Oxidation-Reduction Reactions (REDOX)

involves the transfer of electrons

ex. $2\,Na_{(s)} + Cl_{2(g)} \longrightarrow 2\,NaCl$

$Na \xrightarrow{e^-} Cl \rightarrow Na^+ Cl^-$

Classic example

electron will experience stronger attraction force

ex. $CH_{4(g)} + 2\,O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

- Covalent compounds
- Need to use oxidation states

$2\delta^-$ O

δ^+ H   H δ^+

attracted to O

assumption in oxidation state $\Longrightarrow$

takes electronegativity to an extreme

O^{2-}

H^+ H^+

as if it were ionic

ex. SF_6

$+6$ $\quad$ $-1\,(6)$

$2+$ (charge)

$+2$ (oxidation state)

ex. NO_3^-

$+5$ $\quad$ $-2\,(3)$

not $+6$ cuz '-1' charge

ex. $H^+ClO_4^-$

$+1$ $\quad$ $+7$ $\quad$ $-2\,(4)$

ex. $Na_2^{2+}Cr_2O_7^{2-}$

$+1\,(2)$ $\quad$ $+6\,(2)$ $\quad$ -14

ex. Fe_3O_4

$+\frac{8}{3}\,(3)$ $\quad$ $-2\,(4)$

ex. $CH_{4\,(g)} + 2\,O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2H_2O_{(l)}$

CH_4: -4 $\quad$ $+1\,(4)$

O_2: 0 pure element

CO_2: $+4$ $\quad$ $-2\,(2)$

H_2O: $+1\,(2)$ $\quad$ -2

LOSS OF $8\,e^-$

GAIN of $8\,e^-$ (each Oxygen gains $2\,e^-$)

ex. $Fe_{(s)} + Cu^{2+}SO_4^{2-}{}_{(aq)} \longrightarrow Fe^{2+}SO_4^{2-}{}_{(aq)} + Cu_{(s)}$

Fe: 0

$CuSO_4$: $+2$ $\quad$ $+6$ $\quad$ $-2\,(4)$

$FeSO_4$: $+2$ $\quad$ $+6$ $\quad$ -8

Cu: 0

Reducing Agent

Loss of $2\,e^-$ (oxidation)

Oxidizing Agent

Gain of $8\,e^-$ (reduction)

what undergoes oxidation is known as the reducing agent

OIL Oxidation involves loss of e^-

RIG Reduction involves gain of e^-

Balancing REDOX RXNS

OXIDATION STATES METHOD

Only works for rxns in the solid state (s)

$$3\,MnO_{2(s)} + Al_{(s)} \rightarrow Mn_{(s)} + 2Al_2O_{3(s)}$$

+4   -4   0   0   +3(2)   -2(3)

GAIN OF 4 e^- (red)

LOSS OF 3 e^- (ox)

Doesn't match (e^- gained needs to match e^- lossed)

HALF-REACTION METHOD

$$MnO_{4\,(aq)}^{-} + SO_{3\,(aq)}^{2-} \rightarrow MnO_{2\,(aq)} + SO_{4\,(aq)}^{2-}$$

+7   -2(4)   +4   -2(3)   +4   -2(2)   +6   -2(4)

Reduction

Oxidation

Break into 2 parts

1) Balance all elements except O and H

2) Balance Oxygen using H_2O molecules

3) Balance Hydrogens using H^+ ions

4) Balance charges using electrons.

5) Add up the 1/2 rxns making sure electrons exchanged are matching.

OX 1/2	RED 1/2
$H_2O + SO_3^{2-} \rightarrow 2e^- + SO_4^{2-} + 2H^+$	$3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$
	x2
• $3H_2O + 3SO_3^{2-} \rightarrow \cancel{6e^-} + 3SO_4^{2-} + 6H^+$	$\cancel{6e^-} + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O$

$$3H_2O + 3SO_3^{2-} + 8H^+ + 2MnO_4^- \rightarrow 3SO_4^{2-} + 6H^+ + 2MnO_2 + 4H_2O$$

September 21, 2016

$$MnO_{4\,(aq)}^- + Fe^{2+}_{(aq)} \xrightarrow{ACID} Fe^{3+}_{(aq)} + Mn^{2+}$$

Mn: +7, O: −2(4), Fe^{2+}: +2, Fe^{3+}: +3, Mn^{2+}: +2

Gain of 5 e^- Reduction

Loss of an e^- oxidation

Ox. 1/2	Red. 1/2
$5\left(Fe^{2+} \rightarrow Fe^{3+} + e^-\right)$ $5Fe^{2+} \rightarrow 5Fe^{3+} + \cancel{5e^-}$	$+7 \qquad\qquad +2$ $\cancel{5e^-} + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$$5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$+17 \qquad\qquad\qquad +17$$

ex. __Basic__

$$MnO_{4\,(aq)}^- + Fe^{2+}_{(aq)} \xrightarrow[\text{BASIC}]{\cancel{\text{ACID}}} Fe^{3+}_{(aq)} + Mn^{2+}$$

$+7 \quad -2(4) \qquad +2 \qquad +3 \qquad +2$

Gain of 5 e^- Reduction

loss of an e^-

oxidation

All steps are identical except the end.

