

Disproportionation of Aqueous Sulfur and Sulfide: Kinetics of Polysulfide Decomposition

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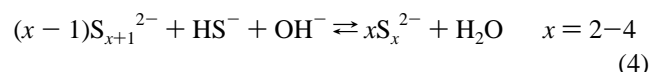
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Thermodynamically, aqueous polysulfide solutions are unstable, and sulfur, dissolved as polysulfide species, S_x^{2-} , $x = 2-5$, will decompose to thiosulfate, $S_2O_3^{2-}$ in accord with the net consumption of dissolved sulfur: $S_{\text{dissolved}} + OH^- \rightarrow 1/4 S_2O_3^{2-} + 1/2 HS^- + 1/4 H_2O$. The distribution of species, and measured and modeled rate of polysulfide decomposition, are investigated for a wide range of polysulfide solution compositions from 25 to 85 °C. The observed decomposition of sulfur concentration, C_S , is consistent with an activation energy for sulfur decomposition of $104(\pm 5)$ kJ mol⁻¹ in accord with the following rate of sulfur loss: $-dC_S/dt = -k_f[S_5^{2-}][OH^-]/[HS^-]$; $k_f = 10^{-(10.7-5430/T(K))}$, where C_S is the concentration of dissolved zerovalent sulfur distributed among all polysulfide species. At temperatures up to 85 °C, polysulfide solutions are extremely stable under conditions of high polysulfide concentration (> 5 m K_2S_4) and low KOH concentrations. Under these conditions, zerovalent sulfur dissolved in these solutions should be stable on the order of years.

Introduction

Aqueous polysulfide electrolytes are regularly used for fundamental photoelectrochemical studies,¹⁻¹² and for the development of high energy conversion efficiency^{13,14} and highly stable¹⁵ photoelectrochemical solar cells. Aqueous polysulfide solution chemistry is also of importance to the pulp and paper industry,¹⁶ and provides an opportunity for a battery cathode based on the high storage capacity of zerovalent sulfur in concentrated aqueous polysulfide electrolytes.^{17,18} The study of both photoelectrochemistry and polysulfide chemistry fascinated the later Professor Heinz Gerischer, to whom this special issue is dedicated.^{19,20}

The chemistry of aqueous polysulfide solutions is complex. Controlled modification of polysulfide solution chemistry has a substantial impact on the electrochemistry and photoelectrochemistry in these electrolytes.^{12,18} The aqueous alkali-metal polysulfide system is known to contain, in addition to H_2O and alkali-metal cations, OH^- , H^+ , H_2S , HS^- , S^{2-} , S_2^{2-} , S_3^{2-} , S_4^{2-} , and S_5^{2-} . The polysulfide equilibrium constants, interrelating polysulfide speciation, K_A , K_B , and K_C , have been well established.^{21,22} The species in solution are related by the equilibria



which provide the following equilibrium constants:

$$K_1 = [H^+][HS^-]/[H_2S] \quad (5)$$

$$K_2 = [H^+][S^{2-}]/[HS^-] \quad (6)$$

$$K_w = [H^+][OH^-]/[H_2O] \quad (7)$$

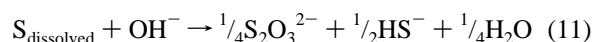
$$K_A = [S_2^{2-}]^2/([HS^-][OH^-][S_3^{2-}]) \quad (8)$$

$$K_B = [S_3^{2-}]^3/([HS^-][OH^-][S_4^{2-}]^2) \quad (9)$$

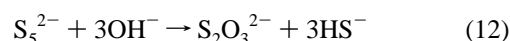
$$K_C = [S_4^{2-}]^4/([HS^-][OH^-][S_5^{2-}]^3) \quad (10)$$

The water equilibrium constant, K_w , and the first acid dissociation constant of H_2S , K_1 , are both well documented. Several studies have confirmed that the H_2S second acid dissociation constant, K_2 , previously²³ thought to have a room temperature value of 10^{-12} , has a measured value²³⁻²⁸ of 10^{-17} . This results in a substantial revision of known metal sulfide solubilities and rest potentials.²⁹

Thermodynamically, aqueous polysulfide solutions are unstable, and sulfur, dissolved as polysulfide, decomposes to thiosulfate, $S_2O_3^{2-}$ in accord with the observed net consumption of dissolved sulfur:



Each polysulfide S_x^{2-} species contains $(x-1)$ zerovalent sulfur and contributes to $S_{\text{dissolved}}$. Hence, $C_S = [S_{\text{dissolved}}] = 1 \times [S_2^{2-}] + 2 \times [S_3^{2-}] + 3 \times [S_4^{2-}] + 4 \times [S_5^{2-}]$. Whereas the complex equilibrium within polysulfide solutions has been consistently established, there have been few studies on the kinetic decomposition of these solutions. Previous studies were conducted under conditions of extreme pressure and temperature (180–350 °C) to facilitate polysulfide decomposition in reasonable laboratory time scales (minutes).^{30,31} In highly alkaline solution, S_5^{2-} has a lower concentration relative to the other polysulfide species. The relatively slow rate of polysulfide decomposition in highly alkaline solutions was attributed to decomposition via the pentasulfide species, also in accord with eq 11, and the observed net reaction:



At high temperatures, polysulfide decomposition was found to be inverse second order with respect to HS^- , consistent with a

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rate-determining intermediate step



$$-d[\text{S}_5^{2-}]/dt \propto -dC_S/dt = k_f u_4 C_S [\text{OH}^-]/[\text{HS}^-]^2 \quad (14)$$

$$k_f(180-350\text{ }^\circ\text{C}) = 10.9 - 5600/T(\text{K}) \quad (15)$$

where k_f is the decomposition rate constant and C_S is the concentration of dissolved zerovalent sulfur distributed among all polysulfide species. Each S_5^{2-} contains four zerovalent sulfur, and u_4 is the fraction of zerovalent sulfur within S_5^{2-} : $u_4 = 4[\text{S}_5^{2-}]/C_S$. Integration of eq 14, with respect to sulfur (C_S), and assuming constant HS^- , u_4 , and OH^- , led to the predicted half-life, t_h , for half of the initial dissolved zerovalent sulfur to decompose:

