

THE OXIDATION STATE DIAGRAM: STABILITY OF DISSOLVED SULPHUR SPECIES IN SEAWATER

M. DILEEP KUMAR

National Institute of Oceanography, Dona Paula, Goa 403004 (India)

(Received November 18, 1980; revision accepted June 30, 1981)

ABSTRACT

Kumar, M.D., 1981. The oxidation state diagram: stability of dissolved sulphur species in seawater. *Mar. Chem.*, 10: 475–486.

Oxidation state diagrams have been constructed for different sulphur species. Sulphur oxyacids are stressed with respect to their key role in the cycling of inorganic sulphur species, besides sulphides and elemental sulphur. Following the stable sulphate species in seawater, metastable species are $S_4O_6^{2-}$, $S_2O_3^{2-}$ and S^0 . Stability of different species found from these diagrams were compared with the earlier literature. A case study, from Solar Lake (Sinai) is inconcurrent with the results of the present diagrams.

INTRODUCTION

In natural waters the occurrence of chemical equilibrium among the chemical species present is inevitable in attaining stability for that system with regard to the species concerned. In a liquid, such as seawater, in contact with rocks and subject to rapid changes in pressure and temperature, maintenance of equilibrium is not likely (Krauskopf, 1967). Where activity coefficients of electrolytes rarely differ and the activity equilibrium constant is in good agreement with the concentration equilibrium constant, the standard electrode potential will be a good indicator of the oxidizing and reducing capacity of that particular system (Johnson, 1968). Since electrode potential and thermodynamic data (Latimer, 1952; Garrels and Christ, 1965) and equilibrium constants (Sillén and Martell, 1964, 1971) are available, it is possible to predict the stability of different species at equilibrium.

Recently, Wong (1980) proposed the oxidation state diagram which can examine the stabilities of various species. A summary of the normalization procedure for different environmental redox potentials, as used by Wong (1980), is given in Table I.

Sulphur is stated to be one of the redox elements (Breck, 1974) whose chemistry can be influenced by microbiological processes. Many of the sulphur oxyacids (e.g. $S_2O_3^{2-}$) are either unstable or metastable and do not appear in *Eh*–pH diagrams (Krauskopf, 1967) despite their detection in measurable quantities in natural waters (Richards, 1965; Jørgensen et al., 1979). In the present work, redox potentials for various half-cell reactions have been obtained from Latimer (1952) or calculated from the free-energy data (Garrels and Christ, 1965).

TABLE I
Summary of the data used by Wong (1980) in the construction of an oxidation state diagram

Environment	Type of solution	Reaction couple	Half-cell reaction ^a	Electrode potential E° (volts)	Equation for normalization ^b
Anoxic	Acidic	$H^+ - H_2$	$2H^+ + 2e = H_2$	0.000	$VE_A^{\circ} = nE_A^{\circ}$
	Basic	$H_2O - H_2$	$2H_2O + 2e = H_2 + 2OH^-$	+0.828	$VE(OH) = n[E(OH)]^c$
Oxic	Acidic	$O_2 - H_2O$	$O_2 + 4H^+ + 4e = 2H_2O$	+1.230	$VE(O_2/H_2O) = VE_A^{\circ} - n(1.23)$
	Basic	$O_2 - OH$	$O_2 + 2H_2O + 4e = 4OH^-$	+0.400	$VE(O_2/OH) = nE_B^{\circ} - n(0.40)$

^a Half-cell reaction written in the 'European convention', i.e. reduced species on the right side of the reaction.

^b n is the oxidation state number including its sign.

^c $E(OH) = E_B^{\circ} + 0.828$.

