Lecture 19 CH131 Summer 1

Tuesday, June 25, 2019

- Electricity from mixing: Concentration cells
- Practice problems

Final lecture: Answer questions you may have

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Cell line notation (Tro, 4e, p 897)

$Zn(s)|\ Zn^{2+}(aq)\ ||Cu^{2+}(aq)|\ Cu(s)$

- Oxidation on left, "||" is salt bridge, reduction on right
- Phases separated by "|", same phases separated by ","
- If no solid, inert electrode (Pt or graphite)
- Left to right order matches flow of electrons

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Cell line notation (Tro, 4e, p 897)

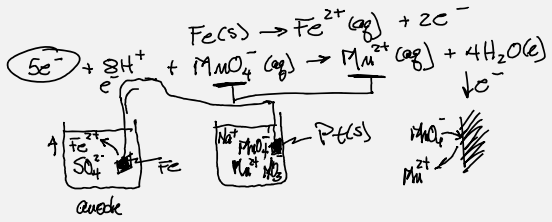
oxidation

$Fe(s)|\ Fe^{2+}(aq)\ ||MnO_4^-(aq),\ Mn^{2+}(aq)|\ Pt(s)$

Write the half reactions …

$Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$

$MnO_4^-(aq) + 5\ e^- + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$



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[TP] The process

$Cl^-(1\ M) \rightleftarrows Cl^-(0.0001\ M)$

is spontaneous. The correct cell line notation is …

0% 1. Pt(s) | Cl^-(0.0001 M) | Cl_2 (1 bar) || Cl^-(1 M) | Cl_2 (1 bar) | Pt(s)

0% 2. Pt(s) | Cl^-(0.0001 M) | Cl_2 (1 bar) || Cl_2 (1 bar) | Cl^-(1 M) | Pt(s)

0% 3. Pt(s) | Cl^-(1 M) | Cl_2 (1 bar) || Cl^-(0.0001 M) | Cl_2 (1 bar) | Pt(s)

100% 4. Pt(s) | Cl^-(1 M) | Cl_2 (1 bar) || Cl_2 (1 bar) | Cl^-(0.0001 M) | Pt(s)

0% 5. None of the above

$2\ Cl^-(1M) \rightarrow Cl_2(1\ bar) + 2e^-$

$2e^- + Cl_2(1\ bar) \rightarrow 2Cl^-(0.0001M)$

$2\ Cl^-(1M) \rightarrow 2Cl^-(10^{-4}M)$

$2\ Cl^-(10^{-4}M) \rightarrow Cl_2(1\ bar) + 2e^-$

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[TP] The voltage of a chloride concentration cell is x V. If the pressure of the chlorine gas in the anode is doubled, the new voltage will ...

0% 1. be larger than x V.
0% 2. remain x V.
100% 3. be smaller than x V.
0% 4. Further information needed.

[Quiz] A concentration cell is constructed with Q corresponding to the Cl^- concentration difference between sea water and river water at 25 °C. Assume that the Cl^- concentration (due to dissolved NaCl) of sea water is 35 g/L and than that of river water is 0.10 mg/L. The voltage of this cell is ...

0% 1. $E = +0.67$ V
0% 2. $E = +0.50$ V
100% 3. $E = +0.33$ V
0% 4. $E = +0.17$ V
0% 5. Something else

$E = -\frac{0.059}{2}\text{ V}\log\left(\frac{10^{-4}}{35}\right)^2$

Recipe for concentration cell reaction and Q

1. Write skeleton reaction, for example
   $A^+(\text{conc}, aq) \rightarrow A^+(\text{dil}, aq)$ or
   $B^-(\text{conc}, aq) \rightarrow B^-(\text{dil}, aq)$
2. Write half reaction for reactant and for product, labelling each component as being in anode or cathode.

$Cl^-(\text{conc}) \rightarrow Cl^-(\text{dil})$

$Pb^{2+}(\text{conc}) \rightarrow Pb^{2+}(\text{dil})$
$2e^- + Pb^{2+}(\text{conc}) \rightarrow Pb(s)$ cathode
$Pb(s) \rightarrow Pb^{2+}(\text{dil}) + 2e^-$ anode
$Pb^{2+}(\text{conc}) \rightarrow Pb^{2+}(\text{dil})$

$Q = \frac{[\text{dilute}]}{[\text{conc}]}$

Recipe for concentration cell reaction and Q

1. Write skeleton reaction, for example
   $A^+(\text{conc}, aq) \rightarrow A^+(\text{dil}, aq)$ or
   $B^-(\text{conc}, aq) \rightarrow B^-(\text{dil}, aq)$
2. Write half reaction for reactant and for product, labelling each component as being in anode or cathode.
3. Combine half reactions, noting the value of n_e.
4. Write expression for Q
5. Use $E = -\frac{0.06}{n_e}\text{ V}\log(Q)$

Electrochemistry practice problems

- 17.15 Reduction potential from cell potential
- 17.23 Reduction potential from free energy change
- 17.33 Concentration from cell potential
- 17.35 Equilibrium constant from cell potential
- 17.39 K_a from cell potential
- 17.41 K_{sp} from cell potential

Electrochemistry practice problem: 17.15

15. In a galvanic cell, one half-cell consists of a zinc strip dipped into a 1.00 M solution of $Zn(NO_3)_2$. In the second half-cell, solid indium adsorbed on graphite is in contact with a 1.00 M solution of $In(NO_3)_3$. Indium is observed to plate out as the galvanic cell operates, and the initial cell potential is measured to be 0.425 V at 25°C.
   (a) Write balanced equations for the half-reactions at the anode and the cathode.
   (b) Calculate the standard reduction potential of an $In^{3+}|In$ half-cell. Consult Appendix E for the reduction potential of the $Zn^{2+}|Zn$ electrode.

(b) $E^\circ = -0.338$ V

Electrochemistry practice problem: 17.23

(a) $E^\circ = -0.18$ V

(b) $E^\circ = -2.54$ V, so no

23. (a) Use the data from Appendix E to calculate the half-cell potential E° for the half-reaction

$$Mn^{3+}(aq) + 3\,e^- \longrightarrow Mn(s)$$

(b) Consider the disproportionation reaction

$$3\,Mn^{2+}(aq) \rightleftharpoons Mn(s) + 2\,Mn^{3+}(aq)$$

Will Mn^{2+} disproportionate in aqueous solution?

Electrochemistry practice problem: 17.33

(a) $E^\circ = 0.31$V

(b) $[Cr^{3+}] = 1.09 \times 10^{-8}$ M

33. The following reaction occurs in an electrochemical cell:

$$3\,HClO_2(aq) + 2\,Cr^{3+}(aq) + 12\,H_2O(\ell) \longrightarrow 3\,HClO(aq) + Cr_2O_7^{2-}(aq) + 8\,H_3O^+(aq)$$

(a) Calculate E° for this cell.
(b) At pH 0, with $[Cr_2O_7^{2-}] = 0.80$ M $[HClO_2] = 0.15$ M, and $[HClO] = 0.20$ M, the cell potential is found to be 0.15 V. Calculate the concentration of $Cr^{3+}(aq)$ in the cell.