

Redox chemistry of H₂S oxidation in the British Gas Stretford Process

Part I: Thermodynamics of sulphur-water systems at 298 K

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The thermodynamics of aqueous sulphur–water systems are summarized in the form of potential–pH diagrams, calculated from recently reported critically assessed standard Gibbs energies of formation of the species considered. However, there is convincing evidence from the literature that a value of $pK_a(\text{HS}^-) = 17\text{--}19$ is appropriate, whereas a value of 13 is widely accepted; hence, the higher value of 19, corresponding to $\Delta G_f^0(\text{S}^{2-}) = 120.5 \text{ kJ mol}^{-1}$, was used in these calculations, rather than $\Delta G_f^0(\text{S}^{2-}) = 86.31 \text{ kJ mol}^{-1}$ quoted in the main data source.

Under ambient conditions, only -2 (sulphide), 0 (elemental sulphur) and $+6$ (sulphate) oxidation states are thermodynamically stable in water, which is predicted to be oxidized by peroxodisulphate ($\text{H}_2\text{S}_2\text{O}_8/\text{SO}_8^{2-}$) and peroxomonosulphate ($\text{HSO}_5^-/\text{SO}_5^{2-}$). However, when sulphate is excluded from the calculations to allow for the large energy of activation/slow kinetics of its formation from sulphide, then other sulphony species appear on the diagram for what is then a metastable system. Similarly, if all sulphony species (i.e. any species with oxidation states > 0) are excluded, then polysulphide ions (S_n^{2-} , $2 \leq n \leq 5$) have areas of predominance at high pH, each with a narrow potential window of predominance. Hence, this information is complemented with $\text{S}_n^{2-}/\text{HS}^-$ activity–potential diagrams at pH 9 and 14.

Some species have no area of stability even on the metastable diagrams. Hence, potential–pH diagrams are also presented for the sulphite–dithionite system (excluding elemental sulphur), and that involving peroxomonosulphate ($\text{HSO}_5^-/\text{SO}_5^{2-}$) in place of peroxodisulphate ($\text{H}_2\text{S}_2\text{O}_8/\text{SO}_8^{2-}$).

1. Introduction – The British Gas Stretford Process

As described elsewhere [1–3], Stretford Processes oxidize hydrogen sulphide from process gases, to elemental sulphur. The H₂S-containing gas is contacted with pH 8–9 aqueous carbonate solutions containing vanadium (V) salts and anthraquinone disulphonates as redox catalysts ultimately for oxygen reduction, H₂S dissolves and deprotonates in the alkaline solution, reacting with the two oxidizing agents. The reduced solution is then passed to an oxidation reactor, in which air is passed through the process solution, reoxidising it and forming elemental sulphur. Being naturally hydrophobic, the sulphur particles are collected by the rising air bubbles and concentrate in the froth at the liquid surface, from where they are recovered and filtered. The oxidized solution is recycled to the gas absorber where it contacts more hydrogen sulphide. However, some plants have experienced over-oxidation of HS⁻ to thiosulphate ions, which constitute an expensive effluent problem.

The four linked redox couples in the process; S(0)/S(-II) [4], anthraquinone/anthraquinol [5], V(V)/

V(IV) [6] and O₂/H₂O, were investigated separately using electrochemical techniques, prior to stopped flow spectrophotometry on the various mixtures [3, 7].

The objectives of the thermodynamic calculations reported here were:

- (i) to provide a framework to describe the redox chemistry of the S/HS⁻ couple, the kinetics of which will be reported in a subsequent paper [4].
- (ii) to help to explain the formation of thiosulphate ions, with a view to defining appropriate conditions to minimise its yield and maximise that of sulphur.

Metastable sulphur–water diagrams are also relevant to processes such as the reductive [8] decomposition of aqueous SO₂ solutions.

2. Thermodynamic data

The potential–pH diagram (Fig. 1) for the S/H₂O system at 298.15 K was constructed by considering reactions between all possible combinations of species given in Table 1. This includes the most recently published critically assessed thermodynamic data [9], from which, unless otherwise stated, all thermodynamic

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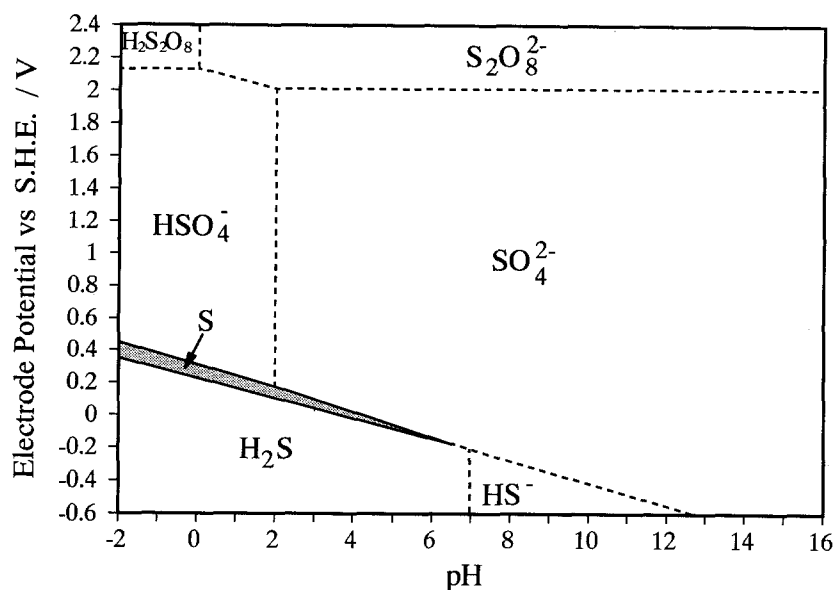


