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Lecture #2 of 20

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Looking forward... our review of Chapter "0"

- Cool applications
- **Redox half-reactions**
- **Balancing electrochemical equations**
- **History of electrochemistry and Batteries**
- *IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$*
- *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*

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... some people think ions are more important than electrons...

... 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 Electroics (pp. 771 – 1534)

2B: Electroics in Chemistry, Engineering, Biology and Environmental Science (pp. 1539 – 2053)

... let's start to discuss ions...

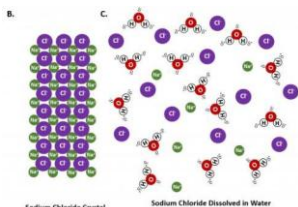
... and how to drive their reactions...

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

... and finish our discussion...

... hopefully, in part, during...

... discussion session on Monday

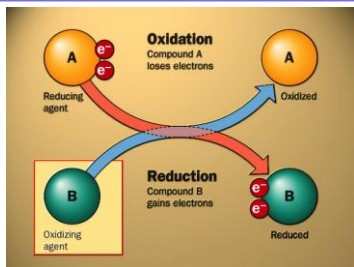


<https://brainly.com/question/14682139>

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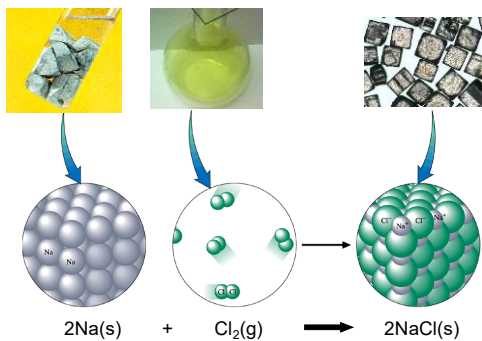
From M3C: Oxidation and reduction⁴¹

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



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Redox reactions⁴²



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Oxidation states⁴³

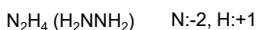
Ionic compound: the oxidation state of an atom is equal to its charge.



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.



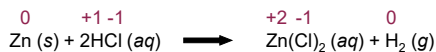
Covalent compound, same type of atoms: charge that the compound would have if the electrons were divided evenly among atoms of the same type.



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Closed (filled) orbital shells are most stable...

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

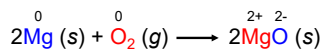
[illegible]

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Oxidation and Reduction

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

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



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

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



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



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Oh (silly) acronyms...

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OIL RIG

- **Oxidation**
- **Is**
- **Loss.** (of electrons)

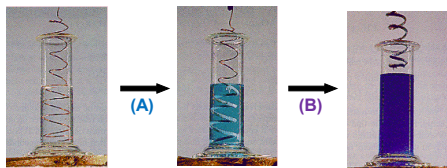
- **Reduction**
- **Is**
Gain. (of electrons)



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Redox reactions, or not?

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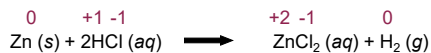
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Redox reactions

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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*).



2. Assign oxidation states.

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

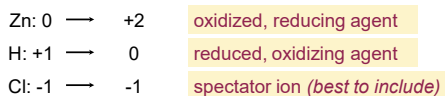
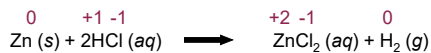
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Redox reactions

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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.

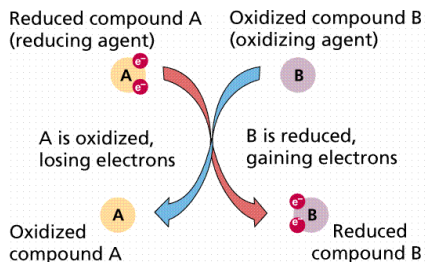


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Half-reactions

Redox reactions can be 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)...*



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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.

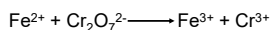
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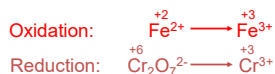
Balancing redox equations

The oxidation of Fe^{2+} to Fe^{3+} by $\text{Cr}_2\text{O}_7^{2-}$ (becomes Cr^{3+}) in **an acidic aqueous** solution?

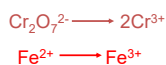
1. Write the unbalanced equation for the reaction in ionic form.



2. Separate the equation into two half-reactions.



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



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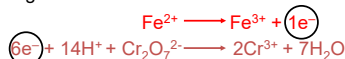
Balancing redox equations

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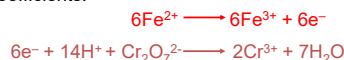
4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.



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



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

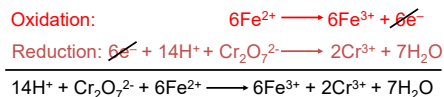


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Balancing redox equations

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



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

$$14 \times 1 - 1 \times 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3 + 7 \times 0$$

... 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...

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Method of half-reactions

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(in aqueous 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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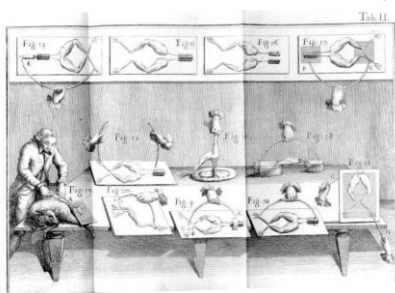
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A Short History Lesson...

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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

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Voltaic pile

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

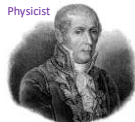
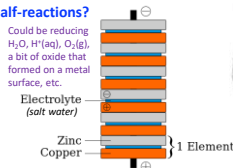
What are the combined half-reactions?

Physicist



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

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



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/Alessandro_Volta

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Galvanic Cells

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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

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Electrolysis of water

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William Nicholson
(1753–1815)



Sir Anthony Carlisle
(1768–1840)

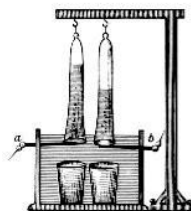
Volta's results were shared with the scientific community and then, **boom**, many people demonstrated electrolysis the same year, and later electroplating!



Johann Wilhelm Ritter
(1776–1810)



William Cruickshank
(1777–1810(1))



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

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Daniell (galvanic) Cell (1836)

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No more H₂ from the (primary) battery!

anode oxidation **cathode reduction**

Half-reactions are physically separated!

$\text{Zn (s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^-$ $\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu (s)}$

NET REACTION: $\text{Zn (s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu (s)}$

Chemist, Meteorologist

John Frederic Daniell
(1790–1845)
from Wiki

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