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Redox chemistry of H_2S oxidation by the British Gas Stretford process
Part IV: V–S–H_2O thermodynamics and aqueous vanadium (V) reduction in alkaline solutions

G. H. KELSALL, I. THOMPSON*, P.A. FRANCIS‡

Department of Mineral Resources Engineering, Imperial College, London SW7 2BP, Great Britain

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The thermodynamics of V–H_2O and V–S–H_2O systems at 298 K are summarized in the form of potential–pH and activity–pH diagrams calculated from recently published critically assessed standard Gibbs energies of formation. At pH 9, as used in Stretford Processes, V–H_2O potential–pH diagrams predicted that the V(V)/V(IV) couple involves $HV_2O_7^{3-}$/$V_4O_9^{2-}$ ions. However, in neutral and alkaline solutions there is difficulty in discriminating between kinetic intermediates and thermodynamically stable solution species, some with V(V)/V(IV) mixed oxidation states. Hence, $V_{18}O_{42}^{12-}$ ions may be the stable V(IV) species, depending on the concentration, though no thermodynamic data are available to enable them to be included in potential-pH calculations. Potential-pH diagrams for V–S–H_2O systems predicted an area of stability for VS_4 in the pH range ≈ 2–8 and over a restricted potential range; neither VS nor VS_2 were predicted to be stable under any conditions considered. In cyclic voltammetric experiments at Hg, Au and vitreous carbon electrodes, reduction of vanadium (V) species (probably $HV_2O_7^{3-}$ ions) was found to be irreversible on a variety of electrode surfaces and, at lower potentials, led predominantly to the formation of solid oxide films (V_3O_5, V_2O_3 and VO) rather than to V(IV) solution species, of which $V_{18}O_{42}^{12-}$ ions probably predominate at equilibrium. In the presence of the large excess of HS^- ions required to form VS_4^{3-} ions, the electrochemical behaviour of a gold electrode was dominated by the former species.

1. Introduction

As described elsewhere [1–3], Stretford Processes oxidize hydrogen sulphide from process gases, to elemental sulphur. The H_2S-containing gas is contacted with an alkaline solution containing vanadium (V) salts and anthraquinone disulphonates; H_2S 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, reoxidizing it and forming elemental sulphur. Being naturally hydrophobic, the sulphur particles 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. Hence, vanadium species and anthraquinone disulphonates act as homogeneous oxygen reduction catalysts.

Previous papers in this series have reported the thermodynamics of sulphur–water systems [4] and the electrochemical behaviour of the S/HS^- [5] and anthraquinone/anthraquinol [6] couples. The objective of the presently reported work was to summarize the thermodynamics of vanadium–water and vanadium–sulphur–water systems, particularly as Stretford plants occasionally suffer from precipitation of ill-defined black solids containing vanadium, so that potential–pH and activity–pH diagrams might provide a framework to explain their occurrence. In addition, the reduction kinetics of vanadium (V) species at pH 9 at a Hg, Au and vitreous carbon eletrodes were investigated briefly, prior to stopped-flow spectrophotometric experiments [7].

2. Experimental details

Cyclic voltammetry and potential pulse studies were carried out using a Taccussel hanging mercury drop electrode (HMDE), the bore of which was cleaned prior to use with 6 kmol HNO_3 m^{-3} and triply distilled water, then rendered hydrophobic by treating it with a solution of dimethyldichlorosilane (2% in 1,1,1-trichloroethane, BDH, Merck Ltd.).

The surface area of one drop was calculated by making 25 complete revolutions of the micrometer drive and measuring the mass of mercury ejected. From this, the average mass of mercury ejected by one revolution was derived; assuming that the drop had a

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* Present address: Lever Development Centre Casalpusterlengo, via Lever Gibbs, 20071 Casalpusterlengo, Italy.
‡ Present address: Billiton Research BV, PO Box 40, 6800 AA Arnhem, The Netherlands.

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spherical shape, the surface area was calculated to be $1.974 \times 10^{-6} m^2$. The capillary bore was $100 \mu m$ in diameter, the area of attachment corresponding to only 0.4% of the total drop area.

Gold, platinum and vitreous carbon rotating discs were also used as working electrodes. All potentials are reported versus the standard hydrogen electrode (S.H.E.), assuming that the potential of the saturated calomel electrode was 0.242 V vs S.H.E. The electrochemical studies were carried out in a three compartment cell using a Wenking MP81 potentiostat. The control potentials were provided by a Hi-Tek PPR1 waveform generator and the current–potential data recorded on a JJ PL4 chart recorder.

Most experiments were at room temperature (≈ 20 °C), but a series were recorded at 40 °C using a jacketed electrochemical cell which contained heated water maintained at 41 °C by a Grants thermostatically controlled water bath. Voltammograms were started from the positive potential limit (0.331 V vs S.H.E. for a mercury electrode) for vanadium (V) solutions, or from the rest potential for vanadium (IV) solutions (−0.193 V vs S.H.E.).

2.1. *Solution preparation*

A carbonate buffer of pH 9.3 was prepared by dissolving the appropriate mass of analytical grade chemicals (BDH, Merck Ltd.) in triply distilled water to produce a solution containing 0.059 kmol Na_2CO_3 + 0.223 kmol Na HCO_3 + 0.1 kmol $Na_2SO_4 m^{-3}$. A borate buffer of pH 9.2, containing 12.5 mol $Na_2B_4O_7.10H_2O$ + 0.9 mol NaOH + 0.1 kmol $Na_2SO_4 m^{-3}$ was prepared similarly.

A stock solution of 0.1 kmol V(V) m^{-3} was prepared by disssolving the appropriate mass of $NaVO_3$ (BDH, Merck Ltd.) in the carbonate buffer, using an ultrasonic bath to enhance the dissolution kinetics. V(V) solutions were also prepared by dissolving vanadium pentoxide (BDH, Merck Ltd.) in dilute sodium hydroxide, according to Reaction 1:

$$V_2O_5 + 3NaOH \longrightarrow HV_2O_7^{3-} + H_2O + 3Na^+ \qquad (1)$$

The colourless stock solutions could be kept for many months without degradation; they were diluted with the appropriate buffer solution before use. All solutions were thoroughly deoxygenated by sparging with White Spot grade nitrogen (BOC plc) for at least an hour before any electrochemical experiments. Identical results were obtained from vanadium (V) solutions which had been prepared from sodium vanadate and vanadium pentoxide starting materials.

A stock solution containing 10 mol vanadium (IV) m^{-3} was prepared by dissolving 0.635 g of blue vanadyl sulphate, $VOSO_4.6H_2O$ (BDH, Merck Ltd.), in 250 cm^3 of oxygen-free carbonate buffer. Since the predominant V(IV) species are thought to be $V_{18}O_{42}^{12-}$ ions [8], 6.7 cm^3 of 1 kmol NaOH m^{-3} solution was added to allow for the hydroxide ion consumption during Reaction 2:

$$18VOSO_4 + 48OH^- \longrightarrow V_{18}O_{42}^{12-} + 18SO_4^{2-} + 24H_2O \qquad (2)$$

The resulting dark brown solution was diluted tenfold with an oxygen-free buffer solution before electrochemical experiments.

