This mixture was stirred and refluxed for 120 hr, during which time hydrogen was slowly liberated. The resulting tan mixture was cooled, filtered, and rotary evaporated to dryness. The solid obtained was dissolved in 50 ml of cold water and was filtered. Addition of 100 ml of 25% CsCl solution precipitated the dianion as the cesium salt. This product was recrystallized from 85 ml of hot water to afford 4.1 g (7.7 mmol, 77%) of colorless plates of $\mathrm{Cs_2}$-7-(7′-7′,8′-$\mathrm{B_9C_2H_{11}}$)-7,8-$\mathrm{B_9C_2H_{11}}$, dec pt >260°. The infrared spectrum of a Nujol mull contained absorptions at 3030 (w), 2500 (s), 1275 (vw), 1240 (w), 1080 (m), 1059 (m), 1032 (m), 1002 (m), 951 (w), 909 (w), 882 (w), 828 (w), 781 (m), 752 (sh), 736 (m), and 706 $\mathrm{cm^{-1}}$ (w). The trimethylammonium salt was prepared by addition of a solution of 50% $\mathrm{(CH_3)_3NHCl}$ to the aqueous potassium salt, and recrystallization of the white precipitate afforded an 80% yield of $\mathrm{[(CH_3)_3NH]_2}$-7-(7′-7′,8′-$\mathrm{B_9C_2H_{11}}$)-7,8-$\mathrm{B_9C_2H_{11}}$, mp 282–283° dec. *Anal.* Calcd for $\mathrm{B_{18}C_{10}H_{42}N_2}$: B, 50.53; C, 31.19; H, 10.99; N, 7.27. Found: B, 50.42; C, 30.80; H, 11.24; N, 7.40.

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CONTRIBUTION FROM THE CHEMISTRY DIVISION,
DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
PETONE, NEW ZEALAND

The Blue Solutions of Sulfur in Water at Elevated Temperatures

BY W. GIGGENBACH

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A blue coloration developing when sulfur is heated together with water and traces of some basic salt was described by Geitner[1] in 1864. These high-temperature solutions are characterized by a strong absorption at 16.8 kK which, in analogy to the blue solutions of sulfur in aprotic, polar organic solvents,[2] is attributed to the hypersulfide ion ($\mathrm{S_2^-}$) formed by the homolytic dissociation of the tetrasulfide ion. Recently a blue solution obtained by electrochemical reduction of elemental sulfur[3] in dimethyl sulfoxide was ascribed to the formation of a $\mathrm{S_8^-}$ species. The absorption spectra of these solutions with a strong band at 16.2 kK are very similar to that of the $\mathrm{S_2^-}$ ion in dimethylformamide;[2] therefore, the possibility of a $\mathrm{S_8^-}$ ion being formed in aqueous polysulfide solutions at elevated temperatures is also considered.

Experimental Section

Materials.—Water was purified as described;[4] hydrogen sulfide and sodium sulfide solutions were prepared by bubbling $\mathrm{H_2S}$ from a tank into water or sufficiently concentrated sodium hydroxide solutions. Sodium tetrasulfide was prepared from sodium and sulfur in liquid ammonia. All solutions were prepared and handled under purified nitrogen, mainly by use of Schlenk-tube techniques.

Spectra.—The spectrophotometer used was the Zeiss PMQ II with the monochromator M4 Q III. High-temperature spectra were determined by use of a cell with a path length d of 0.14 cm as previously described.[5] All spectra were corrected for the expansion of the solutions with temperature and for the background absorption of the cell and of the solvent by subtracting the absorption of the cells filled with water or one of the polysulfide-free solutions at the respective temperature.

The polysulfide spectra were measured in a 0.2 or 0.02 M bisulfide–hydrogen sulfide solution which had been prepared by mixing 5 ml of a 2.0 M (or 0.2 M) sodium sulfide solution with 5 ml of a 0.025 M sodium tetrasulfide solution and varying amounts of 2.0 M (or 0.2 M) hydrochloric acid and water to give a total of 50 ml of solution. The pH of the resulting solution was checked with a glass electrode at room temperature. From these values pH′ at elevated temperatures was estimated by use of the relationship $\mathrm{pH}' = \mathrm{pH} + \mathrm{p}K'_{\mathrm{a}_1} - 7.0$ and the values for K'_{a_1} the first dissociation constant of $\mathrm{H_2S}$ at elevated temperatures.[4] The ionic strength of the less concentrated sulfide solutions was kept at 0.2 by the addition of NaCl. Because of the low and constant ionic strength, concentrations were substituted for activities in eq 3 and 4.

