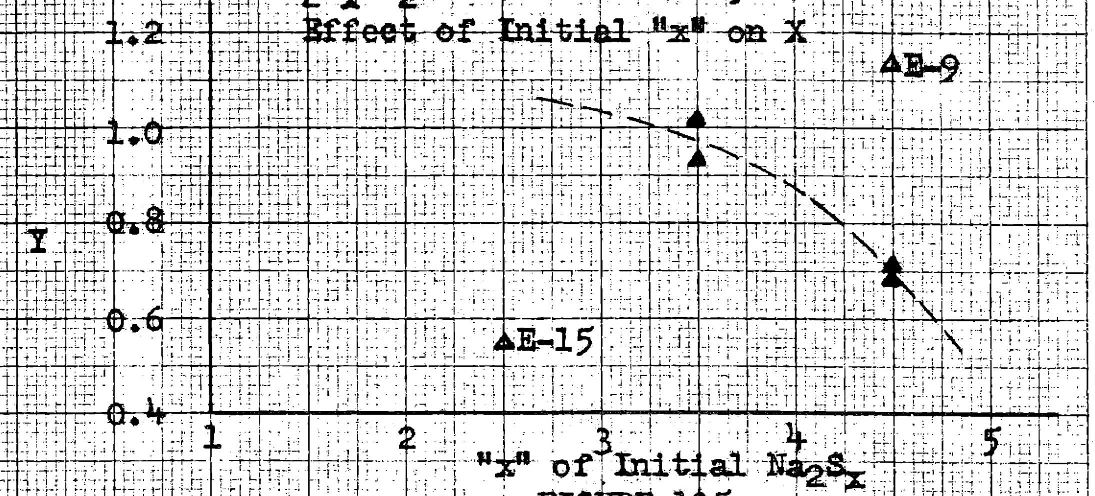


FIGURE 105

Na_2S_x-H_2S Reaction at 25°C:
Effect of Initial "x" on Y

species (not formed during the sodium hydrosulfide - sulfur reaction) would lead to lower Y/X ratios and higher X and Y values than if they were absent. If the higher polysulfides were the non-equilibrium components, the results of the experiments employing higher initial "x" values would be the least likely to approach the numbers obtained from the sodium hydrosulfide - sulfur direction.

If the sodium hydrosulfide - sulfur results are assumed to represent the true equilibrium, examination of Figure 12 then indicates that the non-equilibrium species in effect "added" in the case of the reverse reaction have an average sulfur subscript between 3 and 4 ($\Delta PSS/\Delta S_x^=$ between 2 and 3). If experiment E-15 is assumed to be not too far from sulfur saturation, Figure 12 further implies that the proportion in sodium polysulfide of the ions which are sluggish to react is higher at an "x" of 3.5 than either at 2.5 or 4.5.

The results of the Na_2S-S-H_2S-H_2O measurements of the present thesis thus indicate that one or more of the lower ionic species (probably largely $S_4^=$) either form very slowly or decompose very slowly or both, in neutral solutions at 25°C. The correlations presented in Figures 103-105 imply, however, that these same lower ionic species are formed to some extent in basic solutions in the process of preparing polysulfides from sodium monosulfide and sulfur. No reasonable mechanism has yet been devised to explain why both the formation and the decomposition of these certain ions should be slowed by a shift in pH from about 11 to about 7.

The findings of the present thesis have indicated that the equilibrium "x" in polysulfide solutions saturated with sulfur at room temperature probably is higher than at 75°C (Figure 101). The apparent higher sulfur solubilities at the higher temperatures, as has been pointed out, are considered the result of low reaction rates at the lower temperatures. The precipitation of sulfur upon the rapid cooling of certain hot polysulfide solutions having high "x" values is believed to be due to non-equilibrium adjustments among the various ions, i.e., rates of decomposition faster than rates of formation. Although the "equilibrium" ionic distribution profiles for the two temperatures are but little different (Figure 100), the "suggested" 25°C compositions obviously cannot be considered reliable. Without any quantitative rate data on the slow ionic reactions involved, any further treatment of the non-equilibrium behavior in aqueous polysulfide solutions at low temperatures is beyond the scope of the present thesis.

G. Application of Results to the Raw Oil Synthesis

The production of raw hydrogen persulfide by the acidification of aqueous polysulfide solution should be influenced strongly by the ionic composition of the initial polysulfide. In particular, it should be possible to predict the effects on the process of any changes in the polysulfide variables if the relation between the ionic distribution and these variables is known. Since the raw oil synthesis results of Conway (15) constitute the most reliable research to date on the effects of polysulfide concentration and polysulfide "x", these data were chosen for comparison with the findings of the present thesis. No attempts were made to treat the existing data on the effects of other variables, such as temperature, acid concentration, and mixing rate. Without any quantitative knowledge of the individual components present in raw hydrogen persulfide, such correlations were beyond the scope of the present thesis.

Neither the "suggested" equilibrium ionic compositions at 25°C nor the hypothesized non-equilibrium behavior at this temperature can be considered very dependable. Accordingly, for lack of any better information, the "recommended" polysulfide equilibrium distributions at 75°C will be employed in all correlations with the results of Conway.

1. Effect of Polysulfide Variables on Mol Yield

In Figure 106 the yield curves of Conway (15) (see Figure 1) are compared to the maximum possible mol yields ($S_x^=$/nominal Na_2S_x) derived in the present thesis for sodium ion molalities of 2.0 and 4.0 (sodium polysulfide <u>molarities</u> of approximately 1.0 and 2.0, respectively). Conway attempted to match his curves with constant fractions of the maximum yields based on his proposed ionic compositions of polysulfide solutions. In Figure 108 the percentages, for the four curves of Conway, of the maximum possible mol yields based on the results of the present thesis are plotted versus polysulfide "x". As may be noted, these fractions of the theoretical yield range from about 0.3 to about 0.8, and are far more dependent on mixing rate than on "x". In all instances these "true" mol yields based only on the actual polysulfides present do increase at higher values of "x", however, indicating that the higher polysulfide ions give better yields of the hydrogen persulfides than do the lower ions. This phenomenon could well be due to a greater instability of the lower HS_x^- species formed as reaction intermediates. The flatness of the curves in Figure 108 at lower "x" values might be taken as evidence that the disulfide ion either is absent, or if present is no more unstable than the trisulfide or tetrasulfide HS_x^- species.

The differences between the four curves in Figure 108 are primarily due to mixing rate effects. Owing to the pronounced improvement in mixing when a more dilute polysulfide solution is used, the mol yields at <u>M</u> = 1 are higher than