A solution of the complex VS_4^{3-} was prepared according to the method of Harrison and Howarth [9]. 10 cm^3 of aqueous ammonia '0.880' (BDH, Merck Ltd.) was added to 90 cm^3 of distilled water and the resulting solution was saturated with hydrogen sulphide. 1 cm^3 of stock vanadium (V) solution (prepared from V_2O_5 as detailed above) was then added; this produced a deep purple solution containing 1 mol $VS_4^{3-} m^{-3}$. If this solution was allowed to contact air it turned orange initially and after a longer time became colourless, as elemental sulphur was precipitated. A solution, initially containing 0.2 mol $VS_4^{3-} m^{-3}$, was prepared by diluting the above solution five fold with an oxygen-free carbonate buffer.

3. Thermodynamics of V–S–H_2O systems

The potential–pH diagram for the vanadium–H_2O system shown in Fig. 1 was produced as described previously [4]. The thermodynamic data, in the form of ΔG_f° values from a recently published source [10], are listed in the Appendix, together with all the reactions and equations used to construct the diagrams; parentheses in the equations denote activities. These data differ significantly from those used by Post and Robbins [11], most notably in the predicted predominance of $V_4O_{12}^{4-}$ ions in more concentrated solutions of neutral pH, in the inclusion of peroxy species with predominance areas at high potential and in considering the non-stoichiometric oxides $V_6O_{13}(c)$, $V_3O_5(c)$ and $V_4O_7(c)$, the last of which had no area of predominance (Fig. 1). Data from the most recent National Bureau of Standards (NBS) source [12] are also included in Table 1 for comparison.

Figure 1 predicts that reduction of $HV_2O_7^{3-}$ ions will produce $V_4O_9^{2-}$ ions, with the solid phase $V_3O_5(c)$ forming at lower potentials; however, mixed-valence salts [2,8] are also possible, though no thermodynamic data are yet available for these species to be included in Fig. 1.

The corresponding activity–pH diagrams are shown in Fig. 2a–d for V(V)/V_2O_5(c), V(IV)/V_2O_4(c) V(III)/ V_2O_3(c) and V(II)/VO(c). Again, the main difference between these diagrams and those of Post and Robbins is the predominance area of $V_4O_{12}^{4-}$ ions in Fig. 2a.

Figure 3a shows a potential-pH diagram for the V–S–H_2O system at 298 K and for 0.01 activities of dissolved species. No aqueous sulphur species are included on the diagram for the sake of clarity, their behaviour having been covered in previous papers in this series [4,5]. Only the VS_4(c) phase showed a narrow area of stability in the pH range about 2–7.5 and coexisted with the V_3O_5(c) phase over most of that range. Hence, solid vanadium sulphide phases are

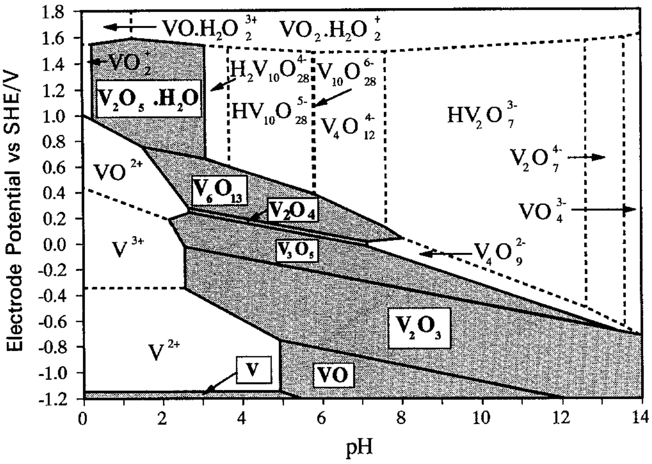

Fig. 1. Potential–pH diagram for the V–H_2O system at 298 K. Activity of dissolved species = 0.01.

not predicted to precipitate from well-controlled Stretford solutions (pH $\approx$ 8.5), which is one reason why they were chosen for that application.

For comparison, Fig. 3b and c shows potential–pH diagrams for V–S–H_2O systems from which, respectively, S(VI) and all sulphoxy species were excluded for reasons explained elsewhere [4,5]. This had the effect of extending the area of stability of VS_4(c) to slightly more positive potentials (by 50 mV at pH 8.5) due to the reaction:

$$V_3O_5(c) + 12S + 10H^+ + 10e^- \rightleftharpoons 3VS_4(c) + 5H_2O \qquad (A73)$$

$$E_{73}/V = 0.2362 - 0.0591pH$$

rather than:

$$V_3O_5(c) + 12SO_4^{2-} + 106H^+ + 82e^- \overset{3VS_4(c)\,+\,53H_2O}{\rightleftharpoons} \qquad (A74)$$

$$E_{74}/V = 0.3384 - 0.0765pH + 0.0086\log(SO_4^{2-})$$

determining the upper potential limit. Particularly if H_2S concentrations were to exceed the design capacity in a Stretford plant, so lowering the pH, it is understandable that conditions could result in precipitation of mixtures of (V_3O_5 + S + VS_4).

4. Results and discussion

A voltammogram of a HMDE in 10 mol V(V) m^{-3} at pH 9.3 is shown in Fig. 4. A sharp reduction peak was observed on the negative-going potential scan at 0.3 V vs S.H.E. together with the corresponding oxidation on the return cycle. There peaks were peculiar to the mercury electrode and the charge under them corresponded to the passage of 1.1 C m^{-2}, independent of the sweep rate, the stirring rate and the vanadium (V) concentration (for > 10^{-3} mol m^{-3}). This is consistent with the process responsible being the reduction of a monolayer of mercury (I) vanadate. The formation of a mercury (I) salt with vanadium anions has been reported [13] and used for analytical determination of dissolved vanadium concentrations. In the concentration range 10^{-4} to 10^{-2} mol m^{-3}, less than a monolayer of mercury (I) vanadate is formed at a HMDE when it is held at an oxidizing potential for 60 s [13]. The vanadium concentration determines the fractional surface coverage and hence the charge that is passed reducing this layer in a subsequent cathodic stripping potential scan, thus enabling determination of dissolved vanadium concentrations by cathodic stripping voltammetry. Calculations show that the close packing of mercury (I) ions results in a charge density of 2.9 C m^{-2}, so it is likely that the monolayer coverage is determined by the packing of the larger vanadium (V) ions (e.g. $HV_2O_7^{3-}$ ions).