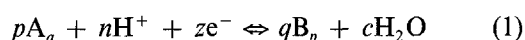
Fig. 1. Potential-pH diagram for the sulphur/water system at 298.15 K. Dissolved sulphur activity = 0.01.

equations quoted in the text or in the Appendix, have been calculated; parentheses indicate activities of the various species. Table 1 incorporates data significantly different to those considered by Pourbaix [10]; data from the most recent NBS source [11] are also included for comparison.

Zhdanov [9] quotes a value of $86.31 \text{ kJ mol}^{-1}$ for $\Delta G_f^0(\text{S}^{2-})$, which corresponds to $\text{p}K_a(\text{HS}^-) = 13$. However, it now appears that this widely accepted value [10, 14], and hence the Gibbs energy of formation of S^{2-} ions, as quoted in Table 1, is in error [15]. U.v. spectrophotometry [16], laser Raman spectroscopy [17] and glass electrode [18] measurements of sulphide solutions at high pH offer convincing evidence that $\text{p}K_a(\text{HS}^-)$ is in the range 17–19, corresponding to $\Delta G_f^0(\text{S}^{2-}) = 109.1\text{--}125.0 \text{ kJ mol}^{-1}$. Information from surface charge measurements on sulphur and from a consideration of the $\text{p}K_a$'s of sulphanes (H_2S_n) [19], indicates that $\text{p}K_a(\text{HS}^-)$ is 18.51 ± 0.56 .

3. Thermodynamic calculations

The various potential-pH diagrams were calculated from the data in Table 1 using the MTDATA program [12, 13]. For reactions such as:



involving polymeric species, (the subscripts q and p define the number of atoms associated with each species), the lines on the equilibrium diagrams presented here correspond to the conditions under which the defined total amount (c_T) of dissolved elemental species is present in each of the two species predominating on either side of a line.

The molar concentrations c_A and c_B of the species A_q and B_p are related to their molar elemental concentrations ($c_{T,A}$ and $c_{T,B}$), by:

$$c_{T,A} = qc_A \quad (2)$$

and

$$c_{T,B} = pc_B \quad (3)$$

Hence, assuming concentrations can be used in place of activities (i.e. activity coefficients are unity) and taking the activity of water as unity, the Nernst equation then is given by:

$$E/V = E^0 - 0.0591 \frac{n}{z} \text{pH} + \frac{0.0591}{z} \log \left\{ \frac{(c_{T,A}/q)^p}{(c_{T,B}/p)^q} \right\} \quad (4)$$

Hence for equal molar elemental concentrations of A and B:

$$E/V = E^0 - 0.0591 \frac{n}{z} \text{pH} + \frac{0.0591}{z} \log \{c_1^{(p-q)} q^{-p} p^q\} \quad (5)$$

Similarly, when Reaction 1 is chemical rather than electrochemical:

$$\log K = \log \{c_1^{-(p-q)} q^p p^{-q}\} + n\text{pH} \quad (6)$$

In the potential-pH diagrams, broken lines correspond to equilibria between solution species and solid lines define the equilibria between elemental sulphur and dissolved species.

4. Results and discussion

Figure 1 is a potential-pH diagram for the sulphur/water system which shows that only the -2 , 0 and $+6$ oxidation states are truly stable in water; $\text{H}_2\text{S}_2\text{O}_8/\text{S}_2\text{O}_8^{2-}$ ions are predicted to be capable of oxidizing water to oxygen, since:

$$E_{\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}}/V > E_{\text{O}_2/\text{H}_2\text{O}}/V = 1.229 - 0.0591\text{pH} \\ + 0.0148 \log p_{\text{O}_2}$$

Oxidation of hydrosulphide at pH 9 is predicted to form sulphate as the predominant product. However, the large activation energy for that reaction is known [14] to result in the production of metastable products such as thiosulphate and sulphite ions.