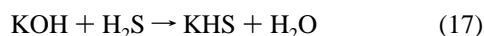
$$t_h = \ln(2) [\text{HS}^-]^2 / (k_f u_4 [\text{OH}^-]) \quad (16)$$

In this study, we present mechanistic evaluation of polysulfide decomposition conducted over periods of several months. These extended measurements permit polysulfide decomposition study at ambient pressure and in the temperature range of 25–85 °C. In this temperature range, unlike higher temperatures, the reaction is inverse first order in HS^- , and surprisingly high stabilities of polysulfide solutions can be achieved.

Experimental Section

Materials. Analytical grade reagents and distilled, doubly deionized water were used throughout and were prepared, stored, and utilized under argon to prevent reaction with oxygen. Concentrated KOH, KHS, and polysulfide solutions were stored in polypropylene vessels.

KHS solutions were prepared by saturation of KOH solutions with $\text{H}_2\text{S}(\text{gas})$. The reaction is exothermic and results in an increase in volume, a proportional mass increase, and a pH decrease all consistent with the equation



As measured by proportional mass increase, the KHS solution synthesis proceeds to $99.3 \pm 0.6\%$ completion. Polysulfide solutions are then formed by addition of KOH and sulfur to these KHS solutions.

Instrumentation and Measurement Techniques. For each polysulfide solution composition investigated, triplicate samples were studied for decomposition. 15 g polysulfide solution samples were capped under argon with Suba-Seal rubber septums. 0.1 g samples for analysis were removed periodically via syringe using Teflon microbore tubing to pierce the septum, rather than a needle, and transferred under argon to 4 g of a solution containing 9 *m* KOH and 9 *m* KHS for analysis. Mass-based concentrations (molal, *m*, rather than molar) are used throughout to enhance measurement precision.

Spectroscopic measurements were performed with a Hewlett Packard 8452A photodiode array UV/vis spectrometer using a Starna Spectrosil 48-Q-0.1 quartz cell with a path length of 0.1 mm. Absorbance measurement of polysulfide solutions at 416 nm yields an isobestic point in solutions containing high constant concentrations of OH^- and HS^- .²¹ At this wavelength, solution absorbance is linearly proportional to the concentration of total zerovalent sulfur. Solutions to be analyzed were added to a constant excess of 9 *m* KOH, 9 *m* KHS electrolyte to ensure a consistent and high constant concentration of OH^- and HS^- and then absorption was measured at 416 nm.

The magnitude of sulfur decomposition may also be determined by analysis of the decomposition product, thiosulfate. Thiosulfate concentration was determined by gravimetric analysis, accomplished by BaS_2O_3 precipitation upon addition of BaCl_2 to solution. Sulfide and unreacted sulfur remain in solution due to the high solubility of barium sulfide and barium polysulfide, BaS and BaS_x . The precipitate was then vacuum filtered and dried, and its mass was determined. At concentrations approaching 1 *m*, the reproducibility of thiosulfate concentration was high ($\pm 2\%$). However, error increased to 20% for gravimetric analysis of thiosulfate concentrations < 0.1 *m*. Due to these poor detection limits, sulfur decomposition was evaluated spectroscopically, with redundant analysis by thiosulfate gravimetric analysis only in cases approaching 1 *m* thiosulfate product.

Results and Discussion

Polysulfide Speciation. In this study, the measured rate of decomposition of dissolved zerovalent sulfur, within polysulfide, will be compared with the distribution of species in the solution. The distribution of species is determined numerically from the equilibria, eqs 5–10. Mass constraints are imposed by the known nominal concentrations of sulfur, KHS, and KOH in the solution respectively, C_S , C_{KHS} , and C_{KOH} . The distributed total sulfide is restricted by that used to form the solution:

$$C_{\text{KHS}} = [\text{H}_2\text{S}] + [\text{HS}^-] + \sum_{i=1}^5 [\text{S}_i^{2-}] \quad (18)$$

The concentration of zerovalent is distributed among the polysulfide species in solution:

$$C_S = \sum_{i=2}^5 (i-1) [\text{S}_i^{2-}] \quad (19)$$

The distributed hydroxide in solution results from (i) the KOH in the solution, (ii) that produced in the protonation of hydrosulfide (eq 1), (iii) that produced in the self-disproportionation of water (eq 3), and (iv) that consumed in the production of divalent sulfide and polysulfide species (eqs 2 and 4):

$$[\text{OH}^-] = C_{\text{KOH}} + [\text{H}_2\text{S}] + [\text{H}^+] - \sum_{i=1}^5 [\text{S}_i^{2-}] \quad (20)$$

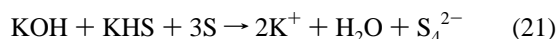
As previously described, the distribution of species in the solution may be determined by numerical iterative convergence, consistent with the known polysulfide equilibria constants, eqs 8–10,²¹ until the mass constraint equations, eqs 18–20, are satisfied to within $\pm 0.001\%$. Equilibria constants for polysulfide speciation have been determined using either an ionic strength correction term²¹ or in accord with variations in mean solvent and solute solution activity coefficients.^{22,28} At temperatures above 70 °C, these activity coefficients are not available, and this study makes use of the ionic strength corrected equilibria constants as summarized in Table 1. Examples of the calculated distribution of species in a variety of polysulfide solutions are included in Table 2. In solutions containing moderate and high concentrations (0.1–10 *m*) of sulfur, hydroxide, and hydrosulfide, the polysulfide species, S_4^{2-} , containing three zerovalent sulfurs tends to predominate. The H_2S first and second acid dissociation constants dictate that free H_2S and S^{2-} concentrations are small in this domain, and the primary polysulfide speciation in this domain from solutions

