The geologic role of polysulfides—Part I

The distribution of ionic species in aqueous sodium polysulfide solutions*

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Abstract—Numerous measurements have been made of the pH, Eh, and the potential of a silver–silver sulfide electrode in sodium sulfide and sodium polysulfide solutions. By suitably estimating the second dissociation constant of hydrogen sulfide and various activity coefficients, it has been possible to derive a consistent model for the distribution of the polysulfide and sulfide species, S^{-2}, S_4^{-2}, S_5^{-2}, S_6^{-2} and HS^{-1}, at strengths up to 1 M and for pH values between 7 and 13. This model differs markedly from the models given previously by PESCHANSKI and VALENSI (1949) and by MARONNY (1959b), who include S^{-2}, S_2^{-2}, S_3^{-2}, S_4^{-2}, S_5^{-2} and HS^{-1}. The free energy of formation values proposed here are $16\cdot36 \pm 0\cdot10$ kcal/mole for S_6^{-2}, $15\cdot97 \pm 0\cdot10$ kcal/mole for S_5^{-2}, and $16\cdot29 \pm 0\cdot10$ kcal/mole for S_4^{-2}. Tentative figures for di- and tri-sulfide ions are $21\cdot0 \pm 3\cdot0$ kcal/mole for S_3^{-2} and $22\cdot7 \pm 3\cdot0$ kcal/mole for S_2^{-2}. These are based on a value of $21\cdot42$ kcal/mole for S^{-2}.

INTRODUCTION

THIS paper is the first of a series dealing with the possible role of polysulfide solutions in the transport and deposition of chalcophile elements in sulfide vein deposits. The suggested Eh and pH values for the hydrothermal solution (BARTON, 1957; NATARAJAN, 1958) lie close to the stability field of elemental sulfur. Since this is exactly the region where polysulfides have their greatest thermodynamic stability, it seems logical that metal-polysulfide complexes may explain hydrothermal transport (BARTON, 1957; BARNES, 1958). Moreover, several sulfides have rather high solubilities in polysulfide solutions.

In order to test this idea further and to determine the influence of changing pH on solubilities, experiments on the solubility of acanthite, Ag_2S, were begun. It soon became apparent that an understanding of the observed solubilities must be based on an adequate interpretation of the distribution of polysulfide ions in aqueous solutions. It is the purpose of this paper to discuss this interpretation and to present the distribution derived from new experimental work. Subsequent papers will deal with the observed solubilities and the significance for geologic processes.

TERMINOLOGY

The following definitions and explanations of terms and symbols will be helpful to the reader in understanding the text.

A, a temperature dependent constant in the Debye–Hückel equation.

a_0, the "mean distance of closest approach" as used in the Debye–Hückel equation.

B, a temperature dependent constant in the Debye–Hückel equation.

c equals $[HS^{-1}] + \sum\limits_{x=1}^{\infty} [S_x^{-2}]$.

$E°$, a standard potential; the sign convention of the American Electrochemical Society is used.

Eh, the oxidation potential in an aqueous solution.

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$E_I°$, the standard potential for the reaction, $S^{-2} = S + 2e^{-1}$.

$E_x°$, the standard potential for the reactions, $xS^{-2} = S_x^{-2} + 2(x - 1)e^{-1}$, where x is an integer.

e^-, symbol for an electron in an oxidation-reduction reaction.

$\Delta^1 F°$ standard Gibbs free energy of reaction or of formation.

$\Delta F°_N$ standard Gibbs free energy of formation of the substance N, where N represents the chemical formula of the substance.

f_N, rational activity coefficient of the substance N.

γ_N^z, stoichiometric molar activity coefficient of the ion N; where N represents the chemical formula of the ion and z its charge.

$\gamma_{\pm Q_q R_r}$, mean molar ionic activity coefficient of the ionic compound $Q_q R_r$.

γ_+, molar ionic activity coefficient of a cation.

γ_-, molar ionic activity coefficient of an anion.

$\gamma_\pm$, mean molar ionic activity coefficient.

hydropolysulfide ion, one of the ions, HS_x^{-1}, where x is an integer greater than 1.

K, an equilibrium constant.

K_w, the dissociation constant of water, equal to (H^{+1}) (OH^{-1});

K_1, the first dissociation constant of H_2S equal to the ratio (H^{+1}) $(HS^{-1})/(H_2S)$.

K_2, the second dissociation constant of H_2S equal to the ratio (H^{+1}) $(S^{-2})/(HS^{-1})$.

K_5', the equilibrium constant $(S_5^{-2})^3(S^{-2})/(S_4^{-2})^4$.

K_5'', the equilibrium constant $(S_5^{-2})/(S_4^{-2})$.

K_6', the equilibrium constant $(S_6^{-2})^4(S^{-2})/S_5^{-2})^5$.

M, molarity of a substance in solution.

monosulfide, the sum $\sum_{x=1}^{\infty} \{[H_2S_x] + [HS_x^{-1}] + [S_x^{-2}]\}$, where x is an integer.

mv, millivolts.

mμ, millimicrons.

μ, ionic strength.

(N), the activity of the substance N in moles/l.

$[N]$, the concentration of the substance N in moles/l.

persulfide, the highly-colored oil produced by adding aqueous polysulfide solutions to cold concentrated HCl; a mixture of various hydrogen polysulfides.

pK, the negative decadic log of K.

pN, the negative decadic log of (N).

polysulfide, (a) when used as a noun, polysulfide means the sum, $\sum_{x=2}^{\infty} (x - 1) \{[S_x^{-2}] + [HS_x^{-1}] + [H_2S_x]\}$; where x is an integer; the sum of monosulfide and polysulfide equals the total amount of S contained in all sulfide and polysulfide species present,

(b) when used as an adjective, polysulfide means "containing or composed of one or more polysulfide species."

polysulfides, the plural of polysulfide species.

polysulfide ion, one of the ions, S_x^{-2}, where x is an integer greater than 1.

polysulfide species, a compound, molecule, or ion containing the group, S_x^{-2}, where x is an integer greater than 1, and not containing oxygen; the negative two charge indicated may be satisfied wholly or in part by covalent bonds. The average valence of the sulfur is between 0 and -2.

$Q_q R_r$, an ionic compound containing q cations of element Q and r anions of element R.

q, the (integral) number of cations in $Q_q R_r$.

r, the (integral) number of anions in $Q_q R_r$.

sulfane, one of the polysulfide species H_2S_x, where x is an integer greater than 1.

sulfide, as a noun; a compound, molecule, or ion containing sulfur having an average valence of -2.

as an adjective; the word sulfide refers to the presence of a sulfide.

species, a solid compound or all of the molecules or all of the ions which can be represented by a single chemical formula.

t, temperature in °C.

V, volts.

x, the number of atoms of sulfur in a sulfide or polysulfide species.

$\bar{x}$, the ratio $\sum\limits_{x=2}^{\infty} x\{[H_2S_x] + [HS_x^{-1}] + [S_x^{-2}]\}/ \sum\limits_{x=2}^{\infty} \{[H_2S_x] + [HS_x^{-1}] + [S_x^{-2}]\}$

the average value of x in all polysulfides in solution.

$\bar{y}$, the ratio of the sum of monosulfide plus polysulfide to monosulfide; the average value of x in all polysulfides and sulfides in solution.

z, the charge on an ion.

Previous Work

The earlier work dealing with aqueous solutions of alkali sulfides is rather extensive. Attention will be focused mostly on work with polysulfide solutions instead of on a review of all the pertinent literature. However, values of certain constants derived from work with sulfides are of interest.

Dissociation constants of H_2S

Values reported for the second dissociation constant of H_2S range over several orders of magnitude. Some of the more recent values for the logarithm of this constant are $-14\cdot00$ (25°C) (ELLIS and GOLDING, 1959), $-13\cdot90$ (25°C)(MARONNY, 1959a), $-12\cdot89$ (25°C)(KURY, ZIELEN, and LATIMER, 1953, using data recalculated from KONOPIK and LEBERL, 1949), $-14\cdot00$ (25°C) (LATIMER, 1952), $-13\cdot10$ (20°C) (KONOPIK and LEBERL, 1949), and $-12\cdot44$ (20°C)(KUBLI, 1946). A considerably older value is $-14\cdot9$ (25°C) (KNOX, 1908).

For the first dissociation constant of H_2S the value of $1\cdot02 \times 10^{-7}$ as given by KURY, ZIELEN, and LATIMER (1953) was accepted.

Work with sodium polysulfides

KÜSTER and HEBERLEIN (1905) studied the solubility of S in Na_2S solutions. They found that $\bar{y}$ varied from $4\cdot47$ to $5\cdot24$ at 25°C depending on the concentration. For a 1 N (1 M in sodium ion) solution they found that the solubility decreased very slightly with increasing temperature. By considering the properties expected to be associated with various possible molecular structures (mostly the expected strengths of the acids, H_2S_x), they concluded that the most likely structure for the acids was a chain designated as H_2S-S-S-S-S, or $H_2S \cdot S_x$. Presumably, therefore, the ions in alkaline solutions are chains such as $(S-S-S-S-S)^{-2}$. Very likely the solubilities reported by KÜSTER and HEBERLEIN are too high since they did not correct for the presence of thiosulfate. As PESCHANSKI and VALENSI (1949) and MARONNY (1959a) point out there is always some oxidation or disproportionation of polysulfides to form thiosulfate, especially at higher temperatures. Because of this the ratio of the total amount of sulfur (dissolved sulfur plus original sulfide) to original sulfide is higher than $\bar{y}$.

PESCHANSKI and VALENSI (1949) have made a rather extensive study of solutions of sodium polysulfides. They equilibrated solutions of Na_2S containing various amounts of dissolved S at 25°C and then measured the pH and Eh of the solutions. These solutions ranged from those saturated in sulfur to ones with very little S. By measuring the thiosulfate, monosulfide, and polysulfide analytically they avoided the difficulties inherent in the method of KÜSTER and HEBERLEIN (1905). In this way they found that $\bar{y}$ never exceeded $5\cdot0$. If they analysed their solutions in the same way as KÜSTER and HEBERLEIN, however, the two sets of measurements were in close agreement. PESCHANSKI and VALENSI then assumed that no ions such as S_6^{-2}, S_7^{-2}, or polysulfide ions containing more sulfur existed in aqueous solution, and that the free energy of the reaction, $S_x^{-2} + S = S_{x+1}^{-2}$ is a linear function of x. The only sulfide and polysulfide species assumed to be present under the experimental conditions were HS^{-1}, S^{-2}, S_2^{-2}, S_3^{-2}, S_4^{-2}, and S_5^{-2}. All of the hydropolysulfide ions were assumed to be absent. They then derived standard potentials for a number of oxidation–reduction reactions from the measurements and used these standard potentials to calculate the pH, Eh, and the concentration of each of the sulfide and polysulfide ions as a function of increasing sulfur content.

The Eh measurements reported by PESCHANSKI and VALENSI (1949) agree well with the

interpolated or extrapolated values obtained in the present study. Their pH measurements, however, agree poorly, differing in some cases by one pH unit. Moreover, their values are apparently inconsistent internally, since in some cases the pH as measured increases with increasing dilution; this is contrary not only to the present measurements but also to their own calculations. Their use of the old value of $1 \cdot 2 \times 10^{-15}$ of KNOX (1908) for the second dissociation constant of hydrogen sulfide has little effect except to change the ratio of $[HS^{-1}]:[S^{-2}]$, but not their sum, and to give too high a pH value in their calculations.

MARONNY (1959a, b) and MARONNY and VALENSI (1955, 1958, 1959) have made additional measurements of the potentials in this system and have adjusted the standard potentials and standard free energies of formation of S_2^{-2}, S_3^{-2}, S_4^{-2}, and S_5^{-2} previously estimated by PESCHANSKI and VALENSI (1949).

ARNTSON, DICKSON, and TUNELL (1958) have measured the solubility of S in Na_2S solutions. They analysed the resultant solutions and reported their results as weight percentages of S, H_2O, and Na_2S. They did not determine thiosulfate. Therefore, as mentioned above in connection with the work of KÜSTER and HEBERLEIN (1905) the ratio of total S to original sulfide is probably higher than $\bar{y}$. Some of their values for the ratio at 50°C are considerably greater than $5 \cdot 0$; this is probably due to marked disproportionation to thiosulfate and hydrosulfide.

In a more recent paper ARNSTON, DICKSON and TUNELL (1960) report the results of solubility measurements of S in NaOH solutions at 25°C. In interpreting their results they assume that Na_2S solutions saturated in S do not disproportionate greatly. At 25°C this appears to be nearly enough correct so as not to affect their conclusions. They found, using this assumption, that their data correspond very closely to the reaction, $(2x + 2)S + 6NaOH = 2Na_2S_x + Na_2S_2O_3 + 3H_2O$.

Work with hydrogen polysulfides or sulfanes

FEHÉR and co-workers have made an extensive study of the nature of hydrogen polysulfides. By using special preparation techniques and fractional distillation they have succeeded in separating as pure substances the compounds H_2S_2 through H_2S_8. The purity of the substances was verified by careful investigations of the compositions, of the Raman spectra, and of the osmotic pressures (summarized in FEHÉR et al., 1956, and in FEHÉR and WINKHAUS, 1956). By studying the molar refractivities and densities of these compounds and of the crystalline alkali polysulfides they concluded that polysulfides form only as chain structures, such as H–S–S–S–S–S–H (FEHÉR and BERTHOLD, 1953b, c, 1954; FEHÉR and NAUSED, 1956; FEHÉR, LAUE and WINKHAUS, 1957).

