Inorganic Polysulfides Sn(2-) and Radical Anions Sn(·-)

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Inorganic Polysulfides S_n^{2-} and Radical Anions $S_n^{\cdot-}$

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Abstract Inorganic polysulfide anions S_n^{2-} and the related radical anions $S_n^{\cdot-}$ play an important role in the redox reactions of elemental sulfur and therefore also in the geobiochemical sulfur cycle. This chapter describes the preparation of the solid polysulfides with up to eight sulfur atoms and univalent cations, as well as their solid state structures, vibrational spectra and their behavior in aqueous and non-aqueous solutions. In addition, the highly colored and reactive radical anions $S_n^{\cdot-}$ with n = 2, 3, and 6 are discussed, some of which exist in equilibrium with the corresponding diamagnetic dianions.

Keywords Sulfur chains · Molecular structures · Radical anions · Spectra · Redox reactions

List of Abbreviations

crypt-2.2.2 $N(C_2H_4OC_2H_4OC_2H_4)_3N$
en   Ethylenediamine
hmpa   Hexamethylphosphoric triamide
pmdeta N,N,N',N'',N'''-pentamethyldiethylenetriamine
teeda   Tetraethylethylenediamine
tmeda   Tetramethylethylenediamine

1
Introduction

Inorganic polysulfides are ionic substances containing chain-like dianions S_n^{2-}. Such ions are formed in numerous reactions, e.g., by oxidation of monosulfide ions HS^- in water or other polar solvents as well as by reaction of aqueous monosulfide with sulfur-rich compounds including elemental sulfur:

$$2HS^- - 2e^- \rightarrow S_2^{2-} + 2H^+ \tag{1}$$

$$2HS^- + S_8 \rightarrow 2S_5^{2-} + 2H^+ \tag{2}$$

Therefore, polysulfide ions play a major role in the global geological and biological sulfur cycles [1, 2]. In addition, they are reagents in important industrial processes, e.g., in desulfurization and paper production plants. It should be pointed out however that only sulfide, elemental sulfur and sulfate are thermodynamically stable under ambient conditions in the presence of water, their particular stability region depending on the redox potential and the pH value [3]:

$$1/2\,S_8 + 4H_2O \rightleftharpoons 3HS^- + SO_4^{2-} + 5H^+ \tag{3}$$
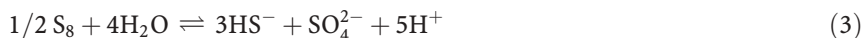
On the other hand, the large activation energy for the formation of sulfate from S_8 and water makes it possible to prepare polysulfides as well as other reduced sulfur compounds as metastable products in aqueous solution at ambient conditions.

Polysulfides are the key reactants in the high-density sodium-sulfur and lithium-sulfur batteries [4] which are based on the following reversible redox reaction taking place in the polysulfide melt:

$$1/2\,S_8 + 2e^- \rightleftharpoons S_4^{2-} \tag{4}$$

In melts and polar solvents polysulfide dianions are usually present as mixtures of species of different chain-lengths as a result of the following types of equilibria which are rapidly established even at 20 °C [5]:

$$2S_4^{2-} \rightleftharpoons S_3^{2-} + S_5^{2-} \tag{5}$$

$$2S_5^{2-} \rightleftharpoons S_4^{2-} + S_6^{2-} \tag{6}$$

The chemistry of polysulfide dianions is closely related to that of the radical-monoanions $S_n^{\cdot-}$ since both types of anions are in equilibrium with each other in solution and in high-temperature melts, e.g.:

$$S_6^{2-} \rightleftharpoons 2S_3^{\cdot-} \tag{7}$$

$$S_5^{2-} \rightleftharpoons S_2^{\cdot-} + S_3^{\cdot-} \tag{8}$$

Furthermore, polysulfide anions are subject to autoxidation if molecular oxygen is present, e.g.:

$$S_4^{2-} + 3/2\,O_2 \rightarrow S_2O_3^{2-} + 1/4\,S_8 \tag{9}$$

In solution this reaction is rather rapid but in the solid state autoxidation takes place much slower. Nevertheless, commercial sulfides and polysulfides of the alkali and alkali earth metals usually contain thiosulfate (and anions of other sulfur oxoacids) as impurities [6]. For all these reasons the chemistry of polysulfides is rather complex, and some of the earlier studies on polysulfides (prior to ca. 1960) are not very reliable experimentally and/or describe erroneous interpretations of the experimental results.

Polysulfides have been prepared with many different types of cations, both monoatomic like alkali metal ions and polyatomic like ammonium or substituted ammonium or phosphonium ions. In this chapter only those salts will be discussed in detail which contain univalent main-group cations although a large number of transition metal polysulfido complexes have been prepared [7–9].

A truly comprehensive review on the chemistry of inorganic (ionic) polysulfides has never been published. Szekeres [10] as well as Hanley and Czech [11] reviewed the classical analytical chemistry (titrimetric and gravimetric analysis) of sulfur acids including sulfides and polysulfides in 1974 and 1970, respectively. Chivers reviewed the chemistry of polychalcogenide anions including the radical monoanions (with the stress on the latter) in 1977 [12]. Hamilton critically reviewed the literature on aqueous polysulfide solutions and proposed a speciation model of his own [13].

Table 1 Properties of some ionic polysulfides

Compound	Color (20 °C)	Melting point [14, 15]	Density (g cm^{-3}) (20 °C)
Na_2S_2	Yellow	470±10 °C (β)	Two allotropes
Na_2S_4	Orange-yellow	290±5 °C	2.08
Na_2S_5	Brown-yellow	265±5 °C	2.08
K_2S_2	Pale yellow	487 °C	1.973
K_2S_3	Yellow-brown	302 °C	2.102
K_2S_4	Orange-yellow	154 °C	
K_2S_5	Orange	206 °C	2.128
K_2S_6	Red	189 °C	2.02

2
Preparation of Solid Polysulfides

2.1
Alkali Metal Polysulfides

The rather complex equilibrium phase diagrams of the sodium-sulfur system [14] and of the potassium-sulfur system [15] have been critically reviewed by Sangster and Pelton in 1997. In the sodium-sulfur system the compounds Na_2S, α-Na_2S_2, β-Na_2S_2, Na_2S_4, and Na_2S_5 exist but neither Na_2S_3 nor polysulfides higher than the pentasulfide do [16]. Na_2S_2 exists as α-form below 160 °C and as β-form above this temperature; both are of hexagonal crystal symmetry. β-Na_2S_2 melts incongruently at 470 °C while the tetra- and pentasulfides show congruent melting points (peritectic) [14]. As higher the sulfur content as lower the melting points (see Table 1). Liquid sodium polysulfides easily supercool and form relatively stable glasses. By Raman spectroscopy it was found that Na_2S_4 and Na_2S_5 can be obtained as several metastable phases depending on the preparation conditions [17,18]. The thermodynamically stable forms at ambient conditions are designated by α.

In the potassium-sulfur system the compounds K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6 exist and there are six eutectics [15]. All sodium and potassium sulfides and polysulfides are hygroscopic and some of them form well defined hydrates.

The preparation of anhydrous Na_2S_2, Na_2S_4, Na_2S_5, K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6 has been described in detail by Fehér et al. [16, 19–21]. These procedures are based on the following reactions (M: Na or K):

$$2M + 1/4\,S_8 \rightarrow M_2S_2 \tag{10}$$

$$M_2S + x/8\,S_8 \rightarrow M_2S_{x+1} \tag{11}$$

$$2MHS + x/8\,S_8 \rightarrow M_2S_{x+1} + H_2S \tag{12}$$

$$M_2S_4 + 2M \rightarrow 2M_2S_2 \tag{13}$$

$$M_2S_x + 1/8\,S_8 \rightarrow M_2S_{x+1} \tag{14}$$

Na_2S_2, K_2S_2, Na_2S_4, K_2S_4, and K_2S_5 may be prepared from the elements in liquid ammonia according to Eq. (10) in a special apparatus which allows the strict exclusion of moisture and oxygen. The alkali metals are soluble in liquid ammonia and reduce the sulfur stoichiometrically. After evaporation of the solvent the product is homogenized by heating under vacuum to a temperature just below the melting point.

