

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

Optical Spectra of Highly Alkaline Sulfide Solutions and the Second Dissociation Constant of Hydrogen Sulfide

By W. GIGGENBACH

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A newly observed band in the uv absorption spectra of highly alkaline sulfide solutions is attributed to the formation of the S^{2-} ion. This band with a maximum at 40.6 kK and a molar absorptivity of 9100 was used to determine upper limits for the second dissociation constant of hydrogen sulfide for temperatures up to 250°. In conjunction with previously reported values for the H^- acidity function, a value of 17.1 ± 0.2 for pK_{a_2} at room temperature was derived.

Introduction

The present experiments began as an attempt to determine the effect of temperature on K_{a_2} , the second dissociation constant of H_2S , by utilizing a method outlined by Ellis and Milestone.¹ By taking advantage of the strong absorption band of the SH^- ion at 43.6 kK they had obtained values for K_{a_2} up to 90°. With preliminary spectroscopic results, however, employing an improved technique to exclude oxygen from the solutions, it was impossible to reproduce their findings. The results given below show that the value for pK_{a_2} is much larger than reported previously. In the light of the present experiments, this discrepancy has to be attributed to the easy oxidation of alkaline sulfide solutions due to the incomplete exclusion of oxygen from the experimental solutions. In previous investigations the loss of SH^- by oxidation during manipulation has been confused with formation of the S^{2-} ion at an OH^- concentration up to 1 *N*, leading to an apparent pK_{a_2} value of about 14 at room temperature.

Blandamer, *et al.*,² ascribed the appearance of an absorption band at 27.5 kK in strongly alkaline sulfide solutions to the formation of S^{2-} ions. No such band, however, could be detected in solutions prepared under strict exclusion of oxygen, whereas a similar absorption band appears regularly in solutions prepared from yellowish, slightly oxidized $Na_2S \cdot 9H_2O$ or in alkaline sulfide solutions in contact with air. On addition of small portions of sulfur this band increases in proportion to the amount of zerovalent sulfur present. The absorbance at 27.5 kK in strongly alkaline sulfide solutions, therefore, is attributed to the presence of polysulfides.

During the present work an absorption band at about 40.0 kK was detected in highly alkaline sulfide solutions and ascribed to the S^{2-} ion. This band, probably representing the first direct evidence of the existence of the S^{2-} ion in aqueous solutions, allowed the determination of a series of experimental dissociation constants for highly concentrated hydroxide solutions which were used to estimate upper limits for the thermodynamic dissociation constant K_{a_2} of H_2S from room temperature up to 250°.

Experimental Section

Materials.—Water was purified by double distillation from alkaline permanganate and Wood's Metal³ under nitrogen.

(1) A. J. Ellis and N. B. Milestone, *Geochim. Cosmochim. Acta*, **31**, 615 (1967).

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

(3) W. A. Patrick and H. B. Wagner, *Anal. Chem.*, **21**, 752 (1949).

Solutions were prepared by dissolving reagent grade $LiCl$, $NaCl$, KCl , $CaCl_2$, $NaBr$, $LiOH$, $NaOH$, and KOH and $Na_2S \cdot 9H_2O$, recrystallized in an N_2 atmosphere, in water, or by bubbling H_2S from a tank in sufficiently alkaline solutions. All solutions were prepared and handled under purified nitrogen mainly by use of Schlenk-tube techniques.

Cl^- and Br^- concentrations were determined in neutral solutions by the Mohr method, OH^- concentrations with HCl and phenolphthalein as indicators, and sulfide concentrations with iodine-thiosulfate in acidic solution.

Spectra.—The spectrophotometer used was the Zeiss PM QII with the monochromator M4 QIII. Spectra at room temperature were determined by use of commercial 0.2-cm stoppered quartz cells and a thin layer cell with a path length of 2.0×10^{-4} cm. This cell consisted of two quartz disks of 1.9-cm diameter and 0.6-cm thickness. One of the disks was provided with a shallow, circular depression obtained by covering the disk partly with paraffin and etching with half-concentrated hydrofluoric acid. After putting 1 drop of the solution to be investigated onto the depression, it was covered with the other plane disk. The combined disks were placed in a thermostated cell holder and pressed together by means of a screw nipple. The path length of the cell was determined by comparison of the absorbances of a series of solutions of $KMnO_4$ and KI obtained in the thin layer cell with those of the same solutions diluted 1000 times in 0.2-cm commercial cells. The measurements were reproducible within $\pm 2\%$; the path length of the cell used in the present investigation was thus found to be $(2.02 \pm 0.04) \times 10^{-4}$ cm.

Spectra at elevated temperatures were determined by use of a cell with a path length of 0.14 cm as previously described.⁴ All spectra were corrected for the background absorption of the cell and the solvent by subtracting the absorption of the cells filled with water or one of the sulfide-free solutions at the respective temperatures.