TABLE 1: Equilibrium Constants for the Aqueous Polysulfide System^a

| p <i>K</i> | <i>a</i> | <i>b</i> | <i>c</i> | <i>d</i> | ref |
|-------------------------|----------|----------|----------|----------|-----|
| p <i>K</i> ₁ | 2830.4 | 0.02083 | -8.7289 | | 22 |
| p <i>K</i> ₂ | 28646 | 0.2657 | -158.255 | | 22 |
| p <i>K</i> _w | 3927.1 | 0.01223 | 2.8334 | | 32 |
| p <i>K</i> _A | | | 4.20 | -0.35 | 21 |
| p <i>K</i> _B | | | 1.75 | -0.35 | 21 |
| p <i>K</i> _C | | | -5.08 | -0.35 | 21 |

^a Equilibria constants are of the form $K = 10^{-pK}$. $pK = a/T + bT + c + dI^{1/2}$; T is the temperature (K), and I is the ionic strength.

prepared with sulfur, KOH and KHS, is approximated by



Sulfur in excess of 3 S per KHS will not dissolve. KOH and KHS, added in excess of the ratio of 3S per KHS, exist as free OH^- and HS^- in solution. In increasingly concentrated solutions ($> 10\text{ m}$) shorter chain length polysulfide, S_3^{2-} , species increasingly dominate.

Ambient Temperature Decomposition Trends. Alkaline solutions of potassium thiosulfate, $\text{K}_2\text{S}_2\text{O}_3$, studied at temperatures of 25–85 °C over a period of several months with spectroscopic evaluation at 416 nm, showed no indication of polysulfide formation. Over a wide range of alkaline polysulfide solutions, addition of $\text{K}_2\text{S}_2\text{O}_3$ to alkali polysulfide solutions also showed no retardation of the rate of polysulfide/dissolved sulfur decomposition to thiosulfate. We conclude that the reverse reaction to eqs 11 and 12 does not occur at a significant rate, in a time domain of months, at this temperature range.

In polysulfide solutions, in accord with eqs 11 and 12, sulfur loss occurs as a polysulfide decomposition measured by absorbance at 416 nm. This is accompanied by a proportional buildup of thiosulfate, as measured by barium precipitation and gravimetric analysis, as discussed in the experimental section. However, in all cases the measured sulfur half-life, t_h , differs from that predicted by eq 16, and in most cases the difference is considerable. For example, compared to a predicted t_h of 10^{-6} days, the measured sulfur half-life is 1.1 days at 85 °C for a polysulfide solution prepared from 1.1 *m* KOH, 0.1 *m* KHS, and 0.3 *m* S, as summarized in the first column of Table 2.

The assumption of a constant fraction of S_5^{2-} , and a constant concentration of HS^- , which are used in the derivation of eq 16, is not consistent with the range of polysulfide composition investigated in this study, and hence the sulfur half-life differs considerably from predictions of that equation. This difference is accentuated in solutions in which the KHS is saturated with sulfur. As seen in the first column of Table 1, initially such polysulfide solutions have little free HS^- . However, a several order of magnitude increase in free HS^- occurs with sulfur decomposition. A several order of magnitude error in calculation of t_h occurs if this variation in HS^- with sulfur decomposition is not incorporated. A better representation of the functional variation of sulfur decomposition takes into account the varying distribution of species in solution which is concurrent with sulfur decomposition:

$$-dC_S/dt = -f_S([\text{S}_5^{2-}], [\text{OH}^-], [\text{HS}^-]) = f_S(C_S, C_{\text{KOH}}(C_S), C_{\text{KHS}}(C_S)) \quad (22)$$

In accord with eq 11, over the time interval occurring between times t_i and t_{i+1} , not only has the total sulfur diminished by ΔS , from a value C_{Si} to a value C_{Si+1} , but total KOH has also diminished by ΔS , and total KHS has increased by $1/2\Delta S$:

$$C_{Si+1} = C_{Si} - \Delta S \quad (23)$$

$$C_{\text{KOH}i+1} = C_{\text{KOH}i} - \Delta S \quad (24)$$

$$C_{\text{KHS}i+1} = C_{\text{KHS}i} + 0.5\Delta S \quad (25)$$

The variation in speciation which occurs during this time, Δt , is determined by numerical iterative convergence of eqs 5–10 and 18–20 using, respectively, C_{Si} , $C_{\text{KOH}i}$, $C_{\text{KHS}i}$, and C_{Si+1} , $C_{\text{KOH}i+1}$, and $C_{\text{KHS}i+1}$. Subsequent numerical trapezoidal integration of eq 22 yields the time, t_{decomp} , for an initial sulfur concentration, C_{Sinitial} , to decompose to a final sulfur concentration, C_{Sfinal} . That is, t_{decomp} is determined using sufficiently small sulfur decomposition steps, ΔS , toward the $\lim_{\Delta S \rightarrow 0}$, over n steps, where $n = (C_{\text{Sfinal}} - C_{\text{Sinitial}})/\Delta S$:

$$t_{\text{decomp}} = \lim_{n \rightarrow \infty} 0.5(C_{\text{Sfinal}} - C_{\text{Sinitial}}) \sum_{i=1}^n (f(S_{i+1}) + f(S_i)) \quad (26)$$

$$t_h = \lim_{\Delta S \rightarrow 0} 0.25C_{\text{Sinitial}} \sum_{i=1}^n (f(S_{i+1}) + f(S_i)) \quad (27)$$

Given a functional description of sulfur decomposition $f_S([\text{S}_5^{2-}], [\text{OH}^-], [\text{HS}^-])$, in eq 22, t_{decomp} is determined from eq 26, using an n equal steps to describe the variation of sulfur, KOH, and KHS concentrations, eqs 23–25. In this study all reported values of t_{decomp} , eq 26, utilize $n = 10\,000$ steps to calculated decomposition of C_{Sinitial} . Increase of n to 100 000 produced no significant change ($\pm 0.01\%$) in the reported values of t_{decomp} , and the values are converged.