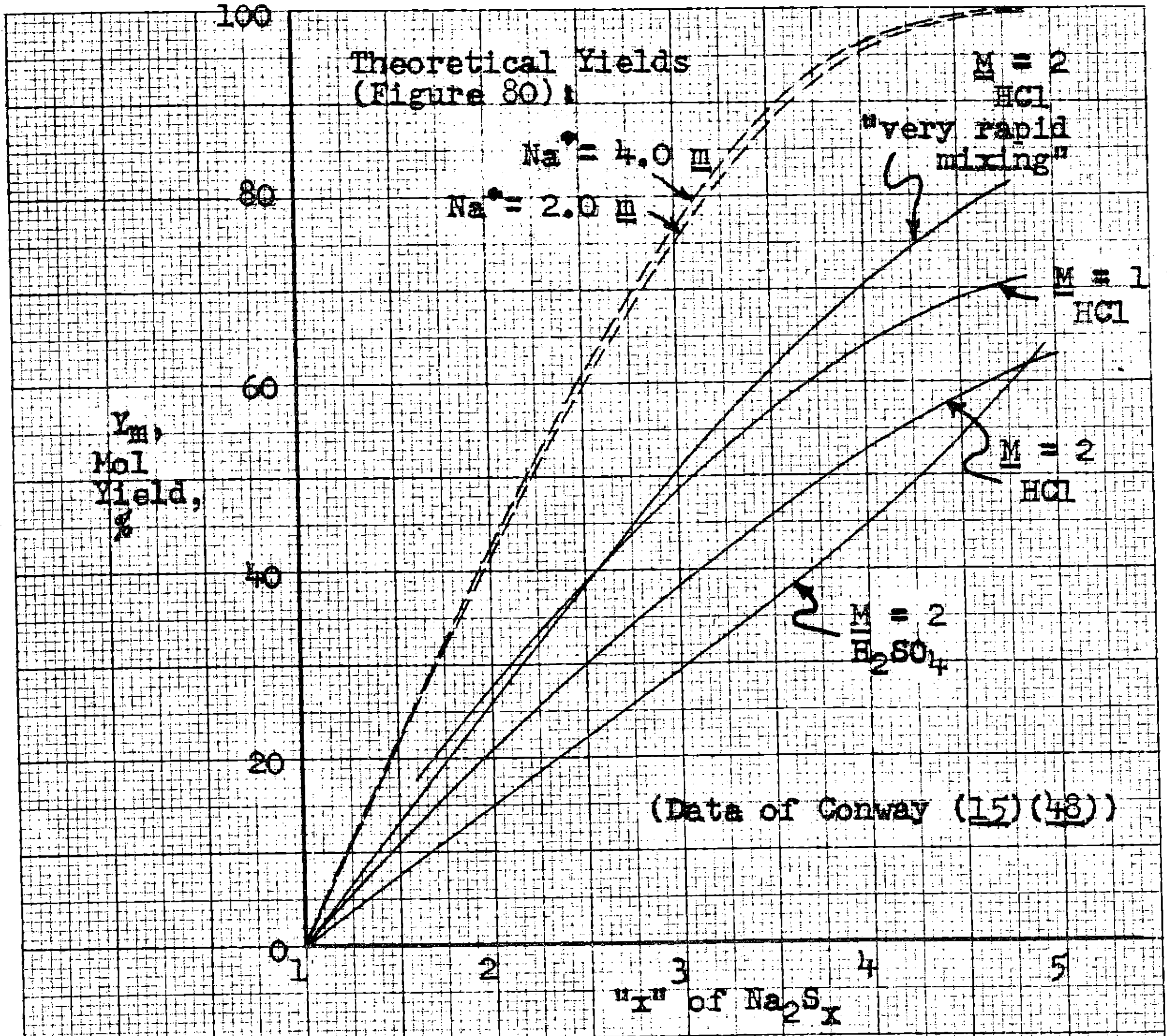


FIGURE 106

Comparison Between Theoretical and Actual Raw Oil Mol Yields

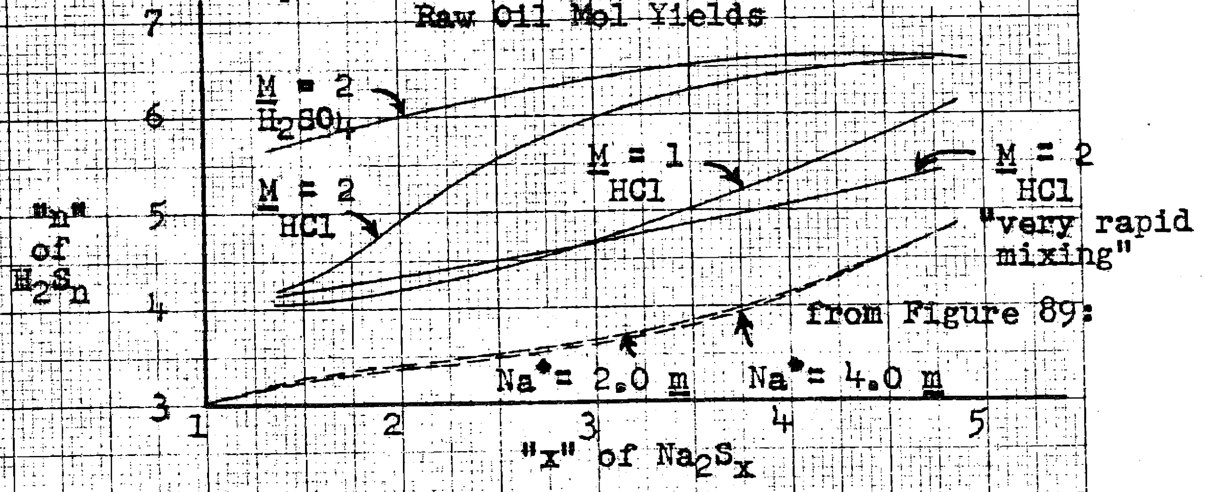


FIGURE 107

Comparison Between Theoretical and Actual Raw Oil Compositions

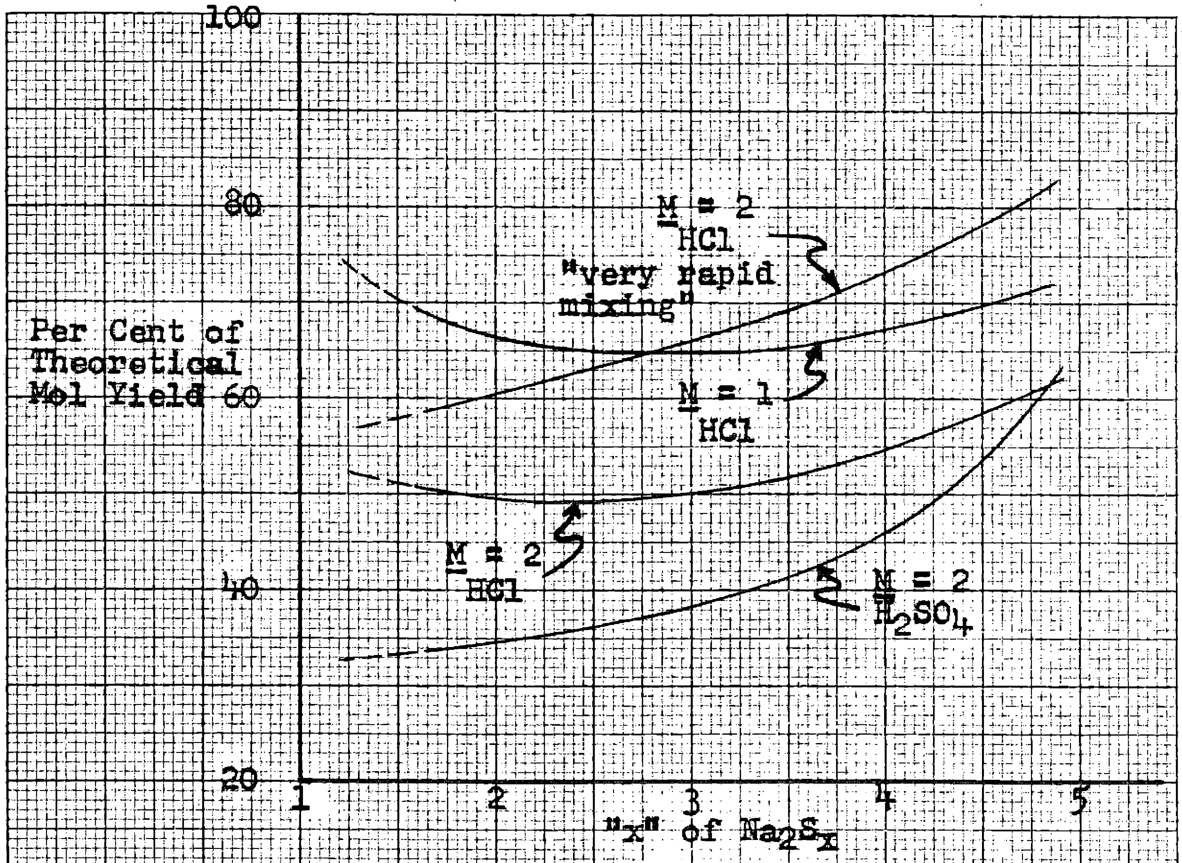


FIGURE 108

Percentages of Theoretical Mol Yields in Raw Oil Synthesis

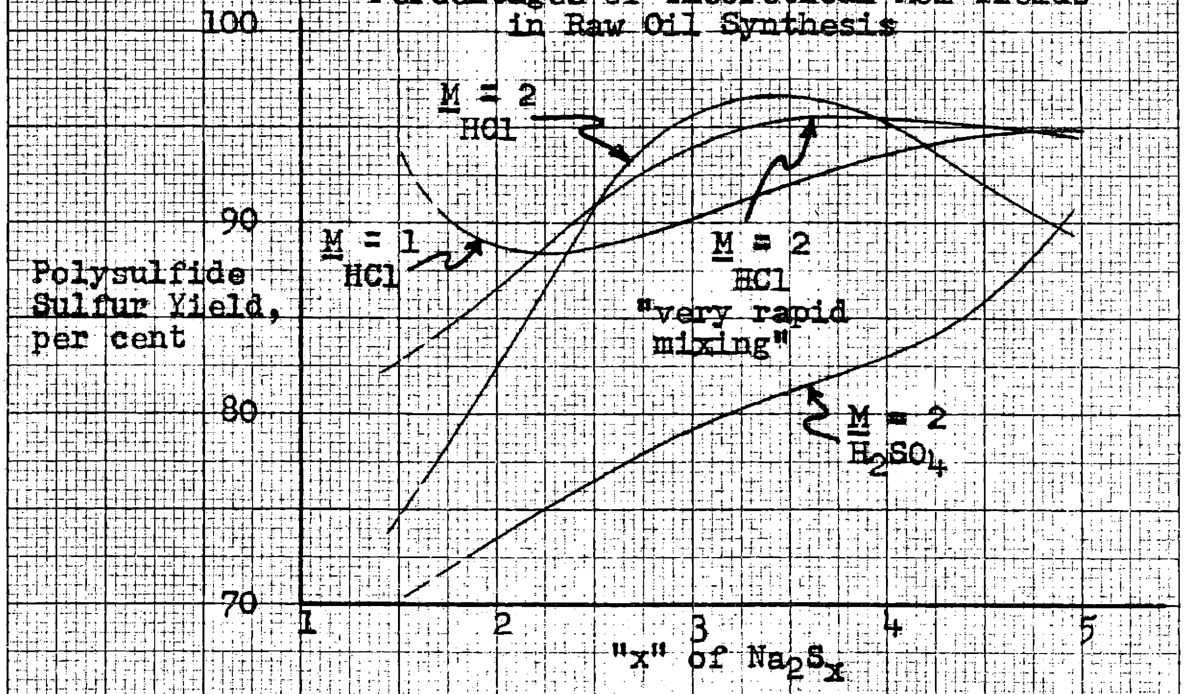


FIGURE 109

Polysulfide Sulfur Yields in Raw Oil Synthesis at M = 2 even though the calculated ratios $S_x^=/Na_2S_x$ are slightly lower in the former case. Since lowered alkalinity of the polysulfide would, in effect, lead to more rapid mixing with the acid, some of the rise in "true" mol yield with increasing "x" (Figure 108) moreover might be only the result of the decreasing polysulfide hydrolysis. No corrections could be made for this unknown effect. The fact that some of the curves in Figure 108 intersect may be taken as further evidence that situations of constant true mixing rate were not represented.

2. Effect of Polysulfide Variables on Sulfur Yield

As was mentioned in the Introduction, "n" in the average formula H_2S_n is always higher than and increases somewhat with the "x" of the polysulfide used. In Figure 107 it is seen that the average "n" of the persulfide is considerably higher than the value which would be expected $((PSS/S_x^=) + 1)$ if each polysulfide species were converted quantitatively. As will be shown, the difference is too great to be explained solely on the basis of the smaller individual percentage yields of the lower persulfide species.

In Figure 109 the polysulfide sulfur yields (defined as per cent of polysulfide sulfur in the initial polysulfide appearing as total sulfur in excess of total hydrogen sulfide in the raw oil) from the data of Conway are plotted versus "x". It is evident that except for the set of runs employing sulfuric acid, the polysulfide sulfur yield remained between 90 and 95 per cent above "x" = 2.5 regardless of the mixing rate. Mixing, in other words, affects the "true" mol yield, but not the sulfur yield.

The data on polysulfide sulfur not appearing in the final product are subject to too much uncertainty to be useful, but it was shown by calculation based on both Figure 106 and Figure 109 that the ratio of "polysulfide sulfur lost" to "polysulfide ions lost" always was less than unity. If all the polysulfide decomposing to sulfur were assumed to be the trisulfide, this ratio would be 2.0; if assumed to be the disulfide, 1.0. It therefore is evident that much of the sulfur released by the decomposition of the lower HS_x^- ions either dissolves in or reacts with the raw oil product. In line with his Raman spectroscopic observations indicating little or no physically-dissolved sulfur in raw oil, Feher (20) hypothesized that the latter must take place, i.e., that the nascent sulfur released by decomposition combines with certain of the hydrogen persulfides (or the acid polysulfide species) to form even higher persulfides. Thus the persulfide compounds present in raw oil might not necessarily correspond to the polysulfide ions present in the starting material.

CONCLUSIONS

1. In the system $Na_2S-S-H_2S-H_2O$ ionic equilibria exist, relating the activities of the various polysulfide species to the monosulfide ion activity and the activity of elemental sulfur:

$$S^{=} + 1/8\ S_8 = S_2^{=}$$

$$S^{=} + 2/8\ S_8 = S_3^{=}$$

etc.

2. Equilibrium in the system $Na_2S-S-H_2S-H_2O$ was approached experimentally at 75°C, but not at 25°C. Even though hydrogen sulfide and the monosulfide and hydrosulfide ions do remain in equilibrium, reactions with solid sulfur and with certain of the lower polysulfide ions are slow at room temperature.

3. The "average" ionic activity coefficient at 75°C, as derived from stoichiometric considerations, increases with concentration above a sodium ion molality of 1.0. Evidence exists that the individual ionic activity coefficients do not all vary with concentration in the same proportion.

4. The absence of the HS_x^- species in the system $Na_2S-S-H_2S-H_2O$ was indicated by the results of pH determinations. This verification of the apparent instability of the acid polysulfides supports the accepted mechanism of the raw oil synthesis.

5. The concentration of physically-dissolved sulfur in aqueous polysulfide solutions is negligible.

6. Elemental sulfur activities in polysulfide solutions can be measured experimentally by the use of o-xylene as a sulfur solvent. The activity coefficients of sulfur dissolved in o-xylene at 75°C are lower in the low concentration region than predicted by ideality.

7. The ionic equilibrium constants relating the various polysulfide species at 75°C could be obtained by the graphical solution of simultaneous equations derived from the experimental data. Several possible sets of constants could be found, however, which fitted the results within the precision of the measurements.

8. The closest agreement with the experimental data was obtained with an ionic distribution which included the $S_3^=$, $S_4^=$, $S_5^=$, and $S_8^=$ ions. Although the trisulfide ion concentrations as recommended are not at all reliable, the existence of at least one polysulfide species below $S_4^=$ is likely.

9. No hypothesized "equilibrium" polysulfide compositions at 25°C could be found which were simultaneously compatible with both the non-equilibrium results of the present thesis and with the heats of formation of polysulfide solutions reported in the literature.

10. Upon the acidification of polysulfide solutions the individual $S_x^=$ ions first may be converted to the unstable intermediates HS_x^-. The yield and composition

of raw hydrogen persulfide thus depends on the rate at which the second hydrogen ion is brought to the scene of reaction.

11. The fraction of initial polysulfide ions converted to hydrogen persulfides upon acidification is primarily dependent on the rate of mixing, and is only weakly a function of polysulfide "x". If the disulfide or trisulfide species do exist in significant proportions in ordinary alkali polysulfide solutions, some additional reason besides the relatively greater instability of the lower HS_x^- species must be sought for their complete disappearance during the formation of raw oil.

12. Much of the nascent sulfur released by the decomposition of the HS_x^- species during polysulfide acidification reacts chemically with the persulfides which are formed, yielding higher sulfur homologues which may not correspond to any ions present in the initial polysulfide.

13. The results of the present thesis should be equally applicable to polysulfide systems in which a cation other than sodium is employed, provided that any differences in ionic activity coefficients are taken into account.

RECOMMENDATIONS

1. The development of an independent analysis for the individual polysulfide ions should be investigated. Ion exchange and visible-range spectroscopy are two approaches which may offer promise.
2. The hydrolyses of polysulfide solutions, both at room and at elevated temperatures, should be determined using the mercuric sulfide solubility method already employed in measurements of monosulfide hydrolyses.
3. The elemental sulfur activities in ordinary sodium polysulfide solutions at room and at elevated temperatures should be measured by means of the solvent extraction technique developed in the present thesis. Operation with dilute polysulfide solutions is recommended in order that the sulfur activities remain large enough to be measured at as low "x" values as possible. The maximum "x" values at sulfur saturation also should be determined with more reliability, allowing sufficient time to approach equilibrium at room temperature.
4. Activities versus concentrations of sulfur in o-xylene or another suitable solvent should be determined by differential vapor pressure measurements, employing a more refined apparatus and technique than those used by Simmons (60).

5. Rate data should be taken for the slow reactions observed in the system $Na_2S-S-H_2S-H_2O$ at low temperatures in an attempt to clarify the non-equilibrium behavior under these conditions.
6. The effect on the production of raw hydrogen persulfide of the time-temperature history of the polysulfide should be investigated in more detail.
7. The possibility of obtaining hydrogen persulfides with selective compositions by taking advantage of the absence of equilibrium in polysulfide solutions at low temperatures should be examined. This study might include acidification of the following:
    - (a) polysulfide solutions saturated with hydrogen sulfide.
    - (b) polysulfides of low "x" prepared by adding monosulfide to polysulfides of high "x" immediately prior to use.
    - (c) the first polysulfides instantaneously formed in a flow system by the reaction of sulfur with solutions of sodium monosulfide or sodium hydrosulfide.
8. The production of raw hydrogen persulfide under extremely high and at the same time closely controlled small-scale mixing rates should be studied to determine how high mol yield can be forced. A different type of

flow apparatus than the system described in the Appendix might be required.

9. Tracer experiments with radioactive S^{35} should be carried out in order to clarify the mechanisms involved in polysulfide preparation, polysulfide acidification, and hydrogen persulfide decomposition. These isotope studies might be expected to indicate under what conditions an exchange between "polysulfide sulfur" and "hydrogen sulfide sulfur" can occur.

10. A quantitative Raman spectroscopic analysis for the individual persulfides in raw oil should be developed. With the proper high vacuum and spectroscopic apparatus and a suitable technique this approach should provide determinations of the individual persulfides up to at least the pentasulfide or hexasulfide.

11. The proposed analyses for physically-dissolved hydrogen sulfide and sulfur in raw oil should be perfected. In both cases the absolute determinations would have to be obtained by extrapolation, using "known" mixtures, since raw oil completely free of these two substances probably could not be prepared.

12. The possibilities, by selective extraction using a partially-miscible solvent such as benzene, either of fractionating raw oil into its components or of analyzing for those components should be investigated

as possible alternatives to high-vacuum distillation and Raman spectroscopy, respectively.

13. The direct, or "gas-phase" synthesis for the hydrogen persulfides should be attempted under more favorable conditions than previously employed, including rapid quenching to avoid decomposition, and the use of a circulating solvent selective for the persulfides.

14. The production of hydrogen disulfide via perthiocarbonic acid should be studied in further detail in order to discover if process modifications can increase the overall disulfide yield above that obtainable by the usual raw oil route. If this approach proves negative, the possibility of substituting the acid itself for the disulfide in its organic reactions should be investigated.

15. Those of the preceding recommendations which constitute <u>applied</u> research on the hydrogen persulfide synthesis should not be followed up until or unless further studies of the organic reactions of the persulfides have indicated one or more reasonably promising commercial applications.

APPENDIX

A. Methods of Analysis

1. Titration for Total Sulfides

The iodine and sodium thiosulfate solutions for use in the titrimetric analyses carried out during the $Na_2S-S-H_2S-H_2O$ equilibrium study were standardized against 0.5 N potassium dichromate solution which had been made up by weight. The pertinent reactions were as follows:

$$Cr_2O_7^{=} + 6S_2O_3^{=} + 14\ H^+ = 2\ Cr^{+++} + 3S_4O_6^{=} + 7H_2O \quad (A1)$$

(6 equivs.)

$$I_2 + 2S_2O_3^{=} = 2\ I^- + S_4O_6^{=} \quad (A2)$$

(2 equivs.)

The standard iodine and thiosulfate solutions as thus prepared ranged from 0.2 N to 0.4 N.

In determining the reducing equivalents in a sample of aqueous sulfide or polysulfide solution the sample first was pipetted slowly into a known excess of rapidly-swirled acidified iodine solution. The reactions taking place may be written:

$$S^{=} + I_2 = 1/8\ S_8 + 2\ I^- \quad (A3)$$

$$S_x^{=} + I_2 = x/8\ S_8 + 2\ I^- \quad (A4)$$

$$HS^- + I_2 = 1/8\ S_8 + 2\ I^- + H^+ \quad (A5)$$

$$H_2S + I_2 = 1/8\ S_8 + 2\ I^- + 2\ H^+ \quad (A6)$$

Thus all the sulfide or polysulfide species yielded two reducing equivalents per gm-mol or gm-ion. Any thiosulfate or sulfite impurities also were oxidized by the iodine. The thiosulfate reacted according to equation A2, while the sulfite was converted as follows:

$$SO_3^{=} + I_2 + H_2O = SO_4^{=} + 2\ I^{-} + 2\ H^{+} \qquad (A7)$$

The excess iodine remaining after the introduction of the unknown was back-titrated with standard sodium thiosulfate solution (equation A2), using starch indicator to mark the endpoint. The titrimetric equivalents in the sample then could be calculated by difference.

Several possible sources of error in performing this analysis had to be considered. If iodine solution were allowed to remain in a highly basic environment for any period of time, the following reaction could take place:

$$6\ OH^{-} + 3\ I_2 = 5\ I^{-} + IO_3^{-} + 3\ H_2O \qquad (A8)$$

If thiosulfate solution, on the other hand, were exposed to a low pH for any length of time, decomposition to sulfite and thence to sulfur dioxide could occur:

$$2\ H^{+} + S_2O_3^{=} = 1/8\ S_8 + SO_2 + H_2O \qquad (A9)$$

In either of these cases an incorrect sulfides analysis would be obtained. Reactions A8 and A9 could be avoided, however, by the use of the procedure just described.

Errors also could arise from hydrogen sulfide evolution upon the addition of the sulfide unknown to the acidified iodine solution, and from the entrainment of aqueous phase within the coagulating mass of pasty sulfur created by incipient raw oil formation upon polysulfide acidification and oxidation. The former could be prevented by mixing sufficiently rapidly that any hydrogen sulfide formed would be oxidized instantly; the latter could be minimized by back-titrating with thiosulfate as soon as possible, and by mechanically squeezing the solution out of the lump of pasty sulfur.

2. Determination of Sulfur in o-Xylene Solutions

The equilibrium xylene sulfur concentrations in the xylene experiments were determined gravimetrically. Two duplicate samples of the organic layer from such an experiment were transferred into tared weighing bottles, which immediately were reweighed to give the amounts of the samples in grams. The bottles then were unstoppered and placed on a hotplate in a strong draft to evaporate the solvent; the final drying was accomplished in an oven at 90°-100°C. When no further losses were evident upon reweighing, the per cent sulfur in solution then could be calculated from the weights of the sulfur residues. No corrections were attempted for the volatile water and hydrogen sulfide also dissolved in the xylene, but these two components by weight percentagewise were very small.

Since the sulfur being weighed was not identified as such, care had to be taken to exclude non-volatile foreign substances which would be calculated as sulfur; two such substances were aqueous phase included in the sample and stopcock grease dissolved in the xylene. The evaporation to dryness moreover had to be sufficient that no xylene remained, but melting of the sulfur which might lead to its volatilization at the same time had to be avoided. Finally, as was mentioned earlier, evidence of a slight chemical reaction between sulfur and the xylene was noted in certain instances, but this could be shown not to affect the sulfur activity-indicating property of the solvent.

