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Potential-pH equilibrium diagrams for the system S-H_2O from 25 to 150°C: Influence of access of oxygen in sulphide solutions*

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Abstract—Equilibrium potential-pH diagrams were constructed using a large set of thermodynamic data for a number of sulphur compounds, from 0 to 150°C. These diagrams were used to determine how access of oxygen in H_2S bearing solutions influences corrosion. It is shown that occasional access of limited amounts of oxygen is not necessarily corrosive, but that continuous access of even traces of oxygen to a same volume of H_2S solution can produce an important pH drop which may be the cause of corrosion.

In the present state of knowledge concerning the reversibility or irreversibility of the reactions, these equilibrium diagrams should be considered as a guide for experimental researches involving systematic electrode potential and pH measurements, which might lead to a perfect understanding and mastering of the corrosions.

FOREWORD

The present work is a tentative extension to higher temperatures of pioneer work first published in 1958 by VALENSI and VAN MUYLDER (1958, 1973) and VALENSI et al. (1963, 1966) on the electrochemical behaviour of system S-H_2O at 25°C, which was performed in the frame of CEBELCOR's "Commission des Etudes Fondamentales et Applications CEFA" (Committee for Fundamental and Applied Studies).

We have kept here, at least provisionally, most of the features of this early publication: (1) the standard free enthalpies of formation $g^0 = h^0 - Ts^0$ (or standard Gibbs free energies of formation ΔG_f^0, or standard chemical potentials u^0) are expressed in calories (1 cal = 4.184 000 6 J). The pressures, P are expressed in atmospheres (1 atm = 1.013 250 bar). Concentration unit c is chosen in mol/L or mol/kg water. As a first approximation, activities have been mostly considered equal to concentrations. The selection of the considered electrochemical reactions has remained as done by G. Valensi and based on their apparent degree of reversibility at 25°C. However, for not extending too much the work to be performed, which related essentially to the corrosion behaviour of metals in the presence of neutral or acid waters containing H_2S and O_2, we did not take into account the polysulphides considered by G. Valensi, which may only exist in alkaline solutions. (2) the symbols used are those that were recommended in the early 1950s by CITCE, CEBELCOR, and the IUPAC Commission of Electrochemistry of which I was the founder and chairman: E for "electrode potential" (E_0 for equilibrium potential, and E_0^0 for standard equilibrium potential), she for "standard hydrogen electrode," $\sum \nu M = 0$ for a chemical reaction (according to the method of Théophile de Donder), and $\sum \nu M + ne = 0$ for an electrochemical reaction, $A = -\sum \nu\mu$ for the "chemical affinity" and $\bar{A} = n(E - E_0)$ for the "electrochemical affinity" PNARW, 1982; VALENSI and VAN MUYLDER (1958, 1973). The methods used for representing graphically the influence of pH and/or of electrode potential on the homogeneous and heterogeneous equilibria are those used in POURBAIX (1973, 1975) and in POURBAIX (1989, 1990).

We are conscious that the present work is imperfect, due notably to the present lack of reliable data on the degree of irreversibility of many electrochemical reactions at different temperatures, and to the presently existing discrepancies concerning the thermodynamic data relating to the dissolved substances, especially at high temperatures.

But, as expressed in two recent publications which in fact include my scientific and moral testament (POURBAIX, 1989, 1990a,b,c), I think that, whatever the progresses that were made during the last decades in the scientific and technical applications of electrochemical thermodynamics, many of the most promising results are still to be obtained, and that some of the presently existing mistakes and misuses in these areas should, if possible, be rectified. Our knowledge in many important fields (including corrosion and geology) might still be greatly improved by more long-range systematic fundamental and applied research work on both the thermodynamics and the kinetics of electrochemical reactions at low and high temperatures, and on their experimental applications. These experiments should preferably include the measurement and the interpretation of electrode potentials versus reliable reference electrodes.

And this is why I am, despite my great age, trying to promote international team work for the preparation of *Atlases of Potential/pH Diagrams* for reactions in the presence of aqueous solutions (from 0 to 325°C), and of *Atlases of Potential/Temperature Diagrams* for reactions in the presence of gaseous atmospheres (from 0 to 6000°K). Readers who would be interested in taking part to these huge works and/or in co-sponsoring them are kindly invited to contact CEBELCOR.

Marcel Pourbaix

INTRODUCTION

BETWEEN 1958 AND 1973, Gabriel Valensi and Jean van Muylder published several papers on equilibrium diagrams for the system sulphur-water (VALENSI and VAN MUYLDER, 1958, 1973; VALENSI et al., 1963, 1966). They considered not only the thermodynamically stable substances, such as sulphur, sulphides, and sulphates, but also metastable substances (sulphites, hyposulphites, hydrosulphites, di-, tri-, tetra-, and pentathionates).

In the present paper, we extend the studies of G. Valensi and we present equilibrium diagrams for the S-H_2O system for several temperatures between 0 and 150°C.

Thirty-five substances were considered. The standard chemical potentials μ^0 (or the free enthalpies of formation ΔG_f^0) of these thirty-five substances at 0, 25, 50, 75, 100, 125, and 150°C found in the literature are listed in Appendix 1. The references of the data used in this study are identified with a black circle in the first column of this table.

* This paper is gratefully dedicated to the beloved memory of Robert Minard Garrels as a special recognition of the excellence of his pioneer work on the application of equilibrium diagrams to geology, which he developed notably in his fundamental book "Solutions, Minerals and Equilibria" published in 1965 with C. L. Christ.

We have selected ninety-six reactions between these thirty-five substances. These reactions and their general equilibrium conditions are listed in Appendix 2.

The equilibrium conditions of these ninety-six reactions are given for the different temperatures in Appendix 3, as a function of potential, pH and, when necessary, the concentration c in total dissolved sulphur (in moles of sulphur per liter).

The equilibria of some of these reactions are represented in diagrams as % vs. pH, $\log c$ – pH, $\log p$ – pH for chemical reactions (Fig. 1 to 3), and in diagrams E – pH for electrochemical reactions (Fig. 4 and 5; PNARW, 1982).

CALCULATION OF EQUILIBRIA

Calculation of Equilibrium Constants of Chemical Reactions and of Equilibrium Potentials of Electrochemical Reactions

The equilibrium conditions of chemical reactions and of electrochemical reactions can be expressed as indicated below. K is the equilibrium constant of a chemical reaction, E_0 is the equilibrium electrode potential of an electrochemical reaction in volts. μ^0 is the standard chemical potential of the reacting substances, in cal/mol, T is the absolute temperature in Kelvin.

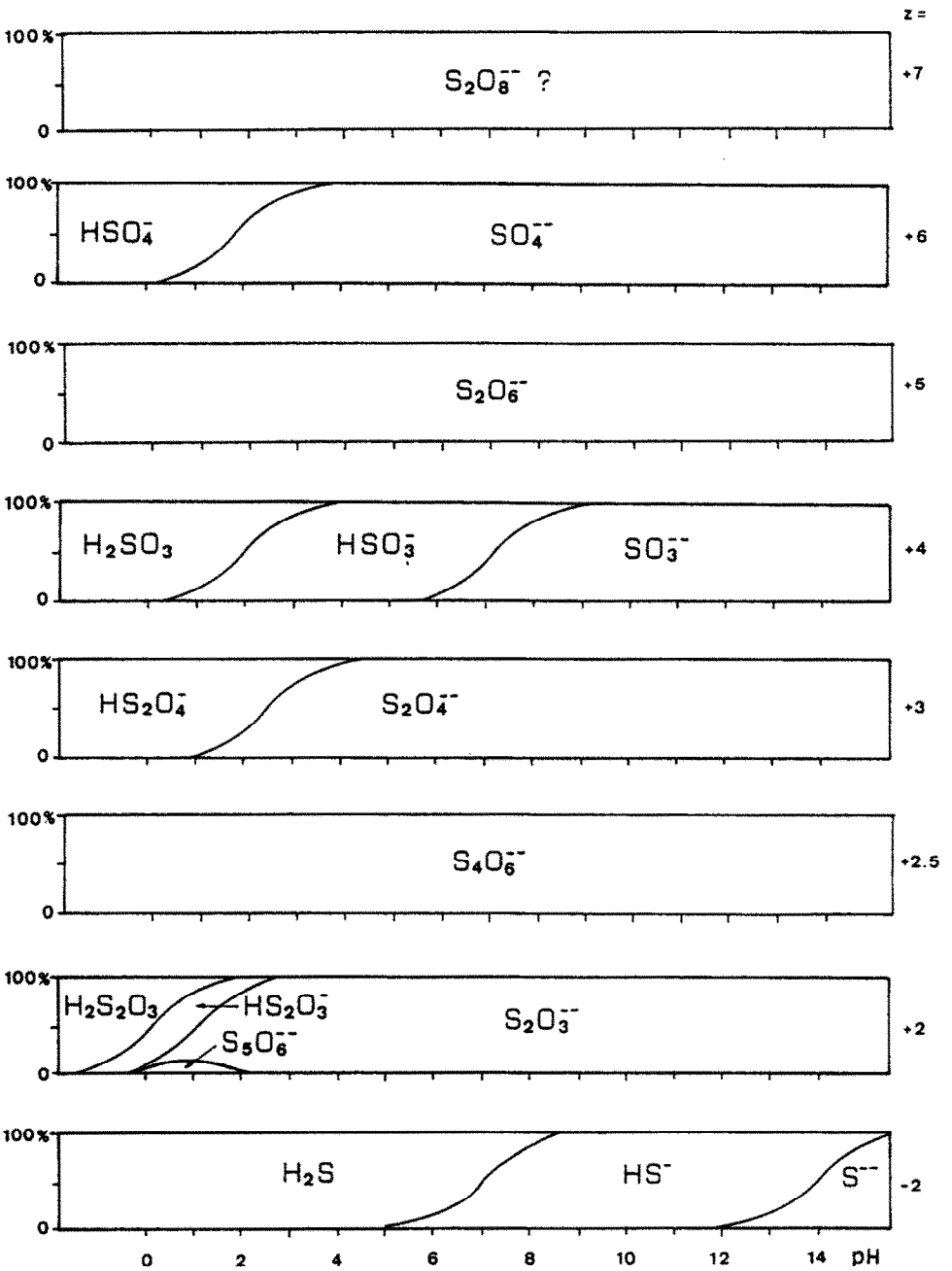

FIG. 1. Influence of pH on the dissociation of the dissolved substances at 25°C (for different "oxidation number z" of sulphur).

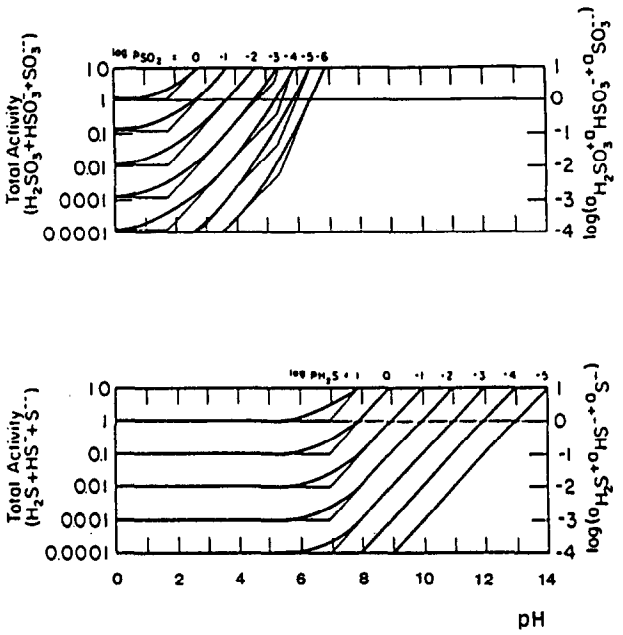

FIG. 2. Influence of pH and pressure on the solubility of gaseous (H_2S) and (SO_2) at 25°C. Equilibrium between H_2S gas and sulphide solutions, and between SO_2 gas and sulphite solutions.

For chemical reactions $\Sigma\ \nu M = 0$, the equilibrium condition is $\Sigma\ \nu \log (M) = \log K$, where

$$\log K = -\frac{\Sigma\ \nu\mu^0}{4.5756\ T}.$$

For electrochemical reactions $\Sigma\ \nu M + ne^- = 0$, the equilibrium condition is

$$E_0 = E_0^0 + \frac{0.1984}{n}\ T\ \Sigma\ \nu \log (M)\ (\text{in } V_{she}),$$

where

$$E_0^0 = \frac{\Sigma\ \nu\mu^0}{23060\ n}.$$

E_0^0 is the standard equilibrium electrode potential of an electrochemical reaction.

Equilibria of the Reactions Between Two Dissolved Substances

For equilibrium diagrams of systems with the same element under different dissolved forms, it is convenient to indicate the domains of relative predominance of each dissolved form. For that, we consider the reactions between the different forms, two by two. When the chemical formulae of these two forms contain the same number of atoms of the element (for example, H_2S and SO_4^{--}), the equation of the line which separates the domains of relative predominance (where the concentrations of the element under the two forms are the same) is a simplication of the equilibrium condition where the logarithmic term with the ratio of the concentrations of the two forms is equal to zero. In this case, the equation of this line does not depend on the total concentration in the element.

For example, for the reaction (34) in Table 2, $H_2S + 4\ H_2O = SO_4^{--} + 10\ H^+ + 8\ e^-$, the equilibrium condition at 25°C is $E_0 = 0.301 - 0.0739\ pH + 0.0074 \log ((SO_4^{--})/(H_2S))$, and the equation of the limit of the areas of relative predominance of sulphur as SO_4^{--} and H_2S is $E'_0 = 0.301 - 0.0739\ pH$.

This is not true when the two dissolved forms do not contain the same number of atoms of the element (for example, H_2S and $S_2O_3^{--}$, or $S_2O_3^{--}$ and $S_4O_6^{--}$).

For example, for the reaction (22) in Table 2, $2\ H_2S + 3\ H_2O = S_2O_3^{--} + 10\ H^+ + 8\ e^-$, the equilibrium condition at 25°C is $E_0 = 0.317 - 0.0739\ pH + 0.0074 \log ((S_2O_3^{--})/(H_2S)^2))$.

The equation of the limit between the areas of relative predominance of sulphur as $S_2O_3^{--}$ and as H_2S is obtained, for a given concentration in total sulphur c, by introducing the concentration in sulphur $c/2$ for each dissolved form, i.e., $c/4$ for $S_2O_3^{--}$ and $c/2$ for H_2S. The equation of the separation line is thus $E'_0 = 0.317 - 0.0739\ pH + 0.0074 (\log c/4 - 2 \log c/2)$ or $E'_0 = 0.317 - 0.0739\ pH - 0.0074 \log c$.

In this case, the equation of the separation line between the domains of relative predominance depends on the total concentration in sulphur.

In the following example, there is another peculiarity: for the reaction (40) in Table 2, $2\ S_2O_3^{--} = S_4O_6^{--} + 2\ e^-$, the equilibrium condition is $E_0 = 0.024 + 0.0295 \log ((S_4O_6^{--})/(S_2O_3^{--})^2)$, and the limit of predominance corresponds to the concentrations in $S_4O_6^{--}$ and in $S_2O_3^{--}$, being both equal to half the total concentration of sulphur c. The limit is given by $E'_0 = 0.024 + 0.0295 (\log c/8 - 2 \log c/4)$ or $E'_0 = 0.024 + 0.0295 (\log c - \log 8 - 2 \log c + 2 \log 4)$ or $E'_0 = 0.033 + 0.0295 \log c$.

In this case, the equation of the line which separates the domains of relative predominance has not only a term in log c, but also an independent term which modifies the value of the "standard potential" ($E'_0 = 0.024 + 0.009 = 0.033$).

This method of calculation was described in general terms by VALENSI and VAN MUYLDER (1958, 1973), VALENSI et al. (1963, 1966). The equilibrium equations presented in Appendix 3 consider the necessary modifications for the equilibria between two dissolved substances.

RESULTS AND EQUILIBRIUM DIAGRAMS

Details on the setting up and the interpretation of these equilibrium diagrams are presented in POURBAIX (1989, 1990).

Chemical Equilibria (at 25°C)

Figure 1 shows the influence of pH on the dissociation of the dissolved substances, for five values of the oxidation number of sulphur, from −2 to +6. Data on the dissociation of $S_4O_6^{--}$ (+2.5), $S_3O_6^{--}$ (+3.3), $S_2O_6^{--}$ (+5), and $S_2O_8^{--}$ (+7) are missing.

The influence of pH and pressure on the solubility of (H_2S) and (SO_2) is represented in Fig. 2, for six values of the partial pressure of (H_2S) and (SO_2), from 10^{-6} to 10^1 atm.

