Lecture #2 of 17

Looking forward… our review of Chapter “0”

- Cool applications
- **Redox half-reactions**
- **Balancing electrochemical equations**
- **History of electrochemistry and Batteries**
- *IUPAC terminology and* $E_{cell} = E_{red} - E_{ox}$
- *Thermodynamics and the Nernst equation*
- *Common reference electrodes*
- *Standard and Absolute potentials*
- *Latimer and Pourbaix diagrams*
- *Calculating* E_{cell} *under non-standard-state conditions*
- *Conventions*

... some people think ions are more important than electrodes...
... and I am one of them!

RECALL:

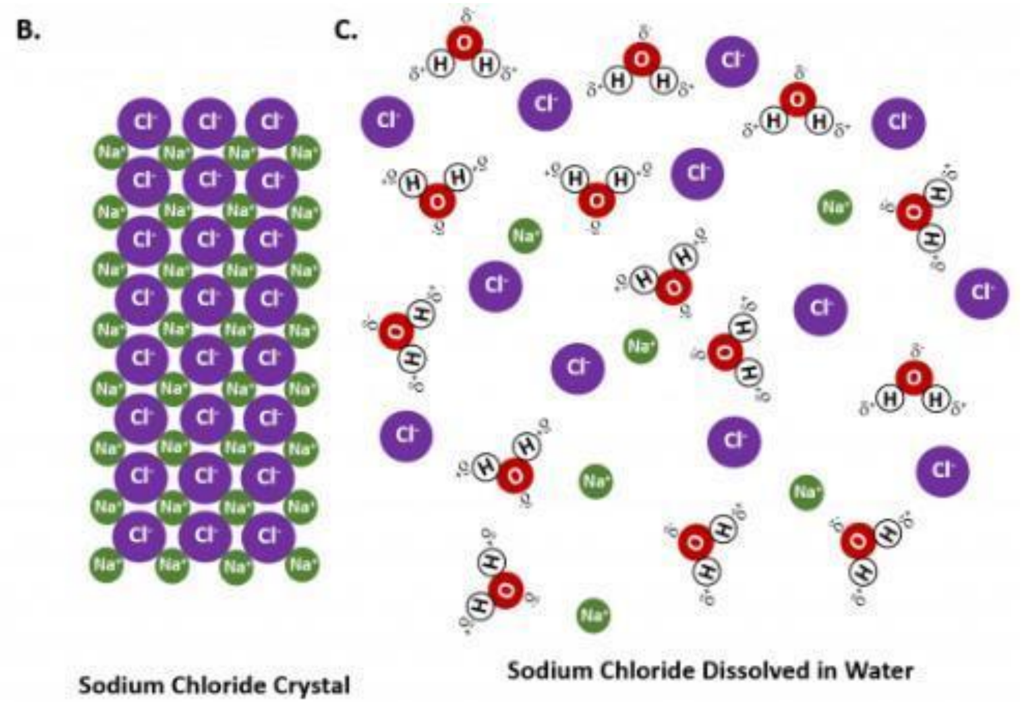
FYI, John O'M. Bockris's Modern Electrochemistry textbook series has the following 3 volumes...

1: Ionics (pp. 1 – 767)
2A: Fundamentals of Electrodics (pp. 771 – 1534)
2B: Electrodics in Chemistry, Engineering, Biology and Environmental Science (pp. 1539 – 2053)

... let's start to discuss ions...
... and how to drive their reactions...

... and let's use the board...