A potential-pH diagram (Fig. 2) showing these

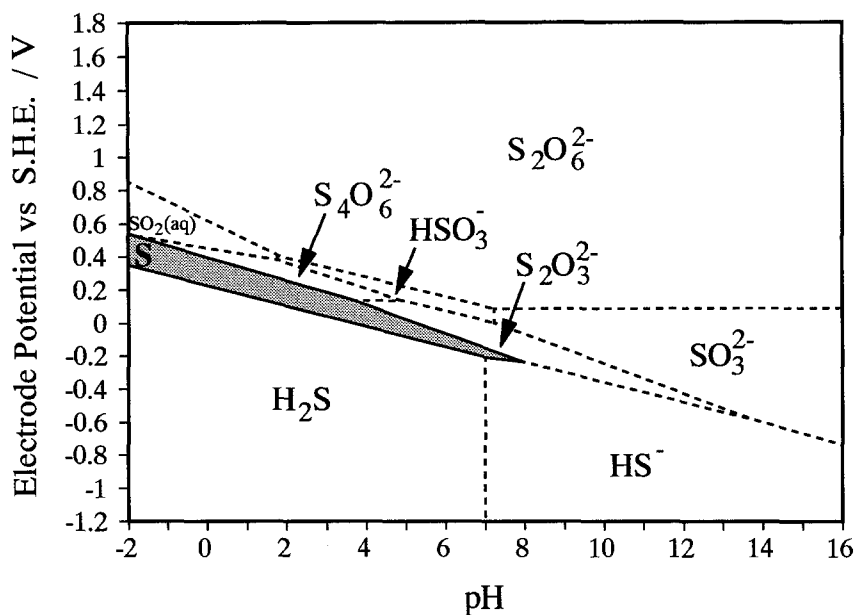


Fig. 2. Metastable potential–pH diagram for the sulphur–water system 298.15 K. S(VI) species excluded. Dissolved sulphur activity = 0.01.

metastable sulphony species can be produced by eliminating sulphur (VI) compounds from the calculations; this is equivalent to adding Gibbs energy to $\Delta G_f^\circ(\text{HSO}_4^-)$ and $\Delta G_f^\circ(\text{SO}_4^{2-})$ to allow for the activation energy associated with their formation from sulphide. Figure 2 predicts that oxidation of a sulphide solution at pH 9 will produce thiosulphate (at > -0.3 V vs SHE), sulphite (> -0.175 V) or dithionate ($> +0.12$ V).

However, yellow-coloured polysulphide solutions [20–24] can result from the atmospheric oxidation of hydrosulphide ions, in mildly alkaline solutions. The conditions under which polysulphides form may be predicted by excluding all sulphony species from the calculations, resulting in the potential–pH diagram shown in Fig. 3. As the polysulphides are of comparable stability, such predominance diagrams may be supplemented by polysulphide activity–potential diagrams, which enable the equilibrium composition of

their solutions to be predicted from the solution potential. The activities/concentrations were calculated by solving numerically the set of simultaneous logarithmic Equations A30–A36 in the Appendix, as functions of potential and for two pH values, using the program TKSOLVER (Software Arts). The results are shown for pH 9 and 14, respectively, in Fig. 4a and Fig. 4b, which indicate that the potential ranges of predominance of the individual polysulphide species are very small.

Some sulphur species in Table 1 have no areas of predominance in the potential–pH diagrams even of metastable sulphur–water systems. These include dithionite species [25, 26], which may be produced by electrochemical reduction of sulphite species [25], in neutral/slightly alkaline electrolytes. The following equilibria for the S(IV)–S(III) system, excluding elemental sulphur from the calculations, are plotted in

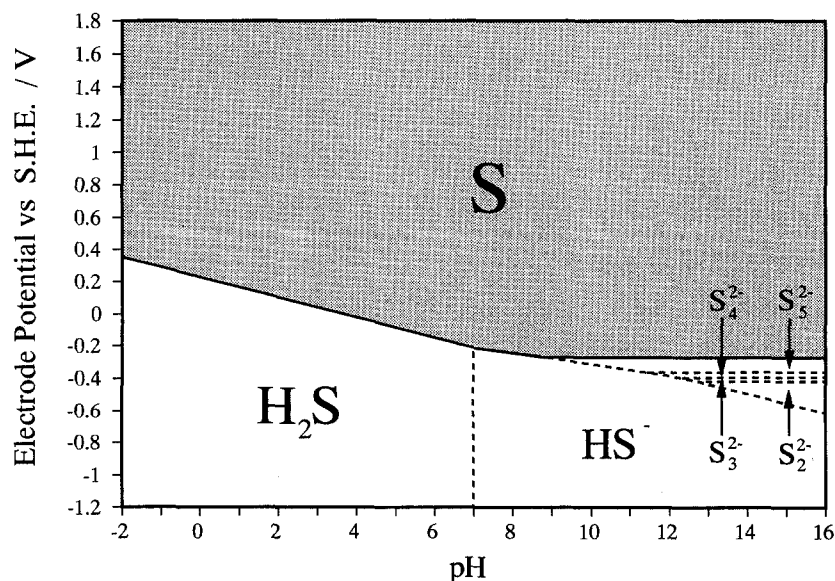


Fig. 3. Metastable potential–pH diagram of the sulphide/polysulphide system at 298.15 K. Dissolved sulphur activity = 0.01.

