Optical Spectra and Equilibrium Distribution of Polysulfide Ions in Aqueous Solution at 20°

BY W. GIGGENBACH

The optical absorption spectra of aqueous polysulfide solutions were investigated over a pH range from 6.8 to 17.5 at 20° and controlled ionic strength ≥ 2.0. The four polysulfide species appearing in these solutions were identified as the di-, tri-, tetra-, and pentasulfide ions. The disulfide ion is characterized by one single band at wave numbers below 36 kK at 27.9 kK. The tri-, tetra-, and pentasulfide ions exhibit two absorption bands in this region at 24.0 and 33.0, 27.2 and 33.0, and 26.7 and 33.4 kK, respectively. Equilibrium constants were derived which permit the calculaton of the equilibrium distribution as a function of $B = [OH^-][SH^-]/S(0)$, with $S(0)$ the total concentration of zerovalent sulfur in solution. The tetrasulfide ion predominates in solutions of intermediate alkalinity, followed at higher pH by the trisulfide ion. The disulfide ion is the predominant species only at extremely high alkalinities. The pentasulfide ion, on the other hand, is formed in significant amounts only in nearly neutral or slightly acidic solutions without ever becoming the sole species present, even in solutions saturated with zerovalent sulfur.

Introduction

Notwithstanding the long history of polysulfide chemistry[1] the problem of the distribution of the various polysulfide species existing in aqueous solutions[2] can still be considered only partly solved. Earlier results based on electrode potential measurements[3,4] and suggesting that all ions S_nS^{2-} with $n = 1–5$ are formed in significant amounts within the small pH range of 10–13 were later disproved by spectroscopic studies[5,6] which showed that the tetra- and pentasulfide ions predominated in solutions of intermediate alkalinity (pH 9–14). The pentasulfide ion was considered[5] to be the only species to dissolve in water without disproportionation. Solubility measurements[7] in the system sulfur–sodium sulfide, however, showed that $\bar{n}$, the average number of atoms of zerovalent sulfur per polysulfide ion, did not exceed 3.8 in solutions saturated with sulfur at 25°, thus precluding the possibility of the formation of pure pentasulfide solutions. Virtually all these investigations were restricted to pH <14 which as will be shown precluded the observation of trisulfide and disulfide ions. The present work reports absorption spectra of the individual polysulfide ions S_nS^{2-}, together with the equilibrium distribution of the various species at room temperature as derived from equilibrium constants governing the $[SH^-]$, $[OH^-]$, and $S(0)$ dependence of these polysulfide equilibria.

Experimental Section

Materials.—Water was purified by distillation under purified nitrogen at atmospheric pressure. It then was stored under purified N_2 and boiled for about 10 min before each use to remove gaseous impurities. The sodium polysulfides Na_2S_2 and Na_2S_4 used in this investigation were prepared and analyzed as described by Schwarzenbach and Fischer.[5] The preparation of the polysulfides in absolute ethanol with the strict exclusion of oxygen and water led to compounds whose analyses corresponded to $Na_{1.98}S_{1.97}$ and $Na_{1.99}S_{3.96}$, respectively. The sulfide–sulfur values obtained by the iodometric and acidimetric method[5] were identical, thus indicating the absence of thiosulfate. Sodium sulfide

$Na_2S \cdot 9H_2O$ was purified by recrystallization from oxygen-free water under nitrogen. Boric acid, sodium chloride, sodium hydroxide, and concentrated HCl were reagent grade and were used without further purification. The sodium hydroxide dissolved up to saturation (20 M) without the formation of a precipitate; thus the presence of significant amounts of Na_2CO_3 impurities could be excluded.

The experimental solutions were obtained by mixing predetermined amounts of concentrated stock solutions and water in a volumetric flask equipped with an N_2 side arm, to give 50-ml quantities of solutions with the desired concentrations. All solutions were prepared and handled under purified nitrogen mainly by use of Schlenk-tube techniques. With respect to the nature of the stock solutions used, three pH regions can be distinguished.

1. pH 6.8–11.—In order to obtain reproducible and stable pH conditions in this intermediate pH range the spectra were investigated in a 0.4 M borate buffer prepared by mixing a 2.0 M (or 0.2 M) solution of $Na_2S \cdot 9H_2O$ with 20 ml of a 1 M solution of boric acid with varying additional amounts of 1.0 M NaOH or HCl solutions to give the required pH. Zerovalent sulfur was introduced in the form of approximately 0.05 M Na_2S_4 solutions. After addition of sufficient amounts of NaCl to raise the ionic strength to 2.0, water was added to give 50 ml. The pH of the resulting solution was determined by use of a calibrated glass electrode at 20° with an accuracy of ± 0.05 unit. Approximate OH^- activities for these solutions were obtained from $pOH^- = 14.00 - pH$. The SH^- concentrations in this pH region were calculated by use of a value of 1.0×10^{-7} for K_{a1} of H_2S.

2. pH 11–14.5.—The OH^- concentrations for this pH range were calculated directly from the concentrations of NaOH and $Na_2S \cdot 9H_2O$ present in the solution by assuming complete hydrolysis of sulfide to form bisulfide and hydroxide ion.[8] Thus $[OH^-]$ is taken as the sum of $[OH^-]$ added in the form of NaOH and $[OH^-] = [SH^-]$ due to the hydrolysis of S^{2-}. Again the solutions were prepared by mixing varying amounts of 1.0 M sulfide, 0.05 M tetrasulfide, and 4.0 M sodium hydroxide stock solutions and sodium chloride and water to give 50 ml of a solution with an ionic strength of 2.0. Variation of ionic strength from 0.4 to 2.0 caused only a $\pm 10\%$ variation in the measured absorbances. In the present investigation, however, no attempt was made to extrapolate experimental values to zero ionic stength, all data reported for solutions with pH 6.8–14 being measured at an ionic strength of 2.0. The equilibrium calculations for this ionic strength were carried out in terms of molar concentrations.