Anhydrous Na_2S_2 and K_2S_2 may also be prepared according to Eq. (11), e.g., by heating of the components in an evacuated glass ampoule to 500 °C until a homogeneous melt is obtained which is then allowed to cool slowly. High-melting glass should be used for the ampoule.

Sodium disulfide for the in situ preparation of organic disulfanes R_2S_2 may also be prepared from the elements in 1,2-dimethoxyethane at 70 °C in the presence of catalytic amounts of an aromatic hydrocarbon or ketone [22].

The reaction at Eq. (12) allows the preparation of Na_2S_4 and K_2S_5 from the alkali metals, hydrogen sulfide and sulfur in anhydrous ethanol (ROH). First the metal is dissolved in the alcohol with formation of ethanolate (MOR) and hydrogen. Bubbling of H_2S into this solution produces the hydrogen sulfide (MHS). To obtain the polysulfide the solution is refluxed with the calculated amount of elemental sulfur. After partial evaporation of the solvent and subsequent cooling the product precipitates.

The alcoholic solution of Na_2S_4 prepared as described above may be reduced to Na_2S_2 by addition of the calculated amount of sodium and refluxing under pure nitrogen; see Eq. (13).

K_2S_6 is obtained if K_2S_5 and sulfur are heated in an evacuated glass ampoule to 220–280 °C for several hours followed by cooling to 20 °C within 10 h; see Eq. (14).

The mechanism of the reaction of solid α-Na_2S_2 with S_8 has been studied by Raman spectroscopy [18]. The reaction begins at the melting temperature of S_8 (120 °C) and the primary product is α-Na_2S_4. Near 160 °C the remaining α-Na_2S_2 first transforms to β-Na_2S_2 which also reacts with S_8 to α-Na_2S_4. If Na_2S is used as a starting material it first reacts with S_8 to Na_2S_2. Heating of α-Na_2S_4 to 500 °C followed by cooling to 120 °C results in a glassy material which on annealing at this temperature forms crystalline γ-Na_2S_4 as a metastable phase which melts at ca. 230 °C. If a mixture of Na_2S and α-Na_2S_4 is heated to 200 °C the Raman lines of β-Na_2S_2 can be observed:

$$2Na_2S + Na_2S_4 \rightarrow 3Na_2S_2 \tag{15}$$

Na_2S_3 is not stable in the solid state, and cooling of a melt of composition Na_2S_3 leads to an eutectic mixture of Na_2S_2 and Na_2S_4 [18, 23]. However, the Raman spectra of melts of this composition show a line at 462 cm^{-1} which has been assigned to S_3^{2-} ions [18], and at low temperatures in liquid ammonia a metastable phase of Na_2S_3 has evidently been prepared by the following reaction [24]:

$$K_2S_3 + 2NaCl \rightarrow Na_2S_3 + 2KCl\downarrow \tag{16}$$

The potassium chloride precipitates from the solution shifting the equilibrium to the right side. On heating to 100 °C this Na_2S_3 sample decomposed exothermically to a 1:1 mixture of Na_2S_2 and Na_2S_4 similar to the one described above.

Heating of α-Na_2S_4 with an excess of sulfur to 500 °C yields mixtures of α-, β-, γ-, and δ-Na_2S_5 with the γ-form predominating. This allotrope converts to the α-form on annealing at 200 °C for 21 h while the β- and δ-form slowly convert to the α-allotrope on cooling also. In other words, these phases are metastable at any temperature [18].

Although solid Na_2S_6 does not exist the adduct $[Na(tea)]_2S_6$ has been isolated as red crystals which were crystallographically characterized (tea = triethanolamine) [25].

The sulfur pressure over liquid sodium polysulfides has been measured in the temperature range 400–1000 °C [26].

For the preparation of rubidium and cesium polysulfides, see [27].

To check the identity and purity of the products obtained in the above reactions it is not sufficient to analyze for the sulfur content since a mixture may incidentally have the same S content. Either X-ray diffraction on single crystals or Raman spectra of powder-like or crystalline samples will help to identify the anion(s) present in the product. However, the most convincing information comes from laser desorption Fourier transform ion cyclotron resonance (FTICR) mass spectra in the negative ion mode (LD mass spectra). It has been demonstrated that pure samples of K_2S_3 and K_2S_5 show peaks originating from $S_n^{\cdot-}$ radical anions which are of the same size as the dianions in the particular sample; no fragment ions of this type were observed [28].

2.2
Sulfur-Rich Polysulfides with Complex Univalent Cations

2.2.1
General

A large number of polysulfides with up to eight sulfur atoms in the anion have been prepared, mostly from non-aqueous solvents. The following donor ligands served to coordinate the alkali metal cations: en = ethylenediamine, tmeda = tetramethylethylenediamine, teeda = tetraethylethylenediamine, hmpa = hexamethylphosphoric triamide, pmdeta = N,N,N',N'',N''-pentamethyldiethylenetriamine, crypt-2.2.2 = $N(C_2H_4OC_2H_4OC_2H_4)_3N$. Often the polysulfide chain-length in the product is different from that in the starting material because of the reactions at Eqs. (5) and (6) taking place in solution. Since the polysulfides are often hygroscopic and air-sensitive their preparation has to be performed under an atmosphere of dry nitrogen or argon.

2.2.2
Tetrasulfides

Na(Et$_4$N)S$_4$ was obtained from Na$_2$S$_4$ and Et$_4$NCl in ethanol and was characterized by X-ray diffraction on single-crystals [29]. Orange needles of [Li(pmdeta)]$_2$S$_4$ crystallized from solutions of pmdeta in toluene in which Li$_2$S$_2$ or Li$_2$S$_4$ was suspended. In the case of Li$_2$S$_4$ the yield is, of course, much higher [30].

2.2.3
Pentasulfides

Ammonium pentasulfide is usually prepared according to Eq. (17) by suspending elemental sulfur in aqueous ammonia (35%) and bubbling hydrogen sulfide into the solution [20, 31, 32]:

$$H_2S + 1/2\, S_8 + 2NH_3 \rightarrow (NH_4)_2S_5 \qquad (17)$$

On cooling (NH$_4$)$_2$S$_5$ crystallizes as yellow to orange-yellow needles which melt at 95 °C in a sealed glass tube but decompose in air [reverse reaction at Eq. (17)] and on dissolution in water. (Et$_4$N)$_2$S$_5$ is obtained by reaction of Et$_4$NCl with Na$_2$S$_5$ in ethanol [33].

