Unit 1 – Deck 1

ELECTROCHEMISTRY

Introduction – Electricity in Chemistry

Topics

1. Introduction to electrochemistry
2. Reduction & oxidation
3. **Assigning oxidation states**
4. Electrochemical cell
5. Cathodes and anodes
6. Cells and half cells

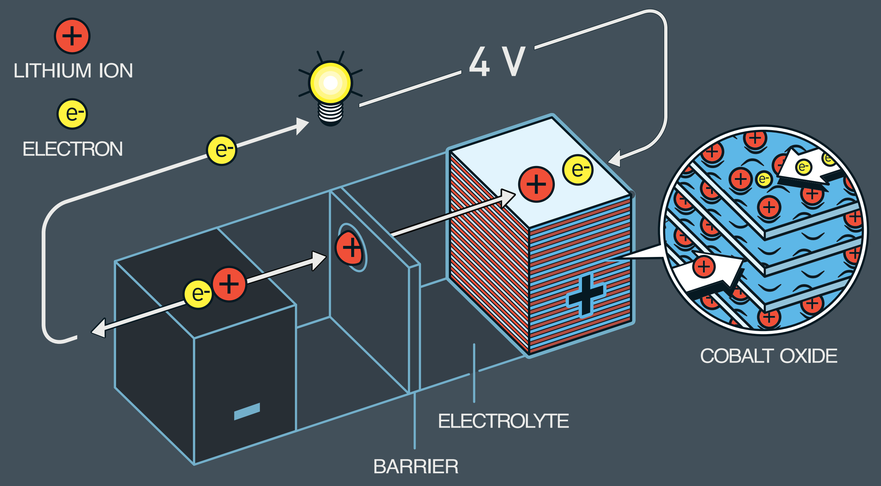
What is Electrochemistry?

Electrochemistry:

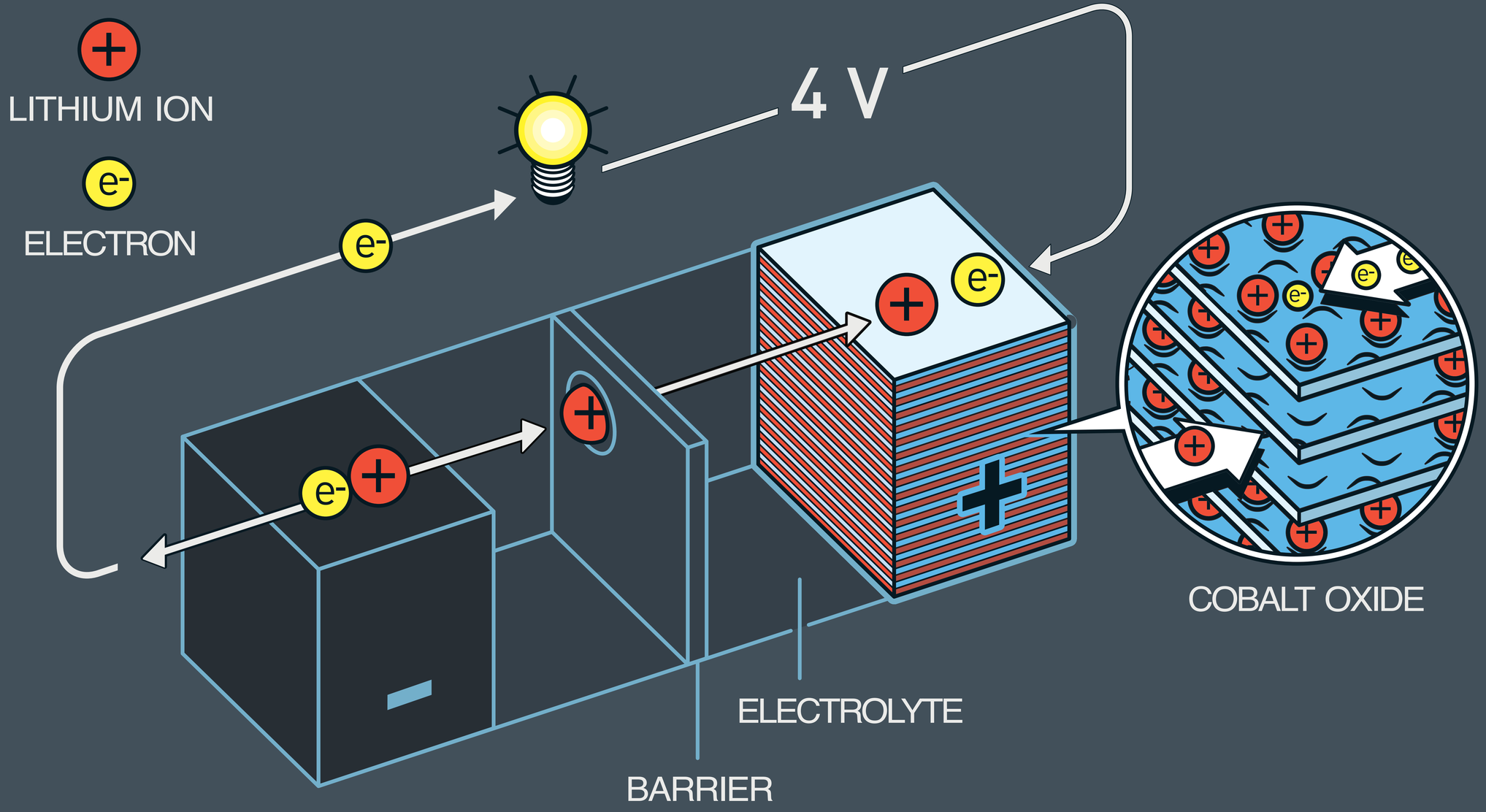
- The study of chemical reactions that generate electricity or can be carried out by running electricity through them.
- *Chemistry that involves the net transfer of charge between discrete components (atoms, ions, molecules, materials…) of a chemical system.*

