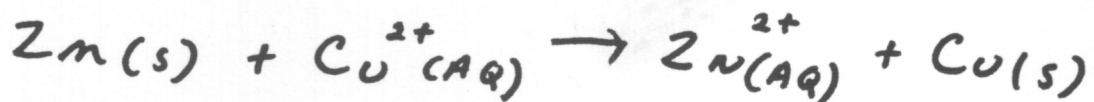


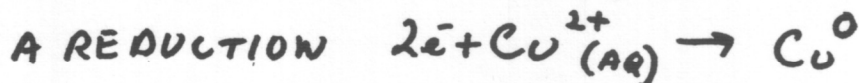
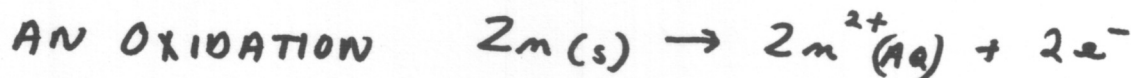
CHAPTER 19 ELECTROCHEMISTRY

IN THIS CHAPTER WE WILL STUDY ELECTROCHEMICAL REACTIONS - REACTIONS WHERE ELECTRONS ARE TRANSFERRED FROM ONE CHEMICAL SPECIES TO ANOTHER. THESE ARE CALLED OXIDATION-REDUCTION REACTIONS OR REDOX REACTIONS. SOME OF THIS MATERIAL WAS COVERED IN CHAPTER 3, P 107-120 ITS IMPORTANT TO GET THE REDOX NOMENCLATURE CORRECT. FOR THE REACTION:

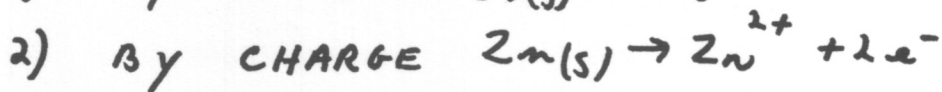


ELECTRONS ARE TRANSFERRED FROM ZINC TO COPPER WE SAY THAT ZINC HAS BEEN OXIDIZED (LOST e^-) AND COPPER HAS BEEN REDUCED TO THE METAL (GAINED e^-)

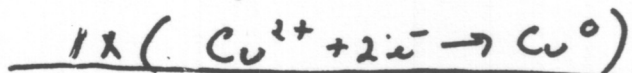
WE WRITE THE REACTION IN TWO HALF-REACTIONS:



TO BALANCE REDOX EQUATIONS, BALANCE HALF REACTIONS



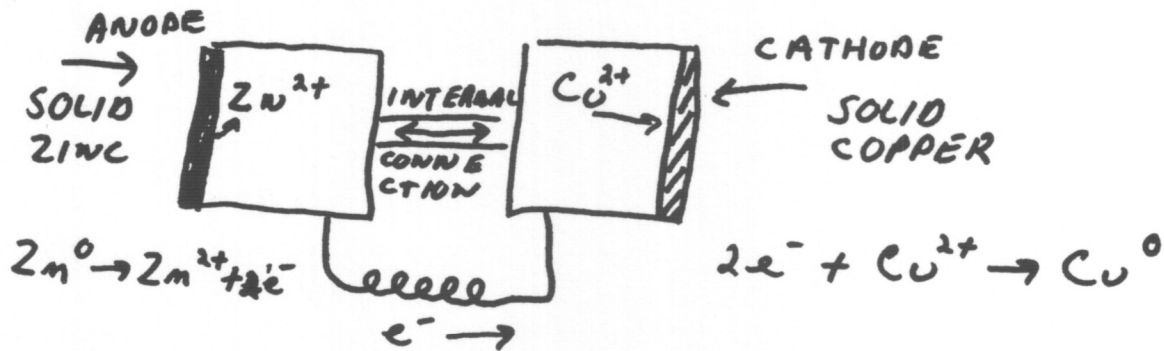
ADD BALANCED HALF REACTIONS, MULTIPLYING TO BALANCE e^-