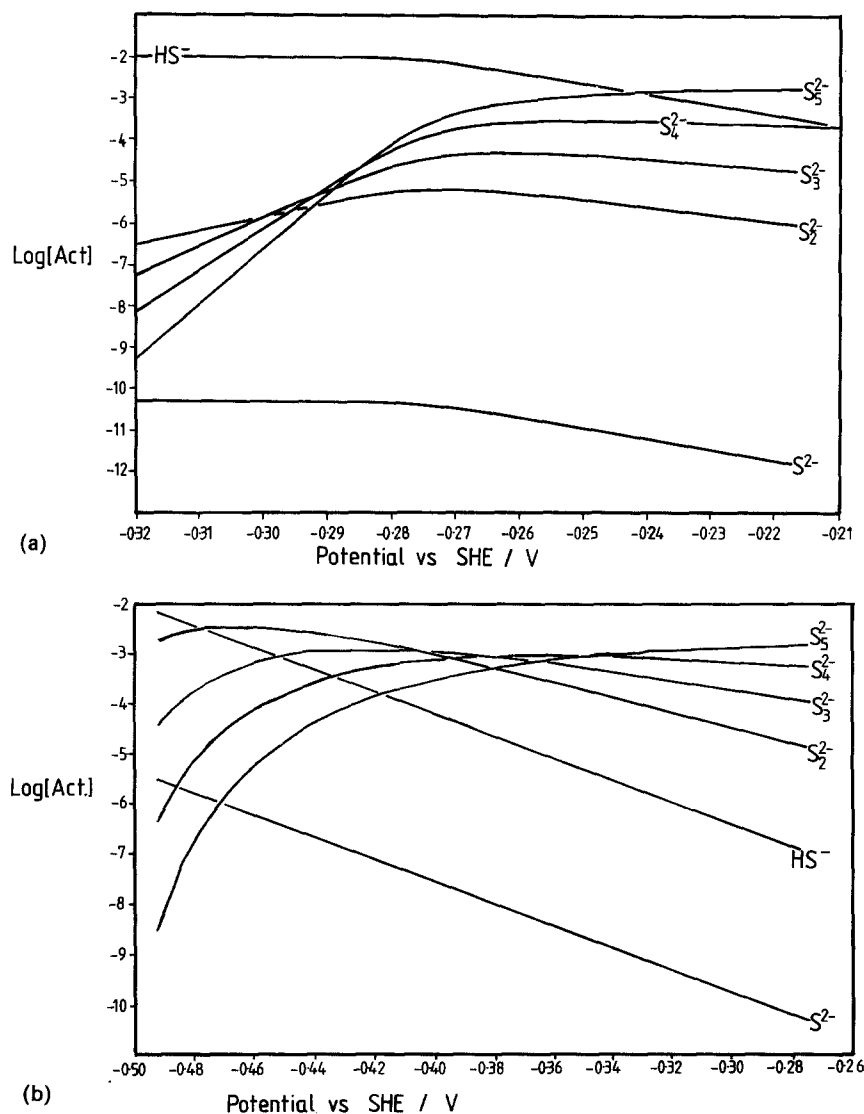
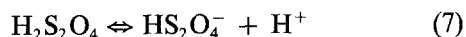
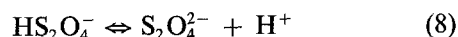


Fig. 4. Polysulphide distribution against electrode potential: (a) pH = 9 at 298.15 K, (b) pH 14 at 298.15 K. Dissolved sulphur activity = 0.01.

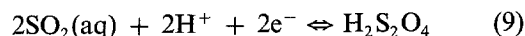
Fig. 5:



$$\log \left\{ \frac{(\text{HS}_2\text{O}_4^-)}{(\text{H}_2\text{S}_2\text{O}_4)} \right\} = \text{pH} - 0.42$$

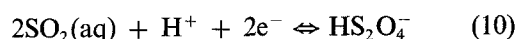


$$\log \left\{ \frac{(\text{S}_2\text{O}_4^{2-})}{(\text{HS}_2\text{O}_4^-)} \right\} = \text{pH} - 2.49$$



$$E/\text{V} = 0.0792 - 0.0591\text{pH} + 0.0591$$

$$\times \log (\text{SO}_2(\text{aq})) - 0.0296 \log (\text{H}_2\text{S}_2\text{O}_4)$$



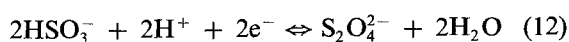
$$E/\text{V} = 0.0683 - 0.0296\text{pH} + 0.0591 \log (\text{SO}_2(\text{aq}))$$

$$- 0.0296 \log (\text{HS}_2\text{O}_4^-)$$



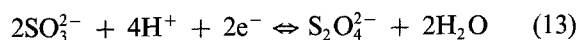
$$E/\text{V} = 0.1728 - 0.0887\text{pH} + 0.059 \log (\text{HSO}_3^-)$$

$$- 0.0295 \log (\text{HS}_2\text{O}_4^-)$$



$$E/\text{V} = 0.0992 - 0.0591\text{pH} + 0.0591 \log (\text{HSO}_3^-)$$

$$- 0.0295 \log (\text{S}_2\text{O}_4^{2-})$$

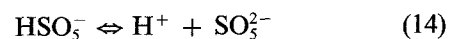


$$E/\text{V} = 0.5263 - 0.1183\text{pH} + 0.0591 \log (\text{SO}_3^{2-})$$

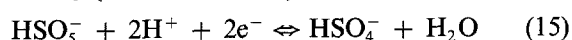
$$- 0.0295 \log (\text{S}_2\text{O}_4^{2-})$$

However, dithionite solutions decompose in acidic solutions [25–28].

