Chemistry 312
Problem Set #1

Due Friday Jan. 12, 2007

1. Use Table 6.1 (below), and the potential vs. pH graph at the end of this problem set, to determine whether the following would be stable in water.
   a. Zn^0 at pH=2.
   b. $[IrCl_6]^{2-}$ at pH= 14.
   c. $[IrCl_6]^{3-}$ at pH= 14.
   d. Fe^{2+} at pH= 0

REDOX HALF-REACTIONS

Table 6.1 Selected standard potentials at 25°C

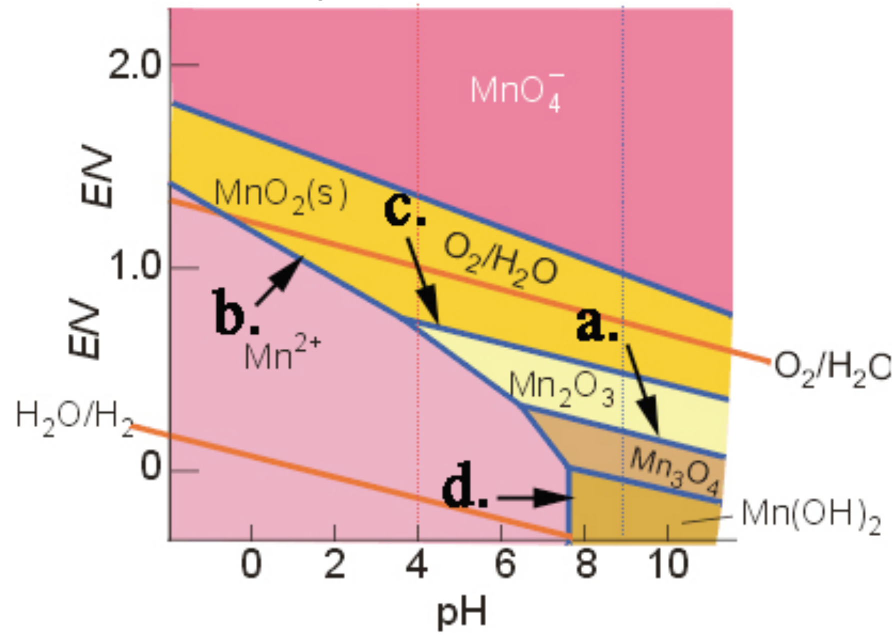
Couple	$E^\ominus$/V
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+3.05
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.76
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(aq)$	+1.23
$[IrCl_6]^{2-}(aq) + e^- \rightarrow [IrCl_6]^{3-}(aq)$	+0.87
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$[PtCl_4]^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4Cl^-(aq)$	+0.76
$I_3^-(aq) + 2e^- \rightarrow 3I^-(aq)$	+0.54
$[Fe(CN)_6]^{3-}(aq) + e^- \rightarrow [Fe(CN)_6]^{4-}(aq)$	+0.36
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0
$AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)$	−0.15
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.68
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	−2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

2. Answer the following questions about the Pourbaix diagram shown below

a. Is MnO_4^- a stronger oxidant at pH= 8, or pH= 2?

b. Is MnO_2(s) easier to reduce at pH= 2, or pH= 10? How do the half rxns differ at pH= 2 vs. pH= 10? Write a balanced eqn for each.

c. What reaction occurs across the line labeled “a”? Is this a redox reaction?

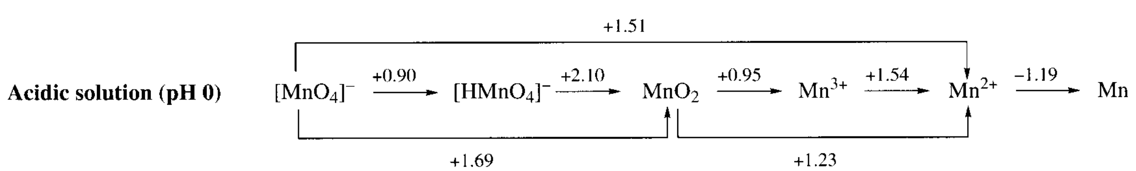


d. What reaction occurs across the line labeled “b”? Is this a redox reaction?

e. What reaction occurs across the line labeled “c”? Is this a redox reaction?

f. What reaction occurs across the line labeled “d”? Is this a redox reaction?

3a. Write balanced half reactions for all of the redox steps shown in the Latimer diagram below.



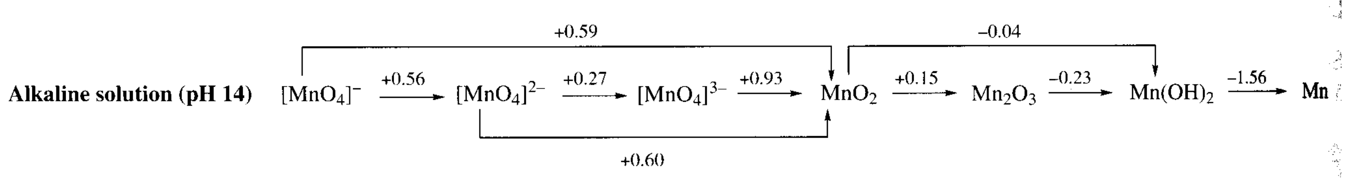


Fig. 7.2 Potential diagrams (Latimer diagrams) for manganese in aqueous solution at pH 0 (i.e. $[H^+] = 1\ mol\ dm^{-3}$), and in aqueous solution at pH 14. For such diagrams, it is essential to specify the pH, and the reason is obvious by comparing the two diagrams.

3b. Determine which Mn species shown in the Latimer diagram above would tend to disproportionate. Do this for both acidic and basic conditions.

3c. Determine the redox potential for MnO_4^- conversion to MnO_4^{3-} at pH= 14.

3d. Determine the redox potential for MnO_4^- conversion to Mn^{3+} at pH= 0.

3e. Determine the redox potential for MnO_4^- conversion to Mn^{3+} at pH= 6.

4. Answer the following questions about the Frost diagram below.

   a. What is the most stable oxidation state of manganese under acidic conditions?

   b. What is the redox potential at which Mn^{2+} is converted Mn^0 to under acidic conditions? Would Mn^0 be a good reductant? Would Mn^{2+} be a good reductant?

   c. What is the redox potential at which $HMnO_4$ is converted H_2MnO_4 to under acidic conditions? Would $HMnO_4$ be a good oxidant? Would H_2MnO_4 be a good reductant?