for interpretation of the physical properties as basic data of the cobaltous oxide system.

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Equilibria Involving Polysulfide Ions in Aqueous Sulfide Solutions up to 240°

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The solubility of elemental sulfur in near-neutral aqueous sulfide solutions was determined from 20 to 200°. The resulting polysulfide solutions contain an approximately equimolar mixture of tetra- and pentasulfide ions with hydropolysulfide ions likely to be present only in very small concentrations. The equilibrium constants governing the formation and rearrangement reactions of the four polysulfide ions S_nS^{2-}, with $n = 1–4$, expressed in terms of m_{SH^-} and m_{OH^-}, show only little variation with temperature. Above 150° the dissociation of polysulfide ions into radicals, S_2^- or S_3^-, and disproportionation into sulfide and thiosulfate become significant. The stability diagram, constructed by use of the equilibrium constants derived, shows that in near-neutral sulfide solutions polysulfide ions are stable with respect to this disproportionation up to 240°; at pH's above 8, however, polysulfide ions become metastable, even at room temperature. Sulfite and sulfate ions apparently are not formed in significant amounts during the disproportionation of polysulfide over the range of conditions studied.

Introduction

The solubility of sulfur in aqueous hydroxide[1] and sulfide[2,3] solutions has been investigated for temperatures up to 80°. The resulting solutions were reported[4] to contain higher polysulfide ions S_nS^{2-} with $\bar{n}$, the average number of sulfur atoms per polysulfide ion, ranging from 3.7 to 4.4 at room temperature. In all these studies hydropolysulfide ions were assumed to be absent. An investigation into the temperature dependence[5] of polysulfide equilibria up to 80° indicated only minor variations in the equilibrium constants governing the rearrangement reactions between the various polysulfide ions. At elevated temperatures polysulfide ions were found[6,7] to disproportionate into thiosulfate and monosulfide (H_2S + SH^-), with the rate and degree of disproportionation proportional[8] to the hydroxide concentration. Based on a previous study[9] supplying information on the equilibrium distribution of polysulfide ions at room temperature, the present work extends quantitative investigations into the effect of temperature on the stability of polysulfide solutions to 240°.

Experimental Section

Experimental procedures were similar to those described in previous studies.[9,10] Starting solutions were prepared by mixing measured amounts of stock solutions of NaHS (0.5 *m*), Na_2S_4 (0.033 *m*), $Na_2S_2O_3·5H_2O$ (0.1 *m*), Na_2SO_3 (0.1 *m*), Na_2SO_4 (0.1 *m*), HCl (0.5 *m*), and NaCl (2.0 *m*) and water to give 50 ml. The NaHS solutions were prepared by bubbling H_2S from a tank into 0.5 *m* NaOH solution. Excess H_2S was removed by purging the saturated solution with purified nitrogen.

All operations were carried out under nitrogen mainly by use of Schlenk-tube techniques. The concentrations of the stock solutions were checked by standard analytical methods. The ionic strength dependence of the equilibrium constants was determined by varying the amount of NaCl added from 0 to 2 *m*, with most measurements carried out at a constant ionic strength of 0.4 *m*, uncorrected for ionic association.

Spectra. Spectroscopic measurements were carried out by use of a gold-lined, high-temperature cell with a solution path length l of 0.80 cm between silica windows as previously described.[11] Polysulfide concentrations were determined by use of molar absorptivities[9] at wave numbers of 2.50 μm^{-1} (waves per micrometer) for the tetrasulfide ion of ϵ_3 1140 and the pentasulfide ion of ϵ_4 2000 and for the supersulfide ion[12] at 1.68 μm^{-1} of ϵ_b 2400. All molar absorptivities were assumed to remain constant with temperature. For the sulfur solubility measurements a small amount of excess elemental sulfur (*ca.* 50 mg) was placed into the cell cavity. In these and the disproportionation measurements, the solution in the cell was replaced by a weak sulfide solution after the cell had cooled down to 80° after a high-temperature run, in order to avoid the deposition of elemental sulfur onto the cell windows. Variations in the distribution of H_2S between liquid and vapor space within the cell with temperature were taken into account by use of the relationship $y_g/y_l = 0.22K_H(1/f - 1/d)/T$, where y_g and y_l are the fractions of H_2S in the gaseous and liquid phases, K_H is the Henry law constant[13] for H_2S at a given temperature, f is the filling factor of the cell, 0.7 for the cell 70% filled with solution at room temperature, and d is the density of the solution at the corresponding temperature.

Temperatures in the cell were measured with a chromel–alumel thermocouple to within 1°. The spectrophotometer used was the Zeiss PM QII with the monochromator M4 QIII.

Results

On heating a sulfide solution at a pH of around 7 at 25°, containing a small amount of zerovalent sulfur, partly present in the form of elemental sulfur and polysulfide, from room temperature to 240°, the color of the solution changes from a deepening yellow through green to blue; at temperatures above 200° this color again starts to fade with the solu-

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tion becoming almost colorless at 240°. On lowering the temperature all of the above changes may again be observed in reverse order. Figure 1 shows absorption spectra of such a solution measured at approximately 25° intervals. With polysulfide ions expected to play a central role in all the equilibria associated with the color changes, first an attempt is made to identify the nature of polysulfide species present in these near-neutral solutions over the temperature range investigated.

