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

(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).

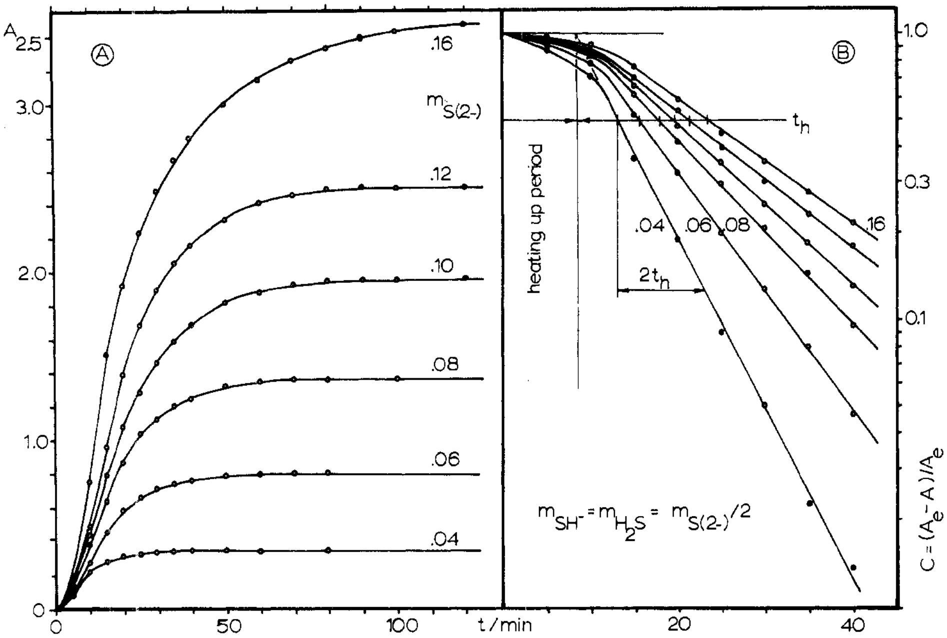

Figure 1. Plots of $A_{2.5}$ (A) and log C (B) *vs.* time for thiosulfate starting solutions as a function of $m_{S^{2-}}$ at 180° ($m_{SH^-} = m_{H_2S} = 0.5 m_{S^{2-}}$).

$$-dm_n/dt = k_f' m_n - k_r'(m_i - m_n) \qquad (4)$$

of A_i, the initial absorbance, and A at time t, at 2.5 μm^{-1}.

For solutions initially containing only thiosulfate, however, an average molar absorptivity $\epsilon_{\bar{n}}$ at 2.5 μm^{-1} for all the polysulfide species present was estimated by use of previously reported[3] values for $K_{3/4}$, $K_{2/3}$, and K_d. This allows the initial concentration of thiosulfate to be expressed in terms of an absorbance according to $A^*_i = m_{ti}\epsilon_{\bar{n}} l d$, where m_{ti} represents the initial molality of thiosulfate, $\epsilon_{\bar{n}}$ the average molar absorptivity of all the polysulfide species expected to form after complete conversion of thiosulfate to polysulfide according to eq 1, l the path length, and d the density of the solution at a given temperature. The resulting rate expression (eq 5) for solutions initially containing thiosulfate then is

$$dA/dt = -k_f'A + k_r'(A^*_i - A) \qquad (5)$$

very similar to that for polysulfide starting solutions

$$-dA/dt = k_f'A - k_r'(A_i - A) \qquad (6)$$

By use of the equilibrium condition

$$k_f'A_e = k_r'(A_i - A_e)$$

where A_e is the polysulfide absorbance at equilibrium, and after separation of variables and integration, expressions are obtained allowing the evaluation of the rate constants k_f' and k_r' from absorbance measurements on solutions initially containing polysulfide or thiosulfate

$$k_f' = -2.303(A_i - A_e)(\log C)/A_i t \qquad (7a)$$

$$k_r' = -2.303 A_e(\log C)/A_i t \qquad (7b)$$

where $C = (A - A_e)/(A_i - A_e)$ for polysulfide starting solutions and $C^* = (A_e - A)/A_e$ for thiosulfate starting solutions. Values for k_f' and k_r', therefore, may be determined from the slopes of plots of log C *vs.* time, with the ratio of k_f'/k_r' being equal to $(A_i - A_e)/A_e$. By use of eq 7 in a form commonly used in studies of simultaneous opposing reactions

$$k_f' + k_r' = -\frac{2.303}{t}\log C \qquad (8)$$

the sum of the two rate constants can be expressed in terms of t_h, the half-time for the pseudo-first-order reaction as given by $t_h = (\ln 2)/(k_f' + k_r')$, which can directly be obtained from the first-order plots of log C *vs.* time.