In the case of the high-temperature spectra, all solutions were remeasured at room temperature after each heating cycle to check for irreversible changes within the solutions due to oxidation by air or reaction with the cell materials. For all measurements reported here, the spectra before and after heating were identical within experimental error.

Because of the strong overlapping absorption of the OH^- ion in highly concentrated sodium hydroxide solutions, accurate determinations of the absorbances of the sulfide species by use of the 0.2-cm cells and the 0.14 cm high temperature block were restricted to intermediate sodium hydroxide concentrations. Nevertheless, values of pK_{a_2}' (K_{a_2}' is the experimental equilibrium constant) obtained with these cells were within ± 0.2 unit of those of the thin layer cell employing solutions about 1000 times more concentrated in sulfide.

Qualitative thin layer absorption spectra of $Na_2S \cdot 9H_2O$ and $Na_2S \cdot 5H_2O$ were obtained by placing 1 drop of the compounds molten under a protective layer of paraffin between two plain quartz plates and allowing it to crystallize. In the case of $Na_2S \cdot 9H_2O$ the plates had to be cooled to prevent the formation of $Na_2S \cdot 5H_2O$ crystals from the melt at temperatures above 50°. The compounds were prepared as described by Bedlivy and Preisinger.⁵

(4) W. Giggenbach, *J. Sci. Instrum.*, in press.

(5) D. Bedlivy and A. Preisinger, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **121**, 131 (1965).

Results and Discussion

The strong band at 43.6 kK in the uv absorption spectrum of slightly alkaline aqueous sulfide solutions has been ascribed to the SH^- ion. On increasing the pH of the solution by the addition of alkali hydroxide this band moves toward higher wave numbers without any significant change in either the shape or the molar absorptivity of the absorption maximum (Figure 1).

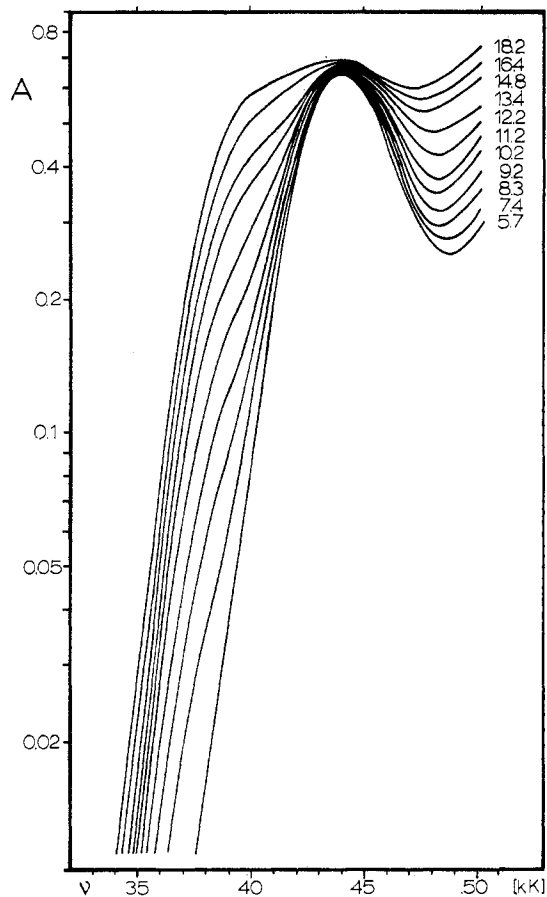


Figure 1.—Spectra of 0.434 *M* solutions of H_2S as a function of the sodium hydroxide concentration in moles per liter at 24° ($d = 2.0 \times 10^{-4}$ cm).

This gradual blue shift with increasing solute concentration is typical⁶ for charge transfer to solvent bands (ctts). It has been demonstrated for the iodide ion⁷ for a wide variety of solutes and has been attributed to a gradual change in the structure of the solvent depending on the structure-making and -breaking properties of the cosolute.⁸ In the case of the SH^- ion addition of LiCl, NaCl, or CaCl_2 up to saturation causes shifts which are directly proportional to the chloride concentration with an increase in ν_{max} of 175 $\text{cm}^{-1}/\text{mol}$ of Cl^- added and almost independent of the nature of the cation (Figure 2). The increase of ν_{max} for SH^- with 95 $\text{cm}^{-1}/\text{mol}$ of OH^- is approximately half that for Cl^- .