The pH of solutions of weak acid solutions and weak base solutions *in pure water* is presented in Fig. 3, as a function

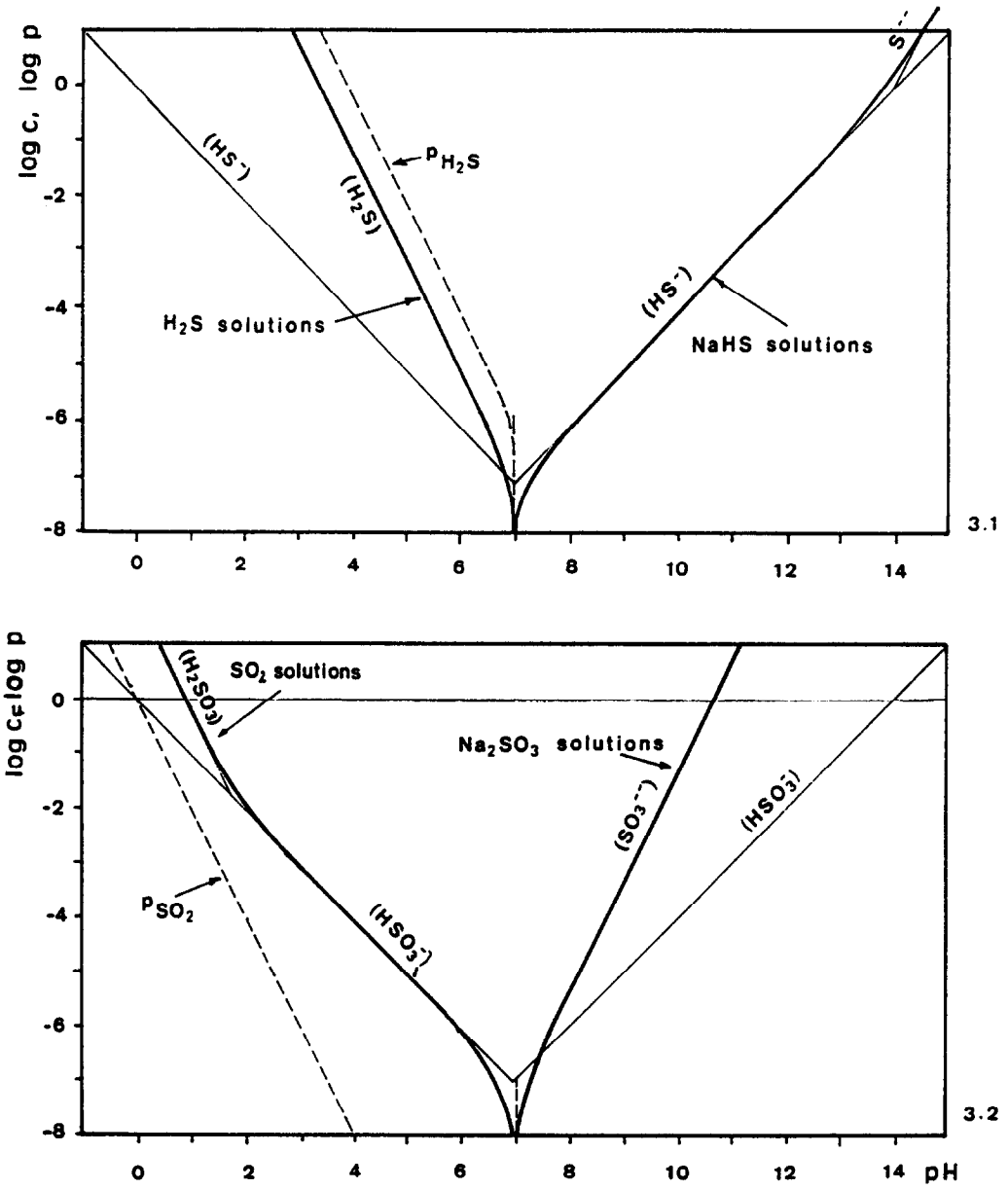

FIG. 3. pH of weak acid and weak base solutions in pure water at 25°C.

of the logarithm of the concentration of solutions of H_2S and NaHS, and of solutions of SO_2, $NaHSO_3$, and Na_2SO_3, and of the logarithm of the partial pressure in (H_2S) and in (SO_2).

Electrochemical Equilibria

Figures 4a–4d present *E*-pH equilibrium diagrams for the system S-H_2O at 25, 50, 100, and 150°C, considering only sulphur, sulphides, thiosulphates, tetrathionates, and sulphites. Sulphates, which have been included in an *E*-pH diagram of system S-H_2O devoted to thermodynamically stable species at 25°C (POURBAIX et al., 1963, p. 551), have not been considered here due to the general irreversibility of their reduction reactions. They should probably be considered sometimes, notably in the case of biological electrochemical reactions involving bacteria, such as vibrio desulphuricans.

Figures 5a–5d present *E*-pH equilibrium diagrams where only the hydrosulphites, sulphites and dithionates are considered.

Figure 6 is a *E*-pH diagram at 25°C, considering sulphur, sulphides, thiosulphates, tetrathionates, and sulphites, in the presence of (H_2S) (below line 69) or (SO_2) (above line 69). This line (69) separates the areas of relative predominance of gaseous (H_2S) and (SO_2) under the same partial pressure.

INTERPRETATION

Among the problems of actual interest for which such diagrams can be useful, there is the theoretical prediction and the experimental verification of the composition of waters containing simultaneously hydrogen sulphide H_2S or sulphur dioxide and oxygen O_2.

The diagram of Fig. 6 is related to such waters, permanently saturated with H_2S or SO_2 under a pressure of 1 atm, shown respectively below and above line (69).

Below line (69), the two families of lines (80) and (82) indicate, respectively, the conditions of metastable equilibria of solutions of thiosulphates $S_2O_3^{--}$ and of tetrathionates $S_4O_6^{--}$ (for concentrations between 10^{-4} and 10^{0} g·atom of sulphur per liter) in the presence of gaseous H_2S under 1 atm. The three vertical lines in the lower part of this figure indicate, from Fig. 2b, the concentration in total sulphur (as H_2S and HS^-) of solutions in equilibrium with gaseous H_2S under a pressure of 1 atm.

Above line (69), the family of lines (89) shows the metastable equilibrium conditions of solutions of tetrathionates $S_4O_6^{--}$ in the presence of gaseous SO_2 under a pressure of 1 atm, with indication of the concentration c in total sulphur ($10^{0.5}$, 10, and $10^{1.5}$ g·atom of sulphur per liter). The three vertical lines in the upper part of this figure show, from Fig. 2a, the concentrations in total sulphur (as H_2SO_3 and HSO_3^-) in solutions in equilibrium with SO_2 under a pressure of 1 atm.

Because of the high concentrations, these values are approximate.

Influence of Temperature and Pressure on the Solubility of Oxygen in Water

The influence of temperature on the solubility of oxygen in pure water, under a partial pressure of oxygen of 0.01 atm, is given in Table 1 (VALENSI et al., 1963, p. 100).

Action of Oxygen on Waters Containing Hydrogen Sulphide H_2S

According to the equilibria presented in Fig. 4a–4c, the oxidation of H_2S can produce successively elementary sulphur S (solid below 119°C and liquid above 119°C) and, depending on the pH, thiosulphate $S_2O_3^{--}$ and tetrathionate $S_4O_6^{--}$.

We do not consider here other substances such as $HS_2O_3^-$ or $H_2S_2O_3$ and pentathionate $S_5O_6^{--}$.

Formation of elementary sulphur

When oxidation is due to oxygen, the reactions from reaction (61) of Appendix 2 are $2\ H_2S \rightarrow 2\ S + 4\ H^+ + 4\ e^-$ and $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ or $2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O$ with formation of 2 moles of S for each mole of O_2, i.e., at 25°C for water saturated with O_2 under a pressure of 0.01 atm, with formation of $2.52\ 10^{-5}$ mole of S (or 0.800 mg S per liter). This reaction does not change the pH.

Formation of thiosulphate $S_2O_3^{--}$

From reaction (22) of Appendix $2\ H_2S + 1.5\ H_2O \rightarrow 0.5\ S_2O_3^{--} + 5\ H^+ + 4\ e^-$ and $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ or $H_2S + O_2 \rightarrow 0.5\ S_2O_3^{--} + 0.5\ H_2O + H^+$ with formation of 0.5 mole $S_2O_3^{--}$ and 1 g·atom H^+ for each mole of O_2 (or, at 25°C and for $P_{O_2} = 0.01$ atm, $0.63\ 10^{-5}$ mole $S_2O_3^{--}$ and $1.26\ 10^{-5}$ g·atom H^+ per liter), with a decrease of the pH.

Formation of tetrathionate $S_4O_6^{--}$

From reaction (25) of Appendix $2\ 4/4.5\ H_2S + 6/4.5\ H_2O \rightarrow 1/4.5\ S_4O_6^{--} + 20/4.5\ H^+ + 4\ e^-$ and $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ or $4/4.5\ H_2S + O_2 \rightarrow 1/4.5\ S_4O_6^{--} + 3/4.5\ H_2O + 2/4.5\ H^+$ with formation of 0.22 mole $S_4O_6^{--}$ and 0.44 g·atom H^+ per mole O_2 (i.e., at 25°C and for $P_{O_2} = 0.01$ atm, $0.28\ 10^{-5}$ mole $S_4O_6^{--}$ and $0.55\ 10^{-5}$ g·atom H^+ per liter). This also decreases the pH.

Characteristics of the Waters in a Potential-pH Diagram at 25°C

According to Fig. 3a, the pH of pure water saturated in gaseous H_2S under a pressure of 1 atm at 25°C is approximately 3.9. The characteristic point of such a water in Fig. 6 is thus about at the point marked 1. When oxygen is added, this point moves upward, at constant pH, until it reaches line (93) which is the equilibrium between (H_2S) and S for a pressure of 1 atm. At this point (marked 2 in Fig. 6), the oxidation of H_2S with formation of elementary sulphur is thermodynamically feasible, according to reactions (61) of Appendix 2 or line (93).

When the characteristic point approaches lines (22) and (25), which relate to the equilibria $H_2S/S_2O_3^{--}$ and $H_2S/S_4O_6^{--}$, the oxidation of H_2S could thermodynamically also produce $S_2O_3^{--}$ and $S_4O_6^{--}$. In these conditions, it may thus be expected that elementary sulphur, thiosulphates, and tetrathionates could be formed simultaneously.

Evolution of the water when the introduction of oxygen is not permanent

If the amount of oxygen initially present ($1.26\ 10^{-5}$ mol/L in the case considered here) is not renewed, the three reactions mentioned above will stop when oxygen will be consumed.

The exact characteristics of the system in these conditions could be determined only from a full knowledge of the kinetics of the three reactions (61), (22), and (25) of Appendix 2. In default of this, it is only possible to make a tentative discussion, in the case of two hypothesis.

Table 1. Influence of temperature on the solubility of oxygen

Temperature (°C)	25	50	75	100	125	150
log dissolved O_2 (mol/L)	−4.90	−5.03	−5.10	−5.12	−5.11	−5.06
dissolved (O_2)						
(mol/L)	$1.26\ 10^{-5}$	$0.93\ 10^{-5}$	$0.80\ 10^{-5}$	$0.76\ 10^{-5}$	$0.78\ 10^{-5}$	$0.87\ 10^{-5}$
(mg/L)	0.403	0.298	0.256	0.243	0.250	0.278

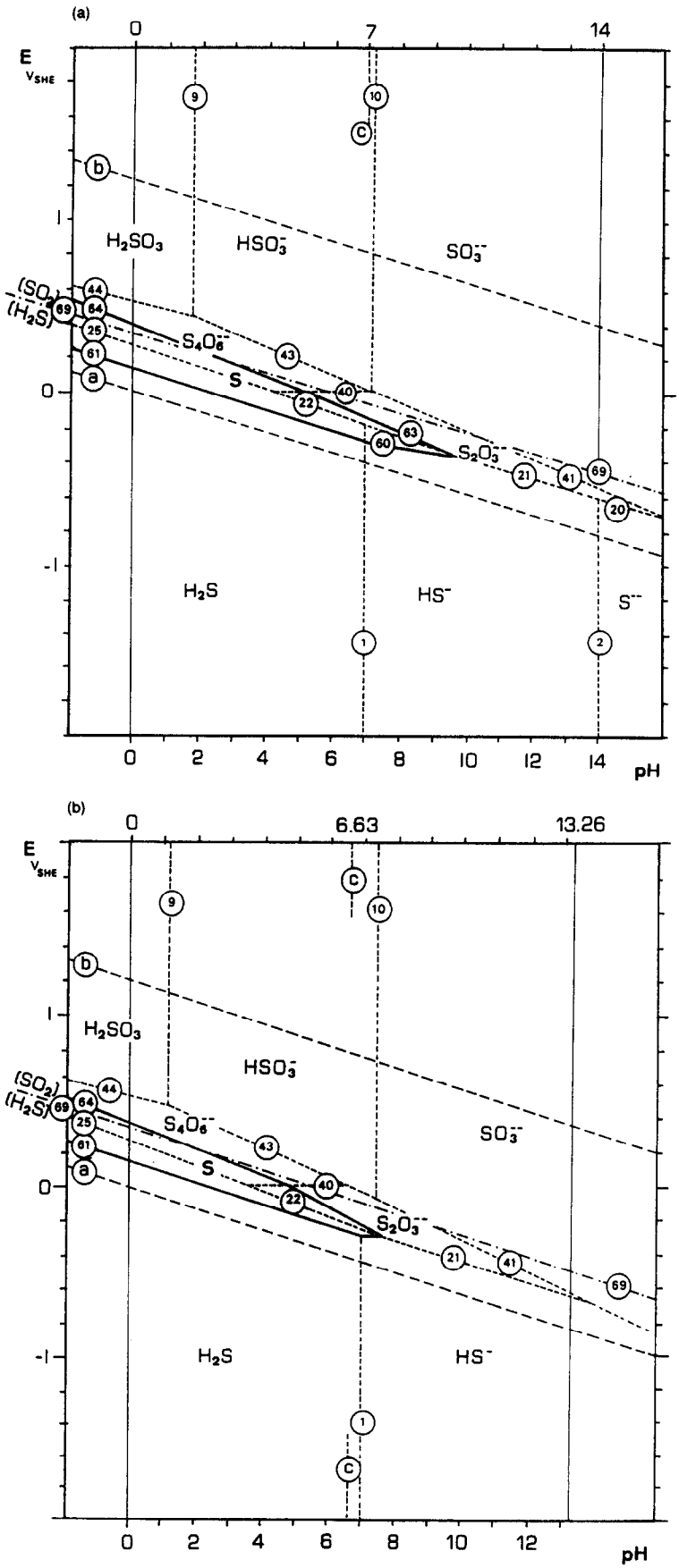

FIG. 4. E-pH equilibrium diagram for the system S-H_2O, considering only sulphur, sulphides, thiosulphates, tetrathionates, and sulphites (log C = 0) at (a) 25°C, (b) 50°C, (c) 100°C, and (d) 150°C.