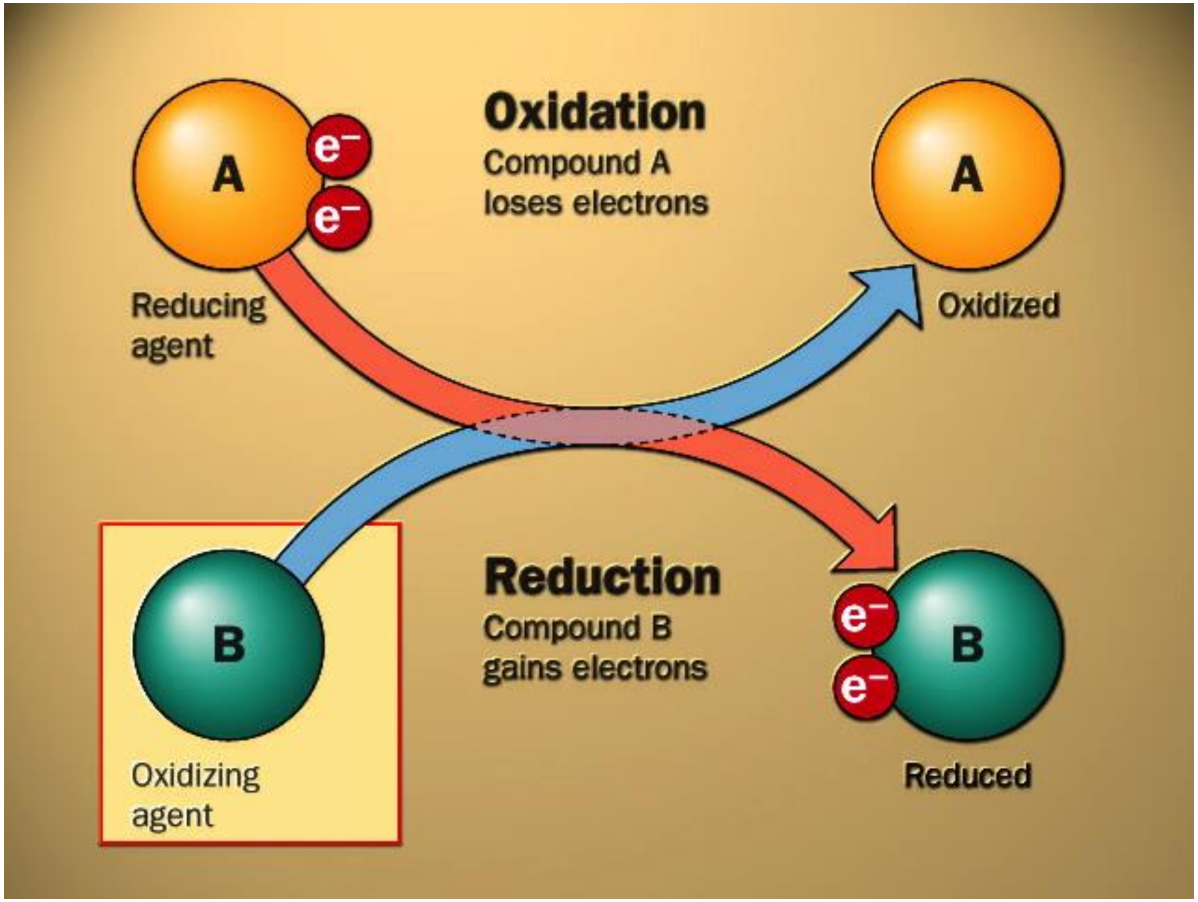
... and finish our discussion...
... during discussion session on Mon.



