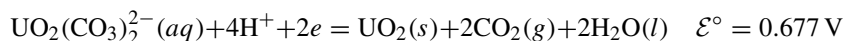
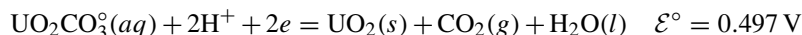
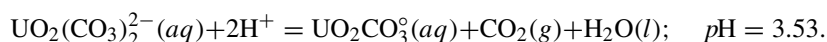
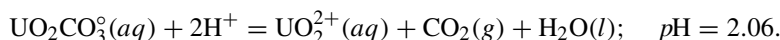


Chapter 12 Answers

1. (a)



(b)



(c) Boundary 1: $Eh = 0.405 \text{ V}$.

Boundary 2: $Eh = 0.349 - 0.0592 \text{ pH}$.

Boundary 3: $Eh = 0.558 - 0.1184 \text{ pH}$.

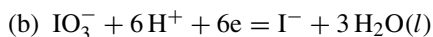
2. (a) $Eh = -0.141 \text{ V}$; $f_{\text{O}_2} = 10^{-68.6} \text{ bar}$.

(b) Using $\Delta_r G_{573}^\circ = \Delta_r G_{298}^\circ - \Delta_r S^\circ(T - 298.15)$, $f_{\text{O}_2} = 10^{-29.01} \text{ bars}$

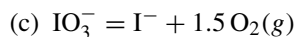
Using $\Delta_r G_{573}^\circ = \Delta_r H_{298}^\circ - 573.15(\Delta_r S_{298}^\circ)$, $f_{\text{O}_2} = 10^{-29.07} \text{ bars}$.

Using $\log K_{573} = \log K_{298} - (\Delta_r H_{298}^\circ / 2.303R)[1/573.15 - 1/298.15]$,
 $f_{\text{O}_2} = 10^{-28.97} \text{ bar}$.

3. (a) I in I^- is -1 ; I in IO_3^- is $+5$.



$\mathcal{E}^\circ = 1.097 \text{ V}$; $Eh = 0.742 \text{ V}$.



(d) $f_{\text{O}_2} = 10^{-8.93} \text{ bar}$; magnetite only stable if $f_{\text{O}_2} \leq 10^{-68.6} \text{ bar}$, so expect iodide, I^- .

5. An Eh of zero just means that the redox conditions happen to be such that the pH and the activity ratio of reduced to oxidized species in the Nernst equation combine to give a voltage equal to the standard voltage \mathcal{E}° . It has no particular theoretical significance. Naturally, however, in any particular system, solutions with a negative Eh will be more reduced than those with a positive Eh .

6. (a) Yes. Near equilibrium, because the samples plot almost on the boundary for their concentration.

(b) It is outside $\text{Fe}(\text{OH})_3$ stability range (actually $\text{Fe}(\text{OH})_3$ is metastable, but can be treated as stable here).

(c) yes, 4 and 5.

(d) sulfate is being reduced.

(e) a little over $\text{pH} 7$.

7. $a_{\text{Fe}} = 10^{-6.20}$; $10^{-2.91}$; 1.0 for $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4 - \text{FeO}$, $\text{Fe} - \text{FeO}$ respectively.

8. $a_{\text{Fe}} = 10^{-5.95}$.
9. (d) At this Eh and sulfate concentration, the equilibrium $\text{H}_2\text{S}(aq)$ activity is enormous. However, it cannot exceed about 0.1 (the solubility of H_2S in water), and so sulfate is being reduced to try to reach the equilibrium concentration.
10. 2 ppb Mn is $10^{-7.439}$ molal. For $a_{\text{Mn}^{2+}} = 10^{-7.439}$, the equations for the numbered reactions are
 1. $Eh = 1.449 - 0.118pH$
 2. $Eh = 1.943 - 0.178pH$
 3. see text.
 4. $pH = 11.26$
 5. $Eh = 0.955 - 0.0592pH$
 6. $Eh = 0.886 - 0.0592pH$
 7. see text.
 8. see text.

It is also useful to calculate the intersections of boundaries as a check. For example reactions 1 and 2 give two equations in two unknowns. Solving for these gives an intersection at $Eh = 0.477$; $pH = 8.23$.

According to assumptions (a) and (b) βMnO_2 should be precipitating from seawater, but it is not (other phases are found in the nodules). Measured Eh values are much lower, because oxygen is used up by decaying organic matter, and they plot in the Mn^{2+} field, indicating that the phases considered should not be precipitating.

Higher $\Delta_f G^\circ$ values for minerals will result in higher \mathcal{E}° values for Mn^{2+} half-cells, so the Mn^{2+} field will enlarge, and so the conclusion that the phases are undersaturated will not be changed.