In addition to the normally observed gradual change in the position of the ctts bands of solutions of a series of anions when the cosolute concentration is increased, another pattern of behavior can be distinguished.⁸ In this second case a decrease of the absorption typical for

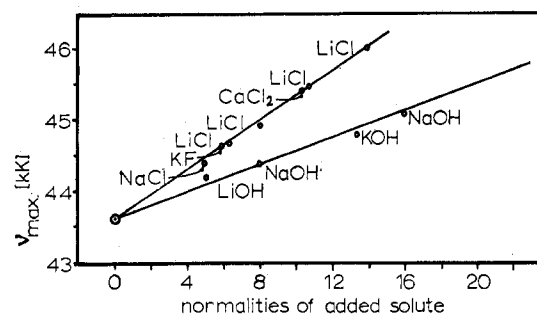


Figure 2.—Position of the absorption maximum ν_{max} for the SH^- ion as a function of the cosolute concentration. The value for KF was taken from ref 2.

the ion in the pure solvent, accompanied by an increase in the intensity of a new band, is ascribed to the possibility of the ion being involved in specific complex formation with a solute molecule or ion or the formation of an entirely new species. For the SH^- ion in strongly alkaline solutions both patterns are observed, as a new band at about 40.0 kK emerges as a shoulder on the SH^- band at concentrations of OH^- above 5 *M*. The appearance of this new band in strongly alkaline solutions and its reversible dependence on the alkali hydroxide concentration strongly suggested the formation of the S^{2-} ion, but possibilities of the band being due to the formation of complexes or ion pairs involving the SH^- or S^{2-} ion have also to be considered.

It was assumed that any ion pair formed in highly concentrated solutions was likely to be preserved in the crystalline state. Therefore, in an attempt to determine the nature of the sulfur species present in compounds crystallizing from alkaline sulfide solutions, thin layer absorption spectra of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$

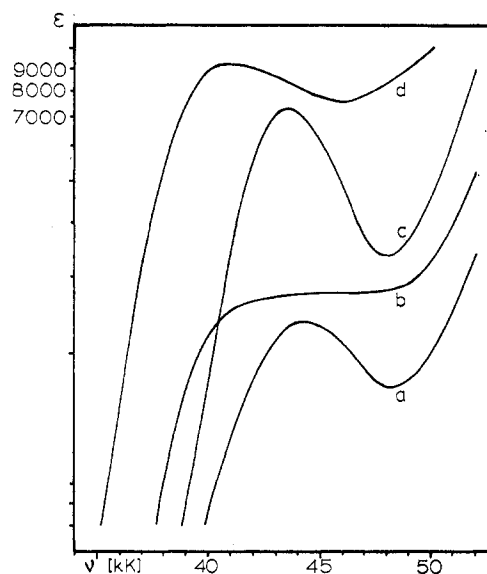


Figure 3.—(a) Thin layer absorption spectrum of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. (b) Thin layer absorption spectrum of $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$. (c) Absorption spectrum of the SH^- ion in 0.025 *M* NaOH solution. (d) The calculated spectrum of the S^{2-} ion in 18 *M* NaOH solution. All spectra measured at 24°. Values for ϵ only refer to curves c and d.

were measured. As seen in Figure 3 the spectrum of the nonahydrate shows one strong band at a wave number close to that for SH^- in a 5 *M* hydroxide solu-

(6) M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, **54**, 338 (1958).

(7) D. Meyerstein and A. Treinin, *J. Phys. Chem.*, **66**, 446 (1962).

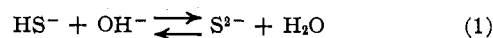
(8) M. J. Blandamer and M. F. Fox, *Chem. Rev.*, **70**, 59 (1970).

tion at 44.2 kK. This similarity of the absorption spectra was taken to indicate either that a complex present in $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ has a spectrum similar to that of the SH^- ion or, more likely, that $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ contains the SH^- ion in an environment resembling closely that in 5 *M* NaOH solution. The crystal structure of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ as recently determined⁵ with 12 oxygen atoms surrounding the sulfur atom at a distance from 3.24 to 3.49 Å does not preclude the formulation of this compound as $\text{NaSH} \cdot \text{NaOH} \cdot 8\text{H}_2\text{O}$ as suggested by its absorption spectrum and does not indicate any ion-pair formation. On the other hand, the thin layer absorption spectrum of $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ (Figure 3b) consists of an ill-defined broad band with a maximum around 41.0 kK. The crystal structure of this compound⁵ shows a sulfur atom surrounded by five oxygen atoms with one sodium atom incorporated in the coordination octahedron and in direct contact with the sulfur atom. The similarity of the spectra of the pentahydrate and of strongly alkaline sulfide solutions, therefore, would suggest the formation of a $\text{Na}^+, \text{S}^{2-}$ contact ion pair in sulfide solutions containing sodium hydroxide in concentrations above 5 *M*, the concentration at which the pentahydrate is formed. The possibility of the formation of an ion pair involving SH^- can be excluded because there is no indication of the presence of such a species in highly concentrated NaCl, LiCl, and CaCl_2 solutions. If the "free" sulfide ion or an ion pair involving S^{2-} is formed, the stabilization of such a species must be attributed to the influence of the adjacent solvent region, as a doubly negative atomic ion, like S^{2-} , with its negative ionization potential⁹ is physically unstable and could not exist in the gaseous phase.¹⁰