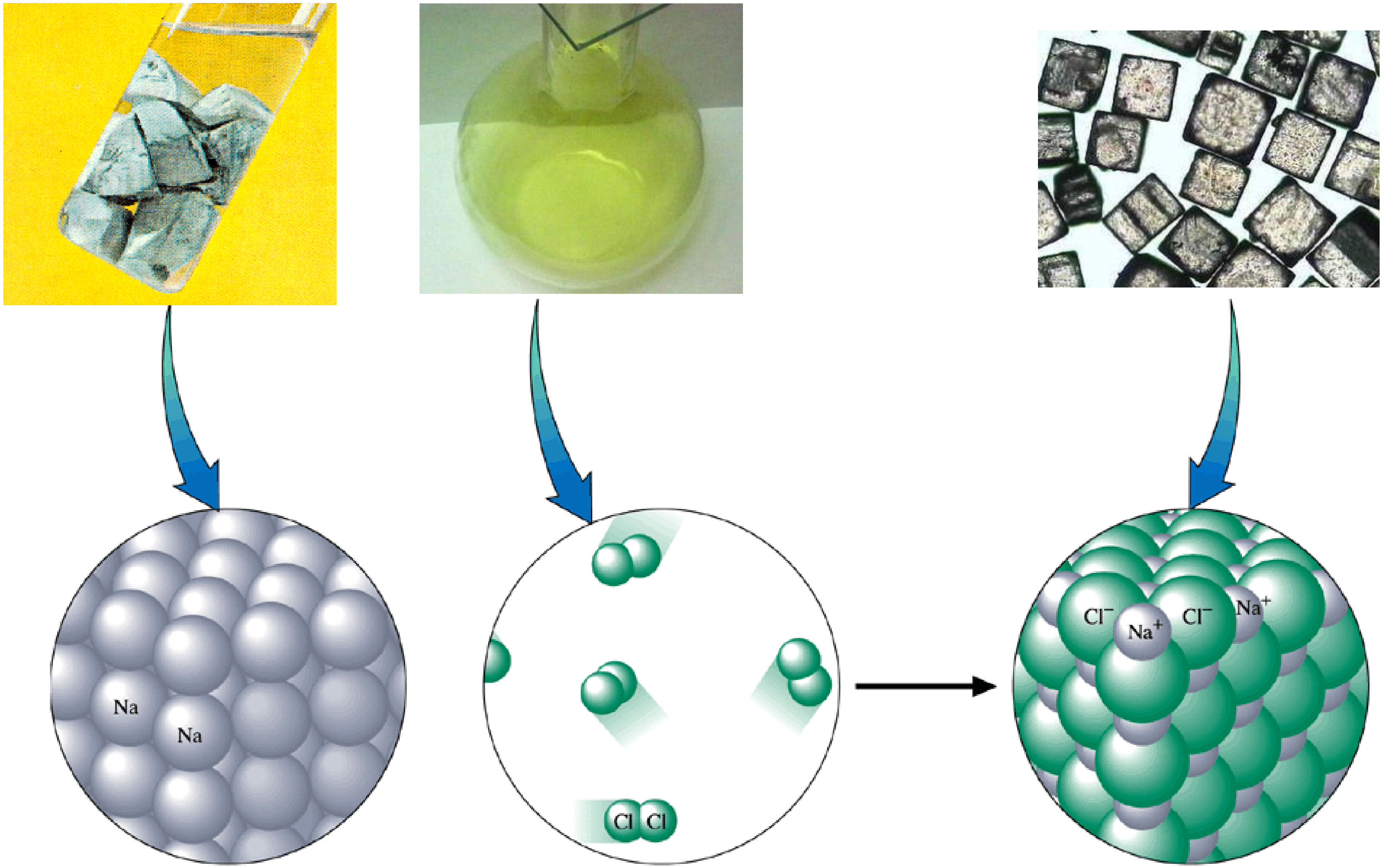
https://brainly.com/question/14682139

From M3C: Oxidation and reduction

An oxidation-reduction, or "redox" reaction is one in which one or more electrons are transferred.



Redox reactions



$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$

Oxidation states

Ionic compound: the oxidation state of an atom is equal to its charge.

KCl K:+1, Cl:-1

Covalent compound, different types of atoms: the oxidation state equals the charge that would result if the electrons were given to the most electronegative atom.

NH_3 N:-3, H:+1

Covalent compound, same type of atoms: charge that the compound would have if the electrons were divided evenly among atoms of the same type.

N_2H_4 (H_2NNH_2) N:-2, H:+1

Closed (filled) orbital shells are most stable…

… in general H (+1), O (-2), halides (-1), etc.

$$\overset{0}{Zn}\,(s) + 2\overset{+1}{H}\overset{-1}{Cl}\,(aq) \longrightarrow \overset{+2}{Zn}(\overset{-1}{Cl})_2\,(aq) + \overset{0}{H_2}\,(g)$$

$$CH_4\,(g) + 2\overset{0}{O_2}\,(g) \longrightarrow C\overset{-2}{O_2}\,(g) + 2H_2\overset{-2}{O}\,(l)$$

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Oxidation and Reduction

Oxidizing agent (oxidant) $\Rightarrow$ molecule that ***gains*** electrons
Reducing agent (reductant) $\Rightarrow$ molecule that ***loses*** electrons

$$\overset{0}{2Mg}\,(s) + \overset{0}{O_2}\,(g) \longrightarrow 2\overset{2+}{Mg}\overset{2-}{O}\,(s)$$