TABLE II

Calculated data for the construction of the oxidation state diagrams

Acidic solution		E_A^0 (volts)	VE_A^0	$VE(O_2-H_2O)$
Oxidation state	Sulphur species			
2.0-	H ₂ S	+0.141	-0.282	+2.180
2.0+	S ₂ O ₃ ²⁻	+0.500	+1.000	-1.460
2.5+	S ₄ O ₆ ²⁻	+0.410	+1.030	-2.040
3.0+	HS ₂ O ₄ ⁻	+0.620	+1.860	-1.830
4.0+	H ₂ SO ₃	+0.450	+1.800	-3.120
5.0+	S ₂ O ₆ ²⁻	+0.470	+2.350	-3.800
6.0+	SO ₄ ²⁻	+0.360	+2.160	-5.220

Basic solution		E_B^0 (volts)	$VE(OH)$	$VE(O_2-OH)$
Oxidation state	Sulphur species			
2.0-	S ²⁻	-0.480	-0.696	+1.760
2.0+	S ₂ O ₃ ²⁻	-0.740	+0.176	-2.280
3.0+	S ₂ O ₄ ²⁻	-0.500	+0.984	-2.700
4.0+	SO ₃ ²⁻	-0.660	+0.672	-4.240
6.0+	SO ₄ ²⁻	-0.750	+0.468	-6.900

RESULTS AND DISCUSSION

Results for acidic and basic solutions, for both anoxic and oxic environments, are summarized in Table II.

Anoxic environment

The oxidation state diagram (Fig. 1) can be compared to that given by Johnson (1968) (for acidic solutions) in general. The difference, in the construction of the diagram for basic solutions, is that potentials given for H⁺-H₂ half-cell reactions as references were not converted to H₂O-H₂ reference half-cell reactions by Johnson (1968). Therefore, the volt equivalents of different species varied widely in basic solutions between these diagrams.

In both the solutions, stability of sulphide is followed by S⁰ and S₂O₃²⁻. Stability of SO₄²⁻ is greater in basic solution, as compared to its stability in acidic solution. This is in accordance with Johnson's (1968) diagram, but the difference may not be to the extent shown by him. In acidic solutions, the instability of oxyacids increases with increasing oxidation state (Johnson, 1968) but is slightly different in basic solution.

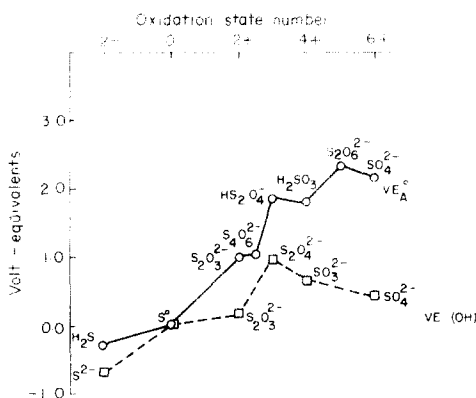


Fig. 1. Oxidation state diagram for sulphur system in the anoxic environment. VE_A^0 , acidic solutions and $VE(OH)$, basic solutions.

In acidic solutions, the strongest oxidizing couple is $S_4O_6^{2-}$ — $HS_2O_4^-$, where SO_4^{2-} is the strongest oxidizing agent. The oxidizing capacity decreases for SO_4^{2-} in basic solution, wherein the oxidizing couple will be $S_2O_3^{2-}$ — $S_2O_4^{2-}$. Despite its disproportionation both in acidic and basic solutions, $S_2O_4^{2-}$ participates in the respective oxidizing couples as an end member.

In acid solutions rapid oxidation occurs up to $S_4O_6^{2-}$ (Johnson, 1968). The oxyacids, $S_2O_3^{2-}$, $HS_2O_4^-$ and $S_2O_6^{2-}$ are readily undergoing disproportionation in acid solution.



In this case, species with lower volt equivalents are formed, i.e. H_2SO_3 , S^0 for the above equations. During the reduction of SO_4^{2-} , di- or polythionates will be formed. Among those considered $S_4O_6^{2-}$ exhibits metastability. H_2SO_3 will be relatively stabilized in acid solution, because it is weaker than sulphuric acid (Johnson, 1968), whose conjugate base has high stability in basic solution.

In basic solution, the disproportionation of $S_2O_4^{2-}$ can be shown as (Johnson, 1968)



and further disproportionation of SO_3^{2-} is thermodynamically feasible.



S^0 can be formed in acidic solution due to its metastability but may not occur in basic solution (Johnson, 1968).