SEE SECTION 3.6 TO REVIEW BALANCING

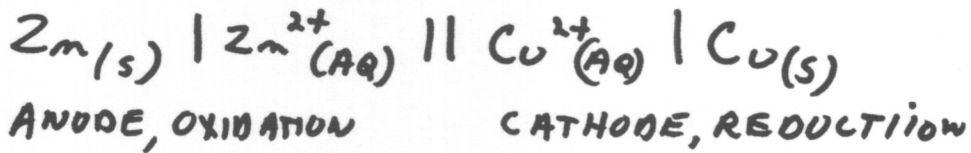
VOLTAIC CELLS

WE USE VOLTAIC CELLS EVERYWHERE. HERE IS HOW THEY WORK: TWO HALF-CELLS ARE CONNECTED

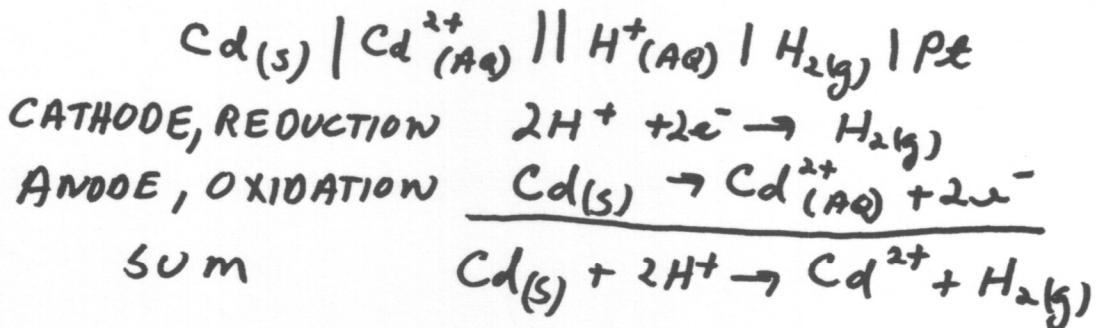


CONNECTED BY A WIRE THROUGH WHICH ELECTRONS FLOW AND CONNECTED INTERNALLY BY AN IONIC PATH CALLED A SALT BRIDGE. IN ORDER FOR USEFUL WORK TO BE DONE, THE HALF-CELL COMPONENTS MUST BE SEPARATED - DIRECT CONTACT OF Cu^{2+} AND Zn^0 WOULD BY PASS THE WIRE THE SALT BRIDGE CONTAINS ELECTROLYTE THAT ALLOWS THE FLOW OF IONS BUT KEEPS THE HALF-CELLS SEPARATE REDUCTION OCCURS AT THE CATHODE OXIDATION OCCURS AT THE ANODE

SHORTHAND FOR CELL LABELLING



GIVEN THE SHORTHAND NOTATION, WRITE THE CELL REACTION

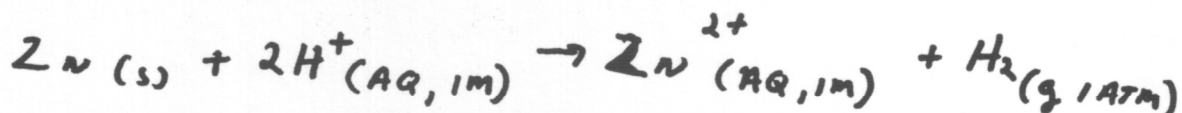


STANDARD VOLTAGES

CHEMISTS ARE INTERESTED IN VOLTIC CELLS BECAUSE A REDOX REACTION WHICH GENERATES ELECTRICAL ENERGY IN A VOLTIC CELL WILL TAKE PLACE SPONTANEOUSLY OUTSIDE THE CELL, IN A BEAKER, TEST TUBE OR ANYWHERE. TO STUDY SUCH REACTIONS WE MAKE USE OF THE PROPERTY OF A VOLTIC CELL KNOWN AS VOLTAGE. THE VOLTAGE IS A MEASURE OF THE "DRIVING FORCE" OR SPONTANEITY OF THE REACTION.

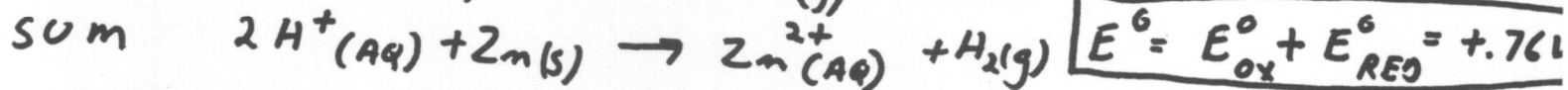
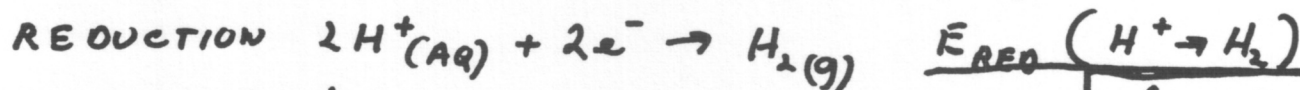
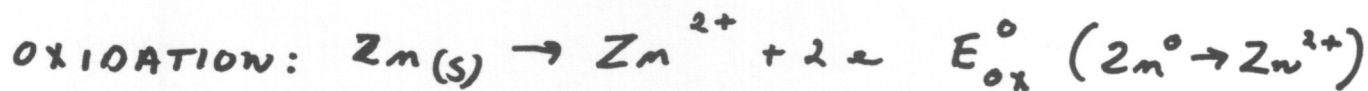
WE DEFINE A STANDARD VOLTAGE, E° FOR EACH GIVEN HALF CELL REACTION AS THAT VOLTAGE PRODUCED WHEN ALL CELL COMPONENTS ARE AT STANDARD CONDITIONS OF 1 M OR 1 ATM