The pH of these polysulfide solutions varied from 4.7 to 10.6 at room temperature. At a pH below 7 the polysulfide solutions became unstable at room temperature and sulfur was precipitated. With increasing temperature, however, the range of stability of polysulfide solutions was found to extend further into the acidic field, and clear solutions containing all the zerovalent sulfur in the form of polysulfide or hypersulfide ions were obtained at a pH of 5.2 and a temperature of 170°. At pH >6 and temperatures above 150°, however, another reaction affected the stability of polysulfide solutions, when zerovalent sulfur, present as polysulfide or hypersulfide, reversibly disproportionated into colorless products. Preliminary investigations showed that both $\mathrm{SO_3^{2-}}$ and $\mathrm{SO_4^{2-}}$ ions are formed together with $\mathrm{SH^-}$. The formation of thiosulfate could not yet be excluded. The small amount of hydrogen ions produced according to

$$n\mathrm{S} + n\mathrm{H_2O} \rightleftarrows \mathrm{SO}_n^{2-} + (n-1)\mathrm{SH}^- + (n+1)\mathrm{H}^+$$

is effectively buffered by the bisulfide–hydrogen sulfide mixture. Any direct influence of the disproportionation reaction on spectra and equilibria involving hypersulfide and polysulfide ions thus can be excluded. The position of the disproportionation equilibrium is strongly dependent on pH and temperature. The rate of the reaction is very slow at temperatures below 150°, whereas at 220° equilibrium is reached within 5 min.

The reversible changes in the concentration of zerovalent sulfur occurring at a conveniently slow rate between 160 and 180° and caused by the second reaction were used to determine $\bar{n}$, the average number of zerovalent sulfur atoms per polysulfide ion as outlined below. It was assumed that the amount of $\mathrm{S_2^-}$ ions formed at a given temperature depends only on the total concentration of zerovalent sulfur S(0) present in the form of polysulfide and hypersulfide ions. By keeping the temperature at 160–180° zerovalent sulfur is used up by the disproportionation reaction until a state of equilibrium which depends on the pH of the solution is reached. By lowering the temperature most of S(0) can be regenerated, thus allowing the concentration of S(0) in the solution to be varied at will.

The concentration of $\mathrm{S_2^-}$ ions was determined by use of a molar absorptivity of 2400 as determined for the strong band at 16.2 kK in organic solution[2] at room temperature. The slight shift in $\nu_{\max}$ from 16.2 kK in dimethylformamide to 16.8 kK in water is assumed to be due to the difference in polarity of the two solvents.

If the oscillator strength of this band is presumed to remain constant with temperature and changing solvent, a lower value for the molar absorptivity should have been used as the width of the band in water at 160° was found to be 3.4 kK as compared to 2.8 kK in DMF at 20°. In the calculation of $\mathrm{p}K'_{\mathrm{d}}$ only the ratio $\epsilon_{\mathrm{S_3S^{2-}}}/\epsilon_{\mathrm{S_2^-}}{}^{2}$ is of significance; thus changes in $\epsilon_{\mathrm{S_2^-}}$ were assumed to be partly compensated for by a corresponding change in $\epsilon_{\mathrm{S_3S^{2-}}}$. Neither the nature nor the molar absorptivities of the polysulfide ions present in aqueous solution at elevated temperatures are known. From the data given by Teder[6] for 25 and 80°, however, it was concluded that in solutions of low pH and a low ratio of S(0) to sulfide sulfur (0.04–0.4 in the present study) the molar absorptivities for these polysulfide ions can be approximated by the relationship $\epsilon_{\mathrm{S}_{\bar{n}}\mathrm{S}^{2-}} = \epsilon_{\mathrm{S(0)}}\bar{n}$. With a value of 350 for $\epsilon_{\mathrm{S(0)}}$, the molar absorptivity at 25.0 kK per atom of zerovalent sulfur, the average concentration of a mixture of polysulfides thus becomes

$$c_{\mathrm{S}_{\bar{n}}\mathrm{S}^{2-}} = A_{25}/350\bar{n}d \tag{1}$$

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[1] C. F. Geitner, *Pharm. Ann.*, **129**, 350 (1864).

[2] W. Giggenbach, *J. Inorg. Nucl. Chem.*, **30**, 3189 (1968).

[3] M. V. Merritt and D. T. Sawyer, *Inorg. Chem.*, **9**, 211 (1970).