Use of the variable speciation description, eqs 26 and 27, provides a considerable improvement in the calculated sulfur decomposition time, compared to the static speciation assumption of eq 16. However, an additional modification is necessary. As will be shown in the next section, eq 14 is not appropriate at lower temperatures, and $f_S([\text{S}_5^{2-}], [\text{OH}^-], [\text{HS}^-])$ is not inverse second order with respect to HS^- .

Decomposition Variation with KHS. Whereas saturated sulfur polysulfide solutions exhibit $[\text{HS}^-]$ which increases by several orders of magnitude during sulfur decomposition, $[\text{HS}^-]$ changes less rapidly in solutions containing lower ratios of C_S : C_{KHS} . These solutions were used to investigate the effect of KHS concentration on the rate of sulfur decomposition. Solutions were prepared containing approximately 1 *m* free OH^- and various concentrations of free HS^- . Representative polysulfide solutions at 85 °C are described in the columns of Table 2. For example, there is 40-fold more HS^- in the solution containing 2 *m* KHS, 2 *m* S than in the solution containing 0.1 *m* KHS, 0.2 *m* S. Hence, the sulfur lifetime should increase by 40² or 1600 according to eqs 16. However, as summarized in Table 2, measured sulfur lifetime increases by 40-fold over this HS^- concentration span. This linear increase in t_h with increasing HS^- was observed in all polysulfide solutions studied. A more rigorous check of this linear variation of t_{decomp} with HS^- is presented in Figure 1.

Figure 1 presents the time variation of the zerovalent sulfur concentration for the polysulfide solutions containing 1 *m* free hydroxide, also containing 0.1, 1, 2, or 9 *m* KHS and either 0.2 or 2 *m* dissolved sulfur. Superimposed on the data are decomposition curves calculated to vary as the inverse first-order reaction in $[\text{HS}^-]^{z=-1.0}$. Small deviations from $z = -1(\pm 0.1)$ result in poor fit of the observed decomposition and we conclude

$$-dC_S/dt \propto [\text{HS}^-]^{-1} \quad (28)$$

TABLE 2: Distribution of Species, and Calculated and Measured Sulfur Lifetimes, for Selected Polysulfide Solutions at 85 °C Containing Various Concentrations of Sulfur, KOH, and KHS^a

| | | | | | | | | | |
|---|------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| KOH (<i>m</i>) | 1.1 | 1.1 | 2 | 2 | 2 | 0.2 | 11 | 2 | 7 |
| KHS (<i>m</i>) | 0.1 | 0.1 | 2 | 2 | 9 | 0.1 | 1 | 1 | 6 |
| S (<i>m</i>) | 0.3 | 0.2 | 2 | 2 | 2 | 0.2 | 2 | 3 | 18 |
| calculated speciation | | | | | | | | | |
| [OH ⁻] | 1.0 | 1.0 | 1.3 | 1.2 | 1.1 | 0.13 | 10. | 1.0 | 1.0 |
| [HS ⁻] | 5 × 10 ⁻⁴ | 0.03 | 0.27 | 1.2 | 8.1 | 0.03 | 0.18 | 4 × 10 ⁻³ | 6 × 10 ⁻³ |
| [H ₂ S] | 7 × 10 ⁻¹⁰ | 4 × 10 ⁻⁸ | 3 × 10 ⁻⁷ | 1 × 10 ⁻⁶ | 9 × 10 ⁻⁶ | 3 × 10 ⁻⁷ | 2 × 10 ⁻⁸ | 5 × 10 ⁻⁹ | 8 × 10 ⁻⁹ |
| [S ²⁻] | 2 × 10 ⁻⁸ | 1 × 10 ⁻⁶ | 1 × 10 ⁻⁵ | 6 × 10 ⁻⁵ | 4 × 10 ⁻⁴ | 2 × 10 ⁻⁷ | 7 × 10 ⁻⁵ | 1 × 10 ⁻⁷ | 2 × 10 ⁻⁷ |
| <i>u</i> ₁ (S ₂ ²⁻) | 7 × 10 ⁻⁵ | 1 × 10 ⁻³ | 2 × 10 ⁻³ | 6 × 10 ⁻³ | 0.03 | 3 × 10 ⁻⁴ | 0.03 | 8 × 10 ⁻⁵ | 9 × 10 ⁻⁵ |
| <i>u</i> ₂ (S ₃ ²⁻) | 0.04 | 0.16 | 0.19 | 0.30 | 0.56 | 0.07 | 0.42 | 0.04 | 0.04 |
| <i>u</i> ₃ (S ₄ ²⁻) | 0.87 | 0.82 | 0.79 | 0.68 | 0.41 | 0.88 | 0.38 | 0.87 | 0.87 |
| <i>u</i> ₄ (S ₅ ²⁻) | 0.10 | 0.02 | 0.02 | 7 × 10 ⁻³ | 1 × 10 ⁻³ | 0.05 | 2 × 10 ⁻³ | 0.09 | 0.09 |
| lifetime (days) | | | | | | | | | |
| <i>t</i> _h , measd | 1.1 | 1.6 | 22 | 71 | ≥290 | 6 | 12 | 79 | ≥290 |
| <i>t</i> _h , eq 16 | 1.2 × 10 ⁻⁶ | 0.017 | 1.6 | 73 | 18200 | 0.07 | 0.4 | 6 × 10 ⁻⁶ | 1 × 10 ⁻⁴ |
| <i>t</i> _h , eqs 27, 29 | 1.1 | 1.5 | 21 | 76 | 1830 | 6 | 13 | 82 | >200000 |

^a The distribution of sulfur within polysulfide species, containing *i* = 1–4 zerovalent sulfur, is given by $u_i = i[S_i^{2-}]/C_{\text{Sinitial}}$.