This reaction can be split into two (hypothetical) ***half-reactions***

Oxidation half-reaction
reactant (= reducing agent) ***loses*** e^-

$$2\,Mg \rightarrow 2\,Mg^{2+} + 4\,e^-$$

Reduction half-reaction
Reactant (= oxidizing agent) ***gains*** e^-

$$O_2 + 4\,e^- \rightarrow 2\,O^{2-}$$

Oh (silly) acronyms…

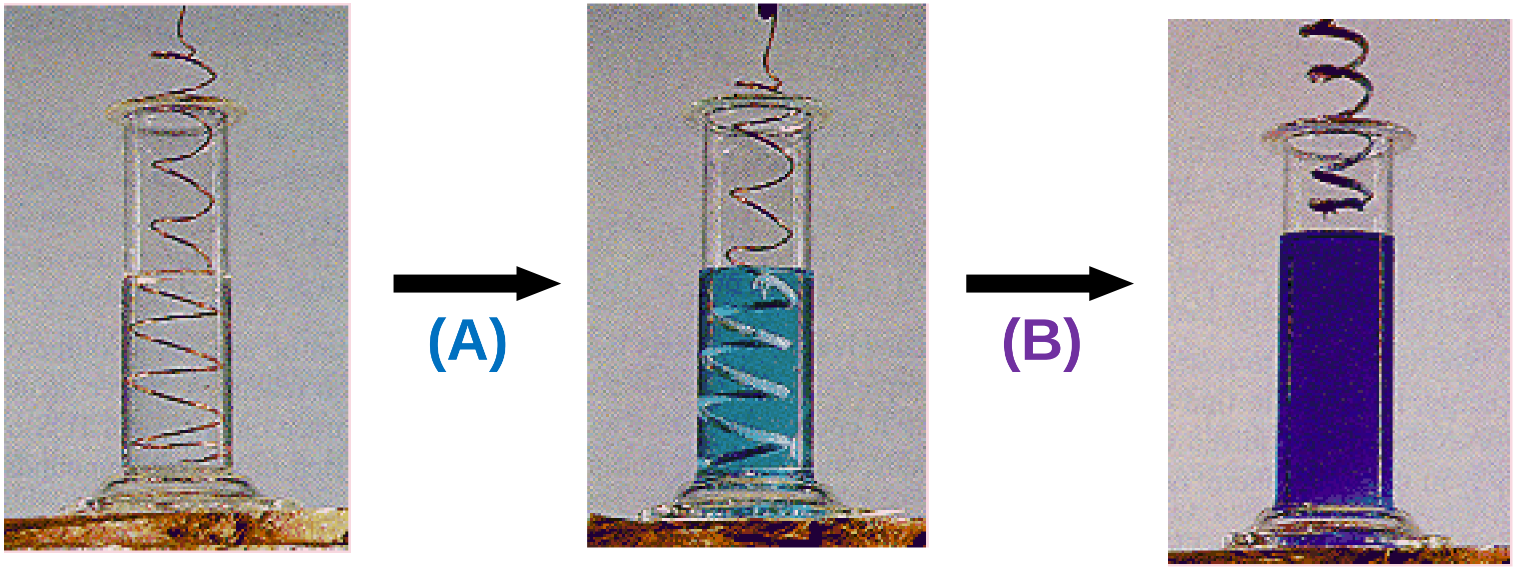
OIL RIG

- **O**xidation
- **I**s
- **L**oss. (of electrons)

- **R**eduction
- **I**s
- **G**ain. (of electrons)

Electrochemistry

Redox reactions, or not?



(A)

$$Cu\ (s) + 2Ag^{+}\ (aq) \xrightarrow[\textit{redox}]{} Cu^{2+}\ (aq) + 2Ag\ (s)$$

(B)

$$Cu^{2+}\ (aq) + 4NH_3\ (l) \xrightarrow[\textit{not redox}]{} [Cu(NH_3)_4]^{2+}\ (\sim aq)$$

Redox reactions

Zinc metal reacts with aqueous hydrochloric acid to form zinc chloride in solution and hydrogen gas. Is this a redox reaction? If yes, identify the oxidizing agent, the reducing agent, and the substances being oxidized and reduced.

