Redox reactions

Today:

- Why do we care about redox reactions?
- What is a redox reaction?
- How do we balance a redox reaction?

Thursday:

- Relationship between Gibbs free energy and Electrode potential (i.e. ability for redox reactions to do work/provide energy)
- Stability of redox species / determination of what species exist in the environment

Redox in nature

- Solar radiation is converted into chemical energy (organic matter) and O_2 is produced
- This chemical energy fuels metabolic processes when that organic matter is broken down
  - The reactions that take place are determined by the environmental conditions and energetic favorability of reactions

"… for every energetically favorable redox reaction, there exists some marine organism, or community of organisms, capable of exploiting that energy resource." – Libes 2009

Electron-transfer reactions

Example: H_2 combining with O_2 to form water:

$2\ H_2 + O_2 \rightarrow 2H_2O$

An electron is transferred from H to O:

the H_2 is oxidized and the O_2 is reduced

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We use the oxidation number (oxidation state) to keep track of electron shifts in chemical reactions. It is defined as "*the charge which an atom appears to have when the net electric charge on a chemical species is apportioned according to certain rules*".

Important because: the binding of atoms can result from the transfer or sharing of electrons.

Reduction-Oxidation Reactions

Oxidation is a chemical process in which an atom shows an *increase* in oxidation number

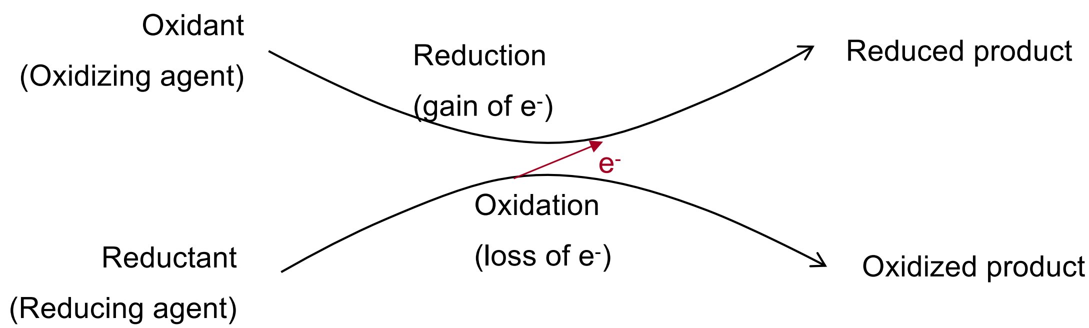
Reduction is a chemical process in which an atom shows a *decrease* in oxidation number

Example: $2\ H_2 + O_2 \rightarrow 2H_2O$

$\quad\quad\ 0 \quad\ 0 \quad\quad\quad 1\ \ -2$

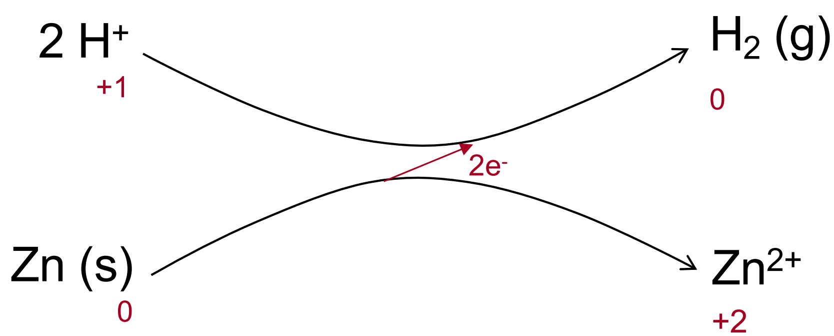
- The hydrogen changes oxidation number from 0 to +1(is oxidized)
- The oxygen changes oxidation number from 0 to –2 (is reduced)

In general



Because there are no free electrons in nature, every oxidation is accompanied by a reduction, and vice versa

Oxidation of zinc: $Zn\ (s) + 2\ H^+ \rightarrow Zn^{2+} + H_2\ (g)$



Zn loses electrons, so it is oxidized

H gains electrons, so it is reduced

Terms used for redox reactions

Term	Change in oxidation number	Change in electrons
Oxidation	Increase	Loss of electrons
Reduction	Decrease	Gain of electrons
Oxidizing agent / Oxidant	Decrease	Accepts electrons
Reducing agent/ Reductant	Increase	Donates electrons
Substance oxidized	Increase	Loses electrons
Substance reduced	Decrease	Gains electrons

Oxidation state / number

Oxidation: Loss of electrons from an element.

