CHEM 205   section 03

LECTURE #14   Tues., Feb.26, 2008

LECTURE TOPICS:

TODAY'S CLASS: continue Ch.5

NEXT CLASS: **finish Ch.5, start Ch.7**

MIDTERM EXAM: **Tues. March 4th during class
Ch.1–5 (all) but not 20.1
see sample MTs on website**

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TITRATIONS: using solution stoichiometry…

Volumetric analysis: How much *analyte "X"* is in a sample?

▪ Consume **X** via quantitative reaction with known stoichiometry
▪ Measure volume of *titrant* solution required to consume all of **X**
  • *Thus: X = limiting reactant*
  • *Use stoichiometry: calculate amount of X originally present*
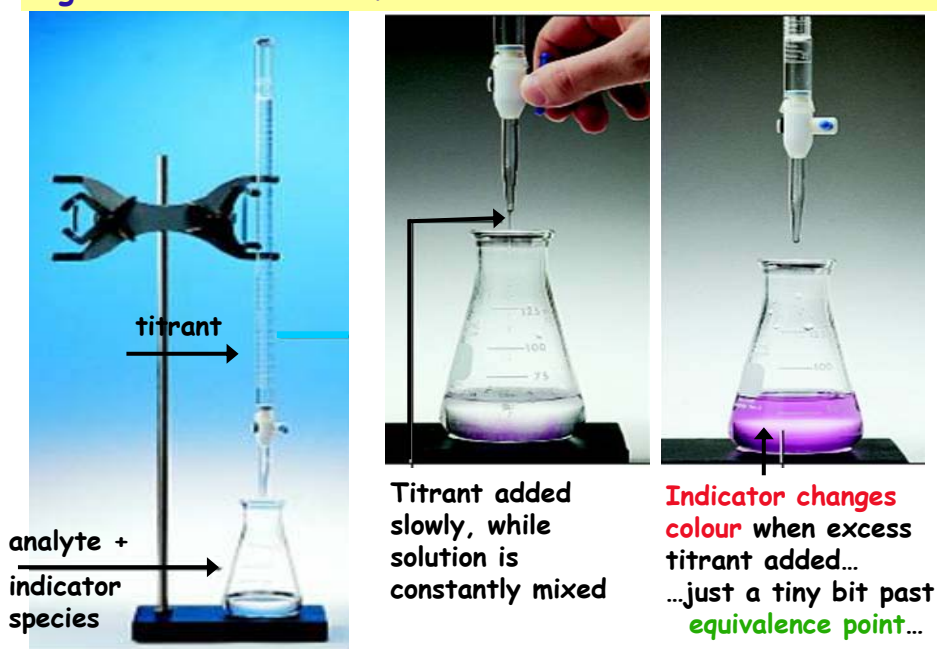
REQUIREMENT FOR ALL TITRATIONS:

Moment when reaction is <u>exactly</u> complete (*equivalence point*)
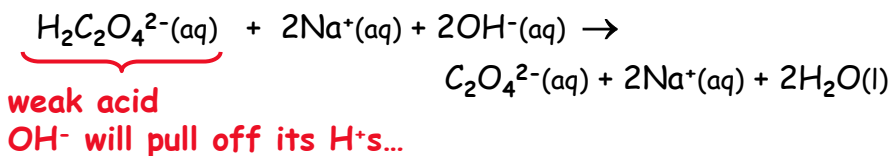must be **accurately** indicated somehow (*end point*)

NOTE:
  • Commonly used with acid-base rxns (often 1:1 stoichiometry)
  • BUT: can be used for <u>any</u> rxn where stoichiometry is known
  • IMPORTANT: do <u>not necessarily</u> have 1:1 ratio of reactants!

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Fig.5.20: Titration of an acid with a base

titrant

analyte + indicator species

Titrant added slowly, while solution is constantly mixed

Indicator changes colour when excess titrant added… …just a tiny bit past equivalence point…

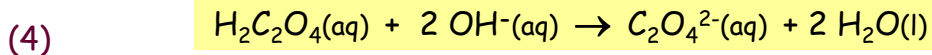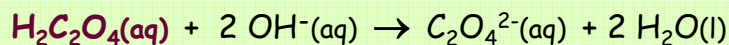## Quality control application of titration…

A production lot of an oxalic acid based cleanser is being analyzed via titration with NaOH(aq). No other acids are present.
   Sample volume: 50.00 mL
   Phenolphthalein end point: 31.66 mL of 1.3057 M NaOH
Calculate the [oxalic acid] in the cleanser, in mol/L.