The very powerful oxidizing agent Caro's acid (H_2SO_5) also has no predominance area. The following equations have been calculated from the data discussed critically by Spiro [29] and are plotted in Fig. 6, excluding peroxodisulphate species from the calculations:

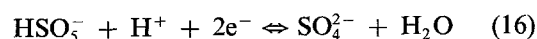


$$\log \left\{ \frac{(\text{SO}_5^{2-})}{(\text{HSO}_5^-)} \right\} = \text{pH} - 9.88$$



$$E/\text{V} = 1.81 - 0.0591\text{pH} + 0.0296$$

$$\times \log \left\{ \frac{(\text{HSO}_5^-)}{(\text{HSO}_4^-)} \right\}$$



$$E/\text{V} = 1.75 - 0.0296\text{pH} + 0.0296$$

$$\times \log \left\{ \frac{(\text{HSO}_5^-)}{(\text{SO}_4^{2-})} \right\}$$

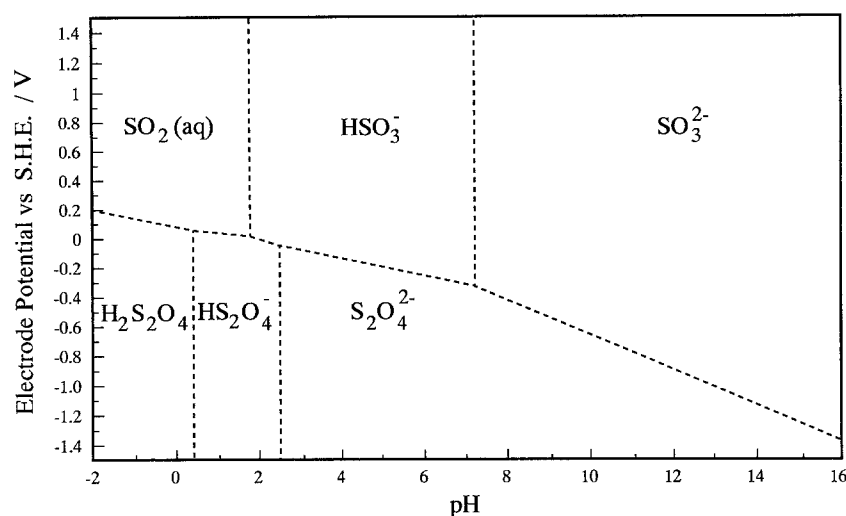
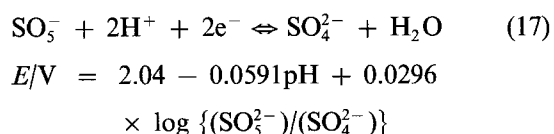


Fig. 5. Metastable potential–pH diagram of the sulphite/dithionite system at 298.15 K, excluding elemental sulphur. Dissolved sulphur activity = 0.01.



As for peroxodisulphate, peroxomonosulphate species are predicted to be capable of oxidizing water to oxygen.

Although sulphur species other than these and those listed in Table 1 have been identified [e.g. 27, 28], their instability has presumably precluded determination of their Gibbs energies of formation. Sulphur itself is the most complex of elements, existing in half a million different forms [30].

5. Conclusions

Only three sulphur oxidation states (–2, 0 and +6) are stable in sulphur–water systems under ambient conditions. A metastable diagram can be produced by eliminating the +6 oxidation state species, which

have a large activation energy barrier associated with their formation from lower oxidation state species such as sulphide. This predicts the metastability of other species, including thiosulphate, sulphite and dithionate, which have been detected in the oxidation of sulphide solutions. By eliminating all sulphony species (i.e. species with oxidation states > 0), the areas of predominance of the metastable polysulphides species can also be calculated. Other sulphony species of technological importance, such as dithionite and peroxomonosulphate have no areas of predominance, reflecting their instability as strong reducing and oxidizing agents, respectively.

Acknowledgements

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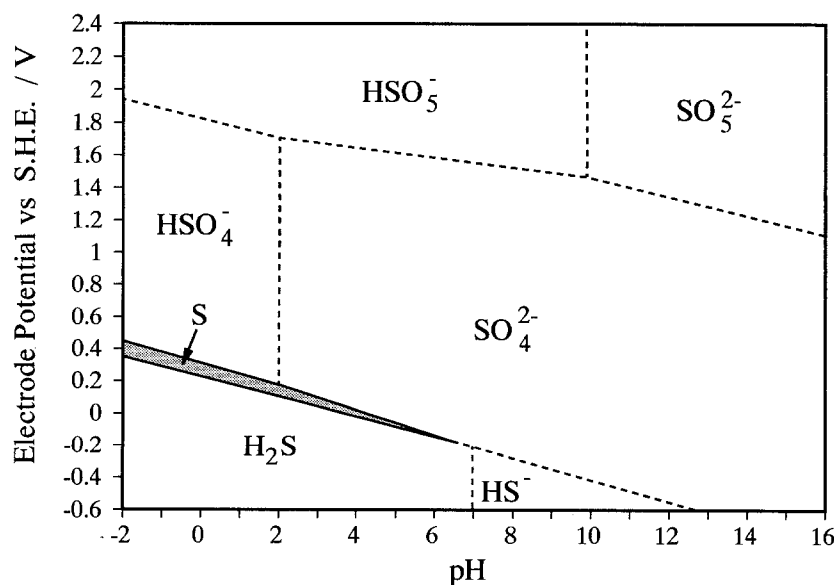


Fig. 6. Metastable potential–pH diagram considering peroxomonosulphate and excluding peroxodisulphate at 298.15 K. Dissolved sulphur activity = 0.01.