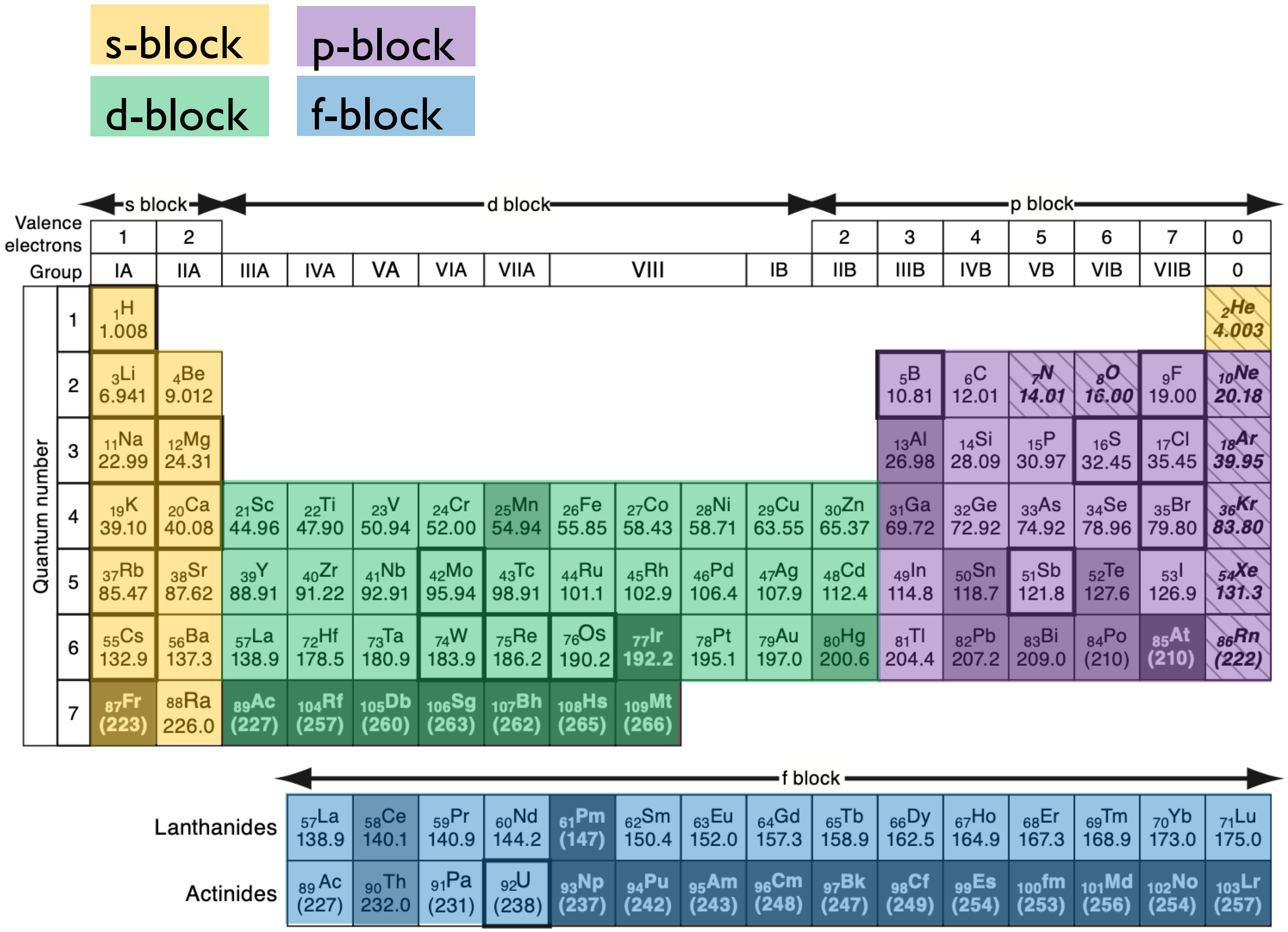
Oxidation number increases

Reduction: Gain of electrons by an element.

Oxidation number decreases

To determine whether reaction is oxidation or reduction:

We need to know oxidation number of the element and how it changes



Likely oxidation states are determined by the number of electrons that can easily be added or stripped away

Orbital configuration determines how many electrons a "block" can hold

s – 2

p – 6

d – 10

f – 14

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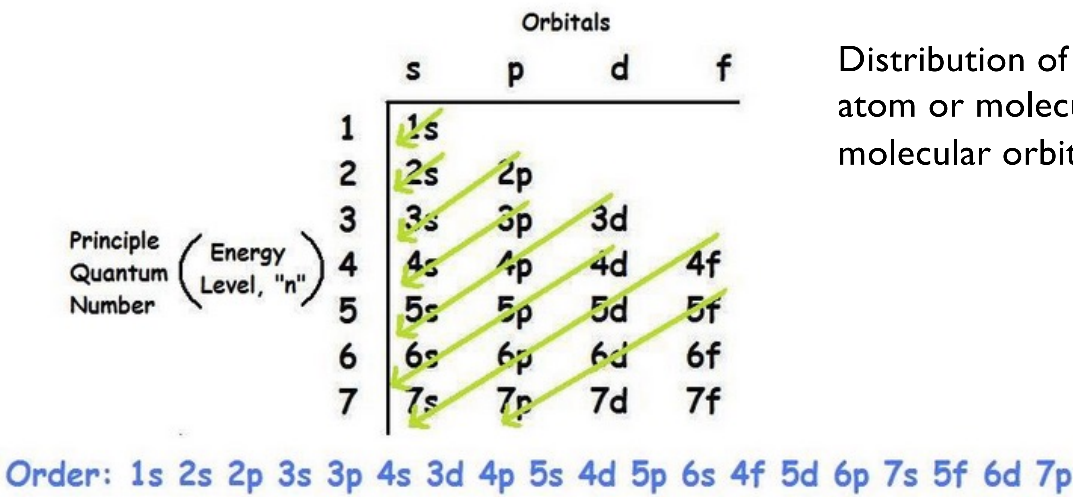