Common Examples:

- **Batteries**
- Nerve impulses in our bodies

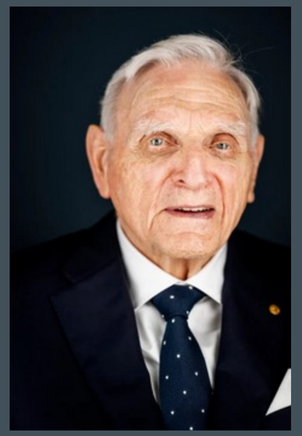


What is a battery?



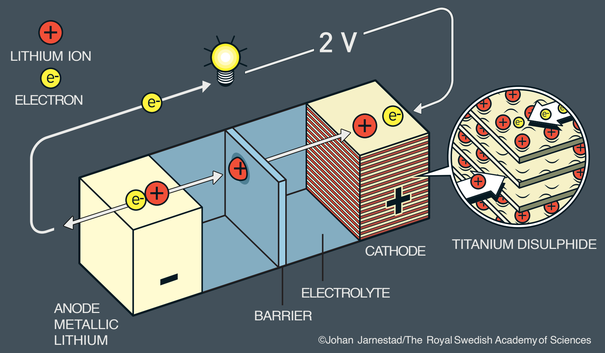
Nobel Prize in Chemistry - 2019

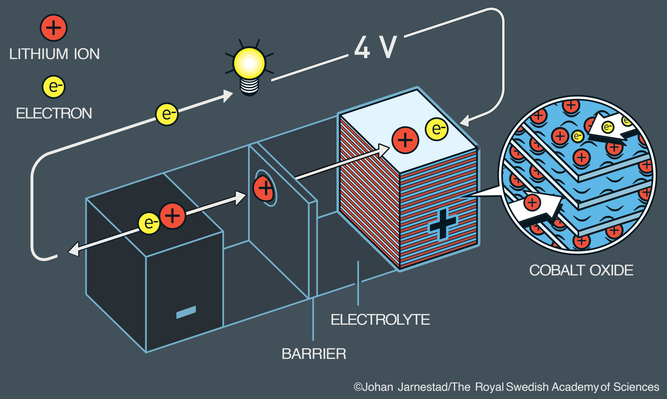
M. Stanley Whittingham
1970

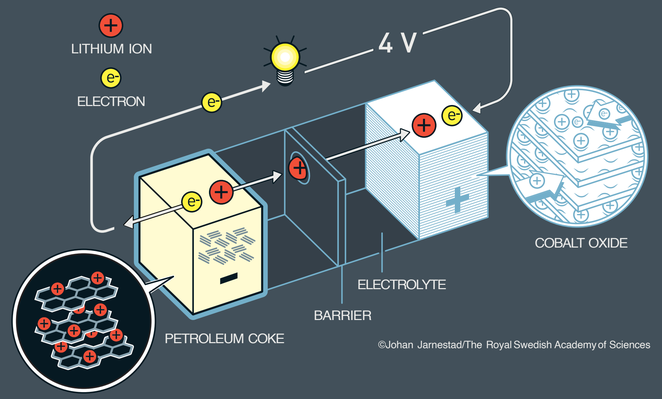


