Chemistry 12

Electrochemistry V

Name: Notes
Date:
Block:

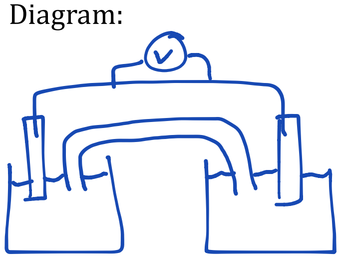
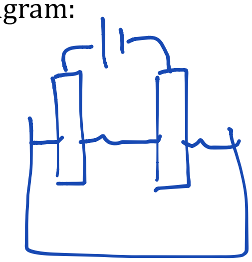
1. **Electrolysis**
2. **Electrolytic Cell**

Electrolysis

Electrolysis: the transformation of electrical energy into chemical energy.

- Used mainly in industry to separate a compound into its elements.
- The electrodes used are often inert (non-reactive) materials – just involved in electron transfer

allows e- flow

Electrochemical Cell	Electrolytic Cell
• Makes electricity. • Transforms chemical energy into electrical energy.	• Takes electricity. • Transforms electrical energy into chemical energy.
• Is a voltage source.	• Requires a voltage source.
• 2 half cells.	• 1 cell.
• Spontaneous redox reaction. • E° is positive.	• Nonspont redox reaction. • E° is negative.
• Needs salt bridge	• No salt bridge.
• Diagram: 	• Diagram: 
• Oxidation half reaction is below the reduction half reaction in the SRP table.	• Oxidation half reaction is above the reduction half reaction in the SRP table.
• Will use the strongest OA and the strongest RA.	• Will use the strongest OA and the strongest RA.
• Electrons travel from the anode to the cathode.	• Electrons travel from the anode to the cathode.

What Am I?

flipped
+0.26V
-0.45V

EC 1. I have 2 half cells.

EL 2. My oxidation half-reaction is: Ni → Ni^{2+} + 2 e- and my reduction half reaction is Fe^{2+} + 2 e- → Fe

Both 3. Oxidation occurs at my anode.

EC 4. I transform chemical energy into electricity

Both 5. In order to flow, the electrical charge requires a complete path or circuit.

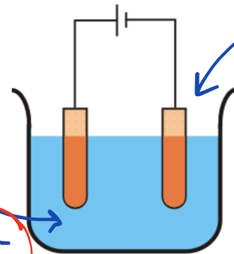
EL 6. You can use the SRP table to calculate how much voltage is "takes" to operate me.

EC 7. My E° is +0.94V.

Electrolytic Cells

(When deciding OA/RA)

THINGS TO CONSIDER:



Liquid Content:

Molten
"melted"

Ex. $NaCl \rightarrow Na^+ + Cl^-$
(no water)

Aqueous
"dissolved in water"

Ex. $NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$
- must consider H_2O as OA or RA

Electrodes:

Inert
"non-reactive"

Ex. Carbon or Platinum

Non-inert
"reactive"

Ex. Any metal
- must consider as OA / RA

Overpotential Effect of WATER:

H_2O exhibits a higher potential than its true position on the table and therefore needs to be re-positioned.

Oxidizing Agents		Reducing Agents	E° (Volts)
$ClO_4^- + 8H^+ + 8e^-$	⇄	$Cl^- + 4H_2O$	+1.39
$Cl_{2(g)} + 2e^-$	⇄	$2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	⇄	$2Cr^{3+} + 7H_2O$	+1.23
$\frac{1}{2}O_{2(g)} + 2H^+ + 2e^-$	⇄	H_2O	+1.23
$MnO_{2(s)} + 4H^+ + 2e^-$	⇄	$Mn^{2+} + 2H_2O$	+1.22
$IO_3^- + 6H^+ + 5e^-$	⇄	$\frac{1}{2}I_{2(s)} + 3H_2O$	+1.20
$Br_{2(\ell)} + 2e^-$	⇄	$2Br^-$	+1.09
$AuCl_4^- + 3e^-$	⇄	$Au_{(s)} + 4Cl^-$	+1.00
$NO_3^- + 4H^+ + 3e^-$	⇄	$NO_{(g)} + 2H_2O$	+0.96
$Hg^{2+} + 2e^-$	⇄	$Hg_{(\ell)}$	+0.85
$\frac{1}{2}O_{2(g)} + 2H^+(10^{-7} M) + 2e^-$	⇄	H_2O	+0.82
$2NO_3^- + 4H^+ + 2e^-$	⇄	$N_2O_4 + 2H_2O$	+0.80
$Ag^+ + e^-$	⇄	$Ag_{(s)}$	+0.80

