Electrochemistry Objective B:

To make quantitative predictions about whether equilibrium will favour products or reactants in a redox reaction.

So far we've seen the following reaction:

$Zn + Cu^{+2} \text{-->} Zn^{+2} + Cu$. (1)

An electrochemical cell can also be setup using

$Cu + 2Ag^{+1} \text{-->} 2\ Ag + Cu^{+2}$ . . (2)

Imagine each of the above as a *competition to gain electrons*. In other word see it as competition between prowlers or oxidizing agents.

In (1), Cu^{+2} wins over Zn^{+2}, and the reaction proceeds not in the reverse reaction but as written.

In (2), however, Cu^{+2} loses to Ag^{+1}.

Tendency to gain electrons = strength of oxidizing agent:

$Ag^{+1} > Cu^{+2} > Zn^{+2}$

If you imagine reactions (1)and (2) as competitions to lose electrons,

then the tendency to lose electrons = strength of reducing agent:

Zn > Cu > Ag.

Consider two more reactions which proceed as written:

$Zn + 2\ H^{+1} \text{-->} Zn^{+2} + H_2$ (3)

$H_2 + Cu^{+2} \text{-->} Cu + 2\ H^{+1}$ (4)

Based on (3) and (4) we can extend our lists:

$Ag^{+1} > Cu^{+2} > H^{+1} > Zn^{+2}$, in terms of oxidizing ability, and

$Zn > H_2 > Cu > Ag$, in terms of reducing ability.

In order to make quantitative predictions about whether equilibrium favours reactants or products, we use the hydrogen half-cell as a reference:

$2H^{+1} + 2e = H_2$ E = 0.00 V *

*under standard conditions of 1.0 M solution for each electrode at a temperature of 25 C and 101.3 kPa

When we set the above reaction at 0V, then we measure the following of other reactions we mentioned:

Ag^{+1} + 1e--> Ag E = 0.80 V

Cu^{+2} + 2e--> Cu E = 0.34 V

$2H^{+1}$ + 2e = H_2 E = 0.00 V

Zn^{+2} + 2e--> Zn E = -0.76 V

Note: For a reverse reaction, E 's sign changes. However since the values represent relative potential differences and not amounts of energy released, the value of E does ***not*** change if we multiply the whole equation by a coefficient.

Example 1: A student sets up an electrochemical cell using Zn and Ag. What will be the anode?

TWO Possibilities:

Possibility 1

Zn + 2 Ag^{+1} --> Zn^{+2} + 2 Ag

Zn^{+2} + 2e--> Zn E = -0.76 V becomes

Zn -->Zn^{+2} + 2e E = 0.76 V .

$2Ag^{+1}$ + 2e--> 2 Ag E = 0.80 V .

Sum = 0.76 + 0.80 V = 1.56 V

Possibility 2

Zn^{+2} + 2 Ag--> Zn + 2 Ag^{+1}

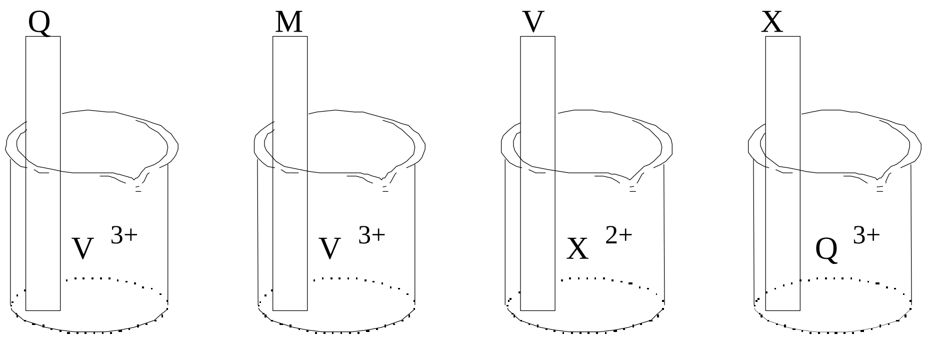
The sum for this reaction would be -0.76 V + -0.80 V = -1.56 V

The reaction with the positive net voltage is the one that occurs spontaneously. Products are favoured over the reactants. So, in possibility (1), Zn is oxidized; Zn will be the anode.

Predictions based on Experiments, not E Values

Example:
In the laboratory, you are given different metallic strips and different solutions containing metal ions.

You place the strips in the solutions and you observe the following.



1.No reaction   2. Reaction   3. Reaction   4. No reaction

Which of the above metals is the strongest reducing agent? The strongest oxidizing agent?

ANSWER

Let's analyze each reaction:

Reaction 1:
If there is no reaction, then presumably the reverse reaction is dominant:
Q^{+3} + V --> Q + V^{+3}.   So V > Q in ability to reduce.

Reaction 2:

M + V^{+3}--> M^{+3} + V   So M > V in ability to reduce.

Reaction 3:

V + X^{+2} --> X + V^{+3} (unbalanced)   So V > X in ability to reduce.

Reaction 4: Again there is no reaction, so the reverse reaction is dominant:
Q + X^{+2}--> Q^{+3} + X (unbalanced)   So Q > X in ability to reduce.

From the above we conclude that M > V > Q > X, so that M is the strongest reducing agent and X is the weakest reducing agent. Also that makes X^{+2} the strongest oxidizing agent and M^{+3} the weakest oxidizing agent.