3. pH >14.—In this extremely high pH range with OH^- concentrations between 1 and 18 M the large increase in the activity of the OH^- ion was taken into account by use of the values for the H_- acidity function as given by Schwarzenbach and Sulzberger[9] and Yagil.[10] For OH^- concentrations exceeding

(1) J. Berzelius, *Ann. Chim. Phys.*, [2] **20**, 113 (1822).
(2) J. S. Thomas and A. J. Rule, *J. Chem. Soc.*, **105**, 188 (1914).
(3) D. Peschanski and G. Valensi, *J. Chim. Phys.*, **46**, 602 (1949).
(4) G. Maronny, *ibid.*, **56**, 140 (1959).
(5) G. Schwarzenbach and A. Fischer, *Helv. Chim. Acta*, **43**, 1365 (1960).
(6) A. Teder, *Ark. Kemi*, **30**, 379 (1969); **31**, 173 (1969).
(7) R. H. Arntson, F. W. Dickson, and G. Tunell, *Science*, **128**, 716 (1958).

(8) W. Giggenbach, *Inorg. Chem.*, **10**, 1333 (1971).
(9) G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, **27**, 348 (1948).
(10) G. Yagil, *J. Phys. Chem.*, **71**, 1034 (1967).

1 M, [OH$^-$] was replaced by values for b_- as derived[11] from

$$b_- = K_w/h_- \qquad (1)$$

with h_- being defined by $H_- = -\log h_-$. Because of $b_- \simeq$ [OH$^-$] at [OH$^-$] < 2.0, the region of constant ionic strength at [OH$^-$] < 2.0 can be expected to join that at [OH$^-$] > 2.0, where the ionic strength is determined by [OH$^-$], without any noticeable break. The solutions were prepared by mixing sulfide and tetrasulfide solutions with varying amounts of 20 M NaOH solutions (80 g of NaOH/100 ml of solution) and water to give 50 ml. At H_- values above 15, where the formation of sulfide ions becomes significant, the SH$^-$ concentrations were estimated by use of a value[8] for K_{a_2}, the second ionization constant of H$_2$S, of 7.0×10^{-18} at 20° and the equation

$$[SH^-] = (S_t h_-)/(K_{a_2} + h_-) \qquad (2)$$

with S_t the total free sulfide concentration, [H$_2$S] + [HS$^-$] + [S^{2-}].

Over the pH range investigated measurements were carried out on solutions varying in total free sulfide concentration, S_t, between 0.1 and 2.0 M and in total zerovalent sulfur $S(0)$ = $\bar{n}$[S$_{\bar{n}}$S^{2-}] between 0.001 and 0.02 g-atom/l. The ratio $S(0)/S_t$ never exceeded 0.1; thus variations in S_t due to variations in the polysulfide concentrations could be neglected. The solutions containing zerovalent sulfur in the form of polysulfide ions were stable at 20° with respect to disproportionation. Even in highly concentrated OH$^-$ solutions no decrease in the polysulfide absorptions was observed for periods of several days. Attainment of equilibrium between the different polysulfide ions after changes in [OH$^-$] or [SH$^-$] is very rapid;[12] 5 min after mixing the stock solutions no changes, due to rearrangement reactions, could be observed in the absorption spectra.

Spectra.—The spectrophotometer used was the Zeiss PMQII with the monochromator M4 QIII. Most of the spectra were measured in commercial 0.2-cm stoppered quartz cells. Only for solutions very low in $S(0)$ (the total concentration of zerovalent sulfur) were cells with a pathlength of 1.0 cm used. Because of the strong ctts transition[13] of the SH$^-$ ion at 43.6 kK the spectral range was limited in the present investigation to wave numbers below 36 kK. The cells were filled by use of an all-glass syringe with the tip drawn out to a capillary.

Results

Considering only equilibria between species differing in one sulfur atom per polysulfide ion and assuming that no gap exists in the series S$_n$S^{2-}, with n = 1, 2, 3, . . ., equilibria between polysulfide ions in aqueous solution can generally be described by the equation

$$n S_m S^{2-} + SH^- + OH^- \rightleftharpoons m S_n S^{2-} + H_2O \qquad (3)$$
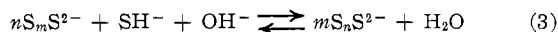
An assumption is made that the condition $n = m - 1$ is applicable to aqueous polysulfide solutions and this will later be shown to be valid. The equilibrium expression for reaction 3 on the molar scale

$$K_{n/m} = \frac{[S_n S^{2-}]^m}{[S_m S^{2-}]^n [SH^-][OH^-]} \qquad (4)$$

describes the dependence of the concentration of an individual polysulfide ion on the product [SH$^-$][OH$^-$] = P.

In Figure 1 a series of spectra obtained by varying log P from about -8.3 to 2.5 are shown. In a solution of 0.005 g-atom of zerovalent sulfur in 0.2 M total monosulfide at a pH of 7.0 (log P = -8.0), the absorption spectrum up to 37 kK exhibits two bands at about 27 and 33 kK. With increasing pH the molar absorptivity of both bands decreases and a slight shift toward higher wave numbers is observed for the low-energy band. At log P exceeding -2.5 a new band appears at

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(13) M. J. Blandamer, J. M. Gross, and M. C. R. Symons, *Trans. Faraday Soc.*, **60**, 494 (1964).
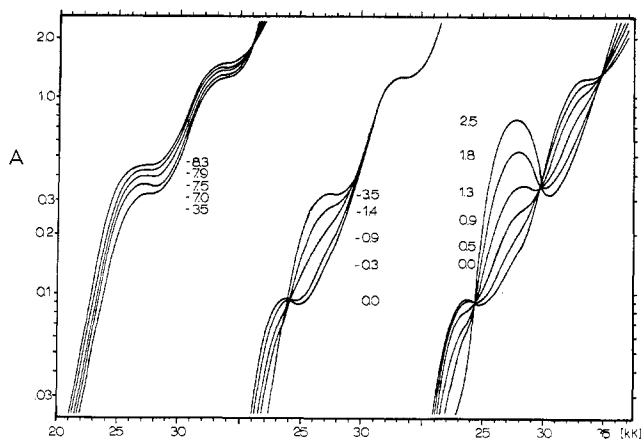

