Corrosion of Copper in Water

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Objectives

- Define the relevant thermodynamics of copper in water by first considering the chemical reactions and then considering the electrochemical reactions.
- Classify copper as being a “noble” or “active” metal.
- Explore the impact of other components, particularly sulfide ion, ammonia, and chloride ion on the “activity” of copper.
- Comment on the range of sulfur species that may exist in ground water environments.
- Sulfur species are considered to be a major threat to the integrity of copper.

Corrosion Domain Diagrams

- **Define regions in concentration versus pH space where corrosion is possible thermodynamically and where it is not possible.**
- **Can be used to characterize, quantitatively, whether a metal is "noble" or "active".**
- **Mysteriously, CDDs are little used in corrosion science (at least compared to Pourbaix diagrams).**
- **An effective tool for exploring whether copper can corrode in ground water systems.**

Corrosion of Copper in Water as a Chemical Reaction

The corrosion of copper may be written in chemical form as:

$$Cu + H^+ = Cu^+ + 1/2H_2$$

Whence $\Delta G = \Delta G^0 + 2.303RT log\left(f_{H_2}^{1/2} a_{Cu^+} / a_{H^+}\right)$

$$log\left(f_{H_2}^{1/2} a_{Cu^+}\right) = \frac{\Delta G - \Delta G^0}{2.303RT} - pH$$

Condition for spontaneity is 0 < ΔG**. Thus, we must map the values for** $P = f_{H_2}^{1/2} a_{Cu^+}$ **in terms of the activities of** Cu^+ **and** H^+ **and the fugacity of hydrogen for which this condition holds.**

$$P = f_{H_2}^{1/2} a_{Cu^+} < f_{H_2}^{e,1/2} a_{Cu^+}^{e}$$

where

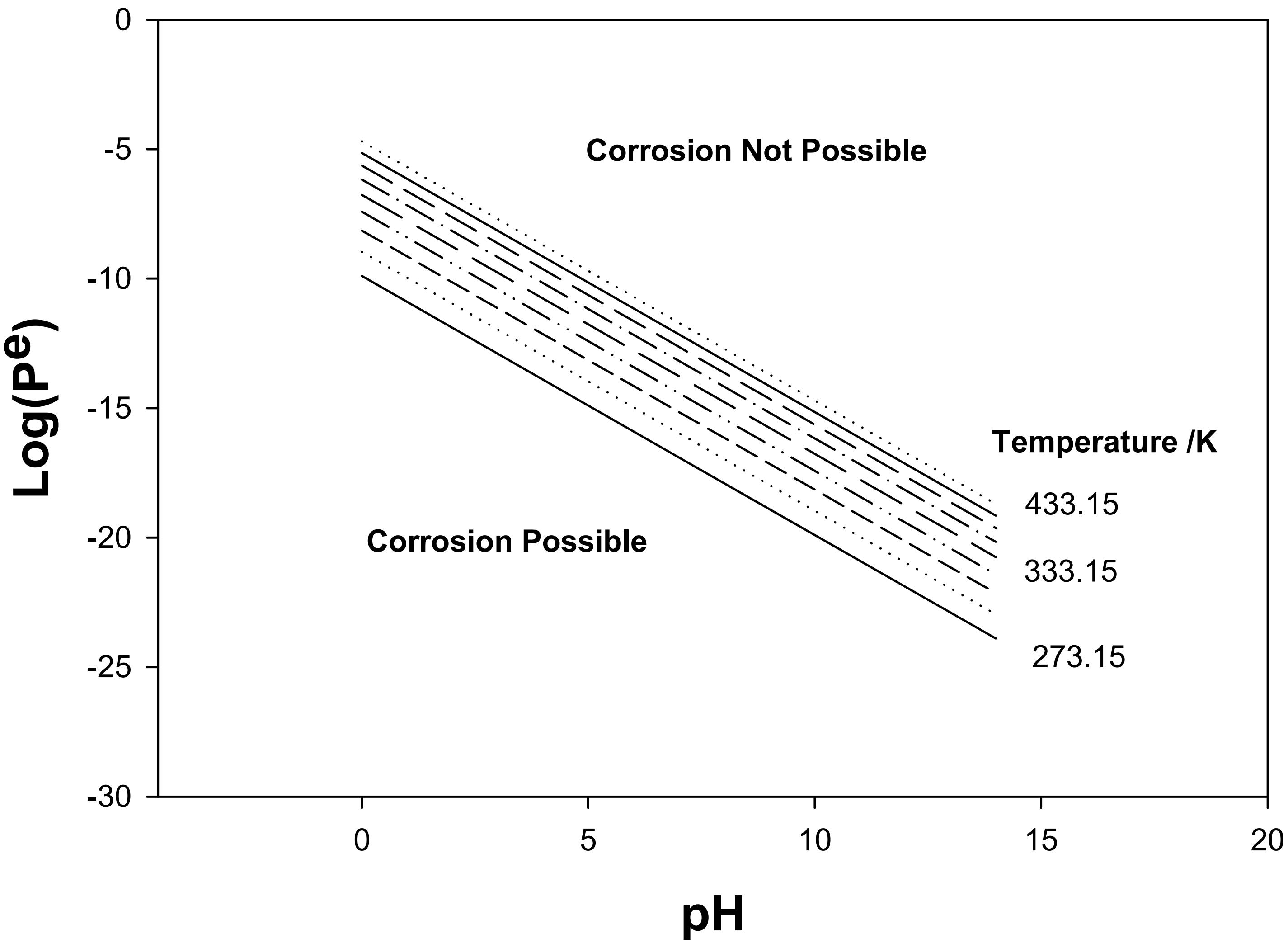
$$f_{H_2}^{e,1/2} a_{Cu^+}^{e} = 10^{-\left(\frac{\Delta G^0}{2.303RT}+pH\right)}$$