Protonation of Species Present in Polysulfide Solutions at Lower pH's. The reaction of elemental sulfur with aqueous sulfide solutions to form polysulfide ions can be described by the equation

$$nS + SH^- + (1-p)OH^- \rightleftarrows H_pS_nS^{p-2} + (1-p)H_2O \tag{1}$$

with p representing the number of protons attached to the species giving rise to the yellow color and the absorption band at 2.5 μm^{-1} of these solutions. With the activities of water and elemental sulfur taken to be unity, n initially assumed to remain constant, and after substituting $A_{2.5}/\epsilon_n l$ for $m_{H_pS_nS^{2-}}$ in the logarithm of the equilibrium expression for reaction 1, $\log (A_{2.5}/m_{SH^-})$ was differentiated with respect to $\log m_{OH^-}$ to yield the relationship

$$\frac{d \log (A_{2.5}/m_{SH^-})}{d \log m_{OH^-}} = 1 - p = \sigma_p \tag{2}$$

which allows the value of $1 - p = \sigma_p$ to be determined from the slope σ of a plot of $\log (A_{2.5}/m_{SH^-})$ *vs.* $\log m_{OH^-}$ for solutions of varying alkalinity. $A_{2.5}$ represents the absorbance of polysulfide ions at 2.5 μm^{-1}. From the least-squares slope of 1.023 close to unity obtained for a series of solutions at 25° with pH's from 6.4 to 7.9 as shown in Figure 2, the value of p was found to be zero. The optical absorption at wave numbers below 3.0 μm^{-1} in aqueous polysulfide solutions, therefore, can safely be considered to be largely due to doubly charged polysulfide ions S_nS^{2-}, with hydropolysulfide ions HS_nS^- either virtually absent or absorbing only at higher wave numbers. However, even in this latter case the sharp breaks in plots of $\log A_{2.5}$ *vs.* $\log (m_{SH^-}m_{OH^-})$ indicate that the amount of protonated polysulfide species present during the reaction of elemental sulfur with near-neutral sulfide sulfide solutions has to be small. On acidifying a polysulfide solution, the absorbance at 2.5 μm^{-1} increases slightly, due to conversion[9] of tetrasulfide into pentasulfide, until elemental sulfur starts to appear. From then on $\log A_{2.5}$ behaves in a manner corresponding to that shown in Figure 2.

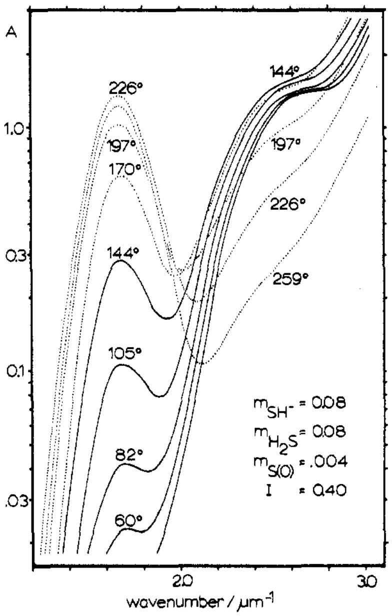

Figure 1. Absorption spectra of polysulfide solutions containing 0.004 m zerovalent sulfur and 0.16 m monosulfide at a room-temperature pH of 7.0, as a function of temperature (l = 0.80 cm).

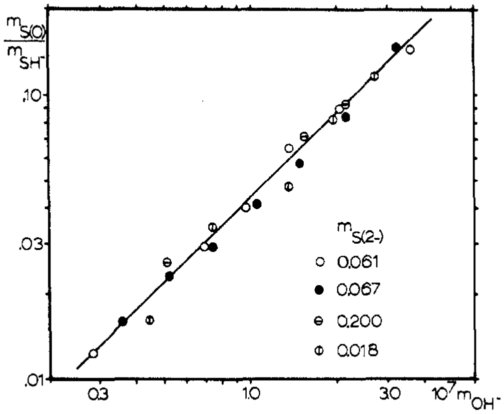

Figure 2. Plot of $\log (m_{S(0)}/m_{SH^-})$ *vs.* $\log m_{OH^-}$ at 25°. $m_{S^{2-}}$ is defined by eq 17.

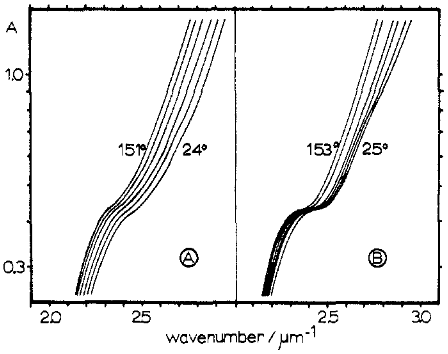

Figure 3. Absorption spectra of polysulfide solutions with log B values of 1.0 (A) and 4.0 (B) from room temperature to about 150° in approximately 25° intervals.

Temperature Dependence of Polysulfide Equilibria. Of the three polysulfide equilibria described in a previous study[9] only those between the lower polysulfides S_nS^{2-} with n = 1-3 could directly be investigated at elevated temperatures. The close similarity between the absorption spectra of tetra- and pentasulfide, already impeding the accurate determination of $K_{3/4}$ at room temperature,[9] made its determination at elevated temperatures impossible. By use of the equilibrium constants derived earlier,[9] solutions containing close to equal amounts of adjoining polysulfide ions at room temperature were selected. Any variation in $K_{n/m}$ with temperature then can be expected to be reflected in changes in the relative strength of the characteristic absorptions of the species S_nS^{2-} and S_mS^{2-}. The somewhat surprising result is that on heating solutions with log B values close to 4.0 and 1.0, where $B = m_{SH^-}m_{OH^-}/m_{S(0)}$, containing approximately equal amounts of di- and trisulfide or tri- and tetrasulfide ions, respectively, no significant changes in the relative strength of the absorption of the two predominant species could be detected (Figure 3). At temperatures up to about 150° only a slight shift of the entire spectrum toward lower wave numbers was observed, at higher temperatures disproportionation of the polysulfide ions to colorless products led to a gradual reduction in the absorption over the visible and near-uv region of the spectrum. With u_1, u_2, and u_3 representing the fractions of zerovalent sulfur present[9] in the form of the polysulfide ions SS^{2-}, S_2S^{2-}, and S_3S^{2-}, the equilibrium constants