2.2.4
Hexasulfides

Dark-red needles of (Bu$_4$N)$_2$S$_6$ were obtained by treatment of an "alloy" of composition Na$_2$S$_3$ (prepared from Na$_2$S+1/4 S$_8$) with aqueous (Bu$_4$N)Br followed by recrystallization from acetone [34]. In a similar fashion (Me$_4$N)$_2$S$_6$ was prepared from Na$_2$S$_5$ and Me$_4$NCl in H$_2$O with exclusion of oxygen [35]. Ethylenediamine reacts with sulfur and H$_2$S to give (enH$_2$)S$_6$ containing diprotonated ligands [36]:

$$H_2S + 5/8\, S_8 + en \rightarrow (enH_2)S_6 \qquad (18)$$

In contrast, the reaction of H$_2$S, S$_8$ and ethylenediamine *in ethanol* at 65 °C produces orange crystals of (enH)$_2$S$_6$ which still contain some elemental sulfur [37]. If trimethylamine is used the product is (Me$_3$NH)$_2$S$_6$ [38]. Dark-red [K(crypt-2.2.2)]$_2$S$_6$ crystallizes from a solution of K$_2$S$_5$, S$_8$ and crypt-2.2.2 in ethylenediamine [39]. Orange crystals of [Li(tmeda)]$_2$S$_6$ were obtained by extracting Li$_2$S$_2$ repeatedly with tetrahydrofuran (THF), evaporation of the solvent from the extracts and suspending the latter in a solution of tmeda in toluene followed by addition of THF and cooling [40,41]. In a similar fashion [Li(hmpa)]$_2$S$_6$, [Li(pmdeta)]$_2$S$_6$, [Na(pmdeta)]$_2$S$_6$, and [K(hmpa)]$_2$S$_6$ [41] as well as [Li(teeda)]$_2$S$_6$ [30] were prepared. The reaction of triorganotelluronium chlorides R$_3$TeCl (R = Me, Ph, etc.) with Na$_2$S$_x$ (x = 4–6) in methanol at 50 °C yields the corresponding bis(triorganotelluroni-

um) hexasulfides $(R_3Te)_2S_6$ regardless of the employed sodium polysulfide or the size of the telluronium cation [42].

2.2.5
Heptasulfides

Bis(tetrapropylammonium)heptasulfide $(Pr_4N)_2S_7$ was obtained from the reaction of Pr_4NBr and Na_2S_5 in water [43]. $[K(crypt-2.2.2)_2]S_7 \cdot$ crystallizes together with other products from a solution of K_2S_5, S_8 and crypt-2.2.2 in ethylenediamine. The red crystals easily lose the solvent molecule [39]. Triclinic orange-red crystals of $(Ph_4P)_2S_7$ have been obtained from a mixture of $(Et_4N)_2MoS_9$, diethyldithiocarbamate trihydrate, and Ph_4PCl in CH_3CN [44]. The compound $(Ph_4P)_2S_7$ and the derivative $(Ph_4P)(NH_4)S_7 \cdot CH_3CN$ are also accessible from Ph_4PBr, polysulfide, S_8, H_2S, and NH_3 in CH_3CN but the details of this synthesis have not been disclosed yet [45]. The reaction of [PPN]SH with S_8 in ethanol yields crystalline $[PPN]_2S_7 \cdot 2EtOH$ in high purity [PPN = $(Ph_3P)_2N^+$] [46]. Saturation of a solution of diisobutylamine and S_8 in a 1:1 mixture of formamide and dimethylformamide with H_2S provides $[(i-C_4H_9)_2NH_2]_2S_7$ [47].

2.2.6
Octasulfides

Treatment of Na_2S_4 with $(Ph_4P)_2Cl$ in ethanol yields $(Ph_4P)_2S_8$ [48]:

$$2Na_2S_4 + 2Ph_4PCl \rightarrow (Ph_4P)_2S_8 + Na_2S_2 + 2NaCl \tag{19}$$

Orange-red crystals of $(Et_3NH)_2S_8$ are formed on reaction of triethanolamine with sulfur and H_2S in formamide at 60 °C and subsequent cooling to 20 °C [49]:

$$2Et_3N + H_2S + 7/8\ S_8 \rightarrow (Et_3NH)_2S_8 \tag{20}$$

There is also a report on the preparation of the *dodecasulfide* $(PPN)_2S_{12}$ [50] but the experimental evidence for such an anion is rather weak.

Polysulfides with two-valent complex cations, e.g., [M(*N*-methylimidazole)$_6$]S_8 have been prepared with M = Mn, Fe, Ni, Mg [51].

3
Properties of Solid Alkali Polysulfides

The alkali polysulfides are hygroscopic crystalline substances which show a pronounced thermochromic effect. The higher members decompose on heating and sinter before melting. The densities given in Table 1 were determined by the pyknometric method [52]. As far as the colors and melting points are concerned rather differing reports can be found in the literature. The melting temperatures cited in Table 1 are "best values" and the colors were taken from Fehér's work.
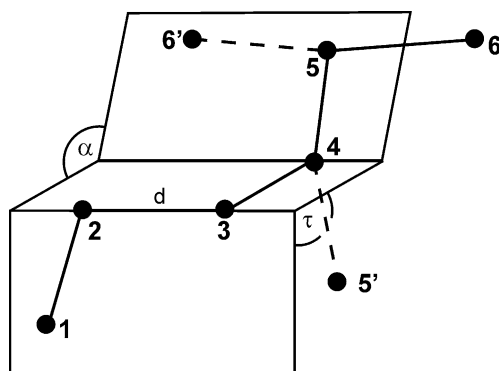
Fig. 1 Possible conformations of the pentasulfide anion S_5^{2-} and of the hexasulfide ion S_6^{2-} depending on the signs of the torsion angles

4
Structures of Polysulfide Dianions

Many of the polysulfides described above have been investigated by X-ray diffraction on either powders or single crystals. In all cases the more sulfur-rich anions ($n>3$) form unbranched chains the symmetry of which varies between C_1, C_2, and C_s. According to Fig. 1 the symmetry C_2 results if all torsion angles have the same sign (right-handed helix: + + +...; left-handed helix: − − −...). If the different torsion angles of the anion vary between + and − the symmetry may be C_s or C_1. The order of the signs of the torsion angles along the chain is called the "motif" of the anion. For structural details, see Table 2.

For powder diffraction studies of Na_2S_2 (hexagonal), α-Na_2S_4 (tetragonal), and α-Na_2S_5 (orthorhombic), see [16, 53]; for those of K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6, see [21]. The hexagonal structures of α- and β-Na_2S_2 contain disulfide anions with SS bonds of length 215 pm (in both cases) while 210 pm were derived for K_2S_2 [54]. The orthorhombic structure of K_2S_3 contains anions of C_{2v} symmetry with SS bonds of 208.3(1) pm and a bond angle of 105.4(1)° [55].

α-Na_2S_4 crystallizes in a tetragonal space group with Z=8. The anions are located on a twofold axis (C_2 symmetry) with internuclear SS distances of 207.4(1) pm for the terminal bonds and 206.1(1) pm for the central bond, an SSS bond angle of 109.76(2)° and a torsion angle of 97.81° [56].

The crystals of α-Na_2S_5 are orthorhombic and contain anions of C_s symmetry (*cis* conformation) with SS bond lengths of 206.1(2) pm (terminal) and 206.6(2) pm (central), SSS angles of 107.3(1)° (terminal) and 108.1(1)° (central), and torsion angles of 88.6°. The terminal sulfur atoms have four, their next neighbors two and the central S atom one sodium cation in the distance range 285–303 pm [57]. In contrast, the anions of K_2S_5 [58], Rb_2S_5 [59], $Cs_2S_5 \cdot H_2O$ [60] and Tl_2S_5 [61] are all of C_2 symmetry (helical conformation). The only alkali metal hexasulfide which has been studied by single

Table 2 Structure data of sulfur-rich polysulfides with univalent cations (for abbreviations, see text)