References

- [1] B. M. Wilson and R. D. Newell, *Chem. Eng. Prog.* **80**(10) (1984) 40.
- [2] I. Thompson, Ph.D. Thesis, University of London (1987).
- [3] G. H. Kelsall and I. Thompson, in Proc. Gas Research Institute (GRI) Symposium on 'Liquid Redox Processes for Hydrogen Sulphide Removal'. Austin, Texas, May 1989, GRI, Chicago, (1989) pp. 34-50.
- [4] G. H. Kelsall and I. Thompson, *J. Appl. Electrochem.* **23** (1993) 287.
- [5] *Idem*, *J. Appl. Electrochem.* **23** (1993) 296.
- [6] G. H. Kelsall, I. Thompson and P. A. Francis, *J. Appl. Electrochem.* **23** (1993) in press.
- [7] G. H. Kelsall and I. Thompson, *J. Appl. Electrochem.* **23** (1993) in press.
- [8] G. H. Kelsall and D. J. Robbins, in 'Electrochemical Engineering', I. Chem. E. Symposium Series No. 112, I. Chem. E., Rugby, UK (1989) pp. 277-87.
- [9] S. Zhdanov, in 'Standard Potentials in Aqueous Solution', (edited by A. J. Bard, R. Parsons and J. Jordan), Marcel Dekker, New York (1985) pp. 93-111.
- [10] M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions', Pergamon, Oxford (1966).
- [11] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11**(supplement 2), (1982).
- [12] T. I. Barry, R. H. Davies, J. A. Gisby, S. M. Hodson and N. J. Pugh, 'MTDATA Handbook: Documentation for the NPL Metallurgical and Thermochemical Databank', National Physical Laboratory, Teddington, UK (1989).
- [13] T. I. Barry, R. H. Davies, J. A. Gisby, S. M. Hodson and N. J. Pugh, Proc. 6th Conf. High Temperatures, Chemistry of Inorganic Materials, 3-7 April 1989, NIST, Gaithersburg, MA, USA.
- [14] A. T. Kuhn, G. H. Kelsall and M. S. Chana, *J. Chem. Tech. Biotechnol.* **33A** (1983) 406.
- [15] R. J. Meyers, *J. Chem. Ed.* **63**(8) (1986) 687.
- [16] W. Giggenbach, *Inorg. Chem.* **10** (1971) 1333.
- [17] B. Meyer, K. Ward, K. Koshap and L. Peter, *Inorg. Chem.* **22** (1983) 2345.
- [18] S. Licht and J. Manassen, *J. Electrochem. Soc.* **134**(4) (1987) 918.
- [19] M. A. A. Schoonen and H. L. Barnes, *Geochem. Cosmochim. Acta* **52** (1988) 649.
- [20] G. Maronney, *J. Chim. Physique* **56** (1959) 202, 214.
- [21] G. Valensi, Proc. 2nd CITCE Meeting, Milan, 1951, (Butterworths, London, 1952) pp. 51-67.
- [22] G. Maronny and G. Valensi, Proc. 6th CITCE Meeting, Poitiers, 1954, (Butterworths, London, 1955) pp. 180-9.
- [23] *Idem*, Proc. 7th CITCE Meeting, Lindau, 1955, (Butterworths, London, 1957) pp. 266-73.
- [24] *Idem*, Proc. 8th CITCE Meeting, Madrid, 1956 (Butterworths, London, 1958) pp. 204-17.
- [25] S. I. Zhdanov, in 'Encyclopedia of Electrochemistry of the Elements', Vol. 4, (edited by A. J. Bard), Marcel Dekker, NY (1974) pp. 273-360.
- [26] M. S. Chao, *J. Electrochem. Soc.* **133**(5) (1986) 954.
- [27] D. Lyons and G. Nickless, in 'Inorganic Sulphur Chemistry', (edited by G. Nickless), Elsevier, Amsterdam (1968) Chap. 14.
- [28] M. Schmidt and W. Siebert, in 'Comprehensive Inorganic Chemistry', Vol. 2, Pergamon, Oxford, Chap. 23, pp. 795-933.
- [29] M. Spiro, *Electrochim. Acta* **24** (1979) 313.
- [30] B. Meyer, *Chem. Revs.* **64** (1964) 429.

Appendix — 1. Thermodynamic data for S-H₂O systemsTable 1. Standard Gibbs energies of formation of species in the S-H₂O system at 298 K