$$K_{1/2} = 2u_1^2/u_2B \tag{3}$$

and

$$K_{2/3} = 9u_2^3/8u_3^2B \tag{4}$$

may be considered to be largely unaffected by changes in temperature, as $B = m_{SH^-}m_{OH^-}/m_{S(0)}$ too remains practically constant with temperature at the high pH's required. The associated enthalpy changes, $\Delta H_{n/m}$, for these reactions, therefore, are very small; "extrapolating" these findings to the similar tetrasulfide-pentasulfide equilibrium, the constant

$$K_{3/4} = 64u_3^4/81u_4^3B \tag{5}$$

may also be assumed to show little change with temperature. Indirect support for this assumption is provided by the findings of a previous investigation[12] where the dissociation of tetrasulfide into supersulfide ions, S_2^-, at 160° was used to estimate values of $\bar{n}$, the average number of atoms of zerovalent sulfur per polysulfide ion, as a function of solution pH. By recalculating these results in terms of $B = m_{SH^-}m_{OH^-}/m_{S(0)}$ for a temperature of 160° the values of $\bar{n}$ for $\log B$ values at around -4.0 are found to be 3.0-3.2, very close to that determined for such solutions at room temperature. In the following calculations the equilibrium constants $K_{n/m}$, therefore, were taken to remain constant with increasing temperature.

Solubility of Sulfur in Aqueous Sulfide Solutions at Elevated Temperatures. By use of previous findings[3,9] and those derived above, the solubility of zerovalent sulfur in aqueous sulfide solutions can be described by the equation

$$K_s = \frac{m_{S(0)}}{m_{SH^-}m_{OH^-}} = \frac{1}{B} \tag{6}$$

With $m_{S(0)}$ calculated from $m_{S(0)} = A_{2.5}/\epsilon_{\bar{n}}ld$ by initially assuming $\epsilon_{\bar{n}} = (\epsilon_3 + \epsilon_4)/2$, the value for $K^0{}_s$, at 25° and extrapolated to zero ionic strength, was found to be $(2.1 \pm 0.3) \times 10^5$, with the dependence of K_s on the molal ionic strength I given by $\log K_s = 5.32 + 0.31\sqrt{I}$.

In the determination of the equilibrium constants $K_{n/s}$ governing the formation of a particular polysulfide ion (n) S_nS^{2-} in aqueous sulfide solution in contact with excess elemental sulfur (s), only the formation of penta- and tetrasulfide ions was considered.[9] Thus with $\bar{n} = \Sigma nu_n$, together with $u_3 + u_4 = 1$ and $B^0{}_s = 1/K^0{}_s$ inserted into

$$K^0{}_{3/4} = 64(4-\bar{n})^4/81(\bar{n}-3)^3B^0{}_s = 1.2 \times 10^5 \tag{7}$$

the value for $\bar{n}$ was found to be 3.48, close to that used in the initial estimation of $\bar{n}$, thus rendering iterations to obtain a consistent set of values unnecessary. For such a saturated solution, found to contain equal amounts of tetra- and pentasulfide ions, the equilibrium constants, expressed in terms of activities

$$K^0{}_{n/s} = \frac{a_{S_nS^{2-}}}{a_{SH^-}a_{OH^-}} \approx \frac{u_n}{nB^0{}_s} = \frac{u_nK^0{}_s}{n} \tag{8}$$

for the formation of tetrasulfide and pentasulfide are seen to be $K^0{}_{3/s} = 3.5 \times 10^4$ and $K^0{}_{4/s} = 2.6 \times 10^4$ at 25°, respectively.

As shown above changes in temperature are likely to have only a small effect on the relative proportions of the various polysulfide ions present in solutions of a given B value. Any variation with temperature in $B^0{}_s = 1/K^0{}_s$, therefore, can be assumed to be due to a change in $\bar{n}_s$, the average number of atoms of zerovalent sulfur per polysulfide ion at saturation. With $m_{S(0)} = A_{2.5}/\epsilon_{\bar{n}}ld$, the influence of changes in $\bar{n}$ on $\epsilon_{\bar{n}}$, the average molar absorptivity of the polysulfide mixture at 2.5 μm^{-1}, was taken into account by employing an iterative procedure. With $\epsilon_{\bar{n}}$ initially assumed to be $(\epsilon_3 + \epsilon_4)/2$, the resulting values of $m_{SH^-}{}^2K_w/m_{S(0)}m_{H_2S}K_1 = B$ calculated for given buffer ratios of m_{SH^-}/m_{H_2S} and temperatures then were inserted into eq 7 to obtain corrected values of $\bar{n}$ and hence corrected values of $\epsilon_{\bar{n}} = (4-\bar{n})\epsilon_3 + (\bar{n}-3)\epsilon_4$. K_w and K_1 represent the first ionization constants of water and H_2S, respectively. After two iterations the values for $\bar{n}$ converged to within 0.01 unit. Again the effect of temperature on K_s is very small leading to variations in $\bar{n}$ from 3.48 at 25° to 3.55 at 80° and 3.40 at 180° for solutions with an ionic strength up to 0.4. At temperatures above 150° the formation[12] of radical ions S_n^- becomes significant. If the supersulfide ion S_2^- is assumed to predominate, the amount of zerovalent sulfur present in solution is given by $m_{S(0)} = \Sigma nm_{S_nS^{2-}} + 1.5m_{S_2^-}$, and the equilibrium expression describing the formation of this blue species (b) in sulfur-saturated (s) sulfide solutions is represented by

$$K^0{}_{b/s} = \frac{a_{S_2^-}{}^2}{a_{SH^-}a_{OH^-}} = K^0{}_{3/s}K^0{}_d \approx 0.167K^0{}_sK^0{}_d \tag{9}$$

with K^0_d the equilibrium constant for the dissociation of tetrasulfide to supersulfide.[12] The experimental values for these equilibrium constants are summarized in Table I.