Have used HSC-5 software to calculate $P^e = f_{H_2}^{e,1/2} a_{Cu^+}^{e}$ **as a function of temperature and pH for the following reactions:**

$Cu + H^+ = Cu^+ + 1/2H_2$

$Cu + 2NH_3 + H^+ = Cu(NH3)_2^+ + 1/2H_2$

$2Cu + HS^- + H^+ = Cu2S + H_2$



Corrosion domain diagram for copper in water as a function of temperature.

Table 3: Prediction of copper corrosion in pure water as a function of solution composition at 273.15 K. Activity coefficients assumed to be one. Log(P^e) = - 16.895.

Case	a_{Cu+}	ppb_{Cu+}	f_{H2}	ppb_{H2}	**Log(P)**	**Corrosion possible?**
1	10^{-6}	63	10^{-6}	0,002	-9	No
2	10^{-6}	63	10^{-12}	2×10^{-9}	-12	No
3	10^{-6}	63	10^{-18}	2×10^{-15}	-15	No
4	10^{-6}	63	10^{-24}	2×10^{-21}	-18	Yes
5	10^{-6}	63	10^{-30}	2×10^{-27}	-21	Yes
6	10^{-6}	63	10^{-18}	2×10^{-15}	-15	No
7	10^{-12}	63×10^{-6}	10^{-18}	2×10^{-15}	-21	Yes
8	10^{-18}	63×10^{-12}	10^{-18}	2×10^{-15}	-27	Yes
9	10^{-24}	63×10^{-18}	10^{-18}	2×10^{-15}	-33	Yes
10	10^{-30}	63×10^{-24}	10^{-18}	2×10^{-15}	-39	Yes

Copper in the Presence of Bi-Sulfide (HS^-)

Reaction is:

$$2Cu + HS^- + H^+ = Cu_2S + H_2$$

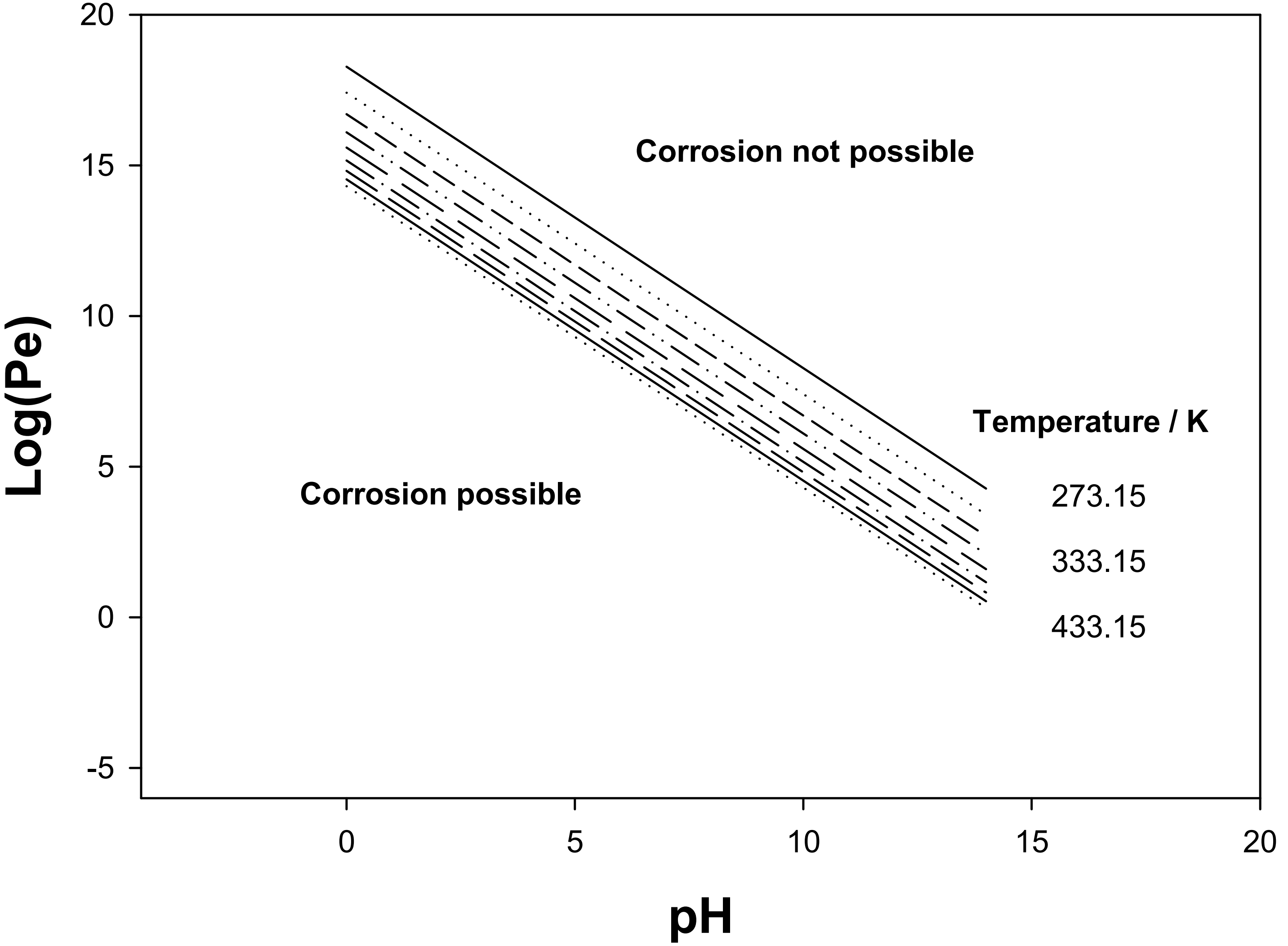
$$\Delta G = \Delta G^0 + 2.303RT\log\left(f_{H_2}^{1/2}/a_{HS^-}.a_{H^+}\right)$$