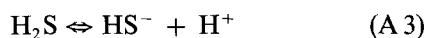
Species	$\Delta G_f^0/\text{kJ mol}^{-1}$ [9]	$\Delta G_f^0/\text{kJ mol}^{-1}$ [10]	$\Delta G_f^0/\text{kJ mol}^{-1}$ [11]
H ₂ S (g)	-33.56	-33.020	-33.56
H ₂ S	-27.87	-27.363	-27.83
HS ⁻	12.05	12.594	12.08
S ²⁻	120.5 (see text)	91.872	85.8
HS (g)	113.30	-	113.29
S ₂ ²⁻	79.5	82.630	79.5
S ₃ ²⁻	73.6	75.178	73.7
S ₄ ²⁻	69.0	69.517	69.1
S ₅ ²⁻	65.7	65.64	65.7
S _{rhombic}	0	0	0
S _{monoclinic}	0.188	0.096	-
S ₈ (g)	49.66	-	49.63
S ₂ (g)	79.33	-	-
S (g)	238.28	-	238.250
S ₂ O (g)	-138.833	-	-
SO	-19.836	-53.473	-19.853
S ₂ O ₃ ²⁻	-518.8?	-532.205	-522.5
H ₂ S ₂ O ₃	-	-543.502	-
S ₂ O ₆ ²⁻	-956.0?	-956.04	-
S ₄ O ₆ ²⁻	-1022.2?	-1022.2	-1040.4
S ₂ O ₄ ²⁻	-600.4	-577.392	-600.3
HS ₂ O ₄ ⁻	-614.6	-591.651	-614.5
H ₂ S ₂ O ₄	-616.7	-	-616.6
S ₃ O ₆ ²⁻	-958?	-958.136	-
SO ₂ (g)	-300.194	-300.369	-300.194
SO ₂	-300.708	-	-300.676
H ₂ SO ₃	-537.90	-538.439	-537.81
HSO ₃ ⁻	-527.81	-527.184	-527.77
SO ₃ ²⁻	-486.6	-485.762	-486.5
S ₂ O ₃ ²⁻	-791?	-	-
S ₂ O ₆ ²⁻	-966?	-966.504	-
SO ₃ (g)	-371.08	-370.368	-371.06
H ₂ SO ₄ (g)	-662.91	-	-
H ₂ SO ₄	-744.63	-741.990	-744.53
HSO ₄ ⁻	-756.01	-752.869	-755.91
SO ₄ ²⁻	-744.63	-741.991	-744.53
S ₂ O ₈ ²⁻	-1110.4	-1096.208	-1114.9
H ₂ S ₂ O ₈	-1110.4	-	-
SO ₅ ²⁻	-587.519 [26]	-	-
HSO ₅ ⁻	-643.914 [26]	-	-
H ₂ SO ₅	-	-	-
H ₂ O	-237.178	-237.191	-237.129

Appendix – 2. Thermodynamic equations for S–H₂O systems
Thermodynamically stable S–H₂O systems
(a) Chemical reactions


$$\log (\text{H}_2\text{S}) = -0.90 + \log p_{\text{H}_2\text{S}}$$



$$\log \{(\text{S}^{2-})/(\text{HS}^-)\} = \text{pH} - 19$$



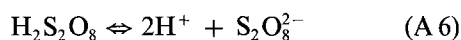
$$\log \{(\text{HS}^-)/(\text{H}_2\text{S})\} = \text{pH} - 6.99$$



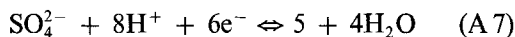
$$\log \{(\text{SO}_4^{2-})/(\text{HSO}_4^-)\} = \text{pH} - 1.994$$



$$\log p_{\text{SO}_3} = -25.89 + \log (\text{HSO}_4^-) - \text{pH}$$



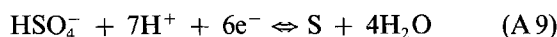
$$\log \{(\text{S}_2\text{O}_8^{2-})/(\text{H}_2\text{S}_2\text{O}_8)\} = 0 + 2\text{pH}$$

(b) Electrochemical reactions


$$E/V = 0.3525 + 0.0099 \log (\text{SO}_4^{2-}) - 0.078\text{pH}$$



$$E/V = 0.1444 - 0.0591\text{pH} - 0.0296 \log (\text{H}_2\text{S})$$

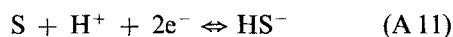


$$E/V = 0.3329 - 0.0690\text{pH} + 0.0098 \log (\text{HSO}_4^-)$$



$$E/V = 0.3005 - 0.0739\text{pH} + 0.0074$$

$$\times \log \{(\text{SO}_4^{2-})/(\text{H}_2\text{S})\}$$

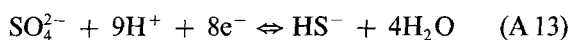


$$E/V = -0.0624 - 0.0296\text{pH} - 0.0296 \log (\text{HS}^-)$$



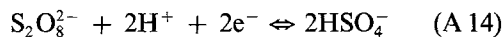
$$E/V = 0.2858 - 0.0666\text{pH} + 0.0074$$

$$\times \log \{(\text{HSO}_4^-)/(\text{H}_2\text{S})\}$$



$$E/V = 0.2488 - 0.0666\text{pH} + 0.0074$$

$$\times \log \{(\text{SO}_4^{2-})/(\text{HS}^-)\}$$

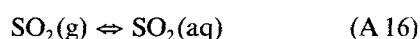


$$E/V = 2.0813 - 0.0591\text{pH} + 0.0296$$

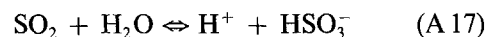
$$\times \log \{(\text{H}_2\text{S}_2\text{O}_8^{2-})/(\text{HSO}_4^-)^2\}$$



$$E/V = 1.9633 + 0.0296 \log \{(\text{S}_2\text{O}_8^{2-})/(\text{SO}_4^{2-})^2\}$$