Disproportionation of Polysulfide Ions at Elevated Temperatures. As already described in previous work,[12] increasing temperature leads to partial or complete disappearance of the color of polysulfide solutions, with the degree of decoloration largely depending on the pH of the starting solution. At temperatures below 150°, however, the rate of decoloration is slow and polysulfide solutions were found to persist metastably at lower temperatures, even at high pH's. At temperatures above 150° reaction rates are sufficiently fast to allow a detailed study of the reversible disproportionation equilibria involved. Preliminary investigations into the nature of the disproportionation products showed that the effect of additions of sulfate ion on the final position of the equilibrium was very small and likely to be due only to associated changes in ionic strength, whereas small additions of sulfite or thiosulfate led to considerable increases in the equilibrium concentration of polysulfide at 160°.

In order to obtain some information on the nature of the actual species involved in this equilibrium the following general reaction scheme was considered

$$S_nS^{2-} + qOH^- \rightleftarrows S_{n-q}SO_q{}^{2-} + qSH^- \tag{10}$$

For solutions containing an approximately equimolar mixture of tetra- and pentasulfide a plot of $\log[(A_i/A_e) - 1]$ *vs.* $\log(m_{OH^-}/m_{SH^-})$ should, in the case of the disproportionation of polysulfide to either sulfite or thiosulfate, show a linear relationship with a slope close to +3. A_i and A_e represent the initial and equilibrium absorbances of polysulfide at 2.5 μm^{-1}. Because of the low sensitivity of $\bar{n}$ to variations in m_{SH^-} and m_{OH^-} over the pH range considered, the least-squares slope of 2.82 as obtained from Figure 4 can be assumed to confirm the proposed reaction scheme; however, it does not allow one to distinguish between the two possible reaction products, sulfite or thiosulfate. A decision

Table I. Temperature and Ionic Strength Dependence of Equilibrium Constants (Molal) Used or Derived in This Investigation and Fitted to the Equation $\log K = A/T + BT + C + D\sqrt{I}$

K	A	B	C	D	Error	T range, °C	Ref
K_1	−2,780.4	0.02133	8.8489	*c*	±0.1[a]	20–270	10
K_w	−3,927.1	0.01223	2.8334	*c*		0–280	*d*
K_s	−1,573.9	0.01365	14.671	0.31	±0.1[a]	20–200	*e* (6)
$K_{1/2}$			−4.20	0.35	±0.2[b]	20–140	*e* (3)
$K_{2/3}$			−1.75	0.35	±0.2[b]	20–140	*e* (4)
$K_{3/4}$			5.08	0.35	±0.3[b]	20	*e* (5)
$K_{t/3}$	−48,168	−0.28551	261.2	0.90	±0.5[a]	150–210	*e* (14)
K_d	−4,533.0		6.42	*c*	±0.2[a]	100–250	12

[a] Standard deviation of experimental values with respect to those described by eq 15. [b] Estimated error taking into account approximations made in deriving equilibrium constants. [c] Equilibrium constants used only in conjunction with calculations at a hypothetical ionic strength of zero. [d] J. R. Fisher and H. L. Barnes, *J. Phys. Chem.*, 76, 90 (1972). [e] This work; number of defining equation is in parentheses.

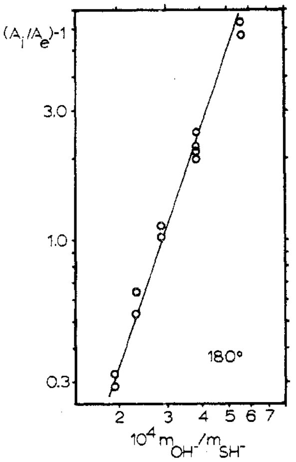

Figure 4. Plot of $\log (A_i/A_e) - 1$ *vs.* $\log (m_{OH^-}/m_{SH^-})$ at 180°. Line drawn represents a slope of 3.

is made possible by the observation that for larger additions the effects of sulfite and thiosulfate start to diverge with the equilibrium concentrations of polysulfide continuing to increase in proportion to thiosulfate added but to decrease with increasing sulfite concentration (Figure 5).

At present no full explanation for this behavior can be given. The initial increase in the equilibrium concentrations of polysulfide ions after small additions of sulfite is considered to be due to the reaction

$$S_nS^{2-} + nSO_3^{2-} + H_2O \rightleftarrows nS_2O_3^{2-} + SH^- + OH^- \qquad (11)$$

according to which addition of sulfite to a polysulfide solution leads to the formation of thiosulfate which in turn causes a fourfold increase in the equilibrium concentration of polysulfide by way of the proposed disproportionation reaction

$$nS_2O_3^{2-} + 2(n+2)SH^- \rightleftarrows 4S_nS^{2-} + 4(n-1)OH^- \qquad (12)$$

Reaction 11 already takes place at room temperature as indicated by the reduction in $A_{2.5}$ after addition of sulfite to the polysulfide solution. With increasing sulfite concentration, therefore, a point is reached where all zerovalent sulfur present is converted into thiosulfate and the solution at room temperature becomes coloreless. On heating such a solution to 160°, however, a maximum amount of polysulfide is produced, only after addition of further sulfite the equilibrium concentration of polysulfide at 160° starts to decrease. The reactions responsible for this behavior thus are likely to involve thiosulfate and sulfite possibly leading to the irreversible formation of polythionates[14] according to

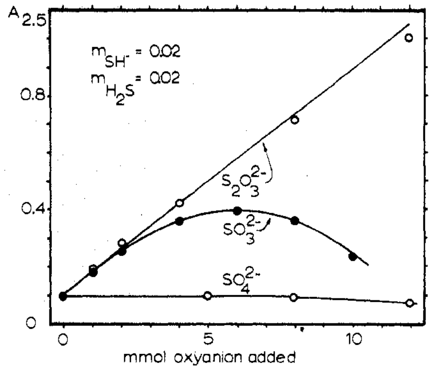

Figure 5. Dependence of $A_{2.5}$, the equilibrium absorbance of polysulfide at 2.5 μm^{-1}, on the amount of sulfate, sulfite, and thiosulfate added at 180° ($m_{SH^-} = m_{H_2S} = 0.02$; initial $m_{S(0)} = 0.004$).

$$S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \rightleftarrows 2S_3O_6^{2-} + 6OH^- \qquad (13)$$

which in turn may disproportionate further into monosulfide and sulfate.