With

$$k_f' + k_r' = (\ln 2)/t_h \qquad (9)$$

and

$$k_f'/k_r' = (A_i - A_e)/A_e \qquad (10)$$

the individual values of k_f' and k_r' are calculated from the experimental values of A_i, A_e, and t_h according to

$$k_f' = \frac{(A_i - A_e)\ln 2}{A_i t_h} \qquad (11)$$

and

$$k_r' = \frac{A_e \ln 2}{A_i t_h} \qquad (12)$$

These pseudo-first-order rate constants, valid only for solutions of a given excess monosulfide concentration and a given pH, are related to the overall rate constants k_f and k_r as required by the general expression expected to describe fully the kinetics of the polysulfide disproportionation, expressed in terms of m_{SH^-} and m_{OH^-}

$$-dm_{S_nS^{2-}}/dt = k_f m_{S_nS^{2-}} m_{SH^-}{}^{-a} m_{OH^-}{}^{-b} - k_r m_{S_2O_3{}^{2-}} m_{SH^-}{}^{-a^*} m_{OH^-}{}^{-b^*} \qquad (13)$$

by the equation

$$k' = k m_{SH^-}{}^{-a} m_{OH^-}{}^{-b} \qquad (14)$$

After insertion of eq 11 and 12, and taking logarithms, the following relationships are obtained

$$\log\,[(A_i - A_e)/t_h] = a \log m_{SH^-} + b \log m_{OH^-} \qquad (15)$$

$$\log (A_e/t_h) = a^* \log m_{SH^-} + b^* \log m_{OH^-} \qquad (16)$$

which allow values for *a* and *b* for forward and reverse (asterisked) reactions to be determined from plots of log $[(A_i - A_e)/t_h]$ or log (A_e/t_h) *vs.* the logarithm of one of the variables m_{SH^-} or m_{OH^-}, with the other kept constant. Both equations are applicable to solutions initially containing polysulfide or thiosulfate.

The coefficients for forward and reverse reaction as obtained from Figure 2 yield the overall rate equation

$$-\mathrm{d}m_{S_nS^{2-}}/\mathrm{d}t = k_f m_{S_nS^{2-}} m_{SH^-}{}^{-2} m_{OH^-} - k_r m_{S_2O_3{}^{2-}} m_{SH^-} m_{OH^-}{}^{-2} \qquad (17)$$

corresponding to the symbolic reaction

$$(S_nS^{2-}) - 2SH^- + OH^- \rightleftarrows S_2O_3{}^{2-} + SH^- - 2OH^- \qquad (18)$$

The simple stoichiometry thus implied, however, can only be reconciled with the pentasulfide ion being the main active species, for any other polysulfide ion more complicated expressions should result. Over the concentration range investigated the tetrasulfide ion is expected to be the predominant species, related to the concentration of pentasulfide by the equation

$$m_{S_3S^{2-}}{}^4 = K_{3/4} m_{S_4S^{2-}}{}^3 m_{SH^-} m_{OH^-} \qquad (19)$$

Thus by assuming the forward reaction to be described by

$$-\mathrm{d}m_{S_4S^{2-}}/\mathrm{d}t = k_f m_{S_4S^{2-}} m_{SH^-}{}^{-2} m_{OH^-} \qquad (20)$$

the rate for solutions predominantly containing tetrasulfide becomes

$$-\mathrm{d}m_{S_4S^{2-}}/\mathrm{d}t = -(3/4)\mathrm{d}m_{S_3S^{2-}}/\mathrm{d}t = k_f m_{S_3S^{2-}}{}^{4/3} m_{SH^-}{}^{-7/3} m_{OH^-}{}^{2/3}/K_{3/4}{}^{1/3} \qquad (21)$$

The relatively high scatter of experimental values as shown in Figure 2, however, renders the distinction between these values for *a* and *b* and the integral values as derived earlier impossible.

