Topic 9: Oxidation + Reduction

9.1

Oxidation → gain of O_2 / loss of H^+ / loss of e^-

reduction → loss of O_2 / gain of H^+ / gain of e^-

Lose	Oxidation
E^-	Is
Oxidized	Loss
Gain	Reduction
E^-	Is
Reduced	Gain

Redox Rxns
one cannot occur w/o other

Half rxns: what happens to one reactant in terms of e^-

$2Mg + O_2 \rightarrow 2MgO$

$2Mg \rightarrow 2\overset{\text{ion}}{Mg^{2+}} + \overset{\text{match}}{\boxed{4e^-}}$

2 per Mg

$O_2 + \boxed{4e^-} \rightarrow 2\overset{\text{ion}}{O^{2-}}$

$3Mg + N_2 \rightarrow Mg_3N_2$

$3Mg \rightarrow 3\overset{\text{ion}}{Mg^{2+}} + \boxed{6e^-}$

$N_2 + \boxed{6e^-} \rightarrow 2\overset{\text{ion}}{N^{3-}}$

Oxidation state (number):
Value to each atom → measures e^- control / possession it has relative to the atom in pure element
(apparent charge of atom)

ionic cmpd → predict based off charge

covalent cmpd → exaggerate unequal sharing (based off electronegativity) → gain/loss track relative e^- density in cmpd

Signs: + : atom has lost e^- control
− : atom has gained e^- control

Value: number of e^- over which control has changed

(2+ → charge of atom / +2 → oxidation state)

Assigning oxidation states:

1) Atoms in elemental state = 0
Mg, O_2, N_2

2) Simple ions, oxidation state = charge on ion
$\underset{+2}{Mg^{2+}}$ $\underset{-2}{O^{2-}}$ $\underset{-3}{N^{3-}}$

3) oxidation state of all atoms in neutral cmpd must = 0 $H_2SO_4 = 0$

4) oxidation state of all atoms in polyatomic ion must = charge of ion $SO_4^{2-} = -2$

5) usual oxidation state → charge of most common ion
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6) Some elements ox states vary in diff. cmpds → depends on other elements
ex: N, P, S, all transitions, Sn, Pb

★ Best to identify 'easy' ox states 1st, then variable species ex : Which compound does S have more e^- control?

H_2SO_4
$\uparrow\ \uparrow\ \uparrow$
$2(+1)\ ?\ 4(-2) = 0$
$\uparrow$
$+6$

SO_3^{2-} ★
$\uparrow\ \uparrow$
$?\ 3(-2) = 2-$
$\uparrow$
$+4$

Transiton metal in complex ion:
1) charge of ligand
2) overall charge

$[Co(NH_3)_6]^{3+}$
$\uparrow\ \uparrow$
$+3$ neutral

$[CuCl_4]^{2-}$
$\uparrow\ \uparrow$
$+2\ 4(-1) = -2$

During rxn, ox state may change in value
more (−), more reduced, more control
more (+), more oxidized, less control

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$
$0 \quad 0 \quad +1\ -2$
H ($0 \rightarrow +1$) ox
O ($0 \rightarrow -2$) red

$Ca_{(s)} + Sn^{2+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + Sn_{(s)}$
$0 \quad +2 \quad +2 \quad 0$
Ca ($0 \rightarrow +2$) ox
Sn ($+2 \rightarrow 0$) red

$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + H_2O_{(l)}$
$-3\ +1 \quad 0 \quad +2\ -2 \quad +1\ -2$
N ($-3 \rightarrow +2$) ox
H ($+1 \rightarrow +1$) N/A
O ($0 \rightarrow -2$) red

★ Roman numerals for transiton metals represent ox state
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V2

Writing half equations

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

1) $0 \quad +2 \quad +2 \quad 0$

2) Zn $(0 \rightarrow +2)$ ox ∴ $Zn \rightarrow Zn^{2+} + \boxed{2e^-}$
Cu $(+2 \rightarrow 0)$ red ∴ $Cu^{2+} + \boxed{2e^-} \rightarrow Cu$

Must be equal # of e^- in ½ eq so when added together they cancel out (like intermediates)

Writing redox equations from ½ eq
make sure it is balanced for atoms / charges
most rxns occur in acidified solns ∴ use H_2O/H^+ to balance ½ rxns

ex: NO_3^- + Cu react together in acidic soln to NO + Cu^{2+}

1) assign ox state:

$$NO_3^- + Cu \rightarrow NO + Cu^{2+} \text{ (unbalanced)}$$
$+5\ -2 \quad 0 \quad +2\ -2 \quad +2$

N $(+5 \rightarrow +2)$ red
Cu $(0 \rightarrow +2)$ ox
O $(-2 \rightarrow -2)$ spectator

