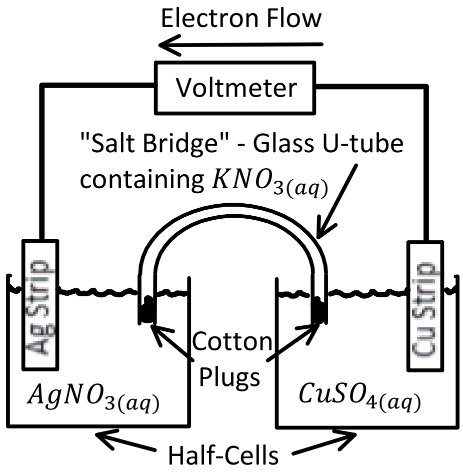
C12 - 5.0 - Electrochemistry

Electrochemistry - The conversion of chemical energy to electric energy and back.

Electrochemical Cell - A system which produces electrical energy or causes a chemical reaction.



Reduction-Oxidization Reaction (Redox Reaction)

$2Ag^+_{(aq)} + Cu_{(s)} \rightarrow 2Ag_{(S)} + Cu^+_{(aq)}$ Add two half reactions.

Half (Cell) - Reactions

Reduction Reaction - Species gain electrons.

$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(S)}$

Oxidation Reaction - Species lose electrons.

$Cu_{(s)} \rightarrow Cu^+_{(aq)} + 2e^-$

Ag is the Oxidizing Agent (Reduced)

Cu is the Reducing Agent (Oxidized)

Oxidization Number - Charge an atom would possess if the species containing the atom were made up of ions.

The sum of the positive charges and the negative charges must equal the overall charge on the species.

$H_4P_2O_7$

$$\begin{array}{ccc} H & P & O \\ +1 & +x & -2 \\ \times 4 & \times 2 & \times 7 \\ \hline +4 & +2x & -14 = 0 \end{array}$$

Charge # of Neutral

$$2x - 10 = 0$$
$$x = 5$$

$Phosphorus\ Oxidation\ \# = 5$

P_4

$$\begin{array}{c} P \\ +x \\ \times 4 \\ \hline 4x = 0 \end{array}$$

$$4x = 0$$
$$x = 0$$

$Phosphorus\ Oxidation\ \# = 0$

Oxidation Number of an atom in its elemental form is Zero

Cr^{3+}

$Chromium\ Oxidation\ \# = +3$

Oxidation Number of a monatomic ion is its charge.

SO_4^{2-}

$$\begin{array}{ccc} S & O_4 & -2 \\ +x & -2 & \\ \times 1 & \times 4 & \\ \hline +x & -8 = -2 & \end{array}$$

$$x - 8 = -2$$
$$x = 6$$

$Sulpher\ Oxidation\ \# = 6$

$ClO_2 + C \rightarrow ClO_2^- + CO_2^{2-}$

$Cl = +4$ $\quad Cl = +3$

$C = 0$ $\quad C = +4$

C is Oxidized

Case #1 100% Spontaneous Reaction

$\boxed{Cu^{2+}} + 2e^- \rightarrow Cu$ $\quad E^o = +0.34$

$Zn^{2+} + 2e^- \leftarrow \boxed{Zn}$ $\quad E^o = -0.76$

$Cu^{2+} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}$

No Reaction

$Cu^{2+} + 2e^- \leftarrow \boxed{Cu}$

$Zn^{2+} + 2e^- \leftarrow \boxed{Zn}$

No Reaction

$\boxed{Cu^{2+}} + 2e^- \rightarrow Cu$

$\boxed{Zn^{2+}} + 2e^- \rightarrow Zn$

Case #2 No Reaction

$Cu^{2+} + 2e^- \leftarrow \boxed{Cu}$ $\quad E^o = +0.34$

$\boxed{Zn^{2+}} + 2e^- \rightarrow Zn$ $\quad E^o = -0.76$

$Cu^{2+} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}$

A reaction will be spontaneous if and only if there is a reactant to be reduced (on the left side) which is above a reactant on a reactant to be oxidized (on the right side).

C12 - 5.0 - Electrochemistry

SO_4^{2-} in solution with Na_2SO_4 will reduce? (Only if H^+ is present) P.199

$$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + 2H_2O$$

A^{2+} reacts with $C(s)$ but not with $B(s)$.