The above reaction scheme suggests that under the conditions employed, only thiosulfate reacts reversibly with monosulfide (H_2S, SH^-) to form zerovalent sulfur. This agrees with the observation that no polysulfide is formed on adding greatly varying amounts of sulfite to near-neutral sulfide solutions up to 240°, whereas on addition of thiosulfate to similar sulfide solutions proportional amounts of polysulfide are produced. The equilibrium between thiosulfate and polysulfide can be approached from both sides. The final solutions appear to be stable with time; even up to 240° no changes in the equilibrium absorption A_e were observed for periods of several hours.

By plotting $\log (A_i - A)$, the differences between the initial absorbance at 2.5 μm^{-1} and that at the time t, *vs.* time, for polysulfide solutions at 180°, the reaction was found to be first order in polysulfide and thiosulfate. A more detailed discussion of the kinetics of this reaction will be given elsewhere.

As in the evaluation of $K_{n/s}$, the actual concentrations of a particular polysulfide ion required in the calculation of $K_{t/n}$, the equilibrium constant governing the formation of thiosulfate (t) from polysulfide (n), were estimated by assuming $K_{n/m}$ to remain constant with temperature. Thus for given values of m_{SH^-}-m_{OH^-} and a given temperature, $m_{S_nS^{2-}}$ was calculated by use of an iterative procedure to find $\bar{n}$ similar to that described for $K_{n/s}$. The values of $\log B$ for the solutions used in the disproportionation measurements were in the region −1 to −3 within which the tetrasulfide predominates.[9] The experimental data available, therefore, are most suitable for the evaluation of

$$K_{t/3} = \frac{m_{S_2O_3^{2-}}{}^3 m_{SH^-}{}^{10}}{m_{S_3S^{2-}}{}^4 m_{OH^-}{}^8} \qquad (14)$$

the equilibrium expression describing the disproportionation of tetrasulfide to monosulfide and thiosulfate. Table I gives the constants representing the temperature and ionic strength dependence of $\log K_{t/3}$, together with a series of other data

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(14) F. H. Pollard, D. J. Jones, and G. Nickless, *J. Chromatogr.*, 15, 393 (1964).

used or determined in this work, in the form of a general equation

$$\log K^0 = A/T + BT + C \qquad (15)$$

with the ionic strength dependence given by

$$\log K = \log K^0 + D\sqrt{I} \qquad (16)$$

The experimental errors given in Table I represent either standard deviations for a series of measurements on solutions covering a wide range of concentrations or the likely range of deviation possible considering the effects of approximations made in evaluating an equilibrium constant. The temperature limits show the range over which equilibrium measurements have been carried out.

Equilibrium Distribution of Sulfur Species as a Function of pH and Temperature. By use of the equilibrium constants derived in the preceding sections, the equilibrium distribution of species present may be calculated. Figure 6 shows such diagrams for solutions with a total monosulfide concentration

$$m_{S^{2-}} = m_{H_2S} + m_{SH^-} + \Sigma m_{S_nS^{2-}} + {}^1/_2 m_{S_2^-} - 2m_{S_2O_3^{2-}} \qquad (17)$$

of 0.1 m and a zerovalent sulfur concentration

$$m_{S(0)} = \Sigma n m_{S_nS^{2-}} + 1.5 m_{S_2^-} + 4m_{S_2O_3^{2-}} + \Sigma n m_{S_n} \qquad (18)$$

of 0.01 m. In these calculations the variations in m_{SH^-} and $m_{S(0)}$ with pH are taken into account. The disproportionation reaction, however, could only be investigated down to 150° when reaction rates became too slow to be measured conveniently. Extrapolation to room temperature would indicate that polysulfide solutions of the above concentrations in S(0) and S^{2-} become thermodynamically unstable at pH's above 8-9. The high kinetic stability of the lower polysulfides S_2S^{2-} and SS^{2-}, however, is illustrated by the fact that their solutions in 0.1 m total sulfide may, at the required pH, be heated to above 100° for considerable time without noticeable changes in their optical absorptions. Only from 150° on does decoloration become rapid.

In the construction of a stability diagram the possibility of polysulfide and thiosulfate disproportionating into sulfide and sulfate has to be taken into account but there was no indication of this reaction occurring at a sufficient rate over the concentration and temperature range (<240°) used in this investigation. Previously derived data[10] on sulfur hydrolysis suggest that zerovalent sulfur should already disproportionate into sulfide and sulfate at temperatures considerably lower than those found for the thiosulfate reaction. A kinetic study[15] on the disproportionation of thiosulfate, however, showed that the formation of sulfate is very slow at temperatures below 250°, making it possible for thiosulfate to form as a metastable intermediate.