FOR EXAMPLE



FOR THIS REACTION, THE STANDARD VOLTAGE, $E^{\circ} = +0.76\text{V}$

FOR THE HALF REACTIONS:



WHILE THE RELATIVE VOLTAGE FOR ANY CELL CAN BE MEASURED, WE CANNOT DETERMINE THE HALF-CELL POTENTIALS EXPERIMENTALLY

SO, ARBITRARILY, WE DEFINE THE STANDARD VOLTAGE FOR THE REDUCTION OF H^+ IONS TO H_2 GAS TO BE ZERO.

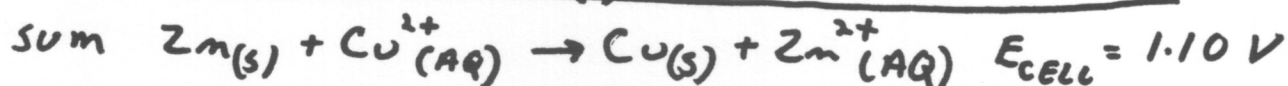
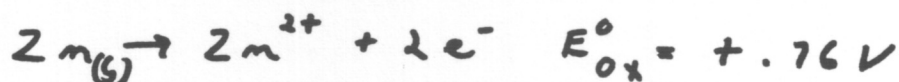
THEREFORE, E° FOR $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- = +0.76V$

ONCE ONE REFERENCE VOLTAGE IS ESTABLISHED, OTHERS CAN BE DETERMINED EXPERIMENTALLY

FOR EXAMPLE THE CELL:

$Zn|Zn^{2+}||Cu^{2+}|Cu$ PRODUCES 1.10 VOLT

IN THIS CELL ZINC IS BEING OXIDIZED AND Cu^{2+} REDUCED



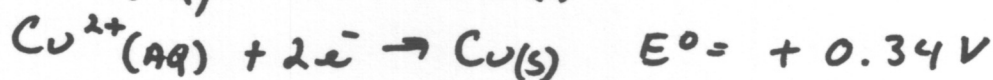
$$E^\circ_{ox} + E^\circ_{red} = E^\circ$$

$$0.76V + E_{red} = 1.10V$$

$$E^\circ_{red} = 1.10V - 0.76V = +0.34V$$

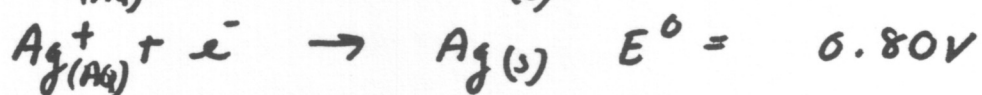
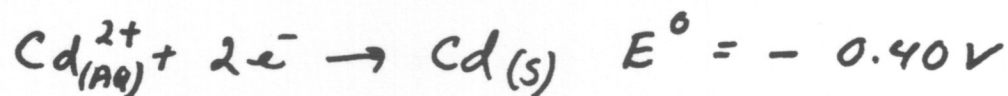
WE CAN NOW TABULATE THE RESULTS OF MANY SUCH MEASUREMENTS IN THE STANDARD POTENTIAL TABLE PG 799 THE POTENTIALS LISTED GIVE US DIRECTLY THE STANDARD VOLTAGES FOR REDUCTION HALF-REACTIONS.

NOTE: FOR OXIDATION HALF-REACTIONS, CHANGE THE SIGN OF THE STANDARD POTENTIAL

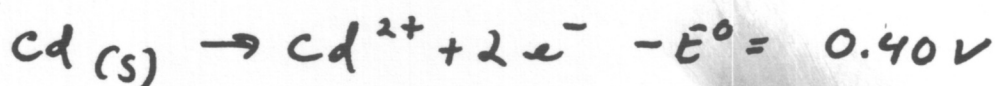


CALCULATING CELL VOLTAGES FROM STANDARD POTENTIALS
 OVERALL CELL VOLTAGES ARE EASILY CALCULATED FROM
 THE STANDARD POTENTIALS.