A small reduction current was also observed at −0.18 V vs S.H.E., a potential which is accessible using H_2S as a reducing agent [3–5]. The reversible potential for the V(V)/V(IV) couple according to equation (A51) at this pH is −0.10 V vs S.H.E. Therefore, it is possible that reduction of vanadium (V) to (IV) may be responsible for this peak, producing $V_{18}O_{42}^{12-}$ or $V_4O_9^{2-}$ ions, according to Equations 3 and 4, though no thermodynamic data are yet available for $V_{18}O_{42}^{12-}$ ions.

$$2HV_2O_7^{3-} + 3H_2O + 4e^- \rightleftharpoons V_4O_9^{2-} + 8OH^- \qquad (A51)$$

$$E_{A51}/V = 0.9999 - 0.1183pH + 0.0147\log\{(HV_2O_7^{3-})^2/(V_4O_9^{2-})\}$$

$$9HV_2O_7^{3-} + 12H_2O + 18e^- \rightleftharpoons V_{18}O_{42}^{12-} + 33OH^- \qquad (3)$$

The large structural rearrangement required explains why the reduction current was less than an order of magnitude lower than that predicted for a reversible one electron transfer. The absence of a steady state diffusion controlled current at potentials < −0.25 V can be ascribed to the further reduction of $V_4O_9^{2-}$ ions to an adsorbed product:

$$3V_4O_9^{2-} + 14H^+ + 8e^- \rightleftharpoons 4V_3O_5(c) \qquad (A64)$$

$$E_{64}/V = 0.7414 - 0.1035pH + 0.0222\log(V_4O_9^{2-})$$

A third reduction was observed with a current onset at −0.6 V and a peak at −0.9 V vs S.H.E. As shown in

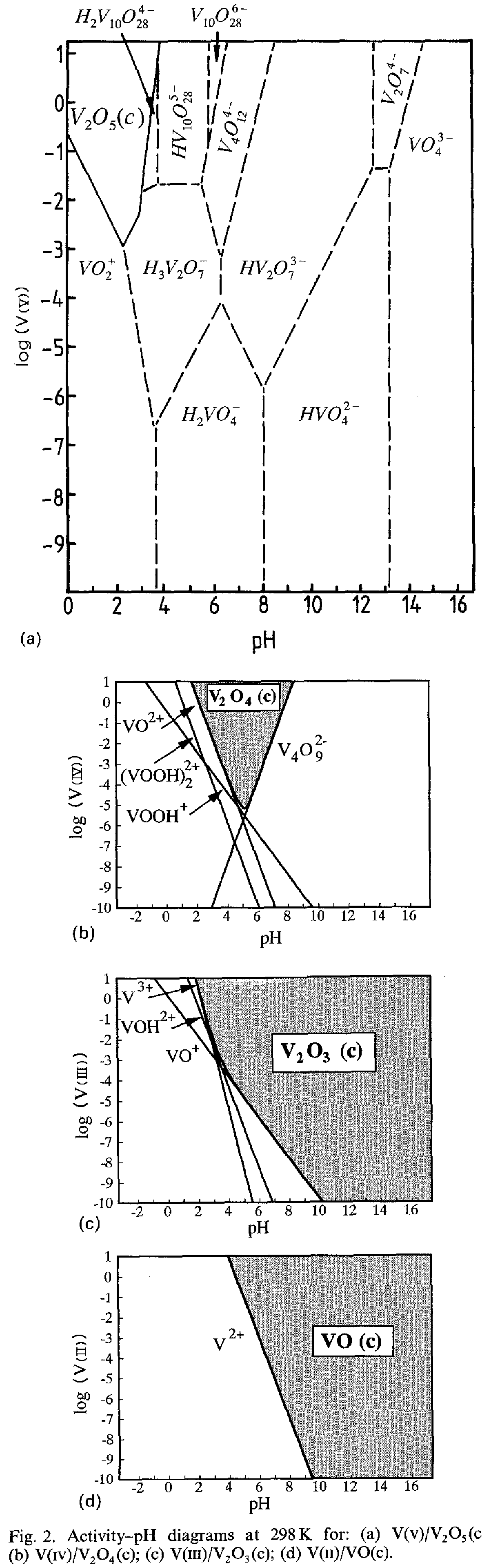

Fig. 2. Activity-pH diagrams at 298 K for: (a) $V(v)/V_2O_5(c)$; (b) $V(IV)/V_2O_4(c)$; (c) $V(III)/V_2O_3(c)$; (d) $V(II)/VO(c)$.

Fig. 1, these potentials at pH 9.3 are sufficient to produce first $V_3O_5(c)$:

$$3HV_2O_7^{3-} + 8H_2O + 10e^- \rightleftharpoons 2V_3O_5(c) + 19OH^- \quad (4)$$

then V_2O_3:

$$HV_2O_7^{3-} + 3H_2O + 4e^- \rightleftharpoons V_2O_3(c) + 7OH^- \quad (5)$$

with vanadium (II) oxide forming at lower potentials:

$$HV_2O_7^{3-} + 4H_2O + 6e^- \rightleftharpoons 2VO\ (c) + 9OH^- \quad (6)$$

$$V_2O_3(c) + 2H^+ + 2e^- \overset{f}{\rightleftharpoons} 2VO\ (c) + H_2O \quad (A67)$$

$$E_{A67}/V = -0.4841 - 0.0591pH$$

The presence of vanadium oxide phases facilitated hydrogen evolution, which is consistent with the known catalytic activity of vanadium [14].

The increasing reduction current with increasing potential on the positive-going potential sweep was probably due to potential-dependent changes in the electronic properties of the vanadium oxide film. At lower dissolved vanadium concentrations, small oxidation currents were observed in that potential region, so that in Fig. 4, a net current was detected at −0.9 V vs S.H.E. on the positive-going potential scan, due to oxide oxidation reactivating the electrode to V(v) reduction. Stirring did not suppress the re-oxidation peak at −0.1 V vs S.H.E., implying again that the reduction product was primarily an adsorbed film.

Figure 5 shows a voltammogram recorded on a gold flag electrode in a carbonate buffer solution (pH 9.3) containing 10 mol V(v) m^{-3}. The peaks at 0.4 V vs S.H.E. on the positive going scan and 0.3 V on the negative going scan, were due to gold oxide formation and reduction, respectively. For vanadium concentrations of 10 mol m^{-3} and above, a small reduction current due to the reduction of vanadium (v) to (IV) (approximately 0.1 of the magnitude of a reversible one electron reduction), was observed at a potential of −0.55 V vs S.H.E. The re-oxidation peak at 0.02 V vs SHE was observed only when a potential of −0.7 V vs SHE was exceeded on the negative going scan, which suggested than a film of reduced vanadium oxide was again formed at these lower potentials.