John B. Goodenough
1980

Akira Yoshino
1985



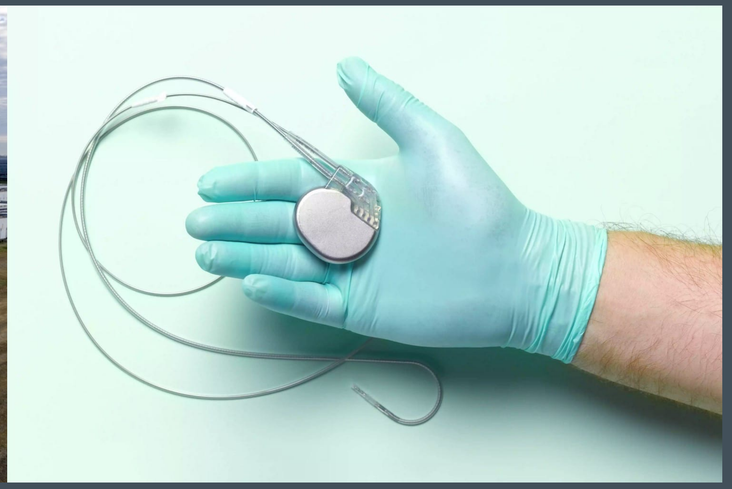




Applications

Electric vehicles

Grid Storage for wind, solar, and load balancing



Medical devices

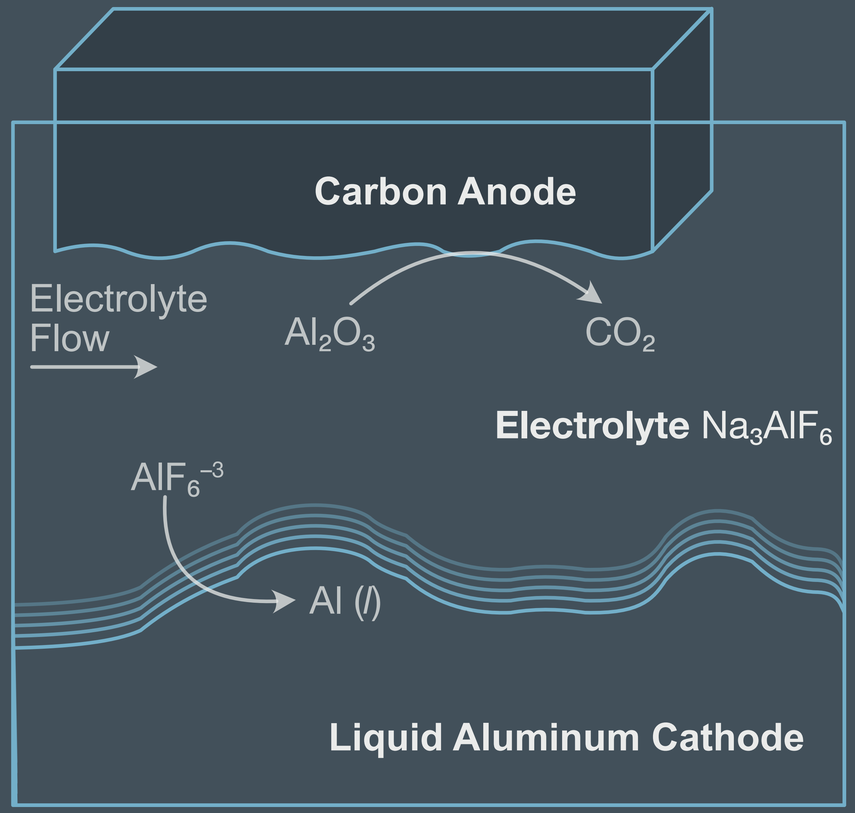
Armand, M., Tarascon, JM. Building better batteries. *Nature* **451**, 652–657 (2008).