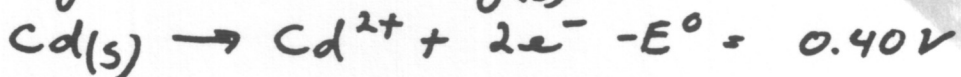
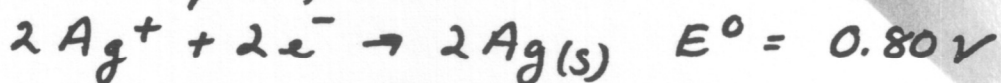
FOR EXAMPLE:



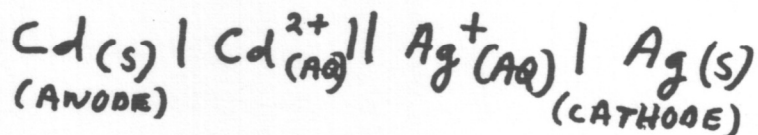
THE REACTION WITH THE POSITIVE E° IS SPONTANEOUS
 THE REACTION WITH THE LESS POSITIVE E° MUST BE REVERSED



TO BALANCE ELECTRONS, THE SILVER REACTION MUST BE
 MULTIPLIED BY 2, E° DOES NOT CHANGE



THE CELL NOTATION



NOTE THAT THE EMF (VOLTAGE) OF THE CELL EQUALS THE
 STANDARD POTENTIAL OF THE CATHODE (FROM TABLE) MINUS
 THE STANDARD POTENTIAL OF THE ANODE. (FROM TABLE, BUT
 THE MINUS SIGN IN THIS EQUATION MEANS THE REACTION IS
REVERSED FROM ITS APPEARANCE IN THE TABLE)

$$E^{\circ}_{\text{CELL}} = E^{\circ}_{\text{AG}} - E^{\circ}_{\text{CD}} = 0.80\text{V} - (-0.40\text{V}) = 1.20\text{V}$$

STRENGTHS OF OXIDIZING AND REDUCING AGENTS

FROM THE STANDARD POTENTIAL TABLE YOU CAN DECIDE WHICH SPECIES ARE THE BEST REDUCING AGENTS. THEY ARE AT THE TOP OF THE TABLE AND HAVE THE MOST

NEGATIVE E° SUCH AS $Li^+(aq) + e^- \rightarrow Li(s)$ $-3.04V$

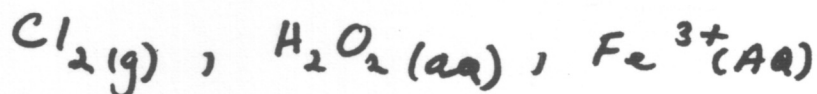
THE BEST OXIDIZING AGENTS ARE AT THE BOTTOM OF THE TABLE AND HAVE THE MOST

POSITIVE E° SUCH AS $F_2 + 2e^- \rightarrow 2F^-(aq)$ $E^{\circ} = +2.87V$

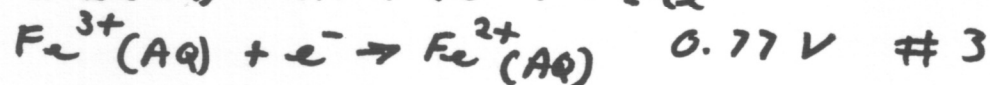
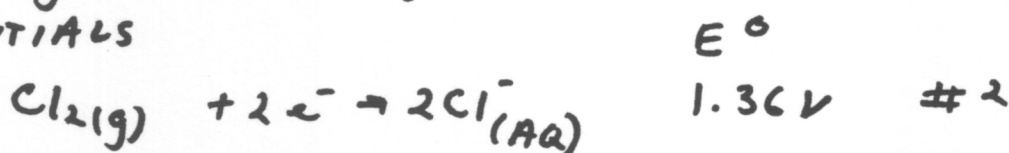
REMEMBER, THAT POSITIVE E° MEANS SPONTANEOUS

FOR EXAMPLE:

ARRANGE THE FOLLOWING IN ORDER OF INCREASING STRENGTH AS AN OXIDIZING AGENT

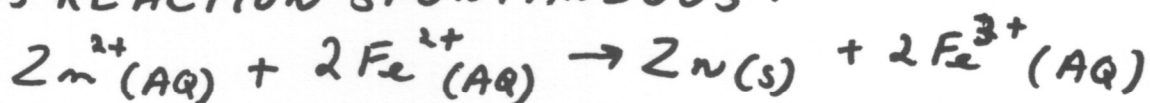


STANDARD POTENTIALS

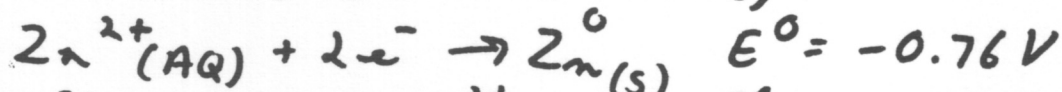


DETERMINING SPONTANEITY DIRECTION

IS THIS REACTION SPONTANEOUS?