Because of the limited solubility of any alkali salt in solutions of sufficiently high alkalinity, the cation concentration can only be varied within a small range. However, no significant change in the absorption spectra due to the addition of LiCl, NaCl, KCl, or NaBr could be observed. On addition of NaBr to a 9.5 *M* NaOH solution (thus increasing the Na^+ concentration to 12.1 *M*), even a slight decrease in A_{40} was observed instead of an increase which would be expected if the absorption band at 40.0 kK was largely due to ion-pair formation. As in the case of the HS^- ion, changes in the cosolute concentrations other than hydroxide apparently do not lead to drastic changes in the absorption or in the concentration of the species causing the absorptions at 43.6 and 40.0 kK, respectively. It was, therefore, concluded that the absorption at 40.0 kK was due to a S^{2-} ion surrounded by water and cosolvent molecules, without the formation of a specific complex. Any changes in the position of the cts absorption of S^{2-} due to variations in the cosolute concentration probably remained undetected because of the closeness of the SH^- and S^{2-} bands.

Analysis of Data.—As Figure 1 shows, there is no significant difference in the SH^- absorption in 5 *M* NaOH compared with that for a less alkaline solution. This already shows that $\text{p}K_{a_2}$ of H_2S has to be higher by at least 2 units than the previously reported value of 14 which would require about 87% of the total sulfur to be present as S^{2-} at this OH^- concentration. It is not possible, even in saturated NaOH solutions, to force

the equilibrium



so far to the right that virtually all of the sulfur is present in the form of S^{2-} ions. Consequently, the molar absorptivity ϵ of the S^{2-} species cannot be calculated directly from the relationship

$$\epsilon_{\text{S}^{2-}} = A_{40}/c_{\text{S}^{2-}}d \quad (2)$$

A_{40} is the absorbance at 40.0 kK, c the S^{2-} concentration in moles per liter, and d the path length in centimeters. Therefore, an extrapolation method as devised by Stearns and Wheland¹¹ for weak organic acids was used to estimate $\epsilon_{\text{S}^{2-}}$ from the data available. This method assumes that at high, experimentally unobtainable OH^- concentrations all the sulfur is present as S^{2-} . The application of this method is complicated by the facts that the solvent (water) concentration and activity are not constant in the range of OH^- concentrations considered, that there is presently no way of estimating the ratio of activity coefficients for $[\text{S}^{2-}]/[\text{SH}^-][\text{OH}^-]$ in solutions of extremely high ionic strength, and that the absorption of the SH^- ion extending to 40.0 kK overlaps the S^{2-} absorption. Therefore, the following modified procedure was adopted.

The equilibrium expression for reaction 1 is

$$K_e = \frac{[\text{S}^{2-}]A_w}{[\text{SH}^-][\text{OH}^-]} \frac{y_{\text{S}^{2-}}}{y_{\text{SH}^-}y_{\text{OH}^-}} = K_e' Y_{\pm} \quad (3)$$

The first term represents a modified experimental concentration quotient, and the second term, the activity coefficient ratio of the ionic reactants. As the ratio of the ionic activity coefficients Y_{\pm} for the divalent S^{2-} ion, $y_{\text{S}^{2-}}/y_{\text{SH}^-}y_{\text{OH}^-}$, can be expected to be less sensitive to changes in the ionic strength of the solution, the experimental concentration quotient $[\text{S}^{2-}][\text{H}_2\text{O}]/[\text{SH}^-][\text{OH}^-]$ was modified by including the activity of water A_w as represented by $[\text{H}_2\text{O}]y_{\text{H}_2\text{O}}$ with $[\text{H}_2\text{O}]$ being the analytical concentration of water in moles per liter and $y_{\text{H}_2\text{O}}$ the activity coefficient of water as calculated from the osmotic coefficients given by Robinson and Stokes¹² for concentrated NaOH solutions. From eq 3 and 4 as given by Stearns and Wheland, eq 5 is de-

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon} + \frac{1}{\epsilon K_e' [\text{OH}^-]} \quad (4)$$

$$\frac{c_T d}{A_{40}} = \frac{1}{\epsilon_{\text{S}^{2-}}} + \frac{1}{\epsilon_{\text{S}^{2-}} K_e' [\text{OH}^-]} A_w \quad (5)$$

rived, where c_T is the total sulfur concentration in moles per liter. This equation represents a relationship, linear for constant K_e' , between $1/\epsilon_{40}'$ and $A_w/[\text{OH}^-]$, with ϵ_{40}' the apparent molar absorptivity for incomplete dissociation of SH^- . Large variations in K_e' with $A_w/[\text{OH}^-]$ have to be expected, but if K_e' approaches some constant value at high OH^- concentrations (see below), eq 5 is still applicable. Then the intercept of a line obtained by plotting $c_T d/A_{40} = 1/\epsilon_{40}'$ against $A_w/[\text{OH}^-]$ is equal to $1/\epsilon_{40}$. In order to eliminate the effect of the SH^- absorption at 40 kK, an iterative procedure was used. With a preliminary value for ϵ_{40} obtained by use of the uncorrected absorbances at

(11) R. S. Stearns and G. W. Wheland, *J. Amer. Chem. Soc.*, **69**, 2025 (1947).