Electrochemistry in synthesis – the electrolytic cell

Hall-Héroult process

Smelting | reduction in molten state

$$Al_2O_3 + \frac{3}{2}C \longrightarrow 2\,Al(l) + \frac{3}{2}CO_2$$



0.5 PWh per year

Oxidation of one Al can will power your laptop for ~3 hours

Aerospace Superalloys

Structural materials


1.5 km potline
Powerlines from oil fields
~3000 kg/day per pot
3D


Austin
Austin

Reduction-Oxidation Chemistry

Reduction-Oxidation (redox) chemistry is the study of the movement of electrons from one atom to another in chemical reactions.

- Sometimes strong bonds are broken/formed:

- Sometimes only weaker bonding interactions involved:

Definitions

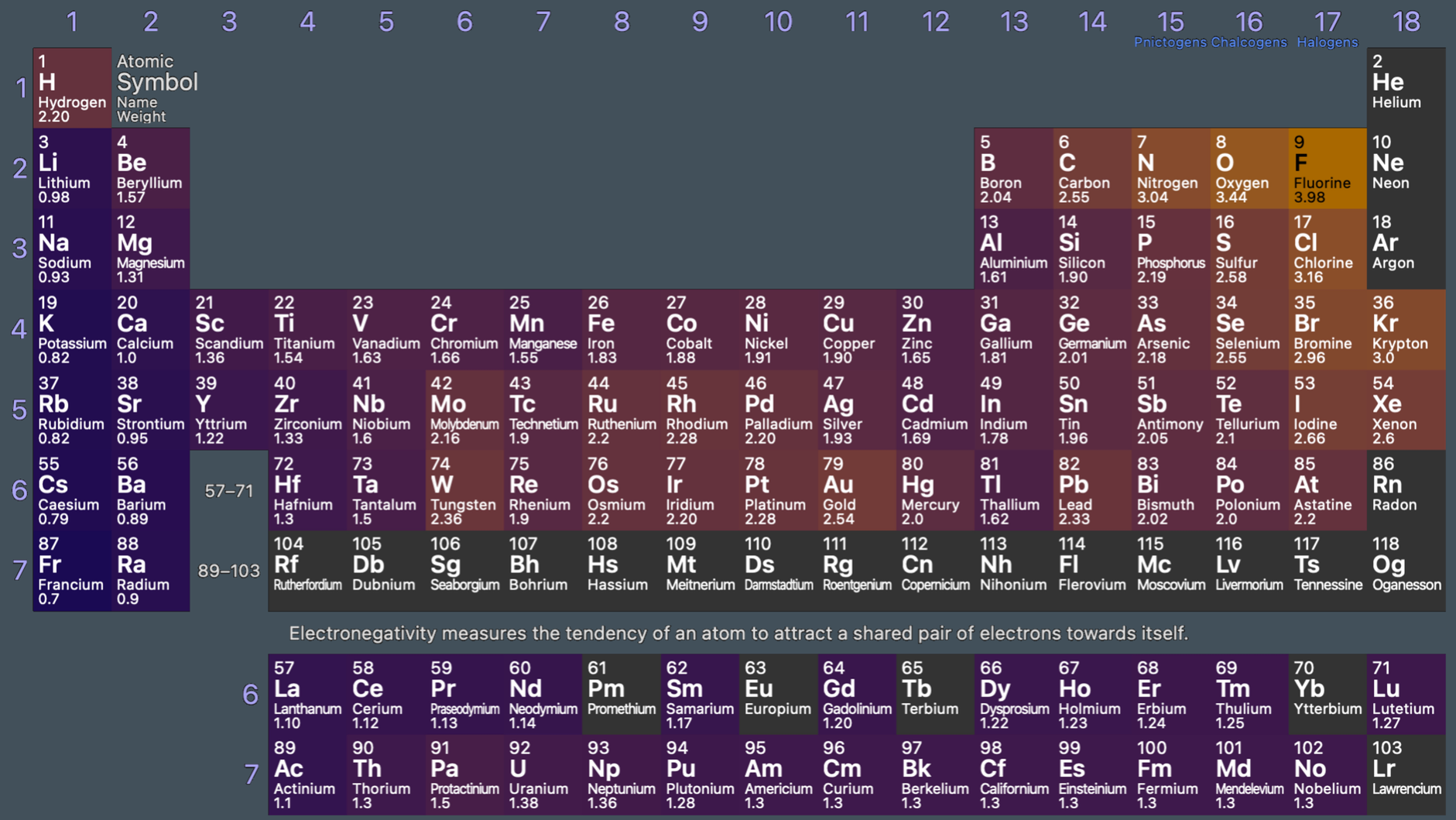
Oxidation Reactions

- Gaining oxygen (O_2)
- Losing hydrogen (H_2)
- Losing electrons

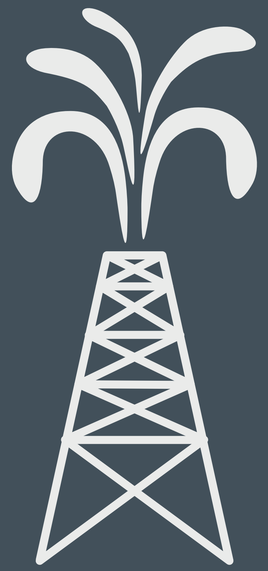
Reduction Reactions

- Losing oxygen (O_2)
- Gaining hydrogen (H_2)
- Gaining electrons

Electronegativity



Redox Mnemonics



OIL RIG

Oxidation **I**s **L**oss of electrons

Reduction **I**s **G**ain of electrons

LEO says **GER!**

Lose **E**lectrons **O**xidation

Gain **E**lectrons **R**eduction

Example – Reduction and Oxidation

Which of the following is an oxidation reaction?

1. $Br_2 + 2e^- \rightarrow 2\,Br^-$

2. $Li \rightarrow Li^+ + e^-$

Who is the oxidizing agent?
Who is the reducing agent?
Who is the oxidant?
Who is the reductant?

Oxidation vs reduction how to tell