Which side has an excess of H^+?

$$8OH^- + 5Fe^{2+} + \underline{8H^+} + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O + 8OH^-$$

$$5Fe^{2+} + \cancel{8}_{4}H_2O + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + \cancel{4H_2O} + 8OH^-$$

* great for titrations b.c. we don't need an indicator, color changes by itself

Breathalizer test

Ethanol

$$H^+_{(aq)} + Cr_2O_7{}^{2-}{}_{(aq)} + C_2H_5OH_{(l)} \rightarrow Cr^{3+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

H: +1

Cr: +6, O: -2(7) Orange

C: -2(2), H: +1(5), O: -2, H: +1

Cr: +3 Green

C: +4, O: -2(2)

H: +1(2), O: -2

REDUCTION

OXIDATION

Sort of like spectators

LEAVE THEM OUT

Ox. ½	Red. ½
$3H_2O + C_2H_5OH \rightarrow 2CO_2 + 12H^+ + 12e^-$ 0 +12	$(6e^- + 14H^+ + Cr_2O_7{}^{2-} \rightarrow 2Cr^{3+} + 7H_2O)\times 2$ +12 +6 $12e^- + 28H^+ + 2Cr_2O_7 \rightarrow 4Cr^{3+} + 14H_2O$

$$\cancel{3H_2O} + C_2H_5OH + \cancel{28}\,{}_{16}H^+ + 2Cr_2O_7 \rightarrow 2CO_2 + \cancel{12H^+} + 4Cr^{3+} + \cancel{14}\,{}_{11}H_2O$$

+24   +24

ex. Peroxide, H_2O_2

$$H_2O_2 + Fe^{2+} \xrightarrow{acid} Fe^{3+} + ?\,H_2O$$

H: $+1(2)$, O: $-1(2)$; Fe^{2+}: $+2$; Fe^{3+}: $+3$

oxidized

Reduced

ex. $$H_2O_2 + MnO_4^- \xrightarrow{acid} 2\,Mn^{2+} + O_2$$

H: $+1(2)$, O: $-1(2)$; Mn: $+7$, O: $-2(4)$; Mn^{2+}: $+2$

Reduction

Oxidation

ex. $$Cl_2 + H_2O \longrightarrow HCl + HClO$$

Cl_2: 0; H: $+1(2)$, O: -2; HCl: $+1$, -1; $HClO$: $+1$, $+1$, -2

Reduction

Oxidation

Same species being both oxidized & reduced

called: DISPROPORTIONATION RXN.

(2 Cl in Cl_2, one oxidized, one reduced)

Remainder must acquire proper char

$$Pb_{(s)} + PbO_{2\,(s)} + 2\,H_2^{+}\cancel{SO_4}^{2-}{}_{(aq)} \longrightarrow Pb^{2+}\cancel{SO_4}^{-2}{}_{(s)}$$

0	+4	-2(2)	+1(2)	+6	-2(4)	+2	+6	-2(4)

Oxidation

Reduction

Ox. ½	Red. ½
$Pb \rightarrow Pb^{2+} \cancel{+2e}$	$\cancel{2e} + 4H^+ + PbO_2 \rightarrow Pb^{2+} + 2H_2O$

$$Pb_{(s)} + 4H^+_{(aq)} + PbO_{2\,(s)} \longrightarrow 2Pb^{2+} + 2H_2O$$

+4

+4

REDOX REACTIONS
(IN CLASS PROBLEMS)

1. A 1.164 gram sample containing some Fe_2O_3 is dissolved, and all the iron is reduced to the Fe^{2+} ions. The resulting solution is titrated with 19.68 mL of a 0.1104 M $KMnO_4$ solution. Calculate the percent of Fe_2O_3 in the original sample.

$$Fe^{2+}(aq) + MnO_4^-(aq) \text{ -----------> } Fe^{3+}(aq) + Mn^{2+}(aq)$$

2. A 13.38 grams sample of a material that contains some As_4O_6 was dissolved in water and required 5.330 grams of iodine for complete reaction according to the reaction:

$$As_4O_6 + I_2 \text{ -----------> } As_2O_5 + HI$$

a) Balance the equation by the 1/2 reaction method (acidic media).
b) Determine the mass of As_4O_6 that reacted with iodine.
c) Determine the mass percent of As_4O_6 in the original sample.