WRITE THE HALF REACTIONS (AS REDUCTIONS)

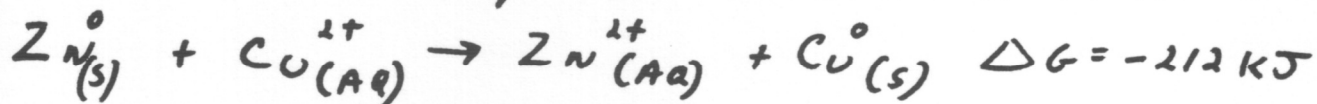


THE HALF-REACTION WITH THE MOST POSITIVE E° IS SPONTANEOUS. THE REACTION IN QUESTION IS NON SPONTANEOUS

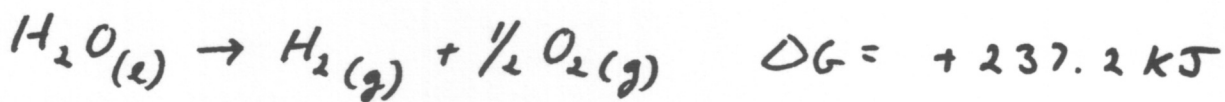
CALCULATING ΔG° FROM STANDARD POTENTIALS

EASILY THE MOST IMPORTANT RESULT OF ELECTROCHEMICAL STUDIES FOR CHEMISTS IS THE ABILITY TO MEASURE ΔG° FROM CELL VOLTAGES. THIS IS BASED ON A PRINCIPLE FIRST DEVELOPED BY GIBBS. HE SHOWED THAT ΔG IS A MEASURE OF THE "USEFUL WORK" THAT CAN BE OBTAINED FROM A REACTION. ELECTRICAL WORK IS USEFUL WORK WE DISTINGUISH BETWEEN TWO CASES:

- 1) A SPONTANEOUS REACTION TAKING PLACE IN A VOLTAGE CELL. ΔG IS NEGATIVE, NUMERICALLY EQUAL TO THE MAXIMUM AMOUNT OF ENERGY THAT CAN BE OBTAINED FROM THE CELL



- 2) A NONSPONTANEOUS REACTION TAKING PLACE IN AN ELECTROLYTIC CELL: ΔG IS POSITIVE. TO MAKE THE REACTION OCCUR, WE MUST SUPPLY AN AMOUNT OF ELECTRICAL ENERGY AT LEAST EQUAL TO ΔG . FOR EXAMPLE, THE ELECTROLYSIS OF WATER:



TO ELECTROLYZE ONE MOLE OF WATER WE MUST SUPPLY AT LEAST 237.2 kJ OF ELECTRICAL ENERGY.

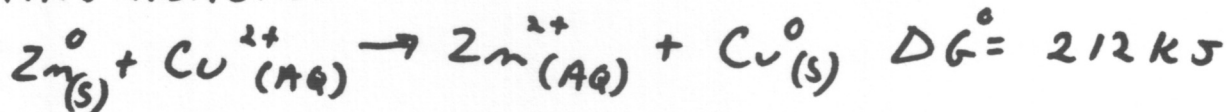
FROM THESE TWO CASES, WE CAN SEE THAT WE CAN OBTAIN THE VALUE OF ΔG FROM THE AMOUNT OF ELECTRICAL ENERGY PRODUCED OR EXPENDED IN A CELL. THE CELL VOLTAGE IS SIMPLY RELATED TO ΔG

$$\Delta G^\circ = -96.5 \text{ n } E^\circ \quad (\text{AT } 25^\circ\text{C})$$

(IN KJ) n = # OF ELECTRONS

NOTE THAT ΔG° AND E° HAVE OPPOSITE SIGNS
 SPONTANEOUS $\rightarrow \Delta G^\circ$ NEGATIVE, E° POSITIVE
 NONSPONTANEOUS $\rightarrow \Delta G^\circ$ POSITIVE, E° NEGATIVE

FOR THIS REACTION:



AND CELL VOLTAGE =

$$\text{Zn}^\circ \rightarrow \text{Zn}^{2+} \quad E^\circ = -(-0.76)$$

$$\text{Cu}^{2+} \rightarrow \text{Cu}^\circ \quad E^\circ = +0.34$$

$$1.10 \text{ V}$$

$$\Delta G^\circ = -96.5 \times 2 \times 1.10 \text{ V} = 212.3 \text{ KJ}$$

SINCE YOU CAN NOW CALCULATE ΔG° FROM E° , YOU
 CAN ALSO CALCULATE K_{eq} FROM E°

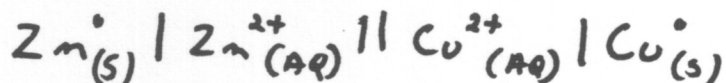
$$\text{IF } \Delta G^\circ = -5.71 \log K$$

$$\text{AND } \Delta G^\circ = -96.5 \text{ m } E^\circ$$

$$\text{THEN } E^\circ = \frac{-5.71}{-96.5 \text{ m}} \log K \text{ OR } E^\circ = \frac{0.059}{\text{m}} \log K$$

$$\text{OR, SOLVING FOR } K, \log K = \frac{-96.5 \text{ m } E^\circ}{-5.71} = 16.9 \text{ m } E^\circ = \log K$$

CALCULATING K FOR OUR COPPER-ZINC CELL



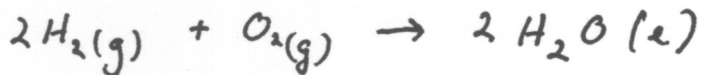
$$1.10 \text{ V} = \frac{0.059}{2} \log K$$

$$\log K = \frac{1.10}{\frac{0.059}{2}} \approx \frac{1.10 \times 2}{0.059} = 37.2$$

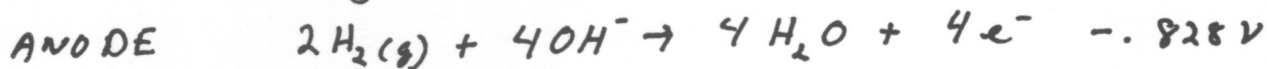
$$K = 10^{37.2} = 2 \times 10^{37}$$

EXAMPLE 2 CALCULATE E° , ΔG , K

FOR THIS REACTION:



HALF REACTIONS:



$$E^\circ = E^\circ_{\text{CAT}} - E^\circ_{\text{AN}} = .401 - (-.828) \rightarrow 1.229\text{V}$$

$$\Delta G^\circ = -96.5 \text{ m} E^\circ$$

$$= -96.5 (4) (1.229)$$

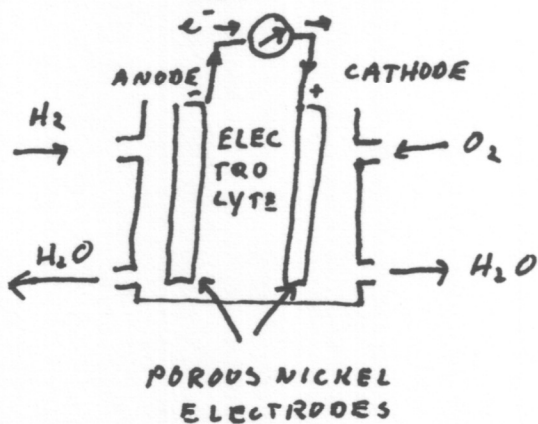
$$\Delta G^\circ = -474.4 \text{ KJ/MOLE O}_2 \quad 237.2 \text{ KJ/MOLE H}_2$$

$$E^\circ = \frac{0.059}{n} \log K$$

$$1.229 = \frac{.059}{4} \log K$$

$$\log K = \frac{1.229 \times 4}{.059} = 83.3 \quad \text{SO } K \approx 10^{83.3} \approx 2 \times 10^{83}$$

THIS IS THE REACTION EXPLOITED IN FUEL CELLS



ONE OF THESE
IS FAMOUS FOR
EXPLODING ON
APPOLO 13

PERHAPS THE CLEAN ENERGY
OF THE FUTURE

SINCE WE NOW HAVE SIMPLE RELATIONSHIPS BETWEEN ΔG° , E° AND K , WE CAN TAKE THE LAST STEP AND RELATE THE STANDARD POTENTIAL OF A CELL TO ITS ACTUAL POTENTIAL AT NONSTANDARD CONDITIONS -

(NEXT TIME YOUR CAR WON'T START BECAUSE THE BATTERY IS DEAD, YOU CAN BLAME THE NERNST EQUATION, WHICH IS AN EQUATION RELATING CELL VOLTAGE TO THE REACTION QUOTIENT Q)

AT NONSTANDARD CONDITIONS THE VOLTAGE OF A CELL EQUALS:

$$E_{\text{CELL}} = E_{\text{CELL}}^\circ - \frac{0.059}{n} \log Q$$

WHERE Q IS SOLVED FOR EXACTLY AS K , BUT NONSTANDARD CONCENTRATIONS.