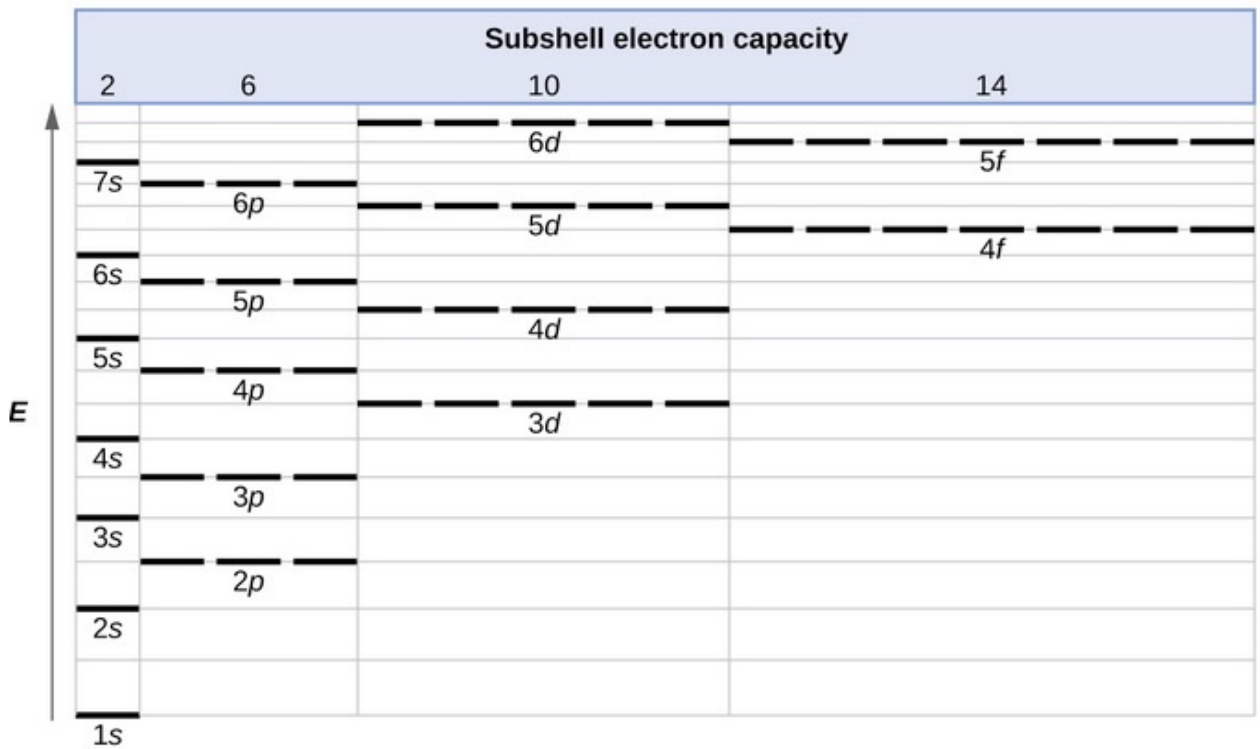
Distribution of electrons of an atom or molecule in atomic molecular orbitals

Electron configurations describe electrons as moving independently in an orbital, mathematically predicted by average orbital fields

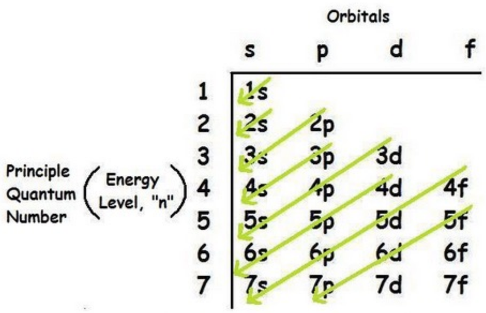
Knowing electron configurations is useful in understanding structure

Element	Electron configuration
H	$1s^1$
He	$1s^2$
Li	$1s^2$ 2s1
Be	$1s^2\ 2s^2$
Bo	$1s^2\ 2s^2\ 2p^1$
C	$1s^2\ 2s^2\ 2p^2$
N	$1s^2\ 2s^2\ 2p^3$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
O	$1s^2\ 2s^2\ 2p^6$