3. Analysis of Hydrogen Sulfide - Nitrogen Mixtures

The gaseous hydrogen sulfide concentrations in those experiments in which nitrogen was used as a diluent were determined titrimetrically. During such an experiment gas samples were withdrawn from the inlet line at periodic intervals. A known excess of iodine solution then was added to each sample tube, taking care that no gas was lost in the process. The tube was shaken until all the hydrogen sulfide in the mixture had been oxidized (reaction A6). The liquid contents then was washed into a flask and was back-titrated with standard thiosulfate solution. From the equivalents of hydrogen sulfide thus determined and the known total number of mols contained in the sample tube the per cent hydrogen sulfide in the gas entering the reaction vessel could be calculated. It was found that if the proper needle valves were used to control the flow rates of the two gases, the mixture composition could be maintained essentially constant over a period of several hours.

Errors in this procedure could result from the absorption of iodine either by the sulfur precipitated during the hydrogen sulfide oxidation or by the Tygon tubing used to introduce the iodine solution into the sample tubes. These two effects combined to give an apparent assay of about 102 per cent in an analysis of the undiluted "purified" grade hydrogen sulfide as obtained from the cylinder. In the usual case, however, it was shown by analyses that the iodine remaining in the small amount of precipitated sulfur could be neglected. The absorption by the Tygon further could be minimized by using as short an exposure of flexible tubing as possible, and by presaturating the Tygon with iodine before use.

B. Purity of Sodium Sulfide

1. Overall Analysis of Sodium Sulfide

At periodic intervals the sodium sulfide crystals used in the $Na_2S-S-H_2S-H_2O$ equilibrium study were sampled and were titrated for total reducing equivalents per unit weight of sodium sulfide. These values, arranged in chronological order, are compared in Table AI to those obtained for the various polysulfide solutions prepared during the course of the work:

TABLE AI-a

Analyses of Sodium Sulfide and Polysulfide Solutions

Run	Temp. of Prep., °C	M of Na_2S_x	"x" of Na_2S_x	$\left(\frac{240.2\ (\text{Mols } Na_2S_x)}{\text{Gm } Na_2S \cdot 9H_2O}\right)$
-	25	1.94	1.0	0.983
E-9	25	1.94	4.60	0.970
E-12	25	1.95	3.56	0.972
-	25	1.94	4.82	0.972
E-14	25	1.93	4.59	0.970
E-15	25	1.93	2.53	0.967
E-16	25	1.93	4.60	0.968
-	25	1.92	1.0	0.965
E-19	75	1.78	3.06	0.969
E-20	25	1.92	3.59	0.963
E-21	75	1.79	3.06	0.970
-	25	1.92	1.0	0.965
E-23	75	1.84	2.04	0.960
E-24	75	1.83	2.04	0.963
-	75	1.91	1.0	0.967
-	75	1.92	1.0	0.974
E-25	75	1.82	2.05	0.948
E-26	75	1.68	4.59	0.957
E-27	75	1.72	4.57	0.979
E-29	75	1.73	3.61	0.955
E-30	75	1.71	3.66	0.940
E-31	75	1.93	1.0	0.977
E-32	75	1.75	3.10	0.951
E-33	75	1.77	3.08	0.960
E-34	75	1.71	4.61	0.969
E-35	75	1.77	3.08	0.961

TABLE AI-b

Analyses of Sodium Sulfide and Polysulfide Solutions

Run	Temp. of Prep., °C	$\underline{M}$ of Na_2S_x	"x" of Na_2S_x	$\left(\frac{240.2\ (\text{Mols}\ Na_2S_x)}{\text{Gm}\ Na_2S \cdot 9H_2O}\right)$
-	25	1.93	1.0	0.977
E-36	75	1.67	3.91	0.945
E-37	75	1.72	3.87	0.958
E-38	75	1.71	3.87	0.957
E-39	75	1.71	3.88	0.954
E-43	75	1.71	4.52	0.994
E-44	75	3.07	4.49	1.000
E-45	75	0.918	4.54	0.999
E-46	75	0.481	4.46	1.004
E-47	75	0.456	4.46	1.005
E-48	75	3.06	4.51	0.999
E-49	75	0.916	4.52	0.995
E-50	75	0.0564	3.76	1.04
E-51	75	0.490	4.44	1.014
-	75	0.473	4.25	1.004
E-52	75	0.491	4.36	1.018
E-53	75	0.152	4.22	1.033
E-54	75	0.149	4.34	1.041
E-55	75	0.0517	3.58	0.99
E-56	75	0.477	4.43	1.005
E-57	75	0.142	4.26	1.020
E-58	25	1.95	1.0	0.976
E-59	25	1.92	1.0	0.972
-	25	0.625	1.0	0.974
-	25	0.622	1.0	0.991
E-60	75	1.78	3.75	1.007
E-61	75	1.77	3.35	1.001
E-62	75	1.81	2.94	0.997
E-63	75	1.76	4.44	1.013
E-64	75	1.79	3.66	1.010
E-65	75	1.81	3.32	1.003
E-66	75	1.79	2.98	0.994
E-67	75	1.76	3.99	1.018
E-68	75	0.480	3.49	1.006
E-69	75	0.477	3.08	0.995
E-70	75	0.480	2.68	0.993
E-71	75	0.481	3.47	1.009
E-72	75	0.476	3.07	0.996
E-73	75	0.478	2.68	0.992

Since the hygroscopic sodium sulfide crystals tended to pick up more water than the nine molecules per mol indicated by the theoretical formula, most of the analyses listed in Table AI range lower than expected from the weights of sodium sulfide used. In some instances the reducing equivalents after polysulfide formation were higher than indicated by the adjacent monosulfide assays, while in other cases they were less. Since no conclusive trend with "x" was evident, it was assumed that during polysulfide preparation the formation of impurities such as thiosulfate and sulfite could be neglected.

The presence of either excess hydrosulfide or excess hydroxyl in the sodium sulfide crystals could be ascertained by comparing the initial reducing equivalents to the equivalents obtained upon hydrogen sulfide saturation to convert all species to the hydrosulfide. These data, corrected for physically-dissolved hydrogen sulfide, are summarized in Table AII:

TABLE AII

Analyses of Sodium Hydrosulfide Solutions

Initial Mols Na_2S	Temp. °C	Vol., liters	Final Equivs.	True Mols NaHS	$\left(\frac{\text{True NaHS}}{2(Na_2S)}\right)$
0.934	25	0.518	3.772	1.857	0.994
0.917	75	0.525	3.682	1.833	1.000
0.917	75	0.527	3.688	1.836	1.001
(0.305)	25	0.598	1.288	0.594	0.982 ?
(0.307)	75	0.601	1.230	0.602	0.982 ?

Notes: Parentheses () indicate values estimated from weights of sodium sulfide crystals used and chronologically adjacent assays of the sodium sulfide.

Examination of Table AII indicates that within the limits of experimental precision the corrected mols hydrosulfide in all cases was twice the original mols monosulfide. It therefore was assumed that in all monosulfide and polysulfide solutions prepared (without hydrogen sulfide addition or subtraction) from the sodium sulfide crystals available the hydrosulfide concentration equalled the hydroxyl concentration.

2. Thiosulfate and Sulfite Impurities in Sodium Sulfide

Since the overall titrimetric analyses for reducing equivalents could not indicate the true proportions of oxidation impurities (thiosulfate and sulfite) in the initial sodium sulfide, a separate procedure for determining these constituents had to be followed in order that corrections to the stoichiometric equilibrium data could be made where necessary. It was found most convenient to measure approximately the sum of thiosulfate plus sulfite by the sulfur precipitated upon controlled acidification of the monosulfide. Under the proper conditions the sulfite would be decomposed, yielding 3 gm-atoms sulfur per mol, according to the following equation:

$$SO_3^{=} + 2\ H^+ + 2\ H_2S = 3/8\ S_8 + 3\ H_2O \qquad (A10)$$

The decomposition of the thiosulfate according to equation A9 ultimately should yield 4 gm-atoms sulfur per mol:

$$S_2O_3^{=} + 2\ H^+ + 2\ H_2S = 4/8\ S_8 + 3\ H_2O \qquad (A11)$$

The acidification analysis for oxidation impurities was performed as follows: From 25 to 50 gm sodium sulfide crystals first was dissolved in about 300 ml water at room temperature, under a nitrogen purge. The monosulfide solution then was converted to the hydrosulfide by saturation with hydrogen sulfide. While continuing the hydrogen sulfide purge, excess hydrochloric acid slowly was added, with continual swirling. As soon as the equivalent amount of acid had been added, the solution would turn turbid to an extent depending on the amounts of thiosulfate and sulfite impurities. The hydrogen sulfide purge was continued at least 30 minutes after the acidification had been completed. The mixture then was digested overnight at elevated temperature in order to coagulate the suspended sulfur. The precipitated sulfur finally was filtered off, washed, dried, and weighed.

Employing the preceding procedure, it was found that the incremental sulfur obtained upon the addition of a known quantity of sodium sulfite was nearly the theoretical 3 gm-atoms per mol, provided that sulfur dioxide was not lost during the acidification. In the case of sodium thiosulfate the incremental sulfur yields averaged somewhat lower than predicted by equation A11, probably owing to the relatively slow rate at which the thiosulfuric acid ($H_2S_2O_3$) first formed decomposed. Since with the proper precautions to prevent oxidation no precipitated sulfur was obtained when sodium hydrosulfide prepared by the hydrogen sulfide saturation of initial sodium hydroxide was acidified, any sulfur precipitated upon the acidification of the sodium sulfide crystals could be assumed to represent only the oxidation impurities in the original material.

From the results of the acidification tests shown in Table AIII it was concluded that the sodium sulfide crystals as commercially available contained from 1.2 up to 2.8 mol per cent oxidation impurities, or from 3 to 7 times as much as the maximum amount of thiosulfate plus sulfite (0.10 weight per cent as SO_2) prescribed by the reagent specifications.

Attempts to obtain reagent-grade sodium sulfide which, as received, did conform to the maximum limits of impurities were unsuccessful. A procedure for purifying the crystals, however, was developed. It was found that by washing with water to remove the outer layers essentially all the oxidation impurities could be eliminated; the "washed" crystals analyzed well below the specification limits for thiosulfate plus sulfite. In practice, unfortunately, one-third to one-half or more of the original sodium sulfide was dissolved in this manner before the crystals could be separated from the washing liquor, even though the impurities probably could have been concentrated in a much smaller fraction. A more permanent solution to the problem of sodium sulfide oxidation would be complete air exclusion during preparation and packaging.

The acidification results for "washed" sodium sulfide also are given in Table AIII.

TABLE AIII

Sulfur Precipitation upon Sodium Sulfide Acidification

Test	Na_2S Source	Mols Na_2S or Equiv.	Mols $Na_2S_2O_3$ Added	Mols Na_2SO_3 Added	Total Gm S Pptd.	Atoms S/Mol $S_2O_3^=$ Added	Atoms S/Mol $SO_3^=$ Added	Net Atoms S/Mol Na_2S
A	old drum	0.104	0	0	0.32	-	-	0.096
B	old jar #2	0.104	0	0	0.15	-	-	0.045
C*	old jar #2	0.104	0	0	0.31	-	-	0.093
D	old jar #2	0.104	0.0040	0	0.51	2.8	-	(0.045)
E	old jar #2	0.104	0	0.0040	0.51	-	2.8	(0.045)
F	new drum (top)	0.210	0	0	0.25	-	-	0.037
G	new drum (bottom)	0.211	0	0	0.52	-	-	0.077
H	new jar #1	0.218	0	0	0.31	-	-	0.044
I	new jar #1	0.222	0.0202	0	1.68	2.1	-	(0.044)
J	from NaOH	0.258	0	0	0.001	-	-	0.000
K#	from NaOH	0.246	0	0	0.0001	-	-	0.000
L#	new jar #1	0.215	0	0	0.24	-	-	0.035
M { M_1	new #1 jar (washed)	0.120	0	0	0.01	-	-	0.003
M_2	new #1 jar (washings)	0.285	0	0	0.48	-	-	0.053
N$	new jar #1	0.210	0	0.0198	1.44	-	1.8	(0.044)
O { O_1	new #2 jar (washed)	0.214	0	0	0.01	-	-	0.001
O_2	new #2 jar (washings)	0.187	0	0	0.23	-	-	0.038
P+	new #1 jar (washed)	0.194	0	0	0.02	-	-	0.0030.003

Notes:
* Air purge during Na_2S solution preparation.
\# Extra precautions taken to prevent exposure to air.
$ Some SO_2 lost during acidification.
\+ About 1/3 removed by washing, washings not analyzed.

C. Sample Calculations

In order to illustrate the treatment of both xylene sulfur and precipitated sulfur, the calculations for run E-63 at 75°C. (an experiment utilized in deriving the "recommended" equilibrium constants and ionic distributions) were chosen for presentation:

Data for Na_2S_x + H_2S Equilibrium Run E-63:

(February 13, 1958)

1. Raw Data

Initial Charge

289.3 gm $Na_2S.9H_2O$, reagent, washed
135.6 gm S, USP pptd., dried
402.1 gm H_2O, distilled, boiled

Sodium Polysulfide Preparation

90 min. under N_2 atmosphere
Final temperature = 74°C.
Solution volume = 695 ml
Water evaporated = 4.6 gm
Unreacted sulfur = about 1.0 gm (not separated)

Sodium Polysulfide Analysis:

(1/10 aliquots of a 25 ml sample)

	A	B
Ml 0.336 $\underline{N}$ I_2 soln	50.0	50.0
Equivs. I_2	0.01680	0.01680
Ml 0.2395 $\underline{N}$ $\underline{S}_2O_3^=$ soln	33.6	33.45+
Equivs. $S_2O_3^=$	0.00804	0.00801
Equivs. sulfides	0.00876	0.00879

$$\text{Equivs. } Na_2S_x = (0.00878)(10)\left(\frac{695}{25}\right) = 2.440 \text{ equivs.}$$

Mols Na_2S_x = 1.220 gm-mols

$\underline{M}$ = 1.76 mols/liter

"x" = 4.44

Hydrogen Sulfide Saturation

1.178 gm-mols Na_2S_x to H_2S reaction (n_1 = 2.356 equivs.)

Added 100 ml o-xylene

150 min. saturation with "purified" grade H_2S

Final temperature = 75.0°C

Final pressure = 752 mm Hg atmospheric + 2 cm dibutyl phthalate = 754 mm Hg

Aqueous soln volume = 673 ml

Xylene soln volume = 104 ml

Precipitated sulfur = 4.3 gm

Final Aqueous Solution Analysis

(1/10 aliquots of a 25 ml sample)

	A	B
Ml 0.336 N I_2 soln	50.0	50.0
Equivs. I_2	0.01680	0.01680
Ml 0.2395 N $S_2O_3^=$ soln	26.75+	26.7
Equivs. $S_2O_3^=$ soln	0.00640	0.00639
Equivs. sulfides	0.01040	0.01041

$$\text{Equivs. Final Soln} = (0.01041)(10)\left(\frac{673}{25}\right) = n_2 = 2.801 \text{ equiv}$$

Xylene Analysis

(25 ml samples)

	A		B	
C	42.7208	gm	42.2777	gm
C + Soln	64.382	"	64.043	"
C + S	44.8840	"	44.3237	"
Soln	21.661	"	21.765	"
S	2.1632	"	2.0460	"
Wt. % S	9.98		9.40	

Avg. Wt. % S = 9.69 %*

* Some uncertainty owing to the tendency of sulfur to precipitate out of saturated xylene solution upon the slightest cooling.