Anion	Cations	Symmetry[a]	d_{SS} (pm)	α_{SSS} (°)	τ_{SSSS} (°)	Ref.
S_4^{2-}	2 Na+ (α)	C_2	206.1/207.4	109.76	97.81	[56]
	Na+, NEt4+	(C_2)	206.1–207.9	109.6/110.3	81.84	[29]
	2 Li(pmdeta)+		204.8–206.7	109.9/109.3	92.1	[30]
S_5^{2-}	2 Na+ (α)	C_s	206.1/206.6	107.3/108.1	88.6	[57]
	2 NH4+	(C_2)	205.8–207.3	106.4–109.0	67.1/68.0	[32]
	2 K+	(C_2)	203.7–207.5	106.4–109.7	68.7/73.6	[58]
	2 Rb+	(C_2)	201.9–210.9	107.5–111.2	68.7/74.5	[59]
	2 Cs+ (H2O)[b]	(C_2)	204.8–207.0	106.9–107.9	69.2/75.7	[60]
	2 Tl+	(C_2)	206–216	107–109	67/73	[61]
S_6^{2-}	2 Cs+	(C_2)	199–212	108.1–109.5	61.4/78.6/81.9	[63]
	2 Li(teeda)+	(C_2)	disordered			[30]
	2 Bu4N+	C_2	206.2–209.0	109.5/110.5		[34]
	2 Me4N+	C_2	202.2–210.1	108.2/112.1	65.3/88.5	[35]
	enH2²+	C_1	202.6–207.7	106.7–109.8	58.9–82.0	<XAppendix>[36]
	2 enH+	(C_2)	202.3–206.7	107.2–110.8	71.2–85.0	[37]
	2 Li(tmeda)+	C_2	disordered			[40,41]
	2 Me3NH+	C_2	203.4–207.9	108.8/111.0	75.5/85.5	[38]
	2 Ph3Te+	(C_2)	203.6–210.3	108.7–113.0	84.7–110.4	[42]
	2 Na(tea)+		203.3–205.9			[25]
S_7^{2-}	2 K(crypt-2.2.2)+	C_2	200.7–207.6	111.8/112.1	83.2/93.0	[39]
	2 Pr4N+	(C_2)	201.0–209.8	107.5–111.4	65.3–78.7	[43]
	2 K(crypt-2.2.2)+ (en)[b]	(C_2)	199.8–208.0	108.8–110.9	75.9–81.5	[39]
	2 Ph4P+	(C_2)	199.0–206.2	106.8–111.3	65.2–79.9	[44]
	Ph4P+, NH4+ (CH3CN)[b]	C_1	196.3–205.9		71.3–96.2	[45]
	2 PPN+ (2 EtOH)[b]	(C_2)	202.6–207.2	107.9–110.9	71.8–94.2	[46]
	2[b]Bu2NH2+	(C_s)	202.0–205.2	106.3–111.0	74.8–85.5	[47]
S_8^{2-}	2 Et3NH+	C_2	204.1–207.3	107.3–110.4	84.3–97.7	[49]

[a] Symmetry of the anion in the crystal. Data in parentheses give the approximate (non-crystallographic) symmetry

[b] Solvent molecule(s) in the crystal structure

crystal X-ray structural analysis is Cs_2S_6 which also contains helical anions [62, 63].

For structures of polysulfides with two-valent cations, see the original literature: SrS_2, BaS_2, SrS_3, and BaS_3 in [64] and $BaS_4 \cdot H_2O$ in [65].

The structures of isolated polysulfide dianions S_n^{2-} with $n = 2–8$ have been studied by ab initio molecular orbital calculations with the DZPD basis set [66]. Generally, small dianions cannot exist as isolated particles but either spontaneously loose one electron ("electron autodetachment") or dissociate into two singly charged fragments ("Coulomb explosion"). In the case of the polysulfide dianions it was found that at least seven sulfur atoms are needed to accommodate two negative charges. In the ground state all dianions exhibit a helical structure of C_2 symmetry; other chain-like conformers are only slightly less stable. The negative charges are essentially localized at the terminal atoms (0.7 e$^-$ each in the case of hepta- and octasulfide). The dissociation of S_7^{2-} and S_8^{2-} into polyatomic monoanions is exothermic and most so if the two fragments are of similar or identical size. On the other hand, the dissociation into $S^{\cdot-}$ and $S_{n-1}^{\cdot-}$ is endothermic and there may be a substantial activation barrier for this process. In other words, all polysulfide dianions are either unstable or metastable in the gas phase. Surprisingly, branched polysulfide dianions like the tetrahedral S_5^{2-} ion (analogous to the sulfate ion) and the D_{3d} structure of S_8^{2-} (in analogy to the dithionate ion, $S_2O_6^{2-}$) are also local minima but much less stable than the helical chain isomers.

5
Polysulfide Solutions

5.1
Aqueous Solutions

Water-soluble sulfides like those of the alkali and alkali earth metals dissolve in H_2O with hydrolysis to give strongly alkaline solutions:

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \tag{21}$$

This equilibrium is practically completely on the right side and therefore the pH of sodium sulfide solutions increases from 12 at a concentration of 0.04 mol l^{-1} to 13 at 1.00 mol l^{-1} [67]. In other words, the pH of these solutions are almost identical to those which one would obtain if pure NaOH had been dissolved instead of Na_2S. Due to the extremely low value of the second dissociation constant of H_2S the sulfide ion S^{2-} exists in water at extremely high pH values only but even then it remains a minority species compared to the HS$^-$ ion [68]. The value of $K_{a2}(H_2S)$ is not known exactly and depends on the ionic strength but has been estimated experimentally at 20 °C as somewhere between 10^{-14} and 10^{-17} mol l^{-1} [68–70] with the latter value being more likely in strongly alkaline solutions (high ionic strength).

Remarkably, in the structure of the solid hydrate $Na_2S \cdot 9H_2O$ the sulfide ion is coordinated by 12 hydrogen atoms but no SH^- ion is formed [71].

Solutions containing the nucleophiles S^{2-} and/or HS^- dissolve elemental sulfur by reactions according to the following equations (nucleophilic degradation):

$$S_8 + HS^- + OH^- \rightleftharpoons S_9^{2-} + H_2O \qquad (22)$$

$$S_9^{2-} + HS^- + OH^- \rightleftharpoons 2S_5^{2-} + H_2O \qquad (23)$$

The generated polysulfide dianions of different chain-lengths then establish a complex equilibrium mixture with all members up to the octasulfide at least; see Eqs. (5) and (6). For this reason, it is not possible to separate the polysulfide dianions by ion chromatography [6]. The maximum possible chain-length can be estimated from the preparation of salts with these anions in various solvents (see above). However, since the reactions at Eqs. (22) and (23) are reversible and S_8 precipitates from such solutions if the pH is lowered below a value of 6, the nonasulfide ion must be present also to generate the S_8 molecules by the reverse of the reaction at Eq. (22). The latter reaction (precipitation of S_8 on acidification) may be used for the gravimetric determination of polysulfides [11]. There is no evidence for the presence of monoprotonated polysulfide ions HS_n^- in aqueous solutions [67, 72].
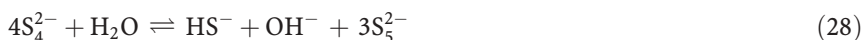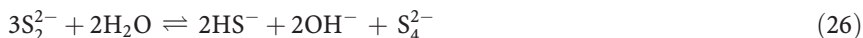
If S_8 is dissolved in a polysulfide solution the reactions according to Eqs. (24) and (25) are faster than the reactions at Eqs. (22) and (23) since disulfide (and also trisulfide) anions are evidently stronger nucleophiles than HS^-:

$$S_2^{2-} + S_8 \rightleftharpoons S_{10}^{2-} \qquad (24)$$

$$S_{10}^{2-} + S_2^{2-} \rightleftharpoons 2S_6^{2-} \rightleftharpoons S_5^{2-} + S_7^{2-} \qquad (25)$$

Consequently, sulfur dissolves in polysulfide solutions much faster than in equimolar monosulfide solutions [73]. In this context it is of interest that the analogous decaselenium dianion Se_{10}^{2-} has been prepared and structurally characterized in solid $[PPN]_2Se_{10}$ [74]. This anion is however bicyclic.