Figure 1.—Spectra of polysulfide solutions containing 5.0 × 10^{-3} g-atom of zerovalent sulfur as a function of log P = log [SH$^-$][OH$^-$]) (d = 0.2 cm).

lower wave numbers at about 24 kK and increases in strength until a value for log P of about 0.0 is reached. From then on the band at 24 kK decreases again while another band at about 28 kK rapidly increases with increasing P. No additional bands were observed in solution with log P up to 3.0. Over the entire range of P values the yellow color of the solutions remained essentially unchanged; the observed changes in the absorption spectra, however, indicate the formation of at least three different species, with the species present at the highest P values being designated as S$_a$S^{2-}, followed at lower P values by S$_b$S^{2-}, S$_c$S^{2-}, . . ., S$_n$S^{2-}.

Identification of Species.—It follows from eq 3 that n, the number of atoms of zerovalent sulfur per polysulfide ion, decreases with increasing P, with the smallest ion existing being present in the most alkaline solution. By substituting [S$_a$S^{2-}] = $A_a/\epsilon_a d$ and [S$_b$S^{2-}] = $A_b/\epsilon_b d$ for [S$_n$S^{2-}] and [S$_m$S^{2-}] in eq 4, with A_n and ϵ_n the absorbance and molar absorptivity of the species S$_n$S^{2-} and d the pathlength of the cell, and taking the logarithm a relationship for constant P is obtained

$$\log A_b = \frac{b}{a} \log A_a + C \qquad (5)$$

which allows the ratio b/a to be determined from the slope σ of a plot of log A_b vs. log A_a for solutions varying in $S(0)$.

Because of the strong overlap of the bands of the two species S$_a$S^{2-} and S$_b$S^{2-} (Figure 1) it was not possible to use the directly measured absorbances at 28 and 24 kK, respectively. With $r_{b/a}$ representing the ratio of the absorbance of the species S$_b$S^{2-} measured at a position close to its absorption maximum (28 kK) and that of the species S$_a$S^{2-} (24 kK) and with $r_{a/b}$ being the absorbance ratio of the species S$_a$S^{2-} determined at 24 and 28 kK, a relationship

$$A_b' = \frac{r_{b/a}(A_b r_{a/b} - A_a)}{r_{a/b} r_{b/a} - 1} \qquad (6)$$

is obtained which allows, by use of the law of additive absorbances, the calculation of A_b' the corrected absorbance of the species S$_b$S^{2-} at its absorption maximum. A corresponding relationship is used to obtain corrected values of A_a'. Equation 6 is generally applicable in the resolution of overlapping bands of two

species into their individual absorbances. Values for $r_{a/b}$ and $r_{b/a}$ were obtained from spectra measured on solutions with P values favoring the presence of only one species. For S_aS^{2-}, absorbing at about 28 kK, these conditions were achieved by use of almost saturated sodium hydroxide solutions (18 N in OH$^-$). The value for $r_{b/a}$ for the species S_bS^{2-} could only be estimated approximately as, at the P value at which $A_b = \epsilon_b c_b d$ reaches a maximum, appreciable amounts of the third species S_cS^{2-} with an absorption at about 27 kK are formed. Therefore, preliminary values for A_b' were calculated by use of an estimated value of $r_{b/a}$, which later was found to be close to the "true" value of 2.1.

In the determination of A_a' and A_b' it is desirable for the two species to be present in comparable amounts. The measurements on the solutions containing varying amounts of $S(0)$, therefore, were carried out at a value of log P of 0.87 (0.4 M total monosulfide, 4.4 M NaOH). But even at this rather high alkalinity the absorption of the third species S_cS^{2-} with its absorption at around 27 kK, close to that of S_bS^{2-} at 28 kK, cannot be neglected. With $c > b > a$ the amount of S_cS^{2-} is likely to increase with increasing $S(0)$; the actual value for $\sigma_{b/a} = $ log A_{24}/log A_{28}, therefore, can be expected to be somewhat higher than the measured value, especially at higher $S(0)$. From Figure 2 where values for log A_b' are
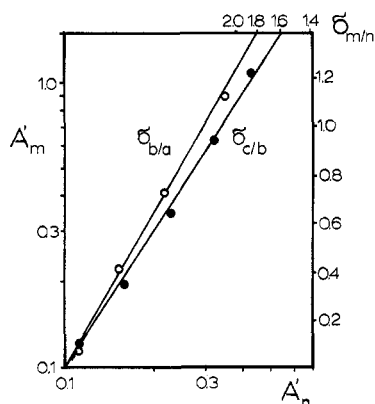

Figure 2.—Plot of log A_m vs. log A_n for a series of polysulfide solutions containing varying amounts of zerovalent sulfur at constant [SH$^-$] and [OH$^-$]; the measured points are shifted vertically to $A_m = 0.1$ for $A_n = 0.1$.

plotted vs. log A_a' a value of 1.8 is derived. With possible values for a of 4, 3, 2, and 1 the ratio σ may assume the values 1.2, 1.33, 1.5, and 2.0, respectively. Considering the fact that the measured σ is likely to be too low the next higher value of 2.0 is adopted, leading to values of 1 and 2 for a and b, respectively. The additional possibilities of a and b being 2 and 4 or 1 and 3 were also taken into consideration but had to be abandoned because of strong evidence favoring the first possibility as shown below.