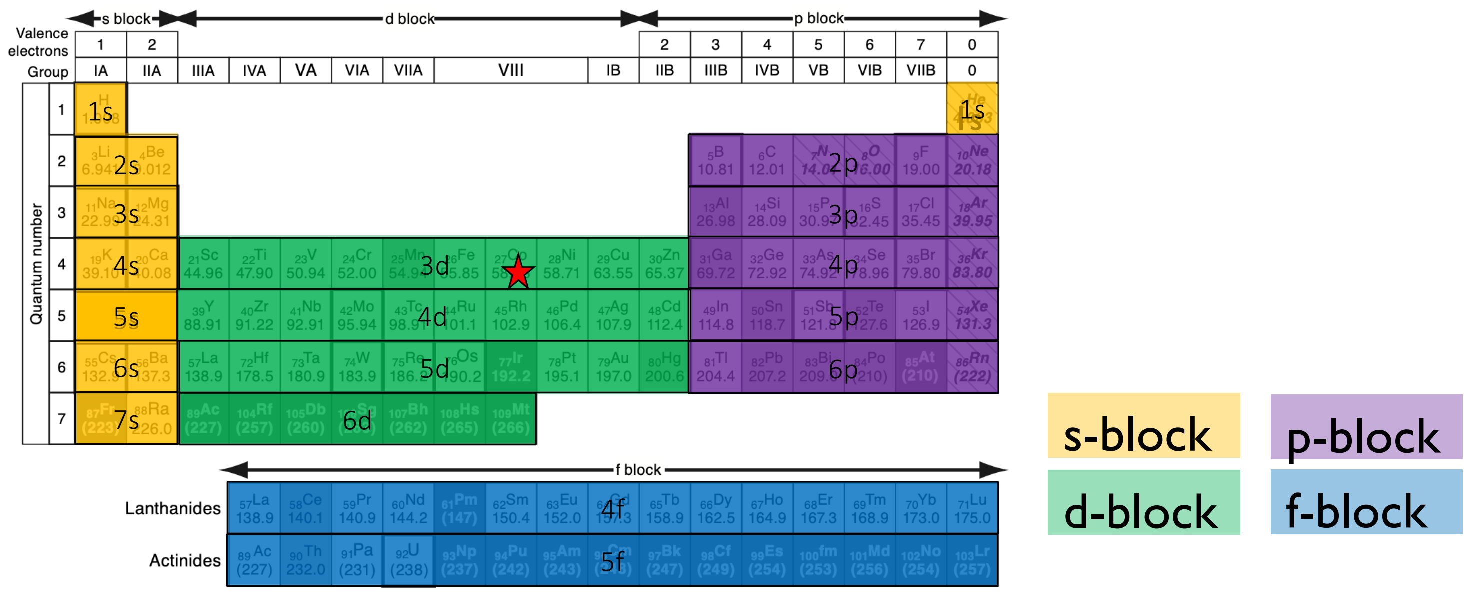
- Electron shells are filled in order of increasing energy (and emptied in the same manner)



What is the electron configuration of Cobalt?



Order: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p



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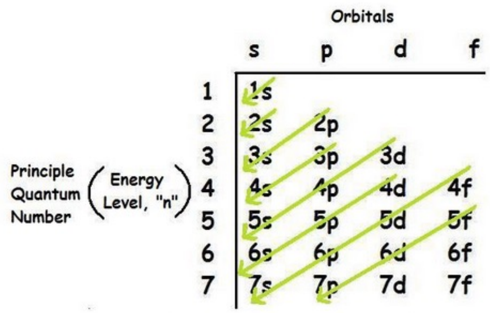
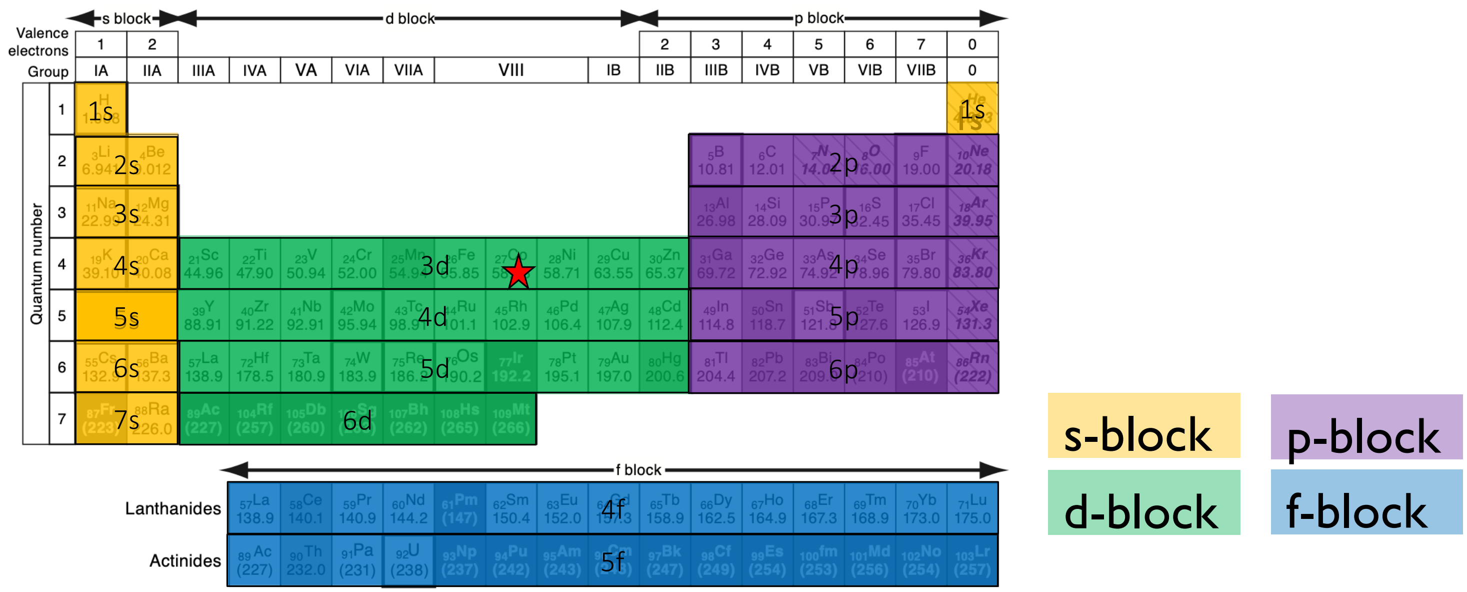


Order: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

What is the electron configuration of Cobalt?