Ionic Strength Dependence of the Rate Constants. The ionic strength dependence for the forward and reverse rate constants was determined by straightforward application of the Debye-Huckel equation and eq 11 and 12 for equimolar 0.03 *m* solutions of H_2S and SH^-, with the ionic strength varied from 0.08 to 1.36 *m* by the addition of NaCl. The rather small dependence (Figure 3), with slopes of −0.16 and −0.33 for plots of log *k'* *vs.* $I^{1/2}$, for forward and reverse reactions, respectively, were taken to indicate the involvement of only singly charged or uncharged reactants in the main rate-determining steps, with interactions involving doubly charged particles restricted to fast preequilibration steps.

By combining eq 11, 12 and 14 the overall rate constants for forward and reverse reaction are calculated in terms of the pentasulfide ion being the main reactive polysulfide species. The values found at 180° and zero ionic strength are

$$k_f = k_f' m_{SH^-}{}^{2} m_{OH^-}{}^{-1} = 3.5 \times 10^{-2} \text{ mol kg}^{-1} \text{ sec}^{-1} \qquad (22)$$

and

$$k_r = k_r' m_{SH^-}{}^{-1} m_{OH^-}{}^{2} = 7.6 \times 10^{-12} \text{ mol kg}^{-1} \text{ sec}^{-1} \qquad (23)$$

Temperature Dependence of the Rate Constants. The temperature dependence of the rate of equilibration for solutions initially containing polysulfide or thiosulfate was determined at 153, 181, and 206° on 0.04 *m* equimolar SH^--H_2S solutions at an ionic strength of 0.20 *m*. From the Arrhenius slopes, $-E/2.3R$, activation energies E_f and E_r of 107 and 187 kJ mol⁻¹ for forward and reverse reactions, respectively, were derived. The value for polysulfide decomposition is within the range of 80-125 kJ mol⁻¹ reported by Teder[2] for a series of polysulfide solutions. The temperature dependence of the rate constants at zero ionic strength expressed in terms of $\log k = A + B/T$ then is given by the values of 10.9 and 10.5 for *A* and −5600 and −9800 for *B* for forward and reverse reactions, respectively.

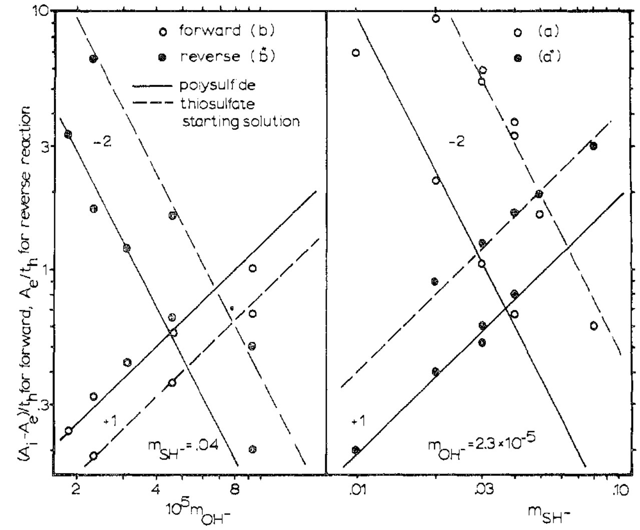

Figure 2. Plots of log $(A_i - A_e)/t_h$ for the forward reaction and log (A_e/t_h) for the reverse reaction *vs.* m_{SH^-} and m_{OH^-} at 180°. Lines drawn correspond to nearest integral slope; arbitrary ordinate scale.