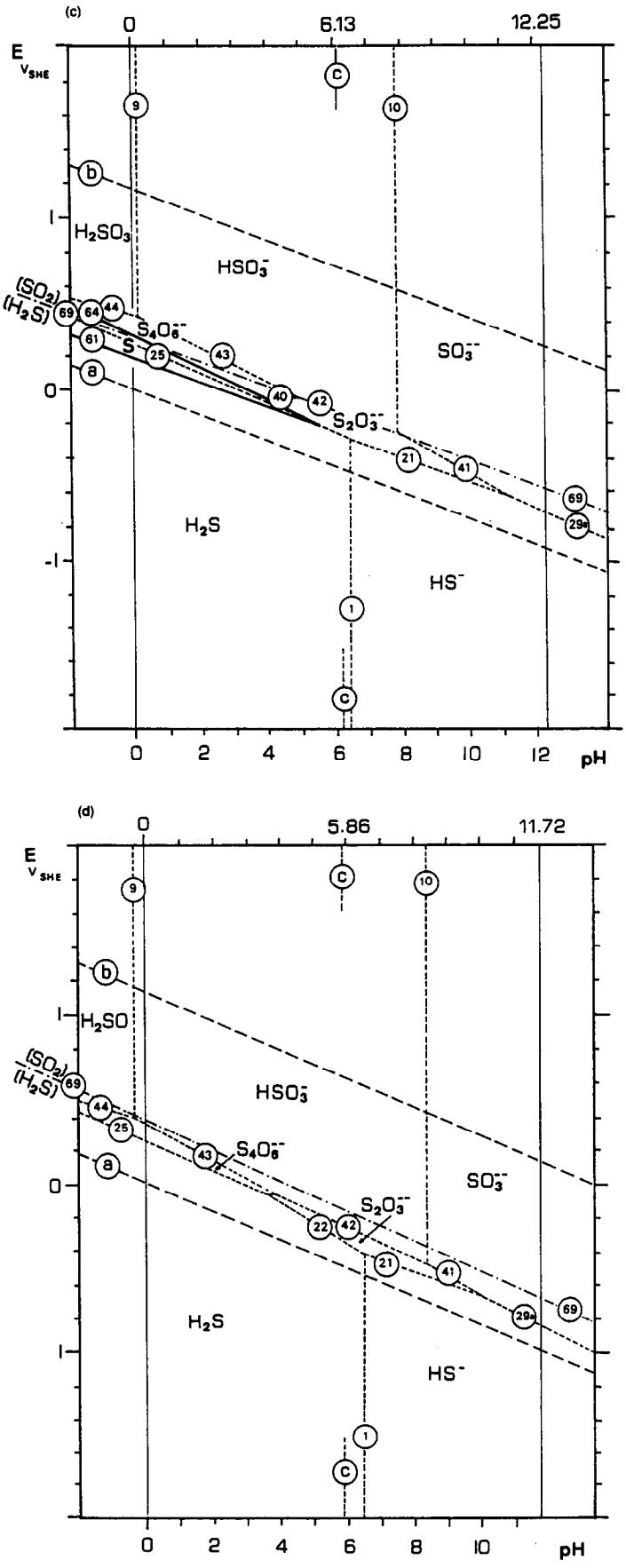

FIG. 4. (Continued)

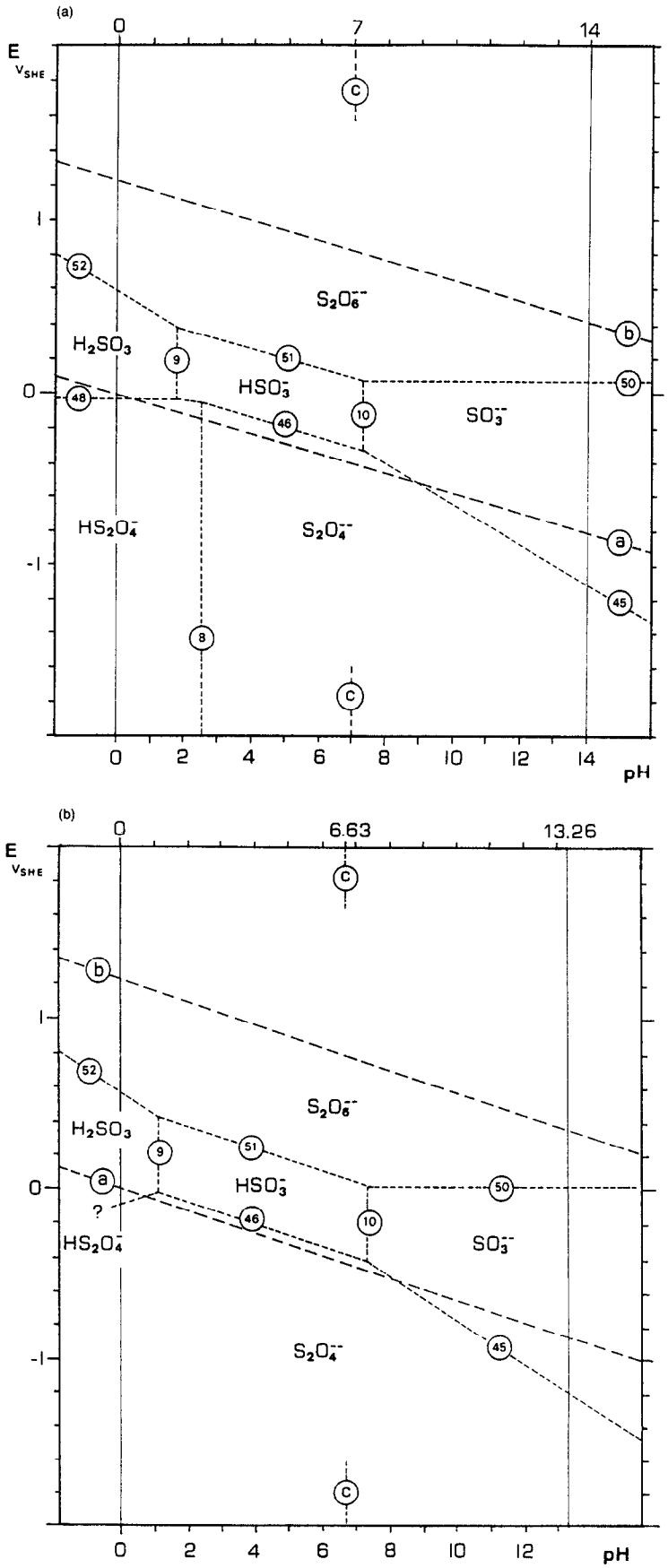

FIG. 5. *E*-pH equilibrium diagram for the system S-H_2O, considering only hydrosulphites, sulphites, and dithionates (log C = 0) at (a) 25°C, (b) 50°C, (c) 100°C, and (d) 150°C.

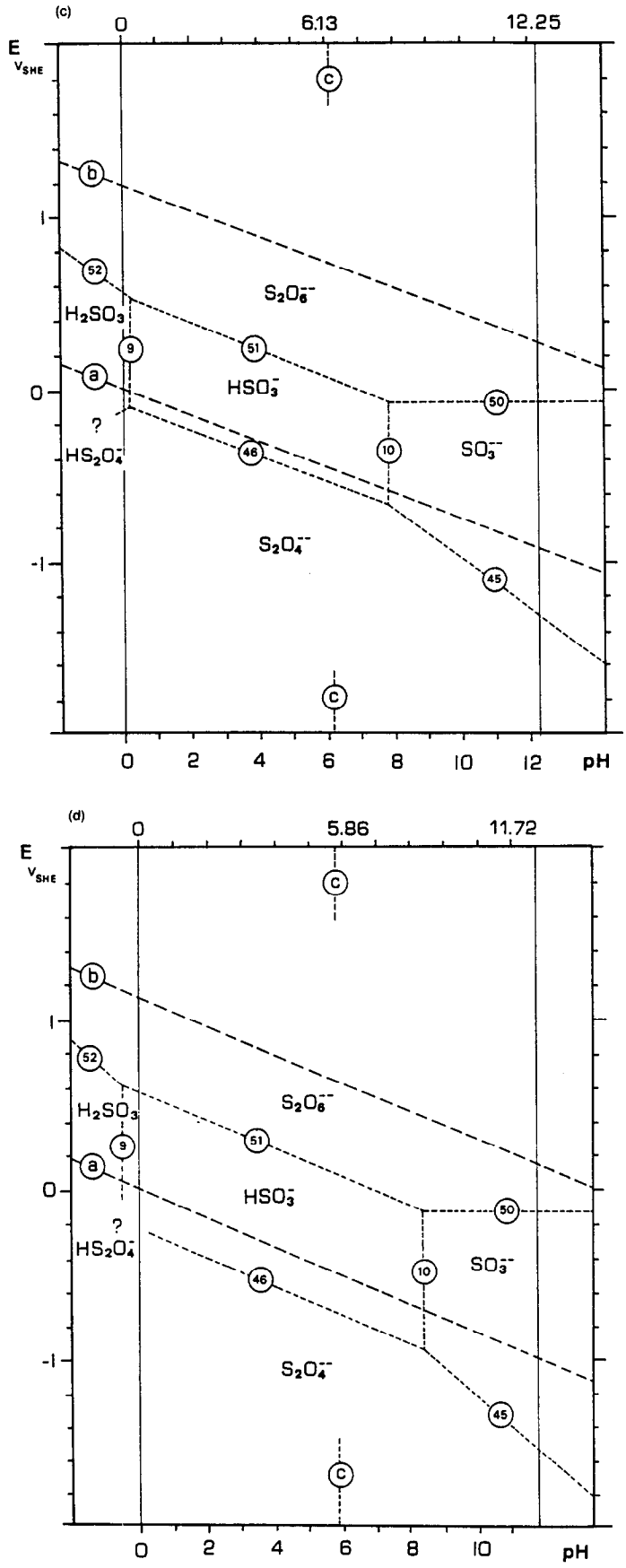

FIG. 5. (Continued)

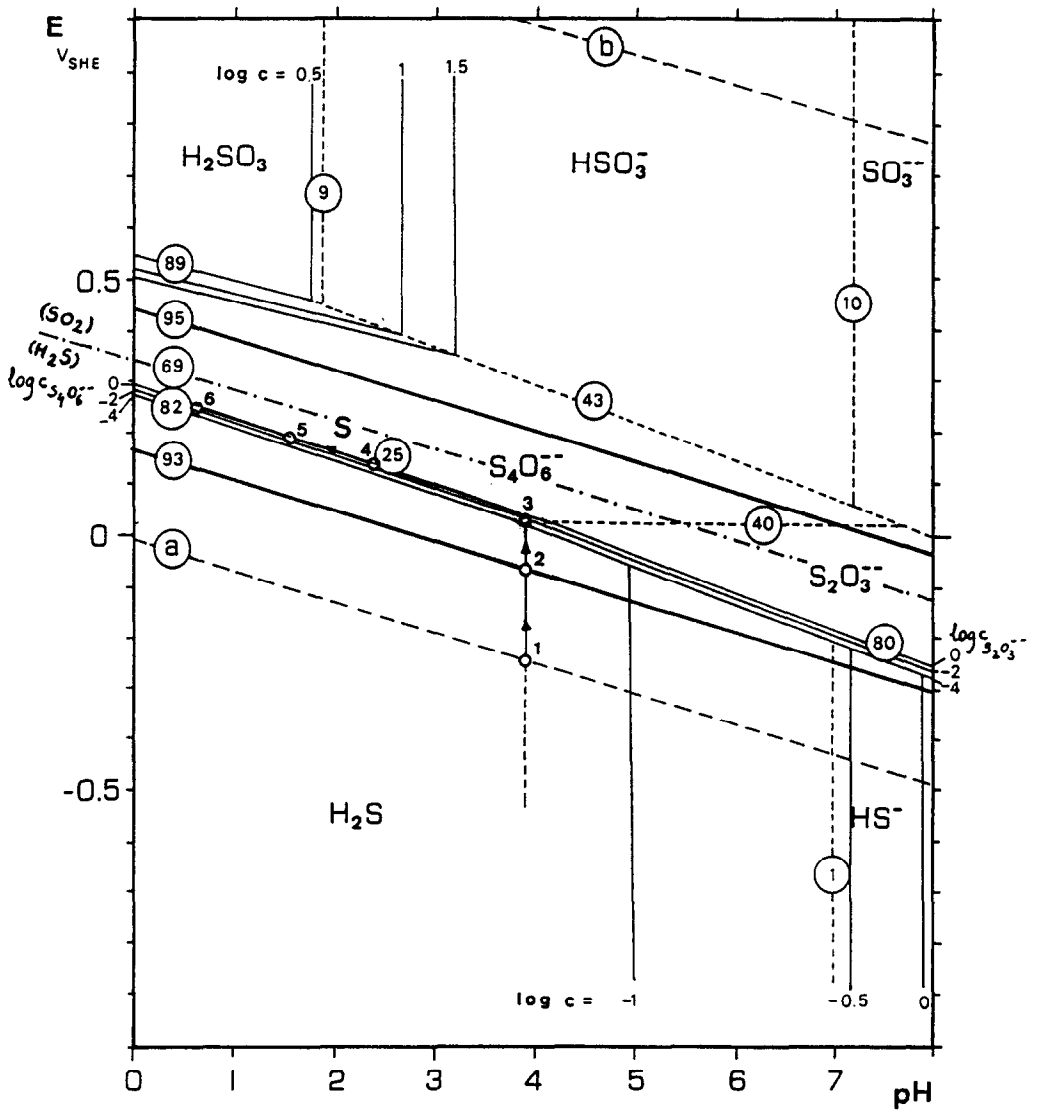

FIG. 6. *E*-pH equilibrium diagram for the system S-H_2O, considering sulphur, sulphides, thiosulphates, tetrathionates, and sulphites at 25°C, in the presence of gaseous H_2S or SO_2 under a pressure of 1 atm.

First hypothesis. The reaction H_2S/S (reaction 61) is reversible. In this case, only that reaction will occur, and neither $S_2O_3^{--}$ nor $S_4O_6^{--}$ will be formed. The characteristic point stabilizes at the point marked 2 in Fig. 6.

Second hypothesis. The equilibrium H_2S/S is not reversible, and the equilibria $H_2S/S_2O_3^{--}$ (reaction 22), Appendix 2 and $H_2S/S_4O_6^{--}$ (reaction 25) of Appendix 2 are reversible. The characteristic point will then move approximately along lines (80) and (82), for a pressure in gaseous H_2S equal to 1 atm. At 25°C, the equations of these lines are, respectively, for $(H_2S)/S_2O_3^{--}$:

Reaction 7 of Appendix 2—

$$E = 0.333 - 0.0739\ \text{pH} + 0.0074 \log c \quad (V_{she})$$

for $(H_2S)/S_4O_6^{--}$:

Reaction 8 of Appendix 2—

$$E = 0.299 - 0.0657\ \text{pH} + 0.0033 \log c \quad (V_{she}).$$

As mentioned previously, both these oxidation reactions of H_2S to $S_2O_3^{--}$ and to $S_4O_6^{--}$ produce H^+ (1 g·atom H^+ per mole O_2 for reaction 7 of Appendix 2 and 2/4.5 = 0.44 g·atom H^+ per mole O_2 for reaction 8 of Appendix 2. As indicated by Fig. 6, tetrathionate $S_4O_6^{--}$ is predominant versus thiosulphate $S_2O_3^{--}$ and, in this case, the amount of H^+ formed due to the amount of oxygen present ($1.26\ 10^{-5}$ mole O_2 per liter) is approximately $1.26 \times 0.44\ 10^{-5} = 0.55\ 10^{-5}$ g·ion H^+. This does not produce any significant change of pH. If it is assumed that the total dissolved sulphur (as $S_4O_6^{--} + S_2O_3^{--}$) is about $10^{-4.9}$ mol/L (about 0.3 mg S per liter), the characteristic point is near pH 3.9 and $E = 0.027$ V_{she} (marked 3 in Fig. 6).

The validity of this second hypothesis is not demonstrated, and we are enclined to consider that, in reality, the solution will contain a small amount of suspended solid sulphur and that the characteristic point will be between the points marked 2 and 3 in Fig. 6 (pH 3.9).

Table 2.

O_2 added (g/L of water)	Point in Fig. 6	Concentration c in dissolved S (mol S/L)	log c	pH	E V_{she}
0.1	4	0.003 to 0.006	−2.5 to −2.2	2.5	0.126
1	5	0.03 to 0.06	−1.5 to −1.2	1.5	0.195
10	6	0.3 to 0.6	−0.5 to −0.2	0.5	0.264

Evolution of the water when the introduction of oxygen is permanent

If the water is in permanent contact with an atmosphere containing H_2S under 1 atm and O_2 under a pressure of 0.01 atm, the oxidation of H_2S will continue permanently with simultaneous formation of all or part of the three oxidation products S, $S_2O_3^{--}$, and $S_4O_6^{--}$. It is also possible that as shown in Fig. 1, $HS_2O_3^-$, $H_2S_2O_3$, and $S_5O_6^{--}$ will be formed at a pH value lower than 3 by hydrolysis of thiosulphate $S_2O_3^{--}$ with about 1 to 2 mole sulphur (32 to 64 g) per mole oxygen (32 g), i.e., 1 to 2 g sulphur per g oxygen.

For instance, an access of 0.1, 1, or 10 g oxygen to 1 L of solution forms, respectively, 0.1 to 0.2, 1 to 2, or 10 to 20 g sulphur per liter, (as elementary S and/or dissolved $S_2O_3^{--}$, $S_4O_6^{--}$, $HS_2O_3^-$, $H_2S_2O_3$, and $S_5O_6^{--}$). If it is assumed that the amount of elementary sulphur is negligible compared to the dissolved sulphur, the solution would be a solution of thiosulphate and polythionates with a total dissolved sulphur concentration c equal to about 0.003 to 0.006, 0.03 to 0.06, or 0.3 to 0.6 mole sulphur per liter (or log c = −2.5 to −2.2, −1.5 to −1.2, or −0.5 to −0.2, respectively). In this case, the characteristic point would move in Fig. 6 from the points marked 2 and 3, towards the left, and along lines (82) for log c = −2.5 to −0.2, up to a point for which the concentration in sulphur c, the pH, and the electrode potential E are approximately those indicated in Table 2, as a function of the cumulated amount of oxygen added. (pH was calculated without consideration of a buffer effect due to the hydrolysis of thiosulphate $S_2O_3^{--}$, although Fig. 1a shows that such an effect indeed exists below pH 3.)