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The combined effects of errors in $\epsilon_{S_2^-}$ and $\epsilon_{S_{\bar{n}}S^{2-}}$ on pK'_d were estimated to be less than 0.1 p*K* unit and, therefore, within the deviation of ±0.14 p*K* unit caused by variations in pH.

Results and Discussion

Figure 1 shows spectra of a 2.5×10^{-3} *M* solution of sodium tetrasulfide in a 0.2 *M* HS^-–H_2S buffer solution at pH 5.6 as a function of temperature. At room temperature the spectra of aqueous polysulfide solutions show two bands[6,7] in the near-uv region at 27.5 and 31.0 kK. Up to about 100° these two bands move toward lower wave numbers without any significant change in either the shape or the molar absorptivity at the absorption maxima. At temperatures above 100°, however, a new band at 16.8 kK appears and increases in strength with increasing temperature causing the color of the solution to change from yellow through green to blue. By investigating the temperature dependence of the spectra of a series of solutions of Na_2S_4 in various mixtures of dimethylformamide and water, it can be demonstrated that decreasing DMF content simply leads to a gradual increase in the temperature required to produce a certain amount of the blue species as indicated by its absorption around 16.5 kK. The species formed in aqueous solution, therefore, was assumed to be identical with the S_2^- ion (or hypersulfide ion) present in solutions of polysulfides in DMF.

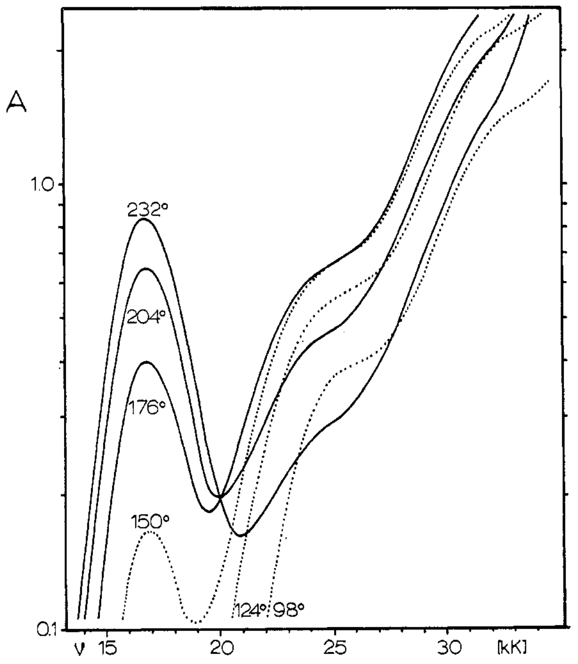

Figure 1.—Spectra of a 2.5×10^{-3} *M* solution of Na_2S_4 in a 0.2 *M* HS^-–H_2S buffer (pH 5.6 at 20°) as a function of temperature.

In analogy to the solutions of alkali polysulfides in aprotic, polar solvents[2] the equilibrium in aqueous solutions at elevated temperatures can be formulated as

$$S_3S^{2-} \rightleftharpoons 2S_2^- \qquad (2)$$

The equilibrium expression for this reaction

$$K_d = [S_2^-]^2/[S_3S^{2-}] \qquad (3)$$

requires the knowledge of the concentrations of the tetrasulfide ion S_3S^{2-}. Recent studies, however, have shown that aqueous polysulfide solutions generally contain a variety of species S_nS^{2-}, with *n* ranging from 2 to 5 and S_3S^{2-} being the predominant species only under certain, limited conditions.[6] As these previous investigations were restricted to temperatures up to 80° the actual concentration of S_3S^{2-} at elevated temperatures as required by eq 3 could not be determined. In order to obtain some estimate for the distribution of polysulfides at temperatures above 100° the following procedure was used.