Discussion

Formation and Rearrangement Reactions of Polysulfide Ions. Previous work on the solubility of sulfur in aqueous solution[1,2] had mostly been carried out at relatively high starting alkalinities where influences of variations in K_1 and K_w, the ionization constants of H_2S and water, with temperature could be neglected. The amount of sulfur dissolving in these solutions was shown to vary only little with temperature in agreement with the present findings according to which the equilibrium constants $K^0{}_{n/s}$ expressed in terms of a_{SH^-} and a_{OH^-} are virtually temperature independent. At lower pH's, however, the values for $a_{SH^-}a_{OH^-}$ vary in proportion to K_w/K_1 for a given buffer ratio a_{SH^-}/a_{H_2S} which in turn means a rapid increase with temperature in the absolute amounts of elemental sulfur soluble in an aqueous sulfide solution at a near-neutral starting pH. On heating a 0.1 m sulfide solution containing an equimolar mixture of SH^- and H_2S in contact with excess elemental sulfur from 25 to 150° the amount of zerovalent sulfur in solution increases from 0.001 to 0.08 m, an 80-fold increase.

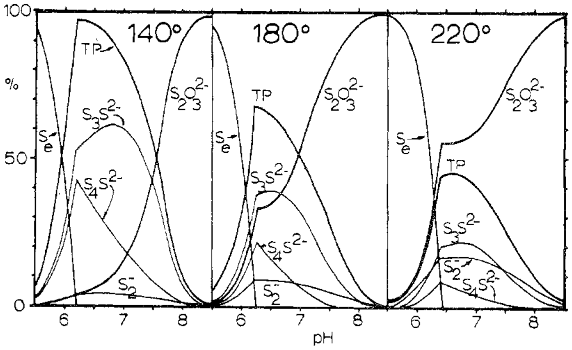

Figure 6. Calculated equilibrium distribution of sulfur species at 140, 180, and 220° as a function of pH ($m_{S^{2-}} = 0.1$, $m_{S(0)} = 0.01$; TP = total polysulfide sulfur, S_e = elemental sulfur).

Contrary to the findings by Teder,[3] both $\bar{n}$ and K_s were found to increase slightly up to about 125°; these increases, however, have only little effect on the overall solubility of zerovalent sulfur at near-neutral pH's. Also, the values for $\bar{n}$ derived in this study of around 3.5 are considerably lower than those of 3.7 and 4.4 at 25° and 4.0 and 5.0 at 50 and 80°, respectively, reported by previous workers.[2,3] This discrepancy is possibly related to the large differences in the concentration and pH conditions used. In dilute, near-neutral solutions $\bar{n}$ is unlikely to exceed 3.6 at any temperature; it would appear, however, that $\bar{n}$ increases with increasing starting pH, implying the formation of ions S_nS^{2-} with $n > 4$ in the resulting, highly concentrated polysulfide solutions in contact with elemental sulfur. The existence of these long-chain ions in aqueous solution is also suggested by the formation[16] of polysulfanes S_nSH_2 with $n > 4$ from acidified highly concentrated polysulfide solutions.

The necessity for extremely rapid acidification in the preparation of these polysulfanes from polysulfide solutions is thought to be due to the instability of hydropolysulfide ions. They can be expected to form at intermediate pH's and are assumed to decompose rapidly according to

$$S_nSH^- \rightleftarrows nS + SH^- \qquad (19)$$

with the formation of elemental sulfur and monosulfide. By use of the second ionization constants $K_{n/h}$ for the tetra- and pentasulfanes (h) as derived by Schwarzenbach and Fischer,[4] together with the equilibrium constant $K_{n/s}$ derived in this study, the concentrations of hydropolysulfide ions possibly present in low pH polysulfide solution can be estimated according to

$$m_{S_nSH^-} = K_{n/s}K_w m_{SH^-}/K_{n/h} \qquad (20)$$

The concentration of hydropolysulfide ions thus is a function of m_{SH^-} only, as long as excess elemental sulfur is present. For a solution 0.1 m in SH^- the equilibrium concentrations of S_3SH^- and S_4SH^- are found to be 6.0 × 10^{-5} and 1.2 × 10^{-5} m, respectively. For solutions at pH 7 and 25° this

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(15) W. A. Pryor, *J. Amer. Chem. Soc.*, **82**, 4794 (1960).

(16) F. Feher and M. Baudler, *Z. Anorg. Allg. Chem.*, **288**, 132 (1949).

would amount to about 10% of the concentration of tetra- and pentasulfide ions present. At pH's below 7 the polysulfide concentrations decrease in proportion to the product $m_{SH^-} m_{OH^-}$; in moderately acidic solutions hydropolysulfide ions thus could be expected to become the predominant zerovalent sulfur-containing species in solution, although present in very low concentrations. These findings may be reconciled with the spectroscopic observations as described earlier, by assuming hydropolysulfide ions to have optical absorptions only at wave numbers above those for polysulfide ions.

The low sensitivities of the equilibrium constants $K^0_{n/s}$ and $K^0_{n/m}$ to variations in temperature indicate very small values for the corresponding standard enthalpy changes $\Delta H^\circ_{n/s}$ and $\Delta H^\circ_{n/m}$ for the formation and rearrangement reactions of the polysulfide ions S_nS^{2-}. Variations in $K^0_{n/m}$ with n and m thus have to be ascribed largely to differences in the reaction entropy changes as derived from $\Delta S^\circ_{n/m} = R \ln K^0_{n/m}$, with $\Delta H^\circ_{n/m}$ and $\Delta C^\circ_{n/m}]_{25^\circ}^{T}$, the average standard heat capacity change of the reaction from 25° over the temperature range investigated, taken to be zero. The standard entropies S°_n for the polysulfide ions S_nS^{2-} thus estimated by use of the standard thermodynamic functions[17] for SH^-, OH^-, and H_2O and the equilibrium constants $K^0_{n/m}$ and $K^0_{n/s}$ show the expected increases with increasing n with $S^\circ_1 = 10\ J\ K^{-1}\ mol^{-1}$, $S^\circ_2 = 72\ J\ K^{-1}\ mol^{-1}$, $S^\circ_3 = 105\ J\ K^{-1}\ mol^{-1}$, and $S^\circ_4 = 102\ J\ K^{-1}\ mol^{-1}$. On the other hand, the standard enthalpies of formation of the various polysulfide ions then are required to be very similar and close to $\Delta H^\circ_{OH^-} + \Delta H^\circ_{SH^-} - \Delta H^\circ_{H_2O} = 37\ kJ\ mol^{-1}$. The resulting standard free energies of formation for the ions S_nS^{2-} with $n = 1$-4 at 298 K then become 85, 77, 66, and 67 kJ mol^{-1}, respectively. These thermodynamic data are internally consistent and describe the experimental findings adequately; however, considering the simplifications made, they could be subject to considerable modifications.