- Row number 4: n=4 for s-orbital
- Energy level for d orbital is n-1, so n=3 for d-orbital
- Co: [Ar] $4s^2$ $3d^7$



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Common oxidation states of elements

Periodic Table with Oxidation Numbers

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H -1,+1																	He -
2	Li +1	Be +2											B +3	C -4 to +4	N -3,+3 +5	O -2	F -1	Ne -
3	Na +1	Mg +2											Al +3	Si -4,+4	P -3,+3 +5	S -2,+2 +4,+6	Cl -1,+1,+3 +5,+7	Ar -
4	K +1	Ca +2	Sc +3	Ti +3,+4	V +2,+3 +4,+5	Cr +3,+6	Mn +2,+4 +7	Fe +2,+3 +6	Co +2,+3	Ni +2	Cu +1,+2	Zn +2	Ga +3	Ge -4,+2 +4	As -3,+3 +5	Se -2,+2 +4,+6	Br -1,+1,+2 +3,+5,+7	Kr +2
5	Rb +1	Sr +2	Y +3	Zr +4	Nb +5	Mo +4,+6	Tc +4,+7	Ru +2,+3 +4	Rh +3	Pd +2,+4	Ag +1	Cd +2	In +3	Sn +2,+4	Sb -3,+3 +5	Te -2,+4 +6	I -1,+1,+3 +5,+7	Xe +2,+4 +6
6	Cs +1	Ba +2	*	Hf +4	Ta +5	W +4,+6	Re -1,+2,+4 +6,+7	Os +2,+3,+4 +6,+8	Ir +3,+4	Pt +2,+4	Au +1,+3	Hg +1,+2	Tl +1,+3	Pb +2,+4	Bi +3	Po +2,+4	At -1,+1	Rn -
7	Fr +1	Ra +2	**	Rf +4	Db +5	Sg +6	Bh -	Hs -	Mt -	Ds -	Rg -	Cn -	Nh -	Fl -	Mc -	Lv -	Ts -	Og -

Lanthanide Series*	La +3	Ce +3,+4	Pr +3	Nd +3	Pm +3	Sm +3	Eu +2,+3	Gd +3	Tb +3	Dy +3	Ho +3	Er +3	Tm +3	Yb +3	Lu +3
Actinide Series**	Ac +3	Th +4	Pa +5	U +4,+6	Np +5	Pu +4	Am +3	Cm +3	Bk +3	Cf +3	Es +3	Fm +3	Md +3	No +2	Lr +3

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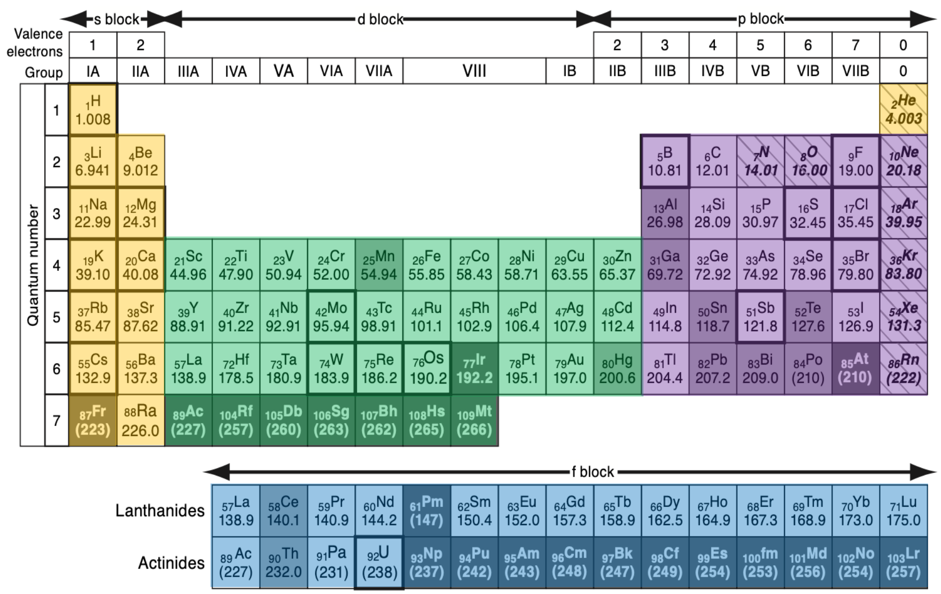
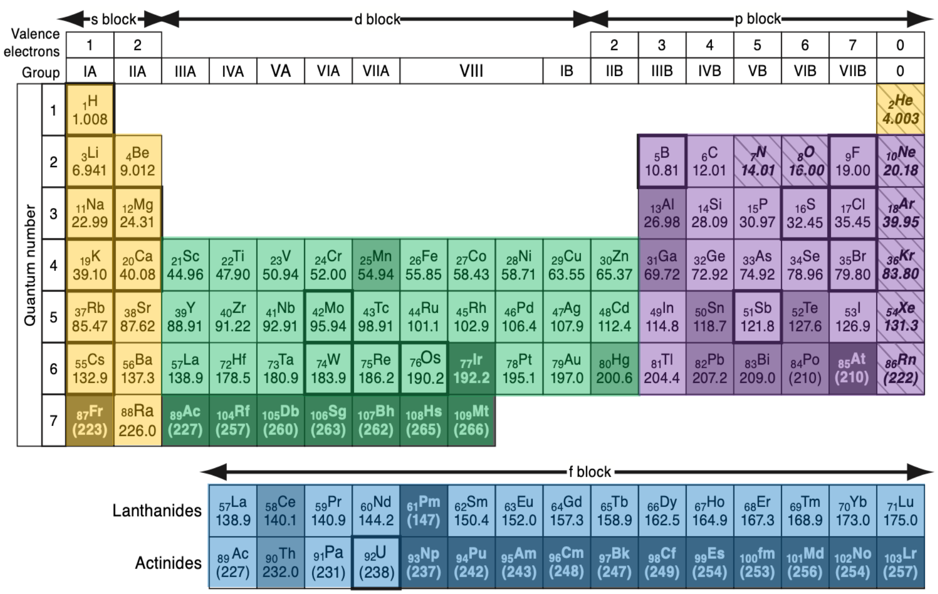
Determining the oxidation number of elements and compounds