Polysulfide Sulfur in Final Solution

Total sulfur charged = 135.6 gm

Polysulfide sulfur removed in Na_2S_x sample $= \frac{25}{695}(135.6-1.0)$

$= 4.8$ gm

Polysulfide sulfur in xylene layer $= \frac{104}{50}(2.1632 + 2.0460)$

$= 8.8$ gm

Final precipitated sulfur = 4.3 gm

Polysulfide Sulfur in Final Soln = 117.7 gm

= 3.666 gm-atoms

2. Gross Ionic Composition

Hydrogen Sulfide Partial Pressure

"Total ionic concentration" $= \mu' \cong \frac{2.356+1.401}{0.673}$

$= 5.58$ mols/liter

Water partial pressure $= p_{H_2O} = 289-3.6(5.58)$

$= 269$ mm Hg

Xylene partial pressure $= p_{Xyl} = 79-0.3(9.69)$

$= 76$ mm Hg

Hydrogen Sulfide Partial Pressure $= p_{H_2S} = 754-269-76$

$= 409$ mm Hg

$f_{H_2S} = 0.538$ atm

Hydrogen Sulfide in Final Solution

Hydrogen sulfide concentration $= [H_2S]$

$= (0.04)(0.538)(e^{-(0.07)(5.58)}) = 0.0146$ gm-mols/liter

Hydrogen sulfide in final solution $= (0.0146)(0.673)$

$= 0.0097$ gm-mols

Corrected Final Titration $= n_{2_c} = 2.801-2(0.0097)$

$= 2.782$ equivs.

Ionic Proportions

Mols Sodium Ion = $Na^+ = n_1$ = 2.356 gm-mols

Mols Polysulfide Ion = $S_x^= = n_1 - 0.5\ n_{2_c}$

= 2.356-0.5(2.782) = 0.956 gm-mols

Mols Hydrosulfide Ion = $HS^- = n_{2_c} - n_1$

= 2.782-2.356 = 0.426 gm-mols

Ionic Molarities

Sodium Molarity = $\frac{Na^+}{V} = \frac{2.356}{0.673}$ = 3.50 gm-mols/liter

Polysulfide Molarity = $\frac{S_x^=}{V} = \frac{0.965}{0.673}$ = 1.435 gm-mols/liter

Hydrosulfide Molarity = $\frac{HS^-}{V} = \frac{0.426}{0.673}$ = 0.634 gm-mols/liter

Polysulfide Sulfur Molarity = $\frac{PSS}{V} = \frac{3.666}{0.673}$

= 5.45 gm-atoms/liter

Ionic Molalities

Since the final solution in run E-63 was not weighed, its density had to be estimated from the correlation in Figure 11:

$$\frac{PSS}{Na^+} = \frac{3.666}{2.356} = 1.559$$

Estimated density = ρ = 1.172 gm/ml

Final solution weight = (1.172)(0.673) = 789 gm

Weight sodium ion = 2.356(23.0) = 54.1 gm

Weight equiv. monosulfide ion = 0.965(32.1)

= 31.0 gm

Weight polysulfide sulfur = 3.666(32.1)= 117.7 gm

(or weight polysulfide ion = 148.7 gm)

Weight hydrosulfide ion = 0.426(33.1) = 14.1 gm

Weight dissolved hydrogen sulfide = 0.010(34.1
= 0.3 gm

Total weight dissolved substances = 217.2 gm

Weight water in solution = 789-217.2 = 572 gm

Sodium Molality = $[\mathrm{Na}^+] = \frac{2.356}{0.572} = 4.11$

Polysulfide Molality = $[\mathrm{S}_x^{=}] = \frac{0.965}{0.572} = 1.688$

Hydrosulfide Molality = $[\mathrm{HS}^-] = \frac{0.426}{0.572} = 0.745$

Polysulfide Sulfur Molality = $[\mathrm{PSS}] = \frac{3.666}{0.572} = 6.40$

3. Derived Numbers

$$\text{"A"} = \frac{\mathrm{PSS}}{\mathrm{Na}^+} = \frac{3.666}{2.356} = 1.559$$

$$\text{"B"} = \frac{\mathrm{S}_x^{=}}{\mathrm{Na}^+} = \frac{0.965}{2.356} = 0.410$$

$$A/B = \frac{\mathrm{PSS}}{\mathrm{S}_x^{=}} = \frac{3.666}{0.965} = 3.80$$

$$\text{"X"} = \frac{[\mathrm{S}_x^{=}]\, f_{H_2S}}{[\mathrm{HS}^-]^2} = \frac{(1.688)(0.538)}{(0.745)^2} = 1.638$$

$$\text{"Y"} = \frac{[\mathrm{PSS}]\, f_{H_2S}}{[\mathrm{HS}^-]^2} = \frac{(6.40)(0.538)}{(0.745)^2} = 6.20$$

D. Error Analysis

For purposes of estimating the experimental measurement errors in the Na_2S-S-H_2S-H_2O equilibrium study (for comparison with the actual scatter of the data), "average" rather than "maximum" errors were evaluated. In view of the approximations required, no attempt was made to treat separately random errors and possible systematic errors. The average error in a calculated sum or difference was assumed to be the root mean square of the absolute average errors of the components, while the average error in a computed product or quotient was taken to be the root mean square of the relative average errors of the components.

Based largely on the approximate values encountered in the experiments at 4.0 m sodium ion concentration (which were employed in the derivation of equilibrium constants and polysulfide ionic distributions), the errors in the experimental measurements indicated in Table AIV were estimated. The propagation of these errors through the calculation of results then could be followed.

I. Sodium Polysulfide Analysis

A. Equivs. $I_2 = V \times \underline{N} \cong (0.050)(0.34) = 0.01700$

Error in $V = 0.02\%$
Error in $\underline{N} = 0.1\%$

Error in Equivs. $I_2 = 0.10\% = 0.000017$

TABLE AIV

Estimated Experimental Measurement Errors

Quantity Measured or Estimated	Approximate Value	Estimated Average Error
Weight initial sulfur	134 gm	0.1 gm
	60 gm	0.1 gm
Weight precipitated sulfur	13 gm	0.1 gm
	0 gm	-
Volume Na_2S_x solution	700 ml	1.0 ml
Volume final solution	675 ml	1.0 ml
Density of sulfur included in volume	2.0	10%
Pipetted samples	50 ml	0.01 ml
	25 ml	0.005 ml
	10 ml	0.002 ml
Dilution in volumetric flask	1000 ml	0.2 ml
	250 ml	0.05 ml
$\underline{N}$ of I_2 solution	0.34	0.1%
	0.068	0.1%
$\underline{N}$ of $S_2O_3^=$ solution	0.24	0.1%
	0.048	0.1%
Volumes dispensed by burette	35 ml	0.05 ml
	25 ml	0.05 ml
	5 ml	0.05 ml
Unreacted sulfur in Na_2S_x solution	0.5 gm	0.5 gm
	0 gm	-
Atmospheric pressure	760 mm Hg	0.5 mm Hg
Manometer pressure difference	2 mm Hg	0.5 mm Hg
Water partial pressure	270 mm Hg	3.0 mm Hg
Xylene partial pressure	78 mm Hg	0.5 mm Hg
Temperature	75°C	0.2°C
	25°C	0.2°C
Volume xylene layer	100 ml	1.0 ml
Weight xylene sample	20 gm	0.002 gm
Weight sulfur residue	2 gm	0.0002 gm
	0.03 gm	0.0002 gm
pH	7.5 to 8.5	0.05 pH unit
Gas Sample Volume	250 ml	0.5 ml
Physically-dissolved H_2S	0.01 gm-mol	10%
Final solution density	1.150 gm/ml	0.005 gm/ml

B. Equivs. $S_2O_3^=$ = V x $\underline{N}$ ≅ (0.035)(0.24) = 0.00840

Error in V = 0.14%
Error in $\underline{N}$ = 0.1%

Error in Equivs. $S_2O_3^=$ = 0.17% = 0.000014

C. Equivs. Sulfides ≅ 0.01700 – 0.00840 = 0.00860

Error in Equivs. Sulfides = 0.000022 = 0.26%

D. Total Equivs. Sulfides ≅ $\left(\frac{250}{25}\right)\left(\frac{700}{25}\right)$(0.00860) = 2.40

Error in 250 ml = 0.02%
Error in 25 ml = 0.02%
Error in 700 ml = 0.14%
Error in 25 ml = 0.02%
Error in 0.00860 = (0.26%)/$\sqrt{2}$ (since two duplicate samples)
= 0.18%

Error in Total Na_2S_x Equivs. = 0.23%

II. Final Aqueous Solution Analysis

A. Equivs. I_2 = V x $\underline{N}$ ≅ (0.050)(0.34) = 0.01700

Error in Equivs. I_2 = 0.10% = 0.000017

B. Equivs. $S_2O_3^=$ = V x $\underline{N}$

Case 1. ≅ (0.025)(0.24) = 0.00600

Error in V = 0.20%
Error in $\underline{N}$ = 0.1%

Error in Equivs. $S_2O_3^=$ = 0.22% = 0.000013

Case 2. ≅ (0.005)(0.24) = 0.00120

Error in V = 1.0%
Error in $\underline{N}$ = 0.1%

Error in Equivs. $S_2O_3^=$ = 1.01% = 0.000012

C. Equivs. Sulfides

Case 1. $\cong$ 0.01700 − 0.00600 = 0.01100

Error in Equivs. Sulfides = 0.000021 = 0.19%

Case 2. $\cong$ 0.01700 − 0.00120 = 0.01580

Error in Equivs. Sulfides = 0.000021 = 0.13%

D. Volume Final Solution = $V_{app.} - \left(\frac{Gm\ S}{\rho}\right)$

Case 1. $\cong 681.5 - \frac{13}{2.0} = 675$ ml

Error in Volume = 1.2 ml = 0.18%

Case 2. $\cong$ 675 ml

Error in Volume = 1.0 ml = 0.15%

E. Total Equivs. Sulfides = $\left(\frac{250}{25}\right)\left(\frac{675}{25}\right)$ (Equivs. Sulfides)

Case 1. $\cong$ 2.90

Error in 250 ml = 0.02%
Error in 25 ml = 0.02%
Error in 675 ml = 0.18%
Error in 25 ml = 0.02%
Error in 0.01100 = $(0.19\%)/\sqrt{2}$ (since two duplicate samples) = 0.14%

Error in total final equivs. = 0.23%

Case 2. $\cong$ 4.20

Error in 250 ml = 0.02%
Error in 25 ml = 0.02%
Error in 675 ml = 0.15%
Error in 25 ml = 0.02%
Error in 0.01580 = $(0.13\%)/\sqrt{2}$ (since two duplicate samples) = 0.09%

Error in Total Final Equivs. = 0.18%

III. Xylene Analysis

A. Weight Per Cent Sulfur = $\left(\frac{\text{Gm S}}{\text{Gm Soln}}\right) \times 100$

Case a. $\cong$ 2/20 x 100 = 10%

Error in % S = (0.014%)/$\sqrt{2}$ (2 samples) = 0.01%

Case b. $\cong$ 0.03/20 x 100 = 0.15%

Error in %S = (0.67%)/$\sqrt{2}$ (2 samples) = 0.47%

B. Sulfur in Xylene Layer = (Gm S) x $\left(\frac{100 \text{ ml}}{25 \text{ ml}}\right)$

Case a. $\cong$ 8 gm

Error in Gm S = 0.01%
Error in 100 ml = 1.0%
Error in 25 ml = 0.02%

Error in Sulfur in Xylene Layer = 1.00% = 0.08 gm

Case b. Sulfur in xylene layer not significant.

IV. Polysulfide Sulfur in Final Solution

(PSS) = (Initial S) - (S in Na_2S_x Sample) - (Xylene S) - (Pptd.S)

A. Sulfur in Na_2S_x Sample = $\left(\frac{25}{700}\right)$ x [(Initial S)- (Unreacted S)]

Case 1. $\cong$ $\left(\frac{25}{700}\right)$ x (134 - 0.5) = 4.8 gm S

Error in 25 ml = 0.02%
Error in 700 ml = 0.14%
Error in 133.5 gm = 0.38%

Error in S in Na_2S_x Sample = 0.41% = 0.019 gm

Case 2. $\cong$ $\left(\frac{25}{700}\right)$ x 60 = 2.1 gm S

Error in 25 ml = 0.02%
Error in 700 ml = 0.14%
Error in 60 gm = 0.17%

Error in S in Na_2S_x Sample = 0.22% = 0.0046 gm

B. Polysulfide Sulfur in Final Solution

Case 1. $\cong$ 134 - 4.8 - 8 - 13 = 115 gm = 3.60 gm-atoms

Error in 134 gm = 0.1 gm
Error in 4.8 gm = 0.02 gm
Error in 8 gm = 0.08 gm
Error in 13 gm = 0.1 gm

Error in PSS in Final Soln = 0.16 gm = 0.14%

Case 2. $\cong$ 60 − 2.1 − 0 − 0 = 58 gm = 1.80 gm-atoms

Error in 60 gm = 0.1 gm
Error in 2.1 gm = 0.005 gm

Error in PSS in Final Soln = 0.10 gm = 0.17%

V. Hydrogen Sulfide Partial Pressure

$$p_{H_2S} = (\pi + \Delta p) - p_{H_2O} - p_{Xyl}$$

$$\cong (760 + 2) - 270 - 78 = 414 \text{ mm Hg} \cong 0.55 \text{ atm}$$

Error in 760 mm Hg = 0.5 mm Hg
Error in 2 mm Hg = 0.5 mm Hg
Error in 270 mm Hg = 3.0 mm Hg
Error in 78 mm Hg = 0.5 mm Hg

Error in H_2S Partial Pressure = 3.1 mm Hg = 0.75%

VI. Ionic Species

A. Corrected Final Titration = $n_2 - 2\,(H_2S)_{aq.}$

Case 1. $\cong$ 2.90 − 2(0.01) = 2.88 equivs.

Error in 2.90 = 0.0067
Error in 0.02 = 0.0020

Error in n_{2_c} = 0.0070 = 0.24%

Case 2. $\cong$ 4.20 − 2(0.01) = 4.18 equivs.

Error in 4.20 = 0.0076
Error in 0.02 = 0.0020

Error in n_{2_c} = 0.0079 = 0.19%

B. Sodium Ion = $n_1 \cong$ 2.30 gm-mols

Error in Na^+ = 0.23% = 0.0053

C.

C. Polysulfide Ion = $n_1 - 0.5\, n_{2_c}$

Case 1. $\cong 2.30 - 0.5\,(2.88) = 0.86$ gm-mols

Error in 2.30 = 0.0053
Error in 1.44 = 0.0035

Error in $S_x^{=}$ = 0.0064 = 0.74%

Case 2. $\cong 2.30 - 0.5(4.18) = 0.21$ gm-mols

Error in 2.30 = 0.0053
Error in 2.09 = 0.0040

Error in $S_x^{=}$ = 0.0066 = 3.05%

D. Hydrosulfide Ion = $n_{2_c} - n_1$

Case 1. $\cong 2.88 - 2.30 = 0.58$ gm-mols

Error in 2.88 = 0.0070
Error in 2.30 = 0.0053

Error in HS^- = 0.0088 = 1.52%

Case 2. $\cong 4.18 - 2.30 = 1.88$ gm-mols

Error in 4.18 = 0.0079
Error in 2.30 = 0.0053

Error in HS^- = 0.0095 = 0.51%

E. Molalities

(Assume 0.44% error in gm H_2O in solution.)