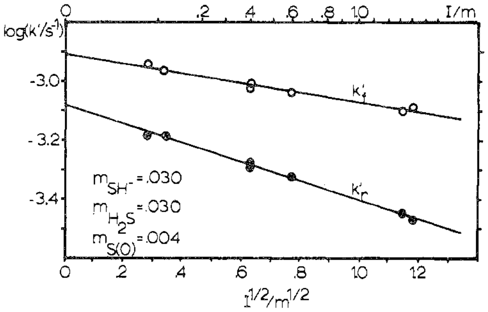

Figure 3. Ionic strength dependence of log k_f' and log k_r' at 180° ($m_{SH^-} = m_{H_2S} = 0.03$, $m_{S(0)} = 0.004$).

Discussion

The experimental data as described above may be used to derive possible mechanisms for the polysulfide-thiosulfate equilibration, to discuss relationships between rate constants and equilibrium constants, and to explain the high kinetic stability of the lower polysulfides in alkaline solutions.

Possible Mechanism for the Polysulfide-Thiosulfate Equilibration. By considering fast proton-transfer equilibria among SH^-, H_2S, OH^-, and H_2O, eq 17 can be shown to represent only one out of a wide range of kinetically equivalent rate expressions. The simple fact that oxygen atoms have to be added to the polysulfide ion during the sequence of reactions finally leading to the formation of thiosulfate and the low ionic strength dependence would suggest that the initial step in the conversion of pentasulfide to thiosulfate consists in the attack of a water molecule on one of the inner sulfur atoms of the polysulfide chain followed by a proton rearrangement reaction and expulsion of SH^- (or H_2S) as represented by the reactions

$$S_5{}^{2-} + H_2O \rightleftarrows (S_5OH_2)^{2-} \rightleftarrows (S_4OH)^- + SH^- \tag{24}$$

The intermediate $(S_4OH)^-$ is then attacked by another H_2O or OH^- on the same sulfur atom followed by the loss of another terminal sulfur atom according to

$$(S_4OH)^- + OH^- \rightleftarrows (S_4(OH)_2)^{2-} \rightleftarrows (S_3O_2H)^- + SH^- \tag{25}$$

In the resulting protonated dithiosulfate ion one of the outer sulfur atoms is hydrolyzed off to give H_2S and bithiosulfate ion which then deprotonates to form thiosulfate ion. In the reverse reaction a protonated thiosulfate ion then is thought to be attacked by H_2S or SH^- replacing the hydroxy group.

None of the intermediate species is considered to be present in significant amounts making it possible to express the kinetics of the proposed rather complicated reaction sequence in terms of the two end products only.

Relationship between Rate Constants and the Polysulfide-Thiosulfate Equilibrium Constant. With the equilibrium constant for a reversible reaction related to the rate constants for forward and reverse reaction by

$$K = k_f/k_r \tag{26}$$

the value for the constant governing the polysulfide-thiosulfate equilibrium as derived earlier may be compared to the ratio k_f/k_r derived in this study. For this purpose the value $K_{t/4}$ has to be expressed in terms of the species used in the evaluation of k_f and k_r; thus

$$K_{t/4} = k_f/k_r = \frac{m_{S_2O_3{}^{2-}} m_{SH^-}{}^{3}}{m_{S_4S^{2-}} m_{OH^-}{}^{3}} = K_{t/3}{}^{1/3} K_{3/4}{}^{1/3} \tag{27}$$

The values for $\log K_{t/4}$ calculated in this way, however, are with 10.7, 10.2, and 9.8 somewhat higher than those derived from the rate constants of 10.3, 9.7, and 9.2 at 153, 181, and 206°, respectively, and would indicate that some of the assumptions made in the evaluation of k_f, k_r, $K_{t/3}$, and $K_{3/4}$ may not be completely justified. From the temperature dependence of $K_{t/4}$ the free enthalpy change for the reaction is calculated to be around -69 kJ mol^{-1} as compared to that obtained from the difference in E_f and E_r of -80 kJ mol^{-1}.

