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CONCEPT: ELECTROLYSIS

Electrolysis deals with passing an electrical current through a substance in order to produce chemical changes.

- The use of outside energy is indicative of a non-spontaneous reaction.

The passing of an electrical current through water helps to generate its standard components:

$$2\,H_2O\,(l) \rightarrow O_2\,(g) + 2\,H_2\,(g)$$

Electrical Current

The units for electrical current are in __________ (A):

moles of electrons

The moles of electrons within a reaction are determined by:

Ohm's Law

The Ohmic potential, E, is the voltage necessary to overcome resistance, R, when the current, I, is flowing:

Overpotential is the voltage required to overcome the activation energy for a reaction at a given electrode.

Concentration polarization occurs when there is a difference in the concentrations of reactants and products on the surface of electrodes when compared to the solution.

Electrolysis is made more difficult by *ohmic potential, overpotential* and *concentration polarization*.

$$E_{Cell} = E_{Cathode} - E_{Anode} - E_{Ohmic} - \text{Overpotentials}$$

PRACTICE: ELECTROLYSIS CALCULATIONS 1

EXAMPLE 1: Aluminum can be electroplated at the cathode of an electrolysis cell by the half-reaction:

$$Al^{3+}\ (aq) + 3\ e^- \rightarrow Al\ (s)$$

How much time would it take for 825 mg of aluminum to be plated at a current of 4.1 A?

EXAMPLE 2: In the electrolysis of molecular iodine to iodide ions for 0.15 M NaI solution containing 4.2 x 10^{-4} M I_2 at a pH = 6.00 with P_{O_2} = 1.25 bar, calculate the voltage needed to drive the reaction.

$$O_2\ (g) + 4\ H^+\ (aq) + 4\ e^- \rightarrow 2\ H_2O\ (l) \qquad E^o_+ = -0.41\ V$$

$$I_2\ (aq) + 2\ e^- \rightarrow 2\ I^-\ (aq) \qquad E^o_- = 0.54\ V$$

PRACTICE: During electrolysis the concentration of I_2 increases to 8.3 x 10^{-3} M, while all other concentrations remain unchanged. If the electrical resistance is 1.8 ohms, the current is 71 mA, the anode overpotential is 0.013 V and the cathode overpotential is 0.115 V, what is the voltage needed?

CONCEPT: ELECTRICAL CURRENT

EXAMPLE 1: Gold can be plated out of a solution containing Au^{3+} based on the following half reaction:

$$Au^{3+} (aq) + 3\, e^{-} \longrightarrow Au\ (s)$$

a) What mass of gold is plated by a 41 minute flow of 6.8 A current?

EXAMPLE 2: A solution of Mn^{+5} is used to plate out Mn in an electrochemical cell. If a total of 1.13 g of Mn is plated out in a total time of 1600 seconds, what was the electrical current used? (**MW of Mn is 54.94 g/mol**)

PRACTICE: ELECTRIC CURRENT (CALCULATIONS 1)

EXAMPLE: If steady current of 15 amperes is provided by a stable voltage of 12 Volts for 600 seconds, answer each of the following questions.

a) Calculate the **total charge** that passes through the circuit in this time.

b) Calculate the **total number of moles of electrons** that pass through the circuit in this time.

c) Calculate the **total amount of energy** that passes through the circuit in this time.

d) Calculate the **power** that the battery provides during this process.

CONCEPT: GRAVIMETRIC ANALYSIS

In *gravimetric analysis* the mass of a product in a chemical reaction is used to calculate the amount of the original analyte.

EXAMPLE: A 25.00 mL solution containing Br^- was treated with excess $PbSO_4$ to precipitate 0.7550 g of $PbBr_2$. What was the molarity of the Br^- in the unknown?

$$PbSO_4\,(s) + 2\,Br^-\,(aq) \longrightarrow PbBr_2\,(s) + SO_4^{2-}\,(aq)$$

PRACTICE: The Fe in a 1.1530 g sample of iron ore is precipitated as $Fe_2O_3 \bullet x\,H_2O$ by the addition of NH_3. The residue is ignited at high temperatures to give 0.6310 g of pure Fe_2O_3. Calculate the weight percent of Fe in the ore.

$$2\,Fe^{3+}\,(aq) + 6\,OH^-\,(aq) \longrightarrow Fe_2O_3 \bullet x\,H_2O$$

$$Fe_2O_3 \bullet x\,H_2O + \text{heat} \longrightarrow Fe_2O_3 + 6\,x\,H_2O$$

CONCEPT: TITRATION CALCULATIONS 1

EXAMPLE 1: Magnesium reacts with HCl according to the reaction below. How many grams of 5.310% by weight of aqueous magnesium are required to provide a 25% excess to react with 75.0 mL of 0.0550 M HCl.

$$Mg\,(s) + 2\,HCl\,(aq) \longrightarrow MgCl_2\,(aq) + H_2\,(g)$$

EXAMPLE 2: The amount of iron within an ore sample was determined by an oxidation-reduction titration using potassium permanganate, $KMnO_4$, as the titrant. A 0.5600 g sample of the ore was placed into acid and the newly freed Fe^{3+} was then reduced to Fe^{2+}. The titration of this solution required 39.82 mL of 0.0315 M $KMnO_4$ to reach the end-point. Determine the mass percent of Fe_2O_3 in the sample.

