<u>Redox</u> – Short for **Oxidation – Reduction**

<u>Redox identification</u>

Charge on <u>neutral</u> atom or molecule = 0

[redacted] – Charge gets more **+** (loses electrons)

[redacted] – Charge gets more **–** (gains electrons)

Reduction (charge decreases)

E.g.) $Pb^{2+}_{(aq)} + Mg^{0}_{(s)} \rightarrow Pb^{0}_{(s)} + Mg^{2+}_{(aq)}$

Oxidation (Charge increases)

<u>Question</u>

In the reaction:

$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$

<u>Identify:</u>

a) The Oxidizing Agent: Cl_2
b) The species being oxidized: Fe^{2+}
c) The reducing agent: Fe^{2+}
d) The species being reduced: Cl_2
e) The species gaining electrons: Cl_2
f) The species losing electrons: Fe^{2+}
g) The product of oxidation Fe^{3+}
h) The product of reduction Cl^-

<u>Do Ex. 1 (a-e) pp. 192 SW</u>

<u>Half-Reactions</u>

-Redox reactions can be broken up into oxidation & reduction half reactions.

e.g.) Redox rx: $Pb^{2+}_{(aq)} + Zn_{(s)} \rightarrow Pb_{(s)} + Zn^{2+}_{(aq)}$

$Pb^{2+} + 2e^- \rightleftharpoons Pb$

The Pb^{2+} (loses/gains) gains 2 electrons.

<u>Reduction Half-rx:</u> $Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$

Electrons on the LEFT side (or GER)
Means REDUCTION

Write the **oxidation** half reaction for the following redox rx.

$Pb^{2+}_{(aq)} + Zn_{(s)} \rightarrow Pb_{(s)} + Zn^{2+}_{(aq)}$

Ox half rx: $Zn \rightarrow Zn^{2+} + 2e^-$

(In oxidation reactions, e⁻'s are lost and are found on the product side.) (LEO)

Note: Half-rx's always have e⁻'s, redox (oxidation-reduction) reactions never show e⁻'s!

Given the redox reaction:

$F_{2(g)} + Sn^{2+}_{(aq)} \rightarrow 2F^-_{(aq)} + Sn^{4+}_{(aq)}$

Write the **oxidation** half-rx: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

Write the **reduction** half-rx: $F_2 + 2e^- \rightarrow 2F^-$

Do ex. 2 a-c on p. 192 SW

Oxidation numbers

-Real or apparent charge on an atom in a molecule or ion

In SW. p. 193 -the charge that an atom would possess if the species containing the atom was made up of ions (even if it's not!)

Rules to find oxidation number of an atom

1) **In elemental form**:

(Single atoms of monatomic elements) or (diatomic molecules of diatomic elements)

Oxidation number of atoms = 0

Eg) $\underbrace{\text{Mn, Cr, } N_2\text{, } F_2\text{, Sn, } O_2\text{, etc.}}$

The oxidation # of each atom = 0

2) In **monatomic ions**: oxidation # = charge

Eg) In Cr^{3+} -oxidation # of Cr = +3

S^{2-} -oxidation # of S = -2

3) In **ionic compounds**

a) the oxidation # of **Alkali Metals** is always **+1**

eg) $\underline{Na}Cl$ $\underline{K_2}CrO_4$

Ox # of Na & K = +1

b) the oxidation # of **Halogens** when at the end (right side) of the formula is always **–1**

eg) $Ca\mathbf{Cl_2}$ $Al\mathbf{Br_3}$ $K\mathbf{F}$

Ox # of Cl, Br and F = -1

Note: Halogens are **not** always –1! (Only when it is written **last** in formula.)

4) In **molecules** or **polyatomic ions**:

a) Ox. # of **oxygen** is almost always **–2**

e.g.) $\underbrace{K\underline{O}H \quad Cr\underline{O_4}^{2-} \quad Li_3P\underline{O_4}}_{\text{Ox \# of O is –2}}$

b) An exception is **Peroxides** in which ox. # of O = **-1**

Hydrogen Peroxide: H_2O_2
Alkali Peroxides: Na_2O_2 } Ox # of O's = -1

(Remember, "O" in O_2 has an Ox. # of Zero**)**

5) In **molecules** or **ions**:

a) **Hydrogen** is almost always **+1**

e.g.) $\underline{H}NO_3$ $\underline{H_2}SO_4$ $\underline{H}PO_4^{2-}$ } Every "H" has an ox # of +1

b) An exception is **metallic hydrides**, which have an ox # of **-1**

e.g.) $Na\underline{H}$ $Ca\underline{H_2}$ (In each one of these Ox. # of H = -1)