1. $[Na^+] = \left(\frac{Na^+}{Gm\ H_2O}\right) \times 1000 \cong \left(\frac{2.30}{0.575}\right) \cong 4.0\ \underline{m}$

Error in $[Na^+]$ = 0.50% = 0.020

2. $[S_x^{=}] = \left(\frac{S_x^{=}}{Gm\ H_2O}\right) \times 1000$

Case 1. $\cong \left(\frac{0.86}{0.575}\right) \cong 1.50\ \underline{m}$

Error in $[S_x^{=}]$ = 0.86% = 0.013

Case 2. $\cong \left(\frac{0.21}{0.575}\right) \cong 0.40\ \underline{m}$

Error in $\left[S_x^{=}\right] = 3.08\% = 0.012$

3. $\left[HS^{-}\right] = \left(\frac{HS^{-}}{Gm\ H_2O}\right) \times 1000$

Case 1. $\cong \left(\frac{0.58}{0.575}\right) \cong 1.00\ \underline{m}$

Error in $\left[HS^{-}\right] = 1.58\% = 0.016$

Case 2. $\cong \left(\frac{1.88}{0.575}\right) \cong 3.30\ \underline{m}$

Error in $\left[HS^{-}\right] = 0.67\% = 0.022$

4. $\left[PSS\right] = \left(\frac{PSS}{Gm\ H_2O}\right) \times 1000$

Case 1. $\cong \left(\frac{3.60}{0.575}\right) \cong 6.20\ \underline{m}$

Error in $\left[PSS\right] = 0.46\% = 0.028$

Case 2. $\cong \left(\frac{1.80}{0.575}\right) \cong 3.10\ \underline{m}$

Error in $\left[PSS\right] = 0.47\% = 0.015$

VII. Derived Numbers

A. "A" $= \frac{PSS}{Na^{+}}$

Case 1. $\cong \frac{3.60}{2.30} \cong 1.60$

Error in "A" $= 0.27\% = 0.0043$

Case 2. $\cong \frac{1.80}{2.30} \cong 0.80$

Error in "A" $= 0.29\% = 0.0022$

B. "B" $= \frac{S_x^{=}}{Na^{+}}$

Case 1. $\cong \frac{0.86}{2.30} \cong 0.40$

Error in "B" $= 0.78\% = 0.0030$

Case 2. $\cong \frac{0.21}{2.30} \cong 0.10$

Error in "B" = 3.06% = 0.0031

C. $A/B = PSS/S_x^{=} = Y/X$

Case 1. $\cong \frac{3.60}{0.86}$

Error in A/B = 0.75%

Case 2. $\cong \frac{1.80}{0.21}$ (?)

Error in A/B = 3.06%

D. $"X" = \frac{[S_x^{=}]\, f_{H_2S}}{[HS^-]^2}$

Case 1. $\cong \frac{0.86 \times 0.55 \times 0.575}{(0.58)^2}$

Error in 0.86 = 0.74%
Error in 0.55 = 0.75%
Error in 0.575 = 0.44%
Error in 0.58 = 1.52%
Error in 0.58 = 1.52%

Error in "X" = 2.4%

Case 2. $\cong \frac{0.21 \times 0.55 \times 0.575}{(1.88)^2}$

Error in 0.21 = 3.05%
Error in 0.55 = 0.75%
Error in 0.575 = 0.44%
Error in 1.88 = 0.51%
Error in 1.88 = 0.51%

Error in "X" = 3.3%

E. $"Y" = \frac{[PSS]\, f_{H_2S}}{[HS^-]^2}$

Case 1. $\cong \frac{3.60 \times 0.55 \times 0.575}{(0.58)^2}$

Error in 3.60 = 0.14%
Error in 0.55 = 0.75%
Error in 0.575 = 0.44%
Error in 0.58 = 1.52%
Error in 0.58 = 1.52%

Error in "Y = 2.3%

Case 2. $\cong \dfrac{1.80 \times 0.55 \times 0.575}{(1.88)^2}$

Error in 1.80 = 0.17%
Error in 0.55 = 0.75%
Error in 0.575 = 0.44%
Error in 1.88 = 0.51%
Error in 1.88 = 0.51%

Error in "Y" = 1.1%

VIII. Hydrogen Sulfide Partial Pressure in Nitrogen Diluent Runs

$$\% \; H_2S = \frac{\text{Mols } H_2S}{\text{Mols sample}} \times 100$$

A. Mols Sample $= \dfrac{P\,V}{R\,T} \cong \dfrac{(760)(250)}{(62,400)(298)} \cong 0.0100$ gm-mols

Error in P = 0.07%
Error in V = 0.20%
Error in T = 0.07%

Error in Mols Sample = 0.22%

B. Mols H_2S in Sample = 0.5 (Equivs. H_2S)

1. Equivs. $I_2 \cong (0.050)(0.068) = 0.00340$

Error in V = 0.02%
Error in N = 0.1%

Error in Equivs. I_2 = 0.10% = 0.0000035

2. Equivs. $S_2O_3^=$ $\cong (0.040)(0.048) = 0.00190$

Error in V = 0.13%
Error in N = 0.1%

Error in Equivs. $S_2O_3^=$ = 0.16% = 0.0000031

3. Equivs. $H_2S \cong 0.00340 - 0.00190 = 0.00150$

Error in Equivs. H_2S = 0.0000047 = 0.31%

(no duplicate titration)

C. Per Cent $H_2S \cong \frac{0.5\ (0.00150)}{0.0100} \times 100 = 7.50\%$

Error in % H_2S = 0.38%

D. H_2S Partial Pressure

From V and VIII-C, Error in p_{H_2S} = 0.84%

IX. pH Determination

Error in pH = 0.05 pH unit

Error in $a_{H+} \cong 11\%$

E. Raw Oil Continuous Synthesis

During the course of the present thesis a preliminary investigation was made concerning the effect of mixing rate on the production of raw hydrogen persulfide in a continuous system. The qualitative mixing rate correlations of Conway (15) and the quantitative results of Haritatos (34), both obtained using batch systems, indicated that the polysulfide acidification reaction should be studied under conditions where concentration and mixing variables did not vary with time, i.e., in a flow system. The adverse effect at high stirring speeds of back-mixing of the raw oil product with the incoming polysulfide solution, as observed by Haritatos (see Figure 3 in the Introduction), moreover suggested that a flow system should be designed for as efficient as possible continuous removal of the raw oil from the scene of reaction.

A scheme employing turbulent mixing between concentric jets was considered. Owing to problems such as the removal of the heat of reaction, the continuous separation of the product, and the recycle of the large excess of acid required, this system, however, was not selected for use in the preliminary study. Chosen instead was the mixing situation previously employed by Haritatos; the baffled cylindrical vessel, stirred by a single-blade impeller.

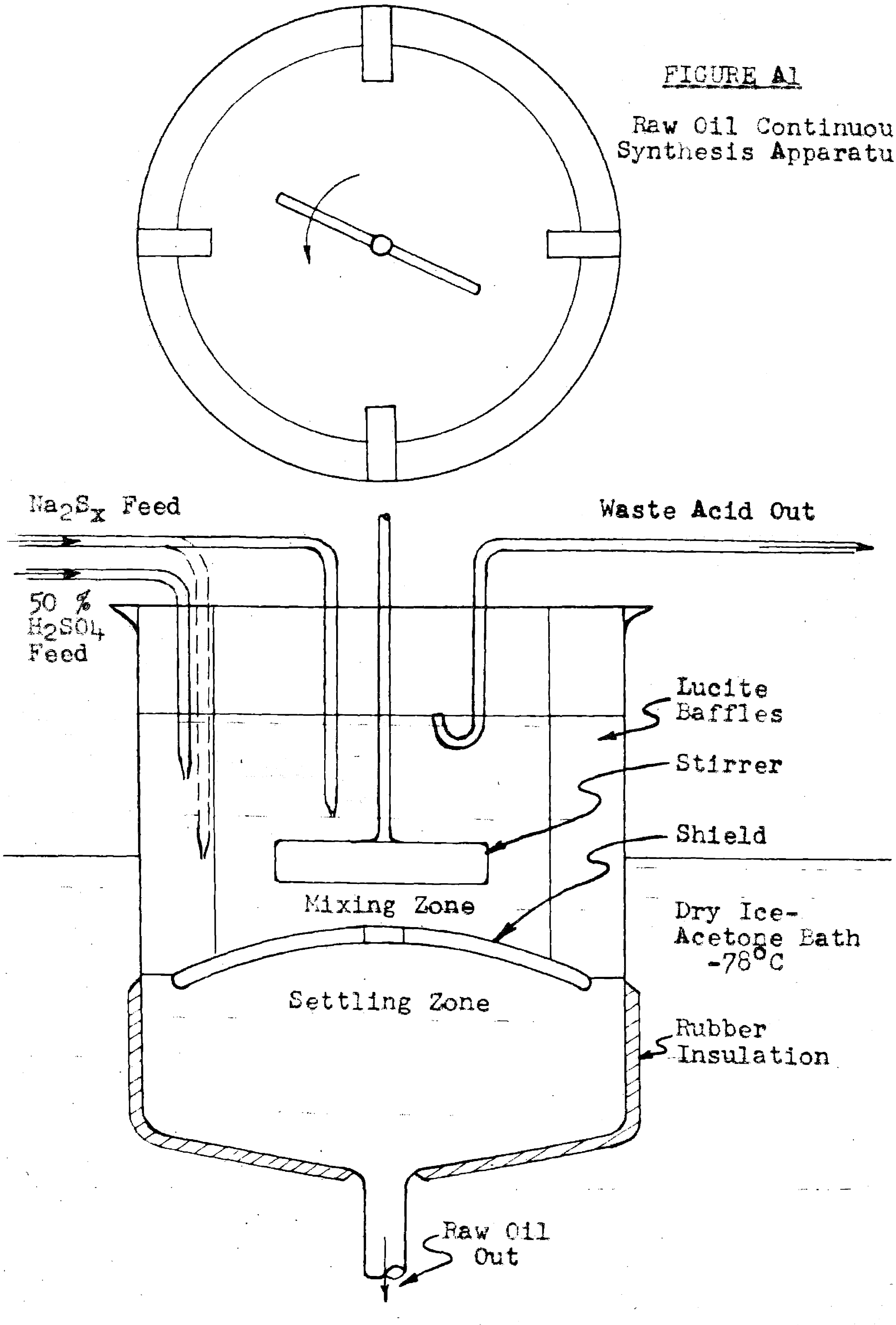
1. Apparatus and Procedure

The apparatus used in the continuous synthesis experiments of Laplane (42) and the present thesis is shown in Figure A1. The reaction vessel consisted of a 1500-ml beaker fitted with a bottom outlet tube and divided by a horizontal shield into an upper mixing section and a lower settling section, as indicated in the drawing. The four vertical baffles and the impeller were scaled up roughly from the dimensions used by Haritatos (34). In the bottom section, which was insulated to prevent supercooling and solid phase formation, the suspended raw oil droplets formed during the reaction coagulated and separated continuously during the course of a run. Even with this scheme as much as 50 per cent of the persulfide oil failed to settle out at some of the higher stirring speeds used. The exact dimensions of the Figure A1 apparatus are given in the thesis of Laplane.

The acid and sodium polysulfide feed streams were

FIGURE A1

Raw Oil Continuous Synthesis Apparatus



controlled by hand stopcocks, were metered by a capilliary flowmeter and a rotameter, respectively, and were introduced as jets beneath the liquid surface. The polysulfide nozzle diameter was approximately 1/16-inch. In two experiments the polysulfide stream was directed into the sweep of the impeller, as indicated by the solid arrow in Figure A1, rather than to the side.

The outlet aqueous phase plus any raw oil which did not separate were removed under a slight vacuum, maintaining a constant liquid level in the reaction vessel. The raw oil product which did settle out could be drained periodically or continuously via the bottom outlet. Since the system was open to the air, any gaseous hydrogen sulfide formed escaped into the hood as rapidly as it was evolved. The small amount of free sulfur liberated by decomposition for the most part remained suspended in the aqueous phase.

The reaction temperature was controlled by adjusting the level of an external acetone - dry ice bath. The stirring rate for each experiment was set using a motor with a calibrated variable-speed transmission having a range up to 1200 rpm. The agitation was so violent at this highest stirring speed that a plastic cover had to be placed over the reaction vessel to prevent splashing from the free liquid surface.

With the exception of the distribution of suspended raw oil essentially all the concentration and mixing variables could be fixed at their chosen steady-state values at the beginning of a run. Since the raw oil "concentration" was considered important in determining the extent of back-mixing, it still was felt necessary to take data under conditions of constant raw oil distribution. Accordingly, in most experiments the raw oil "concentration", initially zero, was allowed to build up during a "start-up" period of about one hour, followed by a test period of somewhat shorter duration during which time it was hoped that true "steady-state" conditions prevailed. From measurements of the suspended hydrogen persulfide in incremental waste acid samples it later was shown that such was not always the case.

At the conclusion of an experiment raw oil had been collected as follows: (a) drained from the reaction vessel during the start-up period, (b) suspended in the waste acid from the start-up period, (c) drained from the reaction vessel during the "steady-state" period, (d) suspended in the waste acid from the "steady-state" period, and (e) drained from the reaction vessel after the run. If a true steady-state was attained, the increments (c) and (d) could be combined to give the test period yield, while the remaining three lots of raw oil had to correspond to the polysulfide fed during the start-up period. The raw oil products were analyzed gravimetrically using the quartz powder technique described by Conway (15) and others, yielding the total hydrogen sulfide content from the difference between the initial sample weight and the weight of decomposition sulfur. No attempts were made to correct these analyses for physically-dissolved hydrogen sulfide and sulfur.

All experiments were carried out using "technical" grade sulfuric acid and sodium polysulfide prepared from "purified" grade sodium sulfide. The polysulfide solution fed in all runs was approximately 1.95 M in $Na_2S_{4.6}$ (nominal composition 2 M $Na_2S_{4.5}$), while the vessel acid concentration was held constant throughout at 25 weight per cent free H_2SO_4 (in excess of that combined as $NaHSO_4$). The temperature in every case was maintained at 0°C ± 0.5°. The system was operated with approximately 1100-1150 ml liquid holdup in the reaction vessel. In all except one run the polysulfide solution was introduced at a rate of about 15 ml per minute. The feed rate of 50 per cent sulfuric acid thus was dictated by the requirement that the vessel acid concentration remain constant.

The primary variable in the raw oil continuous synthesis study was the stirring speed. In the experiments which were made the rate of stirring was varied from 300 rpm up to 1200 rpm, the maximum obtainable with the equipment at hand.

2. Results

The conditions and the results for the 18 raw oil continuous synthesis experiments which were performed are presented in Table AV. Runs C-1, C-2, and C-3 were preliminary experiments which proved unsatisfactory and hence invalid. Runs C-1 through C-13 have been reported previously in the thesis of Laplane (42), but the yields listed in Table AV have been corrected, based on the assumed analyses of the sodium polysulfide fed, rather than on the weights of initial sodium sulfide crystals used. It was found that the yields and compositions obtained during the test periods were not significantly different from those for the corresponding start-up periods. In addition, as was mentioned, the amounts of suspended raw oil in some experiments were not constant with time during the supposed "steady-state" periods. For these two reasons only the total yields and average compositions for start-up period plus steady-state period are reported in Table AV.

TABLE AV

Raw Oil Continuous Synthesis Results
(data from Laplane (42) and present thesis)

All runs using ~1.95 M $Na_2S_{4.6}$ fed at 15 ml/min. except as noted, 25% free H_2SO_4, temperature 0°C, volume 1100-1150 ml.

Run	Stirring Rate, rpm	Total Mols Na_2S_x Fed	Time min.	Total Gm Raw Oil	Total Mol Yield %	"n" of H_2S_n	Final Oil Conc. gm/l
C-4	500	(2.524)	83	306	60.3	6.21	30.0
C-5	300	(2.358)	84	285	55.0	6.78	32.7
C-6	700	(2.580)	83	311	60.3	6.16	23.6
C-7	900	(2.497)	75	303	62.2	6.02	40.9
C-8	500	?	77	278	52.4 ?	6.68	19.1
C-9	500	(2.358)	84	300	62.1	6.37	19.8
C-10	700	(2.456)	84	297	60.6	6.17	26.4
C-11	1200	(2.244)	72	277	68.0	5.59	49.1
C-12*	700	(2.570)	26.5	305	56.7	6.46	40.9
C-13	1200	(2.540)	81	311	62.7	6.04	54.5
C-14	1200	(2.650)	93	314.4	61.7	5.93	69.0
C-15	1200	(2.636)	90	314.8	62.6	5.90	74.9
C-16	1200	(0.352)	9	40	58.9	5.97	33.6
C-17	1200	(0.287)	10	33.6	61.4	5.90	27.5
C-18#	1200	(0.349)	10	39.2	64.4	5.36	32.4
C-19	1200	(2.540)	90	325.5	70.3	5.63	56.7
C-20δ	1200	2.600	85	332.6	68.4	5.76	69.4
C-21δ	1200	2.543	90	327.5	68.5	5.78	50.8

Notes: Parentheses () indicate values estimated assuming 97 % Na_2S assay.