THIS IS AN INTUITIVE CONCEPT - AT FIRST, WITH REACTANTS AND FREE ENERGY AT MAXIMUM LEVELS, THE CELL PRODUCES MAXIMUM VOLTAGE E° . AS THE REACTION PROGRESSES, REACTANTS DECREASE, ΔG DECREASES AND THE CELL VOLTAGE DECLINES. USEFUL WORK IS BEING DONE.

AT EQUILIBRIUM, THERE IS NO MORE NET REACTION, $\Delta G = 0$ AND NO VOLTAGE EXISTS. THE CELL IS DISCHARGED.

EXAMPLE OF A NERNST CALCULATION

WHAT IS THE VOLTAGE OF OUR COPPER-ZINC CELL ($E^\circ = 1.10\text{V}$)

IF THE $[Zn^{2+}] = 1.0 \times 10^{-5} \text{M}$ AND $[Cu^{2+}] = 0.100 \text{M}$?

EVALUATE Q $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$ $n = 2$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad (\text{SOLIDS DO NOT APPEAR IN } Q)$$

$$Q = \frac{1 \times 10^{-5}}{1 \times 10^{-1}} = 1.0 \times 10^{-4}$$

SUBSTITUTE THIS VALUE FOR Q INTO THE NERNST EQN.

$$E_{\text{CELL}} = E_{\text{CELL}}^{\circ} - \frac{0.059}{2} \log Q \quad Q = 1 \times 10^{-4}$$

$$\begin{aligned} E &= 1.10 - 0.03 \times -4 \\ &= 1.10 - (-0.12) = 1.22 \text{ V} \end{aligned}$$

IS THIS REASONABLE? SHOULD THERE BE A LARGER DRIVING FORCE FOR THIS REACTION THAN THE STANDARD ONE?

FROM THE ABOVE, YOU CAN SEE THAT IT IS POSSIBLE TO CONSTRUCT A CELL WHOSE VOLTAGE IS PROPORTIONAL TO THE CONCENTRATION OF ANY REACTANT. ALL YOU HAVE TO DO IS KEEP ALL BUT ONE REACTANT CONSTANT (BY KEEPING THEIR CONCENTRATION RELATIVELY LARGE) AND THEN THE CELL VOLTAGE DEPENDS ONLY ON THE CONCENTRATION OF ONE REACTANT.

THE MOST COMMON OF SUCH ELECTROCHEMICAL CELLS IS THE pH METER SEE PAGE 809-810 FOR A DESCRIPTION MANY OTHER CELLS ARE COMMERCIALY AVAILABLE. THEY ARE REFERRED TO AS ION-SELECTIVE ELECTRODES. THEY CONTAIN ELECTROCHEMICAL CELLS WHERE THE CURR VOLTAGE IS PROPORTIONAL TO K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} OR ANY OF A WIDE VARIETY OF ELECTROLYTES AND EVEN SOME NON ELECTROLYTES.

EXAMPLE 2 NERNST CALCULATION

FOR THE CELL: $\text{Cd}_{(s)} | \text{Cd}^{2+} 0.01 \text{M} || \text{H}^+ 0.05 \text{M} | \text{H}_2 1.0 \text{ATM} | \text{Pt}_{(s)}$

THE REACTION IS: $\text{Cd}^0 + 2\text{H}^+ \rightleftharpoons \text{Cd}^{2+} + \text{H}_2(\text{g})$

THE EQUILIBRIUM CONSTANT IS: $K = \frac{[\text{Cd}^{2+}][\text{H}_2]}{[\text{H}^+]^2}$ ↙ PRESSURE OF H_2

$$Q = \frac{[.01][1]}{[.05]^2} = \frac{.01}{.0025} = 4$$

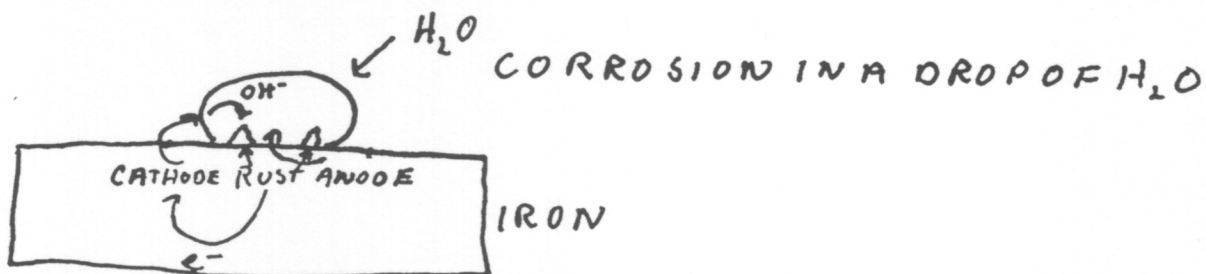
$$E_{\text{CELL}} = E_{\text{CELL}}^0 - \frac{.059}{n} \log Q$$