Arrange in decreasing tendency to reduce.

$$B^{2+} + 2e^- \rightleftharpoons B_{(s)}$$
$$A^{2+} + 2e^- \rightleftharpoons A_{(s)}$$
$$C^{2+} + 2e^- \rightleftharpoons C_{(s)}$$

F^{2+} reacts with $D(s), E(s)$ & $G(s)$.

No reaction between D^{2+} with any metals.

G^{2+} only reacts with $D(s)$.

Arrange in decreasing strengths as oxidization agents .
(Greatest tendency to reduce 1st.)

$$F^{2+} + 2e^- \rightleftharpoons F_{(s)}$$
$$E^{2+} + 2e^- \rightleftharpoons E_{(s)}$$
$$G^{2+} + 2e^- \rightleftharpoons G_{(s)}$$
$$D^{2+} + 2e^- \rightleftharpoons D_{(s)}$$

	Fe^{2+}	Au^{3+}	Ni^{2+}	Pb^{2+}
Fe		RX	RX	RX
Au	—		—	—
Ni	—	RX		RX
Pb	—	RX	—	

RX - Reaction Occurred (— No)

Acidic Solution

$$RuO_2 \rightleftharpoons Ru$$
$$RuO_2 \rightleftharpoons Ru + 2H_2O$$
$$4H^+ + RuO_2 \rightleftharpoons Ru + 2H_2O$$
$$4e^- + 4H^+ + RuO_2 \rightleftharpoons Ru + 2H_2O$$

Major!
O
H
e

$$-4 + 4 = 0$$

Acidic Solution

$$Cr_2O_7^{2-} \rightleftharpoons 2Cr^{3+}$$
$$Cr_2O_7^{2-} \rightleftharpoons 2Cr^{3+} + 7H_2O$$
$$14H^+ + Cr_2O_7^{2-} \rightleftharpoons 2Cr^{3+} + 7H_2O$$
$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightleftharpoons 2Cr^{3+} + 7H_2O$$

$$-6 + 14 - 2 = 6$$

$$\boxed{H_2 \rightleftharpoons 2H^+ + 2e^-}$$

Basic Solution

$$Pb \rightleftharpoons HPbO_2^-$$
$$Pb + 2H_2O \rightleftharpoons HPbO_2^-$$
$$Pb + 2H_2O \rightleftharpoons HPbO_2^- + 3H^+ + 2e^{-1}$$

$$0 = -1 + 3 - 2$$

$$Pb + 2H_2O \rightleftharpoons HPbO_2^- + 3H^+ + 2e^{-1}$$
$$3H^+ + 3OH^- \rightleftharpoons 3H_2O$$
$$\overline{Pb + OH^- \rightleftharpoons 2e^- + H_2O + HPbO_2^-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$3(H_2O \rightleftharpoons H^+ + OH^-)$$
$$3H_2O \rightleftharpoons 3H^+ + 3OH^-$$

Convert to Basic w/ water equilibrium to cancel H^+.

$$NO_2^- \rightleftharpoons NO_3^-$$
$$+3 \qquad +5$$

$$\Delta ON = (+5) - (+3) = +2$$

Acidic Solution

$$H_2O + NO_2^- \rightleftharpoons NO_3^- + 2H^+ + 2e^-$$

$$-1 = -1 + 2 + 2$$

Oxidization (ON # Increases)

$$MnO_4^- \rightleftharpoons MnO_2$$
$$\mathbf{+7} \qquad \mathbf{+4}$$

$$\Delta ON = (+4) - (+7) = -3$$

Acidic Solution

$$e^- + 2H^+ + MnO_4^- \rightleftharpoons MnO_2 + H_2O$$

$$-1 + 2 - 1 = 0$$

Reduction (ON # Decreases)

C12 - 5.0 - Electrochemistry

$Os + IO_3^- \rightarrow OsO_4 + I_2$ Acidic Solution

$$Os \rightarrow OsO_4$$
$$5(4H_2O + Os \rightarrow OsO_4 + 8H^+ + 8e^-)$$
$$0 = 8 - 8$$

$$IO_3^- \rightarrow I_2$$
$$4(10e^- + 12H^+ + 2IO_3^- \rightarrow I_2 + 6H_2O)$$
$$-10 + 12 - 2 = 0$$