? Leak in polysulfide feed line, run C-8.

* Polysulfide feed rate 53.3 ml/min., run C-12.

H_2S purge to reaction mixture before and during run C-18.

δ New feed nozzle position (see Figure A1).

3. Discussion of Results

The total mol yields for the raw oil continuous synthesis are plotted versus stirring speed in Figure 4 (taken from the Introduction). In spite of the scatter of the data it may be seen that mol yield apparently continued to increase as high as stirring speed could be taken. The absence of any maximum in yield such as was observed by Haritatos (34) might be taken as evidence that back-mixing did not play so important a role in the continuous synthesis. In Figure A2 the values of "n", the average sulfur subscript of the persulfide, similarly are plotted against stirring rate. As might be anticipated from the results of previous batch studies, the increase in yield with mixing was accompanied by a decrease in "n". The sulfur yields based on polysulfide sulfur (not shown) indeed remained essentially constant. From the one point at 53.3 ml/min. polysulfide feed rate it might be concluded that at a given stirring speed the true mixing rate dropped as the rate of polysulfide introduction was increased.

A comparison of Figures 4 and A2 with the results of Conway (15) obtained using sulfuric acid in a batch system (Figures 1 and 2) shows that higher mol yields and lower "n" values were attained in the continuous synthesis than under the best conditions tested batchwise. At 1200 rpm stirring speed mol yields as high as 70 per cent and

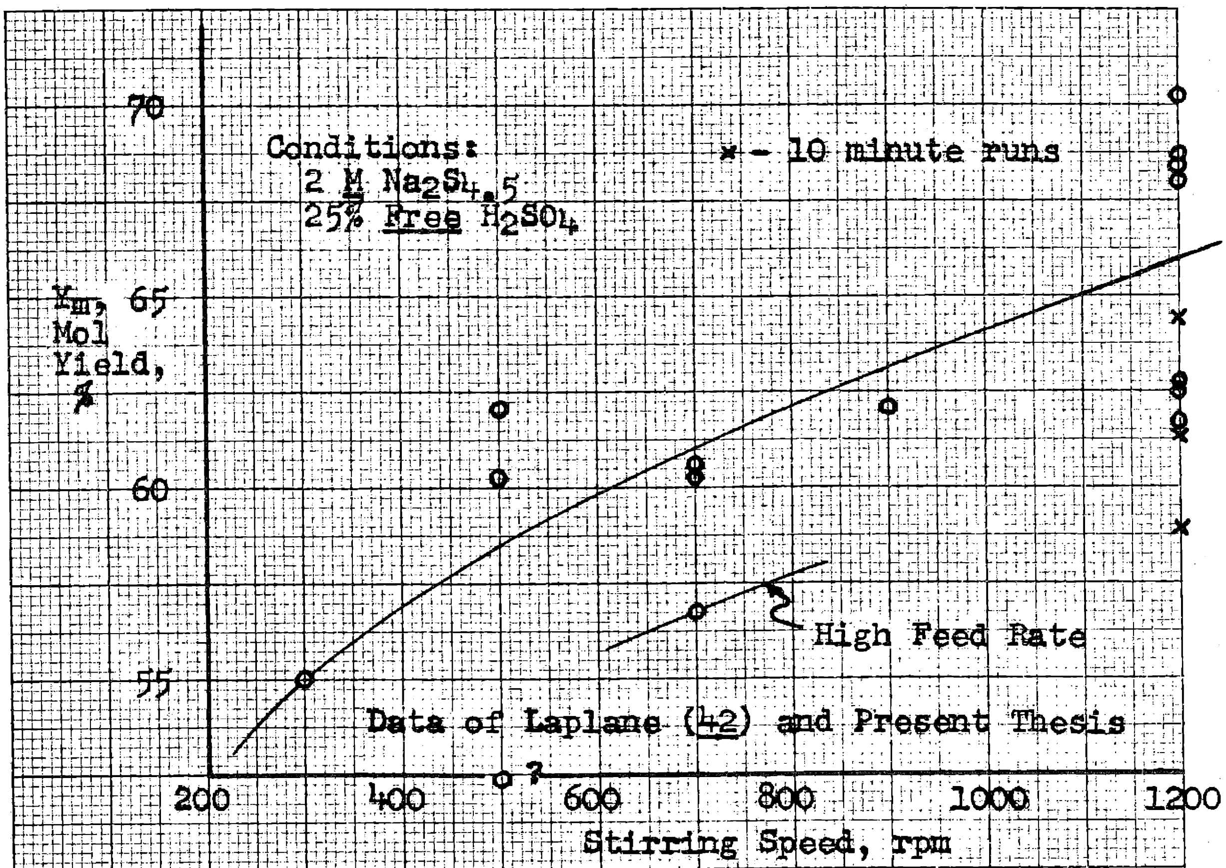


FIGURE 4

Mol Yields for Na_2S_x-H_2SO_4 Reaction at 0°C
(Continuous Synthesis)

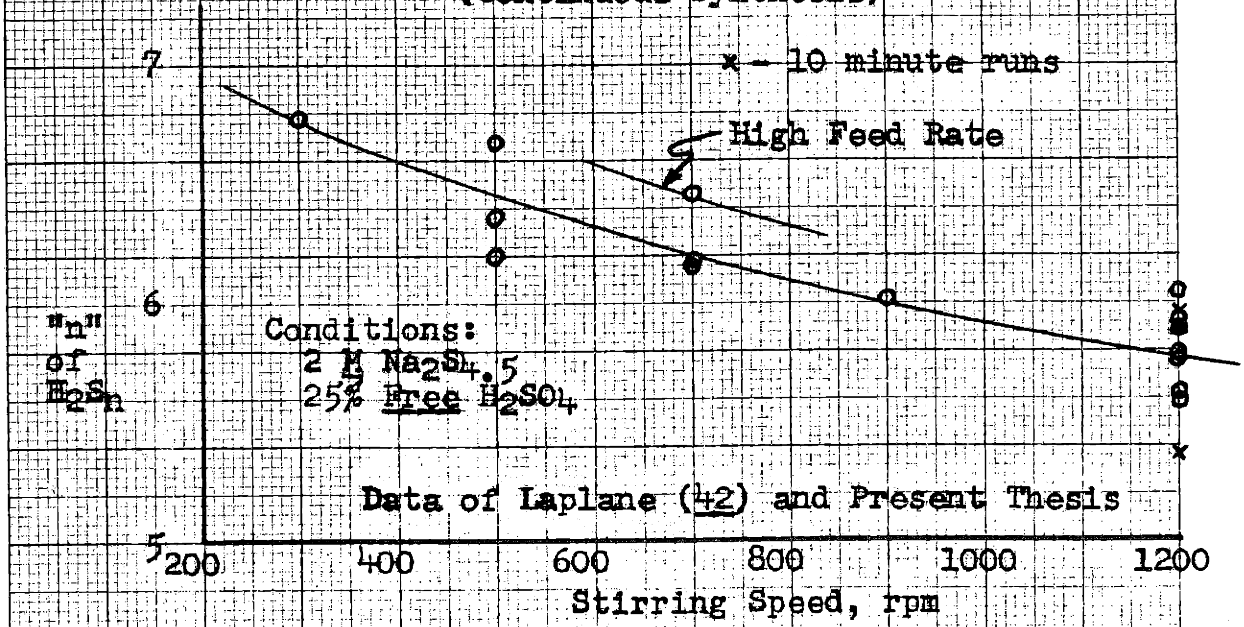


FIGURE A2

Raw Oil Compositions for Na_2S_x-H_2SO_4 Reaction at 0°C
(Continuous Synthesis)

averaging at least 65 per cent were obtained in the present thesis, compared to the 55 per cent estimated at "x"=4.6 from the data of Conway.

In an attempt to obtain better reproducibility at 1200 rpm stirring speed, experiments C-20 and C-21 were performed with the polysulfide feed jet directed into the path of the impeller. An examination of Table AV indicates that the yield and "n" values for these two runs were remarkably close, but that the final suspended raw oil "concentrations" differed. The close check in yield and composition might result from a more reproducible small-scale mixing rate at the point of feed injection; the discrepancy in suspended raw oil is considered to be due to phenomena unconnected with the initial mixing process.

Even though a true steady-state may not always have been reached, the apparent final suspended oil "concentrations" listed in Table AV (obtained by dividing the total raw oil in the reaction vessel at the end of each run by the estimated liquid holdup for that run) should be a close approximation to the true equilibrium values, except of course in the three experiments of only 10-minute duration. These final raw oil concentrations are plotted versus stirring speed in Figure A3. The steady-state quantity of raw oil in suspension may pass through a minimum as mixing rate is increased; at lower speeds

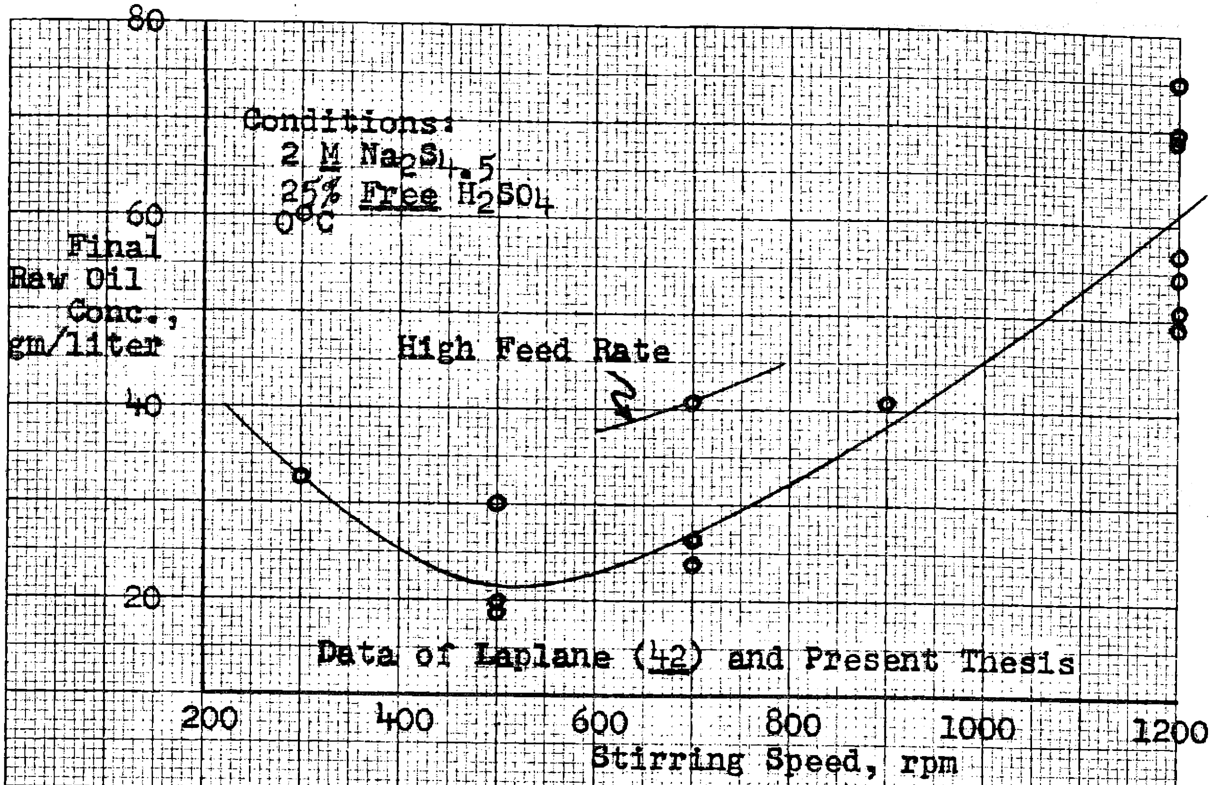


FIGURE A3

Continuous Synthesis Final Raw Oil Concentrations

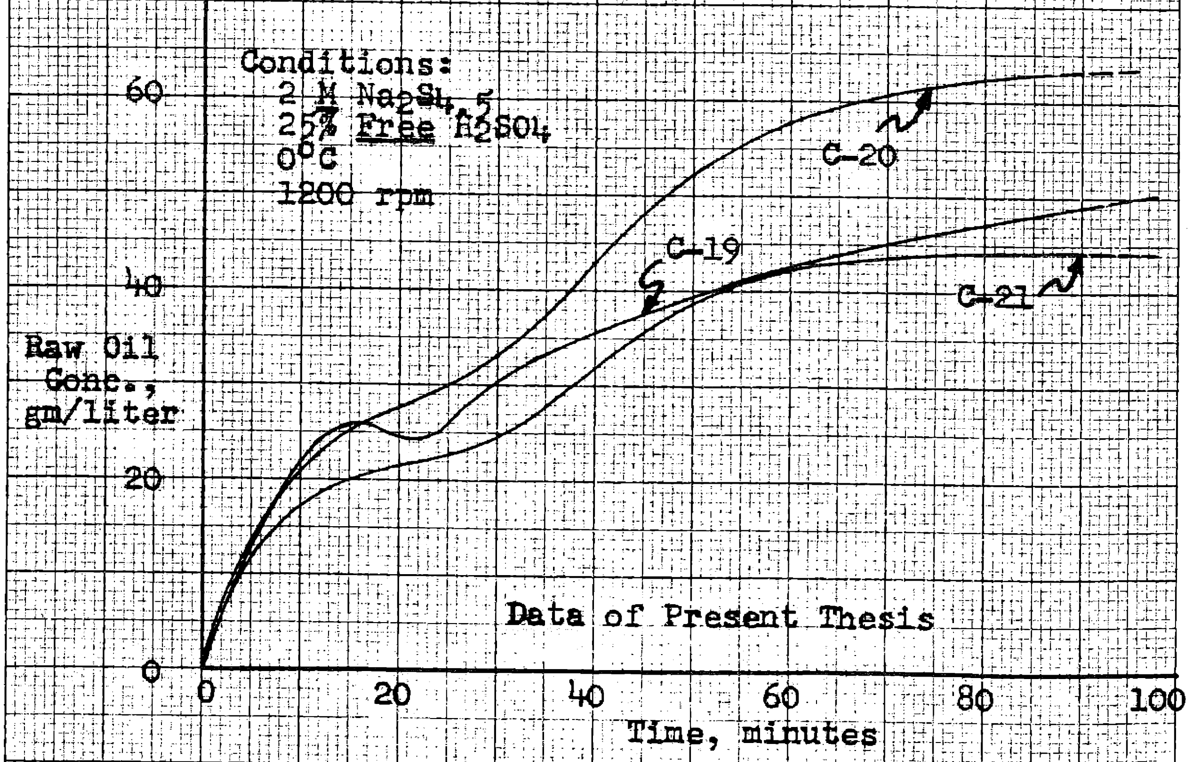


FIGURE A4

Continuous Synthesis Raw Oil Concentration Profiles settling might be hindered by the hydrogen sulfide gas evolved by greater decomposition, while at the higher speeds the coagulation of raw oil droplets might be impeded by the greater eddy shear stresses present.

In Figure A4 are shown the suspended raw oil "concentration" versus time profiles obtained in runs C-19, C-20, and C-21 by collecting the waste acid stream in 10-minute increments and measuring the entrained hydrogen persulfide in each. Apparently in only one of these three experiments at 1200 rpm stirring speed did the raw oil in suspension truly reach an "equilibrium" condition even after 90 minutes run time. In other words, steady-state conditions were not present during the test periods begun after only 50-60 minutes elapsed time.