2) write ½eq for ox + red

- balance atoms (other than H + O)
  - ox: $Cu \rightarrow Cu^{2+}$ } already balanced
  - red: $NO_3^- \rightarrow NO$

- balance each ½eq for O by adding H_2O
  - ox: n/a
  - red: $NO_3^- \rightarrow NO + \underline{2H_2O}$ (3 on ea. side)

- balance each ½eq for H by adding H^+
  - ox: n/a
  - red: $NO_3^- + 4H^+ \rightarrow NO + 2H_2O$

- balance each ½eq for charge by adding e⁻ to sides w/ more positive charge
  - ox: $Cu \rightarrow Cu^{2+} + 2e^-$
  - red: $\underset{+5}{NO_3^-} + 4H^+ + \underset{\text{difference}}{3e^-} \rightarrow \underset{+2}{NO} + 2H_2O$

3) Equalize # of e⁻ (should equal atoms too)

ox: $\times 3 \rightarrow 3Cu \rightarrow 3Cu^{\cancel{2+}} + \cancel{6e^-}$

red: $\times 2 \rightarrow 2NO_3^- + 8H^+ \underline{+} \cancel{6e^-} \rightarrow 2NO + 4H_2O$

4) Add 2 ½eq - cancel out commonalities

$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$

V3 Oxidizing & Reducing Agents

oxidizing agent → accepts e⁻ (being reduced) oxidant

reducing agent → supplies e⁻ (being oxidized) reductant ex: $\underset{+3\ \ -2}{Fe_2O_3}(s) + 3\underset{0}{C}(s) \rightarrow 2\underset{0}{Fe}(s) + 3\underset{+2\ -2}{CO}(g)$

Fe (+3 → 0) red **oxidizing agent**
C (0 → +2) ox **reducing agent**

Useful oxidizing agents: O_2, O_3, H^+/MnO_4^-, $H^+/Cr_2O_7^{2-}$,
F_2, Cl_2, conc. HNO_3, H_2O_2

reducing agents: H_2, C, CO, SO_2, reactive metals

Classification depends on other reactant (think amphoteric)

o.a. $2\underset{+1}{H_2O}(l) + 2\underset{\text{reactive metal}}{Na}(s) \rightarrow NaOH(aq) + \underset{0}{H_2}(g)$

r.a. $2\underset{-2}{H_2O}(l) + 2\underset{0}{F_2} \longrightarrow 4\underset{-1}{HF}(aq) + \underset{0}{O_2}(g)$

H_2O → weak o.a./r.a. → why good solvent

More reactive metals are strong r.a.
b/c metals lose e⁻ (trend of ionization energy)

Tested by reacting 2 metals (switching ions)
↓
Reactivity series: predict redox rxns b/w a metal + ions of another metal (pg 417)

Mg ↑ Strogest r.a. (readily oxidizes)
Al
Zn
Fe
Pb
Cu
Ag Weakest r.a. (least readily oxidizes)

$Zn_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + Zn\underline{SO_4}_{(aq)}$

Spectator ion

Cu^{2+} ion being displaced from soln as Zn is reducing them.

ionic eq: $\underline{Zn} + Cu^{2+} \rightarrow Zn^{2+} + Cu$ + heat displacement rxn

r.a. → more reactive metal

$ZnCl_{2(aq)} + \underset{weaker}{Ag_{(s)}} \rightarrow 2AgCl_{(aq)} + Zn_{(s)}$ NR

$2FeCl_{3(aq)} + \underset{stronger}{3Mg_{(s)}} \rightarrow 3MgCl_{2(aq)} + 2Fe_{(s)}$ Rxn

More reactive non-metals stronger o.a.
b/c non-metals gain e- (electron affinity)

$F_2 \rightarrow Cl_2 \rightarrow Br_2 \rightarrow I_2$

strongest o.a. (readily reduced) weakest o.a. (least readily reduced)

$\underset{stronger}{Cl_{2(aq)}} + 2KI_{(aq)} \rightarrow 2KCl_{(aq)} + I_{2(aq)}$

Redox Titrations

- used to determine unknown conc. of substance in soln
- eq pt: reacted stoichiometrically by transferring e-

A / B	Vs.	Redox
• neutralization b/w A + B		• redox b/w o.a. + r.a.
• H^+ transfer from A → B		• e^- transfer from r.a. → o.a.

Same method

- burrette / pipette (vol) against std soln
- indicator for eq. pt. (maybe)
- from volume of titre used → conc. of unknown can be determined using ½ eq.