Further evidence that reduction of vanadium (v) results in the production of a solid film at potentials < 0.6 V vs S.H.E. was provided by voltammetry at a vitreous carbon disc electrode. This showed vanadium (v) reduction and re-oxidation behaviour similar to that observed in Fig. 4 and Fig. 5; large reduction currents were observed only at highly negative potentials, there was an extremely large potential separation between the reduction and re-oxidation peaks and current densities decreased with successive potential sweeps. Visual inspection of the electrode after such

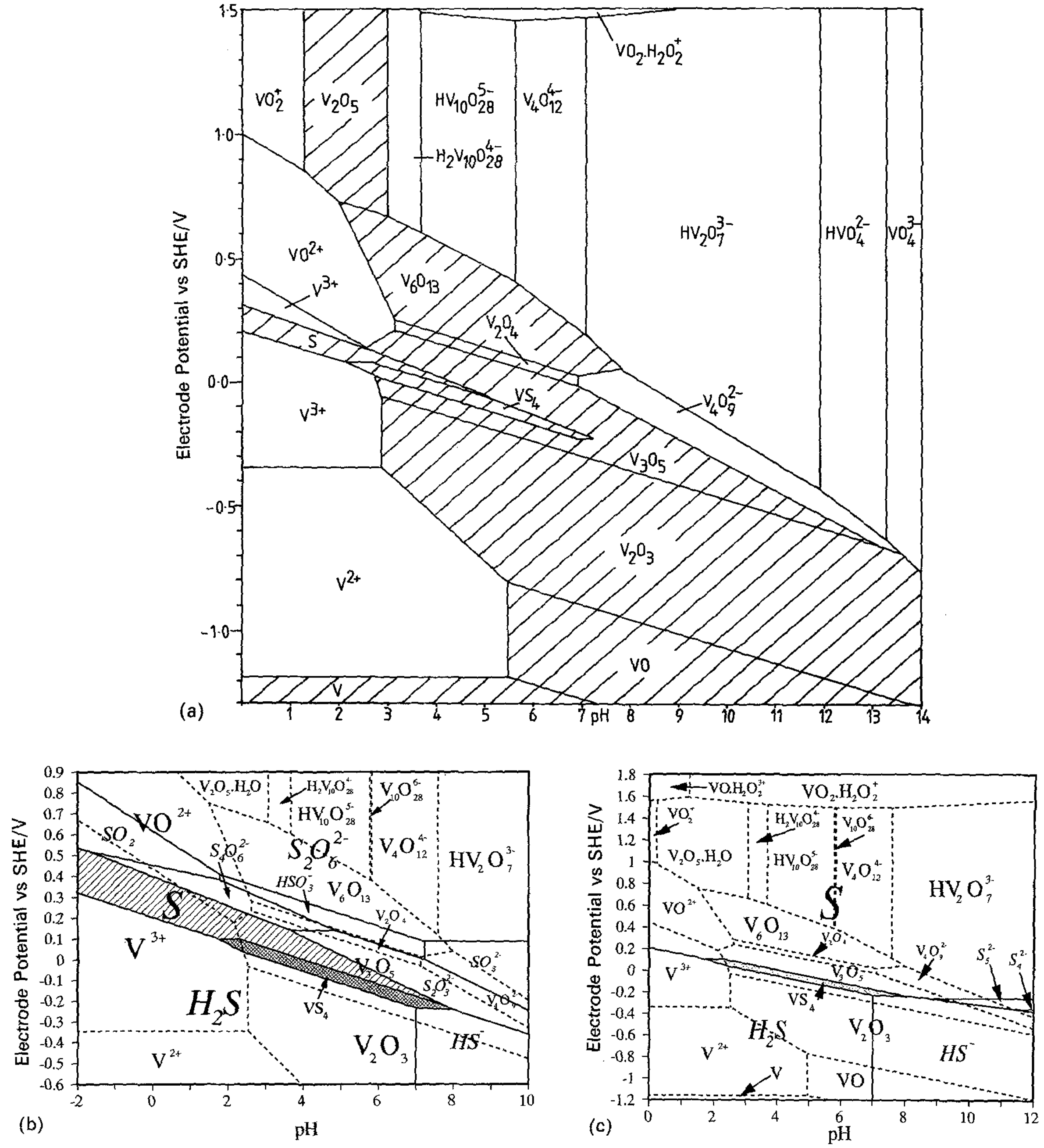

Fig. 3. Potential–pH diagrams for (a) the V–S–H$_2$O System at 298 K. Dissolved S species not shown (see [4] for S–H$_2$O diagrams). Activity of dissolved species = 0.01. (b) Excluding S(VI) species. Activities of dissolved vanadium and sulphur species 0.1 and 0.01, respectively. (c) Excluding all sulphoxy species. Activities of dissolved vanadium and sulphur species 0.1 and 0.01, respectively.

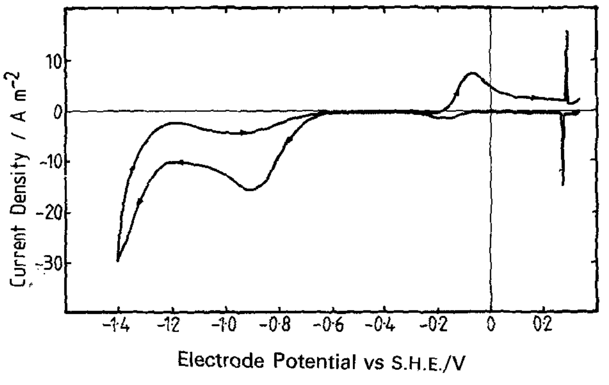

Fig. 4. Voltammogram of HMDE in 10 mol V(V) m^{-3} in pH 9.3 carbonate buffer at 40 °C. 1st potential sweep started at 0.33 V vs SHE, 50 mV s^{-1}.

treatment showed blue, green or purple interference patterns characteristic of a thin film, the thickness of which increased on holding the electrode at a potential of − 1.0 V vs S.H.E.

Voltammetry of a solution containing 1 mol V(IV) m^{-3} on a gold disc electrode revealed that no additional currents could be detected above the background currents in the carbonate buffer, in the potential range − 0.6 to + 0.3 V vs S.H.E. Since the reversible potential for V(V)/(IV) at pH 9.3 is about − 0.10 V vs S.H.E., based on Equation A51, an anodic limit of 0.3 V represents an oxidizing overpotential of 0.4 V.

The above evidence demonstrates that in alkaline solutions, the reduction of V(V) to V(IV) and the oxidation of V(IV), are irreversible processes at a range of electrode surfaces. If the vanadium (V) and V(IV)

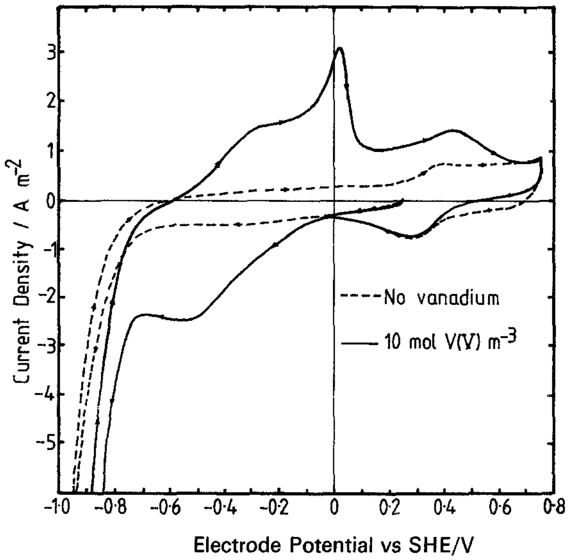

Fig. 5. Voltammogram of gold electrode in 10 mol V(v) m^{-3} in pH 9.3 carbonate buffer at 19 °C. 1st potential sweep started at 0.245 V vs S.H.E., 50 mV s^{-1}.

species are $HV_2O_7^{3-}$ ions (Fig. 2b) and $V_{18}O_{42}^{12-}$ ions [8], respectively, then it is not surprising that V(v) reduction is slow, since the formation of $V_{18}O_{42}^{12-}$ ions requires a considerable structural rearrangement. The overpotential requirement for this reduction is so high that the potential has to be lowered to values at which other reduction reactions can occur, producing oxide phases such as V_3O_5, V_2O_3 and VO.