Many authors have tried to determine the speciation of the various polysulfide anions in water as a function of sulfur content, pH value, concentration, and temperature. However, since there is no direct method to determine single species either analytically or spectroscopically the results are somewhat speculative and rest on certain assumptions. Most authors agree that tetra- and pentasulfide ions are the dominating species at higher sulfur concentrations and that S_n^{2-} ions with $n > 6$ can be neglected to a first approximation [67]. Schwarzenbach and Fischer [69] demonstrated that aqueous alkali polysulfides can be titrated with hydrochloric acid in a flow apparatus allowing a very rapid mixing with simultaneous measurement of the pH value and exclusion of dioxygen. The authors concluded that at polysul-

fide concentrations of 0.05 mol l^{-1} only Na_2S_5 dissolves undecomposed, while di-, tri-, and tetrasulfides (of Na or K) hydrolyze almost quantitatively according to the following equations (at 20 °C):

$$3S_2^{2-} + 2H_2O \rightleftharpoons 2HS^- + 2OH^- + S_4^{2-} \tag{26}$$

$$3S_3^{2-} + H_2O \rightleftharpoons HS^- + OH^- + 2S_4^{2-} \tag{27}$$

$$4S_4^{2-} + H_2O \rightleftharpoons HS^- + OH^- + 3S_5^{2-} \tag{28}$$

Therefore, the pH values of these solutions are between 11 and 12. The speciation model used by Schwarzenbach and Fischer is certainly too simple but these authors have been the first to demonstrate the strong dependence of the polysulfide anion distribution on the alkalinity. According to Eqs. (26)–(28) higher pH values in dilute solutions will favor smaller anion sizes.

Teder has been the first to analyze successfully aqueous sodium polysulfide solutions by UV-Vis absorption spectroscopy in the range of 200–600 nm and at pH values ranging from 11 to 13.8 [75]. He observed eight overlapping bands one of which could be assigned to the HS^- ion (at 230 nm) while the other seven (240–400 nm) all seemed to have contributions from polysulfide ions with up to six sulfur atoms. The spectra were analyzed by varying the alkalinity, the ratio of sulfide: polysulfide excess sulfur (i.e., the sulfur atoms of formal oxidation number zero in the polysulfide chain) and the temperature (25 and 80 °C). The results could be interpreted with the assumption that tetra-, penta-, and hexasulfide ions are the dominating species besides trisulfide ions and hydrogen monosulfide while the concentration of S^{2-} was negligible at 25 °C. Also, monoprotonated polysulfide ions were not observed. However, several models with differing polysulfide species could explain the experimental data equally well! The mean size of the polysulfide ions increased with temperature and decreased with increasing alkalinity (see Eq. 23) and reached maximum values of 5 atoms at 25 °C and 6.5 atoms at 80 °C. Interestingly, in ethanolic solution the maximum size of the polysulfide ions is even larger resulting in additional absorption bands in the visible region at 476 and 588 nm. The wings of the polysulfide bands in the near UV stretching into the visible region cause the yellow color of dilute polysulfide solutions. At higher concentrations the color changes via orange to red; it has been shown above that solid hexa-, hepta- and octasulfides are red (see above).

The composition of sodium polysulfide solutions *saturated* with sulfur of zero oxidation number (S°) has also been studied at 25 and 80 °C (solutions in contact with elemental sulfur) [76]. In this case the ratio $S°:S^{-2}$ per polysulfide ion increases with increasing alkalinity. The maximum average number of sulfur atoms per polysulfide molecule was obtained as 5.4 at 25 °C and 6.0 at 80 °C and pH values of >12. Equilibrium constants for reactions as in Eqs. (26) and (27) have been derived assuming various models with differing numbers of polysulfide ions present.

The isotopic exchange between radioactive elemental sulfur containing traces of ^{35}S and aqueous polysulfide at pH=7.6 has been shown to be very rapid. Within less than 2 min half of the tracer from [35]S° had exchanged [77].

Optical measurements on polysulfide solutions at 20 °C similar to those described above have also been carried out by Giggenbach who varied the pH value between 6.8 and 17.5 and recorded spectra of *dilute solutions* at wavelengths of between 250 and 500 nm [5]. Depending on the concentrations of OH^-, SH^-, and S° the spectra showed five absorption bands which were assigned to specific ions as follows: S_2^{2-}: 358, S_3^{2-}: 417, S_4^{2-}: 368, S_5^{2-}: 375 nm. This order is rather surprising since one would expect the wavelengths to steadily increase with increasing chain-length as has been observed for covalent polysulfanes [78]. On the other hand, the λ_{max} values for tetra- and pentasulfide are in agreement with earlier measurements [69]. These absorption bands are however too close to each other for an accurate quantitative analysis. The maximum average number of 4.5 sulfur atoms in the polysulfide ions derived by Giggenbach for solutions saturated with sulfur at temperatures of between 20 and 180 °C and an ionic strength of 0.4 [72] is relatively low and in contrast to the results of Teder [76] and Jordan et al. [79] which was explained by the lower concentrations [80]. Giggenbach later extended his studies up to temperatures of 240 °C [80]. Licht et al. [81] duplicated Giggenbach's work using a different numerical analysis of the data without obtaining more reliable results, partly because ions larger than S_5^{2-} were neglected. The following peaks were assigned to the polysulfide ions considered (wavelengths in nm): S^{2-}: 358, S_3^{2-}: 429, S_4^{2-}: 372, S_5^{2-}: 377.

Hamilton [13] assumed the presence of all ions S_n^{2-} with n ranging from 1 to 8 in aqueous polysulfide solutions which is by far the most acceptable model but since there is insufficient experimental data available this model cannot be worked out quantitatively without additional assumptions. The general idea is that those species are most abundant which are close to the average composition of the particular solution, e.g., S_4^{2-} and S_5^{2-} for a solution of composition $Na_2S_{4.5}$, and that the larger and smaller ions are symmetrically less abundant. Equilibrium constants for the various reactions

$$n/8\, S_8(\text{solid}) + HS^- + OH^- \rightleftharpoons S_{n+1}^{2-} + H_2O \tag{29}$$
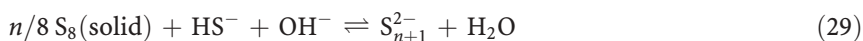
in water were derived for a number of different speciation models ($n = 1$–7). The presence of several ions larger than S_5^{2-} in aqueous polysulfide solutions has in fact been demonstrated by laser desorption mass spectroscopy [28].

Giggenbach observed that the absorption band of HS^- at 230 nm in solutions of H_2S in concentrated aqueous NaOH developed a shoulder at ca. 250 nm with increasing OH^- concentration; he assigned the new band to the hydrated sulfide ion S^{2-}(aq) [68].

5.2
Non-Aqueous Solutions

Ionic polysulfides dissolve only in media of high polarity like water, liquid ammonia, alcohols, nitriles, amines, and similar solvents. In all of these solvents S_8 can be reduced electrochemically to polysulfide anions. On the other hand, the electrochemical oxidation of polysulfide anions produces elemental sulfur:

$$S_8 + 2e^- \rightleftharpoons S_8^{2-} \tag{30}$$

The chemistry of elemental sulfur and sulfur-rich molecules including polysulfides in liquid ammonia [82] and in primary as well as secondary amines [83] is complex because of the possible formation of sulfur-nitrogen compounds. Therefore, polysulfide solutions in these solvents will not be discussed here. Inert solvents which have often been used are dimethylformamide (DMF) [84–86], tetrahydrofuran (THF) [87], dimethylsulfoxide (DMSO) [87], and hexamethylphosphoric triamide (HMPA) [86, 88].

Ionic polysulfides dissolve in DMF, DMSO, and HMPA to give air-sensitive colored solutions. Chivers and Drummond [88] were the first to identify the blue $S_3^{\cdot-}$ radical anion as the species responsible for the characteristic absorption at 620 nm of solutions of alkali polysulfides in HMPA and similar systems while numerous previous authors had proposed other anions or even neutral sulfur molecules (for a survey of these publications, see [88]). The blue radical anion is evidently formed by reactions according to Eqs. (5)–(8) since the composition of the dissolved sodium polysulfide could be varied between Na_2S_3 and Na_2S_{14} with little impact on the visible absorption spectrum. On cooling the color of these solutions changes via green to yellow due to dimerization of the radicals which have been detected by magnetic measurements, ESR, UV-Vis, infrared and resonance Raman spectra [84, 86, 88, 89]; see later.