1. In uncombined or free elements (not ionized), each atom has an oxidation number of 0.
   - e.g., all of the atoms in these molecules: H_2, Na, S_8, O_2, P_4.
2. In simple ions (*i.e.*, charged species which contain only one atom), the oxidation number is equal to the charge on the ion.
   - e.g., Na and K only form +1 ions; thus, their oxidation numbers are +1 in all compounds

Determining the oxidation number of elements and compounds



3. Oxidation state of certain elements is the same in (almost) all of their compounds

e.g.,

Group 1A elements: Li, Na, K, Rb, Cs = +1

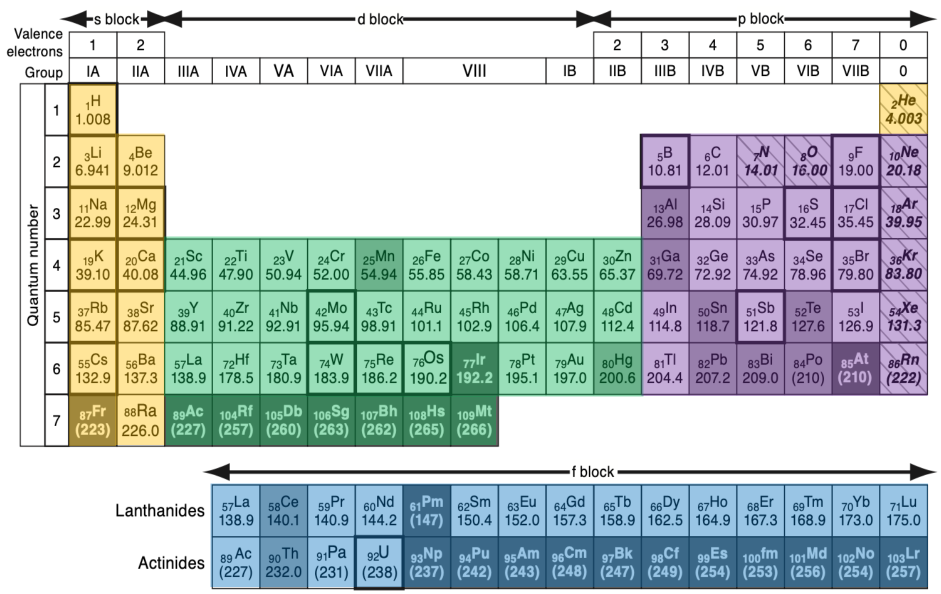
Group 2A elements: Be, Mg, Ca, Sr, Ba, Ra = +2

Group VIIb elements: F, Cl, Br, I, At = -1 in binary compounds

Oxygen is almost always -2 (except when bonded to O or F)

H is almost always +1 (except with a metal; NaH, CaH_2 is -1)

Determining the oxidation number of elements and compounds



4. Oxidation numbers must be consistent with conservation of charge. e.g., The sum of charge must be 0 for neutral molecules.

For H_2O:

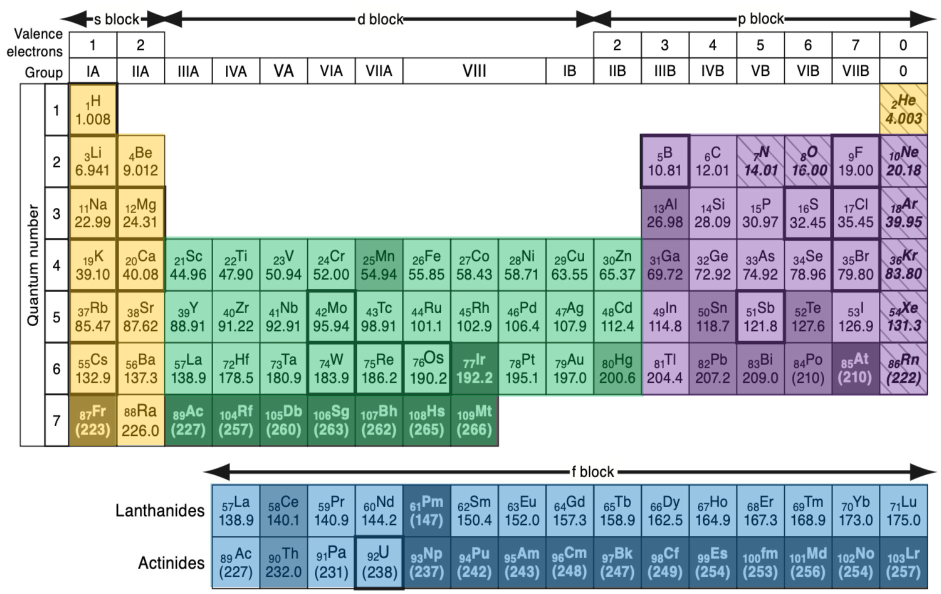
H: oxidation number is +1

O : oxidation number is –2

Net charge = 2(+1) + 1(-2) = 0

For MnO_4^- : O= -2x4= -8, thus Mn= 8-1= 7

Determining the oxidation number of elements and compounds



5. Fractional oxidation numbers are possible. e.g., in $Na_2S_4O_6$ (*sodium tetrathionate*), S has an oxidation number of +10/4:

   O: 6(-2) = -12

   Na: 2(+1) = 2

   Residual = -10, which must be balanced by S:

   S: 4(+10/4) = +10

6. The oxidation number is designated by:

   Arabic number below the atom, or

   Roman numeral or arabic number after the atom (in parentheses)

Organic matter formation

RKR equation:

$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O$ + trace elements (e.g. *Fe, Zn, Mn…*) → $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2$

- Reduction half reactions:

$$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$$

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$$

Oxidation state:

CO_2: **C**H_2O:

NO_3^-: **N**H_3:

- Oxidation half reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

H_2**O**: **O**$_2$:

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Oxidation state:

CO_2:	+IV	**C**H_2O:	0
NO_3^-:	+V	**N**H_3:	-III

- Oxidation half reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

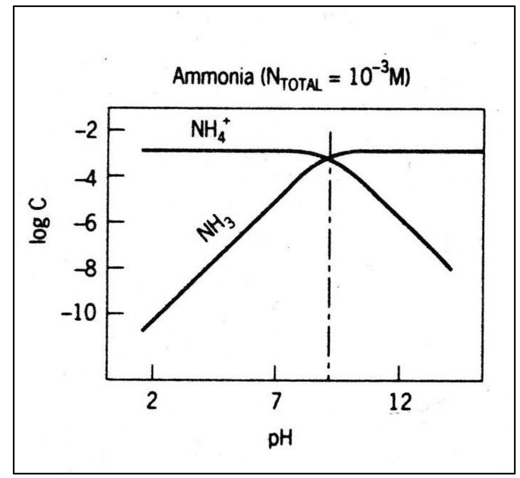
H_2**O**:	-II	**O**$_2$:	0

Nitrogen chemical speciation

- Redox-dependent speciation of dissolved forms:

	Species	Oxid State of N
Dissolved Inorganic Nitrogen (DIN)	NO_3^- (*nitrate*)	+V
	NO_2^- (*nitrite*)	+III
	N_2O (*nitrous oxide*)	+I
	N_2 (*dinitrogen*)	0
	NH_4^+	-III
Dissolved Organic Nitrogen (DON)	Organic-N	-III

(e.g., Urea $H_2N\text{-}CO\text{-}NH_2$)



NH_4^+ (*ammonium ion*)

NH_3 (*ammonia*)

Oxidation states for important N, S, and C compounds

Nitrogen Compounds		Sulfur Compounds		Carbon Compounds	
Substance	Oxidation States	Substance	Oxidation States	Substance	Oxidation States
NH_4^+	N = −III, H = +I	H_2S	S = −II, H = +I	HCO_3^-	C = +IV
N_2	N = 0	$S_8(s)$	S = 0	HCOOH	C = +II
NO_2^-	N = +III, O = −II	SO_3^{2-}	S = +IV, O = −II	$C_6H_{12}O_6$	C = 0
NO_3^-	N = + V, O = −II	SO_4^{2-}	S = +VI, O = −II	CH_3OH	C = −II
HCN	N = −III, C = +II, H = +I	$S_2O_3^{2-}$	S = +II, O = −II	CH_4	C = −IV
SCN^-	S = −I, C = +III, N = −III	$S_4O_6^{2-}$	S = +2.5, O = −II	C_6H_5COOH	C = −2/7
		$S_2O_6^{2-}$	S = +V, O = −II		

Procedure for balancing redox reactions in aqueous solutions

1. Identify the principal reactants and products, that is, species other than H^+, OH^-, and H_2O, in the oxidation half-reaction and the reduction half-reaction and write each half-reaction in crude form.
2. Then to obtain balanced half-reactions, balance the atoms other than hydrogen and oxygen by multiplying the reactants or products by appropriate integers.
3. Balance the oxygen using H_2O.
4. Balance the hydrogen with H^+.
5. Balance the charge with electrons.
6. Multiply each half-reaction by an appropriate integer so that both contain the same number of electrons.
7. Add the two balanced half-reactions.
8. Steps 1 to 7 will sometimes produce an equation that has H^+ as a reactant or a product. If it is known that the reaction takes place in alkaline solution, add the reaction for dissociation of water to the balanced equation to eliminate H^+ and form H_2O.

Example 7-1

Balance the reaction in which ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}) by permanganate (MnO_4^-), which itself is reduced to manganese dioxide ($MnO_{2(s)}$). The reaction takes place in alkaline solution.

Solution

1. The reactants and products are

$$Fe^{2+} \rightleftharpoons Fe^{3+} \qquad \text{(oxidation)}$$
$$MnO_4^- \rightleftharpoons MnO_{2(s)} \qquad \text{(reduction)}$$

2.

3.

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$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$
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The equation is now balanced. In some instances it may be desirable to modify it to take into account other reactions and to make it more useful, as shown in steps (7) and (8).