The electrode potentials were estimated using formula (33) of Appendix 2:

$$E = 0.299 - 0.0657\ \text{pH} + 0.033 \log c.$$

The characteristic point of the water saturated with H_2S under a pressure of 1 atm which is exposed temporarily to oxygen under a pressure of 0.01 atm moves thus along the points 1 → 2 → 3. When the water is exposed permanently to the same oxygen atmosphere, the characteristic moves further along the points 3 → 4 → 5 → 6, with formation of an acid solution concentrated in thiosulphate and in polythionates $S_4O_6^{--}$ and $S_5O_6^{--}$ and in H_2S, probably with some suspended elementary sulphur.

CONCLUSION

This interpretation of the diagram of Fig. 6 is based on several assumptions on the reacting substances and on the kinetics of the reactions considered. The kinetics of most of these reactions is, however, far from sufficiently known. *In the present state of knowledge, the diagrams presented in this paper must be considered as a guide for experimental research.*

An experimental research programme should include systematic experiments where increasing quantities of oxygen would be added to such waters, with continuous measurement of the pH and the redox potential, and with analysis of the solution and with corrosivity tests for iron, steels, and other alloys.

We believe that such a research programme would produce significant progress in the understanding of the corrosion phenomena which occur when oxygen has access to waters containing hydrogen sulphide.

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Appendix 1. Standard Chemical Potentials, μ^0, or free enthalpies of formation, ΔG_f^0 (cal/mol)

z^*	Substances	T°C: 0 / T°K: 273	25 / 298	50 / 323	75 / 348	100 / 373	125 / 398	150 / 423
System H-O								
	Gaseous							
	(H_2)	0	0	0	0	0	0	0
	(O_2)	0	0	0	0	0	0	0
	$(H_2O)^a$		−54 635					
	$(H_2O)^{b,\dagger}$	−54 898	−54 636	−54 368	−54 095	−53 819	−53 539	−53 255
	$(H_2O)^c$	−54 897	−54 634	−54 367	−54 094	−53 817	−53 538	−53 254
	Liquid							
	H_2O^a		−56 690					
	$H_2O^{b,\dagger}$	−57 671	−56 687	−55 719	−54 765	−53 824	−52 895	−51 936
	H_2O^c	−57 670	−56 686	−55 719	−54 766	−53 827	−52 900	−51 985
	Dissolved							
	H^+	0	0	0	0		0	0
	$OH^{-\,a}$		−37 595			0		
	$OH^{-\,b,\dagger}$	−38 943	−37 581	−36 122	−34 566	−32 911	−31 156	−29 259
	$OH^{-\,c}$	−38 996	−37 596	−36 095	−34 521	−32 887	−31 196	−29 443
	$OH^{-\,d}$	−37 615	−37 594	−37 500	−37 356	−37 167	−36 934	−36 662
System H-O-S								
	Gaseous							
−2	$(H_2S)^a$		−7 892					
	$(H_2S)^c$	−7 756	−8 020	−8 274	−8 520	−8 758	−8 979	−9 174
	$(H_2S)^{c,\dagger}$	−7 739	−7 975	−8 211	−8 447	−8 683	−8 920	−9 094
+2	$(SO)^a$		12 780					
	$(SO)^{c,f}$		−5 030					
	$(SO)^{c,\dagger}$	− 4 521	−5 030	−5 540	−6 047	−6 559	−7 068	−7 531
+4	$(SO_2)^a$		−71 790					
	$(SO_2)^g$		−71 741					
	$(SO_2)^{c,\dagger}$	−71 690	−71 741	−71 791	−71 842	−71 892	−71 943	−71 993
+6	$(SO_3)^a$		−88 520					
	$(SO_3)^g$		−88 689					
	$(SO_3)^{c,\dagger}$	−89 202	−88 689	−88 176	−87 664	−87 285	−86 781	−86 071
	Solid and liquid							
0	S_{sol}	0	0	0	0	0		
0	S_{liq}						0	0
	Dissolved							
−2	$S^{--\,a,\dagger}$		21 958					
	$HS^{-\,a}$		3 010					
	$HS^{-\,c}$	2 296	2 817	3 474	4 216	5 055	5 882	6 826
	$HS^{-\,d,\dagger}$	3 296	2 860	2 434	2 124	1 809	1 530	1 285
	H_2S^a		−6 540					
	H_2S^c	−6 935	−6 659	−6 440	−6 290	−6 180	−6 210	−6 250
	$H_2S^{d,\dagger}$	−5 973	−6 674	−7 446	−8 333	−9 265	−10 528	−11 306
−1	$S_2^{--\,a}$		19 749					

Appendix 1. (Continued)

z*	Substances	T°C: 0 / T°K: 273	25 / 298	50 / 323	75 / 348	100 / 373	125 / 398	150 / 423
	S_2^{--} [d,†]	19 253	19 001	18 892	18 890	18 984	19 176	19 456
−0.67	S_3^{--} [a]		17 968					
	S_3^{--} [d,†]	18 069	17 601	17 260	17 014	16 855	16 784	16 973
−0.50	S_4^{--} [a]		16 615					
	S_4^{--} [d,†]	17 182	16 500	15 931	15 444	15 033	14 701	14 442
−0.40	S_5^{--} [a]		15 689					
	S_5^{--} [d,†]	16 595	15 700	14 901	14 173	13 512	12 920	12 394
+2	$S_5O_6^{--}$ [a]		−228 200					
	$S_5O_6^{--}$ [d,†]	−227 951	−229 000	−229 964	−230 865	−231 706	−232 486	−233 205
	$S_2O_3^{--}$ [a]		−127 200					
	$S_2O_3^{--}$ [d,†]	−124 427	−124 899	−125 245	−125 498	−125 664	−125 744	−125 743
	$HS_2O_3^-$ [a]		−129 500					
	$HS_2O_3^-$ [c,e,†]	−126 317	−127 249	−128 165	−129 118	−130 084	−131 064	−132 063
	$H_2S_2O_3$ [a,†]		−129 900					
+2.5	$S_4O_6^{--}$ [a]		−244 300					
	$S_4O_6^{--}$ [d,†]	−247 135	−248 701	−250 218	−251 701	−253 149	−254 557	−255 924
+3	$S_2O_4^{--}$ [a]		−138 000					
	$S_2O_4^{--}$ [d,†]	−142 883	−143 300	−144 000	−144 414	−144 748	−145 001	−145 178
	$HS_2O_4^-$ [a,†]		−141 408					
+3.33	$S_3O_6^{--}$ [a]		−229 000					
	$S_3O_6^{--}$ [a,†]	−228 119	−229 000	−229 783	−230 495	−231 139	−231 714	−232 222
+4	SO_3^{--} [a]		−116 100					
	SO_3^{--} [d,†]	−116 378	−116 299	−116 052	−115 681	−115 197	−114 602	−113 908
+4	HSO_3^- [a]		−126 100					
	HSO_3^- [d,†]	−125 291	−126 130	−126 965	−127 799	−128 632	−129 459	−130 280
	H_2SO_3 [a]		−128 690					
	H_2SO_3 [d,e,†]	−128 730	−128 668	−128 713	−128 851	−129 072	−129 367	−129 492
	$S_2O_5^{--}$ [d,†]	−188 311	−189 000	−189 577	−190 072	−190 491	−190 831	−191 099
+5	$S_2O_6^{--}$ [a]		−231 000					
	$S_2O_6^{--}$ [d,†]	−230 191	−231 000	−231 706	−232 336	−232 896	−233 383	−233 801
+6	SO_4^{--} [a]		−177 340					
	SO_4^{--} [c]	−181 132	−177 974	−174 564	−170 978	−167 302	−163 444	−159 372
	SO_4^{--} [d,†]	−177 735	−177 929	−177 982	−177 934	−177 795	−177 564	−177 252
	HSO_4^- [a]		−179 940					
	HSO_4^- [c]	−183 207	−180 685	−178 027	−175 298	−172 565	−169 769	−166 813
	HSO_4^- [d,†]	−179 885	−180 630	−181 386	−182 152	−182 925	−183 700	−184 475
+7	$S_2O_8^{--}$ [a]		−262 000					
	$S_2O_8^{--}$ [d,†]	−265 008	−266 501	−267 937	−269 333	−270 689	−272 000	−273 265
+8	HSO_5^- [d,†]	−151 137	−152 371	−153 667	−155 011	−156 396	−157 813	−159 257

* z is the oxidation number for sulphur.
† The references of the data used in this paper.
[a] VALENSI and VAN MUYLDER (1958); VALENSI et al. (1963).
[b] POURBAIX and YANG (1981).
[c] COBBLE et al. (1982).
[d] E. L. Shock, pers. commun. (1988).
[e] M. Pourbaix and A. Pourbaix (unpubl. data).
[f] ZHANG et al. (1984).
[g] STULL et al. (1971).

Appendix 2. Reactions and general equilibrium conditions

	z	EQUILIBRIUM	REACTION EQUILIBRIUM CONDITION
		REACTIONS INVOLVING TWO DISSOLVED SUBSTANCES	
Chemical reactions			
1	−2	H_2S/HS^-	$H_2S = HS^- + H^+$ $\log((HS^-)/(H_2S)) = -\log K + pH$
2	−2	HS^-/S^{--}	$HS^- = S^{--} + H^+$ $\log((S^{--})/(HS^-)) = -\log K + pH$
3	+2	$H_2S_2O_3/HS_2O_3^-$	$H_2S_2O_3 = HS_2O_3^- + H^+$ $\log((HS_2O_3^-)/H_2S_2O_3)) = -\log K + pH$
4	+2	$HS_2O_3^-/S_2O_3^{--}$	$HS_2O_3^- = S_2O_3^{--} + H^+$ $\log((S_2O_3^{--})/(HS_2O_3^-)) = -\log K + pH$

Appendix 2. (Continued)

	z	EQUILIBRIUM	REACTION EQUILIBRIUM CONDITION
5	+2	$S_5O_6^{--}/HS_2O_3^-$	$2\ S_5O_6^{--} + 3\ H_2O = HS_2O_3^- + 5\ H^+$ $\log((HS_2O_3^-)^5/(S_5O_6^{--})^2) = -\log K + \text{pH}$
6	+2	$S_5O_6^{--}/S_2O_3^{--}$	$2\ S_5O_6^{--} + 3\ H_2O = 5\ S_2O_3^{--} + 6\ H^+$ $\log((S_2O_3^{--})^5/(S_5O_6^{--})^2) = -\log K + 6\ \text{pH}$
7	+2	$H_2S_2O_3/S_5O_6^{--}$	$5\ H_2S_2O_3 = S_5O_6^{--} + 3\ H_2O + 4\ H^+$ $\log((S_5O_6^{--})^2/(H_2S_2O_3)^5) = -\log K + 4\ \text{pH}$
8	+3	$HS_2O_4^-/S_2O_4^{--}$	$HS_2O_4^- = S_2O_4^{--} + H^+$ $\log((S_2O_4^{--})/(HS_2O_4^-)) = -\log K + \text{pH}$
9	+4	H_2SO_3/HSO_3^-	$H_2SO_3 = HSO_3^- + H^+$ $\log((HSO_3^-)/(H_2SO_3)) = -\log K + \text{pH}$
10	+4	HSO_3^-/SO_3^{--}	$HSO_3^- = SO_3^{--} + H^+$ $\log((SO_3^{--})/(HSO_3^-)) = -\log K + \text{pH}$
11	+6	HSO_4^-/SO_4^{--}	$HSO_4^- = SO_4^{--} + H^+$ $\log((SO_4^{--})/(HSO_4^-)) = -\log K + \text{pH}$
Electrochemical reactions			
12	−2/−1	S^{--}/S_2^{--}	$2\ S^{--} = S_2^{--} + 2e^-$ $E_0 = E_0^0 + 0.0992\ T \log((S_2^{--})/(S^{--})^2)$
13	−1/−0.67	S_2^{--}/S_3^{--}	$3\ S_2^{--} = 2\ S_3^{--} + 2e^-$ $E_0 = E_0^0 + 0.0992\ T \log((S_3^{--})^2/(S_2^{--})^3)$
14	−0.67/−0.50	S_3^{--}/S_4^{--}	$4\ S_3^{--} = 3\ S_4^{--} + 2e^-$ $E_0 = E_0^0 + 0.0992\ T \log((S_4^{--})^3/(S_3^{--})^4)$
15	−0.50/−0.40	S_4^{--}/S_5^{--}	$5\ S_4^{--} = 4\ S_5^{--} + 2e^-$ $E_0 = E_0^0 + 0.0992\ T \log((S_5^{--})^4/(S_4^{--})^5)$
16	−2/−1	HS^-/S_2^{--}	$2\ HS^- = S_2^{--} + 2\ H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\ T\ \text{pH} + 0.0992\ T \log((S_2^{--})/(HS^-)^2)$
17	−2/−0.67	HS^-/S_3^{--}	$3\ HS^- = S_3^{--} + 3\ H^+ + 4e^-$ $E_0 = E_0^0 - 0.1448\ T\ \text{pH} + 0.0496\ T \log((S_3^{--})/(SH^-)^3)$
18	−2/−0.5	HS^-/S_4^{--}	$4\ HS^- = S_4^{--} + 4\ H^+ + 6e^-$ $E_0 = E_0^0 - 0.1323\ T\ \text{pH} + 0.0331\ T \log((S_4^{--})/(HS^-)^4)$
19	−2/−0.4	HS^-/S_5^{--}	$5\ HS^- = S_5^{--} + 5\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.1240\ T\ \text{pH} + 0.0248\ T \log((S_5^{--})/(HS^-)^5)$
20	−2/+2	$S^{--}/S_2O_3^{--}$	$2\ S^{--} + 3\ H_2O = S_2O_3^{--} + 6\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.1488\ T\ \text{pH} + 0.0248\ T \log((S_2O_3^{--})/(S^{--})^2)$
21	−2/+2	$HS^-/S_2O_3^{--}$	$2\ HS^- + 3\ H_2O = S_2O_3^{--} + 8\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.1984\ T\ \text{pH} + 0.0248\ T \log((S_2O_3^{--})/(HS^-)^2)$
22	−2/+2	$H_2S/S_2O_3^{--}$	$2\ H_2S + 3\ H_2O = S_2O_3^{--} + 10\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.2480\ T\ \text{pH} + 0.0248\ T \log((S_2O_3^{--})/(H_2S)^2)$
23	−2/+2	$H_2S/HS_2O_3^-$	$2\ H_2S + 3\ H_2O = HS_2O_3^- + 9\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.2232\ T\ \text{pH} + 0.0248\ T \log((HS_2O_3^-)/(H_2S)^2)$
24	−2/+2	$H_2S/H_5O_6^-$	$5\ H_2S + 6\ H_2O = S_5O_6^{--} + 22\ H^+ + 20e^-$ $E_0 = E_0^0 - 0.2182\ T\ \text{pH} + 0.0099\ T \log((S_5O_6^{--})/(H_2S)^5)$
25	−2/+2.5	$H_2S/S_4O_6^{--}$	$4\ H_2S + 6\ H_2O = S_4O_6^{--} + 20\ H^+ + 18e^-$ $E_0 = E_0^0 - 0.2204\ T\ \text{pH} + 0.0110\ T \log((S_4O_6^{--})/(H_2S)^4)$
26	−2/+3	$S^{--}/S_2O_4^{--}$	$2\ S^{--} + 4\ H_2O = S_2O_4^{--} + 8\ H^+ + 10e^-$ $E_0 = E_0^0 - 0.1587\ T\ \text{pH} + 0.0198\ T \log((S_2O_4^{--})/(S^{--})^2)$
27	−2/+3	$S^{--}/HS_2O_4^-$	$2\ S^{--} + 4\ H_2O = HS_2O_4^- + 7\ H^+ + 10e^-$ $E_0 = E_0^0 - 0.1389\ T\ \text{pH} + 0.0198\ T \log((HS_2O_4^-)/(S^{--})^2)$
28	−2/+4	S^{--}/SO_3^{--}	$S^{--} + 3\ H_2O = SO_3^{--} + 6\ H^+ + 6e^-$ $E_0 = E_0^0 - 0.1984\ T\ \text{pH} + 0.0331\ T \log((SO_3^{--})/(S^{--}))$
29	−2/+4	S^{--}/HSO_3^-	$S^{--} + 3\ H_2O = HSO_3^- + 5\ H^+ + 6e^-$ $E_0 = E_0^0 - 0.1653\ T\ \text{pH} + 0.0331\ T \log((HSO_3^-)/(S^{--}))$
29a	−2/+4	HS^-/SO_3^{--}	$HS^- + 3\ H_2O = SO_3^{--} + 7\ H^+ + 6e^-$ $E_0 = E_0^0 - 0.2315\ T\ \text{pH} + 0.0331\ T \log((SO_3^{--})/(HS^-))$
30	−2/+4	HS^-/HSO_3^-	$HS^- + 3\ H_2O = HSO_3^- + 6\ H^+ + 6e^-$ $E_0 = E_0^0 - 0.1984\ T\ \text{pH} + 0.0331\ T \log((HSO_3^-)/(HS^-))$
31	−2/+4	H_2S/HSO_3^-	$H_2S + 3\ H_2O = HSO_3^- + 7\ H^+ + 6e^-$ $E_0 = E_0^0 - 0.2315\ T\ \text{pH} + 0.0331\ T \log((HSO_3^-)/(H_2S))$
32	−2/+6	S^{--}/SO_4^{--}	$S^{--} + 4\ H_2O = SO_4^{--} + 8\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.1984\ T\ \text{pH} + 0.0248\ T \log((SO_4^{--})/(S^{--}))$
33	−2/+6	HS^-/SO_4^{--}	$HS^- + 4\ H_2O = SO_4^{--} + 9\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.2232\ T\ \text{pH} + 0.0248\ T \log((SO_4^{--})/(HS^-))$
34	−2/+6	H_2S/SO_4^{--}	$H_2S + 4\ H_2O = SO_4^{--} + 10\ H^+ + 8e^-$ $E_0 = E_0^0 - 0.2480\ T\ \text{pH} + 0.0248\ T \log((SO_4^{--})/(H_2S))$