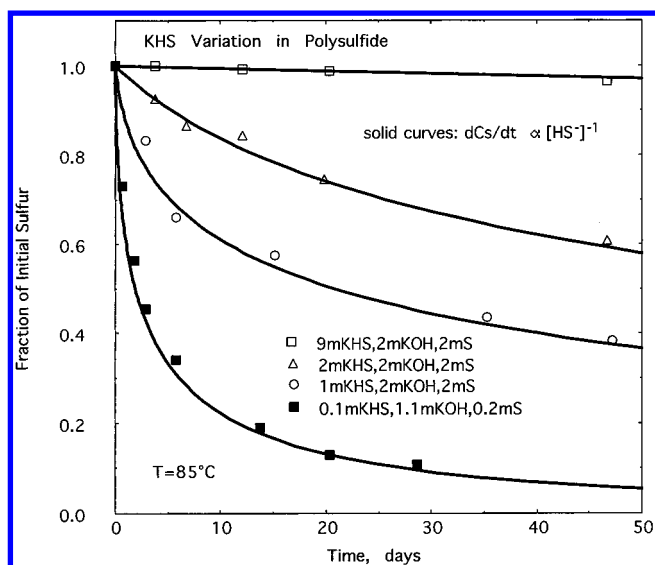


Figure 1. Variation, with KHS concentration, of the rate of relative sulfur decomposition in various polysulfide solutions at 85 °C. Sulfur concentration, C_S , measured at 416 nm absorbance, is expressed as the (zerovalent) sulfur fraction in solution compared to the initial dissolved sulfur concentration, C_S/C_{Sinitial} . KHS concentration is varied from 0.1 to 9 *m*. The nominal concentration of KOH differs (either 1.1 or 2.0 *m* KOH in the solutions containing 0.2 or 2 *m* or sulfur, respectively) to maintain approximately 1 *m* free OH⁻, as shown in Table 2, in the solutions. Solid curves are calculated, in accord with rate eq 29, using the numerical procedure described in the text.

Calculated sulfur decomposition, the solid curves in Figure 1, are determined between an initial and final sulfur concentration using the numerical trapezoidal integration procedure discussed in the previous section and summarized by eq 26, and using the functional description of sulfur decomposition, f_S :

$$-dC_S/dt = -f_S([S_5^{2-}], [OH^-], [HS^-]) = k_f[S_5^{2-}][OH^-]/[HS^-] \quad (29)$$

Decomposition Variation with KOH. The variation of speciation, with KOH concentration, in various polysulfide solutions at 85 °C is presented in Table 2. KOH concentration is varied from 0.2 to 11 *m* KOH. KOH affects the relative distribution of polysulfide species, u_1 , u_2 , u_3 , and u_4 . As seen in Table 2, there is a shift toward longer chain polysulfides in solutions containing less hydroxide, and a distribution shift toward shorter polysulfide species in the concentrated hydroxide solution. This makes hydroxide effects on sulfur decomposition effects less distinct, although general trends are evident.

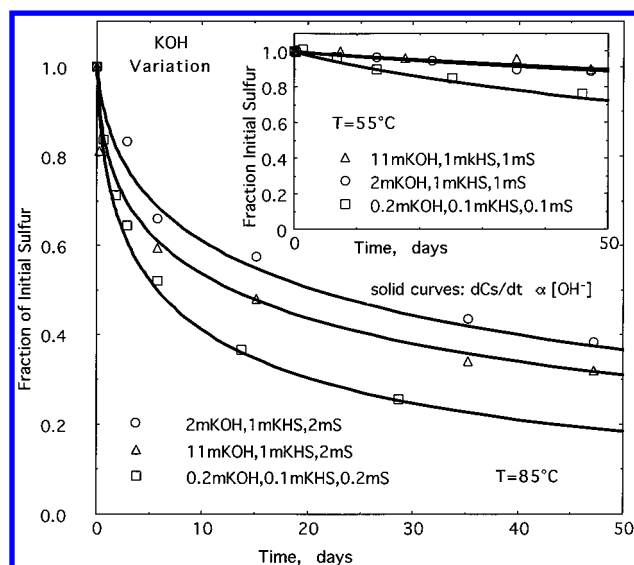


Figure 2. Variation, with KOH concentration, of the rate of relative sulfur decomposition in various polysulfide solutions at either 85 or 55 °C (inset). KOH concentration is varied from 0.2 to 11 *m*. Solutions are prepared with either a 2:1 ratio of sulfur to KHS, $C_{\text{Sinitial}}/C_{\text{KHSinitial}}$, or a 1:1 ratio of sulfur to KHS (inset). Solid curves are calculated in accord with rate equation (29), and the fraction of initial sulfur is as described in the Figure 1 legend.