A further examination of Figure A4 indicates that (a) the three profiles obtained under supposedly identical conditions were not reproducible, and (b) in all three cases a decided inflection was exhibited between 20 minutes and 40 minutes elapsed time. Both these phenomena are considered the result of variations in the draining pattern of the raw oil leaving via the bottom outlet (Figure A1). From raw oil draining increments sampled in run C-9 and reported in the thesis of Laplane (<u>42</u>) it was shown that essentially no persulfide oil appeared in the drain tube until after about 20 minutes operation, at which time a sudden surge was observed. Thus the inflections in suspended oil "concentration" are considered the result of this unsteady-state accumulation of raw oil in the reaction vessel. At 1200 rpm stirring speed this settled oil easily could be picked up again by the rapid swirl induced in the unbaffled lower section.

A comparison between the final "concentrations" indicated in Figure A4 and those tabulated for the same three runs in Table AV indicates that the values based on all the raw oil remaining in the reaction vessel are slightly higher than those calculated from the waste acid increments. This difference, due to the non-homogeniety of the suspended persulfide distribution throughout the reactor, was judged not great enough to justify attempting to correct the numbers tabulated for all 18 runs.

Since the similarity between "start-up" yields and compositions and those from the corresponding "steady-state" periods indicated no significant effect of suspended raw oil concentration, attempts were made to measure the initial incremental yields and compositions obtained with as little opportunity for back-mixing as possible. Experiments C-16 and C-17 (Table AV) yielded, surprisingly enough, results poorer, if anything, than those determined in the presence of relatively high proportions of suspended raw oil. A hydrogen sulfide purge was introduced in run C-18 in an effort to minimize any initial decomposition due to the absence of hydrogen sulfide in the surrounding solution at the beginning of a run. No change was noted other than that accountable for by the physical solution of hydrogen sulfide into the product. Since variation in suspended raw oil "concentration" at a given stirring speed thus did not affect the results, it was concluded that in the continuous system investigated back-mixing had no deterimental effect on yield at oil "concentrations" up to at least 70 gm/liter.

Recommended future work might include the following: (a) a study of feed injection position, or more generally, of reactor design, (b) an investigation of very high stirring speeds, with the free liquid surface eliminated, in an attempt to discover how high mol yield can be forced, and (c) studies with hydrochloric rather than sulfuric acid, with the hope of exceeding the maximum 73 per cent yield obtained in batch operation with this acid (15)(34).

F. Preparation of Individual Hydrogen Persulfides

In the attempt made during the present thesis to develop a quantitative analysis for the individual hydrogen persulfides present in raw oil, samples of the pure persulfides had to be prepared for use as standards. In line with previous practice, it was decided to prepare these pure compounds by the thermal cracking or high-vacuum distillation of raw oil.

1. Batch Synthesis of Raw Oil

The raw hydrogen persulfide employed as the starting material in the preparation of the pure persulfides was produced in relatively large batches in a baffled, stirred reaction vessel (2000-ml beaker) roughly scaled up from the apparatus of Haritatos (34). The mixing rate was set qualitatively by a rheostat stirrer, and the reaction temperature was maintained at 0°C or below by an external cooling bath. The polysulfide feed solution was introduced below the liquid surface through a 1/16-inch nozzle at a rate such that approximately one liter of solution was added to the initial one liter of semi-concentrated acid during the 15-30 minute run period. Since no streams were withdrawn during a run, the liquid level and the amount of suspended raw oil both increased with elapsed time.

Except as will be noted later, all runs were made using "purified" grade sodium sulfide and "technical" grade sulfuric acid. In almost all cases the polysulfide was approximately a 1.95 M solution having the average composition $Na_2S_{4.6}$ (nominally 2 M $Na_2S_{4.5}$). The sulfuric acid concentration in most runs varied from an initial 50 per cent by weight down to about 12 per cent at the end of an experiment.

The raw oil products from the batch synthesis runs were separated, washed, and analyzed by the quartz powder decomposition technique mentioned previously. In those cases in which the oil was to be cracked to hydrogen disulfide or trisulfide it was dried with phosphorous pentoxide, filtered, and again analyzed gravimetrically. Owing to decomposition during the drying process the "n" values of the dried raw oil invariably were higher than those of the crude product.

Since neither stirring speed nor back-mixing were at all controlled in these batch experiments, the results were not reproducible. For the sake of completeness these data nevertheless are presented in Table AVI. In the calculation of mol yields the assay of the initial sodium sulfide used (i.e., the mols actual sodium polysulfide obtained from 240.2 gm monosulfide crystals) was assumed constant at 97 per cent. In those instances in which both the "wet" and the "dry" product analyses were not determined separately, the "n" value after drying was taken to be 0.25 greater than that found for the untreated raw oil.

TABLE AVI

Raw Oil Batch Synthesis Results

All runs except where noted were performed using 1.95 M $Na_2S_{4.6}$ solution, sulfuric acid from 50% down to 12%, temperature -10° to 0°C, and "moderate" stirring. All experiments were carried out in a 2000-ml baffled beaker with run times ranging from 15 to 30 minutes.

Run	Mols Na_2S_x Fed	Gm Raw Oil	Mol Yield %	"n" of H_2S_n
A-1	(1.940)	240	62.8	6.09
A-2	(1.940)	201	44.6	7.24
A-3	(1.940)	240	54.5	(7.10) 7.35 dried
A-4	(1.940)	219	54.1	6.45
A-5	(1.940)	218	48.3	7.23
A-6a	(1.940)	223	52.4	6.78
A-6b	(1.940)	228	52.1	6.96
A-7	(1.940)	232	57.0	6.50
A-8	(1.940)	225	51.4	6.99
A-9	(1.940)	207	46.2	7.16
A-10	(1.940)	219	48.2	7.26
A-11a	(1.940)	242	60.5	6.37
A-11b	(1.940)	198	48.0	6.58
A-12a*	(0.485)	53	54.2	6.23
A-12b*	(0.485)	52	51.8	6.40
A-13a*	(0.485)	52	46.1	7.19
A-13b*	(0.485)	52	58.4	5.68
A-13c*	(0.485)	54	54.9	6.29
A-13d*	(0.485)	56	56.7	6.29
A-14#	(1.940)	64	17.8	5.72
A-15	(1.940)	243	61.6	6.29

<u>Notes</u>: Parentheses () indicate assumed values.

* Runs A-12a through A-13d were duplicate experiments involving smaller quantities of materials. These runs were performed in the 2000-ml vessel at -5°C, "moderate" stirring speed, 4-minute run time, with the sulfuric acid concentration varying from an initial 33% down to 22%. In runs A-13a through A-13d reagent grade chemicals were used. In experiment A-13b 0.05 gm-mol $Na_2S_2O_3$ and 0.05 gm-mol Na_2SO_3 were added to the polysulfide feed; in experiment A-13c the polysulfide was prepared under nitrogen.

\# The polysulfide used in run A-14 had the approximate composition 1.95 M $Na_2S_{2.03}$.

2. Cracking of Raw Oil

The apparatus for the preparation of the various pure hydrogen persulfides, designed according to the practice of Feher and Baudler (23)(24)(25)(26), is shown in Figure A5. The packed bed used for the cracking of raw oil to hydrogen disulfide and hydrogen trisulfide consisted of a Pyrex glass column 2 inches in diameter and 24 inches long, filled with 1/4-inch beryl saddles and jacketed internally and externally with circulating Nujol at 120°-150°C. By the utilization of two water aspirators in parallel the system absolute pressure was maintained at 15-30 mm Hg.

As raw oil was allowed to drip into the top of the column, it either cracked or else completely decomposed as it trickled downward; the residue collected in the bottom flask was mainly sulfur. In the production of hydrogen disulfide most of the higher persulfides vaporizing over were condensed out either in the air-cooled bulb above the column or in the water-cooled condenser, and thus were refluxed to the packed bed for further cracking. The last traces of heavier components were removed in the ice-cooled trap, and the hydrogen disulfide product then was collected in the dry ice-acetone trap at -78°C. The remaining hydrogen sulfide gas was exhausted to the aspirators. In the production of hydrogen trisulfide the lower set of traps shown in Figure A5 was employed. The trisulfide

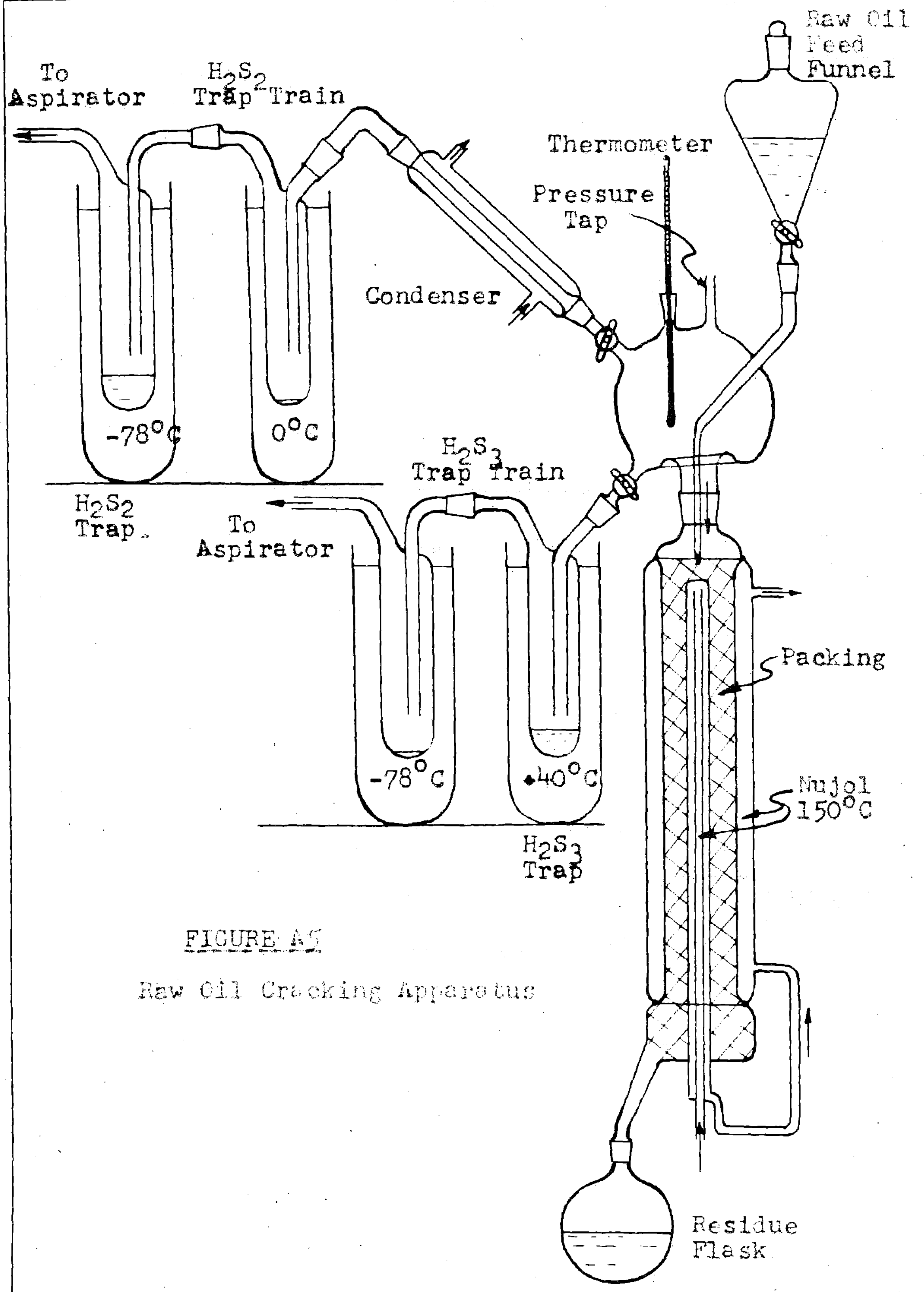


FIGURE A5

Raw Oil Cracking Apparatus

vapors condensing out in the air-cooled bulb were held up in the 40°C trap, while the more volatile disulfide again was collected at dry ice temperature. In order to maximize the conversion to trisulfide no reflux to the column was employed. Any species higher than hydrogen trisulfide for the most part were condensed out below the air-cooled bulb.

By removing the packing the column shown in Figure A5 also could be converted, by modifications not indicated in the drawing, into a falling-film molecular still for the separation of some of the higher persulfides (H_2S_4 through H_2S_6) present in raw oil. Since the planned quantitative Raman spectroscopic analysis for the individual persulfides in raw oil was not successful, no attempts were made to operate the apparatus under molecular distillation conditions.

The raw oil to be cracked in the Figure A5 system first was dried with phosphorous pentoxide. In some cases the dried oil was partially degassed under vacuum to remove dissolved hydrogen sulfide. The raw oil was fed continuously to the cracking column at a rate of about 200 gm in from 2 to 5 hours. This feed rate was limited partly by foaming and partly by the aspirator capacity.

The conditions and the results for the 12 raw oil cracking runs performed in the present thesis are presented in Table AVII. Experiments B-1 through B-6 and also B-12 were carried out at a column temperature of 150°C in order

TABLE AVII

Production of Hydrogen Disulfide and Trisulfide from Raw Oil

All runs were carried out in a packed bed at 120°-150°C and 15-30 mm Hg absolute pressure. Run times usually ranged from 2 to 5 hours.

Run	Mols Raw Oil Fed	"n" of Raw Oil	H_2S_2 Trap Mol Yield %	"n" of H_2S_2	H_2S_3 Trap Mol Yield %	"n" of H_2S_3	Total Mol Yield %
B-1	1.095	(6.34)	10.6	2.18	1.9	(3.0)	12.5
B-2	0.674	(7.49)	41.4	2.07	-	-	41.4
B-3	0.890	7.35	33.3	2.05	2.3	(3.0)	35.6
B-4	0.811	(6.70)	27.5	2.035	?	(3.0)	27.5
B-5	0.806	7.63	17.0*	2.005*	-	-	17.0
B-6#	1.735	7.21	29.7	(2.0)	-	-	29.7
B-7	0.908	6.85	36.2	2.32	?	(3.0)	36.2
B-8	0.843	7.13	23.4	(2.0)	3.5	3.10	26.9
B-9	0.702	7.41	29.0	2.27	1.5	(3.0)	30.5
B-10	0.767	7.32	21.8	(2.0)	12.0	3.00	33.8
B-11	1.840	6.65	20.6	(2.0)	10.9	3.05	31.5
B-12#	1.996	6.87	26.2	(2.0)	-	-	26.2

Notes: Parentheses () indicate values estimated or assumed.

* Yield and composition in run B-5 taken after redistillation of the disulfide.

\# The reported yields in runs B-6 and B-12 are based on estimated values before redistillation of the disulfide. The redistilled products analyzed "n" = 1.74 in run B-6 (probably in error) and "n" = 2.03 in run B-12.

to produce mainly hydrogen disulfide. The remaining five runs were made at somewhat lower column temperatures so that the trisulfide yield could be maximized by less drastic cracking conditions. These attempts to produce hydrogen trisulfide, however, always resulted in the formation of considerable disulfide. Redistillation under vacuum was employed to improve the quality of some of the hydrogen disulfide products. Owing to a tendency to decompose upon vaporization, the trisulfide could not be redistilled.

Inspection of Table AVII indicates that the total cracking yields ranged from as low as 12.5 per cent up to 41.4 per cent, compared to the 60-70 per cent mol yields reported by previous workers. The poor performance in the present thesis is attributed both to less than optimum column design and to the use of feed oils with relatively high "n" values. Better cracking yields of the two lower persulfides might have been obtained from raw oil having a lower average sulfur subscript, but since polysulfide with a lower "x" then would be required as starting material, the overall yields based on the initial sodium sulfide probably would not have been improved.

