Today's News

New HW Posted

Not sure if I will be on campus tomorrow-call or email ahead of time if you need to see me.

Exam Comments: "Most of the students could do most of the problems most of the time."

Exemplary Question: A student reports that the reaction of fluoride ion with $C_2H_5NH_3^+$ results in complete conversion of the fluoride ion into HF. Is this the expected result? Explain your answer.(6 points)

Basic ideas in electrochemistry

- Sections 4.6 to 4.10 (p.125-142) should be reviewed
- Oxidation-process whereby one or more electrons is lost. The species undergoing oxidation is also called the reducing agent (RA)
- Reduction-process whereby one or more electrons is gained. Species being reduced is also called the oxidizing agent(OA).
- Just as acid-base chemistry is treated as proton transfer, oxidation-reduction chemistry is viewed as electron transfer. As these processes are generally reversible (and equilibria), they can be described as:

$$\text{OA} + \text{RA} \Leftrightarrow \text{RA} + \text{OA}$$

- Tracking of electrons is most easily done by use of oxidation numbers (see p. 127).
  - The oxidation number is simply the comparison of the electron count for an element in a compound or ion with that of the element in its elemental form, where it is assigned an oxidation number of 0.
  - One needs to be mindful that oxidation numbers are a bookkeeping formalism and are not a true measure of electron distribution in a compound.
  - an **increase** in oxidation number is indicative of an **oxidation**
  - a **decrease** in oxidation number is indicative of a **reduction**

Oxidation Numbers

- You should be aware that oxidation numbers are used to track electron changes, and will not represent the actual distribution of electrons in a complex species
- General Rules
  - Elements in their elemental forms have ON=0
  - A monoatomic ion has an oxidation number equal to its charge
  - In chemical compounds or polyatomic ions(there is a hierarchy here, a higher rule trumps a lower one.
    - fluorine is always 1-
    - oxygen is 2- except in peroxides(1-). These compounds have O-O single bonds
    - other halogens are 1- except for interhalogen compounds or when bound to oxygen. In an interhalogen compound, the more electronegative element is assigned ON=1-
    - H is 1+ except when bound to a metal (NaH)
    - the sum of the oxidation numbers must equal the charge on the compound or ion.
- What are the oxidation number of all of the atoms in the following: $Na_2C_2O_4$, $Pd(OH)_4$, $NaBF_4$, Au_2S_3, $H_2PO_4^-$, Na_3PO_3, $Cu(NO_3)_2$, ClF_3, $POCl_3$

Breaking down Redox Processes

- Describe each of the following in as many different ways as possible-I'll explain what that means.
- $ClO_4^- + Th \Leftrightarrow Cl^- + Th^{4+}$
- $Cl_2 + Be \Leftrightarrow Cl^- + Be_2O_3^{2-}$
- $AsO_2^- + Fe^{2+} \Leftrightarrow As + Fe^{3+}$
- $Sb_2O_3 + Mo \Leftrightarrow Sb + Mo^{3+}$
- $ClO_2 + F^- \Leftrightarrow ClO_2^- + F_2$
- $Al^{3+} + SO_2 \Leftrightarrow Al + SO_4^{2-}$

Balancing redox equations

- The balancing of redox equations is a special challenge as the balancing must result in neither a production or consumption of electrons. Further, there is often no "mass linkage" between the oxidizing and reducing agents (Na(s) + MnO_4^- ⇔ Na^+ + Mn^{2+}) and for a given redox process there are often numerous mass balanced equations.
  - There are a number of different methods for balancing redox equations. We will be using the ion-electron method(p138). A slight modification in the approach will be suggested. It's interesting that this method makes no use of oxidation numbers. The half reaction method is also presented in your text.
  - If we don't actually use them to balance redox equations, what good are oxidation numbers?
- Acidic vs basic solution. Many redox reactions "require" that the medium be either basic or acidic.
  - In real terms this describes the availability of H^+ or OH^- as products or reagents. Chemically their roles normally involve extra "O" and are summarized by the following equations,which can be written in either direction:
  - acidic $2H^+$(aq) +"O" ⇔ H_2O
  - basic $2OH^-$ (aq) ⇔ H_2O + "O"

Two Examples

- $Cr_2O_7^{2-}(aq) + Fe(s) \Leftrightarrow Cr^{3+}(aq) + Fe^{2+}(aq)$ (acid)
- Separate the reaction into two half reactions:
  - $Cr_2O_7^{2-}(aq) \Leftrightarrow Cr^{3+}(aq)$
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq)$
- Mass balance each half reaction without concern for oxygen or hydrogen
  - $Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq)$
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq)$
- Complete mass balance for H and O, based upon nature of the medium
  - $14H^+(aq) + Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq) + 7H_2O$
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq)$
- Charge balance each half reaction by adding the appropriate number of electrons
  - $6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq) + 7H_2O$
- Combine the half reactions in a manner that achieves e- balance
  - $6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq) + 7H_2O$ (x1)
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq) + 2e^-$ (x3)
- Combine the half reactions and "clean up" as necessary
  - $14H^+(aq) + Cr_2O_7^{2-}(aq) + 3Fe(s) \Leftrightarrow 2Cr^{3+}(aq) + 3Fe^{2+}(aq) + 7H_2O$

- $Cr^{3+}(aq)$ + $MnO_2(s)$ ⇔ $Mn^{2+}(aq)$ + $CrO_4^{2-}(aq)$ (basic)
- half reactions:
  - $Cr^{3+}(aq)$ ⇔ $CrO_4^{2-}(aq)$
  - $MnO_2(s)$ ⇔ $Mn^{2+}(aq)$
- both half reactions are already mass balanced except for O, so go directly to that step(basic solution)
  - $8OH^-(aq) + Cr^{3+}(aq)$ ⇔ $CrO_4^{2-}(aq) + 4H_2O$
  - $2H_2O + MnO_2(s)$ ⇔ $Mn^{2+}(aq) + 4OH^-(aq)$
- add electrons
  - $8OH^-(aq) + Cr^{3+}(aq)$ ⇔ $CrO_4^{2-}(aq) + 4H_2O + 3e-$
  - $2e- + 2H_2O + MnO_2(s)$ ⇔ $Mn^{2+}(aq) + 4OH^-(aq)$
- common factor is 6
  - $8OH^-(aq) + Cr^{3+}(aq)$ ⇔ $CrO_4^{2-}(aq) + 4H_2O + 3e-$ (x2)
  - $2e- + 2H_2O + MnO_2(s)$ ⇔ $Mn^{2+}(aq) + 4OH^-(aq)$ (x3)
  - $16OH^-(aq) + 2Cr^{3+}(aq) + 6H_2O + 3MnO_2(s)$ ⇔ $2CrO_4^{2-}(aq) + 8H_2O$ $3Mn^{2+}(aq) + 12OH^-(aq)$
  - this reaction is "cleaned up" by removing 12 OH- and 6 H_2O from each side, yielding the following final result
  - $4OH^-(aq) + 2Cr^{3+}(aq) + 3MnO_2(s)$ ⇔ $2CrO_4^{2-}(aq) + 2H_2O + 3Mn^{2+}(aq)$

- ClO_4^- + NO_2 => Cl^- + NO_3 (acid)
- same as above in base
- MnO_2 + Sb => Mn^{2+} + Sb_2O_3 (base)
- same as above in acid
- Cl_2 ⇔ Cl^- + ClO_3^-