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

CONCEPT: TITRATION CALCULATIONS 2

EXAMPLE 1: A 0.4317 g sample of $CaCO_3$ (MW: 100.09 g/mol) is added to flask that also contained 12.50 mL of 1.530 M HBr.

$$CaCO_3\ (aq) + 2\ HBr\ (aq) \longrightarrow CaBr_2\ (aq) + H_2O\ (l) + CO_2\ (g)$$

Additional water is then added to create a 250.0 mL of Solution A. Next 20.00 mL aliquot of solution A is taken and titrated with 0.0980 M NaOH. How many milliliters of NaOH were used?

$$NaOH\ (aq) + HBr\ (aq) \longrightarrow H_2O\ (l) + NaBr\ (aq)$$

EXAMPLE 2: A 9.2476 g sample of $M(OH)_2$ was mixed with 15.00 mL of 1.530 M HI and diluted to a final 125.0 mL of solution.

$$M(OH)_2\ (aq) + 2\ HI\ (aq) \longrightarrow 2\ H_2O\ (l) + MCl_2\ (aq)$$

A 12.00 mL aliquot of this diluted solution was taken and titrated with 18.23 mL of 0.0695 M NaOH.

$$NaOH\ (aq) + HI\ (aq) \longrightarrow H_2O\ (l) + NaCl\ (aq)$$

What is the identity of the metal representing M?

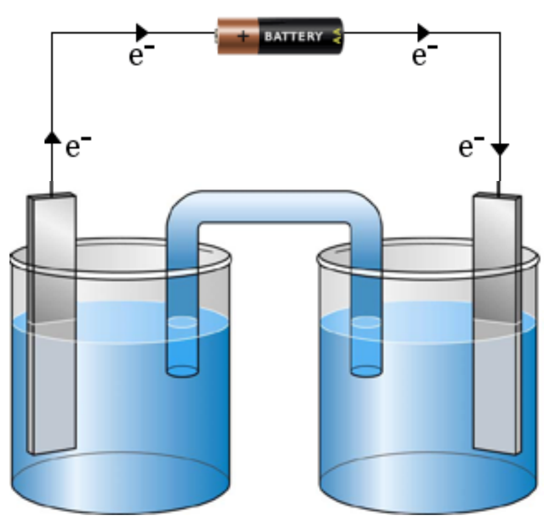
CONCEPT: ELECTROLYTIC CELLS

In terms of spontaneity the following correlations between the following variables can be made:

ΔG°	K	E°	ΔS°	Q vs. K	Reaction Classification	Cell Type
< 0	> 1	> 0	> 0	Q < K		
> 0	< 1	< 0	< 0	Q > K		
= 0	= 1	= 0	= 0	Q = K		

Electrolytic Cell: A non-spontaneous electrochemical cell that _______________ electricity and so requires a battery.

Electron Affinity ___________



Ionization Energy __________

______________ (–)

______________ (+)

Electrolytic Cell

CONCEPT: GALVANIC CELLS

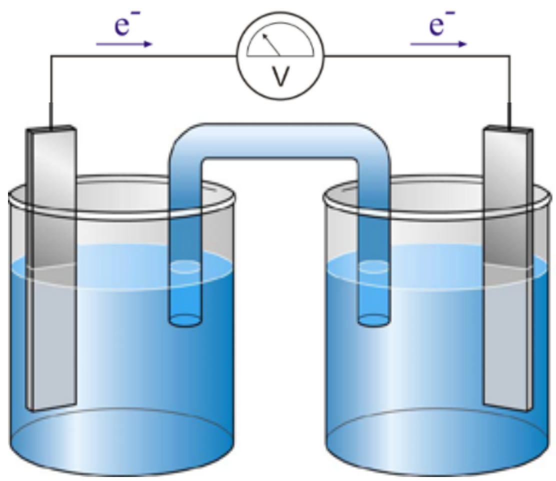
Galvanic/Voltaic Cell: A spontaneous cell that ______________ or ______________ electricity.

Ionization Energy __________

Electron Affinity __________

Anode ______________

Cathode ______________



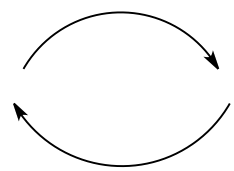
Producing ⇧ Voltage

[Anode] ________

[Cathode] ________

______________ (–)

______________ (+)



Galvanic/Voltaic Cell

$$\text{Cathode: } 3\,Cu^{2+}(aq) + \cancel{6\,e^-} \rightleftharpoons 3\,Cu\,(s)$$

$$\text{Anode: } 2\,Cr\,(s) \rightleftharpoons 2\,Cr^{3+}(aq) + \cancel{6\,e^-}$$

Reduction Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-$	2.890
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$	2.075
⋮	
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.507
⋮	
$Ag^+ + e^- \rightleftharpoons Ag(s)$	0.799
⋮	
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	0.339
⋮	
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
⋮	
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.402
⋮	
$K^+ + e^- \rightleftharpoons K(s)$	−2.936
$Li^+ + e^- \rightleftharpoons Li(s)$	−3.040