The equilibrium between polysulfide ions leading to the formation of tetrasulfide ions can be described by the reaction

$$nS_3S^{2-} + (n-3)H_2O \rightleftharpoons 3S_nS^{2-} + (n-3)SH^- + (n-3)OH^- \qquad (4)$$

Combined with eq 3 the formation of S_2^- from a particular polysulfide ion is given by

$$[S_nS^{2-}]^{3/n}([SH^-][OH^-])^{1-(3/n)} = [S_2^-]^2K_n^{1/n}/K_d \qquad (5)$$

with K_n the constant for the equilibrium between the polysulfide ion S_nS^{2-} and S_3S^{2-}. In solutions containing a large excess of monosulfide sulfur at constant pH and temperature, the effect of variations in the amount of zerovalent sulfur on $\bar{n}$, the number of zerovalent atoms of sulfur per polysulfide ion, was assumed to be negligible. Therefore, by replacing *n* by $\bar{n}$ and $[S_2^-]$ and $[S_nS^{2-}]$ by $A_{17}/\epsilon_{S_2^-}d$ and $A_{25}/\epsilon_{S(0)}\bar{n}d$, respectively, and taking the logarithm, a relationship

$$2 \log A_{17} = (3/\bar{n}) \log A_{25} + C \qquad (6)$$

is obtained which allows the average chain length of a mixture of polysulfides at a given SH^- and OH^- concentration and temperature to be measured against that of the tetrasulfide ion dissociating into hypersulfide ions. The slope σ of a plot of $\log A_{17}$ against $\log A_{25}$ for a series of solutions differing in S(0) thus gives

$$\bar{n} = 3/2\sigma \qquad (7)$$

From Figure 2 for solutions at 160° with pH's of 6.2, 6.5, 6.8, 7.0, 7.1, and 10.5, $\bar{n}$ values of 3.9, 3.2, 3.0, 2.9, 2.7, and 2.2, respectively, are derived. These values show that at pH 6.8 and 160° and a sulfide concentration of 0.2 *M*, eq 5 is reduced to eq 3 with $K_{\bar{n}}$ becoming unity. In this case $[S_3S^{2-}]$, however, does not represent the actual concentration of tetrasulfide ions, rather that of a mixture of polysulfides with an average com-

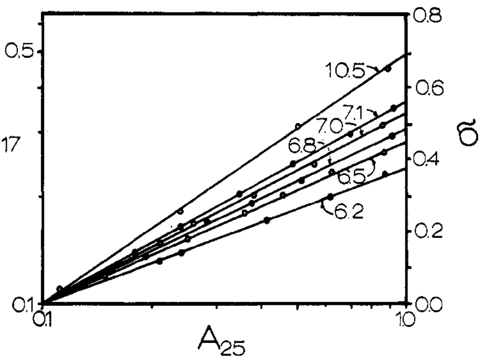

Figure 2.—A plot of $\log A_{17}$ *vs.* $\log A_{25}$ for a series of 2.5×10^{-3} *M* solutions of Na_2S_4 in a 0.2 *M* HS^-–H_2S buffer as a function of pH at 160°. The lines were shifted vertically to A_{17} of 0.1 for A_{25} of 0.1.

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(7) G. Schwarzenbach and A. Fischer, *Helv. Chim. Acta*, **43**, 1365 (1960).

position S_3S^{2-}. For any other values of $[SH^-][OH^-]$ and any other temperature, $\bar{n}$ is different from 3 and the formation of S_2^- ions is described by eq 5. In the present study no attempt was made to estimate values of K_n and thence the actual concentrations of the various polysulfides. Therefore, the experimental values of K'_d for reaction 2 obtained by assuming the absorption at 25.0 kK to be due to the sole presence of tetrasulfide ions may differ considerably from the theoretical values K_d. In order to obtain some estimate of the influence of $[OH^-]$, experimental values at 160° for K'_d at pH 6.2, 6.5, 6.8, and 7.1 are shown in Figure 3. It is obvious that the effect of $[OH^-]$ on K'_d is significant but small compared with that of temperature. The uncorrected values of K'_d, therefore, can be used to describe the formation of S_2^- ions in solutions of polysulfides containing an excess of sulfide sulfur in a simplified way by neglecting any changes in $\bar{n}$ due to variations in pH and temperature. In Figure 3 a series of values of K'_d is plotted against $1/T$. These values were obtained from solutions varying in pH from 4.7 to 10.6 and in total sulfide from 0.02 to 0.2 M. The standard deviation of $\mathrm{p}K'_d$ with respect to values as represented by a line fitted by the method of least squares is ± 0.14. This also shows that the ratio K'_d/K_d is close to unity at all temperatures and SH^- and OH^- concentrations investigated. The thermodynamic data calculated from the temperature dependence of $\mathrm{p}K'_d$ as given by

$$\mathrm{p}K'_\mathrm{d} = -\frac{4533}{T} + 6.42 \tag{8}$$

are $\Delta H'_d = 20.7 \pm 1.2$ kcal/mol and $\Delta S'_d = 29 \pm 4$ cal/deg mol.