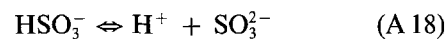
Metastable S–H₂O systems excluding S(VI) species
(a) Chemical reactions


$$\log (\text{SO}_2(\text{aq})) = 0.09 + \log p_{\text{SO}_2(\text{g})}$$

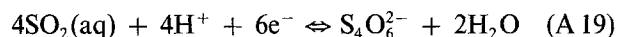


$$\log (\text{HSO}_3^-) = -1.77 + \text{pH} + \log (\text{SO}_2(\text{aq}))$$

$$\log (\text{HSO}_3^-) = -1.68 + \text{pH} + \log p_{\text{SO}_2(\text{g})}$$

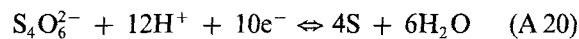


$$\log \{(\text{SO}_3^{2-})/(\text{HSO}_3^-)\} = \text{pH} - 7.22$$

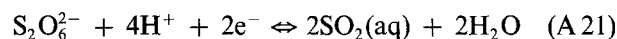
(b) Electrochemical reactions


$$E/V = 0.5074 - 0.0394\text{pH} + 0.0394 \log (\text{SO}_2(\text{aq}))$$

$$- 0.0098 \log (\text{S}_4\text{O}_6^{2-})$$

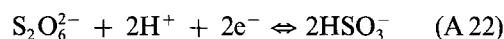


$$E/V = 0.4155 - 0.071\text{pH} + 0.0059 \log (\text{S}_4\text{O}_6^{2-})$$



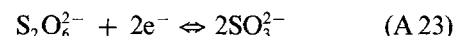
$$E/V = 0.5689 - 0.1183\text{pH} + 0.0296 \log (\text{S}_2\text{O}_6^{2-})$$

$$- 0.0591 \log (\text{SO}_2(\text{aq}))$$



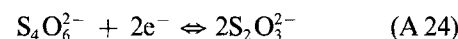
$$E/V = 0.4644 - 0.0591\text{pH} + 0.0296 \log (\text{S}_2\text{O}_6^{2-})$$

$$- 0.0591 \log (\text{HSO}_3^-)$$



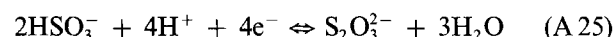
$$E/V = 0.0373 + 0.0296 \log (\text{S}_2\text{O}_6^{2-}) - 0.0591$$

$$\times \log (\text{SO}_3^{2-})$$



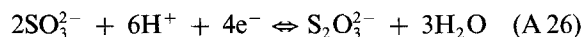
$$E/V = 0.0798 + 0.0296 \log (\text{S}_4\text{O}_6^{2-}) - 0.0591$$

$$\times \log (\text{S}_2\text{O}_3^{2-})$$



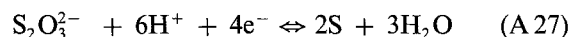
$$E/V = 0.4527 - 0.0591\text{pH} + 0.0296 \log (\text{HSO}_3^-)$$

$$- 0.0148 \log (\text{S}_2\text{O}_3^{2-})$$

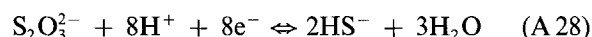


$$E/V = 0.6663 - 0.0887\text{pH} + 0.0296 \log (\text{SO}_3^{2-})$$

$$- 0.0148 \log (\text{S}_2\text{O}_3^{2-})$$

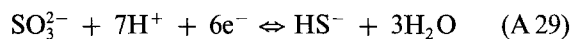


$$E/V = 0.4994 - 0.0887\text{pH} + 0.0148 \log (\text{S}_2\text{O}_3^{2-})$$



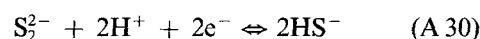
$$E/V = 0.2185 - 0.0591\text{pH} + 0.007 \log (\text{S}_2\text{O}_3^{2-})$$

$$- 0.0148 \log (\text{HS}^-)$$

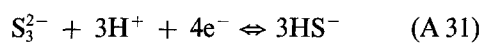


$$E/V = 0.3677 - 0.069\text{pH} + 0.0098$$

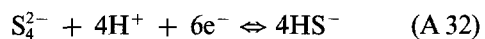
$$\times \log \{(\text{SO}_3^{2-})/(\text{HS}^-)\}$$

Metastable S–H₂O systems excluding species with oxidation states > 0
(a) Electrochemical reactions


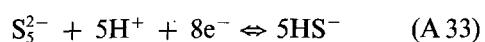
$$E/V = 0.2871 - 0.0591\text{pH} + 0.0296 \log (S_2^{2-}) - 0.0591 \log (HS^-)$$



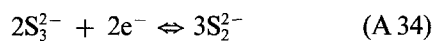
$$E/V = 0.0970 - 0.0444\text{pH} + 0.0149 \log (S_3^{2-}) - 0.0444 \log (HS^-)$$



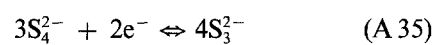
$$E/V = 0.0359 - 0.0394\text{pH} + 0.0099 \log (S_4^{2-}) - 0.0394 \log (HS^-)$$



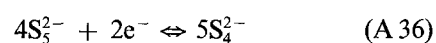
$$E/V = 0.0071 - 0.0370\text{pH} + 0.0074 \log (S_5^{2-}) - 0.0370 \log (HS^-)$$



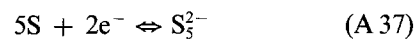
$$E/V = -0.4731 - 0.0887 \log (S_2^{2-}) + 0.0591 \times \log (S_3^{2-})$$



$$E/V = -0.4529 - 0.1183 \log (S_3^{2-}) + 0.0887 \times \log (S_4^{2-})$$



$$E/V = -0.426 - 0.1479 \log (S_4^{2-}) + 0.1183 \times \log (S_5^{2-})$$



$$E/V = -0.3405 - 0.0296 \log (S_5^{2-})$$