Reduction	Oxidation
Gain of electrons	Loss of electrons
Decrease in oxidation number	Increase in oxidation number
Increase in number of hydrogens	Decrease in number of hydrogens
Decrease in number of oxygens	Increase in number of oxygens

Careful here! There are plenty of exceptions.

Oxidation States

Each atom in a compound has its own oxidation state.

- Oxidation states are *not* real ionic charges.
- Oxidation states typically range from –4 to +7.
- Oxidation states can be 0 and can even be fractions (unusual).

Assigning Oxidation States

Step #1:
Start with elements that have the below conditions

- Free, uncombined element = zero
- Monatomic ion = charge on ion
- Group IA in compounds = +1
- Group IIA in compounds = +2
- F = –1 in compounds

Step #2:
Assign oxidation states for H and O

- H = +1 (in metal hydrides H = –1)
- O = –2 (in peroxides O= –1; H–O–O–H)

Consideration of ⊿EN can help in cases like peroxide

For now, we will assign oxidation states only to individual atoms.

Assigning Oxidation States

Step #3:
Work on “The Others”

- Sum of oxidation numbers in compound = 0
- Sum of oxidation numbers in polyatomic ion = charge on ion

Step #4:
Work on “The Unknowns” by choosing the “best guess” to start assigning oxidation numbers

- More electronegative element assigned negative
- Less electronegative element assigned positive

For now, we will assign oxidation states only to individual atoms.