Oxic environment

Irrespective of pH, SO_4^{2-} shows the highest stability (Sillén, 1961). SO_4^{2-} stability is followed by other sulphur oxyacids in decreasing oxidation number with decreasing stability (Fig. 2). In an oxic environment, HS_2O_4^- is also disproportionate in both the solutions, as shown above (eqs. 2 and 4). While $\text{S}_4\text{O}_6^{2-}$ shows metastability in acidic solution, $\text{S}_2\text{O}_3^{2-}$ is unstable but is metastable in basic solution (Johnson, 1968). $\text{S}_2\text{O}_6^{2-}$ disproportionates in acidic solution [eq. 1]. As under anoxic conditions, S^0 shows metastability in acidic solution and is unstable in basic solution. SO_4^{2-} — $\text{S}_2\text{O}_6^{2-}$ and SO_3^{2-} — $\text{S}_2\text{O}_4^{2-}$ are the two reducing couples in acidic and basic solutions, respectively. Since conjugate bases of acids are stable in basic solution (Wong, 1980), the difference in volt equivalents between basic solution and acidic solution will be a measure of power of acidity. This is relatively greater for sulphuric acid than sulphurous acid.

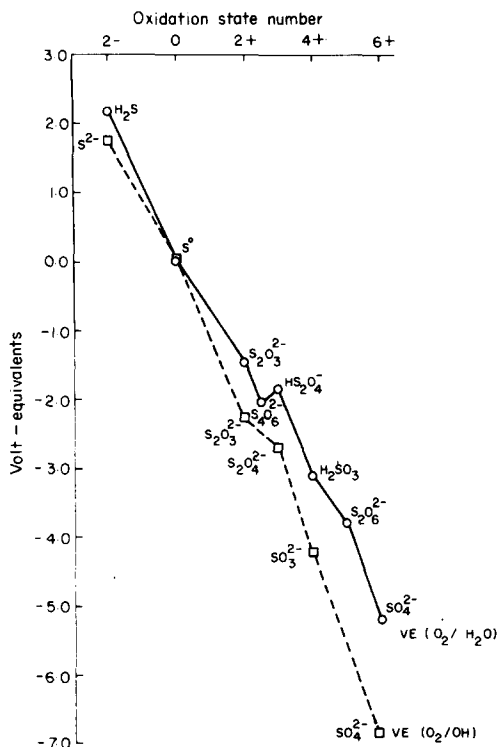
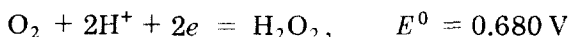


Fig. 2. Oxidation state diagram for sulphur system in the oxic environment. $VE(\text{O}_2/\text{H}_2\text{O})$, acidic solutions and $VE(\text{O}_2/\text{OH})$, basic solutions.

Seawater

The crucial aspect in discussing redox levels in the sea is the selection of a redox couple which maintains the redox potential in seawater. Breck (1974) noted the importance of the $O_2-H_2O_2$ couple; here it is assumed that both the O_2-H_2O and $O_2-H_2O_2$ couples are important for oxygenated seawater. H_2O_2 is an intermediate product in the complicated reduction process of dissolved oxygen to water molecule. The formation of H_2O_2 can be written (Breck, 1974) as



Thus, in the calculation of volt equivalents for the construction of the oxidation state diagram in seawater, the equation given by Wong (1980)

$$VE' = nE_A^0 - 0.472nh - 0.746n \quad (6)$$

may be given as

$$VE(O_2-H_2O_2) = nE_A^0 - 0.472nh - 0.680n \quad (7)$$

where the $O_2-H_2O_2$ couple is considered. The term h is the number of protons considered in the equation.

Stability of sulphur species in seawater, according to Fig. 3, followed the same trend as in an oxic acidic solution (i.e. O_2-H_2O couple). This diagram is constructed for seawater with the two equations given above, i.e. eqs. 6 and 7. Though volt equivalents are lower for all sulphur species for eq. 6 than for eq. 7, the trend has remained the same throughout.