(12) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(9) H. O. Pritchard, *Chem. Rev.*, **52**, 529 (1953).

(10) H. S. W. Massey, *Discuss. Faraday Soc.*, **12**, 24 (1952).

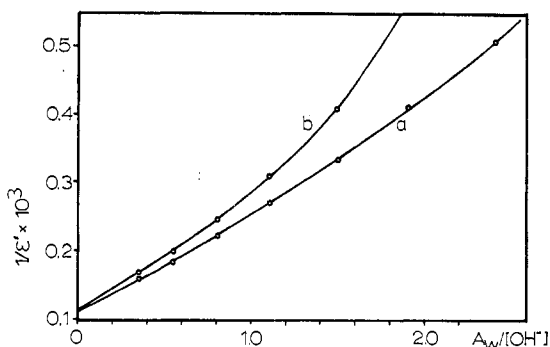


Figure 4.—Evaluation of $\epsilon_{S^{2-}}$ by use of (a) the uncorrected values and (b) the corrected values for A_{40} .

40 kK (Figure 4a), the concentrations of S^{2-} and thus that of SH^- together with its absorbance at 40 kK were calculated. With the corrected absorption at 40 kK a new value for ϵ_{40} was obtained. After two iterations a constant value of $\epsilon_{S^{2-}} = 8900$ was obtained. In correcting the absorption at 40 kK for the SH^- absorption, the shift of the SH^- band with increasing $[OH^-]$ was taken into account. The curvature of the lines in Figure 4 is due to the change of K_e' with $A_w/[OH^-]$.

With the value of ϵ_{40} the complete absorption spectrum for the species formed in highly alkaline sulfide solutions can be constructed. As shown in Figure 3d it consists of a rather broad band with a maximum at 40.6 kK, a molar absorptivity of 9100, and an oscillator strength of $f = (4.32 \times 10^{-9}) \epsilon_{\max} \Delta\nu_{1/2} = 0.23$. This f value is typical for ctt transitions as reviewed by Blandamer and Fox.⁸ The difference between this value and that for the SH^- ion of 0.16 probably reflects the difference in size between the two ions, as a rough correlation exists between oscillator strength and radius for a series of simple ions.⁴

Determination of K_{a_2} .—As shown in Figure 1, the lowest hydroxide concentration at which the absorbance of the S^{2-} ion could be determined with sufficient reliability is about 8.0 M. This concentration is by far too high to permit any evaluation of Y_{\pm} , the ratio of activity coefficients $\gamma_{S^{2-}}/\gamma_{SH^-}\gamma_{OH^-}$. In order to obtain some estimate or an upper limit for the thermodynamic dissociation constant K_{a_2} a correlation was sought permitting the extrapolation of the experimental values measured at high ionic strength to low ionic strength. Figure 5 where K_e' is plotted against $[OH^-]$ shows that K_e' appears to approach some constant value K_e'' at high OH^- concentrations. On the other hand, at low OH^- concentrations K_e' is expected to approach K_e , the thermodynamic equilibrium constant, with Y_{\pm} becoming unity. A relationship describing the smooth transition of K_e' between the two extreme situations as represented by K_e and K_e'' was obtained by assuming K_e and K_e'' to contribute to K_e' in varying ratios depending on the hydroxide concentration as given by $[OH^-]/A_w$. These relative contributions to K_e' from K_e'' were taken to be directly and those from K_e to be inversely proportional to $([OH^-]/A_w)/([OH^-]_{1/2}/A_w)_{1/2}$, with $[OH^-]_{1/2}$ and $A_w)_{1/2}$ representing the alkalinity and water activity at which these relative contributions from K_e and K_e'' to K_e' are equal. Putting $([OH^-]/A_w)/([OH^-]_{1/2}/A_w)_{1/2} = b$ the following relationship is obtained