This suggested that the reduction of V(v) species by HS^- ions in Stretford Processes proceeds via a specific chemical interaction between the two species. Thiovanadate complexes are known [7,9] and are likely reaction intermediates.

The cyclic voltammetric behaviour of VS_4^{3-} ions at a gold electrode is shown in Fig. 6, which is very similar to that in hydrosulphide solutions alone [5]. The saturation of a solution of ammonia with hydrogen sulphide results in the production of ammonium hydrosulphide:

$$NH_3(aq) + H_2S \rightleftharpoons NH_4^+ + HS^- \qquad (7)$$

The 10% aqueous ammonia solution, as used in the preparation of the VS_4^{3-} complex contained 1.8 kmol $NH_3\,m^{-3}$. When this was saturated with hydrogen sulphide, a solution containing 1.8 kmol $HS^-\,m^{-3}$ was formed. This is about 1000 times greater than the VS_4^{3-} concentration and explains why the voltammogram is essentially that of a hydrosulphide solution. If the hydrosulphide concentration was decreased, the complex decomposed. Thus, the redox behaviour of VS_4^{3-} ions was masked by the large background currents due to the presence of HS^- ions.

Results of stopped flow spectrophotometric experiments involving V(v) reacting with other components of Stretford processes, will be reported in Part V [7] of this series.

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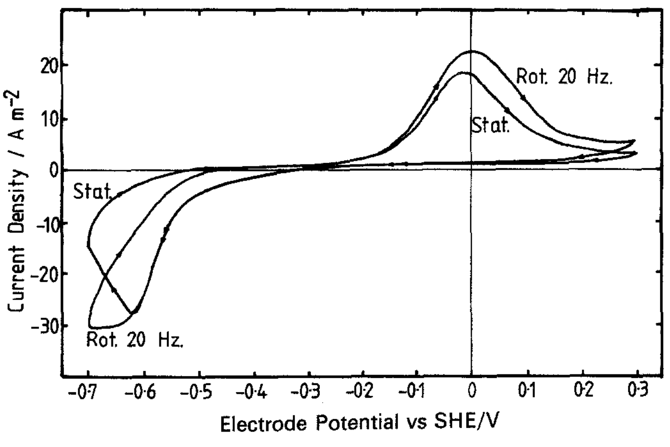

Fig. 6. Cyclic voltammogram of gold rotating disc electrode in 0.2 mol VS_4^{3-} + 360 mol $HS^-\,m^{-3}$ in pH 9.8 carbonate buffer, 100 mV s^{-1}.

Appendix — 1. Thermodynamic data for V–S–H_2O systems

Table 1. Standard Gibbs energies of formation for species in the V–S–H_2O system at 298 K.

Species	ΔG_f°/kJ mol^{-1} [10]	ΔG_f°/kJ mol^{-1} [12]	ΔG_f°/kJ mol^{-1} [11]
V^{2+}	−218	–	−226.773
VO(c)	−404.2	−404.2	−404.174
V^{3+}	−251.3	–	−251.375
V_2O_3(c)	−1139	−1139.3	−1139.303
VO^+	−451.8	–	−451.830
VOH^{2+}	−471.9	–	−471.913
V_3O_5(c)	−1816	−1803	–
V_4O_7(c)	−2473	−2456	–
V_2O_4(c)	−1318.6	−1318.3	−1318.378
VO^{2+}	−446.4	−446.4	−446.432
$VOOH^+$	−657	–	−656.880
$(VOOH)_2^{2+}$	−1331	–	−1330.512
$V_4O_9^{2-}$	−2784	–	−2783.615
V_6O_{13}(c)	−4109	–	–
V_2O_5(c)	−1419.4	−1419.5	−1419.631
$V_2O_5 \cdot H_2O$(c)	−1657?	–	–
VO_2^+	−587	−587.0	−587.015
VO_3^-	−783.7	−783.6	−783.663
VO_4^{3-}	−899.1	−899.0	−1020.110
HVO_4^{2-}	−974.9	−974.8	−974.9
$H_2VO_4^-$	−1020.9	−1020.8	−1020
H_3VO_4	−1040.3	–	–
$V_2O_7^{4-}$	−1720	−1719	−1719.624
$HV_2O_7^{3-}$	−1792	−1792.2	−1792.426
$H_3V_2O_7^-$	−1864	−1863.8	−1863.972
$V_3O_9^{3-}$	−2356	–	–
$V_4O_{12}^{4-}$	−3202	–	–
$V_{10}O_{28}^{6-}$	−7675	–	−7669.690
$HV_{10}O_{28}^{5-}$	−7708	−7702	−7702.744
$H_2V_{10}O_{28}^{4-}$	−7729	−7723	−7723.664
$VO_2 \cdot H_2O_2^+$	−746.4	−746.3	–
$VO \cdot H_2O_2^{3+}$	−523.4	−523.4	–
VO_2HO_2	–	−745.1	–
VS(c)	−191.3	–	–
V_2S_3(c)	−516.2	–	–
VS_4(c)	−286.0	–	–
$VOSO_4$(aq)	−1182	−1204.9	–
$VOSO_4$(c)	−1170	−1169.8	–
H_2O (l)	−237.178	−237.127	−237.233
OH^-	−157.293	−157.244	–
H_2O_2	−134.10	−134.03	–
HO_2^-	−67.4	−67.3	–

ΔH_f° and S° values for vanadium sulphides were from Mills [15] and the ΔG_f° values were calculated using S° values of 0.02893 and 0.03182 kJ mol^{-1} K^{-1} for elemental vanadium and sulphur, respectively [10].

Appendix — 2. Thermodynamic equations for V–H_2O systems

Chemical reactions

(a) Peroxy species

$$VO \cdot H_2O_2^{3+} + H_2O \rightleftharpoons VO_2 \cdot H_2O_2^+ + 2H^+ \quad (A1)$$

$$\log\{(VO_2 \cdot H_2O_2^+)/(VO \cdot H_2O_2^{3+})\} = 2pH - 2.48$$

$$HV_2O_7^{3-} + H_2O_2 + 5H^+ \rightleftharpoons 2VO_2 \cdot H_2O_2^+ + 3H_2O \quad (A2)$$