As reported in the earlier literature, SO_4^{2-} is the most stable and major sulphur species in seawater as shown by the diagram (Sillén, 1961; Wilson, 1975). Intermediate species S^0 and oxysulphur acids form during the oxidation of sulphides or vice versa and occur mostly in the region of the chemocline (Richards, 1965; Sorokin, 1972; Jannasch et al., 1974; Jørgensen et al., 1979). The coexistence of HS^- and dissolved oxygen, though thermodynamically unstable, can be expected at the interface of respective water layers as in a steady-state diffusion (Richards, 1965). But Grasshoff (1975) pointed out the non-existence of HS^- and dissolved oxygen in the transition zone in the Black Sea, which probably is due to the short half-life of H_2S , i.e. about 30 min.

The oxidation of HS^- is a controversial aspect regarding its mode of occurrence. Wheatland (1954) indicated it as being purely inorganic. Sorokin (1972) found the chemical oxidation of HS^- to SO_4^{2-} and $S_2O_3^{2-}$ and biological oxidation of $S_2O_3^{2-}$ to SO_4^{2-} ; but this observation was not agreed to by Jannasch et al. (1974). Also, in a study of the rate of oxidation of HS^- in seawater, Almgreen and Hagstrom (1974) could not find any biological influence on the oxidation rate. In spite of this controversy, the role of the microbiological sulphur cycle in the cycling of carbon compounds is well known (Richards, 1965; Jannasch et al., 1974; Jørgensen et al., 1979). Tuttle and Jannasch (1973) observed high values for $S_2O_3^{2-}$ both in the Cariaco Trench

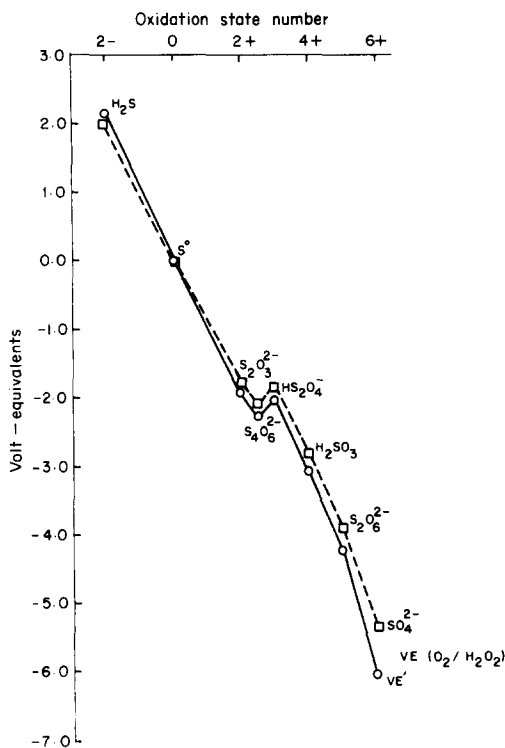
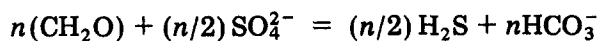


Fig. 3. Oxidation state diagram for sulphur system in seawater. VE' at a pH of 8.0 and pO_2 of 0.21 atm. and $VE (O_2/H_2O_2)$ at the same pH and pO_2 .

and the Black Sea, just in or below the interface. Dark assimilation of CO_2 in this region found by Sen Gupta and Jannasch (1973) explains the high value for $S_2O_3^{2-}$. $S_2O_3^{2-}$ will be the major reduced sulphur species produced during the chemical oxidation of HS^- in seawater (Cline and Richards, 1969). If the ratio of O_2 to HS^- is small, $S_2O_3^{2-}$ and SO_3^{2-} are formed. In the presence of excess O_2 , oxidation proceeds to SO_4^{2-} (Richards, 1965).

During oxidation, $S_2O_3^{2-}$ is a major intermediate, whereas SO_3^{2-} is minor (Richards, 1965; Tuttle and Jannasch, 1973). The latter may be due to its disproportionation into $S_2O_3^{2-}$ and SO_4^{2-} [eq. 5] or because of SO_3^{2-} instability in the presence of small amounts of dissolved oxygen (Rand and Gale, 1967). In some cases, in the oxidation turnover of sulphur species, the rate-limiting step of HS^- oxidation will be the biological oxidation of $S_2O_3^{2-}$ to SO_4^{2-} . From Fig. 3, it is obvious that $S_2O_3^{2-}$ is only metastable in seawater, as supported by the above observations.