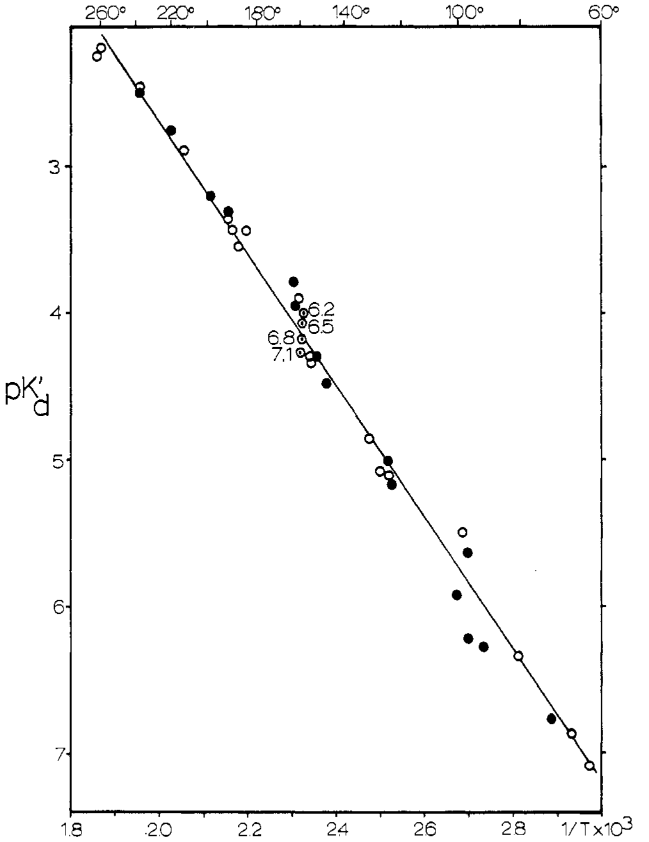

Figure 3.—Values of $\mathrm{p}K'_d$ as a function of $1/T$. For four points at 160° the pH of the solution is given. Open circles represent values obtained from 0.2 M and filled circles those from 0.02 M HS^-–H_2S buffer solutions.

The $\bar{n}$ values determined in this work for 160° are in agreement with the trends indicated by the data given by Teder[6] for 25 and 80°. They show that values for $\bar{n}$ exceed 4 only in solutions very low in $[OH^-]$ and $[SH^-]$ and high in S(0). With m, the number of sulfur atoms in the radical S_m^- produced by the homolytic dissociation of a polysulfide ion, eq 7, written in the more general form $2\bar{n}\sigma = 2m - 1$, indicates that with the values of σ found in this investigation the value of m is unlikely to exceed 3. Thus the possibility of the species S_8^- being formed from polysulfides existing in aqueous solution at elevated temperatures can be excluded. There was no indication of the formation of two other possible particles S_3^- and S_4^-.

Contribution from the Chemistry Division,
Department of Scientific and Industrial Research,
Petone, New Zealand

The Blue Solutions of Sulfur in Salt Melts[1]

By W. Giggenbach

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A deep coloration appearing in molten potassium thiocyanate above 300° was first described by Nöllner[2] in 1856 and later on by Paternò and Mazzuchelli.[3] Greenberg, *et al.*,[4] and Lux and Anslinger[5] measured the absorption spectra of these melts. Blue solutions of sulfur in alkali halide melts at temperatures above 400° were investigated by Delarue[6] and Molina,[7] whereas the preparation of a "boro-ultramarine" was reported by Hoffmann.[8] In all these cases the blue color is attributed to the formation of uncharged sulfur particles such as S_2, S_4, or colloidal sulfur. Recent spectroscopic and chemical evidence, however, suggests that these blue solutions are caused by the hypersulfide ion, S_2^-, as in organic polysulfide solutions[9] at room temperature and aqueous polysulfide solutions[10] at elevated temperatures.

Experimental Section

Materials.—All the salts used to prepare the melts were reagent grade. KSCN was dried at 120° and kept in a desiccator over P_2O_5; the LiCl–KCl eutectic was prepared and purified as described by Laitinen, et al.[11]

Borate glasses were prepared by melting weighed amounts of an equimolar mixture of K_2CO_3 and Li_2CO_3 containing 0.1% w/w of elemental sulfur in an unglazed porcelain crucible at 700°. To this clear, red-brown carbonate melt increasing amounts of B_2O_3 were added until the desired composition was reached. To

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(1) Part of this work has been carried out at the Technische Hochschule München.

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