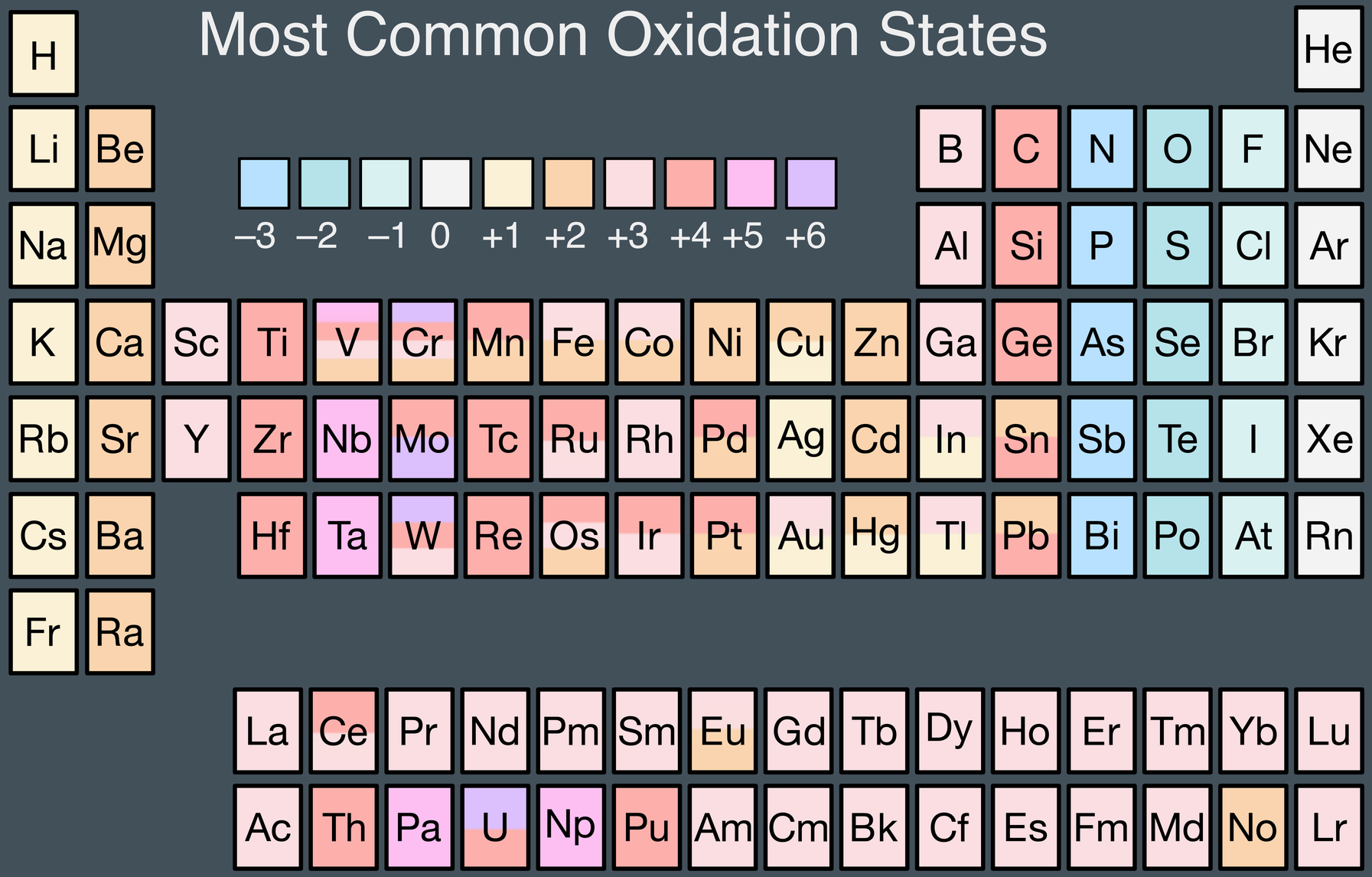
Example

Identify the oxidation state for each element in the below chemical equations.

1. Fe in Fe_2O_3

2. Cs_2CuCl_4

Most Common Oxidation States



WARNING: this list is not at all, in any way, comprehensive.

Example – Reduction and Oxidation

Identify which species is oxidized and which species is reduced in the below chemical equations.

1. $Br_2 + H_2 \rightarrow HBr$

2. $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$

Who is the oxidizing agent?
Who is the reducing agent?
Who is the oxidant?
Who is the reductant?