$$\log\{(VO_2 \cdot H_2O_2^+)^2/(HV_2O_7^{3-})\} = 25.25 + 2\log(H_2O_2) - 5pH$$

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad (A3)$$

$$\log\{(HO_2^-)/(H_2O_2)\} = pH - 11.69$$

(b) V(v) states

$$V_2O_5(c) + 2H^+ \rightleftharpoons 2VO_2^+ + H_2O \quad (A4)$$

$$\log(VO_2^+) = -0.72 - pH$$

$$V_2O_5(c) + 2H_2O \rightleftharpoons H_3V_2O_7^- + H^+ \quad (A5)$$

$$\log(H_3V_2O_7^-) = pH - 5.21$$

$$5V_2O_5(c) + 3H_2O \rightleftharpoons H_2V_{10}O_{28}^{4-} + 4H^+ \quad (A6)$$

$$\log(H_2V_{10}O_{28}^{4-}) = -13.93 + 4pH$$

$$H_2V_{10}O_{28}^{4-} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O \quad (A7)$$

$$\log\{(VO_2^+)^{10}/(H_2V_{10}O_{28}^{4-})\} = 6.73 - 14pH$$

$$5H_3V_2O_7^- + H^+ \rightleftharpoons H_2V_{10}O_{28}^{4-} + 7H_2O \quad (A8)$$

$$\log\{(H_2V_{10}O_{28}^{4-})/(H_3V_2O_7^-)^5\} = 12.13 - pH$$

$$H_2V_{10}O_{28}^{4-} \rightleftharpoons HV_{10}O_{28}^{5-} + H^+ \quad (A9)$$

$$\log\{(HV_{10}O_{28}^{5-})/(H_2V_{10}O_{28}^{4-})\} = -3.68 + pH$$

$$5H_3V_2O_7^- \rightleftharpoons HV_{10}O_{28}^{5-} + 7H_2O \quad (A10)$$

$$\log\{(HVO_{10}O_{28}^{5-})/(H_3V_2O_7^-)^5\} = 8.45$$

$$HV_{10}O_{28}^{5-} \rightleftharpoons V_{10}O_{28}^{6-} + H^+ \quad (A11)$$

$$\log\{(V_{10}O_{28}^{6-})/(HV_{10}O_{28}^{5-})\} = -5.78 + pH$$

$$5V_4O_{12}^{4-} + 8H^+ \rightleftharpoons 2V_{10}O_{28}^{6-} + 4H_2O \quad (A12)$$

$$\log\{(V_{10}O_{28}^{6-})^2/(V_4O_{12}^{4-})^5\} = 50.58 - 8pH$$

$$2HV_{10}O_{28}^{5-} + 4H_2O \rightleftharpoons 5V_4O_{12}^{4-} + 10H^+ \quad (A13)$$