(What is the ox # of "H" in NH_3? +1 **)**

(And remember ox # of "H" in H_2 = 0 **)**

e.g.) Find ox # of P in Li_3PO_4

$Li_3\,P\,O_4$

$3(+1) + x + 4\,(-2) = 0$

$3 + x - 8 = 0$

$x - 5 = 0$

$x = \mathbf{+5}$

Find Ox # of the underlined element in each of the following:

a) $NaH_2\underline{P}O_4$ (+1 +2 +5 -8) __+5__ b) $Na_2\underline{O_2}$ (+2 -2) __-1__ c) $K\underline{H}$ __-1__

Find the ox # of **Fe** in Fe_3O_4

$+8/3$

$\overset{+8}{Fe_3}\,\overset{-8}{O_4}$

Find the ox # of **As** in As_3O_5

$+10/3$

$\overset{+10}{As_3}\,\overset{-10}{O_5}$

Read p. 193-194 of SW. Do Exercise 3 on p. 194 of SW.

<u>Changes in oxidation numbers</u>

When an atom's **oxidation # is <u>increased</u>**, it is **<u>oxidized</u>**.

e.g.) Half-rx: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

<u>More complex:</u>

-When Mn^{3+} changes to MnO_4^-, is Mn oxidized or reduced?

$Mn^{3+} \rightarrow \overset{+7\ -8}{MnO_4^-}$

- What is the ox # of Mn before & after the reaction? Before __+3__ After __+7__

- The ox # of Mn is (de/in)__in__creased.

- In this process, Mn is (*oxidized/reduced*)__oxidized__

Note:

- R.A.O., the **reducing agent** is **oxidized**
- The species **SO_2** is acting as the **reducing agent**.
- The element **S** is being oxidized so **S is losing electrons**.

Look at the species with Cl:

+5 -6

ClO_3^- → Cl^-

Ox. # of Cl = **+5**	Ox. # of Cl = **-1**

Decrease in ox # so Cl is being **reduced**

Therefore, the **species** acting as the **oxidizing agent** is ClO_3^-.

(They may also ask for the **atom** acting as the **oxidizing agent**
– this would be **Cl** in ClO_3^-)

Eg. –given the reaction:

$$2CrO_4^{2-} + 3HCHO + 2H_2O \rightarrow 2Cr(OH)_3 + 3HCOO^- + OH^-$$

Find: a) The species being oxidized
c) The reducing agent
d) The species being reduced
e) The oxidizing agent
f) The species losing electrons
g) The species gaining electrons

Notes:
- For hydrocarbons it's best to rewrite them as simple molecular formulas.
- All O's are in molecules or ions, no O_2 & no peroxides so O remains unchanged as -2
- All H's are in molecules or ions, no H_2 or metallic hydrides so H remains unchanged as +1
- The atoms to check for changes are C and Cr.

$$\overset{0 \xrightarrow{\text{Oxidation}} +2}{}$$
$$2\underline{Cr}O_4^{2-} + 3\underline{C}H_2O + 2H_2O \rightarrow 2\underline{Cr}(OH)_3 + 3H\underline{C}O_2^- + OH^-$$
$$+6 \xrightarrow[\text{Reduction}]{} +3$$

So...
a) the species being **oxidized** is (CH_2O) HCHO (inc. in ox #)
b) the **reducing agent** is (CH_2O) HCHO (RAO)
c) The species being **reduced** is CrO_4^{2-}(decrease in ox #)
d) The **oxidizing agent** is CrO_4^{2-} (OAR)
e) The species **losing e^-'s** is (CH_2O) HCHO (LEO)
f) The species **gaining e^-'s** is CrO_4^{2-} (GER)

+7 -8 – +4 -4

MnO_4 MnO_2

Given the redox reaction:

+6 -8 +3 -8 +4 -4

$$2MnO_4^- + 3C_2O_4^{2-} + 4H_2O \rightarrow 2MnO_2 + 6CO_2 + 8OH^-$$

Find:

a) The species being reduced: MnO_4^-.
b) The species undergoing oxidation: $C_2O_4^{2-}$.
c) The oxidizing agent: MnO_4^-.
d) The reducing agent: $C_2O_4^{2-}$.
e) The species gaining electrons: MnO_4^-.
f) The species losing electrons: $C_2O_4^{2-}$.

Given the balanced redox reaction:

0 +1+5-6 +4-4 +2-2

$$3S + 4HNO_3 \rightarrow 3SO_2 + 4NO + 2H_2O$$

Find:

a) The oxidizing agent: HNO_3.
b) The reducing agent: S.
c) The species being reduced: HNO_3.
d) The species being oxidized: S.
e) The species losing electrons: S.
f) The species gaining electrons: HNO_3.
g) The product of oxidation: SO_2.
h) The product of reduction: NO.