The quantity, *P^e*, is now given as

$$P^e = f_{H_2}^{1/2}/a_{HS^-}.$$

where, as before,

$$f_{H_2}^{e,1/2}/a_{HS^-}^{e} = 10^{-\left(\frac{\Delta G^0}{2.303RT}+pH\right)}$$



Corrosion domain diagram for copper in water + HS^- as a function of temperature.

Volt Equivalent Diagrams

- **Convenient and effective way of summarizing the redox chemistry of an element in aqueous solution.**
- **It is known that the reduction potential is highly pH- and temperature-dependent. Figure 11 shows a volt equivalent diagram for *S/*H_2O system at pH=10.5. It is clear that the shape of the diagram is much different with that shown in Figure 10, with most of the slopes now being negative. The relative positions of some species have also been changed. The observation makes it clear that knowledge of the pH of a system is vital in studying its redox chemistry.**
- **The diagrams presented herein involve species at unit activities. The first feature to note is that the slope of a line joining any two species corresponds to the reduction potential of the associated couple. Consider, for example, the $SO_4^{2-}/S_2O_3^{2-}$ couple in Figure 10. The standard reduction potential E^0 for this couple can be calculated, i.e.**

$$E^0 = \frac{VE_{SO_4^{2-}} - VE_{S_2O_3^{2-}}}{SOS_{SO_4^{2-}} - SOS_{S_2O_3^{2-}}}$$

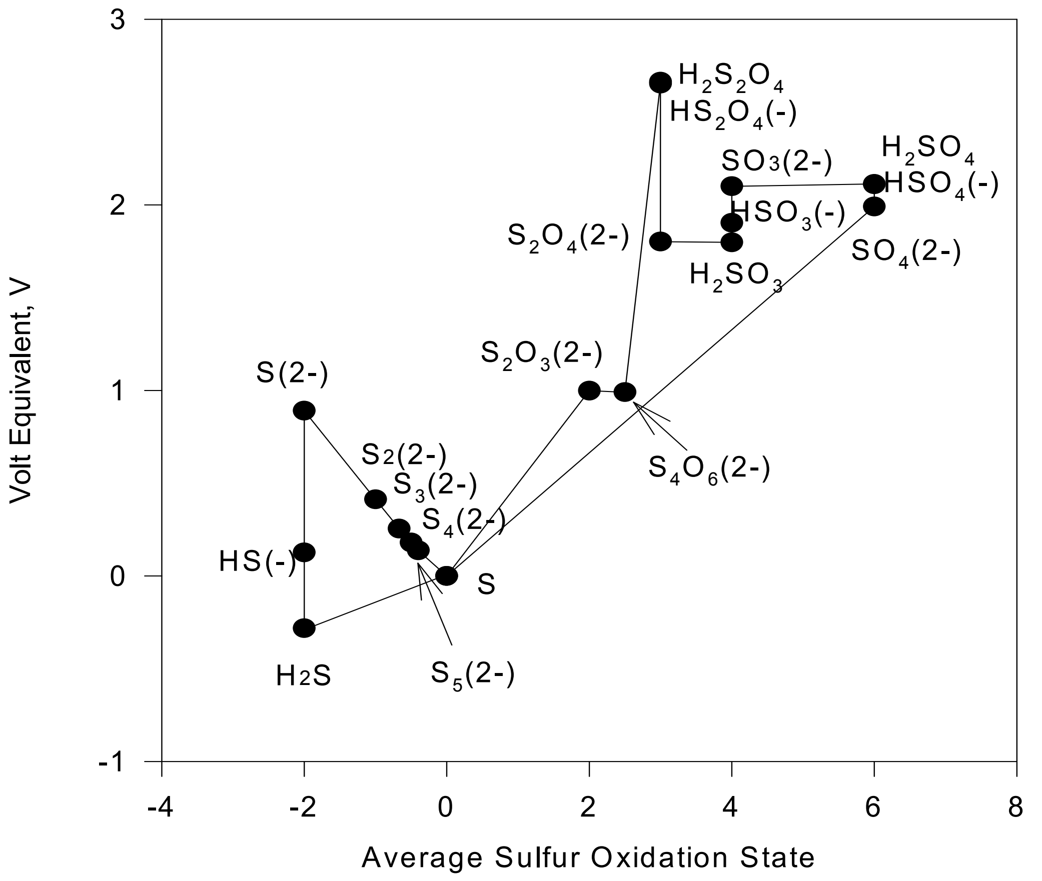
where VE and SOS represent the volt equivalent and the (average) sulfur oxidation state of the species, respectively. In this way, the reduction potential for any conceivable redox couple can be calculated.