FEHÉR and BAUDLER (1949) found by using Raman spectra that when sodium pentasulfide solution was decomposed by cold concentrated hydrochloric acid the persulfide oil which was produced contained only H_2S_4, H_2S_5, and H_2S_6. By using solutions containing less S, such as Na_2S_2, they did not obtain oils containing H_2S_2 or H_2S_3. The proportion of H_2S_4 increased and those of H_2S_5 and H_2S_6 decreased as S decreased. Apparently the production of the persulfide oil involves some change in the chain length. Thus with $\bar{y}$ of $4 \cdot 5$ in the sodium polysulfide solution ($Na_2S_{4 \cdot 5}$) the oily acid produced has a $\bar{y}$ of $5 \cdot 5$. Part of this increase could be due to simple loss of sulfide as H_2S. By considering the facts that the maximum $\bar{y}$ in aqueous polysulfide solutions is 5, that no molecular S is present in the persulfide oil, and that essentially all of the sulfide in a Na_2S solution saturated in sulfur is bound to S, forming polysulfides, it becomes evident that the ratio of sulfur to sulfide in the polysulfide chains themselves has increased. This could take place by some such reaction as

$$H_2S_4(liq.) + H_2S_5(liq.) = H_2S_8(liq.) + H_2S(gas)$$
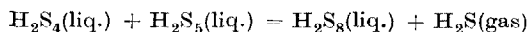
If a sodium polysulfide solution with a $\bar{y}$ of $1 \cdot 5$ is used the persulfide has a $\bar{y}$ of $4 \cdot 5$. In this case it is possible that the entire change could be due to simple loss of H_2S according to the equation,

$$2H^{+1} + S^{-2} = H_2S(gas)$$
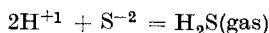
Probably there is some contribution from the other type of reaction, however.

Standard potential of the Ȧg/Ag₂S electrode and the free energy of formation of acanthite

Work by NODDACK and WRABETZ (1955) has shown that the S content of silver sulfide affects the potential of the Ag/Ag₂S electrode. Thus they found that silver sulfide which contained considerable amounts of excess S in solid solution gave potentials differing by as much as 50 mv from silver sulfide with no excess S. Any one electrode, however, gave reproducible potentials and did not drift with time. The significance of this observation for the present work is that, once any given Ag/Ag₂S electrode has been standardized in a solution of known activity of sulfide ion, it can be used with confidence to determine (S^{-2}) in an unknown solution. An unstandardized electrode, however, may give erroneous results.

GOATES *et al.* (1951) determined the free energy of silver sulfide from potentiometric measurements. They obtained -9.562 kcal/mole for the free energy of formation of Ag_2S as compared to the value of -9.62 kcal/mole reported by LATIMER (1952). The $E°$ given by GOATES *et al.*, for the reaction $2Ag^{+1} + S^{-2} = Ag_2S + 2e^{-1}$ is based on an assumed second dissociation constant of H_2S of 1×10^{-15}. Using instead $pK_2 = 13.50$ and their free energy value, the $E°$ becomes -0.6732 V.

SATO (1959) has measured the potentials of a number of sulfide electrodes. From the potential of the reduction reaction of silver sulfide in acid solution,

$$2Ag + H_2S = Ag_2S + 2H^{+1} + 2e^{-1},$$

he obtained -9.36 kcal/mole for the free energy of formation of Ag_2S. Using this figure and $pK_2 = 13.50$, the standard potential for the reaction $2Ag + S^{-2} = Ag_2S + 2e^{-1}$ was calculated as -0.6674 V.

Activity coefficients

Because of the rather strong solutions used in this investigation the choice of activity coefficients became important. The problems involved have been summarized by HARNED and OWEN (1958).

Equilibrium condition in alkali polysulfide solutions

In all of the work with polysulfides described above as well as in the present study, true equilibrium was not attained. This is due to the fact that the reactions,

$$4S_x^{-2} + 4(x-2)OH^{-1} + (5-x)H_2O = 2(x+1)HS^{-1} + (x-1)S_2O_3^{-2},$$
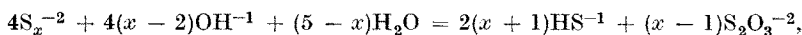
should proceed quantitatively to the right in alkaline solution if $x > 1$. Using the free energy value derived in this paper the equilibrium constant using S_5^{-2} ion is approximately 6×10^{52}. The free energy value given by MARONNY (1959b) yields approximately the same constant. At the measured pH for a sodium sulfide solution 1 M in sodium ion and saturated with sulfur this implies a ratio of thiosulfate to pentasulfide of about 10^{13}. The actual ratio obtained in the present study was about 0.07. As is evident from the Eh–pH diagram for S (cf. VALENSI, 1951 or GARRELS and NAESER, 1958), the thiosulfate should disproportionate also to give sulfide and sulfate.

APPARATUS

The measurements of potentials were made with commercial pH and mv meters and recorded every 18 sec on a multi-record potentiometer. The instruments were carefully adjusted to measure pH to ± 0.02 units and potentials to ± 2 millivolts. Measurements were made with high pH glass electrodes (Beckman type E-2) rated as having no appreciable sodium ion error, thimble style platinum electrodes, and billet style silver–silver sulfide electrodes against sleeve type saturated calomel electrodes. The glass electrodes were standardized with pH 7 and pH 9 buffers, and occasionally with pH 4 buffer as well. The platinum electrode potential was checked against Zobell solution (ZOBELL, 1946) which gives an Eh of 0.430 V at 25°C when freshly prepared. The Ag/Ag₂S electrode was prepared from a silver billet electrode by electrolysis in carefully prepared dilute Na_2S solution. The electrolysis was done with low current density for about twice as long as was required for the surface to become a uniform black. This electrode

was standardized against Na_2S solutions of known strength and periodically re-checked. The potentials were reproducible within a few mv for more than 12 months.

The solutions were placed in Pyrex containers of about 500 ml capacity with a flanged top, which was ground flat. The container was covered with a Plexiglas plate perforated with holes to fit rubber stoppers and sealed to the glass with beeswax or with silicone grease. The electrodes were led into the container through rubber stoppers which were tightly wedged into the holes. The solution was stirred by a teflon-coated magnetic bar and a magnetic stirrer. To prevent conversion of the calomel to mercuric sulfide and mercury by diffusing sulfide ions the calomel electrodes were generally placed in a second identical container and the two connected by a salt bridge containing $1 M NaNO_3$. The junctions were made by means of very finely drawn capillaries such that the flow of solution was no more than 1 ml/day and arranged so that the solution always flowed into the polysulfide container. To guarantee that no junction potentials arose in this way the calomel electrodes were occasionally transferred to the polysulfide container for short periods and the cell potentials measured.

A separate platinum electrode was used for a solution ground for each of the three meters. In addition a thermocompensator (resistance thermometer) was immersed in the solution and connected to the pH meter. There were thus six electrodes, a thermocompensator, a thermometer, and one end of the salt bridge in the polysulfide container, and three calomel electrodes and the other end of the salt bridge in the other container. The second container was filled by $1 M$ $NaNO_3$ solution.

EXPERIMENTAL METHODS

Preparation of Na_2S solutions

Stock solutions of Na_2S were prepared by dissolving clear washed crystals of $Na_2S \cdot 9H_2O$ (any yellow portions were discarded) in distilled water treated for two hours by rapidly flowing nitrogen. The nitrogen was obtained from commercial tanks and passed through a CO_2 absorbent, next through either a solution containing V^{+2} and V^{+3} (maintained in a reduced condition by amalgamated Zn and dilute H_2SO_4) or through copper turnings at $400°C$ to remove O_2, and finally through distilled water. This Na_2S solution was analysed for total S, thiosulfate, and sulfide.

Analysis of sulfide solutions

Total S was determined by either of two methods. In the first a slight excess of sodium hydroxide was added to an aliquot of the sulfide or polysulfide solution, and all sulfur species were oxidized to sulfate by an excess of H_2O_2. The solution was boiled to remove the excess peroxide, acidified by HCl, and the sulfate precipitated and weighed as barium sulfate. Later in the experimental work total S was determined by adding an aliquot of the sulfide or polysulfide to a measured excess of standard NaOH, and oxidizing by H_2O_2. The excess of hydroxide was then back titrated by standard HCl or H_2SO_4 after the method of Fehér and Berthold (1953a).

Thiosulfate was found by adding an aliquot to an excess of zinc acetate solution, filtering, acidifying by acetic acid, and titrating with iodine. The amount of S as thiosulfate was always less than 0·1 per cent of the total S. The amount of monosulfide was determined by adding an aliquot to an excess of acidified iodine solution, and back titrating with standard thiosulfate.

The total S estimated from the sum of that present as sulfide and thiosulfate in the Na_2S solutions (without excess S) agreed with the amount found by either direct method for total S.

Experiments with polysulfide solutions

In one set of experiments weighed amounts of flowers of sulfur were placed in polyethylene flasks and the air displaced by nitrogen. Then an aliquot of the stock solution of Na_2S, pipetted under a nitrogen atmosphere, and 10 ml of a suspension of N_2-treated distilled water and carefully precipitated acanthite* were added. Finally enough nitrogen-treated distilled water was added to dilute the sulfide to some desired strength. After stirring for 24 to 100 hr with a teflon coated bar and the magnetic stirrer, the solutions were transferred to an electrode container, either completely under a N_2 atmosphere or by pouring rapidly through a funnel while a N_2

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* The solubilities of acanthite in these solutions will be reported in a separate paper.

stream was played over the surface of the liquid. The electrode potentials were then measured. Both methods of transfer gave identical potential readings.

A second set of experiments was performed by adding the constituents directly to the electrode container. In this set the starting solutions were either standard NaOH, carbonate and oxygen free, or Na_2S. As before S, H_2O, and acanthite were added. In addition H_2S from a Kipp's generator was bubbled slowly through the solution. The supply of H_2S was either continued to saturation or stopped at some desired intermediate point. The potentials were recorded every 18 sec throughout the experiment. The H_2S was generated from sticks of ferrous sulfide in a N_2 atmosphere by N_2-treated H_2SO_4. The reducing effect of the H_2, doubtless produced from unsulfidized metallic iron, did not seem to affect the Eh in 2 days time. Hydrogen sulfide from commercial tanks was found to contain oxidizing substances which were not readily removed.

The solutions from both types of experiments were analyzed as above for total S, monosulfide, and thiosulfate. Since thiosulfate was always negligible, however, some of the solutions were not analysed for total S and monosulfide, but these quantities were calculated from the initial amounts of S and Na_2S.

EXPERIMENTAL RESULTS

The measured data are presented in Tables 1, 2, and 3, or are shown graphically in Figs. 1 and 2. Most of the Ag/Ag_2S electrode potentials in Table 1 (and a few
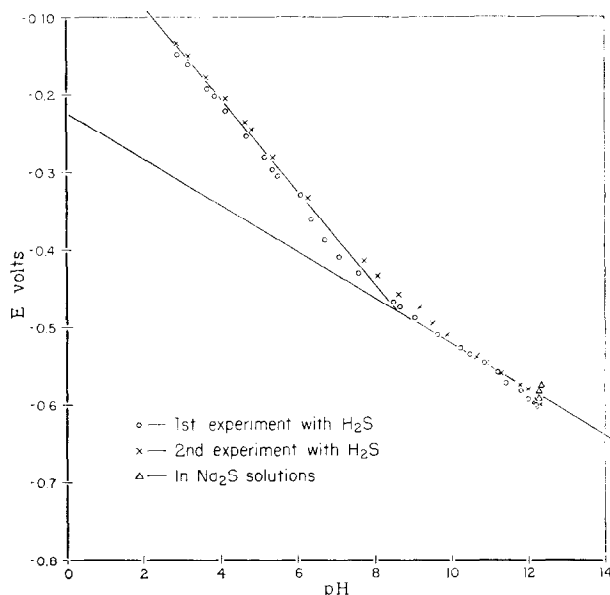

Fig. 1. Measured values of the potentials of the Ag/Ag_2S electrode vs. standard H_2 electrode for sulfide solutions 0·0900 M in Na^{+1}.

others) are also plotted in Fig. 3 against the neg. log of sulfide activity (calculated). The temperature was maintained at approximately 30°C by the heat generated from the motor in the stirrer.

Eh–pH values in sodium polysulfide solutions

The Eh and pH values are plotted against $\bar{y}$ in Fig. 4 for solutions 1 M in Na^{+1}. The solid curves were calculated according to the model derived later in this paper,

Table 1. Measurements with no S added (cf. also Figs. 1 and 2)

Moles $Na^{+1}/l.$	pH	E of Ag/Ag_2S-H_2 couple, V	Eh, V	$t°C$
1·000	13·20	−0·655 (low)		30
1·000	12·80	−0·639 (low)	−0·490	30·0
0·666	12·64*	−0·615	−0·344*	25
$0·370_4$	12·90	−0·607	−0·359	25
$0·256_6$	12·80	−0·604	−0·349 drifts to −0·324	25
$0·183_4$	12·66		−0·442	25
$0·177_6$	12·68	−0·596	−0·321	25
$0·124_0$			−0·474	25
0·1004	12·09	−0·582	−0·421	29·0
0·0986	12·50	−0·589	−0·312	25
0·0900	12·32	−0·584		25
0·0683	12·38	−0·582	−0·310	25
0·0380	12·15	−0·562	−0·291	25
0·0262	12·01	−0·558	−0·289	25
0·0180	11·78	−0·544		25
0·0180	11·86	−0·540		25
0·0180		−0·542		25

* Electrodes probably not immersed deeply enough.

Table 2. Measurements with S added to Na_2S solutions with no addition of H_2S.