Multiply to eliminate electrons

$$20H_2O + 5Os \rightarrow 5OsO_4 + 40H^+ + 40e^-$$
$$40e^- + 48H^+ + 8IO_3^- \rightarrow 4\,I_2 + 24H_2O$$
$$8H^+ + 5O_2 \rightarrow 4H_2O + 5O_2O_4 + 4I_2$$

$MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2 + CO_2$ Basic Solution

$$MnO_4^- \rightarrow MnO_2$$
$$2(3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O)$$
$$-3 + 4 - 1 = 0$$

$$C_2O_4^{2-} \rightarrow CO_2$$
$$3(C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-)$$
$$-2 = -2$$

$$6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O$$
$$3C_2O_4^{2-} \rightarrow 6CO_2 + 6e^-$$

Convert Redox to Basic

$$3C_2O_4^{2-} + 2MnO_4^- + 8H^+ \rightarrow 2MnO_2 + 4H_2O + 6CO_2$$
$$8H_2O \rightarrow 8H^+ + 8OH^-$$
$$3C_2O_4^{2-} + 2MnO_4^- + 4H_2O \rightarrow 2MnO_2 + 6CO_2 + 8OH^-$$

Disproportionation - A redox reaction where the same species is both reduced and oxidized.

$$ClO_2^- \rightarrow ClO_3^- + Cl^-$$
$$3ClO_2^- \rightarrow 2ClO_3^- + Cl^-$$

No H^+ left to convert to basic solutions.

$$U^{4+} + MnO_4^- \rightarrow Mn^{2+} + UO_2^{2+}$$
$$\Delta ON = -5$$
$$\Delta ON = +2$$

Acidic Solution

$$2(MnO_4^- \rightarrow Mn^{2+})$$
$$5(U^{4+} \rightarrow UO_2^{2+})$$
$$\boxed{\Delta ON = 0}$$

$$5U^{4+} + 2MnO_4^- \rightarrow 2Mn^{2+} + 5UO_2^{2+}$$
$$\Delta ON = -10$$
$$\Delta ON = +10$$

$$5U^{4+} + 2MnO_4^- + 2H_2O \rightarrow 2Mn^{2+} + 5UO_2^{2+} + 4H^+$$
$$+20 - 2 = 4 + 10 + 4$$

$$Zn + As_2O_3 \rightarrow 2AsH_3 + Zn^{2+}$$
$$\Delta ON = -12$$
$$\Delta ON = +2$$

Basic Solution

$$1(As_2O_3 \rightarrow 2AsH_3)$$
$$6(Zn \rightarrow Zn^{2+})$$
$$\boxed{\Delta ON = 0}$$

$$6Zn + As_2O_3 \rightarrow 2AsH_3 + 6Zn^{2+}$$
$$\Delta ON = -12$$
$$\Delta ON = +12$$

To balance charge*
To balance H & O

$$6Zn + As_2O_3 \rightarrow 2AsH_3 + 6Zn^{2+} + 12OH^-$$
$$9H_2O + 6Zn + As_2O_3 \rightarrow 2AsH_3 + 6Zn^{2+} + 12OH^-$$

$$P_4 + P_4 \rightarrow 4H_2PO_2^- + 4PH_3$$
$$\Delta ON = +4$$
$$\Delta ON = -12$$

Acidic Solution

$$3(P_4 \rightarrow 4H_2PO_2^-)$$
$$1(P_4 \rightarrow 4PH_3)$$
$$\boxed{\Delta ON = 0}$$

$$P_4 + 3P_4 \rightarrow 12PO_2^- + 4PH_3$$
$$\Delta ON = +4$$
$$\Delta ON = -12$$

Combine/Divide Balance

$$4P_4 \rightarrow 12PO_2^- + 4PH_3$$
$$6H_2O + P_4 \rightarrow 3PO_2^- + PH_3 + 3H^+$$
$$0 = -3 + 3$$

C12 - 5.0 - Redox Titrations Electrochemistry

Oxidizing Agents - $KMnO_4$ is a very useful oxidizing agent. K^+ is a spectator.