Table 1: Reduction reaction for sulfur species

Species[*]	**Reduction Reaction**
$H_2S(a)$	$1/8S_8(s) + 2H^+ + 2e^- = H_2S(a)$
$HS(-a)$	$1/4S_8(s) + H^+ + 2e^- = 2HS(-a)$
$S(-2a)$	$1/8S_8(s)+2e^- = S(-2a)$
$S_2(-2a)$	$1/4S_8(s)+2e^- = S_2(-2a)$
$S_3(-2a)$	$3/8S_8(s)+2e^- = S_3(-2a)$
$S_4(-2a)$	$1/2S_8(s)+2e^- = S_4(-2a)$
$S_5(-2a)$	$5/8S_8(s)+2e^- = S_5(-2a)$
S_8	-
$S_2O_3(-2a)$	$S_2O_3(-2a) + 6H(+a) + 4e^- = 1/4S_8(s)+3H_2O$
$S_4O_6(-2a)$	$S_4O_6(-2a) + 12H(+a) + 10e^- = 1/2S_8(s)+6H_2O$
$H_2S_2O_4(a)$	$H_2S_2O_4(a) + 6H(+a) + 6e^- = 1/4S_8(s)+4H_2O$
$HS_2O_4(-a)$	$HS_2O_4(-a) + 7H(+a) + 6e^- = 1/4S_8(s)+4H_2O$
$S_2O_4(-2a)$	$S_2O_4(-2a) + 8H(+a) + 6e^- = 1/4S_8(s)+4H_2O$
$H_2SO_3(a)$	$H_2SO_3(a) + 4H(+a) + 4e^- = 1/8S_8(s)+3H_2O$
$HSO_3(-a)$	$HSO_3(-a) + H(+a) + 4\text{-}e^- =1/8S_8(s) + 3H2O$
$SO_3(-2a)$	$SO_3(-2a) + 6H(+a) + 4e^- = 1/8S_8(s)+3H_2O$
$H_2SO_4(a)$	$H_2SO_4(a) + 6H(+a) + 6e^- = 1/8S_8(s) + 4H_2O$
$HSO4(-a)$	$HSO_4(-a) + 7H(+a) + 6e^- = 1/8S_8(s) + 4H_2O$
$SO_4(-2a)$	$SO_4(-2a) + 8H(+a) + 6e^- = 1/8S_8(s)+4H_2O$

[*] Specie designation as in HSC-5. “(-2a)” designates an anion of charge –2 in aqueous solution.

Volt Equivalent (VE) = E_{red} x Average Oxidation State of Sulfur



Volt Equivalent Diagram for S/H2O System at pH=0 and at 25 C

Figure 10. Volt-Equivalent diagram for the *S/H_2O* system at 25°C, pH = 0.