Moles $Na^{+1}/l.$	pH	E of Ag/Ag_2S-H_2 couple, V	Eh, V	$\bar{y}$	$S_2O_3^{-2}$ moles/l.	$t°C$
1·000*	12·95	−0·638		1·5		25
1·000	12·86	−0·607	−0·466	2·0	0·023	31·5
1·000*	12·50	−0·625		2·0		30
1·000	12·88	−0·615	−0·442	3·0	0·010	30·0
1·000	12·55	−0·600	−0·437	3·0	0·011	30
1·000*	12·28	−0·607		3·0		30
1·000	12·50	−0·582	−0·420	3·5	0·015	32·8
1·000	12·28	−0·567	−0·401	4·0	0·007	30
1·000	12·37	−0·571	−0·401	4·0	0·007	30
1·000	12·20	−0·575	−0·400	4·0	0·009	30·5
1·000*	11·90	−0·571		4·0		30
1·000	11·75	−0·517	−0·353	4·5	0·011	30·5
1·000	11·34	−0·502	−0·316	4·9	0·004	31·0
1·000	11·00	−0·491	−0·310	4·9	0·023	30·5
1·000	11·25	−0·505	−0·317	4·9		30
1·000*	11·37	−0·522		4·9	0·004	30
0·600	12·50	−0·589	−0·443	2·5	0·008	33·5
0·600	12·35	−0·582	−0·436	3·0	0·010	34·5
0·600	11·80	−0·549	−0·388	4·0	0·006	34·8
0·600	10·33	−0·480	−0·302	4·9	0·006	35·0
0·200	12·05	−0·553	−0·406	3·0	0·006	32·0
0·200	11·53	−0·498	−0·364	4·0	0·006	32·5
0·200	11·59	− 0·513	−0·364	4·0	0·008	33·5
0·200	10·50	−0·462	−0·298	4·9	0·004	32·0

* These 5 sets of values derived from one experiment with successive additions of S; the entire set appears to give incorrect pH and/or pS values.
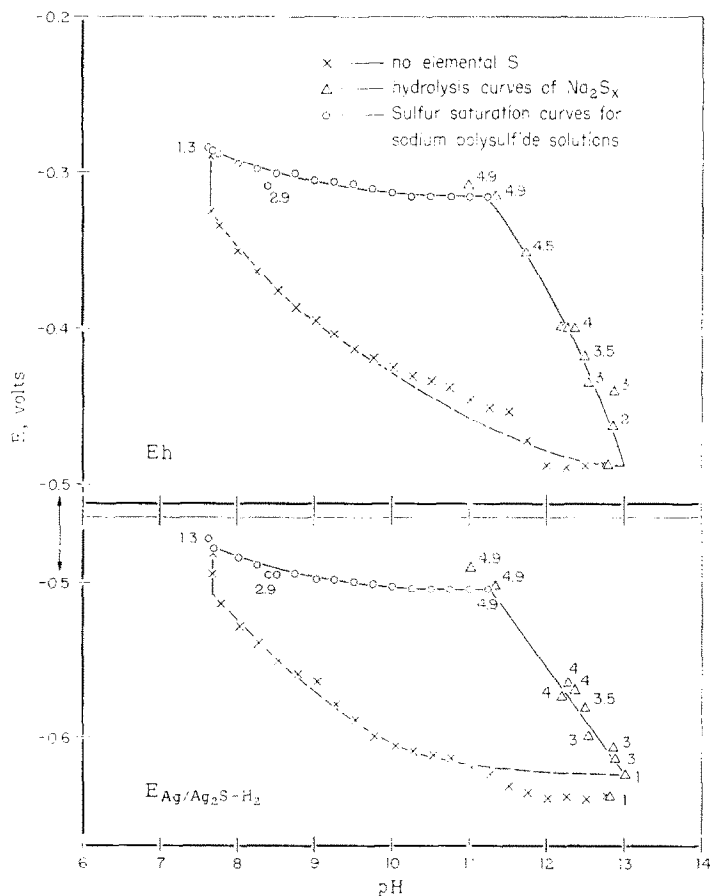
Fig. 2. Measured values of the potentials of the Ag/Ag_2S (lower set of curves) and smooth Pt (upper set) electrodes vs. standard H_2 electrode for sulfide and polysulfide solutions 1·0 M in Na^{+1}. Numbers indicate the $\bar{y}$ of the solutions.

Table 3. Measurements with addition of H_2S and saturated in S (cf. also Fig. 2)

Moles Na^{+1}/l.	pH	E of Ag/Ag_2S-H_2 couple, V	Eh, V	$\bar{y}$	$S_2O_3^{-2}$ moles/l.	$t°C$
1·000*	7·65	−0·478	−0·286	1·3	0·004	30·0
1·000*	7·62	−0·473	−0·284	1·3	0·013	25
1·000*	7·69	−0·482	−0·289	1·3	0·002	28·0
1·000	8·40	−0·495	−0·309	2·9	0·007	30
1·000	11·98	−0·589	−0·429	3·3†		30
0·100*	6·88	−0·429	−0·248	1·03	0·0006	25
0·100*	6·92	−0·424	−0·247	1·01	0·0005	29·5

* Saturated in H_2S.
† Not saturated in S.

and the dashed lines were taken from the calculated curves of PESCHANSKI and VALENSI (1949).

pH values in Na_2S *solutions*

In Fig. 5 the Na_2S hydrolysis pH values measured in this set of experiments are plotted. For comparison the pH's from the work of KONOPIK and LEBERL (1949) and of KUBLI (1946) are also represented. The solid line shows pH's calculated as
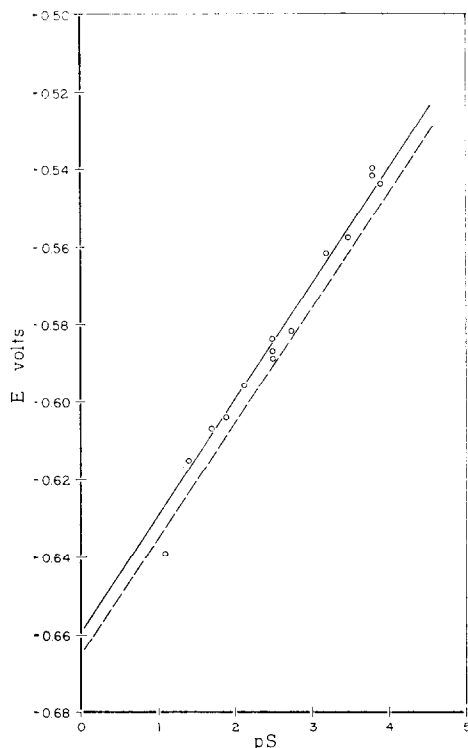

Fig. 3. Plot of pS vs. measured potentials of the Ag/Ag_2S electrode for Na_2S solutions of various concentrations.

described under the section dealing with activity coefficients. All data were recalculated to 25°C.

Temperature corrections

Recalculation to 25°C was done using the equation:

$$(H^{+1}) = \{K_W + \sqrt{K_W{}^2 + 4K_2K_Wc\gamma_{OH^{-1}}^2/\gamma_{S^{-2}}}\}/2\ c\gamma_{OH^{-1}} \tag{1}$$

The activity coefficient of HS^{-1} is taken as equal to that of OH^{-1}. Equation (1) was derived from the relations:

$$K_2 = (H^{+1})(S^{-2})/(HS^{-}) \qquad K_w = (H^{+1})(OH^{-1})$$
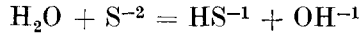$$c = [S^{-2}] + [HS^{-1}] \qquad \gamma_{OH^{-1}}[OH^{-1}] = (OH^{-1})$$
$$\gamma_{HS^{-1}}[HS^{-1}] = (HS^{-1}) \qquad \gamma_{S^{-2}}[S^{-2}] = (S^{-2})$$

and

$$[OH^{-1}] = [HS^{-1}]$$

The last expression is a consequence of the hydrolysis reaction

$$H_2O + S^{-2} = HS^{-1} + OH^{-1}$$

in which equal amounts of hydroxide and hydrosulfide are produced. By dividing both sides of Equation (1) by K_2 an expression is obtained in which the right hand
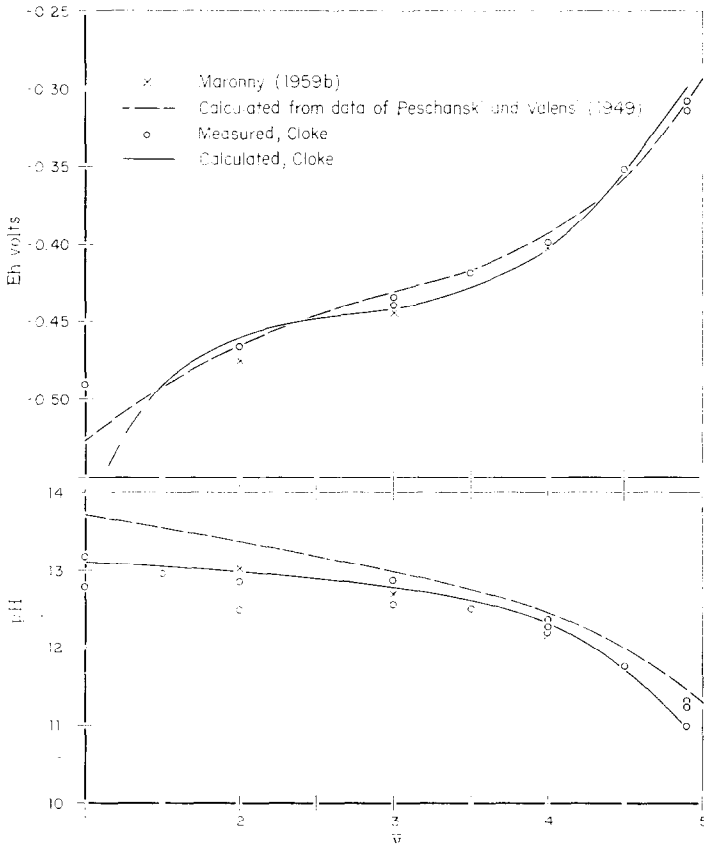

Fig. 4. Redox potential (Eh) and pH of Na_2S_x solutions 1·0 M in Na^{+1}.

member is practically constant since the ratio K_w/K_2 and the γ's change only very slowly with temperature. Writing:

$$(H^{+1})/K_2 = f(c),$$

where $f(c)$ is a function of concentration only, taking logs, and differentiating with respect to temperature, there results:

$$[d \ln (H^{+1})]/dT = (d \ln K_2)/dT$$

i.e. the change of pH with temperature is given closely by the change in pK_2. For a 5° temperature interval this is about 0·15 pH units.

Comparison of results of polysulfide studies with previous work

The agreement of the Eh values for polysulfide solutions (Fig. 4) with those given by PESCHANSKI and VALENSI (1949) is reasonably good, and except for points at $\bar{y} = 1$ the experimental measurements fall quite close to the curves. Theoretically at $\bar{y} = 1$ there should be no polysulfide species and the Eh should be very strongly negative. It would be limited only by the water–hydrogen couple, or determined by couples involving other species, such as thiosulfate. Presumably the wide
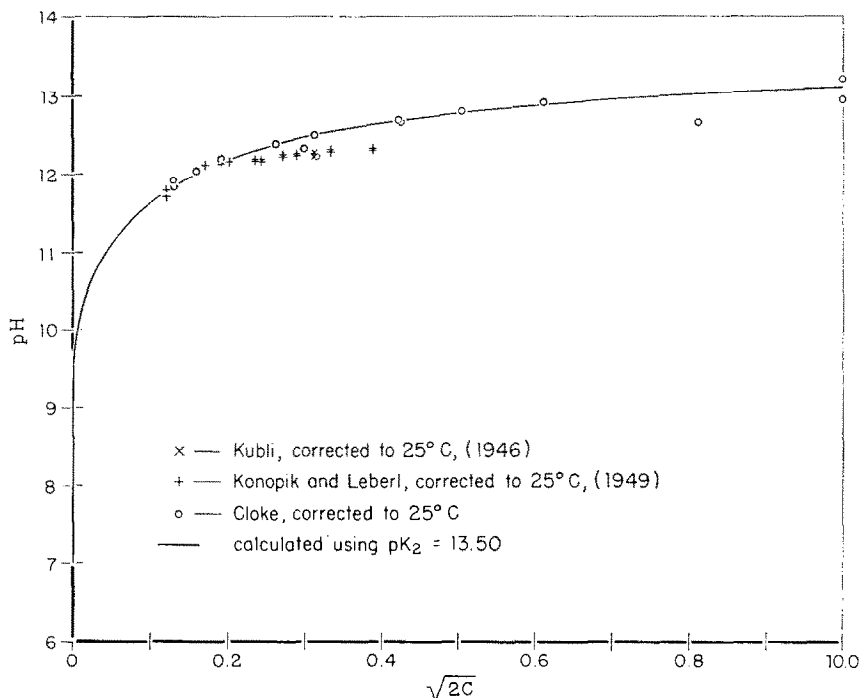

Fig. 5. Measured and calculated pH vs. $\sqrt{[Na^{+1}]}$ for Na_2S solutions. $\sqrt{[Na^{+1}]}$
is approximately the ionic strength for much of the graph.

variation in measured Eh values at very low $\bar{y}$ is due to small changes in the activities of these other species.

The agreement of pH values for polysulfide solutions calculated in this paper with those calculated by PESCHANSKI and VALENSI (1949) is quite poor. However, the measured pH's as reported in Table 1 correspond well with those calculated here and with the experimental data given by MARONNY (1959a, b) and by MARONNY and VALENSI (1955, 1956, 1957, 1958, 1959). The disagreement with PESCHANSKI and VALENSI arises largely from their use of $pK_2 = 14·90$.

Comparison of results of sulfide studies with previous work

The measured pH values for Na_2S solutions are shown in Fig. 5. The solid line which agrees well with the measurements was calculated using equation (1) with $pK_2 = 13·50$. The activity coefficients for this computation were taken from Fig. 6 using the uppermost curve for $\gamma_{OH^{-1}}$ and $\gamma_{HS^{-1}}$ and the upper $\gamma_{S^{-2}}$ line.