5.2.1
Electrochemical Studies

The electrochemical reduction and oxidation of sulfur and of polysulfide dianions at inert electrodes has been studied in aprotic solvents and in liquid ammonia. In the latter case, sulfur-nitrogen compounds are involved and these systems [90] will not be discussed here.

The electrochemical reduction of S_8 in aprotic solvents like DMSO [87, 91, 92], DMF [92, 93], dimethylacetamide [94], acetonitrile [95], or methanol [95] yields primarily S_8^{2-} ions which then equilibrate with other dianions and radical anions like $S_3^{\cdot-}$ and others; see Eqs. (4)–(8). In a second reduction step tetrasulfide ions are formed:

$$S_8^{2-} + 2e \rightleftharpoons 2S_4^{2-} \tag{31}$$

However, the actual mechanism of tetrasulfide formation may be as fol-
lows [93]:

$$S_8^{2-} \rightleftharpoons 2S_4^{\cdot-} \tag{32}$$

$$S_4^{\cdot-} + e \rightleftharpoons S_4^{2-} \tag{33}$$
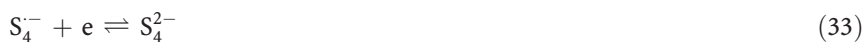
Besides S_8, the homocycles S_6 and S_7 have been reduced electrochemically
in methanol (Au electrode); the reported half-wave potentials are -0.50,
-0.54, and -0.63 V (± 0.03 V each) for S_6, S_7, and S_8, respectively [95].

6
Vibrational Spectra

Vibrational spectroscopy and in particular Raman spectroscopy is by far the
most useful spectroscopic technique to qualitatively characterize polysulfide
samples. The fundamental vibrations of the polysulfide dianions with be-
tween 4 and 8 atoms have been calculated by Steudel and Schuster [96] using
force constants derived partly from the vibrational spectra of Na_2S_4 and
$(NH_4)_2S_5$ and partly from $cyclo$-S_8. It turned out that not only species of dif-
fering molecular size but also rotational isomers like S_5^{2-} of either C_2 or C_s
symmetry can be recognized from pronounced differences in their spectra.
The latter two anions are present, for instance, in Na_2S_5 (C_s) and K_2S_5 (C_2),
respectively (see Table 2).

Reliable spectra of K_2S_3 [97], BaS_3 [98], Na_2S_4 [99–101], Cs_2S_4 [101], Na_2S_5
[99], Rb_2S_5 [101], K_2S_5 [97, 99], K_2S_6 [97], Cs_2S_6 [101], as well as of $(NH_4)_2S_5$
[96] have been published. Corset et al. studied the reactions of sodium sul-
fide and disulfide with elemental sulfur at high temperatures and identified
the solid phases α- and β-Na_2S_2, α-, γ-, and glassy Na_2S_4, as well as α-, β-, γ-
, δ-, and glassy Na_2S_5 by Raman spectroscopy [18].

For Raman spectra of hexa- [30, 40] and heptasulfides [46] with complex
univalent cations, see the original literature.

Several authors studied the changes in the Raman spectra of alkali poly-
sulfides on heating. Heating of pure Na_2S_4 or mixtures of this salt with KSCN
to 300 °C produces the radical anions $S_3^{\cdot-}$ (detected by their resonance Ra-
man effect) [102]. The thermal behavior of the tetra-, penta-, and hexasul-
fides of Na, Rb, and Cs up to 400 °C were studied by Ziemann and Bues
[101] and the formation of $S_3^{\cdot-}$ radicals in the melt of Cs_2S_4 (but not in the
case of Na_2S_4) was observed. Evidently $S_3^{\cdot-}$ results from the reactions accord-
ing to Eqs. (5) and (8). Cs_2S_6 turns black on melting, and the spectrum of
the rapidly quenched melt is different from the original hexasulfide which
has been interpreted in terms of a hexasulfide isomer with the structure
shown in Scheme1.
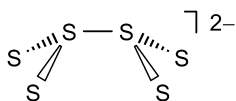
Scheme 1

This black material changed back to the ordinary structure of Cs_2S_6 on annealing. The formation of the isomeric hexasulfide (analogous to the structure of the isoelectronic dithionite anion) was explained by recombination of two trisulfide radical anions [101].

7
Reactions in Solution

Under special conditions the rapid protonation of aqueous polysulfide ions by hydrochloric acid at temperatures of below 0 °C produces polysulfanes:

$$S_n^{2-} + 2H^+ \rightarrow H_2S_x \tag{34}$$

However, some interconversion reactions take place simultaneously and therefore the composition of the sulfane mixture is not a mirror image of the composition of the polysulfide solution [103]. The sulfane mixture forms a yellow oily hydrophobic liquid which precipitates from the aqueous phase. At 20 °C it decomposes more or less rapidly to H_2S and S_8.

Sulfite ions react with polysulfide ions at 50 °C in neutral solution to thiosulfate and monosulfide, e.g.:

$$S_4^{2-} + 3HSO_3^- \rightarrow 3S_2O_3^{2-} + HS^- + 2H^+ \tag{35}$$

This reaction has also been used for the titrimetric determination of polysulfides [10, 11].

In a similar fashion, cyanide ions desulfurize polysulfide ions at 100 °C to the monosulfide level, e.g.:

$$S_4^{2-} + 3CN^- + H^+ \rightarrow 3SCN^- + HS^- \tag{36}$$

After acidification with H_3PO_3 the extremely poisonous HCN and H_2S formed may be evaporated by refluxing under a fume hood; subsequently the thiocyanate can be titrated [10, 11]. The degradation of the polysulfide in the reactions at Eqs. (35) and (36) results in discoloration of the solutions.

Alkaline hydrogen peroxide oxidizes polysulfides to sulfate, e.g.:

$$S_4^{2-} + 13H_2O_2 + 6OH^- \rightarrow 4SO_4^{2-} + 16H_2O \tag{37}$$

Titration of the unreacted hydroxide with standard sulfuric acid allows the determination of the polysulfide [10, 11].

Aqueous polysulfide solutions are thermodynamically unstable with respect to thiosulfate and sulfide. Therefore, on heating to 150–240 °C under anaerobic conditions polysulfide ions disproportionate reversibly [72, 80, 104], e.g.:

$$S_5^{2-} + 3OH^- \rightleftharpoons S_2O_3^{2-} + 3HS^- \tag{38}$$

This equilibrium can be approached from both sides. In other words, thiosulfate and sulfide react at 240 °C to a solution containing polysulfide.

Below 150 °C the forward reaction is very slow because of the high activation energy. The color of a polysulfide solution at a pH around 7 changes on heating from a deepening yellow through green to blue (formation of $S_3^{\cdot-}$, see the following section). At temperatures above 200 °C the color starts to fade with the solution becoming almost colorless at 240 °C due to the reaction at Eq. (38). On lowering the temperature all of the above changes can be observed in reverse order [72]. The reaction rates and activation energies of the forward and reverse reactions have been determined under various conditions [105, 106]. At temperatures above 250 °C thiosulfate also disproportionates or hydrolyzes according to the Eq. (39) [107]:

$$S_2O_3^{2-} + OH^- \rightarrow SO_4^{2-} + HS^- \tag{39}$$
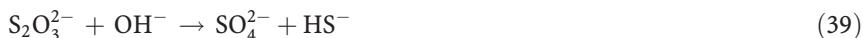
Aqueous polysulfide S_n^{2-} rapidly takes up molecular oxygen to produce thiosulfate and, for chain-lengths $n>2$, elemental sulfur [6, 108]:

$$S_n^{2-} + 3/2\,O_2 \rightarrow S_2O_3^{2-} + (n-2)/8\,S_8 \tag{40}$$

Since this is a spin-forbidden reaction it has been suspected that the reactive species is a radical anion like $S_2^{\cdot-}$ or $S_3^{\cdot-}$ produced by homolytic dissociation of an appropriate polysulfide dianion; see Eqs. (7) and (8) as well as the following section. During the course of the reaction at Eq. (40) the originally yellow solution becomes colorless.