3. A mixture is made by combining 300.0 mL of 0.0200 M $Na_2Cr_2O_7$ with 400.0 mL of 0.060 M $Fe(NO_3)_2$. Initially, the H^+ concentration in the mixture is 0.400 M . Dichromate ion oxidizes Fe^{2+} to Fe^{3+} and is reduced to Cr^{3+}. After the reaction in the mixture has ceased, how many milliliters of 0.0100 M NaOH will be required to neutralize the remaining H^+ ?

4. A mixture of SO_3^{2-} and $S_2O_3^{2-}$ reacts with CrO_4^{2-} in a basic solution to give CrO_2^-. The only sulfur containing product was SO_4^{2-}. Balance the equation using the 1/2 reaction method.

5. In an acidic sol'n HSO_3^- ion reacts with ClO_3^- ion to give SO_4^{2-} ion and Cl^- ion.

a) Write a balanced net ionic eq. for the rxn.
b) How many milliliters of 0.150 M $NaClO_3$ sol'n are needed to react completely with 30.0 mL of 0.450 M $NaHSO_3$ sol'n?

1. $Fe^{2+} + \cancel{K}MnO_4^- \longrightarrow Fe^{3+} + Mn^{2+}$

$+2 \qquad -7 \quad -2(4) \qquad +3 \qquad +2$

Oxidation

Reduction

Ox. ½	Red. ½
$(Fe^{2+} \rightarrow Fe^{3+} + e^-)5$	$\cancel{5e^-} + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
$5Fe^{2+} \rightarrow 5Fe^{3+} + \cancel{5e^-}$	

$$5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$\frac{0.1104 \cancel{\text{ mol } KMnO_4}}{} \times 0.01968 \times \frac{5 \cancel{\text{ mol } Fe^{2+}}}{1 \cancel{\text{ mol } KMnO_4}}$$

$$\times \frac{1 \cancel{\text{ mol } Fe_2O_3}}{2 \cancel{\text{ mol } Fe^{2+}}} \times \frac{159.7 \text{ g } Fe_2O_3}{1 \cancel{\text{ mol } Fe_2O_3}} = 0.867 \text{ g } Fe_2O_3$$

$$\% \, Fe_2O_3 = \frac{0.867 \text{ g } Fe_2O_3}{1.164 \text{ g sample}} \times 100 = 74.5\% \, Fe_2O_3$$

$$\#5 \quad HSO_3^- + ClO_3^- \rightarrow SO_4^{2-} + Cl^-$$

$$+1 \quad +4 \quad -2(3) \qquad +5 \quad -2(3) \qquad +6 \quad -2(4) \qquad -1$$

Ox.

Red.

Ox. 1/2	Red. 1/2
$3(H_2O + \overset{+4}{H}SO_3^- \rightarrow \overset{+6}{SO_4^{2-}} + 3H^+_{(aq)})$ $3H_2O + 3HSO_3^- \rightarrow 3SO_4^{2-} + 9H^+ + \cancel{6e}$	$\cancel{6e^-} + 6H^+ + \overset{+5}{Cl}O_3^- \rightarrow \overset{-1}{Cl^-} + 3H_2O$

$$\cancel{3H_2O} + 3HSO_3^- + \cancel{6H^+} + ClO_3^- \rightarrow 3SO_4^{2-} + \underset{3}{\cancel{9}}H^+ + Cl^- + \cancel{3H_2O}$$

+2 +2

* Nitrogens are spectators

September 23, 2016

$$\frac{0.450\ \cancel{mol\ HSO_3^-}}{\cancel{L}} \times 0.030\ \cancel{L} \times \frac{1\ \cancel{mol\ ClO_3^-}}{3\ \cancel{mol\ HSO_3^-}}$$

$$\times \frac{1.0\ L}{0.150\ \cancel{mol\ ClO_3^-}} = 0.300\ L$$

or 30.0 mL

#4

$$SO_3^{2-} + S_2O_3^{2-} + CrO_4^{2-} \rightarrow CrO_2^- + SO_4^{2-}$$

+4 −2(3) +2(2) −2(3) +6 −2(4) +3 −2(2) +6 −2(4)

RED.

OXID.