The pH values measured here for Na_2S solutions differ from the earlier work by 0·1 to 0·3 pH units. It is presumed that the previous work gave low pH readings. KUBLI (1946) used an ordinary glass electrode and corrected for sodium ion error. At high pH this sodium ion correction becomes large and uncertain. KONOPIK and LEBERL (1949) used colorimetric indicators; the precision of this method is less than that using potential measurements, and possible systematic errors in solutions
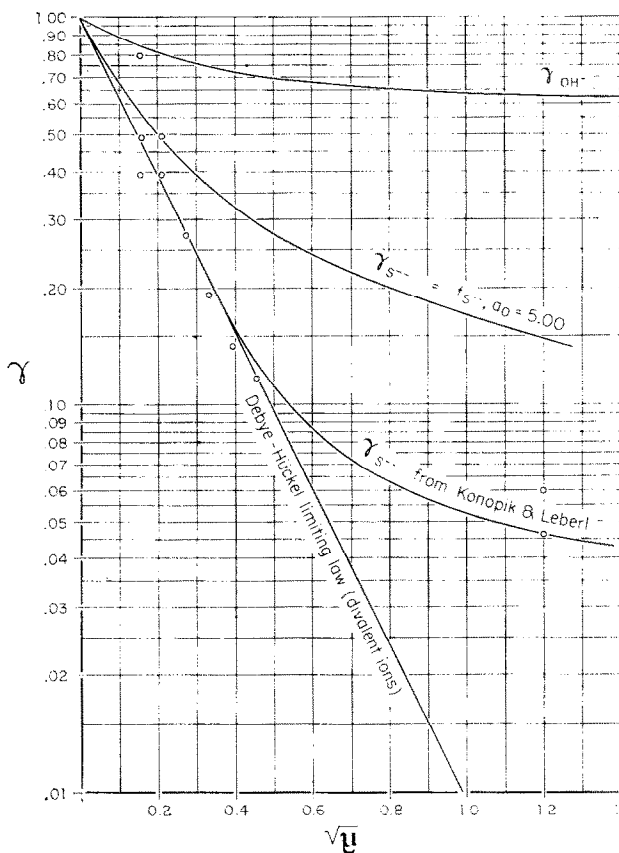

Fig. 6. Activity coefficients for OH^{-1} or HS^{-1} and for S^{-2} plotted on a log scale vs. $\sqrt{\mu}$. The points shown are calculated from pH measurements made by KONOPIK and LEBERL (1949), the value of 12·89 for pK_2 derived from these measurements by KURY, ZIELEN, and LATIMER (1953), and the $\gamma_{OH^{-1}}$ curve shown.

containing sulfide ion do not seem to have been thoroughly investigated. A projection of KONOPIK and LEBERL's data to 0·5 M gives a pH which is considerably lower than the measured values. It seems unlikely that errors in the present data could account for this great a discrepancy at the high concentrations.

Measurements of Ag/Ag$_2$S electrode potentials

Measurements of the potential of the Ag/Ag_2S electrode are plotted in Fig. 1 against the pH of the solution. Values of the free energy of formation of Ag_2S may

7

be obtained from these measurements. If the line of smaller slope in Fig. 1 is projected with the slope -0.0295 V/pH unit to pH = 0, the standard potential for the reaction

$$2Ag + HS^{-1} = Ag_2S + H^{+1} + 2e^{-1}$$
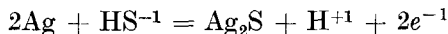
is found to be -0.272 V (corrected to 25°C; (HS^{-1}) is estimated at 0.045×0.74 moles/liter, where $0.045 = [HS^{-1}]$ and $0.74 = \gamma_{HS^{-1}}$). Taking $\Delta F^{\circ}_{HS^{-1}} = 3.00$ kcal/mole, $\Delta F^{\circ}_{Ag_2S}$ is calculated as -9.53 kcal/mole, in good agreement with GOATES *et al.* (1951).

The line of slope -0.059 V/pH unit in Fig. 1 lies too high, probably because of oxidation of sulfide to S (the S was observed) by H_2SO_4, and/or loss of H_2S to the overlying atmosphere. Consequently it could not be used to obtain a standard potential.

In Fig. 3 the measured potentials are plotted against activity of sulfide ion. This activity is calculated either from the measured pH or from equation (1) with $pK_2 = 13.50$, and use of the relations
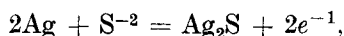
$$pH + pOH = 14.00,$$

$$pOH = pHS,$$

and $$pH + pS - pHS = 13.50$$

Projecting to pH = 0 with the theoretical slope of 0.0295 V/pS unit the standard potential for the reaction,

$$2Ag + S^{-2} = Ag_2S + 2e^{-1},$$

is obtained as -0.659 V. This corresponds to $\Delta F^{\circ}_{Ag_2S} = -9.07$ kcal/mole.

The overall agreement of the standard potential of the electrode Ag/Ag$_2$S with previously determined constants (GOATES *et al.*, 1951; SATO, 1959) indicates that the Ag/Ag$_2$S electrode is functioning properly and gives reproducible results.

For this electrode the two standardization procedures give slightly different standard potentials. It was, therefore, decided to use the average of the two free energies of formation, namely, $\Delta F^{\circ}_{Ag_2S} = -9.30$ kcal/mole. This gives E° for this electrode as -0.665 V. The corresponding line is dashed in Fig. 3.

ACTIVITY COEFFICIENTS

Mean salt approach

One of the most difficult problems in the interpretation of the data is the proper choice of activity coefficients in the strong solutions used. In the final analysis any choice of activity coefficients which is consistent with the pK_2 adopted gives the correct (within experimental error) sum of [HS^{-1}] and [S^{-2}], and gives equal calculated concentrations of HS^{-1} and OH^{-1}. For this work these are the only critical factors related to this problem.

Since only the mean ionic activity coefficients of salts can be measured directly, it is necessary to make some assumption as to how to split the activity coefficient of the cation from that of the anion. In dilute solutions this is usually done by assuming that with KCl the activity coefficient of potassium ion equals that of chloride ion. Activity coefficients of other ions may then be found from the equation

$\gamma_+{}^q \cdot \gamma_-{}^r = \gamma_\pm^{q+r}$ by assuming that the γ's for cations are independent of the particular anions present (except for their charge) and vice versa. Thus the activity coefficient for sodium ion may be estimated from the mean ionic activity coefficient of sodium chloride and the activity coefficient of chloride ion as obtained from potassium chloride.

Other approaches

With more concentrated solutions, however, many types of specific interaction, such as hydration, ion pair formation, change of the dielectric constant etc., become of importance and it becomes questionable whether the mean salt approach gives the proper interpretation (cf. HARNED and OWEN, 1958). To estimate the activity coefficient of hydrosulfide ion, the author has used three different lines of argument, all of which give reasonably consistent answers. Two of these deal mostly with modifications of the mean salt approach, taking into account similarities and differences of the ions involved. The arguments for the activity coefficients of sulfide ion are less satisfactory, but the relation chosen gives results in agreement with experimentally determined pH values.

(a) *Use of similarity of size and charge of* HS^{-1} *and* OH^{-1}. On the basis of the Debye–Hückel equation it is reasonable to expect hydroxide and hydrosulfide ions to have the same activity coefficients, since they have the same charge and KIELLAND (1937) gives the same a_0 for both. Probably, however, OH^{-1} is more hydrated than HS^{-1}. The crystal ionic radius of oxide ion is considerably smaller than that of sulfide ion. If they have the same effective radius in aqueous solution (presumably the addition of the proton will have little effect on the radius) the difference is probably due to water molecules being held more strongly to the hydroxide. According to ROBINSON and STOKES (1949) this hydration effect should increase the activity coefficient of hydroxide ion, but not of hydrosulfide because the crystal radius of sulfide ion is about the same as the radius of HS^{-1} as given by KIELLAND (1937).

On the other hand GIMBLETT and MONK (1954) have concluded that NaOH is partially associated whereas the hydroxides of potassium, rubidium, and cesium are not (for this purpose ion pair formation, localized hydrolysis etc., may be considered as special types of association). The effect of association is to decrease the stoichiometric activity coefficient. By considering the dissociation constants of H_2S and of H_2O it is seen that the attraction of hydrogen ion for sulfide is weaker than its attraction for oxide. By analogy it may be assumed that the attraction of sodium ion for sulfide is likewise weaker than the attraction of Na^{+1} for oxide. It follows that NaHS is probably more completely dissociated than is NaOH. The activity coefficient of HS^{-1} should, therefore, be unaffected by association just as it was unaffected by hydration.

If the effects of hydration and of association for hydroxide ion merely cancel, the approximation that $\gamma_{OH^{-1}} = \gamma_{HS^{-1}}$ should be valid. Going from KCl to KOH, or from RbCl to RbOH gives a fairly good idea of the large effect of hydration of OH^{-1} on the mean ionic activity coefficient in the absence of appreciable association. In the transition from NaCl to NaOH, however, there is practically no change of the mean ionic activity coefficient, which suggests that the hydration and association

do indeed cancel each other. These considerations imply that in strong solutions $\gamma_{OH^{-1}}$ in KOH solutions is not the same as $\gamma_{OH^{-1}}$ in NaOH solutions. Thus although $\gamma_{OH^{-1}}$ in KOH might be obtained directly by going from $\gamma_{\pm KCl}$ to $\gamma_{\pm KOH}$, the value of $\gamma_{OH^{-1}}$ in NaOH would remain unknown. To get $\gamma_{OH^{-1}}$ in NaOH each step of the substitutional chain must involve either no changes in hydration and association or compensating changes. This seems to be true for the sequence: $\gamma_{\pm KCl} = \gamma_{Cl^{-1}}$, $\gamma_{\pm NaCl}, \gamma_{Na^{+1}}, \gamma_{\pm NaOH}, \gamma_{OH^{-1}}$. (Note, also, that going from $\gamma_{\pm KCl}$ to $\gamma_{\pm KOH}$ involves an uncompensated change due to hydration.) $\gamma_{OH^{-1}}$ is then set equal to $\gamma_{HS^{-1}}$. These values, derived from data quoted by LATIMER (1952), were used in subsequent work for ionic strengths greater than 0·15.

(b) *Use of similarity of* HS^{-1} *and* Cl^{-1}. Another approach is to assume that the activity coefficient of HS^{-1} is the same as that for some other anion which has the same charge, and nearly the same size, hydration, etc. This seems to be the case for chloride ion. Writing $\gamma_{HS^{-1}} = \gamma_{Cl^{-1}} = \gamma_{\pm KCl}$ gives activity coefficients slightly lower than the first approach.

(c) *Use of modification of Debye-Hückel theory.* Finally the nature of various theoretical attempts to calculate activity coefficients in strong solutions was considered. According to MACINNES (1939) the mean distance of closest approach, a_0, is "equal to the sum of the radii of oppositely charged ions in contact." This means that to calculate the activity coefficient of hydroxide ion a_0 is not taken equal to the diameter of hydroxide, but the cation present (e.g. sodium ion) must first be known and then the average diameter of this cation and of hydroxide must be computed. Since the same must be done to get the activity coefficient of the cation, it follows that the appropriate a_0 is the same for both cation and the anion in this particular solution. If hydroxide and a different cation (e.g. potassium ion) are considered then the average diameter of this new cation and hydroxide must be used. For any specific symmetrical electrolyte (but not necessarily for mixtures) this means that by considering only the Debye-Hückel expression,

$$\log f_N = -A\, z^2 \sqrt{\mu}/(1 + B\, a_0 \sqrt{\mu})$$

the computed activity coefficient for the cation equals that of the anion. A change in the dielectric constant changes A and B, and may lead to additional terms in μ. Again, however, the dielectric constant affects both cation and anion activity coefficients exactly the same. Similarly ion-pair formation, association, localized hydrolysis etc., affect both cation and anion in the same way since each ion-pair, or associated molecule, in effect removes (for a symmetrical electrolyte) the same number of cations as it does anions from the solution. The hydration of ions according to the theory of ROBINSON and STOKES (1949) has two principal effects on the activity coefficient. The first is to decrease the activity of water, or conversely, to increase the apparent strength of the solute by removing water from the solvent and binding it to the solute. This increase of strength is obviously the same for the cation and the anion. The second effect is to increase the apparent diameter of the ions. Normally the cation seems to be more highly hydrated, but since only the average diameter of cation and anion is used, the effect is, nevertheless, the same for both. Thus, the interesting result emerges that the Debye–Hückel theory and all of the modifications just mentioned treat the anion

and cation of symmetrical electrolytes the same. It seems reasonable that any other effects not considered here will do likewise. It is then permissible to write $\gamma_{HS^{-1}} = \gamma_{\pm NaHS}$. Assuming as above that HS^{-1} is similar to Cl^{-1}, $\gamma_{\pm NaHS}$ may be set equal to $\gamma_{\pm NaCl}$. This approximation gives a curve slightly higher than the first method.

Activity coefficients in mixtures of NaOH and NaHS

The association constant of NaOH is about 5 (GIMBLETT and MONK, 1954). Thus there is very little association of Na^{+1} and OH^{-1} at pH values less than 13·0 even in solutions 1 M in sodium ion. Since only a small percentage of the water is bound to OH^{-1} at this or lower pH values, the decrease of activity of water is slight. The hydration does increase the effective diameter of the OH^{-1}.

Whatever the decrease in activity of water, the increase in strength of both HS^{-1} and OH^{-1} are in the same proportion. After the OH^{-1} is hydrated the size and charge of OH^{-1} are the same as for HS^{-1}. Because little of the OH^{-1} is associated with Na^{+1} under the experimental conditions there is no decrease in concentration of OH^{-1} due to ion-pair formation, localized hydrolysis, etc.; this also appears to be the case for HS^{-1}. Any changes in dielectric constant should affect both of these ions in the same way. Thus the Debye–Hückel equation or modifications of this equation ought to give the same activity coefficients for HS^{-1} and OH^{-1} for the solutions studied. Accordingly the curve for $\gamma_{OH^{-1}}$ was taken the same as that for $\gamma_{HS^{-1}}$. At ionic strengths less than 0·15 the Debye–Hückel equation, using $a_0 = 3·5$ Å as recommended by KIELLAND (1937) was adopted with the approximation that $\gamma_{HS^{-1}} = f_{HS^{-1}}$. At higher ionic strengths the first approximation mentioned above was used. This curve is shown in Fig. 6.