$$K_e'(1 + b^2) = K_e''b^2 + K_e \quad (6)$$

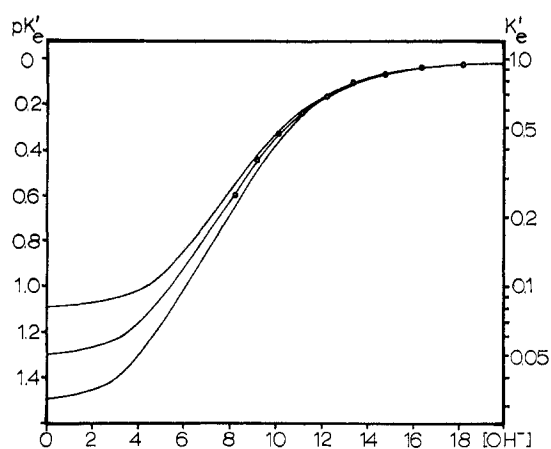


Figure 5.—The experimental equilibrium constant K_e' as a function of the sodium hydroxide concentration in moles per liter. Circles represent experimental values, and the three solid lines represent values calculated by use of eq 6 and values for pK_e of 1.1, 1.3, and 1.5.

To obtain K_e a preliminary value for K_e'' was taken from Figure 5 together with preliminary values for $[OH^-]_{1/2}$ and $A_w)_{1/2}$ at the inflection point of the S-shaped "titration" curve. The value of K_e thus obtained was used to recompute K_e'' and $[OH^-]_{1/2}/A_w)_{1/2}$ and the procedure was repeated until a consistent set of figures with $K_e'' = 0.97 \pm 0.02$ and $[OH^-]_{1/2}/A_w)_{1/2} = 0.45$ resulted. The solid lines in Figure 6 are

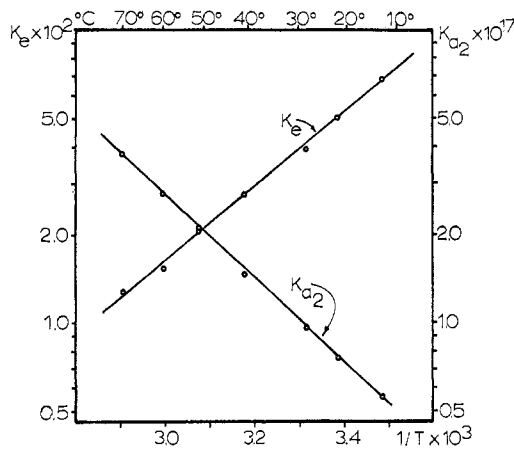
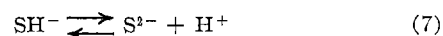


Figure 6.—Values for K_e and K_{a_2} as a function of $1/T$.

drawn by use of these values and eq 6 and values for pK_e of 1.1, 1.3, and 1.5 corresponding to values of K_e of about 0.08, 0.05, and 0.03.

The hydrolysis constant K_h is equal to c_{H_2O}/K_e and related to the conventional dissociation constant K_{a_2} for the reaction



by

$$K_{a_2} = K_w/K_h = K_w K_e/c_{H_2O} \quad (8)$$

where K_w is the ion product of water. With a value of 0.96×10^{-14} for K_w at 24°, K_{a_2} is calculated to 8.7×10^{-18} or $pK_{a_2} = 17.1 \pm 0.2$ at 24°. Because of the uncertainty in the physical significance of eq 6 the value of 17.1 for pK_{a_2} can probably only be considered a lower limit for pK_{a_2} as the possibility that pK_{a_2} is

larger cannot be ruled out. This value, however, is already much higher than most of those previously reported (around 14, with the exception of a value for pK_{a2} of 15.3 at 25° determined by Dickson¹³ from cinnabar solubility data).

Temperature Dependence of K_{a2} .—As above, evaluation of data obtained for sulfide solutions at higher temperatures suffers from the introduction of assumptions required to overcome the lack of activity data at high ionic strengths. Nevertheless, the experimental results may indicate the limits within which the thermodynamic values of K_{a2} may be expected.

The temperature dependence of K_{a2} was investigated in two ways. In order to obtain some estimate of K_{a2} at temperatures up to 270° measurements on a series of SH^- solutions of varying OH^- concentrations were carried out. These measurements, however, were limited to solutions up to 1 M in $[\text{OH}^-]$ because of the rapid attack on the window material (alumina) by more highly concentrated solutions. Also, at higher NaOH concentrations the broadening of the OH^- absorption begins to cover the SH^- absorption at elevated temperatures. Assuming that any changes in the SH^- or S^{2-} concentrations exceeding 10% in 1 M OH^- solutions would not remain undetected, the experimental results indicate that pK_{a2} of H_2S is, at all temperatures investigated, higher by at least 1.2 units than pK_w at the corresponding temperature. That means that pK_{a2} is >13.5 at 100° and >12.5 at 200°. No changes in the absorption spectra attributable to the formation of S^{2-} ions were observed at temperatures up to 270° and OH^- concentrations up to 1 M.