The nature of the species predominant in solutions with log P values between -7 and -1 was determined in a similar way by plotting log $A_c' = $ log A_{28}' vs. log $A_b' = $ log A_{24}' for a series of solutions containing varying amounts of $S(0)$ at a constant value of log $P = -1.05$ (0.1 M monosulfide, 0.9 M NaOH). Again, the influence of the absorption of a third species, that at 28 kK of the disulfide ion SS^{2-}, is expected to lead to σ values, at least at low $S(0)$, somewhat higher than the actual values. The slope σ thus derived from measure-

ments on solutions containing $(0.6-2.4) \times 10^{-2}$ g-atom of zerovalent sulfur is about 1.6. With $b = 2$ and $c = \sigma b$ the absorption at 27 kK reaching a maximum at low P values, therefore, is ascribed to the tetrasulfide ion S_3S^{2-}.

A careful investigation of the pH dependence of the absorption at about 27 kK, however, shows that a further species is formed at very low P values. With decreasing pH at constant $S(0)$ and total monosulfide (0.2 M), the band at 27 kK continually moves toward lower wave numbers, and a plot of A_{27} and A_{33} vs. log P as shown in Figure 3 exhibits a marked rise in absor-
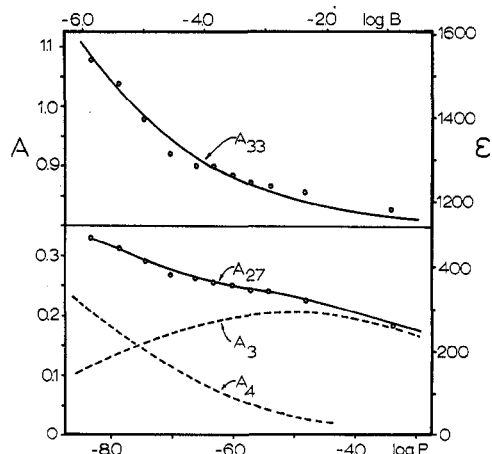

Figure 3.—Plot of A_{27} and A_{33} vs. log P for solutions containing 3.5×10^{-3} g-atom of $S(0)$. Lines represent values for A_{33}, A_{27}, A_3, and A_4 as calculated by use of $K_{3/4} = 4.0 \times 10^5$, ϵ_3' 320, and ϵ_4' 640 ($d = 0.2$ cm).

bance starting at a P value of about -7.0. These discontinuities were ascribed to the formation of a species which is assumed to represent the next member in the series S_nS^{2-}, the pentasulfide ion, with $\bar{n} = 4$. In the present investigation no indications for the presence of an additional polysulfide ion with $n > 4$ could be observed for aqueous solutions at room temperature, in agreement with the fact that $\bar{n}$, the number of atoms of zerovalent sulfur per polysulfide ion at 25°, reaches a maximum of 3.77 for sulfide solutions saturated with sulfur.[7] The existence of a gap in the series S_nS^{2-} of the four polysulfide ions observed can also be excluded, as this should lead to considerably higher $\bar{n}$ values. The limiting value of 3.77 at 25° also precludes the possibility of the pentasulfide ever becoming the sole species present and rather suggests the coexistence of tetra- and pentasulfide ions in solutions saturated in $S(0)$.

Construction of the Absorption Spectra of the Individual Ions S_nS^{2-}.—The only solution containing one single polysulfide species is expected to be that of the disulfide ion at extremely high P values. By analogy to a procedure outlined in a previous study,[8] ϵ_1, the molar absorptivity of the disulfide ion, was obtained by extrapolating $1/\epsilon'$, the reciprocal of the apparent molar absorptivity, to infinite P values by plotting $S(0)d/A_{28} = 1/\epsilon_1'$ vs. $1/P$. The resulting value for ϵ_1 at 27.9 kK is 850 ± 30.

In constructing the spectral bands it was assumed that their shapes can be described[14] by a gaussian curve

(14) W. Kuhn and E. Braun, *Z. Phys. Chem.*, **8**, 281 (1930).

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<div align="center">TABLE I</div>
<div align="center">SPECTRAL CHARACTERISTICS[a] OF THE IONS S_nS^{2-}</div>

n		ν_n', kK	ν_n'', kK	ϵ_n'	ϵ_n''	ϵ_n' $(=n\epsilon_n')$	ϵ_n'' $(=n\epsilon_n'')$	ν_s, kK	$f_{n'}'$	$f_{n'}''$
1	SS^{2-}	27.9	...	850 ± 30	...	850 ± 30	...	2.4	0.0156	...
2	S_2S^{2-}	24.0	33.0	95 ± 5	1140 ± 20	190 ± 10	2280 ± 40	2.8	0.0041	0.0488
3	S_3S^{2-}	27.2	33.0	320 ± 10	1140 ± 20	960 ± 30	3420 ± 60	2.8	0.0206	0.0731
4	S_4S^{2-}	26.7	33.4	640 ± 40	2000 ± 200	2560 ± 160	8000 ± 800	3.2	0.0624	0.1960

[a] Error margins for molar absorptivities give range of variation compatible with internal consistency.