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7. The reaction takes place in alkaline solution. Add the water dissociation equation to eliminate H^+ as a reactant,

$$4\cancel{H^+} + 3Fe^{2+} + MnO_4^- \rightleftharpoons 3Fe^{3+} + MnO_{2(s)} + 2H_2O$$

$$4H_2O \rightleftharpoons 4\cancel{H^+} + 4OH^-$$

$$\overline{2H_2O + 3Fe^{2+} + MnO_4^- \rightleftharpoons 3Fe^{3+} + MnO_{2(s)} + 4OH^-}$$

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$$3 \times (Fe^{2+} \rightleftharpoons Fe^{3+} + e^-)$$

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$$\frac{4H_2O \rightleftharpoons 4\cancel{H^+} + 4OH^-}{2H_2O + 3Fe^{2+} + MnO_4^- \rightleftharpoons 3Fe^{3+} + MnO_{2(s)} + 4OH^-}$$

8. Further, we know that in alkaline solution, Fe^{3+} and OH^- will combine to form $Fe(OH)_{3(s)}$. Adding this reaction, we obtain the final equation.

Q: How do we know that this happens?

$$2H_2O + 3Fe^{2+} + MnO_4^- \rightleftharpoons 3Fe^{3+} + MnO_{2(s)} + 4OH^-$$

$$\frac{3 \times (Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_{3(s)})}{2H_2O + 3Fe^{2+} + MnO_4^- + 5OH^- \rightleftharpoons 3Fe(OH)_{3(s)} + MnO_{2(s)}}$$

This last step would not have been necessary if in step (1) we had taken $Fe(OH)_{3(s)}$ as the product rather than Fe^{3+}.

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Oxidation of organic matter

Oxidation process	Unbalanced equation	Balanced equation	ΔG^0 (kJ/mol) (1 mol CH_2O)
Aerobic respiration	$CH_2O + O_2 = CO_2(g)$		-500.4
Denitrification	$CH_2O + NO_3^- = CO_2(g) + N_2$		
Manganese respiration	$CH_2O + MnO_2(s) = CO_2(g) + Mn^{2+}$		
Iron respiration	$CH_2O + Fe(OH)_3(s) = CO_2(g) + Fe^{2+}$		
Sulfate reduction	$CH_2O + SO_4^{2-} = CO_2(g) + HS^-$		
Methane fermentation	$CH_2O = CO_2(g) + CH_4(g)$		

- Steps:
  - Balance equation
  - Calculate Gibbs free energy
  - What do we learn about energy gain from organic matter oxidation?

Oxidation of organic matter

- What do we learn about energy gain from organic matter oxidation?

Oxidation process	Unbalanced equation	Balanced equation	ΔG^0 (kcal/mol)	ΔG^0 (kJ/mol)	ΔG^0 (kJ/mol) (1 mol CH_2O)
Aerobic respiration	$CH_2O + O_2 = CO_2(g)$	¼ CH_2O + ¼ O_2 = ¼ $CO_2(g)$ + ¼ H_2O	-29.9	-125.1	-500.4
Denitrification	$CH_2O + NO_3^- = CO_2(g) + N_2$	¼ CH_2O + 1/5 NO_3^- + 1/5H^+ = ¼ $CO_2(g)$ + 1/10 N_2 + 7/20 H_2O	-28.4	-118.8	-475.3
Manganese respiration	$CH_2O + MnO_2(s) = CO_2(g) + Mn^{2+}$	¼ CH_2O + ½ $MnO_2(s)$ + H^+= ¼ $CO_2(g)$ + ½ Mn^{2+} + ¾ H_2O	-24.6	-102.9	-411.7
Iron respiration	$CH_2O + Fe(OH)_3(s) = CO_2(g) + Fe^{2+}$	¼ CH_2O + $Fe(OH)_3(s)$ +2H^+= ¼ $CO_2(g)$ + Fe^{2+} + 11/4 H_2O	-12.6	-52.7	-210.9
Sulfate reduction	$CH_2O + SO_4^{2-} = CO_2(g) + HS^-$	¼ CH_2O + 1/8 SO_4^{2-} +1/8 H_+= ¼ $CO_2(g)$ + 1/8 HS^- +1/4 H_2O	-6.1	-25.5	-102.1
Methane fermentation	$CH_2O = CO_2(g) + CH_4(g)$	¼ CH_2O = 1/8 $CO_2(g)$ + 1/8 $CH_4(g)$	-5.6	-23.4	-93.7

What do we learn about energy gain from organic matter oxidation?

- The higher the energy yield, the greater the benefit to organisms that harvest the energy
- In general:
  - There is a temporal and spatial sequence of energy harvest during organic matter oxidation
  - Sequence is from the use of high-yield electron acceptors to the use of low-yield electron acceptors

The bottom line: Oxic-anoxic transitions

There is a principle difference between gradients of compounds used for biomass synthesis and those needed for energy conservation, such as oxygen.

Nutrient limitation leads to a decrease of metabolic activity, but absence of an energy substrate causes a shift in the composition of a microbial community, or forces an organism to switch to a different type of metabolism.

Brune et al. 2000

Readings

- Emerson and Hedges: Ch.3
  - Thermodynamics, activity, equilibrium constants, Redox basics

- More detail (Laulima):
  - Snoeyink and Jenkins, Water Chemistry, Ch. 3 (on Laulima)

  - Appendix 1: Thermodynamics and calculation of energy yields of metabolic processes (on Laulima) from Bacterial Biogeochemistry: The Ecophysiology of Mineral Cycling by Fenchel, King, and Blackburn