In another series of experiments highly concentrated NaOH solutions were investigated at temperatures between 10 and 75°. Again the measurements were limited to intermediate concentrations as in solutions containing more than 15 M OH^- the overlapping uv absorption of the OH^- ion made the accurate determination of $A_{\text{S}^{2-}}$ and A_{SH^-} impossible. At low OH^- concentrations the small amounts of S^{2-} formed led to great errors in estimating its concentration. Therefore, measurements were restricted to NaOH concentrations between 12 and 14 M.

Figure 6 shows the values of K_e measured in a 14 M NaOH solution to decrease with increasing temperature. The thermodynamic data corresponding to this decrease with ΔH_e of about -5.9 kcal/mol and a change in entropy ΔS_e of about -21 cal/mol deg are in agreement with the exothermic nature expected for the "neutralization" reaction as described by eq 1, whereas the negative entropy change may reflect an increased degree of order around the sulfide ion. The thermodynamic data were calculated by assuming the ratio of activity coefficients $Y_{\pm} = K_e'/K_e$ as determined at 24° to remain unchanged for temperatures up to 75°. By use of eq 8 the second dissociation constant for H_2S at various temperatures may be calculated. It is seen to increase from about 0.6×10^{-17} at 14° to 4.0×10^{-17} at 70° corresponding to ΔH_d of $+6.5$ kcal/mol and a rather high negative entropy change of -55 cal/mol deg. These values are comparable to those¹⁴ for similar equilibria, as, e.g., the bicarbonate-carbonate equilibrium ($\Delta H^\circ = 3.6$ kcal/mol, $\Delta S^\circ = -35.16$ cal/

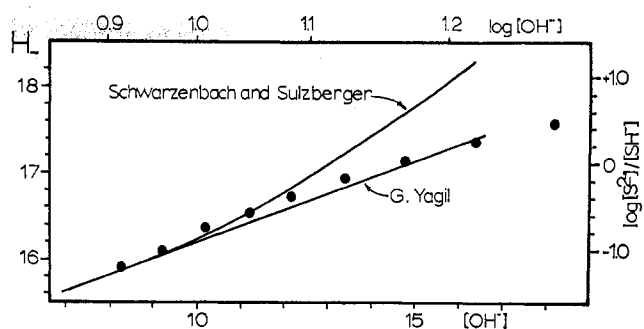


Figure 7.—Values for the H_- acidity function as a function of $[\text{OH}^-]$. Circles represent H_- values calculated from the experimental ionization ratios $[\text{S}^{2-}]/[\text{SH}^-]$ by assuming $pK_{a2} = 17.1$.

deg mol) or the equilibrium $\text{H}_2\text{As}(\text{OH})_8^- \rightleftharpoons \text{H}^+ + \text{HAs}(\text{OH})_8^{2-}$ ($\Delta H^\circ = 5.12$ kcal/mol, $\Delta S^\circ = -66.9$ cal/deg mol).

Correlation between the Measured Ionization Ratios $[\text{S}^{2-}]/[\text{SH}^-]$ and the H_- Acidity Function.—The H_- acidity function is a measure of the proton-abstracting power of strongly alkaline solutions. H_- is defined¹⁵ by

$$H_- = pK_a + \log \left\{ \frac{[\text{B}^-]}{[\text{BH}]} \right\} \quad (9)$$

with K_a representing the conventional acid dissociation constant of BH . Equation 9 assumes the ratio of activity coefficients $\gamma_{\text{B}^-}/\gamma_{\text{BH}}$ for the acid BH and the conjugate base B^- to be unity.¹⁶ Only very few measurements of H_- values for aqueous alkali hydroxide solutions have been made for OH^- concentrations exceeding 8 M. Schwarzenbach and Sulzberger¹⁷ first reported H_- scales for concentrated NaOH and KOH solutions determined by use of indigo derivatives as indicators dissolved in an organic solvent immiscible with the alkaline aqueous phase. Another set of H_- values is reported by Yagil,¹⁸ who used derivatives of indole soluble in the aqueous phase as indicators. As shown in Figure 7, up to 10 M NaOH, both scales agree well with one another but start to deviate at higher NaOH concentrations, with the values by Yagil being considerably lower and almost linearly proportional to $[\text{OH}^-]$.

From the definition of H_- (eq 9) it can be seen that $pK_a = H_-$ for $\text{B}^- = \text{BH}$. In the system S^{2-} – SH^- this point is reached in a 15 M NaOH solution. If it is assumed that the acidity function concept is also valid for the S^{2-} – SH^- equilibrium, pK_{a2} values of 17.1 and 17.7 are derived depending on the H_- scale used (Figure 7). It should be pointed out, however, that the H_- scale presented by Schwarzenbach and Sulzberger may differ largely from the aqueous scale as the water activities and the ratios of the activity coefficients for B^- – BH in the immiscible organic phase are likely to be very different from those in the aqueous phase. Therefore, the first value (based on the H_- values of Yagil) is preferred. It coincides exactly with the value obtained for pK_{a2} obtained by the extrapolation of K_e' to low NaOH concentrations by use of eq 6.