Interpretation of Volt Equivalent Diagrams

- Diagrams are very pH- and temperature-dependent, as noted above.
- Firstly, if a species lies above a line joining any two other compounds, this species will tend to disproportionate into the other two compounds. See Figure 13 and consider, for example, the decomposition of $S_2O_3^{2-}$ in acidic solution. It is clear that $S_2O_3^{2-}$ lies above the line joining S and $S_4O_6^{2-}$. This suggests that, although the decomposition of $S_2O_3^{2-}$ is a complex reaction forming many products, one reaction that may occur is,

  $$5S_2O_3^{2-} + 6H^+ \rightarrow 2S + 2S_4O_6^{2-} + 3H_2O$$

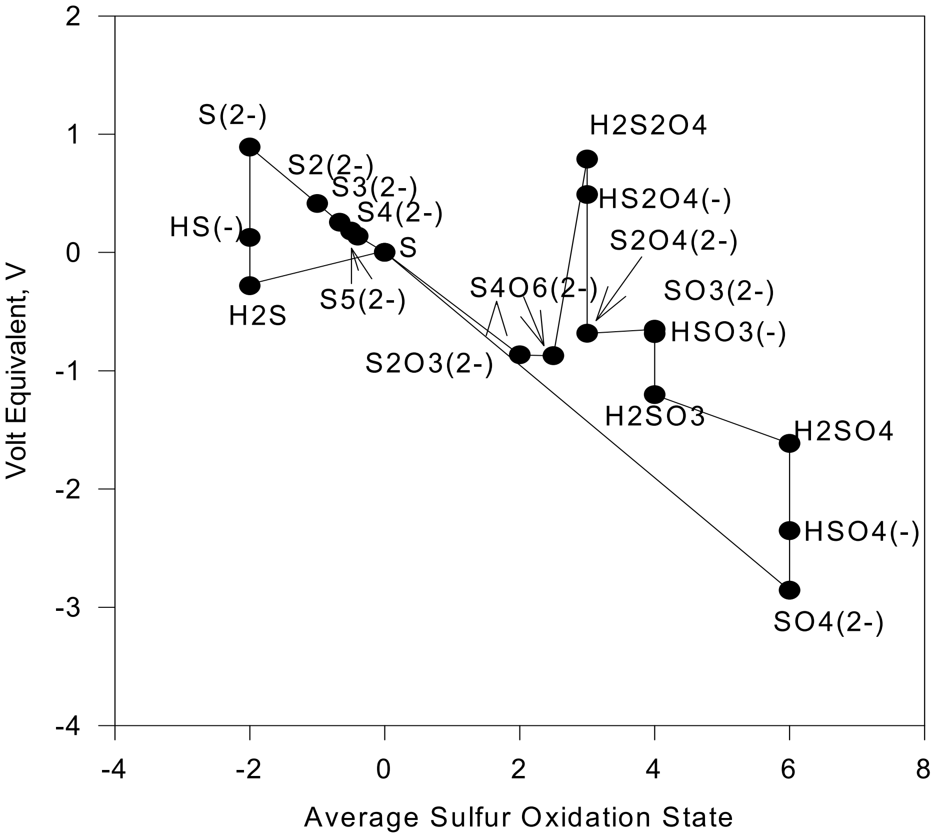
  This shows that it is thermodynamically possible for thiosulfate, i.e., $S_2O_3^{2-}$, to undergo a redox self-disproportionation reaction into a reduction product, S, and an oxidation product, $S_4O_6^{2-}$.
- Secondly, if a species lies below a line joining any two other compounds, the latter will tend to react to produce the former. A good example is found in the reduction of sulfuric acid by hydrogen sulfide. Figure 13 suggests that, at pH = 0 and at 275°C, the following reaction is thermodynamically favorable,

  $$3H_2S + SO_4^{2-} + 2H^+ \Leftrightarrow 4S + 4H_2O$$

  because S lies below the line joining H_2S and SO_4^{2-}.
- Finally, if a species lies between two or more others on the same straight line (or very close to it), it will tend to only partially disproportionate into these species, forming an equilibrium mixture containing substantial amounts of each. For example, it can be seen from Figure 14 that $S_2O_3^{2-}$, SO_4^{2-}, and S are very nearly on a same straight line. Thus, the disproportionation of $S_2O_3^{2-}$ will occur as described by the following reaction,

  $$3S_2O_3^{2-} + 2H^+ \Leftrightarrow 4S + 2SO_4^{2-} + H_2O$$

  Starting with 1M $S_2O_3^{2-}$, a fixed pH of 10.5, and without S and SO_4^{2-} initially in the system, the above reaction will reach an equilibrium position in which all three species are present simultaneously. Similarly, reaction of two species on or near the same line as a third will not go to completion, but will form a mixture containing significant amounts of each species.



Volt Equivalent Diagram for S/H2O System at pH=10.5 and at 25 C

Figure 11. Volt-Equivalent diagram for the *S/H_2O* system at 25°C, pH = 10.5.