G. Raman Spectra of Hydrogen Persulfides

Since other analytical tools such as chromotography, infra-red spectroscopy, thermal diffusion, and nuclear magnetic resonance appeared too speculative, Raman spectroscopy, the approach investigated by Feher and Baudler (26), was selected for use in the attempted development of a quantitative analysis for the individual persulfides in raw oil. When a chemical substance which is a good Raman scatterer (any one of the hydrogen persulfides, for example) is placed in a source of monochromatic light, characteristic Raman lines are emitted at fixed wave-length intervals from the exciting line. These Raman radiations are relatively weak, but nevertheless either may be photographed or may be recorded using a photomultiplier.

It was planned to obtain and thus to standardize the characteristic Raman spectra for as many of the pure hydrogen persulfides as could be isolated. Since the Raman effect is linear with concentration, the mol fraction of any given species in an unknown sample (raw oil) therefore could be taken as the characteristic line intensity ratio, unknown to standard. If an individual characteristic line for each persulfide could not be found, the analysis then would have to be computed from the solution of a set of simultaneous linear equations.

The recorded Raman spectra of the following were obtained under blue 4358 Å excitation, using a Raman spectroscope equipped with a photomultiplier: (1) the redistilled hydrogen disulfide product from cracking run B-6, (2) the hydrogen trisulfide product from run B-11, and (3) the raw oil product from batch synthesis run A-14. The disulfide sample was shown to be quite pure, yielding strong characteristic lines, as found by Feher and Baudler (26), at 510, 882, and 2513 cm^{-1}. The trisulfide proved to be an even more powerful Raman scatterer, exhibiting lines, as previously reported, at 207, 484, 882, and 2513 cm^{-1}; the spectrum, however, was somewhat weakened by absorption in the vicinity of the exciting line. The trisulfide sample also appeared less pure, containing small amounts of the disulfide and of higher hydrogen persulfides. The actual recorded disulfide and trisulfide spectra are on file in the M. I. T. Spectroscopy Laboratory.

Owing to the almost complete absorption by the strongly yellow sample, no Raman spectrum was obtained when raw oil was exposed to blue 4358 Å excitation. From a personal communication (21) it was learned that Feher and Baudler had been forced to change to green 5460 Å excitation, using special filter solutions, in order to obtain even the photographic Raman spectra of the higher persulfides and of raw oil. Since the M. I. T. recording Raman instrument was not suited for work with green excitation, and since photographic spectra were not considered accurate enough for quantitative analysis, the program to develop a method for determining the individual hydrogen persulfides in raw oil had to be abandoned.

H. Production of Hydrogen Disulfide via Perthiocarbonic Acid

All the attempts reported in the literature to prepare hydrogen disulfide, the most reactive of the persulfides, by the direct acidification of substances having the apparent composition Na_2S_2 have resulted in failure. The findings of the present thesis indeed indicate that in aqueous solutions the alkali disulfides largely if not completely disproportionate to the monosulfide and higher polysulfide ions. But if this equilibrium could be distorted artificially such that alignment as the disulfide ion would occur, the direct synthesis of hydrogen disulfide then might be possible, with higher yields and lower potential operating costs than in the present two-step process via raw oil.

The formation of thiocarbonates by the reaction of carbon disulfide with aqueous monosulfide or polysulfide solutions in effect accomplishes this distortion. The findings reported in the literature (49)(71) indicate that carbon disulfide dissolves in the monosulfide solution, yielding, according to the following equation, a red thiocarbonate solution:

$$S^{=} + CS_2 = CS_3^{=} \qquad (A12)$$

It has been found that apparently one perthiocarbonate species can form:

$$S_2^{=} + CS_2 = CS_4^{=} \qquad (A13)$$

Thus if carbon disulfide is allowed to react with an aqueous polysulfide solution, the product is a mixture of trithiocarbonate and tetrathiocarbonate if "x" is less than 2, while if "x" initially is greater than 2, sulfur is precipitated and only the perthiocarbonate is formed.

Upon the acidification of thiocarbonate solutions the corresponding acid species are liberated as bright red liquids which are only slightly soluble in the aqueous phase:

$$CS_3^{=} + 2\ H^{+} = H_2CS_3 \qquad (A14)$$

$$CS_4^{=} + 2\ H^{+} = H_2CS_4 \qquad (A15)$$

Unlike the synthesis of raw oil by the acidification of aqueous polysulfides, perthiocarbonic acid (H_2CS_4) apparently is obtained from sodium perthiocarbonate (equation A15) in very high yields even under ordinary mixing conditions. On the other hand, the yield of thiocarbonic acid (equation A14) as pointed out by Yoeman (<u>71</u>), might depend on the formation of some perthiocarbonate by oxidation; no thiocarbonic acid was obtained by the acidification of sodium thiocarbonate solution with complete exclusion of air and carbon dioxide.

Both thiocarbonic acid and perthiocarbonic acid resemble the hydrogen persulfides in that they are somewhat unstable; their decomposition is accelerated by the same agents which cause breaking down of the persulfides. Mills and Robinson

(49), however, found that under vacuum distillation conditions perthiocarbonic acid on decomposing could be made to yield in part hydrogen disulfide rather than hydrogen sulfide plus sulfur. The best conversion to the disulfide, while percentagewise apparently still small, was obtained when using a brown perthiocarbonic acid product synthesized by the reaction of dry ammonium perthiocarbonate with anhydrous formic acid. The red oil resulting from the ordinary aqueous acidification was asserted to be largely a physical solution of sulfur in thiocarbonic acid (H_2CS_3).

A preliminary study of the production of hydrogen disulfide from perthiocarbonic acid was undertaken in the course of the present thesis.

1. Preparation of Sodium Perthiocarbonate

Upon the addition of carbon disulfide to sodium polysulfide solutions having "x" values greater than 2, sulfur was precipitated with appreciable heat evolution and the perthiocarbonate was formed. As indicated by the results given in Table AVIII this reaction apparently did not go to completion; the sulfur content of the final solution was always a little higher and the carbon disulfide content as determined upon subsequent acidification somewhat lower than expected from stoichiometry. The sodium perthiocarbonate solutions were not analyzed for total reducing equivalents; their molarities were calculated assuming a 97 per cent assay of the initial sodium sulfide from which they were made.

2. Synthesis of Perthiocarbonic Acid

Most of the sodium perthiocarbonate acidification experiments were carried out batchwise in the same reaction vessel used in the raw oil continuous synthesis study (Figure A1), employing hydrochloric acid varying in concentration from an initial 35 per cent down to 10 per cent. The temperature was maintained at 0°C or below and the stirring speed was held at 500 rpm. The perthiocarbonate solution was fed through a nozzle at a rate of about 500 ml in 20 minutes. The product was analyzed by a combination of gravimetric quartz powder decomposition and iodimetric titration, yielding the carbon disulfide-free composition.

The results of the perthiocarbonic acid synthesis runs are given in Table AVIII, along with the data from an experiment in which thiocarbonic acid was prepared. In most cases the perthiocarbonic acid products analyzed slightly higher in sulfur and somewhat lower in carbon disulfide than indicated by the formula H_2CS_4 ; their yields nevertheless were not far from quantitative. The mol yield of thiocarbonic acid in run D-6, on the other hand, apparently was quite low, indicating that perhaps owing to the exclusion of air the initial reaction with carbon disulfide did not proceed very far.

3. Production of Hydrogen Disulfide

In two experiments the perthiocarbonic acid products were subjected to simple vacuum distillation in an attempt to produce hydrogen disulfide by the selective decomposition of the acid. These distillations were performed batchwise at 30-40 mm Hg absolute pressure and a kettle temperature of from 20°C to 40°C; approximately 110 gm initial perthiocarbonic acid was distilled in 1 1/2-4 hours. The distillate was condensed at -78° C in a dry ice trap, and was analyzed by the combination of gravimetric and volumetric techniques outlined previously.

The distillation results also are presented in Table AVIII. Essentially all the carbon disulfide contained in the perthiocarbonic acid was recovered in the low temperature trap. In both the runs however, only a small portion of the potential hydrogen disulfide appeared as such, dissolved in the condensed carbon disulfide. After all the carbon disulfide had been evolved from the distillation flask, a thick yellow residue remained, apparently consisting of a solution of sulfur in higher hydrogen persulfides. No hydrogen disulfide could be produced from this residue upon further distillation. A yellow color in the cold trap condensate was evidence that some of the perthiocarbonic acid had distilled over without breaking down. Since the pure acid was bright red in color, the amount in the distillate was assumed to be small.

In view of the discouraging performance in run D-4, distillation from phosphorous pentoxide was attempted in run D-5. Owing to considerable foaming the distillation had to be carried out at a slower rate; the hydrogen disulfide yield turned out to be even poorer than in experiment D-4. In both cases more that 77 percent of the initial available hydrogen sulfide was exhausted as such into the aspirators. The 9.4 per cent maximum overall hydrogen disulfide yield obtained in the present thesis thus is considerably lower than the 25 per cent optimum reported by Feher and Baudler (<u>23</u>) using the conventional raw oil route.

TABLE AVIII-a

Production of Hydrogen Disulfide via Perthiocarbonic Acid

Run No.	D-1	D-2	D-3		D-4	D-5	D-6
I. Formation of Sodium Perthiocarbonate							
Initial "x"	(4.60)	(4.60)	(4.60)		(2.55)	(4.60)	1.0
"x" after CS_2 Reaction ?		(2.20)	(2.18)		(2.09)	(2.07)	(1.0)
II. Acidification to Perthiocarbonic Acid							
			D-3a	D-3b			
Mols Na_2CS_4 Fed	(0.146)	(0.195)*	(0.504)	(0.420)*	(0.970)	(0.970)	(0.485)$^{+}$
Gm H_2CS_4 Formed	~6	~12	58.3	37.6	118.3	120.5	5.1^{+}
Product % Volatile	76.8	74.7	74.4	68.1	74.1	74.9	98.4
Mol Ratio CS_2/H_2S_n	?	?	0.820	? 0.708	0.868	0.907	?
CS_2-free "n"	?	?	2.03	? 2.29	2.09	2.08	?
H_2CS_4 Mol Yield %	?	?	90.2	? 69.1	90.7	90.4	?$^{+}$
III. Decomposition to Hydrogen Disulfide							
Mols H_2CS_4 Fed	-	-	-	-	0.811	0.805#	-
Mols H_2S_n in Distillate	-	-	-	-	0.0843	0.0473	-
Solvent-free "n"	-	-	-	-	2.15	1.74?	-
H_2S_2 Mol Yield, %	-	-	-	-	10.4	5.9	-
Gm Residue	-	-	-	-	23.7	(30.9)	-
Residue "n"	-	-	-	-	7.34	(7.0)	-
Residue Yield %	-	-	-	-	12.3	(16.9)	-
Total H_2S Recovery %	-	-	-	-	22.7	22.8	-
Overall H_2S_2 Yield %	-	-	-	-	9.4	5.3	-

TABLE AVIII-b

Production of Hydrogen Disulfide via Perthiocarbonic Acid

Notes: Parentheses () indicate values estimated or assumed.

I. Formation of Sodium Perthiocarbonate: All experiments performed using about 1.95 M Na_2S_x solutions (nominally 2M). Analyses based on assumed 97% assay of initial sodium sulfide.

II. Acidification to Perthiocarbonic Acid: Acidifications in runs D-1 and D-2 carried out using hand stirring in an unbaffled vessel. All remaining acidifications carried out in a baffled 1500-ml beaker at 0°C or below, HCl concentration varying from 35% down to 10%, stirring speed 500 rpm, run time 10-20 min.

III. Decomposition to Hydrogen Disulfide: Distillation conditions: system pressure 30-40 mm Hg, boiling temperature 20°-40°C, condensation temperature -78°C, run time 1 1/2 to 4 hours.

* In run D-2 the Na_2CS_4 solution, before being acidified, was heated 80 minutes at 60°C, then cooled. In run D-3b the Na_2CS_4 solution was boiled 30 minutes at 110°C and then cooled.

\+ In run D-6 the values tabulated refer to $Na_2CS_{\underline{3}}$ and $H_2CS_{\underline{3}}$.

\# In run D-5 the perthiocarbonic acid was distilled in contact with phosphorous pentoxide, with 33 gm carbon disulfide added.

4. Recommended Future Work

The following additional studies are suggested:

(a) A more thorough investigation of distillation variables should be undertaken in an effort to improve the yield of hydrogen disulfide from perthiocarbonic acid.

(b) Attempts should be made to prepare hydrogen disulfide from the brown perthiocarbonic acid synthesized from anhydrous chemicals, as suggested by Mills and Robinson (49).

(c) the possibility of using perthiocarbonic acid directly in place of hydrogen disulfide in its organic reactions should be investigated. Since in such cases the point of attack is the disulfide linkage itself rather than the hydrogen sulfide released by decomposition, the acid might well prove an effective substitute for hydrogen disulfide.

I. Nomenclature

Symbol	Definition	Units
a	Thermodynamic activity	
a	Constant in simplified Debye-Huckel equation	
A	Concentration ratio, PSS/Na^+	
B	Concentration ratio, $S_x^=$/Na^+	
$c_1, c_2, ..$	Equilibrium constants for NaS_x^- formation from NaS^-	
C	Complexing constant for NaS^- formation	
d	Differential operator	
e	2.7182818.....	
f	Fugacity (or partial pressure)	atm
F	Free energy	KCal/gm-mol
G_1, G_2	Constants in equation 67	
$h_1, h_2, ..$	Equilibrium constants for HS_x^- formation from HS^-	
H	Enthalpy	KCal/gm-mol
H	Henry's Law constant	gm-mols/liter-atm
$k_1, k_2, ..$	Equilibrium constants for $S_x^=$ formation from $S^=$	
K	Ionization constant	
m	Molality	gm-mols/1000 gm H_2O
M	Molarity	gm-mols/liter soln.

Symbol	Definition	Units
n	Average sulfur subscript of H_2S_n	
n	Total sulfides in solution	gm-eqs
N	Normality	gm-eqs/liter soln
p	Partial pressure	mm Hg
P	Vapor pressure	mm Hg
PSS	Polysulfide sulfur	gm-atoms
$r_1, r_2, ..$	Relative equilibrium constants for $S_x^=$ formation	
R	Gas Law constant = 0.001987	KCal/gm-mol - °K
S	Entropy	KCal/gm-mol - °K
T	Temperature	°K
u,v,w	Polysulfide sulfur subscripts of polysulfide ions	
V	Volume	liters
x	Nominal average sulfur subscript in Na_2S_x	
X	$[S_x^=] f_{H_2S} / [HS^-]^2$	$(\text{molality})^{-1}$ -atm
X_1, X_2, X_3	Defined in text	$(\text{molality})^{-1}$ -atm
y	Mol fraction in liquid xylene solution	
Y	$[PSS] f_{H_2S} / [HS^-]^2$	$(\text{molality})^{-1}$ -atm
Y_1, Y_2, Y_3	Defined in text	$(\text{molality})^{-1}$ -atm
z	Charge on given ionic species	

Symbol	Definition	Units
Z_1	$[S^{=}]/[HS^{-}][OH^{-}]$ or $[S^{=}]/[HS^{-}]^2$	$(\text{molality})^{-1}$
Z_2	$[S_x^{=}]/[HS^{-}]^2$	$(\text{molality})^{-1}$

Greek Symbols

α	Constant in equation 11	liters-mmHg/gm-mol
β	Constant in equation 13	liters/gm-mol
γ	Ionic activity coefficient	$(\text{molality})^{-1}$
Γ	Constant in equations 82 and 83	
Δ	Difference operator	
$\Delta_1, \Delta_2, \Delta_3$	Defined in test	$(\text{molality})^{-1}$-atm
ϵ	Fraction in linear combination	
μ	Ionic strength	(molality)
μ'	"Total ionic concentration"	(molarity)
π	Total pressure	mm Hg
ρ	Density	gm/ml

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