$$\log\{(V_4O_{12}^{4-})^5/(HV_{10}O_{28}^{5-})^2\} = -62.14 + 10pH$$

$$V_4O_{12}^{4-} + 2H^+ + 2H_2O \rightleftharpoons 2H_3V_2O_7^- \quad (A14)$$

$$\log\{(H_3V_2O_7^-)^2/(V_4O_{12}^{4-})\} = 9.05 - 2pH$$

$$V_4O_{12}^{4-} + 2H_2O \rightleftharpoons 2HV_2O_7^{3-} + 2H^+ \quad (A15)$$

$$\log\{(HV_2O_7^{3-})^2/(V_4O_{12}^{4-})\} = -16.18 + 2pH$$

$$HV_2O_7^{3-} \rightleftharpoons V_2O_7^{4-} + H^+ \tag{A16}$$

$$\log\{(V_2O_7^{4-})/(HV_2O_7^{3-})\} = -12.61 + pH$$

$$2VO_4^{3-} + 2H^+ \rightleftharpoons V_2O_7^{4-} + H_2O \tag{A17}$$

$$\log\{(V_2O_7^{4-})/(VO_4^{3-})^2\} = 27.85 - 2pH$$

$$H_3V_2O_7^- + 3H^+ \rightleftharpoons 2VO_2^+ + 3H_2O \tag{A18}$$

$$\log\{(VO_2^+)^2/(H_3V_2O_7^-)\} = 3.77 - 3pH$$

$$H_3V_2O_7^- \rightleftharpoons HV_2O_7^{3-} + 2H^+ \tag{A19}$$

$$\log\{(HV_2O_7^{3-})/(H_3V_2O_7^-)\} = -12.61 + 2pH$$

$$HV_2O_7^{3-} + H_2O \rightleftharpoons 2HVO_4^{2-} + H^+ \tag{A20}$$

$$\log\{(HVO_4^{2-})^2/(HV_2O_7^{3-})\} = pH - 13.91$$

$$2HVO_4^{2-} \rightleftharpoons V_2O_7^{4-} + H_2O \tag{A21}$$

$$\log\{(V_2O_7^{4-})/(HVO_4^{2-})^2\} = 1.29$$

$$HVO_4^{2-} \rightleftharpoons VO_4^{3-} + H^+ \tag{A22}$$

$$\log\{(VO_4^{3-})/(HVO_4^{2-})\} = -13.28 + pH$$

$$H_3V_2O_7^- + H_2O \rightleftharpoons 2H_2VO_4^- + H^+ \tag{A23}$$

$$\log\{(H_2VO_4^-)^2/(H_3V_2O_7^-)\} = pH - 10.40$$

$$HV_2O_7^{3-} + H_2O + H^+ \rightleftharpoons 2H_2VO_4^- \tag{A24}$$

$$\log\{(H_2VO_4^-)^2/(HV_2O_7^{3-})\} = 2.21 - pH$$

$$VO_2^+ + 2H_2O \rightleftharpoons H_2VO_4^- + 2H^+ \tag{A25}$$

$$\log\{(H_2VO_4^-)/(VO_2^+)\} = 2pH - 7.25$$

$$H_2VO_4^- \rightleftharpoons HVO_4^{2-} + H^+ \tag{A26}$$

$$\log\{(HVO_4^{2-})/(H_2VO_4^-) = -8.06 + pH$$

(c) V(IV) states

$$V_2O_4(c) + 4H^+ \rightleftharpoons 2VO^{2+} + 2H_2O \tag{A27}$$

$$\log(VO^{2+}) = 4.25 - 2pH$$

$$V_2O_4(c) + 2H^+ \rightleftharpoons 2VOOH^+ \tag{A28}$$

$$\log(VOOH^+) = -0.40 - pH$$

$$V_2O_4(c) + 2H^+ \rightleftharpoons (VOOH)_2^{2+} \tag{A29}$$

$$\log((VOOH_2^{2+})) = 2.17 - 2pH$$

$$2V_2O_4(c) + H_2O \rightleftharpoons V_4O_9^{2-} + 2H^+ \tag{A30}$$

$$\log(V_4O_9^{2-}) = -15.83 + 2pH$$

$$2VOOH^+ \rightleftharpoons (VOOH)_2^{2+} \tag{A31}$$

$$\log\{((VOOH)_2^{2+})/(VOOH^+)^2\} = 2.98$$

(d) V(III) states

$$V_2O_3(c) + 6H^+ \rightleftharpoons 2V^{3+} + 3H_2O \tag{A32}$$

$$\log(V^{3+}) = 6.58 - 3pH$$

$$V_2O_3(c) + 4H^+ \rightleftharpoons 2VOH^{2+} + H_2O \tag{A33}$$

$$\log(VOH^{2+}) = 3.68 - 2pH$$

$$V_2O_3(c) + 2H^+ \rightleftharpoons 2VO^+ + H_2O \tag{A34}$$

$$\log(VO^+) = 0.16 - pH$$

$$V^{3+} + H_2O \rightleftharpoons VOH^{2+} + H^+ \tag{A35}$$

$$\log\{(VOH^{2+})/(V^{3+})\} = -2.90 + pH$$

$$VOH^{2+} \rightleftharpoons VO^+ + H^+ \tag{A36}$$

$$\log\{(VO^+)/(VOH^{2+})\} = -3.52 + pH$$

(e) V(II) states

$$VO(c) + 2H^+ \rightleftharpoons V^2 + H_2O \tag{A37}$$

$$\log(V^{2+}) = 8.93 - 2pH$$

Electrochemical reactions

(a) Peroxy-vanadates/V(V) couples

$$VO \cdot H_2O_2^{3+} + 2e^- \rightleftharpoons VO_2^+ + H_2O \tag{A38}$$

$$E_{38}/V = 1.5587 + 0.0296 \times \log\{(VO \cdot H_2O_2^{3+})/(VO_2^+)\}$$

$$2VO \cdot H_2O_2^{3+} + 4e^- \rightleftharpoons V_2O_5(c) + H_2O + 2H^+ \tag{A39}$$

$$E_{39}/V = 1.5800 + 0.0296pH + 0.0296 \times \log(VO \cdot H_2O_2^{3+})$$

$$2VO_2 \cdot H_2O_2^+ + 2H^+ + 4e^- \rightleftharpoons V_2O_5(c) + 3H_2O \tag{A40}$$

$$E_{40}/V = 1.6535 - 0.0296pH + 0.0296 \times \log(VO_2 \cdot H_2O_2^+)$$

$$10VO_2 \cdot H_2O_2^+ + 6H^+ + 20e^- \rightleftharpoons H_2V_{10}O_{28}^{4-} + 12H_2O \tag{A41}$$

$$E_{41}/V = 1.6122 - 0.0178pH + 0.0030 \times \log\{(VO_2 \cdot H_2O_2^+)^{10}/(H_2V_{10}O_{28}^{4-})]$$

$$10VO_2 \cdot H_2O_2^+ + 5H^+ + 20e^- \rightleftharpoons HV_{10}O_{28}^{5-} + 12H_2O \tag{A42}$$

$$E_{42}/V = 1.6014 - 0.0148pH + 0.0030 \times \log\{(VO_2 \cdot H_2O_2^+)^{10}/(HV_{10}O_{28}^{5-})\}$$

$$10VO_2\cdot H_2O_2^+ + 4H^+ + 20e^- \rightleftharpoons V_{10}O_{28}^{6-} + 12H_2O \quad (A43)$$

$$E_{43}/V = 1.5843 - 0.0118\text{pH} + 0.0030 \times \log\{(VO_2\cdot H_2O_2^+)^{10}/(V_{10}O_{28}^{6-})\}$$

$$4VO_2\cdot H_2O_2^+ + 8e^- \rightleftharpoons V_4O_{12}^{4-} + 4H_2O \quad (A44)$$

$$E_{44}/V = 1.5095 + 0.0074 \times \log\{(VO_2\cdot H_2O_2^+)^4/(V_4O_{12}^{4-})\}$$

$$2VO_2\cdot H_2O_2^+ + 4e^- \rightleftharpoons HV_2O_7^{3-} + H_2O + H^+ \quad (A45)$$

$$E_{45}/V = 1.3900 + 0.0148\text{pH} + 0.0148 \times \log\{(VO_2\cdot H_2O_2^+)^2/(HV_2O_7^{3-})\}$$

$$VO_2\cdot H_2O_2^+ + 2e^- \rightleftharpoons HVO_4^{2-} + H^+ \quad (A46)$$

$$E_{46}/V = 1.1841 + 0.0296\text{pH} + 0.0296 \times \log\{(VO_2\cdot H_2O_2^+)/(HVO_4^{2-})\}$$

$$VO_2\cdot H_2O_2^+ + 2e^- \rightleftharpoons VO_4^{3-} + 2H^+ \quad (A47)$$

$$E_{47}/V = 0.7913 + 0.0591\text{pH} + 0.0296 \times \log\{(VO_2\cdot H_2O_2^+)/(VO_4^{3-})\}$$

(b) V(V)/V(IV) couples

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad (A48)$$

$$E_{48}/V = 0.9906 - 0.1183\text{pH} + 0.0591 \times \log\{(VO_2^+)/(VO^{2+})\}$$

$$V_2O_5(c) + 6H^+ + 2e^- \rightleftharpoons 2VO^{2+} + 3H_2O \quad (A49)$$

$$E_{49}/V = 0.9584 - 0.1775\text{pH} - 0.0591 \times \log(VO^{2+})$$

$$V_4O_{12}^{4-} + 6H^+ + 4e^- \rightleftharpoons V_4O_9^{2-} + 3H_2O \quad (A50)$$

$$E_{50}/V = -0.7606 - 0.0887\text{pH} + 0.0147 \times \log\{(V_4O_{12}^{4-})/(V_4O_9^{2-})\}$$

$$2HV_2O_7^{3-} + 8H^+ + 4e^- \rightleftharpoons V_4O_9^{2-} + 5H_2O \quad (A51)$$

$$E_{51}/V = 0.9999 - 0.1183\text{pH} + 0.0147 \times \log\{(HV_2O_7^{3-})^2/(V_4O_9^{2-})\}$$

$$4HVO_4^{2-} + 10H^+ + 4e^- \rightleftharpoons V_4O_9^{2-} + 7H_2O \quad (A52)$$

$$E_{52}/V = 1.4112 - 0.1479\text{pH} + 0.0147 \times \log\{(HVO_4^{2-})^4/(V_4O_9^{2-})\}$$

$$4VO_4^{3-} + 14H^+ + 4e^- \rightleftharpoons V_4O_9^{2-} + 7H_2O \quad (A53)$$

$$E_{53}/V = 2.1968 - 0.2071\text{pH} + 0.0147 \times \log\{(VO_4^{3-})^4/(V_4O_9^{2-})\}$$