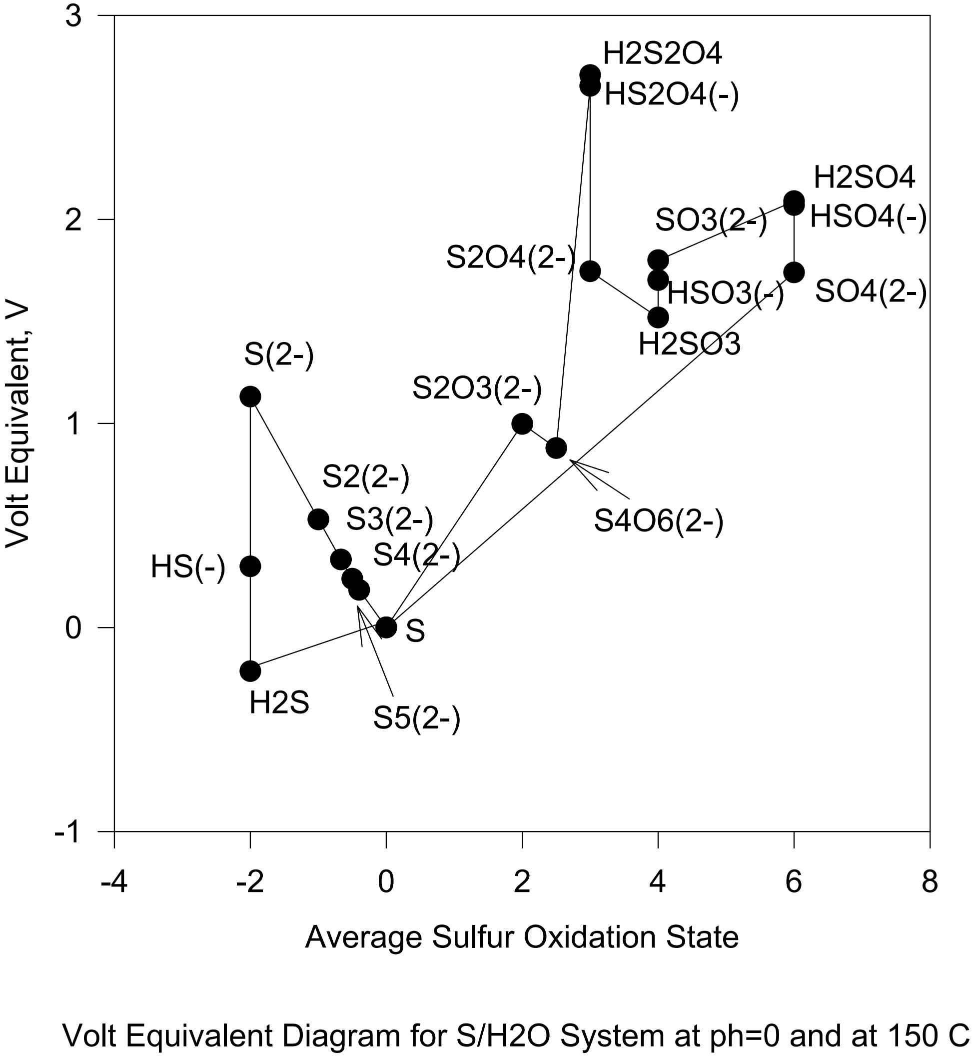


Figure 12. Volt-Equivalent diagram for the S/H_2O system at 150^{o}C, pH = 0.

