CHEMISTRY 225 SEMESTER 01-2010
TUTORIAL QUESTIONS: $E^{\ominus}$ AND REDOX

1) The following questions concerns half-equations.
   a) Write ionic half-equations, including states, for:
      i) the conversion of Fe^{2+} to Fe^{3+}.
      ii) the conversion of Al to Al^{3+}.
      iii) the conversion of Cu^{2+} to Cu.
      iv) the conversion of Cu to Cu^{2+}.
      v) the conversion of Fe to Fe^{2+}.
      vi) the conversion of Ag to Ag^{+}.
      vii) the conversion of Pb to Pb^{2+}.
      viii) the conversion of Mg to Mg^{2+}.
      ix) the conversion of NO_3^- in the presence of acid to NO.
      x) the conversion of NO_3^- in the presence of acid to NO_2.
      xi) the conversion of H_2 to H^+.
      xii) the conversion of MnO_4^- in the presence of acid to Mn^{2+} and water.
      xiii) the conversion of $Cr_2O_7^{2-}$ in the presence of acid to Cr^{3+} and H_2O.
      xiv) the conversion of H_2S to S and H^+.
      xv) the conversion of OH^- to O_2 and H_2O.

   b) In each of the above cases write down the corresponding $E^{\ominus}_{red}$ value (i.e. the standard reduction potential, even though some are oxidation reactions).

   c) Classify each of the above half-equations as either an oxidation or a reduction reaction. Rank the oxidation equations in order of reducing power (since an oxidation process has the power to cause reduction elsewhere) and the reduction equations in order of oxidising power. In each case write the strongest first.

2) The following question concerns ionic equations.
   NB. Ionic equations do not include electrons.
   a) Write balanced overall ionic equations for the following reactions. You may combine some of the half equations you have written in question (1).
      i) The addition of metallic aluminium to a copper(II) nitrate solution results in the precipitation of copper and the formation of Al^{3+} in solution.
      ii) When metallic copper is added to a dilute solution of nitric acid, gaseous NO is evolved and the solution becomes pale blue.
      iii) Potassium permanganate solution is decolourised by acidified iron(II) sulfate solution.
   b) In each of the above cases calculate $E^{\ominus}$ values for the ionic equation from the $E^{\ominus}$ values for the half-equations in the table.

3) Write the cell reactions for the following cells, and use the table of $E^{\ominus}$ values in your textbook to determine the e.m.f.'s of the cells under standard conditions. Make sure the sign of the e.m.f. is correct.
   a) $Zn(s) | ZnSO_4(aq) \| AgNO_3(aq) | Ag(s)$
   b) $Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) \| Cu^{2+}(aq)\ Cu(s)$
   c) $Cd(s) | Cd^{2+}(aq) \| Hg_2Cl_2(s) | Cl^-(aq) | Hg(l)$
   d) $Pb(s) | PbSO_4(s) | SO_4^{2-}(aq) \| Cu^{2+}(aq) | Cu(s)$
   e) $Pt(s) | H_2(g) | H^+(aq), Cl^-(aq) | AgCl(s) | Ag(s)$

   Draw diagrams to illustrate the structure of the cells in parts (a) and (e). Explain the function of the salt bridge in (a). Why is none necessary in (e)?

4) Using $E^{\ominus}$ values from tables, calculate $E^{\ominus}_{cell}$ values

corresponding to each of the following ionic equations and use them to decide whether the reaction described is likely or impossible.

a) $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$

b) $2Fe^{2+}(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + H_2(g)$

c) $2MnO_4^-(aq) + 6H^+(aq) + 5H_2S(g) \rightarrow 5S(s) + 2Mn^{2+}(aq) + 8H_2O(l)$

d) $Br_2(aq) + 2Cl(aq) \rightarrow 2Br(aq) + Cl_2(aq)$

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

f) $Cu(s) + 2H^+(aq) \rightarrow Cu^{2+} + H_2(g)$

5) Using $E^\ominus$ values from your textbook relevant to the following redox couples, answer the questions below:

Ag^+/Ag	Fe^{2+}/Fe
Cu^{2+}/Cu	Zn^{2+}/Zn
Pb^{2+}/Pb	Mg^{2+}/Mg

a) State which species is the strongest oxidant and which is the weakest oxidant.

b) State which species is the strongest reductant and which is the weakest reductant.

c) Lead rods are placed in solutions of each of $AgNO_3$, $Cu(NO_3)_2$, $Fe(NO_3)_2$ and $Mg(NO_3)_2$. In which solutions could you expect a coating of another metal on the lead rod? Explain.

d) Which of the metals: silver, zinc or magnesium, might be coated with lead when immersed in a solution of $Pb(NO_3)_2$?

e) What would be observed if an iron(II) sulphate solution was stored in a copper vessel? What would be observed if a copper(II) sulphate solution was stored in an iron vessel?

6) Use your table of $E^\ominus$ values to decide whether reaction will occur in each of the following cases. In each case look for an oxidising agent and a reducing agent, write the half equations together with the relevant $E^\ominus$ values and, if reaction is predicted, combine them to form a balanced ionic equation.

a) Mercury and dilute hydrochloric acid.

b) Iron metal and copper(II) sulfate solution.

c) Silver metal and copper(II) nitrate solution.

d) Acidified potassium permanganate solution and solid zinc metal.

7) What is meant by the terms *standard hydrogen electrode* and *standard reduction potential*? How are standard reduction potentials determined?

8) Determine $E^\ominus$ for the cell:

$C(s) | Cl^-(aq) | Cl_2(g) \| Cr_2O_7^{2-}(aq), H^+(aq), Cr^{3+}(aq) | Pt(s)$

at 25°C. From your calculated value, what can you say about the spontaneity of the reaction occurring in the cell?

If the pH of the solution in the right hand half-cell is adjusted to -0.50, the concentration of Cr^{3+} adjusted to 0.010 M, and the partial pressure of the Cl_2 adjusted to 0.010 atm, whilst all other conditions are kept at their standard values, calculate the value of E for this non-standard cell.

Use your result to comment on the ability of acidified dichromate solution to oxidise chloride to chlorine.

9) From the standard redox potentials

$E^\ominus(Fe^{3+}/Fe^{2+}) = +0{\cdot}77v$, $E^\ominus(Fe^{2+}/Fe) = -0{\cdot}44v$

a) Explain the assertion that Fe^{2+} may act both as an oxidant and as a reductant.

b) Would you expect metallic iron to dissolve in a 1M acid solution and produce gaseous hydrogen?

c) If so, would the Fe be oxidized to Fe^{2+}, or to Fe^{3+}?

d) Would you expect direct reaction between iron and chlorine in aqueous solution to produce $FeCl_2$ or $FeCl_3$?

e) $E^\ominus(Cl_2/Cl^-) = 1{\cdot}36v$.

f) Use the Nernst equation to calculate the minimum concentration of dilute hydrochloric acid necessary to dissolve metallic iron. (Assume all other conditions are standard.)

10) Calculate the value of $E^\ominus$ for the cell

$Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) \| Ag^+(aq) | Ag(s)$

Write down the cell reaction and determine its equilibrium constant.

11) Calculate the maximum pH at which (a) permanganate ions (b) manganese dioxide can oxidize chloride ions to chlorine in acidic solution. (Assume all other conditions are standard.)