A general equation can be written for the bacterial oxidation of organic matter, using SO_4^{2-} as electron acceptor.



Within a narrow range of pH, the existence of S^0 can be expected (Garrels and Christ, 1965; Krauskopf, 1967). H_2S may be photosynthetically oxidized to S^0 (Richards, 1965; Jørgensen et al., 1979) for which Richards (1965) gave



Further, Almgreen and Hagstrom (1974) showed S^0 formation from the spontaneous decomposition of $S_2O_3^{2-}$ (eq. 3). The stability of the S^0 produced in anoxygenic photosynthesis can be reduced by the presence of either dissolved oxygen or S^{2-} ion. With S^{2-} ion S^0 reacts to give polysulphide ions (Breck, 1974).



The metastable existence of S^0 in seawater can be seen from Fig. 3. Sulphide can exist as $H_2S_{(aq)}$, HS^- , S^{2-} or S_n^{2-} (polysulphides) and their relative stabilities are highly dependent on physicochemical conditions (Field, 1972). At a pH of about 8 in seawater, the major sulphide species are considered to be HS^- ion, followed by H_2S and S^{2-} in minor quantities (Richards, 1965; Goldhaber and Kaplan, 1974). However, in the oxidizing environment of seawater, sulphide species are highly unstable and will not occur, as seen from the diagram (Fig. 3).

According to Table III, in which various sulphur species have been considered, the stability of sulphur species in oxic seawater at a pH of 8 (VE'), generally decreases with the decrease in oxidation number whereas the reverse is the case with anoxic acidic solution (VE_A^0). It is evident that HSO_4^- will be the stable species after SO_4^{2-} as is shown in the Eh -pH diagram (Krauskopf, 1967). Later $S_2O_6^{2-}$ appears as the stable species.

In the highly acidic anoxic environment, H_2S showed highest stability followed by HS^- , polysulphides and S^{2-} (Table III). Krauskopf (1967) and Garrels and Christ (1965) showed high stability for H_2S in acidic anoxic solutions, whereas HS^- becomes stable as the pH rises. S^{2-} can exist at a very high pH. Among polythionates $S_4O_6^{2-}$ and $S_5O_6^{2-}$ showed high stability. $S_4O_6^{2-}$ has been detected as the major species among polythionates in a sedimentary environment (Nriagu et al., 1979). In these circumstances, H_2SO_2 and $S_2O_3^{2-}$ are equally stable.

For practical confirmation, all sulphur species considered should be examined simultaneously. Because of the inherent difficulties (Meyer et al., 1980), the simultaneous detection of sulphur oxyacids is extremely difficult. Using Raman spectroscopy Meyer et al. (1980) tried to study the coexistence of these oxyacids. Based on Eh measurements alone, it is not worthwhile to predict the stable sulphur species, since the Eh value in natural waters is considered as a mixed potential (Stumm and Morgan, 1970).

The applicability of the oxidation state diagram to natural in-situ conditions is limited, since it is completely based on thermodynamic data and does not consider the biological influence (Wong, 1980). In addition, organic

TABLE III

Volt equivalents of various sulphur species in oxic seawater (VE') and acidic anoxic environment (VE_A^0)