Stability of the Lower Polysulfide Ions at Higher pH's. As already pointed out in a preceding study, polysulfide solutions at pH's above 9, containing predominantly tetra-, tri-, and disulfide ions, were heated to temperatures at around 100° without any significant decrease in their optical absorptions. This in spite of the fact that polysulfide solutions can be expected to become thermodynamically unstable at pH's above 8 even at room temperature. This behavior would suggest that the main pathway open for the disproportionation of the lower polysulfide ions leads over one of the higher polysulfide ions with lower polysulfide ions remaining virtually inactive. Assuming the pentasulfide ion to represent the main active species, the rate expression for the disproportionation of zerovalent sulfur at sufficiently high pH's, where the reverse reaction becomes insignificant, can be expressed in the form

$$-dm_{S(0)}/dt = k_f u_4 m_{S(0)} m_{OH^-}/m_{SH^-}{}^{2} \tag{28}$$

where u_4 represents the fraction of zerovalent sulfur S(0) present as pentasulfide ion, calculated by use of the relationship

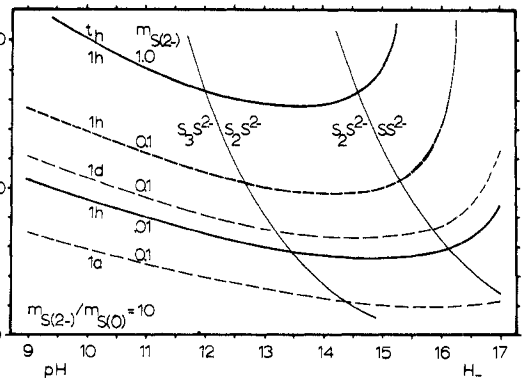

Figure 4. The dependence of T_h, the temperature at which half of the amount of zerovalent sulfur, present in the form of the polysulfide S_nS^{2-} ions, has, within a given period t_h, reacted to thiosulfate, as a function of pH and concentration of monosulfide and zerovalent sulfur in the ratio 10:1. For a solution containing 0.1 m total monosulfide and 0.1 m total zerovalent sulfur, T_h is shown for periods t_h of 1 hr (1h), 1 day (1d), and 1 year (1a).

$$u_1 + u_2 + u_3 + u_4 = 1 \tag{29}$$

and the equilibrium constants $K_{n/m}$ as derived in the preceding study.[3] After integration of eq 28 an expression is obtained allowing the calculation of t_h, the time required for half the pentasulfide, and thus $m_{S(0)}$, to disproportionate into monosulfide and thiosulfate

$$t_h = m_{SH^-}{}^{2}(\ln 2)/u_4 m_{OH^-} k_f \tag{30}$$

By inserting the equation describing the temperature dependence of k_f

$$\log k_f = -5600/T + 10.9 \tag{31}$$

into the logarithm of eq 30 a relationship is obtained allowing the determination of the temperature T_h at which half the zerovalent sulfur can be expected to have been consumed within a given period t_h at a given pH

$$T_h = -5600/[\log (0.69 m_{SH^-}{}^{2} u_4{}^{-1} m_{OH^-}{}^{-1} t_h{}^{-1}) - 10.9] \tag{32}$$

Figure 4 shows values for T_h as a function of pH, t_h, and m_{SH^-}, at a constant ratio of monosulfide sulfur to zerovalent sulfur, $m_{S^{2-}}/m_{S(0)}$, of 10. The kinetic stability of polysulfide solutions accordingly decreases with increasing pH to reach a minimum for solutions containing predominantly trisulfide ions. From then on, the temperatures required for half of the polysulfide ions, then largely present as disulfide ions, to disproportionate increases rapidly, resulting in high kinetic stabilities for extremely alkaline polysulfide solutions. It is obvious that the kinetic stability of polysulfide solutions increases rapidly with increasing monosulfide concentrations; solutions containing monosulfide and zerovalent sulfur in concentrations close to those used in this investigation then are shown to lose half their zerovalent sulfur at room temperature within 1 year only under the most unfavorable conditions at pH's (or H_-) of around 16; at higher or lower alkalinities these solutions can be expected to be even more stable. At higher temperatures, solutions containing predominantly trisulfide ion require about 1 hr at around 100° for half the zerovalent sulfur to disproportionate. These findings thus can be used to explain experimental observations[3] which showed that equimolar tetrasulfide-trisulfide and trisulfide-disulfide solutions may be heated to temperatures above 100° before disproportionation becomes rapid.

Registry No. S_nS^{2-}, 9080-49-3; $S_2O_3{}^{2-}$, 14383-50-7.