Very often inorganic polysulfides have been used to synthesize organic polysulfanes by reaction with, for example, alkyl or aryl halides [109, 110], e.g.:

$$Na_2S_4 + 2RBr \rightarrow R_2S_4 + 2NaBr \tag{41}$$

Finally, it should be mentioned that polysulfides are formed on oxidation of hydrogen sulfide ions in water, either electrochemically [111] or by oxidation with molecular oxygen:

$$2HS^- - 2e \rightleftharpoons S_2^{2-} + 2H^+ \tag{42}$$

$$2HS^- + 1/2\,O_2 \rightarrow S_2^{2-} + H_2O \tag{43}$$

The latter reaction has been studied numerous times because of its relevance for the autoxidation of hydrogen sulfide in seawater and other aqueous systems [112, 113]. Since the polysulfide ions can be further oxidized to elemental sulfur which precipitates from the solution, these reactions are the basis for several industrially important desulfurization processes (e.g., the Stretford, Sulfolin, Lo-Cat, SulFerox, and Bio-SR processes) [114]:

$$2S_4^{2-} - 2e \rightarrow S_8^{2-} \tag{44}$$

$$S_8^{2-} - 2e \rightarrow S_8 \tag{45}$$

The latter reactions are catalyzed by a number of transition metal ions which can exist in several oxidation states in aqueous solution, e.g., $Fe^{2+/3+}$ [28]:

$$S_4^{2-} + Fe^{3+} \rightarrow S_4^{\cdot-} + Fe^{2+} \tag{46}$$

The tetrasulfide radical anion will dimerize to S_8^{2-} which equilibrates with longer chains from which eventually S_8 is formed by the back reaction shown in Eq. (22).

8
Polysulfide Radical Anions

8.1
General

The chemistry of polysulfide radical anions $S_n^{\cdot-}$ ($n = 2$–4) was reviewed by Chivers [12] in 1977, including a historical discussion describing the difficult route to the final identification of these ubiquitous and highly colored species. However, since that time considerable progress has been made. Only the species $S_2^{\cdot-}$, $S_3^{\cdot-}$, and $S_6^{\cdot-}$ have been experimentally characterized in detail while the existence of $S_4^{\cdot-}$ has only been suspected. The nature of the color centers in ultramarine-type solids ($S_2^{\cdot-}$, $S_3^{\cdot-}$) has been reviewed by Reinen and Lindner [115].

8.2
## The Radicals $S_2^{\cdot-}$ and $S_3^{\cdot-}$

The yellow disulfide radical anion and the brilliant blue trisulfide radical anion often occur together for what reason some authors of the older literature (prior to 1975) got mixed up with their identification. Today, both species are well known by their ESR, infrared, resonance Raman, UV-Vis, and photoelectron spectra, some of which have been recorded both in solutions and in solid matrices. In solution these radical species are formed by the homolytic dissociation of polysulfide dianions according to Eqs. (7) and (8). Since these dissociation reactions are of course endothermic the radical formation is promoted by heating as well as by dilution. Furthermore, solvents of lower polarity than that of water also favor the homolytic dissociation. However, in solutions at 20 °C the equilibria at Eqs. (7) and (8) are usually on the left side (excepting extremely dilute systems) and only the very high sensitivity of ESR, UV-Vis and resonance Raman spectroscopy made it possible to detect the radical anions in liquid and solid solutions; see above.

The addition of elemental sulfur to systems containing $S_2^{\cdot-}$ or $S_3^{\cdot-}$ results in the formation of more sulfur-rich species [89]:

$$S_2^{\cdot-} + 1/8\,S_8 \rightleftharpoons S_3^{\cdot-} \tag{47}$$

$$S_3^{\cdot-} + 1/8\,S_8 \rightleftharpoons S_4^{\cdot-} \tag{48}$$

Therefore, on addition of sulfur the color of a solution of Na_2S_4 in DMF changes from originally yellow-green ($S_2^{\cdot-}$) via blue ($S_3^{\cdot-}$) to red (maybe $S_4^{\cdot-}$) [89]. The existence of $S_4^{\cdot-}$ is, however, still disputed (see below).

Heating of certain alkali halides with elemental sulfur also produces colored materials containing the anions $S_2^{\cdot-}$ or $S_3^{\cdot-}$ which replace the corresponding halide ions. For example, NaCl and KI crystals when heated in the presence of sulfur vapor incorporate di- and trisulfide monoanions [116–119] which can be detected, inter alia, by resonance Raman spectroscopy [120, 121]:

$$1/4\,S_8 + I^- \rightleftharpoons S_2^{\cdot-} + 1/2\,I_2 \tag{49}$$

$$3/8\,S_8 + I^- \rightleftharpoons S_3^{\cdot-} + 1/2\,I_2 \tag{50}$$
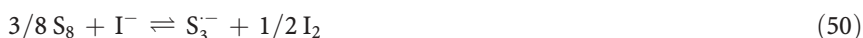
In a KI matrix the electronic absorption maximum of $S_2^{\cdot-}$ is observed at 400 nm, and the SS stretching vibration by a Raman line at 594 cm^{-1}. $S_3^{\cdot-}$ shows a Raman line at 546 cm^{-1} and an infrared absorption at 585 cm^{-1} which were assigned to the symmetric and antisymmetric stretching vibrations, respectively. The bromides and iodides of Na, K, and Rb have also been used to trap $S_2^{\cdot-}$ but the wavenumbers of the SS stretching vibration differ by as much as 18 cm^{-1} from the value in KI. The anion $S_3^{\cdot-}$ has been trapped in the chlorides, bromides and iodides of Na, K, and Rb [120]. While the disulfide monoanion usually occupies a single anion vacancy [116, 122], the trisulfide radical anion prefers a trivacancy (one cation and two halide anions missing) [119].

With the same technique $S_3^{\cdot-}$ has been detected in the mineral ultramarine (lapislazuli) [120]. Lapislazuli is one of the oldest precious stones which was already in use in the Sumerian civilization about 5500 years ago. The underlying pigment ultramarine contains the color centers $S_2^{\cdot-}$ and $S_3^{\cdot-}$ incorporated into the cages of the mineral sodalite $Na_8[Al_6Si_6O_{24}]Cl_2$, an aluminosilicate which belongs to the class of zeolites. The colorless sodalite turns more or less blue if the radical anions $S_2^{\cdot-}$ (yellow) and $S_3^{\cdot-}$ (blue) substitute the chloride anions (as well as a sodium cation) partly or completely, a typical composition being $Na_{6.9}[Al_{5.6}Si_{6.4}O_{24}]S_{2.0}$. Depending on the concentration ratio between the two radical anions the material will be either violet-blue (high ratio $S_3^{\cdot-}:S_2^{\cdot-}$), steel-blue or green (low ratio) [86, 115]. The concentration of $S_3^{\cdot-}$ in commercial blue ultramarine pigments has been determined by quantitative ESR spectrometry. Only one out of two β cages of the sodalite structure were occupied by $S_3^{\cdot-}$ ions (maximum of 54×10^{19} spins per gram). These ions are coordinated by four sodium cations. In addition, $S_2^{\cdot-}$ ions were detected [123].