as given by

$$\epsilon = \epsilon_{max} e^{-[(\nu-\nu_{max})/\nu_s]^2} \qquad (7)$$

with ϵ representing the molar absorptivity at any given wave number ν and ν_s the standard deviation in wave numbers, approximately related to the half-width $\nu_{1/2}$ of the band by $\nu_s = 0.6\nu_{1/2}$. The shape and the position of an absorption band, therefore, are characterized by three parameters: the molar absorptivity ϵ_{max}, at the wave number ν_{max}, with the width of the band ν_s taken at $\epsilon_s = \epsilon_{max} e^{-1} = 0.37\epsilon_{max}$. In Figure 4
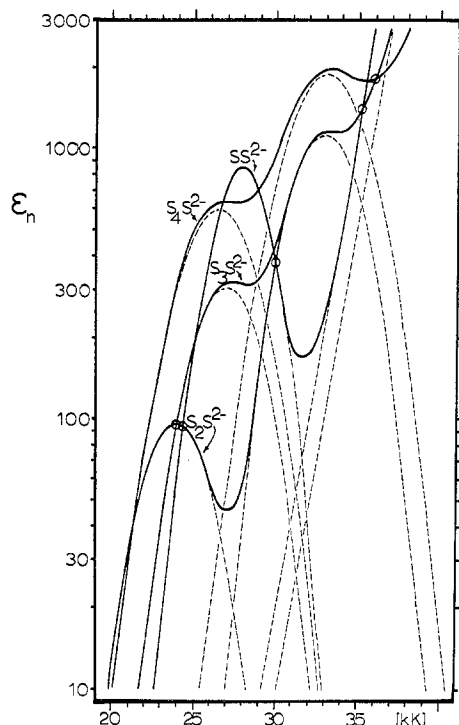

Figure 4.—Absorption spectra of the polysulfide ions S_nS^{2-}. Dashed lines show individual absorption bands as given by eq 7. Circles represent isosbestic points used in the construction of the spectra.

the measured spectrum of the SS^{2-} ion is shown together with a curve calculated by use of $\epsilon_{max} = 850$, $\nu_{max} = 27.9$, and $\nu_s = 2.4$ kK.

The absorption spectra of the overlapping trisulfide and tetrasulfide ions were constructed by taking advantage of the isosbestic points appearing in spectra of solutions containing SS^{2-} and S_2S^{2-} ions at 24.4, 30.0, and 35.0 kK and those containing S_2S^{2-} and S_3S^{2-} ions at 24.0 kK. All values for the molar absorptivities ϵ_n in this investigation are based on the concentration of zerovalent sulfur as defined by

$$A_n = [S_nS^{2-}]n\epsilon_n d = S(0)\epsilon_n d \qquad (8)$$

At the wave number of an isosbestic point the molar absorptivities of two adjoining species, therefore, are

related by $\epsilon_m = \epsilon_n = A_i/S(0)d = \epsilon_i$ with A_i the measured absorbance and ϵ_i the molar absorptivity based on $S(0)$ at the isosbestic point. The spectra of the trisulfide and tetrasulfide ions show two bands at about 24.0 and 33.0 kK, and 27.2 and 33.0 kK, respectively. With approximate values for ν_s taken from the measured spectra at $0.37A_{max}$, preliminary values of ϵ_{max}' and ϵ_{max}'', the molar absorptivities for lower and higher energy transition, respectively, were calculated by inserting ϵ_i and the corresponding values for ν_i, ν_s, and ν_{max} into eq 7. By readjusting ν_s to fit the experimental curves the final values for ϵ_2', ϵ_2'', ϵ_3', and ϵ_3'', the molar absorptivities for the first and second bands of the tri- and tetrasulfide ions, were obtained as shown in Figure 4 and Table I.

Because of the impossibility of preparing pure pentasulfide solutions and the lack of suitable isosbestic points in solutions containing tetra- and pentasulfide ions together, only approximate values for ϵ_4 could be derived. The increase in the absorbance at 27 kK as shown in Figure 3 due to the formation of the S_4S^{2-} ion at log P values below -6.5 was used to obtain an estimate of the fraction of zerovalent sulfur present as S_4S^{2-}. Thus by substituting $(S(0) - 4[S_4S^{2-}])/3$ for $[S_3S^{2-}]$ in the logarithm of the equilibrium expression for the tetrasulfide–pentasulfide equilibrium

$$\log K_{3/4} = 4 \log [S_3S^{2-}] - 3 \log [S_4S^{2-}] - \log P \qquad (9)$$

and by differentiating log P with respect to $[S_4S_2^-]$ and writing $u_4 S(0)/4 = [S_4S^{2-}]$, with u_4 the fraction of zerovalent sulfur present in the form of the pentasulfide ion, a relationship is obtained

$$-\frac{d \log P}{d u_4} = \frac{1.74}{1 - u_4} + \frac{1.30}{u_4} \qquad (10)$$

which shows that for any value of u_4, the change in the fraction of zerovalent sulfur present as S_4S^{2-}, Δu_4, cannot exceed 0.33 for the range of log P values of 1.8 from -6.5 to -8.3, within which the formation of the pentasulfide ion could be observed. With this value for Δu_4 the molar absorptivity of the pentasulfide ion at 27 kK as calculated from

$$\epsilon_4' = \frac{A_{27}}{S(0)\Delta u_4 d} - \frac{\epsilon_3'(1 - \Delta u_4)}{\Delta u_4} \qquad (11)$$

was found to be 620. This value represents only a minimum value; however, by combining eq 10 and 11 and inserting the experimental values of A_{27} for a series of log P values, an average value for ϵ_4' of 640 ± 40 was obtained. In a similar procedure the molar absorptivity ϵ_4'' of the second band of the pentasulfide ion at 33.4 kK was found to be 2000 ± 200. The S_4S^{2-} spectrum is best reconstructed by use of a value for ν_s of 3.2 kK for both bands.

