Homework #3

1. Chemical Dosing

2 points

a. How many mg/L of chlorine (hypochlorous acid) are required to oxidize 0.8 mg/L ferrous iron to ferric iron? Express your answer in mg/L as Cl_2.

Solution to #a

These are both redox (reduction-oxidation) reactions, so the electron transfer must be balanced. This requires that we first separate out the two half reactions,

First the oxidation half reaction involves conversion of ferrous iron to ferric

$$Fe^{+2} \rightarrow Fe^{+3}$$

And taking into account the oxidation states of the participating species, it's clear that this is a one-electron reaction:

$$\overbrace{Fe^{+2}}^{+II} \rightarrow \overbrace{Fe^{+3}}^{+III} + e^{-}$$

Next, hypochlorous must be the substance that is reduced (i.e., it does the oxidizing of the iron). The general stable form of reduced chlorine is chloride (Cl-). So the reduction half reaction is:

$$HOCl \rightarrow Cl^{-}$$

And taking into account the oxidation states of the participating species, it's clear that this is a two-electron reaction:

$$HO\overbrace{Cl}^{+I} + 2e^{-} \rightarrow \overbrace{Cl^{-}}^{-I}$$

Now the half reaction needs to be balance in term of the other elements (by adding H_2O, H^+ or OH^- as needed:

$$HO\overbrace{Cl}^{+I} + 2e^{-} \rightarrow \overbrace{Cl^{-}}^{-I} + OH^{-}$$

Then combine to balance the overall equation:

$$1 \text{ x } \quad (Fe^{+2} \rightarrow Fe^{+3} + e^{-})$$
$$½ \text{ x } (\underline{HOCl + 2e^{-} \rightarrow Cl^{-} + OH^{-}})$$
$$\tfrac{1}{2}HOCl + Fe^{+2} \rightarrow Fe^{+3} + \tfrac{1}{2}Cl^{-} + \tfrac{1}{2}OH^{-}$$

Next calculate the mass requirements

$$chlorine\ requirement = 0.8\frac{mg-Fe}{L}\left(\frac{1mM-Fe}{55.8mg-Fe}\right)\frac{0.5mM-HOCl}{1mM-Fe}\left(\frac{52.5mg-HOCl}{1mM-HOCl}\right)$$

$$= 0.38\frac{mg-HOCl}{L}$$

Since most forms of chlorine are expressed as Cl_2, the more accepted answer would be:

$$chlorine\ requirement = 0.8\frac{mg-Fe}{L}\left(\frac{1mM-Fe}{55.8mg-Fe}\right)\frac{0.5mM-HOCl}{1mM-Fe}\left(\frac{71mg-Cl_2}{1mM-HOCl}\right)$$

$$= 0.51\frac{mg-Cl_2}{L}$$

b. How many mg/L of potassium permanganate[1] are required to oxidize 2 mg/L of cyanide to nitrate and carbon dioxide?

Solution to #b

First separate out the two half reactions,

First the oxidation half reaction involves conversion of cyanide and nitrate to carbon dioxide and the most stable oxidized form of nitrogen (nitrate):

$$CN^- \rightarrow CO_2 + NO_3^-$$

And taking into account the oxidation states of the participating species, it's clear that this is both a two-electron (for carbon) and an eight-electron reaction (for nitrogen). The sum is then 10 electrons.

$$\overbrace{C}^{+II}\overbrace{N^-}^{-III} \rightarrow \overbrace{C}^{+IV}O_2 + \overbrace{N}^{+V}O_3^- + 10e^-$$

Note that I presumed N had a –III oxidation state which is true for most nitrogen in organic compounds. However, if I had assumed another oxidation state, it would have forced me to change the oxidation state on the carbon as well. The end result would have been the same; 10 electrons given up per CN ion.