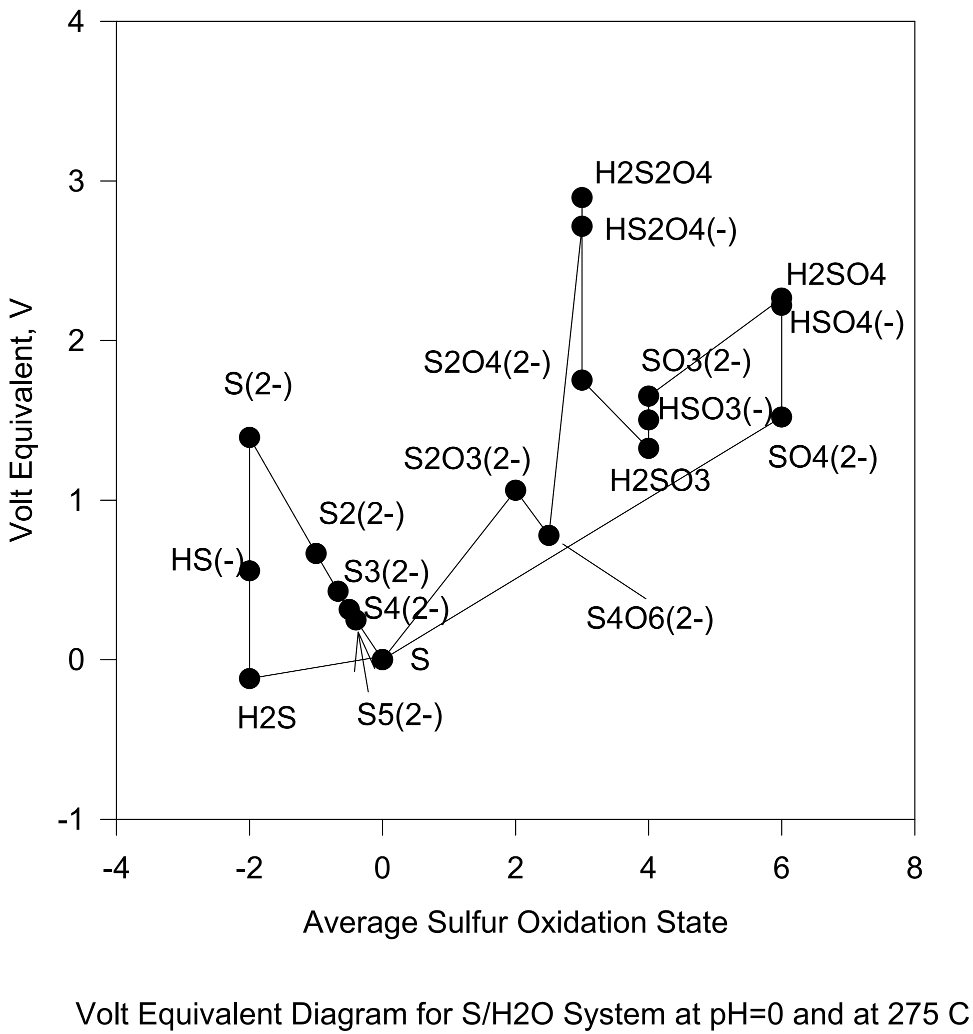
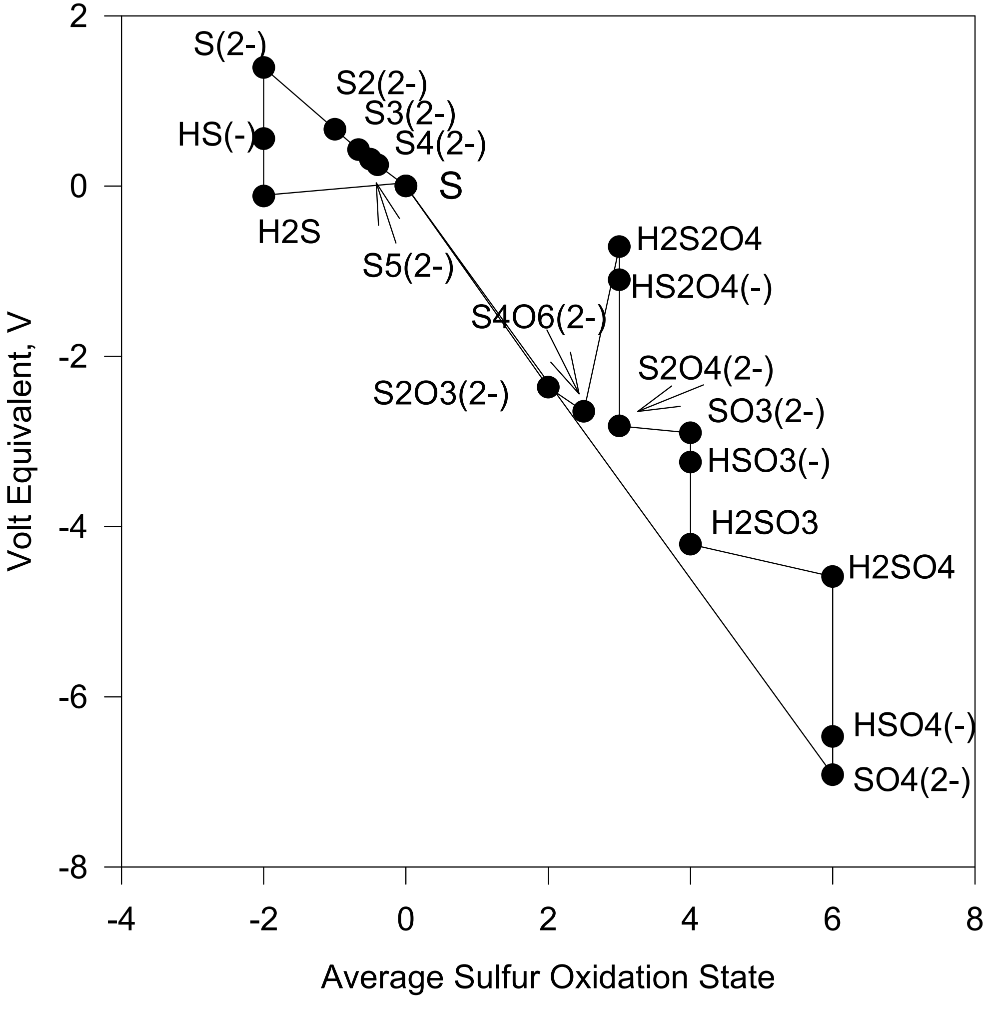


Figure 13. Volt-Equivalent diagram for the S/H_2O system at 275°C, pH = 0.



Volt Equivalent Diagram for S/H2O System at pH=10.5 and at 275 C

Figure 14. Volt-Equivalent diagram for the *S/H_2O* system at 275°C, pH = 10.5.