(c) V(V)/V(III) couples

$$2VO_4^{3-} + 10H^+ + 4e^- \rightleftharpoons V_2O_3(c) + 5H_2O \quad (A54)$$

$$E_{54}/V = 1.3647 - 0.1479\text{pH} + 0.0296\log(VO_4^{3-})$$

(d) V(V)/V(4.33) couples

$$3V_2O_5(c) + 4H^+ + 4e^- \rightleftharpoons V_6O_{13}(c) + 2H_2O \quad (A55)$$

$$E_{55}/V = 0.8425 - 0.0591\text{pH}$$

$$3H_2V_{10}O_{28}^{4-} + 32H^+ + 20e^- \rightleftharpoons 5V_6O_{13}(c) + 19H_2O \quad (A56)$$

$$E_{56}/V = 0.9662 - 0.0947\text{pH} + 0.0088 \times \log(H_2V_{10}O_{28}^{4-})$$

$$3HV_{10}O_{28}^{5-} + 35H^+ + 20e^- \rightleftharpoons 5V_6O_{13}(c) + 19H_2O \quad (A57)$$

$$E_{57}/V = 0.9988 - 0.1035\text{pH} + 0.0088 \times \log(HV_{10}O_{28}^{5-})$$

$$3V_4O_{12}^{4-} + 20H^+ + 8e^- \rightleftharpoons 2V_6O_{13}(c) + 10H_2O \quad (A58)$$

$$E_{58}/V = 1.2745 - 0.1479\text{pH} + 0.0222 \times \log(V_4O_{12}^{4-})$$

$$3HV_2O_7^{3-} + 13H^+ + 4e^- \rightleftharpoons V_6O_{13}(c) + 8H_2O \quad (A59)$$

$$E_{59}/V = 1.6335 - 0.1923\text{pH} + 0.0444 \times \log(HV_2O_7^{3-})$$

(e) V(4.33)/V(IV) couples

$$V_6O_{13}(c) + 2H^+ + 2e^- \rightleftharpoons 3V_2O_4(c) + H_2O \quad (A60)$$

$$E_{60}/V = 0.4352 - 0.0591\text{pH}$$

$$4V_6O_{13}(c) + 2H_2O + 8e^- \rightleftharpoons 6V_4O_9^{2-} + 4H^+ \quad (A61)$$

$$E_{61}/V = -0.2673 + 0.0296\text{pH} - 0.0444 \times \log(V_4O_9^{2-})$$

(f) V(IV)/V(III) couples

$$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O \quad (A62)$$

$$E_{62}/\mathrm{V} = 0.4361 - 0.1183\mathrm{pH} + 0.0591 \times \log\{(\mathrm{VO^{2+}})/(\mathrm{V^{3+}})\}$$

(g) V(IV)/V(3.3) couples

$$3\mathrm{V_2O_4(c)} + 4\mathrm{H^+} + 4\mathrm{e^-} \rightleftharpoons 2\mathrm{V_3O_5(c)} + 2\mathrm{H_2O} \tag{A63}$$

$$E_{63}/\mathrm{V} = 0.3901 - 0.0591\mathrm{pH}$$

$$3\mathrm{V_4O_9^{2-}} + 14\mathrm{H^+} + 8\mathrm{e^-} \rightleftharpoons 4\mathrm{V_3O_5(c)} \tag{A64}$$

$$E_{64}/\mathrm{V} = 0.7414 - 0.1035\mathrm{pH} + 0.0222 \times \log(\mathrm{V_4O_9^{2-}})$$

(h) V(3.3)/V(III) couples

$$2\mathrm{V_3O_5(c)} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightleftharpoons 3\mathrm{V_2O_3(c)} + \mathrm{H_2O} \tag{A65}$$

$$E_{65}/\mathrm{V} = 0.1149 - 0.0591\mathrm{pH}$$

(i) V(III)/V(II) couples

$$\mathrm{V^{3+}} + \mathrm{e^-} \rightleftharpoons \mathrm{V^{2+}} \tag{A66}$$

$$E_{66}/\mathrm{V} = -0.3452 - 0.0591\log\{(\mathrm{V^{3+}})/(\mathrm{V^{2+}})\}$$

$$\mathrm{V_2O_3(c)} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightleftharpoons 2\mathrm{VO(c)} + \mathrm{H_2O} \tag{A67}$$

$$E_{67}/\mathrm{V} = -0.4841 - 0.0591\mathrm{pH}$$

(j) V(II)/V(0) couples

$$\mathrm{V^{2+}} + 2\mathrm{e^-} \rightleftharpoons \mathrm{V} \tag{A68}$$

$$E_{68}/\mathrm{V} = -1.1297 + 0.0296\log(\mathrm{V^{2+}})$$

$$\mathrm{VO(c)} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightleftharpoons \mathrm{V} + \mathrm{H_2O} \tag{A69}$$

$$E_{69}/\mathrm{V} = -0.8655 - 0.0591\mathrm{pH}$$

Appendix — 3. Thermodynamic equations for V–S–H_2O systems

Chemical reactions

$$\mathrm{VOSO_4(c)} \rightleftharpoons \mathrm{VOSO_4(aq)} \tag{A70}$$

$$\log(\mathrm{VOSO_4(aq)}) = 2.10$$

$$\mathrm{VOSO_4(aq)} \rightleftharpoons \mathrm{VO^{2+}} + \mathrm{SO_4^{2-}} \tag{A71}$$

$$\log\{(\mathrm{VOSO_4(aq)})/(\mathrm{VO^{2+}})\} = -1.58 + \log(\mathrm{SO_4^{2-}})$$

Electrochemical reactions

$$\mathrm{V^{3+}} + 4\mathrm{S} + 3\mathrm{e^-} \rightleftharpoons \mathrm{VS_4(c)} \tag{A72}$$

$$E_{72}/\mathrm{V} = 0.1199 + 0.0197\log(\mathrm{V^{3+}})$$

$$\mathrm{V_3O_5(c)} + 12\mathrm{S} + 10\mathrm{H^+} + 10\mathrm{e^-} \rightleftharpoons 3\mathrm{VS_4(c)} + 5\mathrm{H_2O} \tag{A73}$$

$$E_{73}/\mathrm{V} = 0.2362 - 0.0591\mathrm{pH}$$

$$\mathrm{V_3O_5(c)} + 12\mathrm{SO_4^{2-}} + 106\mathrm{H^+} + 82\mathrm{e^-} \rightleftharpoons 3\mathrm{VS_4(c)} + 53\mathrm{H_2O} \tag{A74}$$

$$E_{74}/\mathrm{V} = 0.3384 - 0.0765\mathrm{pH} + 0.0086 \times \log(\mathrm{SO_4^{2-}})$$

$$3\mathrm{VS_4(c)} + 5\mathrm{H_2O} + 2\mathrm{H^+} + 14\mathrm{e^-} \rightleftharpoons \mathrm{V_3O_5(c)} + 12\mathrm{HS^-} \tag{A75}$$

$$E_{75}/\mathrm{V} = 0.2762 - 0.0086\mathrm{pH} - 0.0507\log(\mathrm{HS^-})$$

$$3\mathrm{VS_4(c)} + 5\mathrm{H_2O} + 14\mathrm{H^+} + 14\mathrm{e^-} \rightleftharpoons \mathrm{V_3O_5(c)} + 12\mathrm{H_2S} \tag{A76}$$

$$E_{76}/\mathrm{V} = 0.0791 - 0.0591\mathrm{pH} - 0.0507\log(\mathrm{H_2S})$$

$$\mathrm{VS_4(c)} + 8\mathrm{H^+} + 5\mathrm{e^-} \rightleftharpoons \mathrm{V^{3+}} + 4\mathrm{H_2S} \tag{A77}$$

$$E_{77}/\mathrm{V} = 0.1594 - 0.0946\mathrm{pH} - 0.0118 \times \log(\mathrm{V^{3+}}) - 0.0473\log(\mathrm{H_2S})$$