Activity coefficient of sulfide ion

The derivation of the activity coefficient for sulfide ion is less satisfactory. KIELLAND (1937) recommends the use of a_0 equal to 5·0 in the Debye–Hückel equation. However, as mentioned above, adoption of the value of $pK_2 = 12·89$ recommended by KURY, ZIELEN, and LATIMER (1953) and the use of their pH values in conjunction with the $\gamma_{HS^{-1}}$ curve of Fig. 6 produces the lower $\gamma_{S^{-2}}$ curve of Fig. 6. This curve corresponds to the Debye–Hückel equation with $a_0 = 0$ at ionic strengths less than 0·15. If the pH values obtained in this work, and $pK_2 = 12·89$ were utilized, a different $\gamma_{S^{-2}}$ curve lying above the $\gamma_{HS^{-1}}$ values would result (not shown). It is thus apparent that the calculated activity coefficients for sulfide ion are extremely sensitive to a small error of pH. Conversely, if the values of the activity coefficients are assumed, the calculated values of pK_2 are very sensitive to pH errors. For this work the stoichiometric activity coefficient has been estimated as equal to the rational activity coefficient and the latter calculated from the Debye–Hückel equation using $a_0 = 5·0$ (upper $\gamma_{S^{-2}}$ curve in Fig. 6.) This curve can also be obtained by taking a_0 somewhat smaller, then increasing $f_{S^{-2}}$ in accordance with the hydration effect and lowering it by converting to $\gamma_{S^{-2}}$. This curve and $pK_2 = 13·50$ give good agreement with the measured pH's.

Errors arising from incorrect choices of activity coefficients

Fortunately the sum of $[HS^{-1}]$ and $[S^{-2}]$ is not particularly sensitive to small errors in pH as long as consistent values for the γ's and pK_2 are employed. Thus this

sum calculated using $pK_2 = 12.89$ and the γ's derived from KONOPIK and LEBERL's (1949) data is almost exactly the same as the sum obtained using $pK_2 = 13.50$ and the γ's assumed in this paper. In a similar manner the calculated amount of HS^{-1} will always be the same as the calculated amount of OH^{-1}. If the pH measurements are consistently high, this will lead to a pK_2 that is too high and a pOH that is too low, if the assumed activity coefficient curves are not simultaneously changed. This leads to a change in the free energy of formation of sulfide ion, and this in turn to a change in the standard potential of the Ag/Ag_2S electrode. If this electrode is used to estimate sulfide ion activity, the pS obtained will then be too high. By inserting the activities of hydrogen and sulfide ions into the expression for the second dissociation constant for H_2S, with the new pK_2, a value of pHS is obtained which is too low. Calculation shows that this lowering of pHS is almost exactly the lowering of pOH. A similar result is obtained if the γ's are changed and pK_2 kept constant. In all subsequent work only the sum of $[HS^-]$ and $[S^{-2}]$, or the relative magnitude of $[HS^{-1}]$ and $[OH^{-1}]$ is of critical importance. As long as the activity coefficients are consistent with the accepted pK_2 the sum of $[HS^{-1}]$ and $[S^{-2}]$ will be correct, and $[HS^{-1}]$ will equal $[OH^{-1}]$.

Because the use of the upper $\gamma_{S^{-2}}$ curve in Fig. 6 and $pK_2 = 13.50$ gave consistent and reproducible results in agreement with experiments these values were adopted. This implies that any errors of pH due to oxidation, loss of H_2S etc., are consistent and are in some manner incorporated into the pK_2 and $\gamma_{S^{-2}}$ values chosen. This value of pK_2 lies between those of MARONNY (1959a) and of KURY, ZIELEN, and LATIMER (1953).

All other constants, such as $E°$ for the Ag/Ag_2S electrode, were calculated to agree with these choices.

Activity coefficients for polysulfides

Activity coefficients for polysulfide ions were calculated from the Debye–Hückel equation by choosing the a_0's approximately equal to chain length. For S_4^{-2}, S_5^{-2}, and S_6^{-2}, a_0's were taken as 10, 12, and 14 Å, respectively. These were estimated by taking the radii of the two sulfur atoms on the ends of the chain equal to that of S^{-2}, and the radii of intermediate sulfur atoms equal to that of elemental S. This corresponds to FEHÉR and BERTHOLD's (1954) observation that the molar volume of polysulfide ions can be estimated in a similar way. The length was found by assuming a zigzag chain with tetrahedral bond angles. MARONNY (1959b) used similar values for a_0. Any effects that might arise due to the separation of charge in the longer polysulfide chains have been assumed negligible.

CALCULATIONS BASED ON EXPERIMENTAL RESULTS

By proceeding to the interpretation of the experimental data a model for the distribution of various sulfide and polysulfide species in the solutions studied can be derived. The data for experiments where no H_2S was added will be considered first.

Absence of hydropolysulfide ions

From the measured pH, corrected to 25°C, and the value of pK_w, the pOH can be calculated directly. The measurements of potentials with the Ag/Ag_2S electrode,

with the $E°$ corrected to the temperature of measurement using entropy data from KURY, ZIELEN, and LATIMER (1953), are then employed to calculate pS. Since $d(pK_2)/dt \simeq d(pK_W)/dt$, $d(pS)/dt \simeq 0$. By combining this pS, the measured pH, and the value of pK_2 at 25°C, the pHS is obtained. As is shown in Figs. 7 and 8 pHS
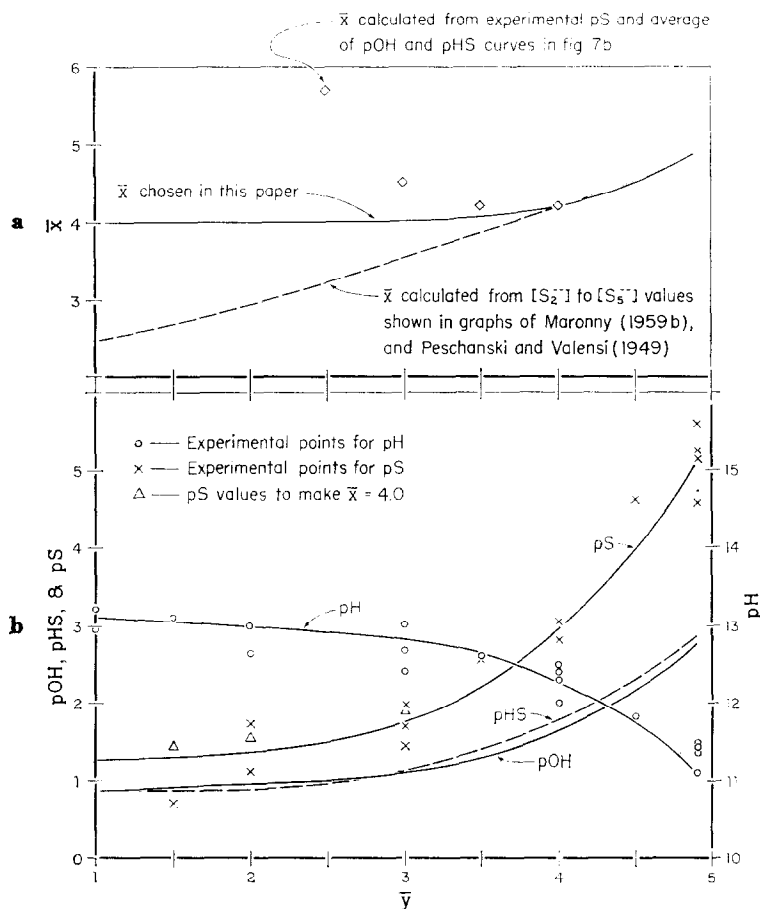

Fig. 7. (a) Plot of $\bar{x}$ vs. $\bar{y}$ for solutions 1·0 M in Na^{+1}. (b) Plot of experimentally determined pH and pS values (corrected to 25°C) vs. $\bar{y}$ in solutions 1·0 M in Na^{+1}. Curves for pH and pS are drawn to give the best fit with the experimental data. pOH is calculated from pH, and pHS is calculated from pH and pS.

equals pOH within the experimental error, but in Fig. 9 the agreement is quite poor. Ignoring this last plot, the data at molarities of sodium ion of 1·0 and 0·6 imply that no hydropolysulfides or hydrogen polysulfides are present. If they were, there should be additional hydroxide produced by the reactions:

(i) $S_x^{-2} + H_2O = HS_x^{-1} + OH^{-1}$,

(ii) $HS_x^{-1} + H_2O = H_2S_x + OH^{-1}$
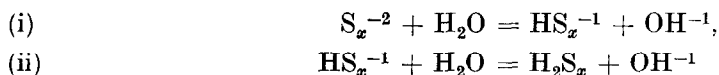
This result thus confirms the assumption of PESCHANSKI and VALENSI (1949) and of MARONNY (1959b) that hydropolysulfides are absent.

Calculation of $\bar{x}$

The procedure for calculating $\bar{x}$ is to subtract the amount of HS^{-1} and S^{-2} from the total S and monosulfide, respectively, and to compute the ratio of these two quantities. Since hydropolysulfide ions and hydrogen polysulfides are absent, the expression for $\bar{y}$ becomes

$$\bar{y} = \{[\text{HS}^{-1}] + [\text{S}^{-2}] + \sum_{x=2}^{\infty} x[\text{S}_x^{-2}]\}/\{[\text{HS}^{-1}] + [\text{S}^{-2}] + \sum_{x=2}^{\infty} [\text{S}_x^{-2}]\} \qquad (2)$$

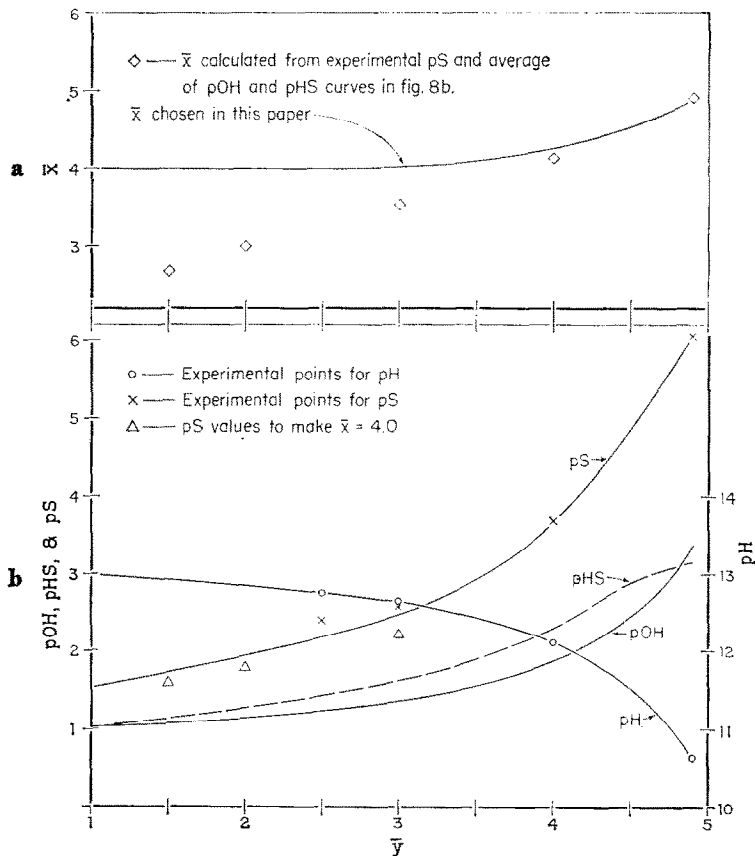From the calculations just made, we know the activity of both HS^{-1} and S^{-2}.

Fig. 8. (a) Plot of $\bar{x}$ vs. $\bar{y}$ for solutions 0·6 M in Na^{+1}. (b) Plot of experimentally determined pH and pS values (corrected to 25°C) vs. $\bar{y}$ in solutions 0·6 M in Na^{+1}. Curves for pH and pS are drawn to give the best fit with the experimental data. pOH is calculated from pH, and pHS is calculated from pH and pS.

