Chem12 Voltages in Electrochemical Cells : Notes/W.S. - 30

In the **<u>Standard Reduction Table</u>**, the voltages for half cell reactions are given. The half-cell reaction : $2H^+ + 2e^- \rightarrow H_2$ is assigned a voltage of 0.0 volts. This is arbitrary as the half-cell reaction : $Cu^{2+} + 2e^- \rightarrow Cu$ which is assigned a voltage of 0.34 volts could have been assigned a voltage of 0.0 volts. This would make the hydrogen half-cell voltage equal to -0.34 volts. These half-cell voltages are <u>relative</u>.

These voltages do not mean anything by themselves, as a reduction cannot occur without an oxidation. The important thing is the difference in voltages between the reduction half-reaction and the oxidation half-reaction. We can then find the voltage that a particular electrochemical cell can produce under standard conditions.

Examples :

1) For a silver-nickel cell we have the following voltages :

$Ag^+ + e^- \rightarrow Ag$	+0.80 volts	reduction
$Ni \rightarrow Ni^{2+} + 2e^-$	+0.26 volts	oxidation

The voltages are found in the table of reduction potentials. To find the voltage of the oxidation half-cell reaction, simply change the sign so that the nickel half-reaction has a voltage of +0.26 instead of -0.26 volts. The voltage of the cell can be found by simply **<u>adding</u>** the two voltages. +0.80 +0.26 = +1.06 volts under standard conditions. The + sign means that the reaction is **<u>spontaneous</u>**. The standard conditions are : the cell electrodes are immersed in solutions with a concentration of 1.0 M, the temperature is 25°C and the pressure is 101.3 kPa (1.0 atmospheres).

2) In the above reaction : $2Ag^+ + Ni \rightarrow Ni^{2+} + 2Ag$, the overall voltage is positive so the reaction is **<u>spontaneous</u>**, therefore, it will proceed. For the reaction : $Ni + Fe^{2+} \rightarrow Ni^{2+} + Fe$, the cell voltage is -0.19 volts. When the cell voltage is negative, the reaction will be **<u>non-spontaneous</u>**. In this case energy must be supplied to the cell to make the reaction proceed.

Problems : 1) Using the Standard Reduction Potential tables, for the following redox reactions, find the cell potential, and indicate whether the reactions are spontaneous, non-spontaneous, or not possible.

a) $Ni^{2+} + Fe \rightarrow Ni + Fe^{2+}$

b) $Ag + H^{+} \rightarrow Ag^{+} + H_2$

c) $Co + Fe^{3+} \rightarrow Co^{2+} + Fe^{2+}$

d) $I^{-} + MnO_4^{-} \rightarrow I_2 + Mn^{2+}$

e) $Ag + Cl^{-} \rightarrow Ag^{+} + Cl_2$

f) $I_2 + Cl^{-} \rightarrow I^{-} + Cl_2$

g) $H_2 + S_2O_8^{2-} \rightarrow H^{+} + SO_4^{2-}$

Answers : 1)a) +0.19V, spontaneous, b) -0.80V, non-spontaneous, c) +1.05V, spontaneous, d) +0.97V, spontaneous, e) not possible (it is not a redox reaction), f) -0.82V, non-spontaneous, g) +2.01V, spontaneous.