Overpotential Effect

H_2O as a REDUCING Agent

Half Reaction: (acidic)

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

E°= -0.82V

$Cr^{3+} + e^-$	⇄	Cr^{2+}	−0.41
$2H_2O + 2e^-$	⇄	$H_2 + 2OH^-(10^{-7} M)$	−0.41
$Fe^{2+} + 2e^-$	⇄	$Fe_{(s)}$	−0.45
$Ag_2S_{(s)} + 2e^-$	⇄	$2Ag_{(s)} + S^{2-}$	−0.69
$Cr^{3+} + 3e^-$	⇄	$Cr_{(s)}$	−0.74
$Zn^{2+} + 2e^-$	⇄	$Zn_{(s)}$	−0.76
$Te_{(s)} + 2H^+ + 2e^-$	⇄	H_2Te	−0.79
$2H_2O + 2e^-$	⇄	$H_{2(g)} + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	⇄	$Mn_{(s)}$	−1.19

Overpotential Effect

H_2O as an OXIDIZING Agent

Half Reaction: (basic)

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

E°= -0.41V

* water is weaker than how it appears

($\ominus$ voltage) (inert) (no water)

Example 1: Identify the half-reactions occurring in an electrolytic cell with carbon electrodes in molten MgI_2 and predict the voltage required to operate this cell.

- Identify the oxidizing agent and the reducing agent.

Mg^{2+} + $2I^-$

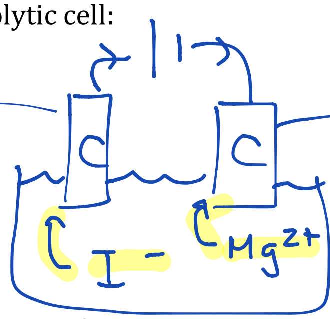
OA	RA
Mg^{2+}	I^-

- Write the two half-reactions and calculate the voltage required.

$$2I^- \rightarrow I_2 + 2e^- \quad -0.54V$$
$$Mg^{2+} + 2e^- \rightarrow Mg \quad -2.37V$$
$$-2.91V$$

- Draw the electrolytic cell:

anode (oxidation) $2I^- \rightarrow I_2 + 2e^-$



cathode (reduction) $Mg^{2+} + 2e^- \rightarrow Mg$

$E°_{total} = -2.91V$

*separating compound!

Example 2: Identify the half-reactions that occur in the electrolysis of an aqueous solution of manganese (II) bromide with platinum electrodes and predict the voltage required to operate this cell.

- Identify the oxidizing agent and the reducing agent.

$$MnBr_{2(aq)} \rightarrow Mn^{2+}_{(aq)} + 2Br^-_{(aq)} \quad (+H_2O)$$

Pt = inert

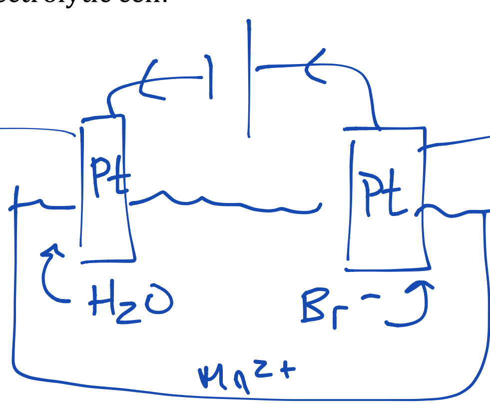
OA	RA
H_2O, Mn^{2+}	H_2O, Br^-

- Write the two half-reactions and calculate the voltage required.

$$2Br^- \rightarrow Br_2 + 2e^- \quad E° = -1.09V$$
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E° = -0.41V$$
$$-1.50V$$

- Draw the electrolytic cell:

Cathode (reduction) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$



anode (oxidation) $2Br^- \rightarrow Br_2 + 2e^-$

(Mn^{2+} spectator)

Example 3: Identify the half-reactions that occur in an electrolytic cell consisting of copper electrodes in an aqueous solution of $CrBr_3$ and predict the voltage required to operate this cell.

Cr^{3+} &

- Identify the oxidizing agent and the reducing agent.

(Note: Cu appear twice - choose stronger RA)

OA: H_2O, Cr^{3+}

RA: H_2O, Cu, Br^-

- Write the two half-reactions and calculate the voltage required.