Oxidation state	Sulphur species	VE'	VE_A^0	Equation considered
2.0-	S_5^{2-}	2.172	0.680	$\frac{5}{2} S^0 + e = \frac{1}{2} S_5^{2-}$
	S_4^{2-}	2.212	0.720	$2 S^0 + e = \frac{1}{2} S_4^{2-}$
	S_3^{2-}	2.268	0.776	$\frac{3}{2} S^0 + e = \frac{1}{2} S_3^{2-}$
	S_2^{2-}	2.368	0.856	$S^0 + e = \frac{1}{2} S_2^{2-}$
	S^{2-}	2.444	0.952	$\frac{1}{2} S^0 + e = \frac{1}{2} S^{2-}$
	HS^-	2.094	0.130	$\frac{1}{2} S^0 + \frac{1}{2} H^+ + e = \frac{1}{2} HS^-$
	H_2S	2.154	-0.282	$\frac{1}{2} S^0 + H^+ + e = \frac{1}{2} H_2S$
2.0+	$S_5O_6^{2-}$	-1.645	0.980	$\frac{1}{10} S_5O_6^{2-} + \frac{6}{5} H^+ + e = \frac{1}{2} S^0 + \frac{3}{5} H_2O$
	H_2SO_2	-1.436	1.000	$\frac{1}{2} H_2SO_2 + H^+ + e = \frac{1}{2} S^0 + H_2O$
	$S_2O_3^{2-}$	-1.908	1.000	$\frac{1}{4} S_2O_3^{2-} + \frac{3}{2} H^+ + e = \frac{1}{2} S^0 + \frac{3}{4} H_2O$
2.5+	$S_4O_6^{2-}$	-2.261	1.025	$\frac{1}{10} S_4O_6^{2-} + \frac{6}{5} H^+ + e = \frac{2}{5} S^0 + \frac{3}{5} H_2O$
3.0+	$HS_2O_4^-$	-2.030	1.860	$\frac{1}{6} HS_2O_4^- + \frac{7}{6} H^+ + e = \frac{1}{3} S^0 + \frac{2}{3} H_2O$
4.0+	$S_2O_5^{2-}$	-3.300	2.044	$\frac{1}{8} S_2O_5^{2-} + \frac{5}{4} H^+ + e = \frac{1}{4} S^0 + \frac{5}{8} H_2O$
	SO_3^{2-}	-3.476	2.340	$\frac{1}{4} SO_3^{2-} + \frac{3}{2} H^+ + e = \frac{1}{4} S^0 + \frac{3}{4} H_2O$
	HSO_3^-	-3.436	1.908	$\frac{1}{4} HSO_3^- + \frac{5}{4} H^+ + e = \frac{1}{4} S^0 + \frac{3}{4} H_2O$
	H_2SO_3	-3.072	1.800	$\frac{1}{4} H_2SO_3 + H^+ + e = \frac{1}{4} S^0 + \frac{3}{4} H_2O$
5.0+	$S_2O_6^{2-}$	-4.212	2.350	$\frac{1}{10} S_2O_6^{2-} + \frac{6}{5} H^+ + e = \frac{1}{5} S^0 + \frac{3}{5} H_2O$
6.0+	HSO_4^-	-5.752	2.028	$\frac{1}{6} HSO_4^- + \frac{7}{6} H^+ + e = \frac{1}{6} S^0 + \frac{2}{3} H_2O$
	SO_4^{2-}	-6.092	2.160	$\frac{1}{6} SO_4^{2-} + \frac{4}{3} H^+ + e = \frac{1}{6} S^0 + \frac{2}{3} H_2O$

sulphur species which were not considered in the diagram may also affect its stability.

A case study

A case study helps in assessing the validity of the constructed oxidation state diagrams. Most of the earlier studies were concerned with either H_2S or SO_4^{2-} and to a lesser extent with $S_2O_3^{2-}$ (R. Sen Gupta, unpublished data). A recent article by Jørgensen et al. (1979) provides profiles for the species $S_2O_3^{2-}$, S^0 , S_n^{2-} (polysulphides) and H_2S studied simultaneously in Solar Lake (Sinai), which is a highly saline shallow (ca. 5 m) water body, having anoxic conditions in the hypolimnion.

Jørgensen et al. (1979) evidenced the coexistence of dissolved oxygen and H_2S , in the interface. The steady downward diffusion of O_2 can be seen which oxidizes the upcoming sulphur species. In Table IV, approximate

TABLE IV

Values for various sulphur species, obtained from the profiles of Jørgensen et al. (1979)

Depth (m)	$S_2O_3^{2-}$ (μM)	S^0 part. (μM)	H_2S (μM)	S_{tot}^0 * (μM)
3.20	28	0.0	0.0	0.0
3.60	125	0.0	14.0	0.0
3.85	170	0.1	>175	16.0
3.95	135	33.0	>175	100.0
4.15	105	6.0	>175	130.0
5.00	38	35.0	4000	125.0