Figure 2 presents the rate of sulfur decomposition in 0.2, 2, and 11 *m* KOH polysulfide solutions. At 85 °C, comparing the 1.1 *m* KOH, 0.1 *m* KHS polysulfide solution in Figure 1 to the 0.2 *m* KOH, 0.1 *m* KHS solution in Figure 2, sulfur lifetime improves with decreasing hydroxide concentration. Similarly, comparing in Figure 2 the 2 *m* KOH, 1 *m* KHS polysulfide solution to the 11 *m* KOH, 1 *m* KHS solution, sulfur lifetime decreases with increasing hydroxide concentration. Incorporating this variation of polysulfide distribution, which occurs with variation in hydroxide concentration, the experimental sulfur decomposition is fit by a linear variation with free hydroxide concentration:

$$-dC_S/dt \propto [OH^-] \quad (30)$$

Calculated sulfur decomposition, the solid curves in Figure 2, is determined using a decomposition rate linearly varying with the hydroxide concentration, eq 30, as contained within eq 29, and using the previously discussed numerical trapezoidal integration procedure summarized by eq 26.

Decomposition Variation with Relative Sulfur. Figure 3 presents the variation, with sulfur to sulfide ratio, of the rate of

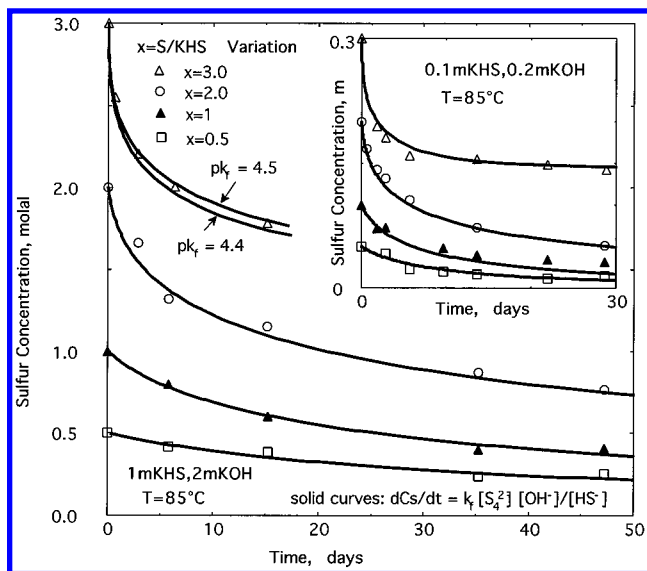


Figure 3. Variation, with sulfur to sulfide ratio, of the rate of sulfur decomposition in various polysulfide solution at 85 °C. Solutions are prepared with either a 3:1, 2:1, 1:1, or 0.5:1 ratio of sulfur to KHS, and with either 1 *m* KHS, 2 *m* KOH or 0.1 *m* KHS, 0.2 *m* KOH (inset). The solid curves are calculated in accord with rate equation (29).

sulfur decomposition in various polysulfide solution at 85 °C. Both the main portion of the figure, as well as the figure inset, summarize time dependence of the sulfur loss at 85 °C for polysulfide solutions prepared with a 3:1, 2:1, 1:1, or 0.5:1 ratio of sulfur to KHS. The main portion of the figure summarizes results for polysulfide solutions containing sulfur and 1 *m* KHS, 2 *m* KOH, and the figure inset is for solutions 10 times more dilute (0.1 *m* KHS, 0.2 *m* KOH). As seen in Table 2, variation over a wide range of sulfur to KHS compositions has little impact on the distribution of polysulfide species in solution. Hence in these solutions, the increase in stability at lower sulfur to sulfide ratio is primarily due to the increase in HS⁻ which is evident in the table.

The forward rate constant, k_f , consistent with eq 29, has been determined by iterative fit of the experimental decomposition data as

$$pk_f(85\text{ }^{\circ}\text{C}, 358.2\text{ K}) = 4.43(\pm 0.05) \quad (31)$$

Equation 29, and rate constant eq 31, provide a good fit, as seen in the solid curves of each figure, for the observed experimental sulfur decomposition in polysulfide solutions. The uncertainty in eq 31 is determined by compared variations in the rate constant to the data scatter. This is illustrated in Figure 3 using alternate calculated sulfur decomposition based on rate constants of either $pk_f = 4.4$ or $pk_f = 4.5$.

Decomposition Variation with Temperature. The decomposition rate may be reduced by either a decrease in temperature or a reduction in the number of sulfur dissolved per KHS. Together, these effects can be substantial. As seen in Figure 2, a relatively rapid rate of sulfur decomposition is observed for 85 °C polysulfide solutions containing two sulfur per KHS, and prepared with either low KHS concentrations or high KOH concentrations. As seen in the figure inset, sulfur is highly stable in solutions of the same KOH and KHS concentration, but at 55 °C and containing one sulfur per KHS.

Figure 4 presents the variation, with temperature, of the rate of sulfur decomposition in various polysulfide solutions. Polysulfide solution temperature is maintained at either 25, 55, or 85 °C as indicated in the figure. Solutions are prepared with 2 *m* KOH and either a 2:1 ratio of sulfur to KHS or a 1:1 ratio

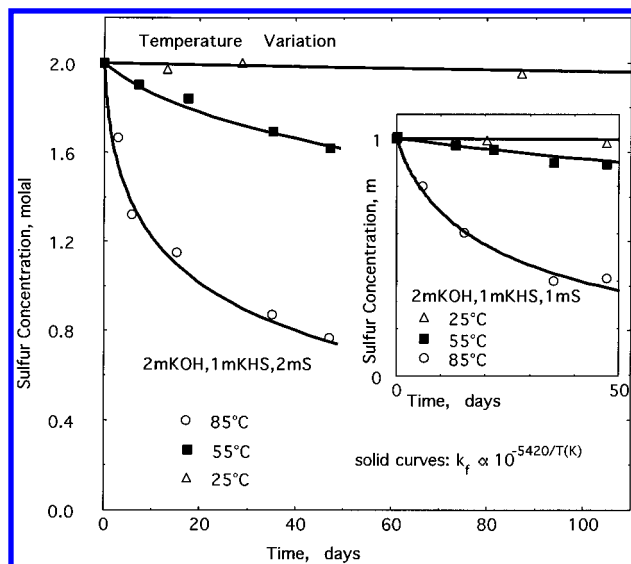


Figure 4. Variation, with temperature, of the rate of sulfur decomposition in various polysulfide solutions. Temperature is 25, 55, or 85 °C as indicated on the figure. Solutions are prepared with 2 *m* KOH and either a 2:1 ratio of sulfur to KHS, $C_{\text{Sinitial}}/C_{\text{KHSinitial}}$, or a 1:1 ratio of sulfur to KHS (inset). The solid curves are calculated in accord with rate equation (29).