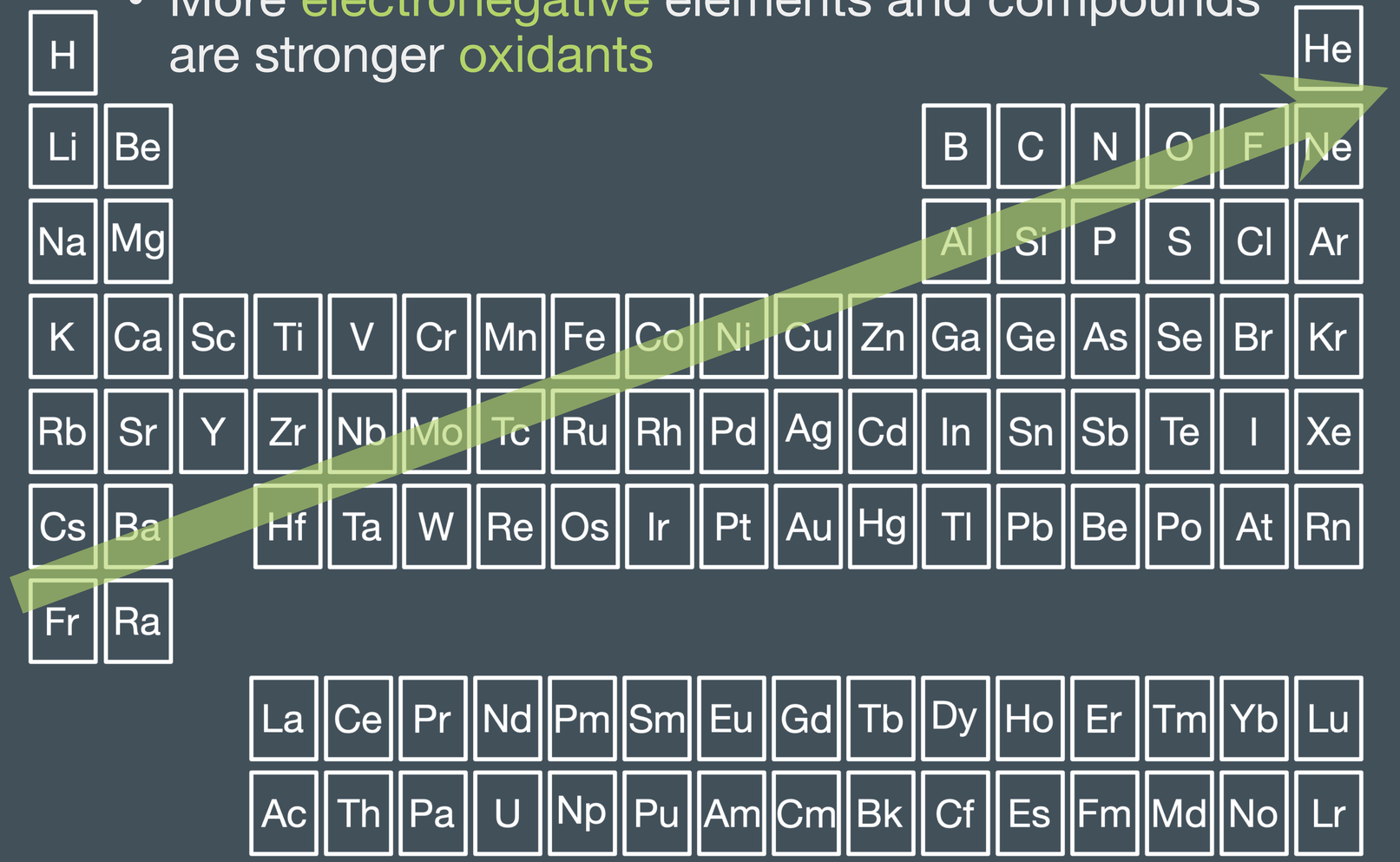
Advanced: Oxidation states for whole molecules

In charge delocalized compounds (and those with multiple resonance structures) assigning an integer *formal oxidation state* (FOS) to single atoms is not very useful. But we can assign partial charges to atoms and a FOS for the whole molecular fragment instead.

quinone semiquinone

Preview: electrochemical series

- More electropositive elements and compounds are stronger reductants
- More electronegative elements and compounds are stronger oxidants



Generally, we must also consider electron counts and relative stabilities of whole compounds, but generally electron poor compounds are more oxidizing

Poll: what is the stronger oxidant?

Which do you expect to be the stronger oxidizing agent?

1. Cl_2 or Cl^-

2. N_2O_5 or N_2O

3. K_2FeO_4 or Fe_2O_3