Table I also contains values for the oscillator strength

f of the individual bands as calculated by use of the equation

$$f = 4.32 \times 10^{-9} \epsilon_{max} \nu_s \sqrt{\pi} \qquad (12)$$

Evaluation of Equilibrium Constants.—The equilibrium expressions for equilibria among disulfide, trisulfide, and tetrasulfide ions are given by

$$K_{1/2} = \frac{[SS^{2-}]^2}{[S_2S^{2-}]P} \qquad (13)$$

$$K_{2/3} = \frac{[S_2S^{2-}]^3}{[S_3S^{2-}]^2 P} \qquad (14)$$

Because of the strong overlap in the absorption spectra and the stability regions of the three species, modified equations were used in evaluating $K_{1/2}$ and $K_{2/3}$. With

$$S(0) = \sum n[S_nS^{2-}] \qquad (15)$$

and

$$A_1{}^* + A_3{}^* = [SS^{2-}]\epsilon_1{}^*d + [S_3S^{2-}]\epsilon_3{}^*d \qquad (16)$$

together with

$$2[S_2S^{2-}]\epsilon_2 d = A_{23} \qquad (17)$$

and eq 13 and 14, respectively, the relationships

$$K_{1/2} = \frac{2(S(0)\epsilon_2\epsilon_3{}^*d - A_{23}\epsilon_3{}^* - A^*\epsilon_2)^2}{A_{23}P\epsilon_2 d(\epsilon_3{}^* - \epsilon_1{}^*)} \qquad (18)$$

$$K_{2/3} = \frac{9A_{23}{}^3(\epsilon_1{}^* - \epsilon_3{}^*)^2}{8\epsilon_2 dP(S(0)\epsilon_1{}^*\epsilon_2 d^* - A_{23}\epsilon_1{}^* - A^*\epsilon_2)^2} \qquad (19)$$

are obtained which take into account any influence due to the presence of the third species coexisting with the species m and n for which $K_{n/m}$ is determined. The asterisked symbols represent the measured absorbance A^* and the absorbances and molar absorptivities of di- and tetrasulfide ion at 27.5 kK, a wave number approximately halfway between ν_1 and ν_3.

Because of the large difference in P values between the stability regions of S_4S^{2-} and the lower polysulfide ions SS^{2-} and S_2S^{2-}, their influence on the equilibrium $S_3S^{2-}-S_4S^{2-}$ was considered to be negligible. In the calculation of $K_{3/4}$ for the tetra- and pentasulfide ions, with their practically identical values of ν_{max} of 27 kK, a relationship was derived by use of eq 15 and

$$A_{27} = A_3 + A_4 = (3\epsilon_3[S_3S^{2-}] + 4\epsilon_4[S_4S^{2-}])d \qquad (20)$$

Together with

$$K_{3/4} = \frac{[S_3S^{2-}]^4}{[S_4S^{2-}]^3 P} \qquad (21)$$

the new expression becomes

$$K_{3/4} = \frac{64(A_{27} - S(0)\epsilon_4 d)^4}{81(A_{27} - S(0)\epsilon_3 d)^3(\epsilon_4 - \epsilon_3)dP} \qquad (22)$$

The values for the equilibrium constants $K_{n/m}$ as calculated by use of the experimental data and eq 18, 19, and 22 are shown in Table II.

Equilibrium Distribution of the Ions S_nS^{2-}.—By use of the experimental values $K_{1/2}$, $K_{2/3}$, and $K_{3/4}$ the concentrations of the polysulfide ions S_nS^{2-} as a function of P, the product $[SH^-][OH^-]$, can be calculated. By introducing[6] the parameter B as defined by

$$B = P/S(0) = [SH^-][OH^-]/S(0) \qquad (23)$$

these concentrations may more conveniently be expressed in fractions of zerovalent sulfur present in the form of a particular polysulfide ion.

By taking

$$u_n = \frac{[S_nS^{2-}]n}{S(0)} \qquad u_m = \frac{[S_mS^{2-}]m}{S(0)} \qquad (24)$$

eq 4 becomes

$$K_{n/m} = \frac{m^n u_n{}^m}{n^m u_m{}^n} \frac{1}{B} \qquad (25)$$

With u_1, u_2, u_3, and u_4 representing the fractions u of $S(0)$ being present in the form of di-, tri-, tetra-, or pentasulfide ion, the expressions for $K_{1/2}$, $K_{2/3}$, and $K_{3/4}$ become

$$K_{1/2} = \frac{2u_1{}^2}{u_2 B} \qquad (26)$$

$$K_{2/3} = \frac{9u_2{}^3}{8u_3{}^2 B} \qquad (27)$$

$$K_{3/4} = \frac{64u_3{}^4}{81u_4{}^3 B} \qquad (28)$$

At high B values the presence of the pentasulfide ion was assumed negligible; thus with $u_1 + u_2 + u_3 = 1$, the relationship describing the dependence of u_1 on B, e.g., is given by

$$3u_1{}^3 + 2u_1{}^2 B(K_{1/2}K_{2/3})^{1/2} -$$
$$(1 - u_1)B^2 K_{1/2}(K_{1/2}K_{2/3})^{1/2} = 0 \quad (29)$$

Values for u_1, u_2, and u_3 were calculated by solving eq 29 for B, whereas u_4 was directly obtained from eq 28. In Figure 5a the calculated values for u_1, u_2, u_3, and u_4 are shown together with a series of experimental points directly obtained from the measured absorbance values by use of the equation

$$u_n = \frac{A_n - \epsilon_m{}^* S(0)d}{(\epsilon_n{}^* - \epsilon_m{}^*)S(0)d} \qquad (30)$$

where $\epsilon_n{}^*$ and $\epsilon_m{}^*$ represent molar absorptivities for two adjoining species S_nS^{2-} and S_mS^{2-} at the position of the absorption maximum ν_n at which A_n is measured.