From estimations of the ionic strength the activity coefficients are approximated and in turn first estimates of the concentrations of HS^{-1} and S^{-2}. It also follows from the previous calculations that [OH^{-1}] = [HS^{-1}]. By subtracting the sum of [HS^{-1}] and [S^{-2}] from the original concentration of Na$_2$S the concentration of polysulfide ion is obtained. This gives first estimates of the sum of the concentrations of divalent ions

and separately of the sum of the concentrations of univalent ions. This makes possible an improved estimate of ionic strength, and the cycle can be repeated until constant values are obtained.
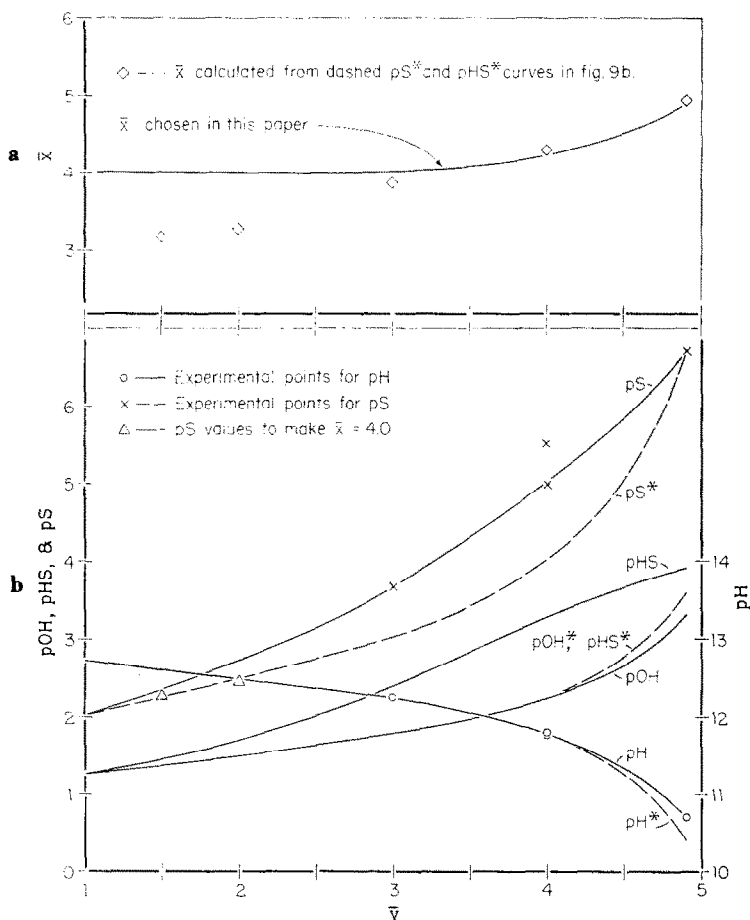

Fig. 9. (a). Plot of $\bar{x}$ vs. $\bar{y}$ for solutions $0 \cdot 2$ M in Na^{+1}. (b) Plot of pH, pS, pOH, and pHS (corrected to 25°C) vs. $\bar{y}$ for solutions $0 \cdot 2$ M in Na^{+1}. Solid curves for pH and pS are drawn to give the best fit to experimental data, and for pHS and pOH are calculated from pH and pS. The dashed pH* and pOH* lines are adjusted so as to give the measured pS at $\bar{y} = 4 \cdot 9$, assuming pHS = pOH. The dashed pOH* line is adjusted to agree with pOH*. pS* is calculated from the adjusted pH* and pHS* lines.

Subtracting the sum of $[HS^{-1}]$ and $[S^{-2}]$ from both numerator and denominator of the right hand member of equation (2) yields

$$\bar{x} = \sum_{x=2}^{\infty} x[S_x^{-2}] / \sum_{x=2}^{\infty} [S_x^{-2}] \tag{3}$$

This value of $\bar{x}$ is plotted in Fig. 7 for solutions 1 M in sodium ion ($0 \cdot 5$ M in monosulfide). It is assumed that the pH data are more reliable than the pS measurements. By correcting the pS values on the hypothesis that pOH = pHS the interesting

relation appears that $\bar{x}$ never decreases below 4 even for solutions with very low $\bar{y}$. Actually some of the originally calculated values at low $\bar{y}$ were much higher (up to 30), but by adjusting the experimental values of pH and pS to a small extent, as shown by triangles in Figs. 7, 8, and 9, the calculated $\bar{x}$ could be decreased sharply. This was done because it seemed quite unreasonable that $\bar{x}$ should increase as $\bar{y}$ decreased. The value of 4 was chosen as a reasonable value because it gave the best fit with the pH and pS values measured here. MARONNY's (1959b) pH data imply that $\bar{x}$ is higher than 4 at low $\bar{y}$, but his final graph of the distribution implies an $\bar{x} < 4$.

The values of $\bar{x}$ obtained differ markedly at low $\bar{y}$ from those derived from the graphical representations given by PESCHANSKI and VALENSI (1949) or by MARONNY (1959b) (cf. Fig. 7). If their total of $[HS^{-1}]$ and $[S^{-2}]$ is recalculated using $pK_2 = 13 \cdot 50$ in order to achieve consistency of pH, pS, and pHS values, it is found that a pH decrease of $0 \cdot 1$ and a pS increase of about $0 \cdot 2$ will convert the data given in the present paper so as to give their $\bar{x}$ curve. Thus $\bar{x}$ is extremely sensitive to small errors in pH and pS.

Comparison with work of Valensi and co-workers

The original experimental pH data of PESCHANSKI and VALENSI (1949) is internally inconsistent and differs markedly from that reported by MARONNY (1959a, b) and by MARONNY and VALENSI (1955, 1958, 1959). The data in the latter four papers agree closely with the present work. By using the latter pH data and pK_W, pOH is easily found. By assuming that pOH $=$ pHS and by using pK_2, pS is computed. Thus a change in pH is a measure of the change in the amounts of hydrosulfide and sulfide ions. The less the pH decreases, the less is the decrease in the concentrations of HS^{-1} and S^{-2}. It is seen from equation (2) with $\bar{y} = 2$, that

$$[HS^{-1}] + [S^{-2}] = \sum_{x=2}^{\infty} x[S_x^{-2}] - 2 \sum_{x=2}^{\infty} [S_x^{-2}],$$

and by using equation (3) that

$$[HS^{-1}] + [S^{-2}] = (\bar{x} - 2) \sum_{x=2}^{\infty} [S_x^{-2}]$$

There is also the relation

$$c = [HS^{-1}] + [S^{-2}] + \sum_{x=2}^{\infty} [S_x^{-2}]$$

Using this to eliminate $\sum_{x=2}^{\infty} [S_x^{-2}]$ the expression becomes

$$[HS^{-1}] + [S^{-2}] = (\bar{x} - 2)(c - [HS^{-1}] - [S^{-2}])*$$

The less the pH changes between $\bar{y} = 1$ and $\bar{y} = 2$ at fixed c, the smaller is the quantity $(c - [HS^{-1}] - [S^{-2}])$ and since $[HS^{-1}] + [S^{-2}]$ has changed only a little, the larger is $\bar{x}$. MARONNY's data show less change of pH from $\bar{y} = 1$ to $\bar{y} = 2$ than the data reported here. Therefore, $\bar{x}$ calculated from his data should be greater than 4 at $\bar{y} = 2$, not less as is implied by his final model which is reproduced here as Fig. 12. Partly because of this the value of $\bar{x}$ is taken as varying only between 4 and 5 in spite of its extreme sensitivity to small errors in pH.

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* More generally this equation is:

$$(\bar{y} - 1)([HS^{-1}] + [S^{-2}]) = (\bar{x} - \bar{y})(c - [HS^{-1}] - [S^{-2}])$$

Implications of $\bar{x} \geqq 4$

In order to get an average value of $x = 4$ various distributions can be postulated. There might be equal amounts of S_2^{-2} and S_6^{-2} with no intermediate polysulfides, or S_4^{-2} only, etc.

There are no gaps in the homologous series of hydrogen polysulfides (cf. FEHÉR *et al.*, 1956; FEHÉR and WINKHAUS, 1956). Because the polysulfide ions are chains it seems unlikely that the energy required to add or subtract a sulfur atom is very great. It therefore seems unlikely that gaps exist in the sequence of polysulfide ions. As a reasonable limiting case it may be assumed that S_2^{-2}, S_3^{-2}, S_4^{-2}, S_5^{-2}, and S_6^{-2} are all equal in amount (i.e. it seems unlikely that S_6^{-2} or S_5^{-2} are greater than S_4^{-2} at low $\bar{y}$ where $\bar{x} = 4$). In this case the amount of S_2^{-2} at low $\bar{y}$ is only 1/5 of the total amount of polysulfide ions. Since this total is small, as calculated by subtracting the sum of $[HS^{-1}]$ and $[S^{-2}]$ from initial sulfide, the amount of S_2^{-2} is at most small. The same applies to the amount of S_3^{-2} but not so strongly.

These relations suggest that both disulfide and trisulfide ions may be negligible in amount at low $\bar{y}$. At higher $\bar{y}$ they are expected to be less abundant because of reaction to form polysulfides containing more S. Since $\bar{x}$ varies only between 4 and 5 the further hypothesis is now adopted that only S_4^{-2} and S_5^{-2} are of importance, and this assumption is tested against the experimental data. With these postulates it is now possible to calculate the amounts of all the ions assumed to be in the solution. The amounts of S_4^{-2} and S_5^{-2} are found from the two equations,

(i) $$\bar{x} = \{4[S_4^{-2}] + 5[S_5^{-2}]\}/\{[S_4^{-2}] + [S_5^{-2}]\},$$

(ii) $$c - [HS^{-1}] - [S^{-2}] = [S_4^{-2}] + [S_5^{-2}]$$

All other concentrations are calculated as described above. The results are compiled in Table 4 for solutions 1 M in sodium ion.

Table 4

$\bar{y}$	$\gamma_{HS^{-1}}$	$\gamma_{S^{-2}}$	pHS	pS	$[HS^-]$	$[S^{-2}]$	$\bar{x}$ calc.	$c - [HS^{-1}] - [S^{-2}]$	$\bar{x}$ ass-umed	$[S_4^{-2}]$	$[S_5^{-2}]$	Eh	E_4°	E_5
1·0	0·640	0·155	0·93	1·31	0·184	0·316	—	0	—	0	0	—	—	—
1·5	0·638	0·153	0·965	1·43	0·170	0·243	3·88	0·087	4·00	0·087	0	−0·485	−0·525	
2·0	0·637	0·152	1·02	1·55	0·150	0·185	4·04	0·165	4·00	0·165	0	−0·466	−0·514	
3·0	0·636	0·149	1·20	1·90	0·099	0·084	4·15	0·317	4·03	0·307	0·010	−0·438	−0·503	−0·490
4·0	0·635	0·147	1·70	3·00	0·031	0·007	4·25	0·462	4·25	0·346	0·116	−0·402	−0·510	−0·503
4·5	0·634	0·146	2·28	4·10	0·008	0·001	4·57	0·491	4·57	0·211	0·280	−0·354	−0·503	−0·498
4·9	0·634	0·145	3·00	5·50	0·002	—	4·91	0·498	4·91	0·044	0·454	−0·314	−0·511	−0·511
													−0·508	−0·500₅

These values of $[S_4^{-2}]$ and $[S_5^{-2}]$ and the experimental Eh uncorrected for temperature variation (cf. Fig. 4) are used to calculate approximate standard potentials for the two reactions,

(i) $$4S^{-2} = S_4^{-2} + 6e^{-1}$$

(ii) $$5S^{-2} = S_5^{-2} + 8e^{-1}$$

The standard potentials thus calculated from the equations,

$$\text{Eh} = E_4{}^\circ + (0\cdot059/6) \log [(S_4{}^{-2})/(S^{-2})^4] \tag{4}$$

and

$$\text{Eh} = E_5{}^\circ + (0\cdot059/8) \log [(S_5{}^{-2})/(S^{-2})^5] \tag{5}$$

are also compiled in Table 4. The nearly constant values over practically the entire range of $\bar{y}$ lends considerable support to the simple model assumed. The average value of $E_4{}^\circ$ is $-0\cdot508$ V and of $E_5{}^\circ$ is $-0\cdot500_5$ V.

Calculated maximum $\bar{y}$

(a) *With no H_2S added.* From these average values it is a simple matter to obtain an approximate standard free energy of the reactions, and in turn to use the free energy of formation of S^{-2} and get that of $S_4{}^{-2}$ and of $S_5{}^{-2}$.

A further test of the hypothesis can be made by noticing that at saturation in sulfur both HS^{-1} and S^{-2} are negligible. Moreover, the reaction,

$$S_4{}^{-2} + S = S_5{}^{-2}$$
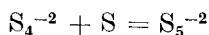
is involved since solid S is present. From the free energies just obtained the equilibrium constant for this reaction is found to be $2\cdot88$. This is the ratio of $S_5{}^{-2}$ to $S_4{}^{-2}$ and since these are the only sulfur species presumed to be present implies a $\bar{y}$ of $4\cdot72$. This is less than the observed maximum, and implies that the model is not yet complete. The same objection can be applied to the work of PESCHANSKI and VALENSI (1949), of MARONNY (1959b), and of MARONNY and VALENSI (1955, 1958, 1959). To correct this discrepancy it was necessary to assume that there is also some hexasulfide, $S_6{}^{-2}$, in the solution. Thus one of the basic assumptions of the work by VALENSI and co-workers was not confirmed.

The necessity for including $S_6{}^{-2}$ can also be shown in another way. The reaction $S^{-2} + 3\ S_5{}^{-2} = 4\ S_4{}^{-2}$ is always involved in polysulfide solutions. By using the relations:

(i) $$\Delta F^\circ = n\mathcal{F}E^\circ, \quad \Delta F^\circ = -RT \log_e K, \text{ and}$$

(ii) $$(S_4{}^{-2})^4/(S^{-2})(S_5{}^{-2})^3 = K,$$

the equation

$$24(E_4{}^\circ - E_5{}^\circ)/0\cdot059 = 4 \text{ p}S_4{}^{-2} - 3 \text{ p}S_5{}^{-2} - \text{p}S^{-2} = \text{p}K$$

is derived. When the solution is saturated in S, pS can be estimated with the Ag/Ag_2S electrode. Because $\bar{y}$ is approximately $4\cdot9$ and only $S_4{}^{-2}$ and $S_5{}^{-2}$ are presumed to be present, it follows that:

$$9[S_4{}^{-2}] = [S_5{}^{-2}] \tag{6}$$

Use of $\gamma_{S_4^{-2}} = 0\cdot320$ and $\gamma_{S_5^{-2}} = 0\cdot375$ for solutions 1 M in Na^{+1} gives the values $\text{p}S_4{}^{-2} = 1\cdot796$ and $\text{p}S_5{}^{-2} = 0\cdot773$. Taking $\text{p}S^{-2} = 5\cdot5$ from Table 4 gives $\text{p}K = -0\cdot635$, or

$$E_4{}^\circ - E_5{}^\circ = -0\cdot0016 \text{ V} \tag{7}$$

This calculated difference of the E°'s is markedly smaller than the difference of

0·006 V determined here from the experimental data or the difference of 0·005 V derived from MARONNY's (1959b) data. It is precisely this very small difference of two relatively large numbers that makes the problem of finding the correct distribution of polysulfide species so difficult.