Ox. 1/2	Red. 1/2
$3\left(SO_3^{2-} + S_2O_3^{2-} + 6H_2O \rightarrow 3SO_4^{2-} + 12H^+ + 10e^-\right)$ -4 $\quad$ $+6$ $18H_2O + 3SO_3^{2-} + 3S_2O_3^{2-}$ $\rightarrow 9SO_4^{2-} + 36H^+ + 30e^-$	$\left(3e^- + 4H^+ + \overset{+6}{Cr}O_4^{2-} \rightarrow \overset{+3}{Cr}O_2^- + 2H_2O\right)10$ $30e^- + 40H^+ + 10CrO_4^{2-}$ $\rightarrow 10CrO_2^- + 20H_2O$

$$\underset{}{18}\cancel{H_2O} + 3SO_3^{2-} + 3S_2O_3^{2-} + \underset{4}{\cancel{40H^+}} + 10CrO_4^{2-} + 40OH^-$$

$$\rightarrow 9SO_4^{2-} + \cancel{36}H^+ + 10CrO_2^- + \underset{2}{\cancel{20}}H_2O + 40OH^-$$

$$3SO_3^{2-} + 3S_2O_3^{2-} + \underset{2}{\cancel{4}}H_2O + 10CrO_4^{2-} \rightarrow 9SO_4^{2-} + 10CrO_4^- + \cancel{2H_2O} + 4OH^-$$

#3 (Problem so long & complicated like this won't be on the test)

others are spectators

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

$+1$ $\quad$ $+6(2)$ $\quad$ $-2(7)$ $\quad$ $+2$ $\quad$ $+3$ $\quad$ $+3$

Red.

Oxid.

Ox. ½	Red. ½
$6(Fe^{2+} \rightarrow Fe^{3+} + e^-)$ $6Fe^{2+} \rightarrow 6Fe^{3+} + \cancel{6e^-}$	$\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$ $+12$ $\quad$ $+6$

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

$Cr_2O_7^{2-}$: $\dfrac{0.0200\ \cancel{mol\ Cr_2O_7^{2-}}}{\cancel{L}} \times 0.300\ \cancel{L} \times \dfrac{7\ mol\ H_2O}{1\ \cancel{mol\ Cr_2O_7^{2-}}}$

$= 0.042\ mol\ H_2O$

Fe^{2+}: $\dfrac{0.0600\ \cancel{mol\ Fe^{2+}}}{\cancel{L}} \times 0.400\ \cancel{L} \times \dfrac{7\ mol\ H_2O}{6\ \cancel{mol\ Fe^{2+}}}$

Limiting Reactant

$= \boxed{0.028\ mol\ H_2O}$

Theoretical Yield

$(0.300 + 0.400)$

H^+: $\dfrac{0.400\ \cancel{mol\ H^+}}{\cancel{L}} \times 0.700\ \cancel{L} \times \dfrac{7\ mol\ H_2O}{14\ \cancel{mol\ H^+}}$

$= 0.14\ mol\ H^+$

H^+ initial: $\dfrac{0.400\ mol\ H^+}{\cancel{L}} \times 0.700\ \cancel{L} = 0.280\ mol\ H^+$

H^+ used up: $\dfrac{0.060\ mol\ Fe^{2+}}{L} \times 0.400 \times \dfrac{14\ mol\ H^+}{6\ mol\ Fe^{2+}}$

$= 0.056\ mol\ H^+$

H^+ remaining: 0.280
$- 0.056$
0.224

$H^+ + OH^- \rightarrow H_2O$

$0.224 \text{ mol } H^+ \times \frac{1 \text{ mol } OH^-}{1 \text{ mol } H^+} \times \frac{1.0 \text{ L}}{0.0100 \text{ mol } OH^-} = 22.4 \text{ L NaOH}$

#2 $As_4O_6 + I_2 \rightarrow AsO_5 + HI$

a) +3(4) -2(6) 0 +5(2) -2(5) +1 -1

Oxid.

Red.

Ox. 1/2	Red. 1/2
$4H_2O + As_4O_6 \rightarrow 2As_2O_5 + 8H^+ + \cancel{8e^-}$	$(2e^- + 2H^+ + I_2 \rightarrow 2HI)4$ (not 1
	$\cancel{8e^-} + 8H^+ + 4I_2 \rightarrow 8HI$

$4H_2O + As_4O_6 + \cancel{8H^+} + 4I_2 \rightarrow 2As_2O_5 + \cancel{8H^+} + 8HI$

b) $5.33 \text{ g } \cancel{I_2} \times \frac{1 \cancel{\text{ mol } I_2}}{253.8 \cancel{\text{ g } I_2}} \times \frac{1 \text{ mol } As_4O_6}{4 \cancel{\text{ mol } I_2}} \times \frac{395.68 \text{ g } As_4O_6}{1 \text{ mol } As_4O_6} = 2.077 \text{ g } As_4O_6$

c) $\% As_4O_6 = \frac{2.077 \text{ g } As_4O_6}{13.38 \text{ g sample}} = 15.5\% \; As_4O_6$