25 mL solution with unknown $[Fe^{2+}]$ is titrated to an endpoint with acidic $KMnO_4$, requires 17.52 mL of acidified 0.1000 M $KMnO_4$. Find $[Fe^{2+}]$.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O\ ; E^o = 1.51\ V$$

$$\begin{array}{c} 5(Fe^{2+} \rightarrow Fe^{3+} + e^-) \\ \underline{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O} \end{array}$$

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

MnO_4^- is purple in solution and Mn^{2+} is colourless.

$$moles\ KMnO_4^- = 0.1000\frac{mmol}{mL} \times 17.52\ L = 1.752\ mmol$$

$$moles\ Fe^+ = 1.752\ mmol\ KMnO_4^- \times \frac{5\ mmolFe^{2+}}{1\ mmolMnO_4^-} = 8.760\ mmol \qquad [Fe^{2+}] = \frac{8.760\ mmol}{25\ mL} = 0.3504\ M$$

Reducing Agents - NaI or KI are common reducing agents.

25 mL of bleach is reacted with excess KI. The I_2 produced requires exactly 46.84 mL 0.7500 M $Na_2S_2O_3$ to endpoint. Using Starch as an indicator find bleach $[OCl^-]$.

$$2H^+ + OCl^- + 2I^- \rightarrow Cl^- + H_2O + I_2$$

I^- is involved in reducing Laundry Bleach $NaOCl$.

$$\begin{array}{c} 2I^- \rightarrow I_2 + 2e^- \\ \underline{2e^- + 2H^+ + OCl^- \rightarrow Cl^{-1} + H_2O} \\ OCl^- + 2H^+ + 2I^- \rightarrow I_2 + Cl^- + H_2O \end{array}$$

I^- is in deliberate excess
$\#\ mol\ OCl^- = \#\ mol\ I_2$ produced.

$$\begin{array}{c} I_2 + 2e^- \rightarrow 2I^- \\ \underline{2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-} \\ 2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4\,O_6 \end{array}$$

I_2 is reduced back to I^-, by a second reducing agent such as $S_20_3^{2-}$ (NaS_2O_3)

When addition of $S_2O_3^{2-}$, reacted most of the I_2, the brown colour of the I_2 almost disappears and a pale yellow remains. Starch is added producing blue colour reacting with I_2. $S_2O_3^{2-}$ is added causing blue to fade. (Last of colour disappears at equivalence point.

$$moles\ S_2O_3^{2-} = 0.7500\frac{mmol}{mL} \times 46.84\ mL = 35.13\ mmol$$

$$moles\ I_2 = 35.13\ mmol\ S_2O_3^{2-} \times \frac{1\ mmol\ I_2}{2\ mmol\ S_2O_3^{2-}} = 17.57\ mmol$$

$$moles\ OCl^- = 17.57\ mmol\ I_2 \times \frac{1\ mmol\ OCl^-}{1\ mmol\ I_2} = 17.57\ mol \qquad [OCl^-] = \frac{17.57mmol}{25mL} = 0.7026\ M$$

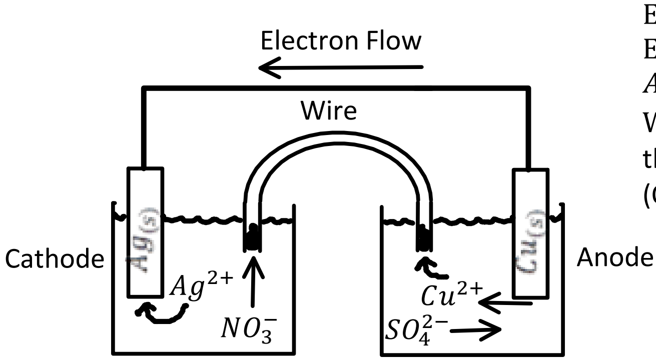
C12 - 5.0 - Electrochemical Cell Electrochemistry

Electrode - A conductor at which a half-reaction occurs.

Anode - (Electrode)
- Which Oxidization occurs.
- Receiving Electrons from substance being Oxidized
- Toward which Anions travel

Cathode - (Electrode)
- Which Reduction occurs.
- Receiving Electrons from substance being Reduced
- Toward which Cations travel

$A_g \rightleftharpoons Ag^+ + e^-$
$Cu \rightleftharpoons Cu^{2+} + 2e^-$ Half-Reactions



Cu has a greater tendency to oxidize than Ag.
Causing an excess of electrons on the Cu Anode.
Electrons flow from Cu to Ag Electrode (via the wire.)
Equilibrium is upset (Le Chatelier's Principle) &
Ag^+ $ions$ are forced to reduce at the Ag Cathode to $Ag_{(s)}$.
Water & certain ions (Cu^{2+} & NO_3^- in above) pass through the salt-bridge but total mixing is prevented.
(Only ions flow in the solution)