Disproportionation of Species Containing Zerovalent Sulfur. By use of the equilibrium constants given in Table I a temperature–pH diagram outlining areas within which one of the species considered predominates may be constructed. Figure 7 shows such a stability diagram for solutions with $m_{S^{2-}} = 0.1$ and $m_{S(0)} = 0.01$. The dotted line in Figure 7 indicates the changes in pH taking place on heating solutions with an initial room-temperature pH of around 7. At a pH of 7 and at 25° part of the 0.01 m zerovalent sulfur is present in the form of undissolved elemental sulfur. With increasing temperature, following the dotted line, the elemental sulfur continues to dissolve to form predominantly pentasulfide ion for a small temperature range to about 60°. From then on most of the zerovalent sulfur is transformed into tetrasulfide until at around 180° half of this disproportionates into sulfide and thiosulfate. For solutions of a lower starting pH, disproportionation is preceded by the dissociation of most of the tetrasulfide into radical ions S_n^-, of which the supersulfide ion S_2^- is here assumed to predominate.

In previous studies on the disproportionation or hydrolysis of zerovalent sulfur, present in the form of elemental sulfur or some polysulfide, the nature of the reaction products was found to depend on solution pH and temperature. At pH's below neutral the reaction proceeds[10] according to

$$4S + 4H_2O \rightleftarrows 3H_2S + HSO_4^- + H^+ \qquad (21)$$

whereas the reaction with hydroxide at higher pH's and temperatures below 250° is reported[7,8] to follow the equation

$$4S + 4OH^- \rightleftarrows S_2O_3^{2-} + 2SH^- + H_2O \qquad (22)$$

At temperatures above 250° thiosulfate again disproportionates[15] according to

$$S_2O_3^{2-} + OH^- \rightleftarrows SO_4^{2-} + SH^- \qquad (23)$$

The final products being in both cases sulfur species in the oxidation states −2 and 6.

The degree to which these reactions proceed again depends on temperature and pH. At higher pH's and temperatures above 250° reactions 22 and 23 lead to virtually complete disproportionation to bisulfide and sulfate, at higher acidities; however, zerovalent sulfur was found to be only partly hydrolyzed.

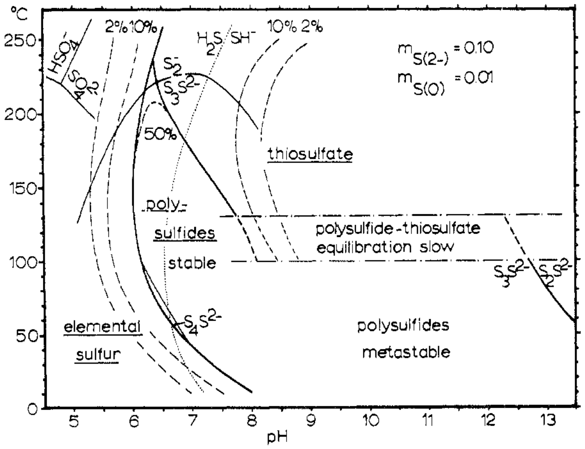

Figure 7. Temperature–pH diagram for solutions 0.1 m in total monosulfide and 0.01 m in total zerovalent sulfur. Dashed lines delineate conditions where 2, 10, or 50% of the total initial zerovalent sulfur are present in the form of polysulfide. The dotted line shows variations in pH with temperature, for a $SH^-:H_2S$ buffer ratio of unity.

By use of the equilibrium constants for the sulfur–water reaction as derived in a previous study[10] the stability field for elemental sulfur can be estimated as shown in the upper left corner of Figure 7. In acidic solutions zerovalent sulfur in equilibrium with hydrogen sulfide and bisulfate or sulfate at around 200° can be expected to be largely present as liquid sulfur. Approaching neutral pH's, however, the formation of polysulfide species is likely to become significant, suggesting the existence of a small range of temperatures and pH's over which polysulfide ions are thermodynamically stable with respect to decomposition into monosulfide and elemental sulfur and disproportionation into monosulfide and sulfate.

With the polysulfide–thiosulfate boundary at temperatures above that for the polysulfide–sulfate equilibrium, reactions between polysulfide and thiosulfate, as described here in detail, have to be considered to involve metastable species, present at the relatively high temperatures and pH's investigated only due to the slow rates of reactions 21 and 23.

From previous work it can be concluded that sulfur in its +4 oxidation state is unlikely to be present in significant amounts or to form an important intermediate species in any of the solutions investigated. Sulfurous acid and sulfur dioxide have been shown[18] to disproportionate rapidly to sulfur and sulfuric acid, whereas sulfite[15] is reported to dis-

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(17) *Nat. Bur. Stand.* (*U. S*), *Tech. Note*, No. 270-3 (1968).