Figure 5c also shows calculated values of $\bar{n}$, the average number of atoms of zerovalent sulfur per polysulfide ion as given by

$$\bar{n} = \sum n[S_nS^{2-}]/\sum[S_nS^{2-}] = \sum n u_n \qquad (31)$$

Discussion

Spectra of the Polysulfide Ions S_nS^{2-}.—In an attempt to interpret the absorption spectra of a series of sulfanes S_nSH_2 and some of their derivatives S_nSR_2, Fehér and Münzner[15] showed that the simple free-electron model, previously proposed for conjugated organic systems,[14] may successfully be used to explain the intensities and positions of the low-energy bands as a function of
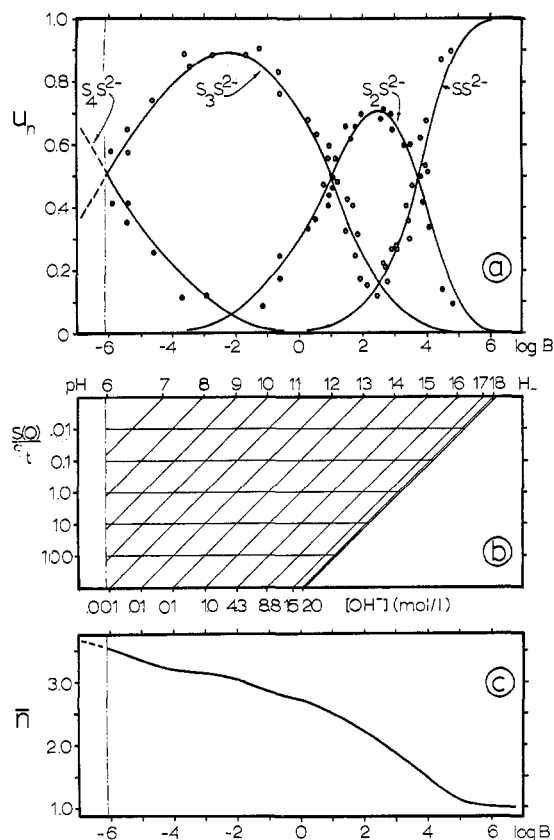
TABLE II
EQUILIBRIUM CONSTANTS $K_{n/m}$ FOR THE SYSTEMS $S_nS^{2-}-S_mS^{2-}$ (IONIC STRENGTH ≥ 2.0, TEMPERATURE 20°)

Equilibrium	$K_{n/m}$	Log $K_{n/m}$
$SS^{2-}-S_2S^{2-}$	2.0×10^{-4}	-3.70 ± 0.15^a
$S_2S^{2-}-S_3S^{2-}$	1.8×10^{-2}	-1.75 ± 0.15^a
$S_3S^{2-}-S_4S^{2-}$	4.0×10^5	5.60 ± 0.30^b

^{a} Standard deviation of values obtained from eq 18 and 19.
^{b} Estimated uncertainty.

(15) F. Fehér and H. Münzner, *Chem. Ber.*, **96**, 1131 (1963).

Figure 5.—Equilibrium distribution of polysulfide ions S_nS^{2-} as a function of log B. Circles in part a represent experimental values of u_n as calculated from eq 30, whereas solid lines were calculated by use of the experimental values for $K_{n/m}$. Part b represents the relationships among log B, $S(0)/S_t$, and solution pH. Part c gives $\bar{n}$, the average number of atoms of zerovalent sulfur per polysulfide ion, as a function of log B.

the length of the polysulfur chain. The wave number of the lowest transition of these compounds decreases steadily with increasing n, whereas the intensity of the first band increases in proportion to $n + 1$, so that $\epsilon_n/(n + 1) \approx$ constant. These findings strongly suggest the presence of a conjugated system extending over the entire length of the polysulfur chain. In order to explain the out-of-plane conjugation as required by the helical structure of the polysulfur chain and to provide partly filled orbitals capable of accommodating the delocalized electrons, some contribution from d orbitals had to be assumed. In agreement with recent calculations[16] which showed that contributions from d orbitals to the ground state in sulfur compounds rapidly decrease with decreasing oxidation state, the influence of these $d\pi$–$d\pi$ interactions on the strength of the S–S bonds was found to be rather small.

On removing the two protons from a sulfane molecule to form a polysulfide ion, the electrons previously localized in the S–H σ bond and now added to the polysulfur chain lead to a decrease in the average oxidation state or charge per sulfur atom by $2/(n + 1)$ units. The influence of this reduction in oxidation state thus should be strongest for the shorter polysulfide ions, whereas with increasing n the pattern as observed for the sulfanes may be approached.

The electronic configuration of the ground state of the homonuclear, diatomic ion SS^{2-} corresponds to a

$^1\Sigma_g$ state, with the lowest energy absorption being expected to be due to the perpendicular, allowed transition according to

$$(\pi_g)^3(\sigma_u)^1\Pi_u \longleftarrow (\pi_g)^4 \, {}^1\Sigma_g$$
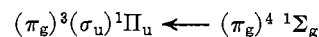
whereas the next transition expected at higher energies

$$(\pi_u)^3(\pi_g)^4(\sigma_u)^1\Pi_g \longleftarrow (\pi_u)^4(\pi_g)^4 \, {}^1\Sigma_g$$
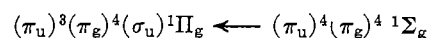
would be both parity and symmetry forbidden. These assignments are in agreement with the experimental findings which show one single, relatively strong (ϵ_1 850) absorption band at 27.9 kK, with no indication of the presence of another band up to about 37 kK. The very strong absorption starting at about 33 kK is ascribed to the charge transfer to solvent transition of the ion.

The 20 valence electrons of the triatomic ion S_2S^{2-} should, according to the rules proposed by Walsh,[17] favor a bent ground-state configuration. The structure of this ion as determined by X-ray diffraction methods[18] shows an SSS angle of 103° and S–S bond distances of 2.15 Å. The ground state of the trisulfide ion, therefore, is probably[17] given by $(a_1)^2(b_1)^2$ $^1A_2$ with the first absorption band being due to the symmetry-allowed transition

$$\ldots (b_1)(a_1) \, {}^1B_1 \longleftarrow \ldots (b_1)^2 \, {}^1A_1$$

The Walsh diagram[17] for triatomic molecules suggests some considerable increase in the apex angle for the $^1B_1$ state as compared with that for the $^1A_1$ ground state. The rather low intensity (ϵ_2' 190) of the first absorption band of the ion S_2S^{2-} at 24.0 kK thus is likely to be due to the $^1B_1 \leftarrow {}^1A_1$ transition being Franck–Condon forbidden. The second much stronger transition (ϵ_2'' 2280) at 33.0 kK is assigned to the fully allowed $^1B_2 \leftarrow {}^1A_2$ transition, as the other two possible transitions $^1A_2 \leftarrow {}^1A_1$ or $^1A_1 \leftarrow {}^1A_1$ involving orbitals of comparable energy[17] are either symmetry forbidden or can be expected to be also Franck–Condon forbidden.