* $S_{tot}^0 = S^0$ part. + S_n^{2-} (polysulphides).

values for various species studied taken from the diagram of Jørgensen et al. (1979), are incorporated. In going from the interface to the bottom, an increase in the stabilization of reduced species is seen. At about a depth of 3.2 m, where the interface lies, H_2S was not detected but $S_2O_3^{2-}$ showed a value of $28 \mu M$. Here, the H_2S must have been oxidized soon after its entry. The maximum $S_2O_3^{2-}$ concentration, observed at 3.85 m, is $170 \mu M$, where H_2S increased rapidly. Below the $S_2O_3^{2-}$ maximum, S^0 showed a maximum value of about $33 \mu M$ at 3.95 m. As discussed above, S^0 may be the product of either oxidation of H_2S or the disproportionation of $S_2O_3^{2-}$. The observed maximum value ($>100 \mu M$) for polysulphides at 4.15 m, will be a consequence of the reaction between S^0 and dissolved sulphide ions as shown in eq. 8 (Breck, 1974). Below this, H_2S increases to give a concentration of $4 mM$. The possible existence of polythionates is not known from this work. However, in sediments, Nriagu et al. (1979) detected $5-40 \mu g g^{-1}$ of polythionates and $S_2O_3^{2-}$ to $0-20 \mu g g^{-1}$ having $0.010 mg l^{-1}$ H_2S in pore water. The above studies support the constructed oxidation state diagram in the present work.

CONCLUSIONS

Oxidation state diagrams showed that sulphur oxyacids are unstable in an acidic anoxic environment and the intensity of instability increases with the increasing oxidation state. The reverse is the case in an oxic environment. Metastable species are S^0 , $S_4O_6^{2-}$ and H_2SO_3 in acidic solution and $S_2O_3^{2-}$ in basic solution, for both the environments. In seawater, sulphur species showed the same order of stability as they showed in oxic acidic solution. Apart from S^0 and $S_4O_6^{2-}$ species, $S_2O_3^{2-}$ shows metastability in seawater. Species stability with respect to the $O_2-H_2O_2$ couple (Breck, 1974) is in close agreement with the O_2-H_2O couple (Wong, 1980). For seawater with pH of 8.0 and pO_2 of 0.21 atm HSO_4^- is the next stable species to SO_4^{2-} . H_2S showed high stability in anoxic acidic solution. Results from a recent article

(Jørgensen et al., 1979) are in agreement with the results of the present diagrams.

ACKNOWLEDGEMENTS

I wish to express my gratefulness to Dr. S.Z. Qasim, Director, National Institute of Oceanography for his constant encouragement. Thanks are due to Dr. R. Sen Gupta for his keen interest and for making suggestions for the modification of the manuscript and Shri C.V.G. Reddy for his constant help and advice. I thank the CSIR for the award of a Junior Research Fellowship.