Given the following:

0 -1 +1 +5 -6

$$6Br_2 + 12KOH \rightarrow 10KBr + 2KBrO_3 + 6H_2O$$

Find:

a) The oxidizing agent: Br_2.
b) The reducing agent: Br_2.
c) The species undergoing oxidation: Br_2.
d) The species being reduced: Br_2.
e) The product of oxidation: $KBrO_3$.
f) The product of reduction: KBr.

Using oxidation numbers to identify half-reactions

They don't have to be balanced

+3 -4 +5 -6

e.g.) If $NO_2^- \rightarrow NO_3^-$ is an example of (oxidation or reduction?) oxidation.

("O" does not change it's ox # (no O_2 or peroxides)) so find ox # of **N** on both sides.

$\underline{N}O_2^- \rightarrow \underline{N}O_3^-$

Ox # = +3 Ox # = +5

Δ O.N. = +2 ← Since ox # increases, this is an *oxidation* e.g.) $H_2O_2 \rightarrow H_2\mathbf{O}$ ← This time "O" is the element changing ox #

Ox # = -1   Ox # = -2

Δ O.N. = -1 ← Ox # if "O" **decreases** so this is a **reduction**

Find the Δ O.N. of the element in which it changes and identify each as an oxidation or reduction

+6
+3 -6
Fe_2O_3

+8
+8/3 -8
Fe_3O_4

+3 +5 -8
H_3PO_4

a) $C_2H_5OH \rightarrow CH_3COOH$ C (-2) → C (0)   Δ O.N. = +2   oxidation

b) $Fe_2O_3 \rightarrow Fe_3O_4$ Fe (+3) → Fe (+8/3)   Δ O.N. = -1/3   reduction

c) $H_3PO_4 \rightarrow P_4$ P (+5) → P (0)   Δ O.N. = -5   reduction

(P_4 is the elemental form of phosphorus)

d) $CH_3COOH \rightarrow CH_3COH$ C (0) → C (-1)   Δ O.N = -1   reduction

0 +4 -4 $C_2H_4O_2$ -2 +4 -2 C_2H_4O

NOTE: When asked if a given reaction is a redox or not:

Look for a change from **an element → compound** or **compound→ an element**

These will **<u>always</u>** be redox, because in **elemental form ox. # = 0** and in compounds usually **ox. # is not = 0**

$$\text{Zn} \xrightarrow{0 \,\to\, +2} \quad \text{Cl}_2 \xrightarrow{0 \,\to\, -1}$$

Eg.) Is the reaction: $Zn + Cl_2 \rightarrow ZnCl_2$ a redox reaction?

Answer: It must be because ΔON of Zn (0 → +2 = +2) and ΔON of Cl (0 → -1 = -1)

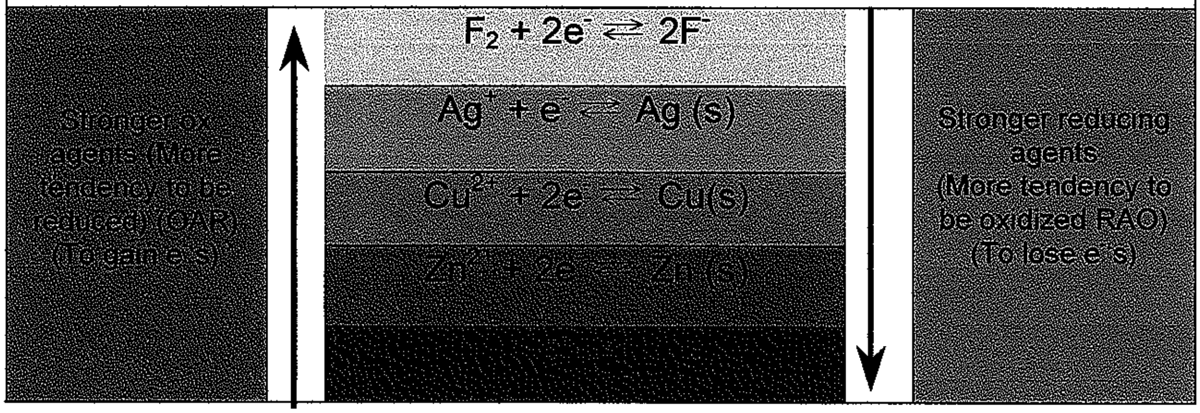
Do Exercises 4, 5 and 6 on p. 194-195 of SW.