Appendix 2. (Continued)

	z	EQUILIBRIUM	REACTION EQUILIBRIUM CONDITION
35	−2/+6	H_2S/HSO_4^-	$H_2S + 4\,H_2O = HSO_4^- + 9\,H^+ + 8e^-$ $E_0 = E_0^0 - 0.2232\,T\,pH + 0.0248\,T \log((HSO_4^-)/(H_2S))$
36	−1/+2	$S_2^{--}/S_2O_3^{--}$	$S_2^{--} + 3\,H_2O = S_2O_3^{--} + 6\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0331\,T \log((S_2O_3^{--})/(S_2^{--}))$
37	−0.4/+2	$S_5^{--}/S_2O_3^{--}$	$2\,S_5^{--} + 15\,H_2O = 5\,S_2O_3^{--} + 30\,H^+ + 24e^-$ $E_0 = E_0^0 - 0.2480\,T\,pH + 0.0083\,T \log((S_2O_3^{--})^5/(S_5^{--})^2)$
38	+2/+2.5	$S_2O_3^{--}/S_4O_6^{--}$	$2\,S_2O_3^{--} = S_4O_6^{--} + 2e^-$ $E_0 = E_0^0 - 0.0992\,T \log((S_4O_6^{--})/(S_2O_3^{--})^2)$
39	+2/+3	$S_2O_3^{--}/S_2O_4^{--}$	$S_2O_3^{--} + H_2O = S_2O_4^{--} + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log((S_2O_4^{--})/(S_2O_3^{--}))$
40	+2/+3	$S_2O_3^{--}/HS_2O_4^-$	$S_2O_3^{--} + H_2O = HS_2O_4^- + H^+ + 2e^-$ $E_0 = E_0^0 - 0.0992\,T\,pH + 0.0992\,T \log((HS_2O_4^-)/(S_2O_3^{--}))$
41	+2/+4	$S_2O_3^{--}/SO_3^{--}$	$S_2O_3^{--} + 3\,H_2O = 2\,SO_3^{--} + 6\,H^+ + 4e^-$ $E_0 = E_0^0 - 0.2976\,T\,pH + 0.0496\,T \log((SO_3^{--})/(S_2O_3^{--}))$
42	+2/+4	$S_2O_3^{--}/HSO_3^-$	$S_2O_3^{--} + 3\,H_2O = 2\,HSO_3^- + 4\,H^+ + 4e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0496\,T \log((HSO_3^-)^2/(S_2O_3^{--}))$
43	+2.5/+4	$S_4O_6^{--}/HSO_3^-$	$S_4O_6^{--} + 6\,H_2O = 4\,HSO_3^- + 8\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.2645\,T\,pH + 0.0331\,T \log((HSO_3^-)^4/(S_4O_6^{--}))$
44	+2.5/+4	$S_4O_6^{--}/H_2SO_3$	$S_4O_6^{--} + 6\,H_2O = 4\,H_2SO_3 + 4\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.1323\,T\,pH + 0.0331\,T \log((H_2SO_3)^4/(S_4O_6^{--}))$
45	+3/+4	$S_2O_4^{--}/SO_3^{--}$	$S_2O_4^{--} + 2\,H_2O = 2\,SO_3^{--} + 4\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.3968\,T\,pH + 0.0992\,T \log((SO_3^{--})^2/(S_2O_4^{--}))$
46	+3/+4	$S_2O_4^{--}/HSO_3^-$	$S_2O_4^{--} + 2\,H_2O = 2\,HSO_3^- + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log((HSO_3^-)^2/(S_2O_4^{--}))$
47	+3/+4	$HS_2O_4^-/HSO_3^-$	$HS_2O_4^- + 2\,H_2O = 2\,HSO_3^- + 3\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.2976\,T\,pH + 0.0992\,T \log((HSO_3^-)^2/(HS_2O_4^-))$
48	+3/+4	$HS_2O_4^-/H_2SO_3$	$HS_2O_4^- + 2\,H_2O = 2\,H_2SO_3 + H^+ + 2e^-$ $E_0 = E_0^0 - 0.0992\,T\,pH + 0.0992\,T \log((H_2SO_3)^2/(HS_2O_4^-))$
49	+3/+4	$S_2O_4^{--}/H_2SO_3$	$S_2O_4^{--} + 2\,H_2O = 2\,H_2SO_3 + 2e^-$ $E_0 = E_0^0 + 0.0992\,T \log((H_2SO_3)^2/(S_2O_4^{--}))$
50	+4/+5	$SO_3^{--}/S_2O_6^{--}$	$2\,SO_3^{--} = S_2O_6^{--} + 2e^-$ $E_0 = E_0^0 - 0.0992\,T \log((S_2O_6^{--})/(SO_3^{--})^2)$
51	+4/+5	$HSO_3^-/S_2O_6^{--}$	$2\,HSO_3^- = S_2O_6^{--} + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log((S_2O_6^{--})/(HSO_3^-)^2)$
52	+4/+5	$H_2SO_3/S_2O_6^{--}$	$2\,H_2SO_3 = S_2O_6^{--} + 4\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.3968\,T\,pH + 0.0992\,T \log((S_2O_6^{--})/(H_2SO_3)^2)$
53	+4/+6	SO_3^{--}/SO_4^{--}	$SO_3^{--} + H_2O = SO_4^{--} + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log((SO_4^{--})/(SO_3^{--}))$
54	+4/+6	HSO_3^-/SO_4^{--}	$HSO_3^- + H_2O - SO_4^{--} + 3\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.2976\,T\,pH + 0.0992\,T \log((SO_4^{--})/(HSO_3^-))$
55	+4/+6	HSO_3^-/HSO_4^-	$HSO_3^- + H_2O = HSO_4^- + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log((HSO_4^-)/(HSO_3^-))$
56	+6/+7	$SO_4^{--}/S_2O_8^{--}$	$2\,SO_4^{--} = S_2O_8^{--} + 2e^-$ $E_0 = E_0^0 - 0.0992\,T \log((S_2O_8^{--})/(SO_4^{--})^2)$
57	+6/+7	$HSO_4^-/S_2O_8^{--}$	$2\,HSO_4^- = S_2O_8^{--} + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log((S_2O_8^{--})/(HSO_4^-)^2)$
58	+7/+8	$S_2O_8^{--}/HSO_5^-$	$S_2O_8^{--} + 2\,H_2O = 2\,HSO_5^- + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log((HSO_5^-)^2/(S_2O_8^{--}))$
		REACTIONS INVOLVING ELEMENTARY SULPHUR (SOLID OR LIQUID) AND ONE DISSOLVED SUBSTANCE	
		Electrochemical reactions	
59	−0.4/0	S_5^{--}/S	$S_5^{--} = 5\,S + 2e^-$ $E_0 = E_0^0 - 0.0992\,T \log(S_5^{--})$
60	−2/0	HS^-/S	$HS^- = S + H^+ + 2e^-$ $E_0 = E_0^0 - 0.992\,T\,pH = 0.0992\,T \log(HS^-)$
61	−2/0	H_2S/S	$H_2S = S + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH - 0.0992\,T \log(H_2S)$
62	0/+2	$S/S_5O_6^{--}$	$5\,S + 6\,H_2O = S_5O_6^{--} + 12\,H^+ + 10e^-$ $E_0 = E_0^0 - 0.2381\,T\,pH + 0.0198\,T \log(S_5O_6^{--})$
63	0/+2	$S/S_2O_3^{--}$	$2\,S + 3\,H_2O = S_2O_3^{--} + 6\,H^+ + 4e^-$ $E_0 = E_0^0 - 0.2976\,T\,pH + 0.0496\,T \log(S_2O_3^{--})$
64	0/+2.5	$S/S_4O_6^{--}$	$4\,S + 6\,H_2O = S_4O_6^{--} + 12\,H^+ + 10e^-$ $E_0 = E_0^0 - 0.2381\,T\,pH + 0.0198\,T \log(S_4O_6^{--})$
65	0/+4	S/H_2SO_3	$S + 3\,H_2O = H_2SO_3 + 4\,H^+ + 4e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0496\,T \log(H_2SO_3)$

Appendix 2. (Continued)

	z	EQUILIBRIUM	REACTION EQUILIBRIUM CONDITION
66	0/+5	$S/S_2O_6^{--}$	$2\,S + 6\,H_2O = S_2O_6^{--} + 12\,H^+ + 10e^-$ $E_0 = E_0^0 - 0.2381\,T\,pH + 0.0198\,T \log (S_2O_6^{--})$
67	0/+6	S/SO_4^{--}	$S + 4\,H_2O = SO_4^{--} + 8\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.2645\,T\,pH + 0.0331\,T \log (SO_4^{--})$
68	0/+6	S/HSO_4^-	$S + 4\,H_2O = HSO_4^- + 7\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.2315\,T\,pH + 0.0331\,T \log (HSO_4^-)$

REACTIONS INVOLVING TWO GASEOUS SUBSTANCES

Electrochemical reactions

69	−2/+4	$(H_2S)/(SO_2)$	$(H_2S) + 2\,H_2O = (SO_2) + 6\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0331\,T \log (P_{SO_2}/P_{H_2S})$
70	+4/+6	$(SO_2)/(SO_3)$	$(SO_2) + H_2O = (SO_3) + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T \log (P_{SO_3}/P_{SO_2})$

REACTIONS INVOLVING ONE GASEOUS AND ONE DISSOLVED SUBSTANCES

Chemical reactions

71	−2	$(H_2S)/HS^-$	$(H_2S) = HS^- + H^+$ $\log (HS^-) = -\log K + pH + \log P_{H_2S}$
72	−2	$(H_2S)/H_2S$	$(H_2S) = H_2S$ $\log (H_2S) = -\log K + \log P_{H_2S}$
73	+4	$(SO_2)/SO_3^{--}$	$(SO_2) + H_2O = SO_3^{--} + 2\,H^+$ $\log (SO_3^{--}) = -\log K + 2\,pH + \log P_{SO_2}$
74	+4	$(SO_2)/HSO_3^-$	$(SO_2) + H_2O = HSO_3^- + H^+$ $\log (HSO_3^-) = -\log K + pH + \log P_{SO_2}$
75	+4	$(SO_2)/H_2SO_3$	$(SO_2) + H_2O = H_2SO_3$ $\log (H_2SO_3) = -\log K + \log P_{SO_2}$
76	+6	$(SO_3)/SO_4^{--}$	$(SO_3) + H_2O = SO_4^{--} + 2\,H^+$ $\log (SO_4^{--}) = -\log K + 2\,pH + \log P_{SO_3}$
77	+6	$(SO_3)/HSO_4^-$	$(SO_3) + H_2O = HSO_4^- + H^+$ $\log (HSO_4^-) = -\log K + pH + \log P_{SO_3}$

Electrochemical Reactions

Reactions involving gaseous (H_2S)

78	−2/−0.4	$(H_2S)/S_5^{--}$	$5\,(H_2S) = S_5^{--} + 10\,H^+ + 8e^-$ $E_0 = E_0^0 - 0.2480\,T\,pH + 0.0248\,T \log (S_5^{--}) - 0.1240\,T \log P_{H_2S}$
79	−2/+2	$(H_2S)/S_5O_6^{--}$	$5\,(H_2S) + 6\,H_2O = S_5O_6^{--} + 22\,H^+ + 20e^-$ $E_0 = E_0^0 - 0.2182\,T\,pH + 0.0099\,T \log (S_5O_6^{--}) - 0.0496\,T \log P_{H_2S}$
80	−2/+2	$(H_2S)/S_2O_3^{--}$	$2\,(H_2S) + 3\,H_2O = S_2O_3^{--} + 10\,H^+ + 8e^-$ $E_0 = E_0^0 - 0.2480\,T\,pH + 0.0248\,T \log (S_2O_3^{--}) - 0.0496\,T \log P_{H_2S}$
81	−2/+2	$(H_2S)/HS_2O_3^-$	$2\,(H_2S) + 3\,H_2O = HS_2O_3^- + 9\,H^+ + 8e^-$ $E_0 = E_0^0 - 0.2232\,T\,pH + 0.0248\,T \log (HS_2O_3^-) - 0.0496\,T \log P_{H_2S}$
82	−2/+2.5	$(H_2S)/S_4O_6^{--}$	$4\,(H_2S) + 6\,H_2O = S_4O_6^{--} + 20\,H^+ + 18e^-$ $E_0 = E_0^0 - 0.2204\,T\,pH + 0.0110\,T \log (S_4O_6^{--}) - 0.0441\,T \log P_{H_2S}$
83	−2/+3	$(H_2S)/S_2O_4^{--}$	$2\,(H_2S) + 4\,H_2O = S_2O_4^{--} + 12\,H^+ + 10e^-$ $E_0 = E_0^0 - 0.2381\,T\,pH + 0.0198\,T \log (S_2O_4^{--}) - 0.0397\,T \log P_{H_2S}$
84	−2/+3	$(H_2S)/HS_2O_4^-$	$2\,(H_2S) + 4\,H_2O = HS_2O_4^- + 11\,H^+ + 10e^-$ $E_0 = E_0^0 - 0.2182\,T\,pH + 0.0198\,T \log (HS_2O_4^-) - 0.0397\,T \log P_{H_2S}$
85	−2/+3.33	$(H_2S)/S_2O_6^{--}$	$3\,(H_2S) + 6\,H_2O = S_3O_6^{--} + 18\,H^+ + 16e^-$ $E_0 = E_0^0 - 0.2232\,T\,pH + 0.0124\,T \log (S_3O_6^{--}) - 0.0372\,T \log P_{H_2S}$

Reactions involving gaseous (SO_2)

86	+2/+4	$S_5O_6^{--}/(SO_2)$	$S_5O_6^{--} + 4\,H_2O = 5\,(SO_2) + 8\,H^+ + 10e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH - 0.0248\,T \log (S_5O_6^{--}) + 0.1240\,T \log P_{SO_2}$
87	+2/+4	$S_2O_3^{--}/(SO_2)$	$S_2O_3^{--} + H_2O = 2\,(SO_2) + 2\,H^+ + 4e^-$ $E_0 = E_0^0 - 0.0992\,T\,pH - 0.0496\,T \log (S_2O_3^{--}) + 0.0992\,T \log P_{SO_2}$
88	+2/+4	$HS_2O_3^-/(SO_2)$	$HS_2O_3^- + H_2O = 2\,(SO_2) + 3\,H^+ + 4e^-$ $E_0 = E_0^0 - 0.1488\,T\,pH - 0.0496\,T \log (HS_2O_3^-) + 0.0992\,T \log P_{SO_2}$