In certain pink and red colored ultramarine varieties an additional red colored species absorbing at $\lambda_{max}=520$ nm has been detected but its identity has been disputed; it may be the radical anion $S_4^{\cdot-}$ or the neutral molecule S_4 [86, 124–126]. In fact, the *cis*-planar isomer of the latter absorbs at $\lambda_{max}=520$ nm in the gas phase and one of its fundamental vibrations (678 cm^{-1}) [127] matches exactly a resonance Raman line of the red chro-

mophore in pink ultramarine. Thus, the assignment to the C_{2v} isomer of S_4 seems justified.

Nowadays, ultramarine-type pigments are produced synthetically. Inside the zeolite structure the highly reactive sulfur radical anions are well protected which explains the stability of the blue color over thousands of years in air. However, the species responsible for the blue color should not be confused with the sulfur radical *cations* responsible for the blue color of sulfur solutions in fuming sulfuric acid (oleum) and similar oxidizing mixtures [128] or with the blue anion S_4N^- (λ_{max}=580 nm) which is also present in solutions of sulfur in liquid ammonia in addition to the radical anion $S_3^{\cdot-}$ [129]. S_4N^- is a planar chain-like anion of connectivity SSNSS [130].

The wavenumbers of the stretching vibrations of the radical anions $S_2^{\cdot-}$ and $S_3^{\cdot-}$ are higher than those of the corresponding dianions (see above) but lower than those of the corresponding neutral molecules. Since there is a systematic relationship between the bond distances and the bond stretching force constants as well as the wavenumbers of polysulfur compounds [131] it can be concluded that the bond lengths in the monoanions are between those of the dianions and the neutrals; the same holds for the bond strengths. In both anions the unpaired electron occupies an antibonding molecular orbital.

The blue color of $S_3^{\cdot-}$ has been observed in numerous experiments. For example, a brilliant blue color occurs if a potassium thiocyanate melt is heated to temperatures above 300 °C [132] or if eutectic melts of LiCl-KCl (containing some sulfide) are in contact with elemental sulfur [132, 133], if aqueous sodium tetrasulfide is heated to temperatures above 100 °C [134], if alkali polysulfides are dissolved in boiling ethanol or in polar aprotic solvents (see above), or if borate glasses are doped with elemental sulfur [132]. In most of these cases mixtures of much $S_3^{\cdot-}$ and little $S_2^{\cdot-}$ will have been present demonstrating the ubiquitous nature of these radicals [12].

The photoelectron spectrum of gaseous $S_2^{\cdot-}$ has been measured and analyzed; it provided the value of the ionization energy of this ion as 1.67 eV [135].

8.3
The Radical $S_4^{\cdot-}$

The red tetrasulfide radical anion $S_4^{\cdot-}$ has been proposed as a constituent of sulfur-doped alkali halides, of alkali polysulfide solutions in DMF [84, 86], HMPA [89] and acetone [136] and as a product of the electrochemical reduction of S_8 in DMSO or DMF [12]. However, in all these cases no convincing proof for the molecular composition of the species observed by either ESR, Raman, infrared or UV-Vis spectroscopy has been provided. The problem is that the red species is formed only in sulfur-rich solutions where long-chain polysulfide dianions are present also and these are of orange to red color, too (for a description of this dilemma, see [89]). Furthermore, the presence of the orange radical anion $S_6^{\cdot-}$ (see below) cannot be excluded in such systems.

More recently, $S_4^{\cdot-}$ may have been identified by ESR spectroscopy of solutions of Li_2S_n ($n>6$) in DMF at 303 K. The lithium polysulfide was prepared from the elements in liquid ammonia. These polysulfide solutions also contain the trisulfide radical anion ($g=2.0290$) but at high sulfur contents a second radical at $g=2.031$ (Lorentzian lineshape) was formed which was assumed to be $S_4^{\cdot-}$ generated by dissociation of octasulfide dianions; see Eq. (32) [137].

The more reasonable formation of the tetrasulfide radical by the reaction shown in Eq. (51)

$$S_7^{2-} \rightleftharpoons S_3^{\cdot-} + S_4^{\cdot-} \tag{51}$$

was not considered by the authors despite the presence of both radicals in the same solution. Most authors discussing the solutions of polysulfide dianions in aprotic solvents assumed the presence of tri-, tetra-, hexa-, and octasulfide ions but usually ignored the equally likely existence of penta- and heptasulfide anions in these systems; see Eqs. (5)–(8) and (51).

8.4
The Radical $S_6^{\cdot-}$

This species has been isolated as the tetraphenylphosphonium salt $(Ph_4P)S_6$ which is produced in the following complex reaction at 20 °C [138]:

$$2Ph_4PN_3 + 20Me_3SiN_3 + 22H_2S \rightarrow 2Ph_4PS_6 + 10(Me_3Si)_2S + 11NH_4N_3 + 11N_2 \tag{52}$$
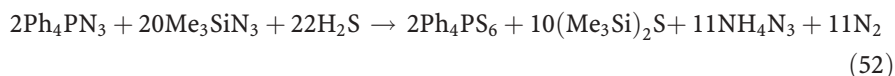
Ph_4PS_6 forms orange needle-like air-sensitive crystals which were characterized by X-ray diffraction. The anions are cyclic and adopt a chair-conformation of C_{2h} symmetry. These rings can be considered to be composed of two S_3 units connected by two extremely long bonds of 263 pm. The ESR spectrum of Ph_4PS_6 at 115 K (g: 2.056/2.036/2.003) is different from those of $S_2^{\cdot-}$ and $S_3^{\cdot-}$ and it is possible that the $S_6^{\cdot-}$ radical is identical to the species which many authors have taken for $S_4^{\cdot-}$ (see above).

8.5
Calculated Structures

The electronic structure and the UV-Vis spectrum of $S_3^{\cdot-}$ have been studied by high-level ab initio MO calculations [139].

The molecular structures of the isolated polysulfide monoanions $S_n^{\cdot-}$ with $n=2$–9 have been studied by density functional calculations and those of the smaller ions also by ab initio MO calculations. Compared to the neutral S_n molecules the extra electron occupies an antibonding orbital resulting in longer SS bonds. The species $S_3^{\cdot-}$ is bent and of C_{2v} symmetry ($\alpha=115°$) [140, 141]. $S_4^{\cdot-}$ was calculated to be a planar ion of C_{2v} symmetry (similar to the neutral molecule S_4) but the planar C_{2h} structure is only slightly less stable [140, 141]. The most stable isomer of $S_5^{\cdot-}$ is a chain of C_s symmetry sim-

ilar to the anion structure in Na_2S_5 (torsion angle motif +–a). However, $S_5^{\cdot-}$ chains of C_1 and C_2 symmetry are by less than 10 kJ mol^{-1} less stable than the global minimum [140, 141]. In the case of $S_6^{\cdot-}$ a chain-like isomer of C_2 symmetry is the global minimum but a ring of the same symmetry (chair conformation) is by only 2 kJ mol^{-1} less stable [138, 141]. The $S_7^{\cdot-}$ anion also exists as many local minima on the potential energy hypersurface. Most stable is a chair-like ring as in the case of neutral S_7 molecules but with one extremely long bond of 289 pm. The global minimum isomer of $S_8^{\cdot-}$ has a geometry which is a distortion of the crown-shaped S_8 molecule. On addition of the extra electron two bonds on opposite sides of the ring increase in length resulting in a lowering of the molecular symmetry from D_{4d} to D_2. The anion $S_9^{\cdot-}$ also forms chain-like and cyclic isomers; most stable is a chain of C_1 symmetry [141].

By mass spectrometry sulfur radical anions with up to 25 atoms have been detected and there is photoelectron spectroscopic evidence for chain-like as well as cyclic isomers of $S_6^{\cdot-}$ and $S_7^{\cdot-}$ [141].

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