$$E_{\text{CELL}} = 0.4 \text{V} - \frac{.059}{2} \log 4 \quad \log 4 = 0.60$$

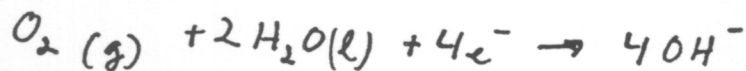
$$= .04 \text{V} - .018$$

$$E_{\text{CELL}} = .022 \text{V}$$

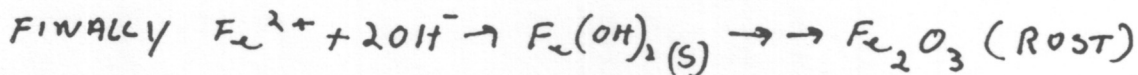
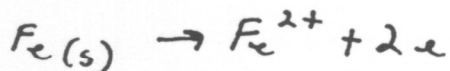
CORROSION



AT THE EDGE, OXYGEN IS REDUCED TO OH^-

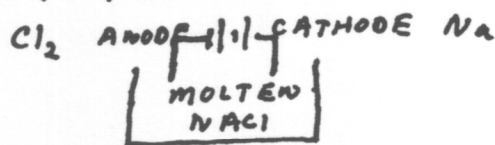
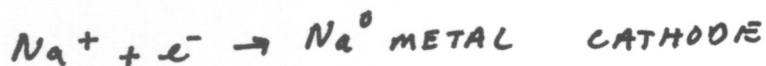
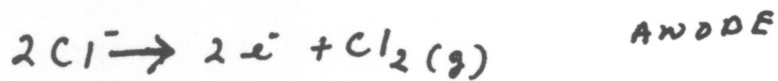


ELECTRONS SUPPLIED BY OXIDATION OF Fe^0 AT THE CENTER



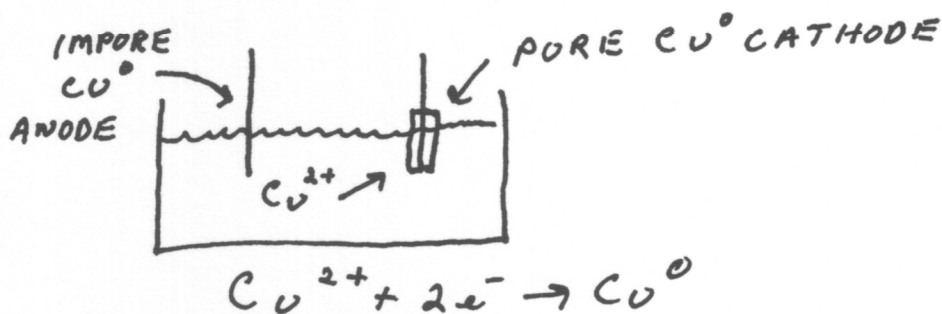
ELECTROLYSIS

IN AN ELECTROLYTIC CELL, AN ELECTRIC CURRENT DRIVES AN OTHERWISE NON SPONTANEOUS REACTION. MANY PURE COMPOUNDS OR ELEMENTS ARE MADE THIS WAY. EXAMPLE Na AND Cl₂



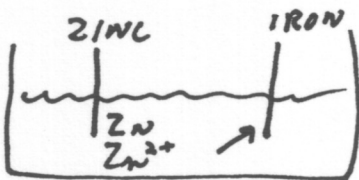
METALS ARE ELECTROPLATED

PURE Cu⁰ IS MADE FROM LESS PURE METAL



GALVANIZING

A COATING OF ZINC CAN BE APPLIED TO IRON BY ELECTROPLATING (OR A THICKER COAT BY DIPPING THE IRON IN MOLTEN ZINC)



STOICHIOMETRY

THE AMOUNT (IN MOLES) OF A SUBSTANCE GENERATED AT THE ELECTRODES IS PROPORTIONAL TO THE # OF MOLES OF ELECTRONS TRANSFERRED. ONE MOLE e⁻ = 9.65 x 10⁴ COULOMBS