REFERENCES

- Almgren, T. and Hagström, J., 1974. The oxidation rate of sulphide in seawater. *Water Res.*, 8: 395–400.
- Breck, W.G., 1974. Redox levels in the sea. In: E.D. Goldberg (Editor), *The Sea*. Wiley Interscience, New York, NY, Vol. 5, pp. 153–179.
- Cline, J.D. and Richards, F.A., 1969. Oxygenation of hydrogen sulphide in seawater at constant salinity, temperature and pH. *Environ. Sci. Technol.*, 3: 838–843.
- Field, C.W., 1972. Sulphur: element and geochemistry. In: R.W. Fairbridge (Editor), *The Encyclopedia of Geochemistry and Environmental Sciences*. Van Nostrand Reinhold, New York, NY, pp. 1142–1148.
- Garrels, R.M. and Christ, C.L., 1965. *Solutions, Minerals, and Equilibria*. Harper and Row, New York, NY, 450 pp.
- Goldhaber, M.B. and Kaplan, I.R., 1974. The sulphur cycle. In: E.D. Goldberg (Editor), *The Sea*, Wiley Interscience, New York, NY, Vol. 5, pp. 569–655.
- Grasshoff, K., 1975. The hydrochemistry of land locked basins and fjords. In: J.P. Riley and G. Skirrow (Editors), *Chemical Oceanography*. Academic Press, New York, NY, Vol. 2, 2nd edn., pp. 455–597.
- Jannasch, H.W., Truper, H.G. and Tuttle, J.H., 1974. Microbial sulphur cycle in the Black Sea. In: E.T. Degens and D.A. Ross (Editors), *The Black Sea: Its Geology, Chemistry and Biology*. Am. Assoc. Petrol. Geol. Mem. 20, Tulsa, OK, pp. 419–425.
- Johnson, D.A., 1968. *Some Thermodynamic Aspects of Inorganic Chemistry*. Cambridge University Press, Cambridge, 224 pp.
- Jørgensen, B.B., Kuenen, J.G. and Cohen, Y., 1979. Microbial transformation of sulphur compounds in a stratified lake, Solar Lake (Sinai). *Limnol. Oceanogr.*, 24: 799–822.
- Krauskopf, K.B., 1967. *Introduction to Geochemistry*. McGraw Hill, New York, NY, 721 pp.
- Latimer, W.M., 1952. *Oxidation Potentials*. Prentice-Hall, New York, NY, 2nd edn., 392 pp.
- Meyer, B., Ospina, M. and Peter, L.B., 1980. Raman spectroscopic determination of oxy-sulphur anions in aqueous systems. *Anal. Chim. Acta*, 117: 301–311.
- Nriagu, J.P., Coker, R.D. and Kemp, A.L.W., 1979. Thiosulphate, polythionates and rhodanese activity in Lakes Erie and Ontario sediments. *Limnol. Oceanogr.*, 24: 383–389.
- Rand, M.C. and Gale, S.B., 1967. Kinetics of the oxidation of sulphites by dissolved oxygen. In: S.D. Faust and J.V. Hunter (Editors), *Principles and Application of Water Chemistry*. Proc. 4th Rudolfs Res. Conf., Rutgers. Wiley, New York, NY, pp. 380–404.
- Richards, F.A., 1965. Anoxic basins and fjords. In: J.P. Riley and G. Skirrow (Editors), *Chemical Oceanography*. Academic Press, New York, NY, Vol. 1, 1st edn., pp. 611–645.

- Sen Gupta, R. and Jannasch H.W., 1973. Photosynthetic production and dark assimilation of CO₂ in the Black Sea. *Int. Rev. Gesamten Hydrobiol.*, 58: 625—632.
- Sillén, L.G., 1961. The physical chemistry of seawater. In: M. Sears (Editor), *Oceanography*. American Association for the Advancement of Science, Washington, DC, pp. 549—581.
- Sillén, L.G. and Martell, A.E., 1964. Stability Constants of Metal—Ion Complexes. Chem. Soc., London, Spec. Publ. 17, 754 pp.
- Sillén, L.G. and Martell, A.E., 1971. Stability Constants of Metal—Ion Complexes. Chem. Soc., London, Spec. Publ. 25 (suppl.).
- Sorokin, Y.I., 1972. The bacterial population and the processes of hydrogen sulphide oxidation in the Black Sea. *J. Cont. Int. Explor. Mer.*, 34: 423—455.
- Stumm, W. and Morgan, J.J., 1970. *Aquatic Chemistry*. Wiley Interscience, New York, NY, 583 pp.
- Tuttle, J.H. and Jannasch, H.W., 1973. Sulphide and thiosulphate oxidizing bacteria in anoxic marine basins. *Mar. Biol.*, 20: 64—71.
- Wheatland, A.B., 1954. *J. Hyg. Camb.*, 52: 194.
- Wilson, T.R.S., 1975. Salinity and major elements of seawater. In: J.P. Riley and G. Skirrow (Editors), *Chemical Oceanography*. Academic Press, New York, NY, Vol. 1, 2nd edn., pp. 365—413.
- Wong, G.T.F., 1980. The oxidation state diagram: a potential tool for studying redox chemistry in seawater. *Mar. Chem.*, 9: 1—12.