(18) S. Oana and H. Ishikawa, *Geochem. J.*, 1, 45 (1966).

proportionate to sulfide and sulfate. These observations are in agreement with present findings according to which no polysulfides were formed on heating sulfite solutions containing sulfide over a wide range of concentrations indicating that the disproportionation

$$4SO_3^{2-} + H^+ \rightleftarrows 3SO_4^{2-} + SH^- \qquad (24)$$

predominates over the comproportionation reaction

$$SO_3^{2-} + 2SH^- + 4H^+ \rightleftarrows 3S + 3H_2O \qquad (25)$$

describing the formation of zerovalent sulfur in analogy to reaction 22. Thiosulfate and polysulfide ions thus emerge as the most stable solution species with intermediate oxidation states at near-neutral pH's. The determination of the actual extent of their thermodynamic stability requires additional information on equilibria involving sulfate species at present not available.

Registry No. SS^{2-}, 16734-12-6; S_2S^{2-}, 12597-05-6; S_3S^{2-}, 12597-07-8; S_4S^{2-}, 36966-99-1; sulfur, 7704-34-9.

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Kinetics of the Polysulfide-Thiosulfate Disproportionation up to 240°

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For temperatures up to 240°, the disproportionation of zerovalent sulfur S(0), present in aqueous solution in the form of polysulfide ions S_nS^{2-}, according to the equilibrium $4S_nS^{2-} + (3n-4)OH^- \rightleftarrows nS_2O_3^{2-} + (2n+4)SH^-$, is shown to be governed by the rate expression $-dm_{S_4S^{2-}}/dt = k_f m_{S_4S^{2-}} m_{SH^-}^{-2} m_{OH^-} - k_r m_{S_2O_3^{2-}} m_{SH^-} m_{OH^-}^{-2}$. The temperature and ionic strength dependencies of the rate constants for forward and reverse reaction are given by $\log k_f = 10.9 - 5600/T - 0.161^{1/2}$ and $\log k_r = 10.5 - 9800/T - 0.33I^{1/2}$. The associated activation energies are $E_f = 107$ kJ mol^{-1} and $E_r = 187$ kJ mol^{-1}. The rate constants were measured in the pH range 6–8 between 150 and 240° and at an ionic strength up to 1.4 *m*. The high kinetic stability of polysulfide solutions at higher pH's is explained in terms of the pentasulfide ion being the main reactive polysulfide species.

Introduction

The stability of polysulfide solutions and the rates and conditions for their decomposition have previously been investigated in connection with studies on the reactions occurring during polysulfide pulp cooking.[1,2] In these studies the stability of polysulfide solutions was found to decrease with increasing temperature and pH and decreasing monosulfide concentration. The present work extends investigations on the thermodynamic stability of polysulfide ions at elevated temperatures[3] to their kinetic stability.

Experimental Section

The experimental techniques were essentially the same as those employed in the preceding study.[3] The ionic strength of the solution was controlled by the addition of NaCl, with most of the measurements carried out at an ionic strength of 0.4 *m*. In the computation of this "arithmetic" ionic strength $I = 0.5(m_i z_i^2)$ no attempts were made to take into account ion association or related effects. The reactions were usually followed for periods corresponding to 10 times the half-time or longer. The half-times t_h for the pseudo-first-order reactions were obtained as shown in Figure 1B.

Results

On heating aqueous polysulfide solutions above 150°, their optical absorption at a wave number of 2.5 μm^{-1} (waves per micrometer) starts to decrease until an equilibrium value is reached,[3] which, together with the speed of equilibration, depends on both the temperature and the composition of the starting solution. In a previous study[3] it was shown that the main chemical equilibrium associated with this decoloration as given by the equation

$$4S_3S^{2-} + 8OH^- + H_2O \rightleftarrows 3S_2O_3^{2-} + 10SH^- \qquad (1)$$

is reversible and can be approached from both sides.

Preliminary checks on polysulfide solutions at 180°, containing excess monosulfide sulfur ($m_{H_2S} + m_{SH^-}$), with the pH kept constant by the SH^--H_2S buffer, showed that a linear relationship exists between time and $\log (A - A_e)$, where A refers to the absorbance at 2.5 μm^{-1} at time t, and A_e, to that at equilibrium. Similarly, first-order plots result by use of $\log (A_e - A)$ for solutions initially containing thiosulfate (Figure 1). The rate expressions describing two simultaneous opposing first-order reactions leading to the establishment of the above equilibrium, in terms of consumption or formation of polysulfide, are given by

$$-dm_n/dt = k_f' m_n \qquad (2)$$

$$dm_n/dt = k_r' m_t \qquad (3)$$

where m_n and m_t represent the molalities of the polysulfide ion S_nS^{2-} and thiosulfate at time t and k_f' and k_r' are the pseudo-first-order rate constants describing consumption and formation of polysulfide.

Over the temperature, concentration, and pH ranges used in this investigation, tri-, tetra-, penta-, and supersulfide ions (S_2S^{2-}, S_3S^{2-}, S_4S^{2-}, S_2^-) can be expected to be present. Due to the high speed at which rearrangements between these ions occur, their relative proportions can be assumed to remain largely constant for solutions containing a constant amount of excess monosulfide ($H_2S + SH^-$) at constant temperature and pH. Any measurable quantity related to the concentration of one of these species thus can be used to evaluate eq 2 and 3. In the present investigation the absorbance at 2.5 μm^{-1} ($A_{2.5}$) is used. All three polysulfide ions S_nS^{2-}, with n ranging from 2 to 4, absorb at this wave number. In the evaluation of the net rate of the reaction describing the consumption of polysulfide ions in solutions initially containing only polysulfide (eq 4) m_i and m_n may be expressed in terms

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(1) J. E. Olsen and O. Samuelson, *Sv. Papperstidn.*, 69, 703 (1966).

(2) L. Gustafsson and A. Teder, *Sv. Papperstidn.*, 72, 249 (1969).

(3) W. Giggenbach, *Inorg. Chem.*, 13, 1724 (1974).