1. Write a balanced chemical equation *(not always easy)*.

$$\overset{0}{Zn}\,(s) + 2\overset{+1}{H}\overset{-1}{Cl}\,(aq) \longrightarrow \overset{+2}{Zn}\overset{-1}{Cl_2}\,(aq) + \overset{0}{H_2}\,(g)$$

2. Assign oxidation states.

3. Determine whether atomic oxidation states change. **Yes**

Redox reactions

Zinc metal reacts with aqueous hydrochloric acid to form zinc chloride in solution and hydrogen gas. Is this a redox reaction? If yes, identify the oxidizing agent, the reducing agent, and the substances being oxidized and reduced.

4. Use the changes in oxidation state for each atom to determine what is being oxidized and reduced.

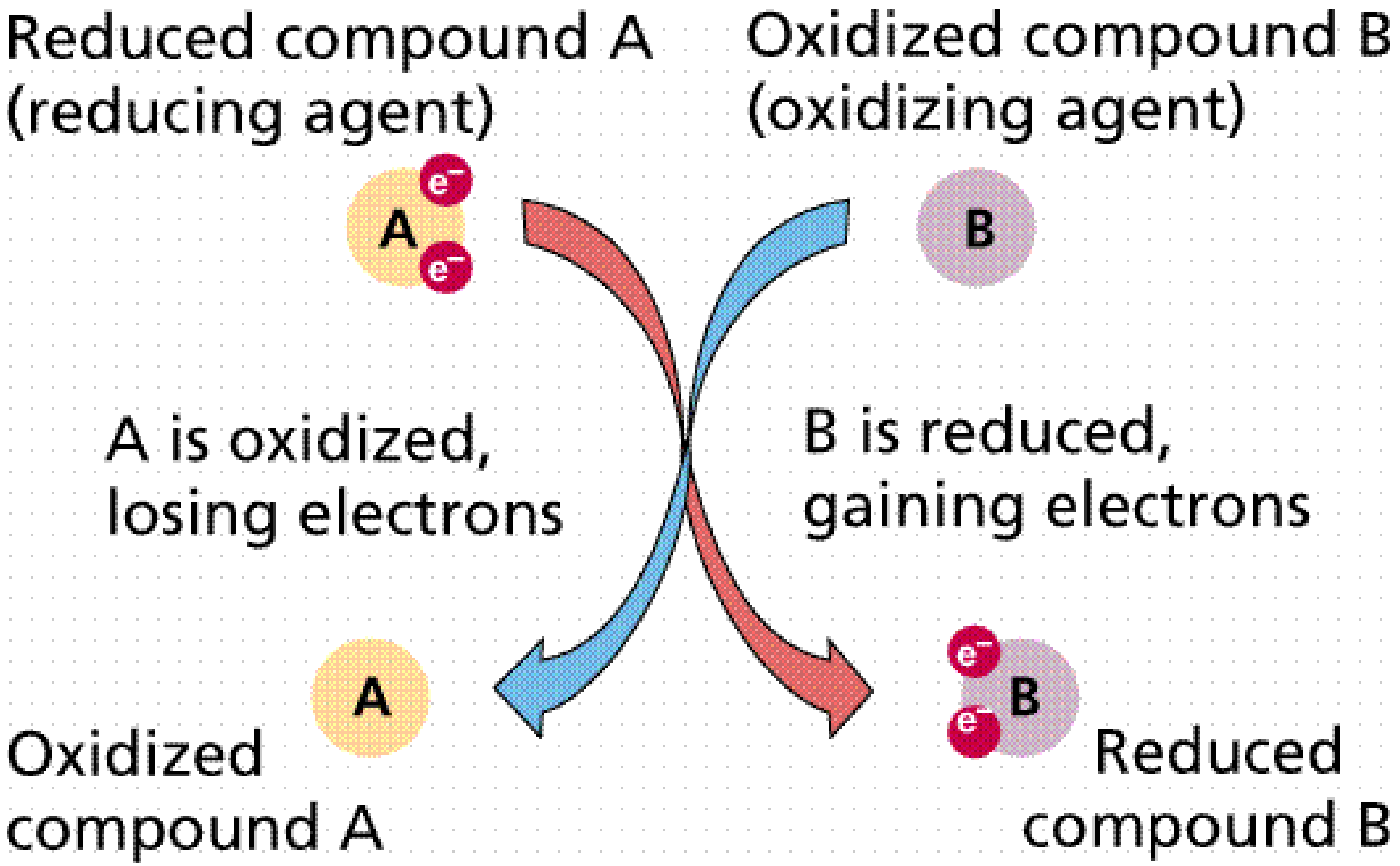
0	+1 -1		+2 -1	0	

$$\overset{0}{Zn}\,(s) + 2\overset{+1}{H}\overset{-1}{Cl}\,(aq) \longrightarrow \overset{+2}{Zn}\overset{-1}{Cl_2}\,(aq) + \overset{0}{H_2}\,(g)$$