It is assumed that at the least

$$E_5° - E_4° = 0·004 \text{ V} \tag{8}$$

The standard potential of the reaction,

$$S^{-2} = S + 2e^{-1}, \tag{9}$$

can be obtained from the second dissociation constant of H_2S and the standard free energy of formation of HS^{-1} ion. This potential, $E_I°$, is $-0·46444$ V. (The last 2 places are not significant, but are useful for consistency in avoiding errors in the calculations due to rounding.)

(b) *Saturated in H_2S assuming no HS_x^{-1}*. From the reaction, $S_4^{-2} + S = S_5^{-2}$, the values of $E_4°$, $E_5°$, $E_I°$, and Eqns. (4) and (5) it is now possible to derive the relation:

$$4E_5° - 3E_4° = -0·49462 \text{ V}, \tag{10}$$

as follows. Multiplying Eqns. (4) and (5) by 6 and 8 respectively, and converting to neg. log. units gives:

$$6Eh = 6E_4° - 0·059pS_4^{-2} + 4 \times 0·059pS^{-2} \tag{11}$$

$$8Eh = 8E_5° - 0·059pS_5^{-2} + 5 \times 0·059pS^{-2} \tag{12}$$

The Nernst equation corresponding to reaction (9) is multiplied by 2 to obtain:

$$2Eh = 2 \times -0·46444 + 0·059pS^{-2} \tag{13}$$

Adding Eqn. (11) and (13) and subtracting Eqn. (12) gives

$$0·059(pS_5^{-2} - pS_4^{-2}) = 8E_5° - 6E_4° + 2 \times 0·46444 \tag{14}$$

From Eqn. (6) and the activity coefficients of pentasulfide and tetrasulfide ions it is found that $pS_5^{-2} - pS_4^{-2}$ equals $-1·02312$ when an 0·5 M solution of Na_2S is saturated in S. Introducing this into Eqn. (14) and simplifying gives Eqn. (10).

Solving Eqn. (8) and (10) yields $E_5° = -0·50662$ and $E_4° = -0·51062$. These values lie below final estimates made here and those calculated from MARONNY's (1959b) free energy values. For the reaction, $S^{-2} + 4S = S_5^{-2}$, the relation,

$$pS_5^{-2} - pS = 8(E_5° - E_I°)/0·059 = -5·72 \tag{15}$$

is valid as long as sulfide ion, pentasulfide ion, and solid S are present at equilibrium. Therefore, it may be used for Na_2S solutions saturated in both S and H_2S. Experimentally, for 1 M Na^{+1} the pH is found to be 7·65 and $\bar{y} = 1·29$. For a pH of 7·65 the relation, $pS = pHS + 5·85$, follows from the use of the second dissociation constant of H_2S. Substituting this expression for pS into Eqn. (15) gives

$$pS_5^{-2} - pHS = 0·13 \tag{16}$$

At this pH, and with solutions saturated in S, the only ions present in appreciable amount (ignoring for the moment HS_5^{-1}, HS_4^{-1}, etc.) are Na^{+1}, HS^{-1}, S_4^{-2}, and S_5^{-2}. Since electrical neutrality must be maintained, the relation

$$[Na^{+1}] = 1 \cdot 000 = [HS^{-1}] + 2[S_4^{-2}] + 2[S_5^{-2}] \tag{17}$$

must hold. Eqn. 16, after the activity coefficients have been estimated, gives the ratio of $(HS^{-1}):(S_5^{-2})$, and Eqn. (6) gives that of $(S_4^{-2}):(S_5^{-2})$. Substituting these ratios into Eqn. (17), it is found that $[HS^{-1}] = 0 \cdot 266$, $[S_4^{-2}] = 0 \cdot 037$, and $[S_5^{-2}] = 0 \cdot 330$. These values yield a $\bar{y}$ of 3·26, which is much too large. By introducing S_6^{-2} this discrepancy can be removed.

(c) *Saturated in H_2S assuming the presence of HS_x^{-1}.* It follows from Eqn. (17) that if hydropolysulfides are present at pH 7·65 the amounts of hydrosulfide, tetrasulfide, and pentasulfide must be less than computed. The ratios of these last three ions, however, are not changed. An extreme case exists if the only anion in the solution is HS_2^{-1}. In this case the $\bar{y}$ would be 2·0; it follows that addition of HS_2^{-1} to any polysulfide solution tends to bring the $\bar{y}$ to 2·0. Thus the assumption that HS_2^{-1} is present would decrease the $\bar{y}$ of 3·26, calculated above, but would not bring it to 1·29 as required by the experimental observations. If the $\bar{y}$ as calculated, assuming the absence of hydropolysulfides, were between 1·29 and 2·00, the inclusion of any hydropolysulfide in the computations would worsen the agreement between experiment and hypothesis. Evidently the introduction of hydropolysulfides into the present discussion will not remove the discrepancies observed.

Final approximation of standard potentials and $\Delta F°$'s of S_4^{-2}, S_5^{-2}, and S_6^{-2}

The only explanation that the present writer found to be satisfactory was to assume the presence of S_6^{-2}. By estimating $E_5°$ and $E_4°$ from the data, except for that at $\bar{y} = 4 \cdot 9$ and then estimating the amount of S_6^{-2} needed to bring $\bar{y}$ up to 4·9 at saturation in S (no H_2S added) a preliminary estimate of $E_6°$ was obtained. By using this estimate for calculations at pH 7·65 (saturated in S and H_2S) corrections could be estimated, and the corrected values used for the case where no H_2S was added. By recycling in this manner estimates were finally obtained which were consistent with all the experimental data. These estimates are as follows:

$$E_4° = -0 \cdot 502; \qquad 4S^{-2} = S_4^{-2} + 6e^{-1}$$
$$E_5° = -0 \cdot 494; \qquad 5S^{-2} = S_5^{-2} + 8e^{-1}$$
$$E_6° = -0 \cdot 486; \qquad 6S^{-2} = S_6^{-2} + 10e^{-1}$$

Estimates of $\Delta F°$ for S_2^{-2} and S_3^{-2}.

By assuming an upper limit of about 0·001 M for the concentrations of disulfide and trisulfide ions their free energies of formation can be estimated. The concentrations of S_2^{-2} and S_3^{-2} cannot be higher without controverting earlier assumptions, and may be far less. These and other data are compiled in Table 5. In Fig. 10 the free energies are plotted against the number of S atoms/ion.

Calculations of distribution of polysulfide ions

Having derived values of the free energies of all ions present in these solutions, it is now possible to calculate the distribution of species throughout the pH range

investigated entirely from theoretical considerations. Since S_2^{-2} and S_3^{-2} are very small in amount, they may be omitted from the equations without serious error. It was possible to get agreement with the experimental data at pH 7·65 without introducing any hydropolysulfides, and consequently these are also presumed to be

Table 5

ion	$\Delta F^{\prime \circ}$	E_x°; reaction	E°; reaction	ΔF° from MARONNY (1959b)
S^{-2}	21·42	—	$-0 \cdot 46444$; $S^{-2} = S + 2e^{-1}$	21·958
S_2^{-2}	22·7 $\pm$ 3·0	$-0 \cdot 436$; $2S^{-2} = S_2^{-2} + 2e^{-1}$	$-0 \cdot 492$; $S_2^{-2} = 2S + 2e^{-1}$	19·749
S_3^{-2}	21·0 $\pm$ 3·0	$-0 \cdot 469$; $3S^{-2} = S_3^{-2} + 4e^{-1}$	$-0 \cdot 455$; $S_3^{-2} = 3S + 2e^{-1}$	17·968
S_4^{-2}	16·29 $\pm$ 0·10	$-0 \cdot 501_5$; $4S^{-2} = S_4^{-2} + 6e^{-1}$	$-0 \cdot 353$; $S_4^{-2} = 4S + 2e^{-1}$	16·615
S_5^{-2}	15·97 $\pm$ 0·10	$-0 \cdot 494_0$; $5S^{-2} = S_5^{-2} + 8e^{-1}$	$-0 \cdot 346$; $S_5^{-2} = 5S + 2e^{-1}$	15·689
S_6^{-2}	16·36 $\pm$ 0·10	$-0 \cdot 486_4$; $6S^{-2} = S_6^{-2} + 10e^{-1}$	$-0 \cdot 355$; $S_6^{-2} = 6S + 2e^{-1}$	($>17 \cdot 0$?)*

* If less than 17·0 appreciable amounts would be present at saturation in S.
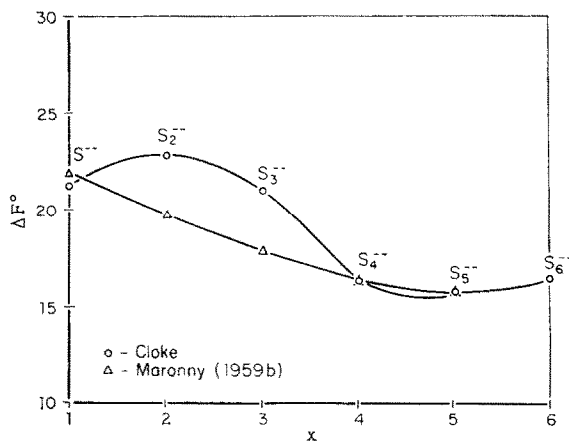

Fig. 10. Plot of Gibbs free energy of formation of sulfide and polysulfide ions vs. no. of S atoms in ion.

negligible. From the free energies the following equilibrium constants were evaluated:

$$(H^{+1})(HS^{-1})/(H_2S) = K_1 = 10^{-6 \cdot 99}, \tag{18}$$

$$(H^{+1})(S^{-2})/(HS^{-1})/ = K_2 = 10^{-13 \cdot 50}, \tag{19}$$

$$(H^{+1})(OH^{-1}) = K_W = 10^{-14 \cdot 00}, \tag{20}$$

$$(S_5^{-2})^3(S^{-2})/(S_4^{-2})^4 = K_5' = 10^{-3 \cdot 23} \tag{21}$$

$$(S_6^{-2})^4(S^{-2})/(S_5^{-2})^5 = K_6' = 10^{-5 \cdot 33} \tag{22}$$

In addition there are within the experimental error the two relations:

$$[Na^{+1}] = [OH^{-1}] + [HS^{-1}] + 2[S^{-2}] + 2[S_4^{-2}] + 2[S_5^{-2}] + 2[S_6^{-2}] \tag{23}$$

and $\bar{y} = \{[HS^{-1}] + [S^{-2}] + 4[S_4^{-2}] + 5[S_5^{-2}] + 6[S_6^{-2}]\}/$

$$\{[HS^{-1}] + [S^{-2}] + [S_4^{-2}] + [S_5^{-2}] + [S_6^{-2}]\} \tag{24}$$

This amounts to 7 eqns. in 10 unknowns since the activity coefficients are known. An additional eqn. is readily obtained by specifying the concentration, i.e. the molarity of sodium ion. The choice of the two remaining eqns. depends on the circumstances.

Calculation of the hydrolysis curve was made by writing

$$[OH^{-1}] = [HS^{-1}], \tag{25}$$

and either assigning a definite value to $\bar{y}$ or specifying that the solution is saturated in S. In the latter case the reaction $S_4^{-2} + S = S_5^{-2}$ and the corresponding eqn.,

$$(S_5^{-2})/(S_4^{-2}) = K_5'' = 1.74, \tag{26}$$

are both valid. The constant for the reaction $S_5^{-2} + S = S_6^{-2}$ can be obtained from equations (21), (22), (26).

Along the S saturation curve use was made of Eqn. (26) and the pH specified. At the acid end of this curve the pressure of H_2S was specified instead of pH. For

Table 6

$\bar{y}$	$[S_6^{-2}]$	$[S_5^{-2}]$	$[S_4^{-2}]$	$[S^{-2}]$	$[HS^{-1}]$	$[H_2S]$	pS_6	pS_5	pS_4	pS	pHS	pH_2S	pH	$[Na^{+1}]$	Eh
					Hydrolysis Curve, $[OH^{-1}] = [HS^{-1}]$										
4.9	0.108	0.234	0.158	—	0.002	—	1.34	1.06	1.30	5.25	2.88	7.01	11.12	1.0	−0.308
4.5	0.044	0.189	0.258	0.001	0.008	—	1.73	1.15	1.09	4.13	2.32	7.01	11.69	1.0	−0.350
4.0	0.010	0.104	0.343	0.010	0.034	—	2.38	1.41	0.96	2.84	1.67	7.01	12.33	1.0	−0.400
3.0	0.002	0.038	0.279	0.081	0.099	—	3.15	1.84	1.05	1.91	1.20	7.01	12.80	1.0	−0.437
2.0		.013	0.148	0.191	0.149	—	3.85	2.32	1.32	1.54	1.02	7.01	12.98	1.0	−0.454
					S saturation curve										
4.5	0.102	0.221	0.149	—	0.055	—	1.37	1.08	1.32	5.27	1.46	4.16	9.69	1.0	−0.308
4.0	0.093	0.205	0.137	—	0.130	—	1.40	1.12	1.36	5.31	1.08	3.36	9.27	1.0	−0.306
3.0	0.074	0.159	0.107	—	0.320	0.002	1.51	1.22	1.46	5.41	0.69	2.48	8.78	1.0	−0.303
2.0	0.044	0.095	0.064	—	0.594	0.011	1.73	1.44	1.68	5.63	0.42	1.72	8.29	1.0	−0.297
1.3	0.016	0.036	0.024	—	0.849	0.056	2.15	1.87	2.11	6.06	0.26	1.00	7.72	1.0	−0.284
					$\bar{y} = 4.5$ curve										
4.5	0.057	0.204	0.229	—	0.018	—	1.62	1.12	1.14	4.42	1.92	5.93	11.00	1.0	−0.339
4.5	0.088	0.219	0.170	—	0.046	—	1.43	1.09	1.27	5.03	1.53	4.54	10.00	1.0	−0.316
					$\bar{y} = 4.0$ curve										
4.0	0.029	0.160	0.272	0.001	0.077	—	1.91	1.22	1.06	3.81	1.31	5.32	11.00	1.0	−0.362
4.0	0.062	0.195	0.191	—	0.106	—	1.58	1.14	1.21	4.67	1.17	4.18	10.00	1.0	−0.330
					$\bar{y} = 3.0$ curve										
3.0	0.004	0.063	0.302	0.026	0.195	—	2.76	1.62	1.01	2.40	0.90	5.91	12.00	1.0	−0.417
3.0	0.012	0.102	0.259	0.003	0.247	—	2.28	1.42	1.08	3.30	0.80	4.81	11.00	1.0	−0.383
3.0	0.032	0.139	0.188	—	0.282	—	1.87	1.28	1.22	4.25	0.75	3.76	10.00	1.0	−0.347
3.0	0.050	0.154	0.145	—	0.302	—	1.67	1.24	1.33	4.82	0.72	3.13	9.40	1.0	−0.325
					$\bar{y} = 2.0$ curve										
2.0	0.001	0.028	0.196	0.055	0.423	—	3.29	1.98	1.20	2.07	0.57	5.58	12.00	1.0	−0.432
2.0	0.004	0.050	0.180	0.007	0.517	—	2.74	1.72	1.23	2.98	0.48	4.49	11.00	1.0	−0.397
2.0	0.012	0.074	0.140	—	0.545	—	2.28	1.55	1.34	3.96	0.46	3.47	10.00	1.0	−0.359
2.0	0.028	0.094	0.094	—	0.572	0.002	1.92	1.45	1.52	4.94	0.44	2.45	9.00	1.0	−0.322