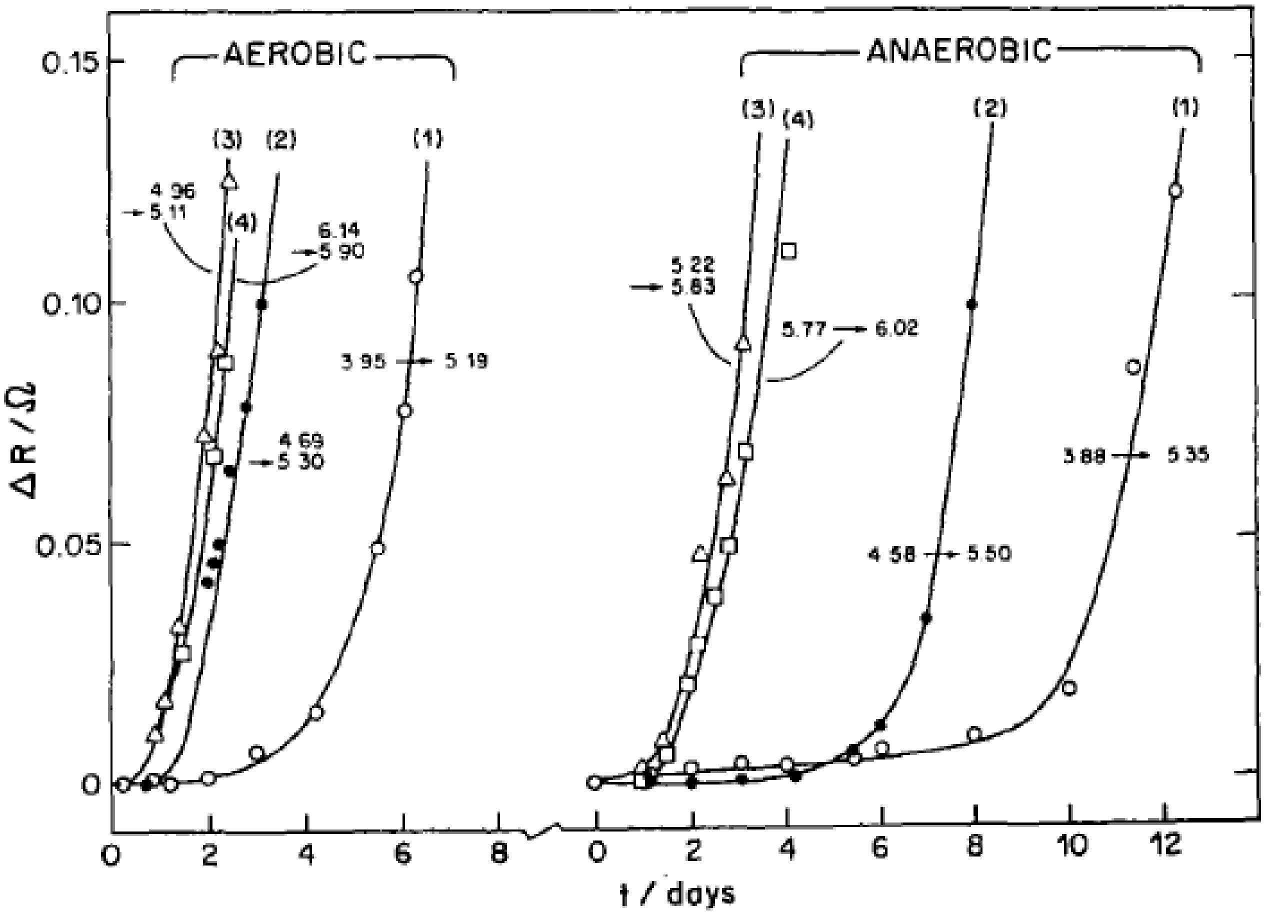


Figure 22: Dependence of the corrosion of carbon steel in wet elemental sulfur on initial pH under aerobic (left hand curves) and anaerobic (right hand curves) conditions. The initial and final pH values are superimposed upon each curve. The solutions comprised various acetic acid/sodium acetate buffers of 3.88 < pH < 6.14. Sulfur particle size = 4.76 – 2.38 mm. The corrosion loss is measured as the change of resistance of the thin, carbon steel wire specimen. After Macdonald, et. al. [1].

Summary and Conclusions

- **The thermodynamic conditions for the corrosion of copper in water have been defined. Copper is not a noble metal.**
- **The results are expressed in corrosion domain diagrams as P^e versus pH, where**

$$P^e = f_{H_2}^{e,1/2} a^e_{Cu^+}$$

- **Corrosion is spontaneous for $P < P^e$.**
- **Certain species commonly found in ground water, e.g. HS^- and NH_3 are deleterious by (thermodynamically) activating copper.**
- **Volt Equivalent diagrams are enormously useful in interpreting and predicting the chemistry of complex systems, such as S-H_2O.**
- **Only the thermodynamic conditions have been examined. The kinetics must also be examined, because, even though copper is active, the rate of corrosion may be sufficiently low to meet the engineering requirements.**