Half-reactions and the reduction table

- Do Experiment 21-A

- Look at "Standard Reduction Table"

Ox agents on left + e⁻'s $\rightleftarrows$ Reducing agents on right



-So F_2 is a stronger ox agent than Ag+, etc.
-The strongest reducing agent on your chart is: Li(s)

Help in Hunting

- Solid metals mostly on bottom right (less active ones Ag, Au, farther up on the right side)
- Halogens (e.g. Cl_2) and oxyanions e.g. BrO_3^-, MnO_4^-, IO_3^- found near top left
- Some metal ions found on both sides e.g. Fe^{2+}, Sn^{2+}, Cu^+, Mn^{2+} can act as OA's or RA's

All the half-rx's are written as **reductions:**

e.g.) $F_2 + 2e^- \rightleftarrows 2F^-$
$Ag^+ + e^- \rightleftarrows Ag_{(s)}$

- The double arrow implies that **oxidation's** can also take place (reverse of reductions)

e.g.) reduction of Ag^+ (Same as table- single arrow)

Specifically just **reduction** → $Ag^+ + e^- \rightarrow Ag_{(s)}$

oxidation of Ag (**Reverse** of that on table- single arrow)

Specifically just **oxidation** → $Ag_{(s)} \rightarrow Ag^+ + e^-$

Write half-reactions for:
- Reduction of Pb^{2+} $Pb^{2+} + 2e^- \rightleftarrows Pb$
- Oxidation of Pb $Pb \rightleftarrows Pb^{2+} + 2e^-$
- Reduction of Sn^{2+} $Sn^{2+} + 2e^- \rightleftarrows Sn$
- Oxidation of Sn^{2+} $Sn^{2+} \rightleftarrows Sn^{4+} + 2e^-$

- Oxidation of Fe^{2+} $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$
- Reduction of Fe^{2+} $Fe^{2+} + 2e^- \rightleftharpoons Fe$
- Oxidation of Fe $Fe \rightleftharpoons Fe^{2+} + 2e^-$
- Reduction of acidified MnO_4- $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$
- Oxidation of H_2 $H_2 \rightleftharpoons 2H^+ + 2e^-$

Which is a stronger oxidizing agent: Ni^{2+} or Ag^+? Ag^+

Fe^{2+} or Cr^{3+}? Cr^{3+}

Must be on the left side when treating these as OA's

Sn^{2+} or Sn^{4+}? Sn^{4+}

Which is a stronger reducing agent: Sn^{2+} or Fe^{2+}? Sn^{2+}

Must look for these on the right side

Zn or Ba? Ba

Cl^- or Br^-? Br^-

Fe^{2+} or Au? Fe^{2+}

Which has a greater tendency to lose electrons, Ni or Zn? Zn (Reducing agent)
Which has a greater tendency to gain electrons, Fe^{3+} or Cr^{3+}? Fe^{3+} (O.A.)
Which solid metal has the least tendency to lose electrons? Au (R.A.)
Which solid metal has the greatest tendency to lose e^-'s? Li
Give the formula for an ion that is a stronger oxidizing agent that Ni^{2+}, but is weaker than Pb^{2+}? Sn^{2+}

Using the reduction table to predict which reactions are spontaneous

- An **oxidizing agent** will react **spontaneously** with (oxidize) a reducing agent **below it on the right**

Look at your reduction chart!		
$F_2(g) + 2e^- \rightleftharpoons 2F^-$	↓	F_2, the strongest OA, oxidize (react spontaneously with) all species below it on the right side from SO_4^{2-} all the way down to Li(s)
$S_2O_8 + 2e^- \rightleftharpoons 2SO_4^{2-}$		
$Li^+ + e^- \rightleftharpoons Li_{(s)}$		

Look at the 4th half rx from the bottom		
$K^+ + e^- \rightleftharpoons K_{(s)}$	↓	K^+ will oxidize only $Rb_{(s)}$, $Cs_{(s)}$ and $Li_{(s)}$, nothing else on the chart.
$Rb^+ + e^- \rightleftharpoons Rb_{(s)}$		
$Cs^+ + e^- \rightleftharpoons Cs_{(s)}$		
$Li^+ + e^- \rightleftharpoons Li_{(s)}$		

- A **reducing agent** on the right will react **spontaneously** with (reduce) any **oxidizing agent on the left above it**

e.g.) Li(s) (bottom right) will **reduce all species** on the **left** side except Li^+.
SO_4^{2-} (near top right) will reduce **only** F_2

- An OA on the left will **not** react spontaneously with a RA on the right above it!

e.g.) Au^{3+} will **not** oxidize (or react spontaneously with) SO_4^{2-}.