1. Analysis of Fe w/ Mangante (VII) (pg 420)

o.a. = $KMnO_4$ (in acidic soln) ($MnO_4^- \rightarrow Mn^{2+}$)
r.a. = Fe ($Fe^{2+} \rightarrow Fe^{3+}$)

(go through ½ rxn) $5Fe^{2+} + \underset{\text{purple}}{MnO_4^-} + 8H^+ \rightarrow 5Fe^{3+} + \underset{\text{colorless}}{Mn^{2+}} + 4H_2O$

Known: 2.000 (g) Fe tablet
27.50 cm^3 of 0.100 mols dm^{-3} $KMnO_4$

1. $n(MnO_4^-) = 0.100 \times 0.02750\ dm^3 = 0.00275$ mol MnO_4^-

2. $MnO_4^- : Fe^{2+} = 1 : 5$
$n(Fe^{2+}) = 0.00275$ mol $MnO_4^- \times 5 = 0.01375$ mol Fe^{2+}

3. $n = \frac{m}{M}$ $m(Fe) = 0.01375mol \times 55.85\ gmol^{-1} = \boxed{0.768g}$

4. % Fe in tablet $= \frac{0.768g}{2.000g} \times 100 = \boxed{38.4\ \%}$

5. obs: MnO_4^- purple in burrette, colorless in flask (as Mn^{2+}), after eq. pt. purple in flask

2. Iodine - Thiosulfate Rxn (422)

$2I^-_{(aq)} + O.a. \rightarrow I_{2(aq)} + \text{reduced product}$

$KMnO_4$, KIO_3, $K_2Cr_2O_7$, $NaOCl$

titrated w/ $Na_2S_2O_3$
w/ starch indicator

ox: $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$
red: $I_2 + 2e^- \rightarrow 2I^-$

complete: $2S_2O_3^{2-} + \underset{\text{deep blue}}{I_2} \rightarrow \underset{\text{colorless}}{2I^-} + S_4O_6^{2-}$

Know: 10.00 cm^3 bleach
38.65 cm^3 of 0.0200 mols dm^{-3} $S_2O_3^{2-}$

1. $n(S_2O_3^{2-}) = 0.0200 \text{ mol dm}^{-3} \times 0.03865 \text{ dm} = 7.73 \times 10^{-4} \text{ mol } S_2O_3^{2-}$

2. $S_2O_3^{2-} : I_2 = 2:1$
$n(I_2) = 7.73 \times 10^{-4} \text{ mol } S_2O_3^{2-} \div 2 = 3.865 \times 10^{-4} \text{ mol } I_2$

3. $OCl^- : I_2 = 1:1$
$n(OCl^-) = \text{mol } I_2 = 3.865 \times 10^{-4} \text{ mol } OCl^-$

4. $c = \frac{n}{V} = \frac{3.865 \times 10^{-4}}{0.01} = \boxed{0.0387 \text{ mol dm}^{-3}}$

3. Winkler Method → calc DO (dissolved O_2)
DO = aquatic life
measures affect of pollution (Biological O_2 demand → BOD)
on aquatic life

high BOD → low O_2 level → due to NO_3^- & PO_4^{3-}
(eutrophication → great quantity of degradable waste)

1. 'fixing' O_2 w/ Mn(II) → Mn (IV) in basic soln

$$2\underset{+2}{Mn^{2+}} + O_2 + 4OH^- \rightarrow 2\underset{+4}{Mn}O_2 + 2H_2O$$

2. Add acidified I^-

x2 $MnO_{2(s)} + 2I^-_{(aq)} + 4H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$

3. Titrate I_2 w/ $Na_2S_2O_3$

x2 $2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow 2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

1mol O_2 : 4 mol $S_2O_3^{2-}$ used

Known: 500cm³ H_2O sample
12.50 cm³ of 0.0500 mol dm^{-3} $Na_2S_2O_3$
? g dm^{-3} DO of H_2O

1. $n(S_2O_3^{2-}) = 0.0500 mol\ dm^{-3} \times 0.01250\ dm^3 = 6.25 \times 10^{-4}$ mol

2. $S_2O_3^{2-} : I_2 = 2:1$
$n(I_2) = 6.25 \times 10^{-4}$ mol $\div 2 = 3.175 \times 10^{-4}$ mol I_2

3. $MnO_2 : I_2 = 1:1$
$n(MnO_2) = 3.175 \times 10^{-4}$ mol MnO_2

4. $MnO_2 : O_2 = 2:1$
$n(O_2) = 3.175 \times 10^{-4}$ mol $\div 2 = 1.5875 \times 10^{-4}$ mol O_2

5. $m(O_2) = n \times M = 1.5875 \times 10^{-4} mol \times 32.00 g\ mol^{-1} = 5.080 \times 10^{-3}$ g
in 500 cm3

6. DO = 0.0102 g dm^{-3}