Zn: 0 ⟶ +2		oxidized, reducing agent
H: +1 ⟶ 0		reduced, oxidizing agent
Cl: -1 ⟶ -1		spectator ion *(best to include)*

Half-reactions

Redox reactions are often difficult to balance by inspection. Instead, we can use the method of half-reactions. *Half-reactions don't actually exist all that often… (read on)…*



Writing half-reactions

1. Assign oxidation states for each element in the reactants and products.

2. Determine what is being oxidized, what is being reduced, and how many electrons are transferred.

3. Write balanced half-reactions, using electrons as reactants or products, as appropriate.

Balancing redox equations

The oxidation of Fe^{2+} to Fe^{3+} by $Cr_2O_7^{2-}$ (becomes Cr^{3+}) in acid solution?

1. Write the unbalanced equation for the reaction in ionic form.

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$$

2. Separate the equation into two half-reactions.

Oxidation: $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

Reduction: $\overset{+6}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}}$

3. Balance the atoms other than O and H in each half-reaction.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Balancing redox equations

4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$$

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

6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

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

Balancing redox equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^{-}}$

Reduction: $\cancel{6e^{-}} + 14H^{+} + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

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

8. Verify that the number of atoms and the charges are balanced.

$$14x1 – 1x2 + 6x2 = \mathbf{24} = 6x3 + 2x3 + 7x0$$

… that’s a lot of spectator anions!

9. *For reactions in basic solutions, add OH^{-} to* ***both sides*** *of the equation for every H^{+} that appears in the final equation…*

Method of half-reactions

(under basic/alkaline conditions)

1. Use the half reaction method for acidic solution to balance the equation as if excess H^+ ions were present.

2. To both sides of the equation, add the number of OH^- ions needed to balance the H^+ ions added in the last step.

3. Form H_2O on the side containing both H^+ and OH^- ions, and cancel out the number of H_2O molecules appearing on both sides of the equation.