Appendix 2. (Continued)

	z	EQUILIBRIUM	REACTION EQUILIBRIUM CONDITION
89	+2.5/+4	$S_4O_6^{--}/(SO_2)$	$S_4O_6^{--} + 2\,H_2O = 4\,(SO_2) + 4\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.1323\,T\,pH - 0.0331\,T\log(S_4O_6^{--}) + 0.1323\,T\log P_{SO_2}$
90	+3/+4	$S_2O_4^{--}/(SO_2)$	$S_2O_4^{--} = 2\,(SO_2) + 2e^-$ $E_0 = E_0^0 - 0.0992\,T\log(S_2O_4^{--}) + 0.1984\,T\log P_{SO_2}$
91	+3/+4	$HS_2O_4^-/(SO_2)$	$HS_2O_4^- = 2\,(SO_2) + H^+ + 2e^-$ $E_0 = E_0^0 - 0.0992\,T\,pH - 0.0992\,T\log(HS_2O_4^-) + 0.1984\,T\log P_{SO_2}$
92	+3.33/+4	$S_3O_6^{--}/(SO_2)$	$S_3O_6^{--} = 3\,(SO_2) + 2e^-$ $E_0 = E_0^0 - 0.0992\,T\log(S_3O_6^{--}) + 0.2976\,T\log P_{SO_2}$

REACTIONS INVOLVING ELEMENTARY SULPHUR (SOLID OR LIQUID) AND ONE GASEOUS SUBSTANCE

Electrochemical reactions

93	−2/0	$(H_2S)/S$	$(H_2S) = S + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH - 0.0992\,T\log P_{H_2S}$
94	0/+2	$S/(SO)$	$S + H_2O = (SO) + 2\,H^+ + 2e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0992\,T\log P_{SO}$
95	0/+4	$S/(SO_2)$	$S + 2\,H_2O = (SO_2) + 4\,H^+ + 4e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0496\,T\log P_{SO_2}$
96	0/+6	$S/(SO_3)$	$S + 3\,H_2O = (SO_3) + 6\,H^+ + 6e^-$ $E_0 = E_0^0 - 0.1984\,T\,pH + 0.0331\,T\log P_{SO_3}$

REACTIONS OF THE SOLVENT

a	Reduction of water in gaseous (H_2)	$(H_2) = 2\,H^+ + 2e^-$
b	Oxidation of water in gaseous (O_2)	$H_2O = (O_2) + 4\,H^+ + 4e^-$
c	Dissociation of liquid water	$H_2O = H^+ + OH^-$
d	Vaporization of liquid water	$H_2O = (H_2O)$

The following table section relates to the influence of temperature on the equilibria of these four reactions:

$n°$		T°C: 0	25	50	75	100	125	150
a	*Equilibrium $H_2O/(H_2)$*							
6, p. 60	E_A (mV) for P_{H_2} = 1 atm	0	0	0	0	0	0	0
	$E_{A'}$ (mV) for $P_{H_2} = P_{H_2O}$	60.1	44.5	29.3	14.5	0	−14.0	−28.6
b	*Equilibrium $H_2O/(O_2)$*							
6, p. 60	E_B (mV) for P_{O_2} = 1 atm	1250.4	1229.1	1208.1	1187.1	1167.0	1146.9	1126.1
	$E_{B'}$ (mV) for $P_{O_2} = P_{H_2O}$	1220.4	1206.9	1193.5	1180.2	1167.0	1153.9	1140.4
c	*Equilibrium $H_2O/H^+ + OH^-$*							
6, p. 60	log $(H^+)(OH^-)$	−14.99	−14.01	−13.26	−12.69	−12.25	−11.94	−11.72
	pH of neutrality	7.50	7.00	6.63	6.35	6.13	5.97	5.26
d	*Equilibrium $H_2O/(H_2O)$*							
6, p. 60	log P_{H_2O}	−2.2200	−1.5050	−0.9146	−0.4198	0.0000	0.3600	0.6719
	P_{H_2O} (atm)	0.0060	0.0317	0.1217	0.3804	1.0000	2.2909	4.6979
	Slope of the isobar lines for (O_2) and (H_2) in the E-pH (mV/pH) diagrams	−54.17	−59.13	−64.04	−69.05	−74.01	−78.97	−83.93

Appendix 3. Equilibrium conditions of the ninety-six reactions considered, from 0 to 150°C

T°C	1. H_2S/HS^-	2. HS^-/S^{--}	3. $H_2S_2O_3^-/HS_2O_3^-$
0	$\log((HS^-)/(H_2S)) = -7.428 + pH$	$\log((S^{--})/(HS^-))$	$\log((H_2S_2O_3)/(HS_2O_3^-))$
25	$= -6.992 + pH$	$= -14.006 + pH$	$= -1.944 + pH$
75	$= -6.699 + pH$		
50	$= -6.567 + pH$		
100	$= -6.488 + pH$		
125	$= -6.621 + pH$		
150	$= -6.505 + pH$		

Appendix 3. (Continued)

T°C	4. $HS_2O_3^-/S_2O_3^{--}$	5. $S_5O_6^{--}/HS_2O_3^-$	6. $S_5O_6^{--}/S_2O_3$
0	$\log((S_2O_3^{--})/(HS_2O_3^-)) = -1.513 + pH$	$\log((HS_2O_3^-)^5/(S_5O_6^{--})^2) = 2.137 + pH$	$\log((S_2O_3^{--})^5/(S_5O_6^{--})^2) = -5.428 + 6\,pH$
25	$= -1.723 + pH$	$= 6.002 + pH$	$= -2.615 + 6\,pH$
50	$= -1.976 + pH$	$= 9.297 + pH$	$= -0.582 + 6\,pH$
75	$= -2.273 + pH$	$= 12.287 + pH$	$= +0.920 + 6\,pH$
100	$= -2.590 + pH$	$= 14.962 + pH$	$= +2.013 + 6\,pH$
125	$= -2.921 + pH$	$= 17.387 + pH$	$= +2.780 + 6\,pH$
150	$= -3.265 + pH$	$= 19.683 + pH$	$= +3.357 + 6\,pH$

	7. $H_2S_2O_3/S_5O_6^{--}$	8. $HS_2O_4^-/S_2O_4^{--}$	9. H_2SO_3/HSO_3^-
0	$\log((S_5O_6^{--})^2/(H_2S_2O_3)^5)$	$\log((S_2O_4^{--})/(HS_2O_4^-))$	$\log((HSO_3^-)/(H_2SO_3)) = -2.760 + pH$
25	$= -15.725 + 4\,pH$	$= 1.534 + pH$	$= -1.861 + pH$
50			$= -1.183 + pH$
75			$= -0.661 + pH$
100			$= -0.258 + pH$
125			$= -0.050 + pH$
150			$= -0.407 + pH$

	10. HSO_3^-/SO_3^{--}	11. HSO_4^-/SO_4^{--}	12. S^{--}/S_2^{--}
0	$\log((SO_3^{--})/(HSO_3^{--})) = -7.135 + pH$	$\log((SO_4^{--})/(HSO_4^-)) = -1.721 + pH$	$E =$
25	$= -7.210 + pH$	$= -1.981 + pH$	$-0.540 - 0.0295 \log c$
50	$= -7.384 + pH$	$= -2.303 + pH$	
75	$= -7.610 + pH$	$= -2.649 + pH$	
100	$= -7.872 + pH$	$= -3.006 + pH$	
125	$= -8.158 + pH$	$= -3.369 + pH$	
150	$= -8.459 + pH$	$= -3.732 + pH$	

	13. S_2^{--}/S_3^{--}	14. S_3^{--}/S_4^{--}	15. S_4^{--}/S_5^{--}
0	$E = -0.462 - 0.0271 \log c$	$E = -0.438 - 0.0271 \log c$	$E = -0.409 - 0.0271 \log c$
25	$-0.466 - 0.0295 \log c$	$-0.441 - 0.0295 \log c$	$-0.412 - 0.0295 \log c$
50	$-0.472 - 0.0320 \log c$	$-0.448 - 0.0320 \log c$	$-0.418 - 0.0320 \log c$
75	$-0.482 - 0.0345 \log c$	$-0.457 - 0.0345 \log c$	$-0.427 - 0.0345 \log c$
100	$-0.494 - 0.0370 \log c$	$-0.469 - 0.0370 \log c$	$-0.439 - 0.0370 \log c$
125	$-0.509 - 0.0395 \log c$	$-0.483 - 0.0395 \log c$	$-0.453 - 0.0395 \log c$
150	$-0.526 - 0.0419 \log c$	$-0.500 - 0.0419 \log c$	$-0.469 - 0.0419 \log c$

	16. HS^-/S_2^{--}	17. HS^-/S_3^{--}	18. HS^-/S_4^{--}
0	$E = 0.275 - 0.0541\,pH - 0.0271 \log c$	$E = 0.091 - 0.0406\,pH - 0.0271 \log c$	$E = 0.032 - 0.0361\,pH - 0.0271 \log c$
25	$0.289 - 0.0591\,pH - 0.0295 \log c$	$0.100 - 0.0443\,pH - 0.0295 \log c$	$0.040 - 0.0394\,pH - 0.0295 \log c$
50	$0.304 - 0.0640\,pH - 0.0320 \log c$	$0.110 - 0.0481\,pH - 0.0320 \log c$	$0.048 - 0.0427\,pH - 0.0320 \log c$
75	$0.317 - 0.0691\,pH - 0.0345 \log c$	$0.117 - 0.0517\,pH - 0.0345 \log c$	$0.053 - 0.0460\,pH - 0.0345 \log c$
100	$0.333 - 0.0740\,pH - 0.0370 \log c$	$0.126 - 0.0555\,pH - 0.0370 \log c$	$0.060 - 0.0493\,pH - 0.0370 \log c$
125	$0.349 - 0.0790\,pH - 0.0395 \log c$	$0.134 - 0.0592\,pH - 0.0395 \log c$	$0.066 - 0.0526\,pH - 0.0395 \log c$
150	$0.366 - 0.0839\,pH - 0.0419 \log c$	$0.143 - 0.0629\,pH - 0.0419 \log c$	$0.071 - 0.0559\,pH - 0.0419 \log c$

	19. HS^-/S_5^{--}	20. $S^{--}/S_2O_3^{--}$	21. $HS^-/S_2O_3^{--}$
0	$E = 0.004 - 0.0338\,pH - 0.0271 \log c$	$E =$	$E = 0.228 - 0.0541\,pH - 0.0068 \log c$
25	$0.011 - 0.0369\,pH - 0.0295 \log c$	$0.007 - 0.0443\,pH - 0.0074 \log c$	$0.214 - 0.0591\,pH - 0.0074 \log c$
50	$0.019 - 0.0400\,pH - 0.0320 \log c$		$0.201 - 0.0640\,pH - 0.0080 \log c$
75	$0.023 - 0.0431\,pH - 0.0345 \log c$		$0.187 - 0.0691\,pH - 0.0086 \log c$
100	$0.029 - 0.0462\,pH - 0.0370 \log c$		$0.174 - 0.0740\,pH - 0.0092 \log c$
125	$0.033 - 0.0493\,pH - 0.0395 \log c$		$0.162 - 0.0790\,pH - 0.0099 \log c$
150	$0.037 - 0.0524\,pH - 0.0419 \log c$		$0.149 - 0.0839\,pH - 0.0105 \log c$

	22. $H_2S/S_2O_3^{--}$	23. $H_2S/HS_2O_3^-$	24. $H_2S/S_5O_6^{--}$
0	$E = 0.328 - 0.0677\,pH - 0.0068 \log c$	$E = 0.318 - 0.0609\,pH - 0.0068 \log c$	$E = 0.322 - 0.0595\,pH - 0.0108 \log c$
25	$0.317 - 0.0739\,pH - 0.0074 \log c$	$0.304 - 0.0665\,pH - 0.0074 \log c$	$0.314 - 0.0650\,pH - 0.0029 \log c$
50	$0.308 - 0.0801\,pH - 0.0080 \log c$	$0.292 - 0.0721\,pH - 0.0080 \log c$	$0.309 - 0.0705\,pH - 0.0032 \log c$
75	$0.301 - 0.0863\,pH - 0.0086 \log c$	$0.281 - 0.0776\,pH - 0.0086 \log c$	$0.304 - 0.0795\,pH - 0.0034 \log c$
100	$0.294 - 0.0925\,pH - 0.0092 \log c$	$0.270 - 0.0832\,pH - 0.0092 \log c$	$0.300 - 0.0814\,pH - 0.0037 \log c$
125	$0.293 - 0.0987\,pH - 0.0099 \log c$	$0.264 - 0.0888\,pH - 0.0099 \log c$	$0.300 - 0.0868\,pH - 0.0039 \log c$
150	$0.285 - 0.1049\,pH - 0.0105 \log c$	$0.251 - 0.0944\,pH - 0.0105 \log c$	$0.294 - 0.0923\,pH - 0.0042 \log c$

	25. $H_2S/S_4O_6^{--}$	26. $S^{--}/S_2O_4^{--}$	27. $S^{--}/HS_2O_4^-$
0	$E = 0.297 - 0.0601\,pH - 0.0090 \log c$	$E =$	$E =$
25	$0.285 - 0.0657\,pH - 0.0098 \log c$	$0.170 - 0.0473\,pH - 0.0054 \log c$	$0.180 - 0.0414\,pH - 0.0054 \log c$
50	$0.275 - 0.0712\,pH - 0.0106 \log c$		
75	$0.266 - 0.0767\,pH - 0.0115 \log c$		
100	$0.258 - 0.0822\,pH - 0.0123 \log c$		
125	$0.254 - 0.0877\,pH - 0.0131 \log c$		
150	$0.244 - 0.0932\,pH - 0.0139 \log c$		

Appendix 3. (Continued)

T°C	28. S^{--}/SO_3^{--}	29. S^{--}/HSO_3^-	29a. HS^-/SO_3^{--}
0	$E =$	$E =$	$E = 0.386 - 0.0632$ pH
25	$0.230 - 0.0591$ pH	$0.159 - 0.0492$ pH	$0.368 - 0.0690$ pH
50			$0.351 - 0.0748$ pH
75			$0.336 - 0.0806$ pH
100			$0.321 - 0.0863$ pH
125			$0.308 - 0.0921$ pH
150			$0.294 - 0.0979$ pH

	30. HS^-/HSO_3^-	31. H_2S/HSO_3^-	32. S^{--}/SO_4^{--}
0	$E = 0.321 - 0.0541$ pH	$E = 0.388 - 0.0632$ pH	$E =$
25	$0.297 - 0.0591$ pH	$0.366 - 0.0690$ pH	$0.146 - 0.0591$ pH
50	$0.273 - 0.0640$ pH	$0.344 - 0.0748$ pH	
75	$0.248 - 0.0691$ pH	$0.324 - 0.0805$ pH	
100	$0.224 - 0.0740$ pH	$0.304 - 0.0863$ pH	
125	$0.200 - 0.0790$ pH	$0.287 - 0.0921$ pH	
150	$0.175 - 0.0839$ pH	$0.266 - 0.0979$ pH	

	33. HS^-/SO_4^{--}	34. H_2S/SO_4^{--}	35. H_2S/HSO_4^-
0	$E = 0.269 - 0.0609$ pH	$E = 0.319 - 0.0677$ pH	$E = 0.308 - 0.0609$ pH
25	$0.249 - 0.0665$ pH	$0.301 - 0.0739$ pH	$0.286 - 0.0665$ pH
50	$0.230 - 0.0721$ pH	$0.284 - 0.0801$ pH	$0.265 - 0.0721$ pH
75	$0.211 - 0.0776$ pH	$0.268 - 0.0863$ pH	$0.245 - 0.0776$ pH
100	$0.193 - 0.0832$ pH	$0.253 - 0.0925$ pH	$0.226 - 0.0832$ pH
125	$0.176 - 0.0888$ pH	$0.241 - 0.0987$ pH	$0.208 - 0.0888$ pH
150	$0.158 - 0.0944$ pH	$0.226 - 0.1049$ pH	$0.187 - 0.0944$ pH

	36. $S_2^{--}/S_2O_3^{--}$	37. $S_5^{--}/S_2O_3^{--}$	38. $S_2O_3^{--}/S_2O_4^{--}$
0	$E = 0.318 - 0.0812$ pH	$E = 0.377 - 0.0677$ pH $+ 0.0068 \log c$	$E = 0.850 - 0.0541$ pH
25	$0.284 - 0.0887$ pH	$0.348 - 0.0739$ pH $+ 0.0074 \log c$	$0.826 - 0.0591$ pH
50	$0.249 - 0.0961$ pH	$0.321 - 0.0801$ pH $+ 0.0080 \log c$	$0.801 - 0.0640$ pH
75	$0.216 - 0.1035$ pH	$0.296 - 0.0863$ pH $+ 0.0086 \log c$	$0.777 - 0.0691$ pH
100	$0.182 - 0.1110$ pH	$0.272 - 0.0925$ pH $+ 0.0093 \log c$	$0.753 - 0.0740$ pH
125	$0.149 - 0.1184$ pH	$0.248 - 0.0987$ pH $- 0.0099 \log c$	$0.729 - 0.0790$ pH
150	$0.115 - 0.1259$ pH	$0.223 - 0.1049$ pH $- 0.0105 \log c$	$0.705 - 0.0839$ pH