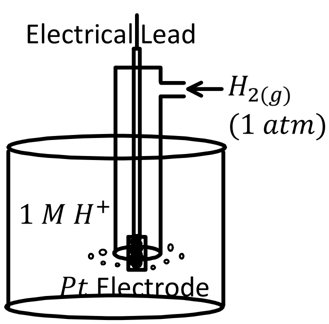
$$A_g \rightleftharpoons Ag^+ + e^-$$
$$Ag^+ + e^- \rightarrow Ag$$

Voltage - Tendency for electrons the flow. $\frac{Work}{e^-\ transferred}$ (Electric Potential). Difference of Half-Cell Voltages*.

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$; $E^o = 0.000\ V$

E^o − Standard Reduction Potential (Volts, V) in Standard State (o).

- 25^oC
- Gases are at 101.3 kPa (1 atm)
- Elements are in Standard States (Normal Phase)
- 1 M concentration for all solutions in half-cell reactions



$H_{2(g)}$ passes over a platinum (Inert) metal electrode which accepts or supplies electrons to the half-cell as required.

C12 - 5.0 - Electrochemical Cell Electrochemistry

Copper metal in 1 $M\ Cu^{2+}$ solution.

$Cu^{2+} + 2e^- \rightleftharpoons Cu \;;\; E^o = 0.34\,V$

$Zn^{2+} + 2e^- \rightleftharpoons Zn \;;\; E^o = -0.76\,V$

$Zn \rightleftharpoons Zn^{2+} + 2e^- \;;\; E^o = +0.76\,V$

Reversing a reduction reaction produces an oxidation reaction.

Sign of E^o is reversed.

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

$\boxed{Ni^{2+}} + 2e^- \rightleftharpoons Ni \;;\; E^o = -0.26\,V$

$Fe^{2+} + 2e^- \rightleftharpoons \boxed{Fe} \;;\; E^o = -0.45\,V$

$$\begin{array}{lll} Ni^{2+} + 2e^- \rightleftharpoons Ni & ; & E^o = -0.26\,V \\ Fe \rightleftharpoons Fe^{2+} + 2e^- & ; & E^o = +0.45\,V \\ \hline Ni^{2+} + Fe \rightarrow Ni + Fe^{2+} & ; & E^o_{CELL} = 0.19\,V \end{array}$$

Spontaneous $E^o > 0$

$$-0.26 - (-0.45) = 0.19\,V$$
$$E^o_{CELL} = E^o_{REDUCTION} - E^o_{OXIDIZATION}$$
$$-0.45 - (-0.26) = -0.19\,V$$

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

$\boxed{Fe^{2+}} + 2e^- \rightleftharpoons Fe \;;\; E^o = -0.45\,V$

$Ni^{2+} + 2e^- \rightleftharpoons \boxed{Ni} \;;\; E^o = -0.26\,V$

$$\begin{array}{lll} Fe^{2+} + 2e^- \rightleftharpoons Fe & ; & E^o = -0.45\,V \\ Ni \rightleftharpoons Ni^{2+} + 2e^- & ; & E^o = +0.26\,V \\ \hline Fe^{2+} + Ni \rightarrow Fe + Ni^{2+} & ; & E^o_{CELL} = -0.19\,V \end{array}$$

Not Spontaneous $E^o < 0$

Lead - Acid Storage Battery (Common in Automobiles) consists of altering pairs of "plates" made of $Pb_{(s)}$ & $PbSO_{2(s)}$, immersed in dilute H_2SO_4 (Sulphuric/Battery Acid).

Anode Reaction (Simply)

$$Pb_{(s)} + HSO_4^- \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^-$$
$$Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$$

Cathode Reaction (Simply)

$$PbO_{2(s)} + HSO^-_{4(aq)} + +3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$
$$Pb^{+4} + 2e^- \rightarrow Pb^{2+}$$

Overall Reaction (Or)

$$Pb_{(s)} + PbO_{2(s)} + 2H^+_{(aq)} + 2HSO^-_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$
$$Pb + Pb^{4+} \rightarrow Pb^{2+} + Pb^{2+}$$

As battery Discharges, spontaneously reacting to produce electrical energy, insoluble $PbSO_{4(s)}$ forms a layer around the plates.

Batteries
Lead-Acid
Zinc-Carbon
Alkaline Dry-Cell
Fuel Cell