×2 $(2Cr^{3+} + \cancel{2e^-} \rightarrow 2Cr^{2+})$ $E° = -0.41\ V$

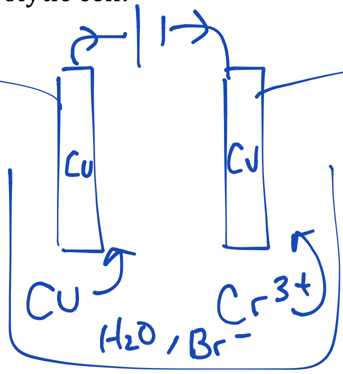
$Cu \rightarrow Cu^{2+} + \cancel{2e^-}$ $E° = -0.34\ V$

$2Cr^{3+} + Cu \rightarrow 2Cr^{2+} + Cu^{2+}$ $E°_{total} = -0.75\ V$

- Draw the electrolytic cell:

anode (oxidation)

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



cathode (reduction)

$Cr^{3+} + e^- \rightarrow Cr^{2+}$

$E°_{total} = -0.75\ V$

(No W/S) is practice

Practice:

For the following, draw the electrolytic cell and the half-reactions occurring within it and the voltage required to operate the cell.

1. Platinum electrodes in $CaSO_{4(aq)}$

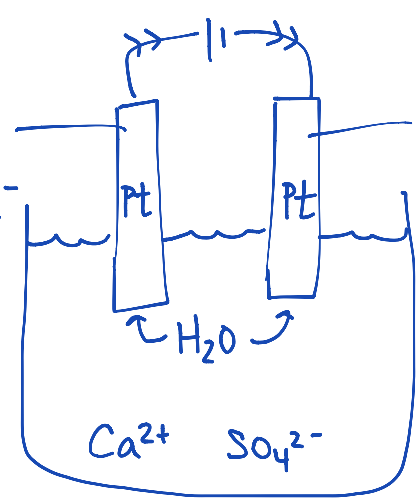
inert

OA: H_2O, Ca^{2+}

RA: H_2O, SO_4^{2-}

anode

$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$



cathode

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

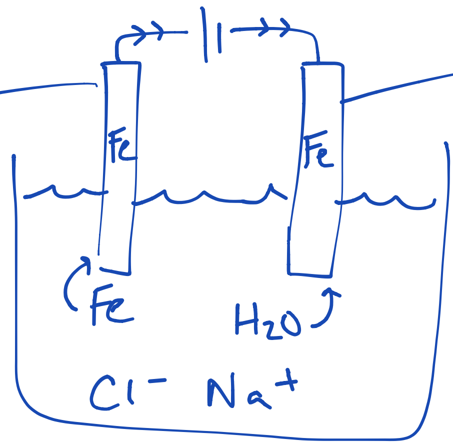
$E°_{total} = (-0.41V) + (-0.82V) = -1.23V$

2. Iron electrodes in NaCl $_{(aq)}$

non-inert

OA: H_2O, Na^+

RA: H_2O, Fe, Cl^-



anode

$Fe \rightarrow Fe^{2+} + 2e^-$

cathode

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$E°_{total} = (-0.41V) + 0.45V$
$= +0.04V$

*note: ⊕ voltage due to H_2O's overpotential effect

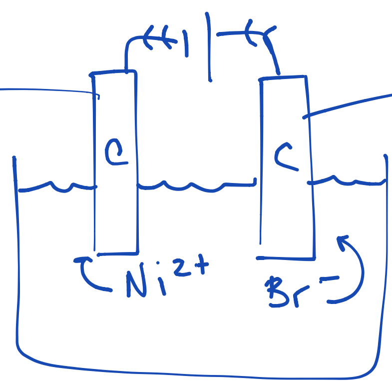
3. Carbon electrodes in molten $NiBr_2$

inert

no H_2O

OA: Ni^{2+}

RA: Br^-



cathode

$Ni^{2+} + 2e^- \rightarrow Ni$

anode

$2Br^- \rightarrow Br_2 + 2e^-$

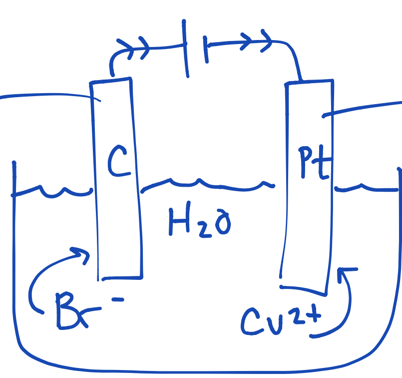
$E°_{total} = (-0.26V) + (-1.09V)$
$= -1.35V$

4. Inert electrodes in $CuBr_2$ $_{(aq)}$

C or Pt

OA: H_2O, Cu^{2+}

RA: H_2O, Br^-



anode

$2Br^- \rightarrow Br_2 + 2e^-$

cathode

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

$E°_{total} = (+0.34V) + (-1.09V)$
$= -0.75V$

Hebden Workbook: Pg. 242 #65-68