If a redox reaction is non-spontaneous, then the reverse reaction will be spontaneous!

e.g.) The reaction $Sr^{2+} + Ca_{(s)} \rightarrow Ca^{2+} + Sr_{(s)}$ is **non**-spontaneous because Ca is **above** Sr^{2+} on the **right** side.

But the rx: $Ca^{2+} + Sr_{(s)} \rightarrow Sr^{2+} + Ca_{(s)}$ **is** spontaneous because $Sr_{(s)}$ is **below** Ca^{2+} on the **right** side

Use the reduction table to answer the following questions:

a) Will Br_2 oxidize $Au_{(s)}$?......... No
b) Will $Pb_{(s)}$ reduce Fe^{2+}?........ No
c) Will Zn^{2+} react with Cr^{3+}?..... No
d) Will Mg^{2+} react with Cr^{3+}?.... No
e) Give the symbol of an ion that will oxidize $Mn_{(s)}$ but not $Cr_{(s)}$..... Zn^{2+}
f) Give the formula for a compound which will reduce Co^{2+} but will not reduce Fe^{2+}.................. H_2Se, Cr^{2+}, $H_2 + 2OH^-$ ($10^{-7}M$)
g) Which is a stronger reducing agent, Sn^{2+} or Fe^{2+}?(Hint – you must look for both on the right side)..... Sn^{2+}
h) Which is a stronger oxidizing agent, Cu^{+} or Sn^{2+}?(Hint – you must look for both on the left side)..... Cu^{2+}

Acidified solutions

-Any reactions on the table with $\mathbf{H^+}$ in them are **acidified** or **acid solutions.**

e.g.) Look at these: at E° = +1.51 (4^{th} from the top)

$$\underbrace{MnO_4^- + 8H^+}_{\text{Called acidified permanganate solution}} + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

Note: Names of many ions can be found on the ion table!

Give the E° corresponding to each of the following:

a) acidified iodate .... E° 1.20
b) acidified dichromate................. E° 1.23
c) acidified manganese (IV) oxide... E° 1.22
d) acidified bromate...................... E° 1.48
e) acidified perchlorate.................. E° 1.39
f) acidified oxygen gas.................. E° 1.23

using overpotential effect

Questions

a) Will neutral water oxidize Fe(s)? NO Cr(s)? No Na(s)? Yes
b) Will neutral water reduce Au^{3+}? Yes Ag^+? No
c) Will acidified permanganate oxidize SO_4^{2-}? No Br^-? Yes Zn? Yes
d) Will nitric acid react with Ag(s)? Yes Au(s)? No I^- Yes Cl^-? No
e) Will nitric acid react with Fe^{2+} Yes
f) Will nitric acid react with Hg to form N_2O_4? No
g) Will nitric acid react with Hg to form NO? Yes
h) Can you safely put a gold ring in acidified dichromate solution? Yes What about acidified bromate solution? Yes
i) If Cl_2 gas is bubbled into water, will it all remain as Cl_2, or will some be converted to Cl^-? No

Finding products of spontaneous reactions

eg) Given $Sn^{4+} + H_2S$ – find the products

See the table at +0.15v and +0.14v

$Sn^{4+} + 2e^- \rightleftarrows Sn^{2+}$ + 0.15v

$S(s) + 2H^+ + 2e^- \rightleftarrows H_2S$ + 0.14v

The **higher** reaction will be **reduction** (→), the lower reaction will proceed to the **left** (←) and be an **oxidation**.

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$

$S(s) + 2H^+ + 2e^- \leftarrow H_2S$ (**reversed**! Lower one is **reversed**-is an **oxidation**)

-So the **products** are Sn^{2+}, S, and H^+

(at this point don't worry about coefficients yet.)

$Sn^{4+} + H_2S \rightleftarrows S + 2H^+ + Sn^{2+}$

Questions

a) What are the products of the reaction of acidified hydrogen peroxide (H_2O_2) and bromide (Br^-)? $H_2O + Br_2$

using overpotential effect

b) What are the products of the reaction when neutral water reacts with:

Ca(s) $Ca^{2+} + H_2 + 2OH^-(10^{-7}M)$

Zn(s) $Zn^{2+} + H_2 + 2OH^-(10^{-7}M)$

Br_2 NR

Acidified MnO_2 NR

Fluorine gas $2F^- + \frac{1}{2} O_2 + 2H^+(10^{-7}M)$

Read SW p. 195-199

Do Ex 7-12 p. 199-200 SW