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Chemistry 505
Environmental Chemistry
University of Pennsylvania
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Problem set 6: Due July 18. Chemical characteristics of natural waters.
1. Write the reversible half reaction for Mn(II) forming Mn(III).
$\mathbf{Mn^{+2} \leftrightarrow Mn^{+3} + e^-}$

2. Write the reversible half reaction for Fe(III) forming Fe(II).
$\mathbf{Fe^{+3} + e^- \leftrightarrow Fe^{+2}}$

3. What reaction is defined to have Eh = 0?
$H^+ + 2\ e^- \leftrightarrow H_2$ and any other reaction at equilibrium (where $\Delta G = 0$).

4. For the reaction in #3, what will the ratio of oxidizers to reducers be in the Nernst equation?

Oxidizer: H^+ (e-acceptor) and Reducer: H_2 (e-donor)
Faure's version:

$$E_h = E^0_{ox} - \frac{0.0592}{2} \log \frac{[H^+]^2}{[H_2]}$$

The ratio $[H^+]^2/[H_2] = 1$ so the ratio of $[H^+]^2$ to $[H_2]$ = 1:1 or 50:50.

5. For the reaction in #3, what is the value of the standard potential?
$E^0_{ox} = 0$ by definition (SHE = 0 potential)

6. Given the value of the standard potential in #5, what is the resulting value of $-\Delta G^o_R$ [take a look at page 22 in Hem].
$-\Delta G^o_R = nFE = 2 \times 96{,}500C \times 0 = 0$

7. The dissociation of water is: $H_2O_{(l)}$ $2H^+ + 0.5\ O_2 + 2e^-$
If ΔG^o_R = +56.687 kcal, what is the standard potential? Use equation 14.24 from Faure. Note here that the sign convention used by Faure is different than Hem.

$\Delta G^o_R = nFE^0$
56.687 kcal = (2 mol e^-) (23.06 kcal $V^{-1}mol^{-1}$)E^0_{ox}
E^0_{ox} = 1.23 V (not spontaneous, Faure's positive sign convention)

8. What is Eh in a natural water system when the partial pressure of $O_2 = 10^{-83.1}$ atm and pH = 8?

$H_2O(l) \rightarrow 2\ H^+ + \frac{1}{2}\ O_2 + 2\ e^-$

$$Eh = E^0_{ox} + \frac{0.05916}{2} \log \frac{[O_2]^{1/2}}{[H^+]^2}$$

$$\begin{aligned} Eh &= 1.23\ V + 0.01479 \log [O_2] - 0.05916\ pH \\ &= 1.23\ V + 0.01479\ (-83.1) - 0.05916\ (8) \\ &= -0.472\ V \end{aligned}$$

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9. Using the same O_2 partial pressure for question 8, what is the value of Eh when pH = 4.5?

Eh $= 1.23\ V + 0.01479\ (-83.1) - 0.05916\ (4.5)$
$= -0.265\ V$

10. Which of the values for problems 8 and 9 represent the more oxidizing environment?

The water system at pH = 4.5. The more oxidizing environment is the one with the higher (more positive according to Faure's convention) Eh.

11. What is the fugacity of O_2 of an environment having pH = 7.0 and Eh = +0.2 V?

$+0.2V = 1.23\ V + 0.01479 \log[O_2] - 0.05916\ (7.0)$
$\text{Log}[O_2] = -41.64$
$[O_2] = 10^{-41.64}$

12. Combine the Ag and Cu electrode half reaction and calculate the Eh (emf) when $[Cu^{2+}]/[Ag^+]2 = 10^{-4}$. Refer to Table 14.3 in Faure.

$Cu + 2\ Ag^+ \rightarrow Cu^{+2} + 2\ Ag \quad E^0_{ox} = 0.34\ V - (0.80\ V) = -0.46\ V$

Eh $= -0.46\ V + \frac{0.0592}{2} \log(10^{-4})$
$= -0.58\ V$

13. Write the half reactions for conversion of iron to rust (assume that rust is Fe_2O_3).

$2\ Fe \rightarrow 2\ Fe^{+3} + 6\ e^-$
$3/2\ O_2 + 6\ e^- \rightarrow 3\ O^{2-}$

14. The ΔG^o_R for the water electrode is 56.867 kcal. Calculate the value of E^o knowing that $\Delta G^o_R = E^o n F$ where n is the number of electrons and F is Faraday's constant.

$H_2O(l) \rightarrow 2\ H^+ + \frac{1}{2} O_2 + 2\ e^-$
$\Delta G^o_R = E^o n F$
$56.867\ \text{kcal} = E^o\ (2\ \text{mol e-})\ (23.06\ \text{kcal}\ V^{-1}\text{mol}^{-1})$
$E^o = 1.23\ V$

15. Refer to Figures and 14.1 and 14.2 in Faure. At equilibrium, what is the condition of the anode (that is, how much of it is left)? Correspondingly, about how many Cu^{2+} ions remain in solution at the cathode at equilibrium?

Anode: Zn (Zn--> Zn^{+2}+ $2e^-$); Cathode: Cu (Cu^{+2} + $2e^-$ → Cu)
At equilibrium, Eh = 0.00 Volts, log $[Zn^{+2}]/[Cu^{+2}] = 37.5$, so $[Zn^{+2}]/[Cu^{+2}] = 10^{37.5}$
This indicates that the anode has been sacrificed (pretty much all of the zinc metal oxidized to soluble zinc ion and there's no anode left) and that the $[Cu^{+2}]$ is very low (pretty much all of the soluble copper II ion has been reduced to form copper metal).