of sulfur to KHS (figure inset). From the measured values of $pk_f(25\text{ }^{\circ}\text{C}) = 7.48$, $pk_f(55\text{ }^{\circ}\text{C}) = 5.82$, and $pk_f(85\text{ }^{\circ}\text{C}) = 4.43$, the temperature variation of the sulfur decomposition rate constant for eq 29 consistent is with

$$k_f = 10^{-(10.7-5430/T(K))} \quad (32)$$

From the Arrhenius slope, $-E_a/2.3R$, where R is the gas constant, an activation energy for sulfur decomposition of $104(\pm 5)\text{ kJ mol}^{-1}$ is determined. The relatively high uncertainty is consistent with the limitations imposed by the small temperature range investigated (298–358 K), and the small extent of sulfur decomposition at the lower temperature.

Decomposition of Concentrated Electrolytes. Aqueous potassium polysulfide solutions are capable of storing unusually large concentrations of sulfur. Under certain conditions, these solutions can contain more sulfur than water.¹⁷ Highly concentrated polysulfide solutions are capable of supporting high electrochemical current densities for photoelectrochemical and storage cells, and the zerovalent sulfur provides a cathode with a high battery storage capacity.^{17,18} The stability of these solutions has not been previously measured and is addressed in Figure 5. This figure presents variation of the rate of sulfur decomposition, at 85 °C, in polysulfide solutions prepared with 6 *m* KHS and up to 18 *m* sulfur. Solutions are prepared with a 3:1, 2:1, 1:1, or 0.5:1 ratio of sulfur to KHS and are prepared with either 7 *m* KOH (open points) or 12 *m* KOH (solid points).

As exemplified for the polysulfide solution containing 6 *m* KHS, 18 *m* S, and 7 *m* KOH, summarized in the last column of Table 2, speciation in these solutions is similar to more dilute polysulfide solutions, but sulfur half-life can be a duration on the order of years, as calculated in accord with the described iterative speciation procedure and numerical integration of eqs 29 and 32. For example, the calculated half-life is in excess of 500 years for the 6 *m* KHS, 18 *m* S, 7 *m* KOH. This is due to the high concentration of HS⁻ which builds up, eq 25, and the simultaneous substantial depletion of OH⁻, eq 24, which occurs, with onset of any sulfur decomposition. Consistent with eq 29, both of these trends substantially diminish the rate of sulfur decomposition. As seen in Figure 5, the small initial sulfur

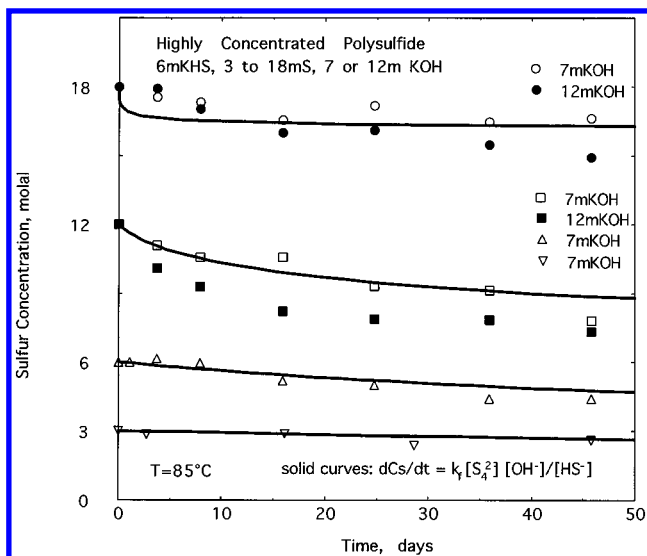
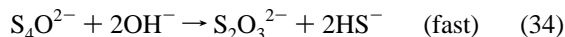
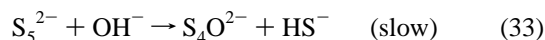


Figure 5. Variation in various highly concentrated polysulfide solutions of the rate of sulfur decomposition, with sulfur to sulfide ratio of 85 °C. Solutions are prepared with 6 m KHS, up to 18 m S (3:1, 2:1, 1:1, or 0.5:1 ratio of sulfur to KHS, $C_{S_{initial}}/C_{KHS_{initial}}$) and are prepared with either 7 m KOH (open points) or 12 m KOH (solid points). The solid curves are calculated in accord with rate equation (29).

decomposition occurring over an initial 50 days is generally consistent with this rate of decomposition predicted by eqs 29 and 32, although the scatter and deviation from the calculated decomposition are somewhat larger than observed for the other polysulfide compositions studied and summarized in Figures 1–4. This deviation may be related to limitations of the ionic strength equilibria correction factors in Table 1, for the very high ionic strength domain of these solutions. Alternately, these small deviations may indicate the initiation of a tendency toward a clustering phenomenon in these highest concentration electrolytes. Clustering, involving several polysulfide species, could be reflected in noninteger powers in eq 29.

Polysulfide Decomposition Mechanism. A mechanism consistent with eq 29 initiates with the reaction of pentasulfide and hydroxide. This reduces and ejects the first sulfur in the polysulfide chain via a rate-limiting S_4O^{2-} intermediate. Once formed, this intermediate readily reacts with hydroxide to form the thiosulfate product.