Now the half reaction needs to be balance in term of the other elements (by adding H_2O, H^+ or OH^- as needed:

$$5H_2O + \overbrace{C}^{+II}\overbrace{N^-}^{-III} \rightarrow \overbrace{C}^{+IV}O_2 + \overbrace{N}^{+V}O_3^- + 10H^+ + 10e^-$$

Next, permanganate is reduced to manganese dioxide. So the reduction half reaction is:

$$KMnO_4 \rightarrow K^+ + MnO_2$$

And taking into account the oxidation states of the participating species, it's clear that this is a two-electron reaction:

[1] Permanganate is a strong oxidant that is widely used in water treatment and for COD tests and some toxic waste treatment systems. Manganese is the oxidized species that does the "work" and its final reduced form after treatment is as manganese dioxide.

$$K\overbrace{Mn}^{+VII}O_4 + 3e^- \rightarrow K^+ + \overbrace{Mn}^{+IV}O_2$$

Now the half reaction needs to be balance in term of the other elements (by adding H_2O, H^+ or OH^- as needed:

$$4H^+ + K\overbrace{Mn}^{+VII}O_4 + 3e^- \rightarrow K^+ + \overbrace{Mn}^{+IV}O_2 + 2H_2O$$

Then combine to balance the overall equation:

$$3 \text{ x } (5H_2O + CN^- \rightarrow CO_2 + NO_3^- + 10H^+ + 10e^-)$$

$$10 \text{ x } (\underline{4H^+ + KMnO_4 + 3e^- \rightarrow K^+ + MnO_2 + 2H_2O})$$

$$10H^+ + 10KMnO_4 + 3CN^- \rightarrow 10K^+ + 10MnO_2 + 3CO_2 + 3NO_3^- + 5H_2O$$

Or

$$10/3\, H^+ + 10/3\, KMnO_4 + CN^- \rightarrow 10/3\, K^+ + 10/3\, MnO_2 + CO_2 + NO_3^- + 5/3\, H_2O$$

Next calculate the mass requirements

$$= 2\frac{mg-CN}{L}\left(\frac{1mM-CN}{26mg-CN}\right)\frac{10mM-MnO_4}{3mM-CN}\left(\frac{158.04mg-KMnO_4}{1mM-KMnO_4}\right)$$

$$= 40.5\frac{mg-KMnO_4}{L}$$

2. List all possible species and write the necessary equations (equilibrium, mass balance, and electroneutrality) to solve the following chemical systems.

2 points

a. 10^{-5} M sodium acetate and 10^{-6} M acetic acid

For all of these reaction in problem #2, you should recognize that they involve exchange of protons (H^+ ions), but no redox reactions or other types of reactions (e.g., breaking of C-C bonds). Also it must be remembered that Alkali metals (Na, K and any other metals in the first column in the periodic table) do not form covalent bonds and therefore completely dissociate in water, leaving the anions that they came with to exist and react (e.g., CH_3COO^-, or $H_2PO_4^-$).

The reactions are:

$$NaAc \rightarrow Na^+ + Ac^-$$

$$HAc \leftrightarrow H^+ + Ac^-$$

$$H_2O \leftrightarrow H^+ + OH^-$$

The species are: $[H^+]$, $[Na^+]$, $[OH^-]$, $[HAc]$ and $[Ac^-]$. Thus five unknowns requiring five equations:

Equilibria:

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = 10^{-4.7}$$

$$K_w = [H^+][OH^-] = 10^{-14}$$

Mass balance:

$$C_{T,Na} = [Na^+] = 10^{-5}\ M$$

$$C_{T,Ac} = [HAc] + [Ac^-] = 10^{-5}\ M + 10^{-6}\ M = 1.1x10^{-5}\ M$$

Electroneutrality:

$$[H^+] + [Na^+] = [OH^-] + [Ac^-]$$

b. 10^{-5} M sodium dihydrogen phosphate and 10^{-6} M disodium hydrogen phosphate

The reactions are:

$$NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-$$

$$Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{-2}$$

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{-2}$$

$$HPO_4^{-2} \leftrightarrow H^+ + PO_4^{-3}$$

$$H_2O \leftrightarrow H^+ + OH^-$$

The species are: $[H^+]$, $[Na^+]$, $[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{-2}]$, $[PO_4^{-3}]$ and $[OH^-]$. Thus seven unknowns requiring seven equations:

Equilibria:

$$K_{a1} = \frac{[H^+][H_2PO_4]}{[H_3PO_4]} = 10^{-2.1}$$

$$K_{a2} = \frac{[H^+][HPO_4^{-2}]}{[H_2PO_4^-]} = 10^{-7.21}$$

$$K_{a3} = \frac{[H^+][PO_4^{-3}]}{[HPO_4^{-2}]} = 10^{-12.3}$$

$$K_w = [H^+][OH^-] = 10^{-14}$$

Mass balance:

$$C_{T,Na} = [Na^+] = 10^{-5}\ M + 2x10^{-6}\ M = 1.2x10^{-5}\ M$$

$$C_{T,PO_4} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{-2}] + [PO_4^{-3}] = 10^{-5}\ M + 10^{-6}\ M = 1.1x10^{-5}\ M$$

Electroneutrality:

$$[H^+] + [Na^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{-2}] + 3[PO_4^{-3}]$$

c. 10^{-4} M hydrochloric acid

The reactions are:

$$HCl \leftrightarrow H^+ + Cl^-$$
$$H_2O \leftrightarrow H^+ + OH^-$$

The species are: [H^+], [OH^-], and [Cl^-]. Since HCl is a strong acid, it will completely dissociate. There will be no appreciable HCl present in solution. Thus, three unknowns requiring three equations:

Equilibrium:

$$K_w = \left[H^+\right]\left[OH^-\right] = 10^{-14}$$

Mass balance:

$$C_{T,Cla} = \left[Cl^-\right] = 10^{-4}\ M$$

Electroneutrality:

$$\left[H^+\right] = \left[OH^-\right] + \left[Cl^-\right]$$

d. 10^{-4} M acetic acid

The reactions are:

$$HAc \leftrightarrow H^+ + Ac^-$$
$$H_2O \leftrightarrow H^+ + OH^-$$

The species are: [H^+], [OH^-], [HAc] and [Ac^-]. Thus four unknowns requiring four equations. Note that acetic acid is a weak acid. Thus some undissociated HAc will be present in contrast to the HCl above. The equilibrium equation for the acid is thus required for the solution:

Equilibria:

$$K_a = \frac{\left[H^+\right]\left[Ac^-\right]}{\left[HAc\right]} = 10^{-4.7}$$
$$K_w = \left[H^+\right]\left[OH^-\right] = 10^{-14}$$

Mass balance:

$$C_{T,Ac} = \left[HAc\right] + \left[Ac^-\right] = 10^{-4}\ M$$

Electroneutrality:

$$\left[H^+\right] = \left[OH^-\right] + \left[Ac^-\right]$$

3. Determine the Percent composition (% acetate, % acetic acid) of a solution of Acetic Acid at the following pHs

1 point

a. pH 3.0

b. pH 4.5

c. pH 5.5

$$K_a = 10^{-4.7} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{10^{-4.7}}{[H^+]}$$

$$1 + \frac{[CH_3COO^-]}{[CH_3COOH]} = 1 + \frac{10^{-4.7}}{[H^+]}$$

$$\frac{[CH_3COOH] + [CH_3COO^-]}{[CH_3COOH]} = 1 + \frac{10^{-4.7}}{[H^+]}$$

$$\frac{[CH_3COOH]}{[CH_3COOH] + [CH_3COO^-]} = \left(1 + \frac{10^{-4.7}}{[H^+]}\right)^{-1}$$

$$\%\text{ acetic acid} = 100\% \frac{[CH_3COOH]}{[CH_3COOH] + [CH_3COO^-]} = 100\% \left(1 + \frac{10^{-4.7}}{[H^+]}\right)^{-1}$$

% acetate = 100%-% acetic acid

Answers:

pH	% acetic acid	% acetate
3.0	98.04	1.96
4.5	61.31	38.69
5.5	13.68	86.32

Or if you used pKa = 4.75, you'd get:

pH	% acetic acid	% acetate
3.0	98.6	1.4
4.5	64.3	35.7
5.5	15.2	84.8

Or if you used Ka = 1.76×10^{-5} (corresponds to pKa = 4.7545), you'd get:

pH	% acetic acid	% acetate
3.0	98.3	1.7
4.5	64.3	35.7
5.5	15.2	84.8