The spectra of both the disulfide and trisulfide ions thus may tentatively be explained by neglecting any contributions from delocalized orbitals in connection with $d\pi$–$d\pi$ interaction. The bond lengths[18] as determined for BaS_4, however, with 2.03 Å for the outer bonds and 2.07 Å for the middle bond already suggest some contribution from doubly bonded, butadiene-like configurations to the ground state of the tetrasulfide ion due to the $d\pi$–$d\pi$ interactions as symbolized by

$$\bar{S}{=}\bar{S}{-}\bar{S}{=}\bar{S}$$
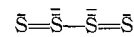
The similarities in the shape of the tetrasulfide and pentasulfide spectra and the shift of the latter toward lower wave numbers further support the assumption that with increasing n the spectral properties of the ions S_nS^{2-} may increasingly be determined by the presence of delocalized orbitals.

The absorption spectrum of the tetrasulfide as determined in this investigation closely agrees with that previously reported.[5] The molar absorptivity, however, of the pentasulfide ion (2560) was found to be considerably higher than the value of 1600 as reported

(16) B. C. Webster, *J. Chem. Soc. A*, 2909 (1968).

(17) A. D. Walsh, *ibid.*, 2266 (1953).

(18) S. C. Abrahams, *Acta Crystallogr.*, **7**, 432 (1954).

by Schwarzenbach and Fischer for the band at about 27 kK. This discrepancy, however, is most readily explained considering the invalid assumption of these authors that pentasulfide would dissolve undecomposed. In view of the present findings on dissolving solid pentasulfide in water an approximately equimolar mixture of tetra- and pentasulfide is obtained with an average molar absorptivity $(\epsilon_4' + \epsilon_5')/2$ of about 1760.

The characteristic spectrum of the disulfide ion with its single band at 27.8 kK had previously been observed by Blandamer, *et al.*,[13] in strongly alkaline sulfide solutions but had erroneously been ascribed to the charge transfer to solvent transition of the sulfide ion S^{2-} The present investigation confirms previous findings[19] according to which the concentration of zerovalent sulfur in an aqueous polysulfide solution for log B between -4.0 and $+5.0$ is most readily obtained from its absorbance at 35 kK. At this wave mumber the molar absorptivities per atom of zerovalent sulfur of all three species present are practically identical with a value ϵ_{35} of 1400 ± 20. For solutions with low values of log B between -6.1 and $+2.0$, however, the absorbance at 36.0 kK with ϵ_{36} 1800 ± 40 is better suited.

Equilibrium Distribution of the Polysulfide Ions S_nS^{2-}.—Figure 5a shows the equilibrium distribution of polysulfide ions as a function of log B = log ($[SH^-]\cdot$ $[OH^-]/S(0)$). In order to facilitate the determination of log B, a diagram taking into account changes in $[SH^-]$ due to the formation of H_2S in the acidic range and those due to the formation of S^{2-} and the increase in OH^- activity at extremely high pH's is added. Thus for a given ratio $S(0)/S_t$, with S_t the total concentration of free monosulfide sulfur as given by $[H_2S] + [SH^-] + [S^{2-}]$, values for log B are obtained by following the horizontal line for a given $S(0)/S_t$ ratio to the 45° line representing the solution pH (Figue 5b).

At low pH's the amount of zerovalent sulfur pres-

ent in solution is determined by its solubility[20] as given by

$$K_s = \frac{S(0)}{[SH^-][OH^-]\bar{n}} = \frac{1}{B\bar{n}} \qquad (32)$$

with K_s = (3.3 ± 0.7) × 10^5 at 20°. With a value for $\bar{n}$ of 3.65 at 20° as extrapolated from data given[7] for 25 and 50° in 0.1 M Na_2S solution, log B for a solution saturated in zerovalent sulfur is found to be -6.1 ± 0.1. With the experimental values for ϵ_3' and ϵ_4' and the resulting value for $K_{3/4}$, however, approximately equal amounts of tetra- and pentasulfide are calculated to be present at this B value. This small discrepancy in $\bar{n}$ is probably due to the considerable uncertainty in the value of ϵ_4' and that of $K_{3/4}$ derived from it. On the other hand, considering the large differences in experimental conditions employed in determining the values for $\bar{n}$ in these saturated solutions, the agreement is satisfactory and would indicate that any aqueous polysulfide solution saturated with zerovalent sulfur at 20° contains approximately equal amounts of tetrasulfide and pentasulfide ions, with $\bar{n}$ = 3.6 ± 0.1.

With increasing pH the tetrasulfide ion remains the predominant species for log B up to $+1.0$, whereas at log B values between 1.0 and 4.0 most of the zerovalent sulfur is present as trisulfide. The disulfide ion is formed only in highly alkaline solutions or in solutions with extremely low ratios $S(0)/S_t$. In systems where virtually all free sulfide S_t is present in the form of the sulfide ion S^{2-}, the distribution of polysulfides becomes independent of $[OH^-]$ and is only determined by $S(0)/S_t$. For aqueous solutions this condition is reached for H_- values above 18, in systems with low H^+ activities, *e.g.*, nonaqueous solvents or salt melts,[21] however, the formation of disulfide ion can be expected to be quite common.

(19) A. Teder, *Sv. Papperstidn.*, **70**, 197 (1967).

(20) W. Giggenbach, unpublished results.
(21) W. Giggenbach, *Inorg. Chem.*, **10**, 1308 (1971).