4. Check to make sure that the equation is balanced.

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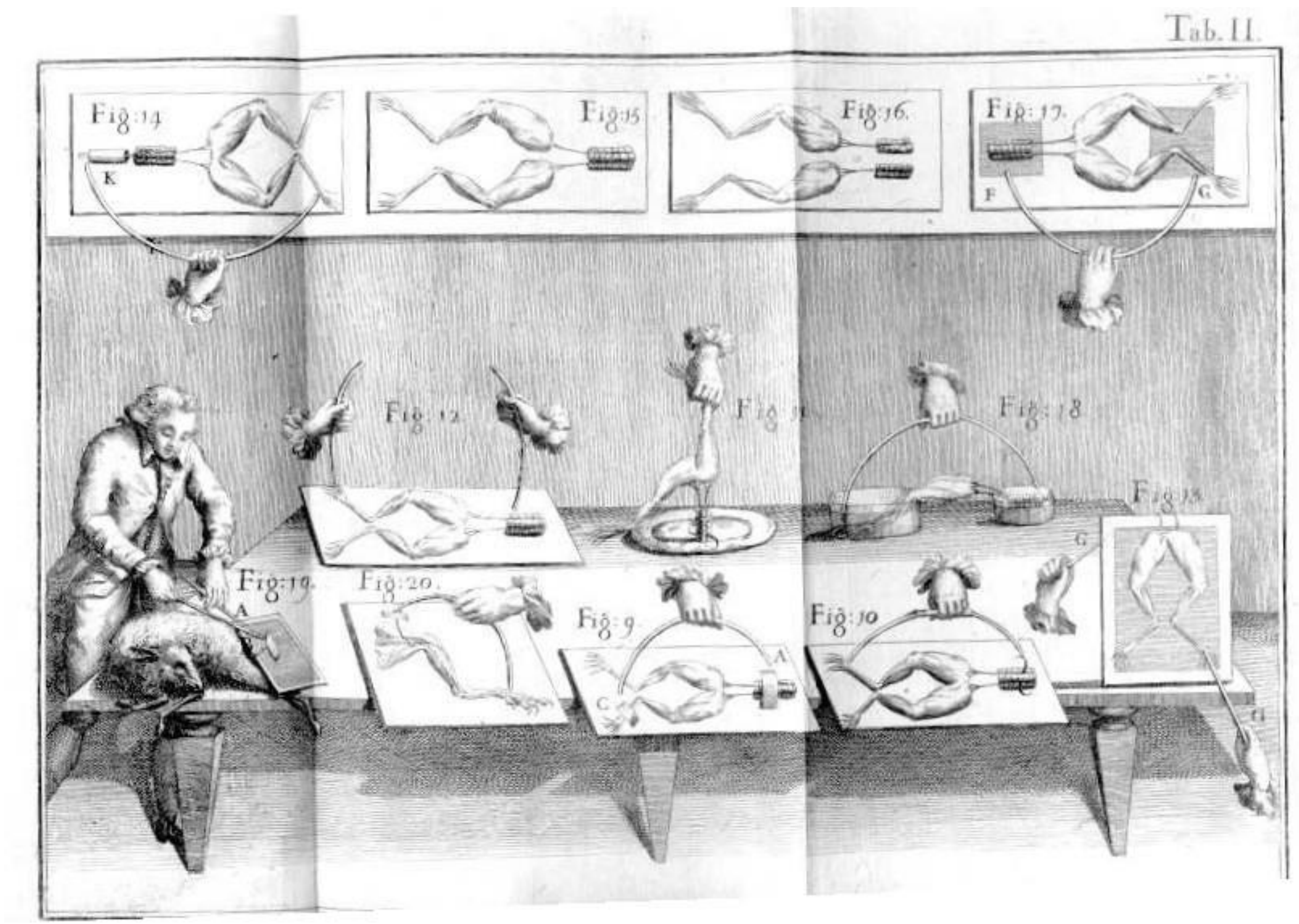
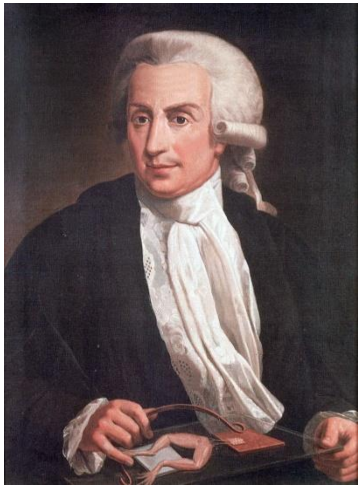
A Short History Lesson…

Electrochemistry is associated with Luigi Galvani who discovered "animal electricity," while trying to Frankenstein frogs legs (1791)