	39. $S_2O_3^{--}/HS_2O_4^-$	40. $S_2O_3^{--}/S_4O_6^{--}$	41. $S_2O_3^{--}/SO_3^{--}$
0	$E =$	$E =$	$E = 0.701 - 0.0812$ pH $+ 0.0135 \log c$
25	$0.871 - 0.0295$ pH	$0.045 - 0.0271 \log c$	$0.676 - 0.0887$ pH $+ 0.0148 \log c$
50		$0.033 - 0.0295 \log c$	$0.653 - 0.0961$ pH $+ 0.0160 \log c$
75		$0.016 - 0.0320 \log c$	$0.633 - 0.1035$ pH $+ 0.0173 \log c$
100		$-0.005 - 0.0345 \log c$	$0.615 - 0.1110$ pH $+ 0.0185 \log c$
125		$-0.028 - 0.0370 \log c$	$0.599 - 0.1184$ pH $+ 0.0197 \log c$
150		$-0.054 - 0.0395 \log c$	$0.582 - 0.1259$ pH $+ 0.0210 \log c$
		$-0.083 - 0.0419 \log c$	

	42. $S_2O_3^{--}/HSO_3^-$	43. $S_4O_6^{--}/HSO_3^-$	44. $S_4O_6^{--}/H_2SO_3$
0	$E = 0.508 - 0.0541$ pH $+ 0.0135 \log c$	$E = 0.662 - 0.0722$ pH $+ 0.0271 \log c$	$E = 0.562 - 0.0361$ pH $+ 0.0271 \log c$
25	$0.463 - 0.0591$ pH $+ 0.0148 \log c$	$0.606 - 0.0788$ pH $+ 0.0295 \log c$	$0.533 - 0.0394$ pH $+ 0.0295 \log c$
50	$0.417 - 0.0640$ pH $+ 0.0160 \log c$	$0.551 - 0.0854$ pH $+ 0.0320 \log c$	$0.501 - 0.0427$ pH $+ 0.0320 \log c$
75	$0.371 - 0.0691$ pH $+ 0.0173 \log c$	$0.495 - 0.0920$ pH $+ 0.0345 \log c$	$0.465 - 0.0460$ pH $+ 0.0345 \log c$
100	$0.324 - 0.0740$ pH $+ 0.0185 \log c$	$0.441 - 0.0986$ pH $+ 0.0370 \log c$	$0.428 - 0.0493$ pH $+ 0.0370 \log c$
125	$0.276 - 0.0790$ pH $+ 0.0197 \log c$	$0.387 - 0.1053$ pH $+ 0.0395 \log c$	$0.390 - 0.0526$ pH $+ 0.0395 \log c$
150	$0.227 - 0.0839$ pH $+ 0.0210 \log c$	$0.331 - 0.1118$ pH $+ 0.0419 \log c$	$0.354 - 0.0559$ pH $+ 0.0419 \log c$

	45. $S_2O_4^{--}/SO_3^{--}$	46. $S_2O_4^{--}/HSO_3^-$	47. $HS_2O_4^-/HSO_3^-$
0	$E = 0.552 - 0.1083$ pH $+ 0.0271 \log c$	$E = 0.166 - 0.0541$ pH $+ 0.0271 \log c$	$E =$ $- 0.0812$ pH
25	$0.526 - 0.1182$ pH $+ 0.0295 \log c$	$0.100 - 0.0591$ pH $+ 0.0295 \log c$	$0.055 - 0.0887$ pH $+ 0.0295 \log c$
50	$0.506 - 0.1281$ pH $+ 0.0320 \log c$	$0.033 - 0.0640$ pH $+ 0.0320 \log c$	$- 0.0961$ pH
75	$0.490 - 0.1381$ pH $+ 0.0345 \log c$	$-0.036 - 0.0691$ pH $+ 0.0345 \log c$	$- 0.1036$ pH
100	$0.477 - 0.1480$ pH $+ 0.0370 \log c$	$-0.105 - 0.0740$ pH $+ 0.0370 \log c$	$- 0.1110$ pH
125	$0.468 - 0.1579$ pH $+ 0.0395 \log c$	$-0.176 - 0.0790$ pH $+ 0.0395 \log c$	$- 0.1184$ pH
150	$0.460 - 0.1678$ pH $+ 0.0419 \log c$	$-0.250 - 0.0839$ pH $+ 0.0419 \log c$	$- 0.1259$ pH

	48. $HS_2O_4^-/H_2SO_3$	49. $S_2O_4^{--}/H_2SO_3$	50. $SO_3^{--}/S_2O_6^{--}$
0	$E =$ $- 0.0271$ pH	$E =$ $0.016 + 0.0271 \log c$	$E =$ $0.056 - 0.0271 \log c$
25	$-0.055 - 0.0295$ pH $+ 0.0295 \log c$	$-0.010 + 0.0295 \log c$	$0.035 - 0.0295 \log c$
50	$- 0.0320$ pH	$-0.043 + 0.0320 \log c$	$0.008 - 0.0320 \log c$
75	$- 0.0345$ pH	$-0.081 + 0.0345 \log c$	$-0.021 - 0.0345 \log c$
100	$- 0.0370$ pH	$-0.125 + 0.0370 \log c$	$-0.054 - 0.0370 \log c$
125	$- 0.0395$ pH	$-0.172 + 0.0395 \log c$	$-0.091 - 0.0395 \log c$
150	$- 0.0419$ pH	$-0.215 + 0.0419 \log c$	$-0.130 - 0.0419 \log c$

Appendix 3. (Continued)

T°C	51. $HSO_3^-/S_2O_6^{--}$	52. $H_2SO_3/S_2O_6^{--}$	53. SO_3^{--}/SO_4^{--}
0	$E = 0.442 - 0.0541\ pH - 0.0271\ \log c$	$E = 0.592 - 0.1083\ pH - 0.0271\ \log c$	$E = -0.080 - 0.0541\ pH$
25	$0.461 - 0.0591\ pH - 0.0295\ \log c$	$0.571 - 0.1182\ pH - 0.0295\ \log c$	$-0.107 - 0.0591\ pH$
50	$0.482 - 0.0640\ pH - 0.0320\ \log c$	$0.558 - 0.1281\ pH - 0.0320\ \log c$	$-0.135 - 0.0640\ pH$
75	$0.504 - 0.0691\ pH - 0.0345\ \log c$	$0.550 - 0.1381\ pH - 0.0345\ \log c$	$-0.162 - 0.0691\ pH$
100	$0.528 - 0.0740\ pH - 0.0370\ \log c$	$0.547 - 0.1480\ pH - 0.0370\ \log c$	$-0.190 - 0.0740\ pH$
125	$0.554 - 0.0790\ pH - 0.0395\ \log c$	$0.550 - 0.1579\ pH - 0.0395\ \log c$	$-0.218 - 0.0790\ pH$
150	$0.580 - 0.0839\ pH - 0.0419\ \log c$	$0.546 - 0.1678\ pH - 0.0419\ \log c$	$-0.247 - 0.0839\ pH$
	54. HSO_3^-/SO_4^{--}	55. HSO_3^-/HSO_4^-	56. $SO_4^{--}/S_2O_8^{--}$
0	$E = 0.113 - 0.0812\ pH$	$E = 0.067 - 0.0541\ pH$	$E = 1.961 - 0.0271\ \log c$
25	$0.106 - 0.0887\ pH$	$0.047 - 0.0591\ pH$	$1.937 - 0.0295\ \log c$
50	$0.102 - 0.0961\ pH$	$0.028 - 0.0640\ pH$	$1.909 - 0.0320\ \log c$
75	$0.100 - 0.1035\ pH$	$0.009 - 0.0691\ pH$	$1.876 - 0.0345\ \log c$
100	$0.101 - 0.1110\ pH$	$-0.010 - 0.0740\ pH$	$1.841 - 0.0370\ \log c$
125	$0.104 - 0.1184\ pH$	$-0.029 - 0.0790\ pH$	$1.802 - 0.0395\ \log c$
150	$0.108 - 0.1259\ pH$	$-0.049 - 0.0839\ pH$	$1.761 - 0.0419\ \log c$
	57. $HSO_4^-/S_2O_8^{--}$	58. $S_2O_8^{--}/HSO_5^-$	59. S_5^{--}/S
0	$E = 2.055 - 0.0541\ pH - 0.0271\ \log c$	$E = 1.693 - 0.0541\ pH + 0.0271\ \log c$	$E = -0.379 - 0.0271\ \log c$
25	$2.055 - 0.0591\ pH - 0.0295\ \log c$	$1.629 - 0.0591\ pH + 0.0295\ \log c$	$-0.361 - 0.0295\ \log c$
50	$2.056 - 0.0640\ pH - 0.0320\ \log c$	$1.562 - 0.0640\ pH + 0.0320\ \log c$	$-0.345 - 0.0320\ \log c$
75	$2.059 - 0.0691\ pH - 0.0345\ \log c$	$1.493 - 0.0691\ pH + 0.0345\ \log c$	$-0.333 - 0.0345\ \log c$
100	$2.063 - 0.0740\ pH - 0.0370\ \log c$	$1.421 - 0.0740\ pH + 0.0370\ \log c$	$-0.319 - 0.0370\ \log c$
125	$2.068 - 0.0790\ pH - 0.0395\ \log c$	$1.348 - 0.0790\ pH + 0.0395\ \log c$	$-0.308 - 0.0395\ \log c$
150	$2.075 - 0.0839\ pH - 0.0419\ \log c$	$1.271 - 0.0839\ pH + 0.0419\ \log c$	$-0.296 - 0.0419\ \log c$
	60. HS^-/S	61. H_2S/S	62. $S/S_5O_6^{--}$
0	$E = -0.071 - 0.0271\ pH - 0.0271\ \log c$	$E = 0.130 - 0.0542\ pH - 0.0271\ \log c$	$E = 0.516 - 0.0648\ pH + 0.0054\ \log c$
25	$-0.062 - 0.0295\ pH - 0.0295\ \log c$	$0.144 - 0.0591\ pH - 0.0295\ \log c$	$0.486 - 0.0709\ pH + 0.0059\ \log c$
50	$-0.052 - 0.0320\ pH - 0.0320\ \log c$	$0.162 - 0.0640\ pH - 0.0320\ \log c$	$0.458 - 0.0768\ pH + 0.0064\ \log c$
75	$-0.046 - 0.0345\ pH - 0.0345\ \log c$	$0.181 - 0.0690\ pH - 0.0345\ \log c$	$0.429 - 0.0829\ pH + 0.0069\ \log c$
100	$-0.039 - 0.0370\ pH - 0.0370\ \log c$	$0.201 - 0.0740\ pH - 0.0370\ \log c$	$0.401 - 0.0888\ pH + 0.0074\ \log c$
125	$-0.033 - 0.0395\ pH - 0.0395\ \log c$	$0.228 - 0.0790\ pH - 0.0395\ \log c$	$0.374 - 0.0948\ pH + 0.0079\ \log c$
150	$-0.028 - 0.0419\ pH - 0.0419\ \log c$	$0.245 - 0.0838\ pH - 0.0419\ \log c$	$0.346 - 0.1007\ pH + 0.0084\ \log c$
	63. $S/S_2O_3^{--}$	64. $S/S_4O_6^{--}$	65. S/H_2SO_3
0	$E = 0.531 - 0.0812\ pH + 0.0148\ \log c$	$E = 0.431 - 0.0648\ pH + 0.0054\ \log c$	$E = 0.480 - 0.0542\ pH + 0.0136\ \log c$
25	$0.494 - 0.0887\ pH + 0.0148\ \log c$	$0.401 - 0.0709\ pH + 0.0059\ \log c$	$0.449 - 0.0591\ pH + 0.0148\ \log c$
50	$0.459 - 0.0960\ pH + 0.0160\ \log c$	$0.369 - 0.0768\ pH + 0.0064\ \log c$	$0.416 - 0.0640\ pH + 0.0160\ \log c$
75	$0.426 - 0.1037\ pH + 0.0173\ \log c$	$0.337 - 0.0829\ pH + 0.0069\ \log c$	$0.384 - 0.0690\ pH + 0.0173\ \log c$
100	$0.394 - 0.1110\ pH + 0.0185\ \log c$	$0.307 - 0.0888\ pH + 0.0074\ \log c$	$0.351 - 0.0740\ pH + 0.0185\ \log c$
125	$0.363 - 0.1185\ pH + 0.0198\ \log c$	$0.277 - 0.0948\ pH + 0.0079\ \log c$	$0.318 - 0.0790\ pH + 0.0198\ \log c$
150	$0.329 - 0.1259\ pH + 0.0210\ \log c$	$0.246 - 0.1007\ pH + 0.0084\ \log c$	$0.285 - 0.0838\ pH + 0.0210\ \log c$
	66. $S/S_2O_6^{--}$	67. S/SO_4^{--}	68. S/HSO_4^-
0	$E = 0.504 - 0.0648\ pH + 0.0054\ \log c$	$E = 0.383 - 0.0722\ pH + 0.0090\ \log c$	$E = 0.367 - 0.0633\ pH + 0.0090\ \log c$
25	$0.475 - 0.0710\ pH + 0.0059\ \log c$	$0.359 - 0.0788\ pH + 0.0098\ \log c$	$0.333 - 0.0689\ pH + 0.0098\ \log c$
50	$0.447 - 0.0768\ pH + 0.0064\ \log c$	$0.324 - 0.0853\ pH + 0.0107\ \log c$	$0.300 - 0.0746\ pH + 0.0107\ \log c$
75	$0.419 - 0.0829\ pH + 0.0069\ \log c$	$0.297 - 0.0920\ pH + 0.0115\ \log c$	$0.267 - 0.0802\ pH + 0.0115\ \log c$
100	$0.392 - 0.0888\ pH + 0.0074\ \log c$	$0.271 - 0.0986\ pH + 0.0123\ \log c$	$0.238 - 0.0864\ pH + 0.0123\ \log c$
125	$0.364 - 0.0948\ pH + 0.0079\ \log c$	$0.246 - 0.1053\ pH + 0.0132\ \log c$	$0.201 - 0.0922\ pH + 0.0132\ \log c$
150	$0.340 - 0.1007\ pH + 0.0084\ \log c$	$0.220 - 0.1117\ pH + 0.0140\ \log c$	$0.168 - 0.1397\ pH + 0.0140\ \log c$
	69. $(H_2S)/(SO_2)$	70. $(SO_2)/(SO_3)$	71. $(H_2S)/HS^-$
0	$E = 0.371 - 0.0542\ pH + 0.0090\ \log P_{SO_2}/P_{H_2S}$	$E = 0.870 - 0.0542\ pH + 0.0271\ \log P_{SO_3}/P_{SO_2}$	$\log (HS^-) = -8.884 + pH + \log P_{H_2S}$
25	$0.358 - 0.0591\ pH + 0.0098\ \log P_{SO_2}/P_{H_2S}$	$0.862 - 0.0591\ pH + 0.0295\ \log P_{SO_3}/P_{SO_2}$	$-7.946 + pH + \log P_{H_2S}$
50	$0.346 - 0.0640\ pH + 0.0107\ \log P_{SO_2}/P_{H_2S}$	$0.853 - 0.0640\ pH + 0.0320\ \log P_{SO_3}/P_{SO_2}$	$-7.203 + pH + \log P_{H_2S}$
75	$0.333 - 0.0690\ pH + 0.0115\ \log P_{SO_2}/P_{H_2S}$	$0.844 - 0.0690\ pH + 0.0345\ \log P_{SO_3}/P_{SO_2}$	$-6.639 + pH + \log P_{H_2S}$
100	$0.321 - 0.0740\ pH + 0.0123\ \log P_{SO_2}/P_{H_2S}$	$0.833 - 0.0740\ pH + 0.0370\ \log P_{SO_3}/P_{SO_2}$	$-6.147 + pH + \log P_{H_2S}$
125	$0.309 - 0.0790\ pH + 0.0132\ \log P_{SO_2}/P_{H_2S}$	$0.825 - 0.0790\ pH + 0.0395\ \log P_{SO_3}/P_{SO_2}$	$-5.738 + pH + \log P_{H_2S}$
150	$0.296 - 0.0838\ pH + 0.0140\ \log P_{SO_2}/P_{H_2S}$	$0.821 - 0.0838\ pH + 0.0419\ \log P_{SO_3}/P_{SO_2}$	$-5.362 + pH + \log P_{H_2S}$