solutions saturated in H_2S but unsaturated in S the pressure of H_2S and the $\bar{y}$ were assigned. For those solutions which do not correspond to any of these situations $\bar{y}$ and pH were specified. Thus in all cases it is possible to choose 10 eqns. in 10 unknowns. These were solved by the method of successive approximations by substituting into each eqn. in turn and making appropriate adjustments until all 10 were satisfied. The results are compiled in Table 6 for solutions 1 M in sodium ion.

This data can be plotted in various ways. Three of the more interesting methods are shown in Figs. 11, 13, and 14. In Fig. 11 the concentrations of the various ionic
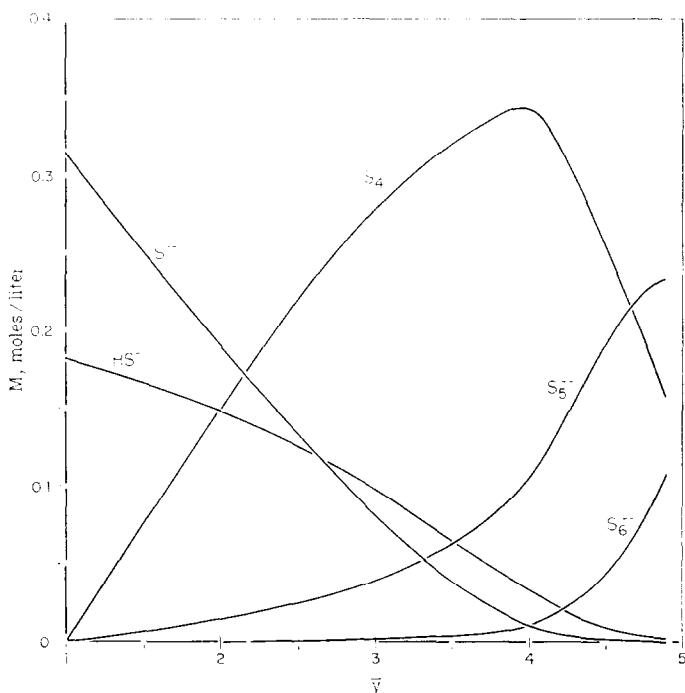
Fig. 11. Distribution of sulfur species on hydrolysis curve
of 0·5 M sodium polysulfide solutions.

species are plotted for the hydrolysis of sodium polysulfides as a function of $\bar{y}$. For comparison Fig. 12 shows the distribution as given by MARONNY for a concentration in sodium ion of 0·186 M. Although S_2^{-2} and S_3^{-2} are undoubtedly present, the work reported here suggests that they are negligible in amount. The entire difference between Figs. 11 and 12 rests on a difference of only 0·1 pH and a small discrepancy between the observed and calculated (assuming no S_6^{-2}) maximum $\bar{y}$ values. It seems reasonable that the actual distribution lies somewhere between these two models.

Figure 13 shows the computed equilibrium concentrations of the various sulfide species in polysulfide solutions at pH 10 as a function of $\bar{y}$. The shift in the maximum for S_4^{-2} to $\bar{y} = 3.5$ is particularly interesting. At lower pH values this intermediate maximum disappears entirely and the concentration of S_4^{-2} increases continuously from $\bar{y} = 1$ to a maximum where the solution is saturated in S.

8

In Fig. 14 the changes in concentrations of S species are shown at a constant $\bar{y}$ of 4·0 as the pH changes from that on the S saturation curve (pH 9) to that on the hydrolysis curve (pH 12·33).

DISCUSSION

The present study has led to a new interpretation of the relative amounts of polysulfide ions in sodium polysulfide solutions. In spite of this the measured pH and Eh values correspond well with those reported previously by MARONNY
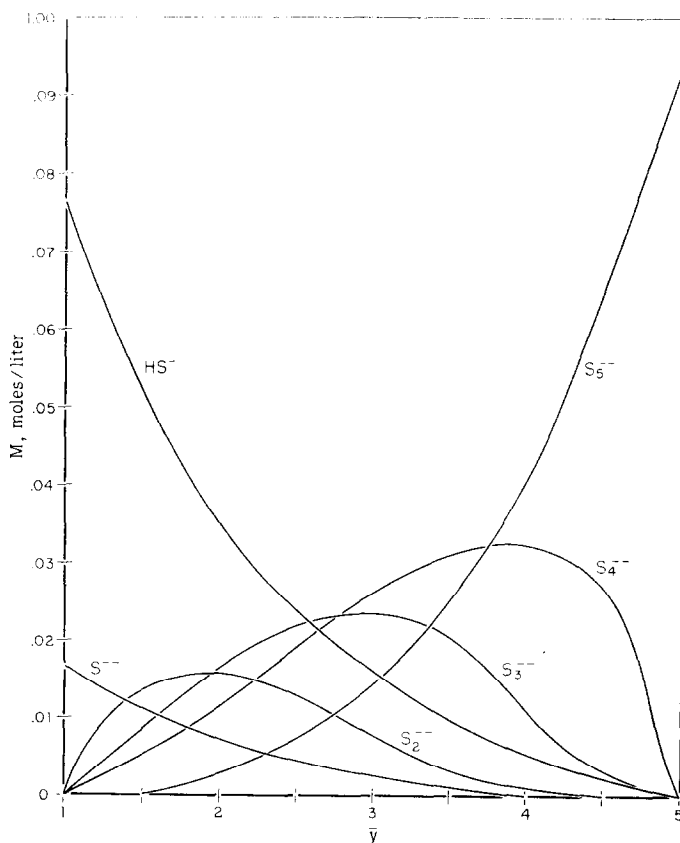

Fig. 12. Distribution of sulfur species on hydrolysis curve of 0·093 M sodium polysulfide solutions after MARONNY (1959b).

(1959a,b) or by MARONNY and VALENSI (1959), and the free energies of formation of the higher polysulfide ions do not differ greatly from MARONNY's (1959b) values. The difference in interpretation rests on quantities that are difficult to measure so that it seems worthwhile to consider the problem from other points of view.

In this respect it is interesting to consider the work of FEHÉR et al. As mentioned above, when he added sodium polysulfide solutions to concentrated HCl, he did not obtain any H_2S_2 or H_2S_3 as determined by Raman spectra (FEHÉR and BAUDLER, 1949) in the resulting oils even though the $\bar{y}$ of the initial polysulfide solution was
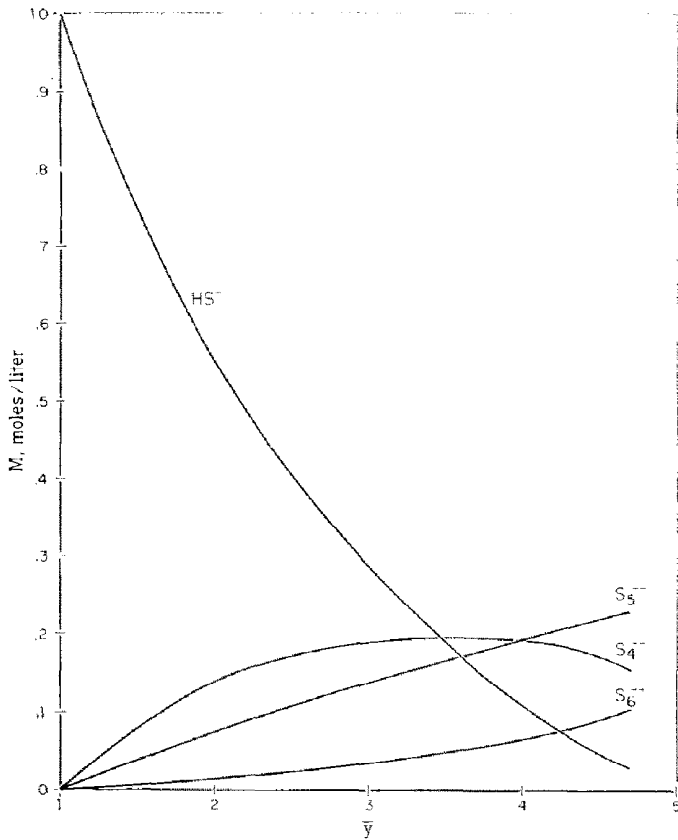
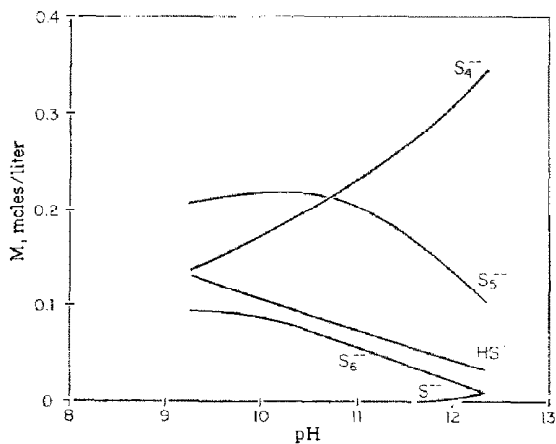Fig. 13. Distribution of sulfur species at pH 10 in sodium polysulfide solutions 1·0 M in Na^{+1}.

Fig. 14. Distribution of sulfur species for $\bar{y} = 4·0$ as a function of pH in sodium polysulfide solutions 1·0 M in Na^{+1}.

low. In terms of the distribution suggested here this is to be expected since there is no appreciable amount of S_2^{-2} or S_3^{-2} ion in the initial solution. In terms of MARONNY's distribution, however, rather large amounts of both S_2^{-2} and S_3^{-2} must be completely and rapidly converted to H_2S and H_2S_4 or H_2S_5. FEHÉR and co-workers (e.g. FEHÉR and BAUDLER, 1947, 1949) on the other hand found this type of splitting reaction to take place slowly. There is no doubt that some splitting does occur, however, as is evident from the fact that some of the persulfide oils have $\bar{y}$ values up to 5·5 or 6. These relations do lend more support to the present model than to MARONNY's.

In an attempt to verify the distribution proposed, absorption spectra of poly-sulfide solutions with $\bar{y}$'s of 2, 3, and 4 were made. The results were not very satisfactory due to the rapid oxidation to S at the dilution required to transmit any light at all at the absorption peaks. One broad peak was found at about 310 mμ and a second about one half as strong at about 365 mμ. They were in the same positions for all three solutions. FEHÉR et al. (FEHÉR and BAUDLER, 1947, 1949; FEHÉR and WINKHAUS, 1956) found the Raman spectra of H_2S_4 and H_2S_5 were very similar to each other, and to higher sulfanes but differed sharply from those of H_2S_2 and H_2S_3. By analogy it might be expected that the absorption peaks of S_4^{-2} and S_5^{-2} are similar to each other but differ from those of S_2^{-2} and S_3^{-2}. Since no shifts were found in the peaks, the absorption data lend a little support to the proposed distribution.

FEHÉR and his co-workers have also concluded that the polysulfides are chain structures. Moreover, as seems very reasonable the properties of the hydrogen polysulfides (or sulfanes) are smooth, approximately linear functions of the chain length or become more and more alike as the length increases. A reasonable extrap-olation of MARONNY's (1959b) free energy data can be made in keeping with this principle by referring to Fig. 10. The estimate thus obtained for the free energy of formation of hexasulfide ion is about 15·4 kcal/mole. This value, however, implies that S_6^{-2} is present in solutions saturated in sulfur to an even greater extent than in the distribution proposed here.

The author feels that the available evidence favors the distribution and free energy values proposed here more strongly than the corresponding ones of MARONNY. Perhaps a study using Raman spectra, or an investigation of maximum $\bar{y}$ values in dioxane-water solutions would help to clarify the problem.

SUMMARY

Calculations based on potential measurements with glass, platinum, and silver–silver sulfide electrodes have led to a different interpretation of the distribution of polysulfide ions in aqueous solution than that proposed previously. This leads to values of the free energy of formation differing from those of MARONNY by 180 cal for S_5^{-2} to 3000 cal for S_3^{-2}. The changes in distribution even though very marked are based on small differences in pH or in the maximum $\bar{y}$. Analogies to the work with hydrogen polysulfides favor the free energy values proposed here.

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