Physician, Physicist, Philosopher





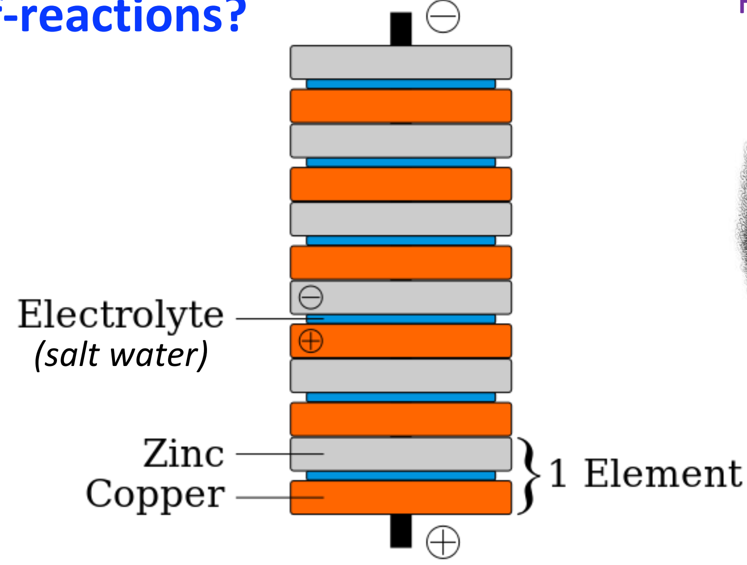
Luigi Galvani
(1737–1798)
from Wiki

Voltaic pile

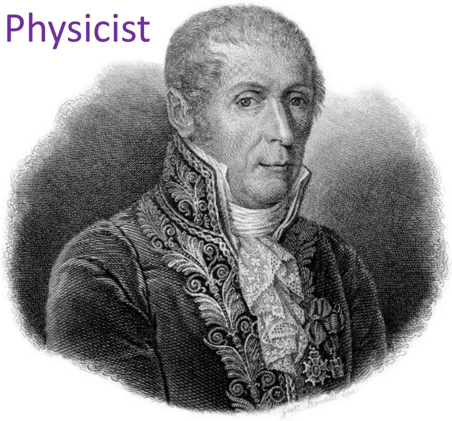
Invented by Alessandro Volta (1800) but the elements of the pile (galvanic cells) were named after Galvani.

What are the combined half-reactions?

At the Tempio Voltiano (the Volta Temple) near Volta's home in Como, Italy.



Physicist



Alessandro Volta (1745–1827)
from Wiki

Volta presenting his "Voltaic Pile" to Napoleon and his court… and now he is a Count!

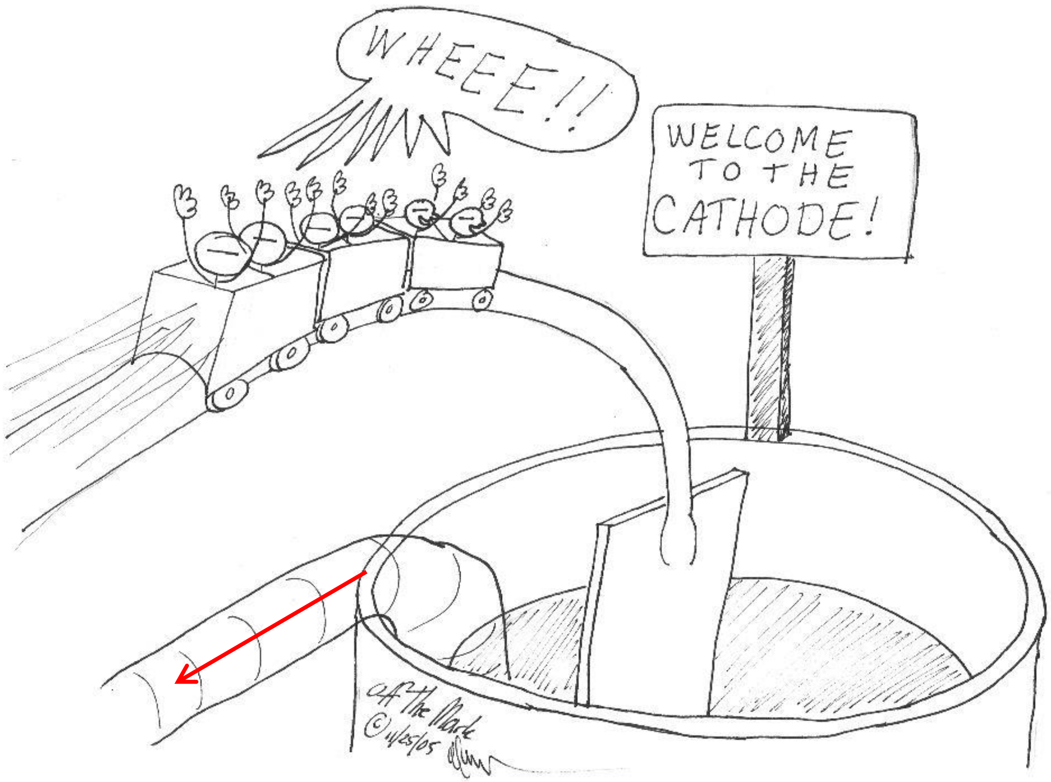
http://en.wikipedia.org/wiki/Voltaic_pile

http://en.wikipedia.org/wiki/Alessandro_Volta

Galvanic Cells

Every non-equilibrium cell is a galvanic cell (in one direction, i.e. the spontaneous direction)

Physically separating the half-reactions allows the electrons to go over a long distance, from the anode to the cathode via a (solid) conductor: basis for conversion of chemical energy into electricity = "Electrochemistry"!



Salt bridge is an ionic conduit to prevent buildup of charge in both compartments and also to prevent bulk mixing of the two solutions