Combined, eqs 33 and 34 are consistent with both reaction rate 29 and the observed net reaction expressed by eq 11. Future studies will be of interest to probe for S_4O^{2-} and will establish if appropriate polysulfide solution composition and temperature conditions can generate significant quantities of this intermediate.

Conclusions

The distribution of species and measured and modeled rate of polysulfide decomposition were investigated for a wide range of polysulfide solution compositions from 25 to 85 °C. Evaluation of aqueous alkaline sulfur solutions was conducted over periods of several months and provides a consistent mechanism for polysulfide solution decomposition in this temperature range. Aqueous polysulfide solutions are unstable in this temperature range, and sulfur, dissolved as polysulfide, will decompose to thiosulfate, $S_2O_3^{2-}$ in accord with the observed net consumption

of dissolved sulfur expressed by eq 11. In this temperature range, the reverse reaction, of thiosulfate to polysulfide, was not observed to be measurable or significant over the period of several months.

The observed decomposition of sulfur concentration, C_S , is consistent with a rate-limiting step that is inverse first order in $[HS^-]$, and first order in $[OH^-]$ and $[S_5^{2-}]$, providing a sulfur decomposition mechanism consistent with eq 29. The measured decomposition rate constant, $k_f = 10^{-(10.7-5430/T(K))}$, is consistent with an activation energy for sulfur decomposition of $104(\pm 5)$ kJ mol⁻¹. In accord with these observations, S_4O^{2-} is proposed as the intermediate in the rate-limiting step as described by the mechanism of eqs 33 and 34.

At temperatures up to 85 °C, polysulfide solutions are extremely stable under conditions of high polysulfide concentration (> 5 m K_2S_4) and low KOH concentrations. Under these conditions, zerovalent sulfur dissolved in these solutions should be stable on the order of years.

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References and Notes

- (1) Ellis, A. B.; Kaiser, S. W.; Bolts, J. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 2839.
- (2) Miller, B.; Heller, A.; Robbins, M.; Menezes, S.; Chanson, K. C.; Thomson, J. *J. Electrochem. Soc.* **1977**, *124*, 1019.
- (3) Manassen, J.; Hodes, G.; Cahen, D. *J. Electrochem. Soc.* **1977**, *124*, 532.
- (4) Licht, S.; Tenne, R.; Flaisher, H.; Manassen, J. *J. Electrochem. Soc.* **1984**, *131*, 950.
- (5) Licht, S.; Manassen, J. *J. Electrochem. Soc.* **1985**, *132*, 1076.
- (6) Licht, S.; Tenne, R.; Flaisher, H.; Manassen, J. *J. Electrochem. Soc.* **1986**, *133*, 52.
- (7) Licht, S.; Manassen, J.; Hodes, G. *J. Electrochem. Soc.* **1986**, *133*, 272.
- (8) Licht, S.; Manassen, J. *J. Electrochem. Soc.* **1986**, *133*, 277.
- (9) Licht, S.; Marcu, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *210*, 197.
- (10) Licht, S. *Nature* **1987**, *330*, 148.
- (11) Miller, B.; Licht, S.; Orazem, M. E.; Searson, P. C. *Crit. Rev. Surf. Chem.* **1993**, *3*, 29.
- (12) Licht, S. *Solar Energy Mater.* **1995**, *38*, 305.
- (13) Licht, S.; Tenne, R.; Dagan, G.; Manassen, J.; Cahen, D.; Triboulet, R.; Rioux, J.; Levy-Clement, C. *Appl. Phys. Lett.* **1985**, *46*, 608.
- (14) Licht, S.; Hodes, G.; Tenne, R.; Manassen, J. *Nature* **1987**, *326*, 863.
- (15) Licht, S. *J. Phys. Chem.* **1986**, *90*, 1096.
- (16) Troshina, A. P.; Dontsov, A. G.; Brach, B. Ya.; Kondraenok, B. M. *Bum. Promst.* **1988**, *9*, 8.
- (17) Licht, S. *J. Electrochem. Soc.* **1987**, *134*, 2137.
- (18) Peramunage, D.; Licht, S. *Science* **1993**, *261*, 1029.
- (19) Gerischer, H. *Z. Anorg. Chem.* **1949**, *259*, 220.
- (20) Heller, A.; Gerischer, H. *J. Electrochem. Soc.* **1992**, *139*, 113.
- (21) Gigenbach, W. F. *Inorg. Chem.* **1974**, *13*, 1724.
- (22) Licht, S.; Hodes, G.; Manassen, J. *Inorg. Chem.* **1986**, *25*, 2486.
- (23) Rao, S. R.; Hepler, L. G. *Hydrometallurgy* **1977**, *2*, 293.
- (24) Meyer, B.; Ward, K.; Koshlap, K.; Peter, L. *Inorg. Chem.* **1983**, *22*, 2345.
- (25) Licht, S.; Manassen, J. *J. Electrochem. Soc.* **1987**, *134*, 918.
- (26) Forouzan, F.; Longo, K.; Licht, S. *Anal. Chem.* **1990**, *62*, 1356.
- (27) Licht, S.; Longo, K.; Peramunage, D.; Forouzan, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *318*, 111.
- (28) Peramunage, D.; Forouzan, F.; Licht, S. *Anal. Chem.* **1994**, *66*, 378.
- (29) Licht, S. *J. Electrochem. Soc.* **1988**, *135*, 2971.
- (30) Gustafsson, L.; Teder, A. *Sv. Papperstidn.* **1969**, *72*, 249.
- (31) Gigenbach, W. F. *Inorg. Chem.* **1974**, *13*, 1730.
- (32) Fisher, J. R.; Barnes, H. L. *J. Phys. Chem.* **1972**, *76*, 90.