(15) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932).

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By accepting a value of 17.1 for pK_{a_2} of H_2S the ionization ratio $[S^{2-}]/[SH^-]$ as determined in the present work may be used to derive additional values for H_- . As shown in Figure 7 they are within ± 0.1 unit of those given by Yagil and thus support the approximately linear dependence of H_- on $[OH^-]$ for $[OH^-] > 8 M$. This result is surprising considering the large difference in the "indicators" used and may only be a chance coincidence. However, it could sug-

gest that the H_- acidity function, after all,¹⁹ is largely independent of the class of indicators used and thus is generally applicable to highly concentrated alkali hydroxide solutions.

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CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, SCHOOL OF CHEMICAL SCIENCES, AND MATERIALS RESEARCH LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

The Effect of Pressure on the Spin State of Iron(II) in Manganese(IV) Sulfide^{1a}

By C. B. BARGERON, M. AVINOR,^{1b} AND H. G. DRICKAMER*

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Mössbauer resonance studies as a function of pressure on iron as a dilute substitutional impurity in MnS_2 have revealed a high-spin to low-spin transition which initiates near 40 kbars and is complete by about 120 kbars. MnS_2 has the cubic structure of pyrites (FeS_2). The iron in FeS_2 is low spin at all pressures. Since FeS_2 has a smaller lattice parameter than MnS_2 , the difference in spin states at 1 atm and the transition from iron in MnS_2 are qualitatively consistent with theory.

The effect of pressure to 165 kbars has been measured on the spin state of ^{57}Fe , presumably as a substitutional impurity in MnS_2 , using Mössbauer resonance. The high-pressure Mössbauer apparatus has been described elsewhere.² The pressures are accurate at least to $\pm 10\%$. It took 6–36 hr to accumulate sufficient counts at each pressure. Consecutive spectra taken at a given pressure showed no differences, so that no time-dependent phenomenon is involved. The MnS_2 was prepared by a hydrothermal method.³ The iron, enriched to 90% in ^{57}Fe , was incorporated by adding the appropriate amount of ^{57}Fe solution to the manganese sulfate solution before precipitation by the polysulfide. MnS_2 has the pyrite structure with a lattice constant $a = 6.102 \text{ \AA}$.⁴ It becomes antiferromagnetic at $47.93^\circ K$.⁵ Most of the data were obtained on a sample containing 2% ^{57}Fe . (Three different high-pressure runs were made at this concentration.) One high-pressure run was also made on a sample containing 0.5% ^{57}Fe , and an atmospheric pressure spectrum was obtained on a sample containing traces of ^{57}Co . The atmospheric pressure values of the isomer shift and quadrupole splitting appear in Table I. At 1 atm the samples were predominantly high spin. The samples containing 2% ^{57}Fe exhibited about 10% low spin, as indicated by the relative areas under the curves obtained by fitting the data with Lorentzian peaks. The samples with lower concentrations of iron showed slightly less low spin (5–6% for the sample containing

traces of ^{57}Co). It should be noted that the isomer shift for the high-spin iron is somewhat lower than that for the normal ferrous iron ($\sim 1.3 \text{ mm sec}$) but comparable to that for ferrous iron in FeS_2 and similar compounds.

The primary effect of pressure was the conversion of $Fe(II)$ from the high-spin to the low-spin state. A change in the amount of high spin first becomes measurable at about 40 kbars, and by 120–130 kbars the conversion is complete. Typical spectra appear in Figure 1. Figure 2 shows conversion as a function of pressure. While it was more difficult to get a quantitative fit for the 0.5% sample under pressure, the pressure-induced conversion clearly initiates near 35–40 kbars and was again complete at 120–130 kbars; *i.e.*, the behavior under pressure was essentially identical with that of the 2% sample. The spin conversion was quite reversible with only a modest hysteresis, almost certainly due to residual strain in the sample. There was a modest decrease in isomer shift with increasing pressure for both spin states and an increase in quadrupole splitting, especially for the high-spin component. These effects are similar to our observations on a wide variety of compounds⁶ and will not be discussed here.

In an earlier paper⁷ Mössbauer resonance studies at high pressure were made on FeS_2 in the pyrite structure. The 1-atm lattice parameter is 5.504 \AA , and this material is low spin at 1 atm. The initial isomer shift (relative to iron metal) and the quadrupole splitting are 0.30 and 0.61 mm/sec, respectively, and these values are reasonably close to the 1-atm values for the low-spin component in MnS_2 , especially when one considers the problems in accurately characterizing a 10%

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