Appendix 3. (Continued)

T°C	72. $(H_2S)/H_2S$	73. $(SO_2)/SO_3^{--}$	74. $(SO_2)/HSO_3^-$
0	$\log (H_2S) = -1.414 + \log P_{H_2S}$	$\log (SO_3^{--}) = -10.393 + 2\,pH + \log P_{SO_2}$	$\log (HSO_3^-) = -3.258 + pH + \log P_{SO_2}$
25	$-0.954 + \log P_{H_2S}$	$-8.895 + 2\,pH + \log P_{SO_2}$	$-1.685 + pH + \log P_{SO_2}$
50	$-0.504 + \log P_{H_2S}$	$-7.753 + 2\,pH + \log P_{SO_2}$	$-0.369 + pH + \log P_{SO_2}$
75	$-0.072 + \log P_{H_2S}$	$-6.862 + 2\,pH + \log P_{SO_2}$	$0.749 + pH + \log P_{SO_2}$
100	$0.341 + \log P_{H_2S}$	$-6.163 + 2\,pH + \log P_{SO_2}$	$1.708 + pH + \log P_{SO_2}$
125	$0.883 + \log P_{H_2S}$	$-5.621 + 2\,pH + \log P_{SO_2}$	$2.537 + pH + \log P_{SO_2}$
150	$1.143 + \log P_{H_2S}$	$-5.177 + 2\,pH + \log P_{SO_2}$	$3.281 + pH + \log P_{SO_2}$

	75. $(SO_2)/H_2SO_3$	76. $(SO_3)/SO_4^{--}$	77. $(SO_3)/HSO_4^-$
0	$\log (H_2SO_3) = -0.498 + \log P_{SO_2}$	$\log (SO_4^{--}) = 24.707 + 2\,pH + \log P_{SO_3}$	$\log (HSO_4^-) = 26.428 + pH + \log P_{SO_3}$
25	$0.176 + \log P_{SO_2}$	$23.874 + 2\,pH + \log P_{SO_3}$	$25.855 + pH + \log P_{SO_3}$
50	$0.814 + \log P_{SO_2}$	$23.064 + 2\,pH + \log P_{SO_3}$	$25.367 + pH + \log P_{SO_3}$
75	$1.409 + \log P_{SO_2}$	$22.298 + 2\,pH + \log P_{SO_3}$	$24.947 + pH + \log P_{SO_3}$
100	$1.966 + \log P_{SO_2}$	$21.495 + 2\,pH + \log P_{SO_3}$	$24.501 + pH + \log P_{SO_3}$
125	$2.487 + \log P_{SO_2}$	$20.805 + 2\,pH + \log P_{SO_3}$	$24.175 + pH + \log P_{SO_3}$
150	$2.874 + \log P_{SO_2}$	$20.277 + 2\,pH + \log P_{SO_3}$	$24.008 + pH + \log P_{SO_3}$

	78. $(H_2S)/S_5^{--}$	79. $(H_2S)/S_5O_6^{--}$
0	$E = 0.302 - 0.0677\,pH + 0.00677 \log c - 0.0338 \log P_{H_2S}$	$E = 0.342 - 0.0590\,pH + 0.00270 \log c - 0.0135 \log P_{H_2S}$
25	$0.303 - 0.0739\,pH + 0.00739 \log c - 0.0369 \log P_{H_2S}$	$0.329 - 0.0650\,pH + 0.00296 \log c - 0.0148 \log P_{H_2S}$
50	$0.305 - 0.0801\,pH + 0.00801 \log c - 0.0400 \log P_{H_2S}$	$0.317 - 0.0705\,pH + 0.00320 \log c - 0.0160 \log P_{H_2S}$
75	$0.308 - 0.0863\,pH + 0.00863 \log c - 0.0431 \log P_{H_2S}$	$0.305 - 0.0759\,pH + 0.00345 \log c - 0.0173 \log P_{H_2S}$
100	$0.311 - 0.0925\,pH + 0.00925 \log c - 0.0462 \log P_{H_2S}$	$0.295 - 0.0814\,pH + 0.00369 \log c - 0.0185 \log P_{H_2S}$
125	$0.315 - 0.0987\,pH + 0.00987 \log c - 0.0493 \log P_{H_2S}$	$0.284 - 0.0868\,pH + 0.00394 \log c - 0.0197 \log P_{H_2S}$
150	$0.317 - 0.1049\,pH + 0.01049 \log c - 0.0524 \log P_{H_2S}$	$0.272 - 0.0923\,pH + 0.00419 \log c - 0.0210 \log P_{H_2S}$

	80. $(H_2S)/S_2O_3^{--}$	81. $(H_2S)/HS_2O_3^-$
0	$E = 0.349 - 0.0677\,pH + 0.00677 \log c - 0.0135 \log P_{H_2S}$	$E = 0.339 - 0.0609\,pH + 0.0068 \log c - 0.0135 \log P_{H_2S}$
25	$0.333 - 0.0739\,pH + 0.00739 \log c - 0.0148 \log P_{H_2S}$	$0.320 - 0.0665\,pH + 0.0074 \log c - 0.0148 \log P_{H_2S}$
50	$0.318 - 0.0801\,pH + 0.00801 \log c - 0.0160 \log P_{H_2S}$	$0.302 - 0.0721\,pH + 0.0080 \log c - 0.0160 \log P_{H_2S}$
75	$0.305 - 0.0863\,pH + 0.00863 \log c - 0.0173 \log P_{H_2S}$	$0.284 - 0.0777\,pH + 0.0086 \log c - 0.0173 \log P_{H_2S}$
100	$0.291 - 0.0925\,pH + 0.00925 \log c - 0.0185 \log P_{H_2S}$	$0.267 - 0.0833\,pH + 0.0093 \log c - 0.0185 \log P_{H_2S}$
125	$0.278 - 0.0987\,pH + 0.00987 \log c - 0.0197 \log P_{H_2S}$	$0.249 - 0.0888\,pH + 0.0099 \log c - 0.0197 \log P_{H_2S}$
150	$0.264 - 0.1049\,pH + 0.01049 \log c - 0.0210 \log P_{H_2S}$	$0.230 - 0.0944\,pH + 0.0105 \log c - 0.0210 \log P_{H_2S}$

	82. $(H_2S)/S_4O_6^{--}$	83. $(H_2S)/S_2O_4^{--}$
0	$E = 0.315 - 0.0602\,pH + 0.0030 \log c - 0.0120 \log P_{H_2S}$	$E = 0.450 - 0.0650\,pH + 0.0054 \log c - 0.0108 \log P_{H_2S}$
25	$0.299 - 0.0657\,pH + 0.0033 \log c - 0.0131 \log P_{H_2S}$	$0.432 - 0.0710\,pH + 0.0059 \log c - 0.0118 \log P_{H_2S}$
50	$0.284 - 0.0712\,pH + 0.0036 \log c - 0.0142 \log P_{H_2S}$	$0.415 - 0.0769\,pH + 0.0063 \log c - 0.0128 \log P_{H_2S}$
75	$0.269 - 0.0767\,pH + 0.0038 \log c - 0.0153 \log P_{H_2S}$	$0.400 - 0.0829\,pH + 0.0069 \log c - 0.0138 \log P_{H_2S}$
100	$0.255 - 0.0822\,pH + 0.0041 \log c - 0.0164 \log P_{H_2S}$	$0.384 - 0.0888\,pH + 0.0074 \log c - 0.0148 \log P_{H_2S}$
125	$0.240 - 0.0877\,pH + 0.0044 \log c - 0.0176 \log P_{H_2S}$	$0.369 - 0.0948\,pH + 0.0079 \log c - 0.0158 \log P_{H_2S}$
150	$0.225 - 0.0932\,pH + 0.0047 \log c - 0.0186 \log P_{H_2S}$	$0.353 - 0.1007\,pH + 0.0084 \log c - 0.0167 \log P_{H_2S}$

	84. $(H_2S)/HS_2O_4^-$	85. $(H_2S)/S_3O_6^{--}$
0	$E =$	$E = 0.384 - 0.0609\,pH + 0.0034 \log c - 0.0102 \log P_{H_2S}$
25	$0.440 - 0.0650\,pH + 0.0059 \log c - 0.0118\ P_{H_2S}$	$0.368 - 0.0665\,pH + 0.0037 \log c - 0.0111 \log P_{H_2S}$
50		$0.352 - 0.0721\,pH + 0.0040 \log c - 0.0120 \log P_{H_2S}$
75		$0.337 - 0.0777\,pH + 0.0043 \log c - 0.0129 \log P_{H_2S}$
100		$0.322 - 0.0833\,pH + 0.0046 \log c - 0.0139 \log P_{H_2S}$
125		$0.308 - 0.0888\,pH + 0.0049 \log c - 0.0148 \log P_{H_2S}$
150		$0.292 - 0.0944\,pH + 0.0052 \log c - 0.0157 \log P_{H_2S}$

	86. $S_5O_6^{--}/(SO_2)$	87. $S_2O_3^{--}/(SO_2)$
0	$E = 0.539 - 0.0542\,pH - 0.0068 \log c + 0.0338 \log P_{SO_2}$	$E = 0.416 - 0.0271\,pH - 0.0135 \log c + 0.0271 \log P_{SO_2}$
25	$0.521 - 0.0591\,pH - 0.0074 \log c + 0.0369 \log P_{SO_2}$	$0.409 - 0.0296\,pH - 0.0148 \log c + 0.0296 \log P_{SO_2}$
50	$0.503 - 0.0640\,pH - 0.0080 \log c + 0.0400 \log P_{SO_2}$	$0.400 - 0.0320\,pH - 0.0160 \log c + 0.0320 \log P_{SO_2}$
75	$0.486 - 0.0691\,pH - 0.0086 \log c + 0.0431 \log P_{SO_2}$	$0.431 - 0.0345\,pH - 0.0173 \log c + 0.0345 \log P_{SO_2}$
100	$0.468 - 0.0740\,pH - 0.0093 \log c + 0.0462 \log P_{SO_2}$	$0.429 - 0.0370\,pH - 0.0185 \log c + 0.0370 \log P_{SO_2}$
125	$0.450 - 0.0790\,pH - 0.0099 \log c + 0.0493 \log P_{SO_2}$	$0.428 - 0.0395\,pH - 0.0197 \log c + 0.0395 \log P_{SO_2}$
150	$0.432 - 0.0839\,pH - 0.0105 \log c + 0.0524 \log P_{SO_2}$	$0.428 - 0.0420\,pH - 0.0210 \log c + 0.0420 \log P_{SO_2}$

	88. $HS_2O_3^-/(SO_2)$	89. $S_4O_6^{--}/(SO_2)$
0	$E = 0.436 - 0.0406\,pH - 0.0135 \log c + 0.0271 \log P_{SO_2}$	$E = 0.541 - 0.0361\,pH - 0.0090 \log c + 0.0361 \log P_{SO_2}$
25	$0.434 - 0.0443\,pH - 0.0148 \log c + 0.0296 \log P_{SO_2}$	$0.537 - 0.0394\,pH - 0.0099 \log c + 0.0394 \log P_{SO_2}$
50	$0.432 - 0.0481\,pH - 0.0160 \log c + 0.0320 \log P_{SO_2}$	$0.531 - 0.0427\,pH - 0.0107 \log c + 0.0427 \log P_{SO_2}$

Appendix 3. (Continued)

T°C		
75	$0.431 - 0.0518\ pH - 0.0173 \log c + 0.0345 \log P_{SO_2}$	$0.527 - 0.0460\ pH - 0.0115 \log c + 0.0460 \log P_{SO_2}$
100	$0.429 - 0.0555\ pH - 0.0185 \log c + 0.0370 \log P_{SO_2}$	$0.522 - 0.0493\ pH - 0.0123 \log c + 0.0493 \log P_{SO_2}$
125	$0.428 - 0.0592\ pH - 0.0197 \log c + 0.0395 \log P_{SO_2}$	$0.516 - 0.0527\ pH - 0.0132 \log c + 0.0527 \log P_{SO_2}$
150	$0.428 - 0.0629\ pH - 0.0210 \log c + 0.0420 \log P_{SO_2}$	$0.511 - 0.0560\ pH - 0.0140 \log c + 0.0560 \log P_{SO_2}$

	90. $S_2O_4^{--}/(SO_2)$	91. $HS_2O_4^{-}/(SO_2)$
0	$E = -0.019 - 0.0271 \log c + 0.0542 \log P_{SO_2}$	$E =$
25	$-0.009 - 0.0296 \log c + 0.0591 \log P_{SO_2}$	$-0.054 - 0.0296\ pH - 0.0296 \log c + 0.0591 \log P_{SO_2}$
50	$-0.001 - 0.0320 \log c + 0.0640 \log P_{SO_2}$	
75	$0.006 - 0.0345 \log c + 0.0690 \log P_{SO_2}$	
100	$0.010 - 0.0370 \log c + 0.0740 \log P_{SO_2}$	
125	$0.013 - 0.0395 \log c + 0.0790 \log P_{SO_2}$	
150	$0.014 - 0.0420 \log c + 0.0839 \log P_{SO_2}$	

	92. $S_3O_6^{--}/(SO_2)$	93. $(H_2S)/S$	94. $S/(SO)$
0	$E = 0.275 - 0.0271 \log c + 0.0812 \log P_{SO_2}$	$E = 0.168 - 0.0542\ pH - 0.0271 \log P_{H_2S}$	$E = 1.152 - 0.0542\ pH + 0.0271 \log P_{SO}$
25	$0.290 - 0.0296 \log c + 0.0887 \log P_{SO_2}$	$0.173 - 0.0591\ pH - 0.0296 \log P_{H_2S}$	$1.120 - 0.0591\ pH + 0.0296 \log P_{SO}$
50	$0.302 - 0.0320 \log c + 0.0961 \log P_{SO_2}$	$0.178 - 0.0640\ pH - 0.0320 \log P_{H_2S}$	$1.088 - 0.0640\ pH + 0.0320 \log P_{SO}$
75	$0.314 - 0.0345 \log c + 0.1036 \log P_{SO_2}$	$0.183 - 0.0690\ pH - 0.0345 \log P_{H_2S}$	$1.056 - 0.0690\ pH + 0.0345 \log P_{SO}$
100	$0.324 - 0.0370 \log c + 0.1110 \log P_{SO_2}$	$0.188 - 0.0740\ pH - 0.0370 \log P_{H_2S}$	$1.025 - 0.0740\ pH + 0.0370 \log P_{SO}$
125	$0.332 - 0.0395 \log c + 0.1184 \log P_{SO_2}$	$0.193 - 0.0790\ pH - 0.0395 \log P_{H_2S}$	$0.994 - 0.0790\ pH + 0.0395 \log P_{SO}$
150	$0.339 - 0.0420 \log c + 0.1259 \log P_{SO_2}$	$0.197 - 0.0839\ pH - 0.0420 \log P_{H_2S}$	$0.963 - 0.0839\ pH + 0.0420 \log P_{SO}$

	95. $S/(SO_2)$	96. $S/(SO_3)$
0	$E = 0.473 - 0.0542\ pH + 0.0135 \log P_{SO_2}$	$E = 0.606 - 0.0542\ pH + 0.0093 \log P_{SO_3}$
25	$0.451 - 0.0591\ pH + 0.0148 \log P_{SO_2}$	$0.588 - 0.0591\ pH + 0.0099 \log P_{SO_3}$
50	$0.430 - 0.0640\ pH + 0.0160 \log P_{SO_2}$	$0.571 - 0.0640\ pH + 0.0100 \log P_{SO_3}$
75	$0.408 - 0.0690\ pH + 0.0172 \log P_{SO_2}$	$0.554 - 0.0690\ pH + 0.0115 \log P_{SO_3}$
100	$0.388 - 0.0740\ pH + 0.0185 \log P_{SO_2}$	$0.536 - 0.0740\ pH + 0.0123 \log P_{SO_3}$
125	$0.367 - 0.0790\ pH + 0.0197 \log P_{SO_2}$	$0.520 - 0.0790\ pH + 0.0132 \log P_{SO_3}$
150	$0.346 - 0.0839\ pH + 0.0210 \log P_{SO_2}$	$0.504 - 0.0839\ pH + 0.0140 \log P_{SO_3}$