$H_2C_2O_4$(aq) + NaOH(aq) $\rightarrow$ **?**

$H_2C_2O_4{}^{2-}$(aq)   + 2Na$^+$(aq) + 2OH$^-$(aq) $\rightarrow$

$C_2O_4{}^{2-}$(aq) + 2Na$^+$(aq) + 2H_2O(l)

weak acid
OH$^-$ will pull off its H$^+$s…

NET IONIC EQUATION:

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$H_2C_2O_4$(aq) + 2 OH$^-$(aq) $\rightarrow$ $C_2O_4{}^{2-}$(aq) + 2 H_2O(l)

$$H_2C_2O_4(aq) + 2\ OH^-(aq) \rightarrow C_2O_4{}^{2-}(aq) + 2\ H_2O(l)$$

Analyte: ❶
- $C =$ _____ M $H_2C_2O_4$
- $V = 0.05000$ L

Rxn stoichiometry = 1 : 2 ❸
- At equiv. point: *all X used*
  $n(H_2C_2O_4) = n(OH^-) / 2$
  $\therefore n(H_2C_2O_4) = 2.067 \times 10^{-2}$ mol

Note: 2 H⁺ came from each
1 $H_2C_2O_4$ in analyte sol'n

$\Rightarrow C = \dfrac{n\text{(oxalic acid)}}{V\text{(sample solution)}}$

$= \dfrac{2.067 \times 10^{-2} \text{ mol}}{0.05000 \text{ L}}$

$\boxed{= 0.4134\ M}$

❷

Titrant:
- $C = 1.3057$ M NaOH
- $V = 0.03166$ L

$n = (1.3057M)(0.03166L)$
$= 4.134 \times 10^{-2}$ mol

Every 1 mol NaOH
yields 1 mol OH⁻
$\therefore n = (1)\ 4.134 \times 10^{-2}$ mol
$= 4.134 \times 10^{-2}$ mol OH⁻
required to consume all the " H⁺ "

THUS: in our cleanser sample,
[oxalic acid] was = **0.4134 M**

5.5 Gas-Forming Rxns: net formation of gas (easy to see…)

Many types of chemical rxn can produce gaseous products:

- **Gas-forming REDOX (e⁻-transfer) rxns:**
  - certain metals + acid → "dissolved" metal + GAS
    $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + \mathbf{H_2(g)}$

- **Gas-forming ACID-BASE (H⁺-transfer) rxns:**   *Table 5.3*
  - sometimes the A/B rxn product is a GAS
    $NH_4Cl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) + \mathbf{NH_3(g)}$

  - products of **some** A/B rxns can DECOMPOSE *(details next…)*
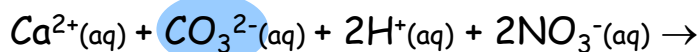 $CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + \mathbf{CO_2(g)}$

THUS: any gas-forming rxn should be described by also
identifying the type of chemistry involved

Limestone + acid rain: $CaCO_{3(aq)} + HNO_{3(aq)} \rightarrow$?

A carbonate salt…   A strong acid
(very weak bond to H^+)

$$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} + 2H^+_{(aq)} + 2NO_3^-_{(aq)} \rightarrow$$

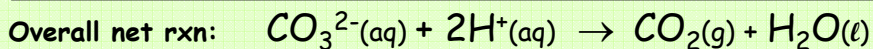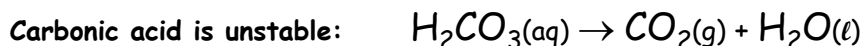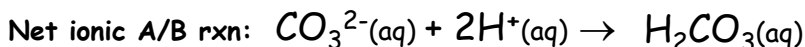$$H_2CO_{3(aq)} + Ca^{2+}_{(aq)} + 2NO_3^-_{(aq)}$$

Anions of
weak acids
are weak bases,
& can accept H^+s
from acids
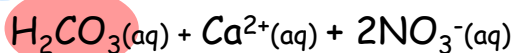
Carbonic acid = a weak acid
(stronger bond to H^+)

H_2CO_3 forms if CO_2 dissolves in H_2O
…& that rxn is reversible…

Net ionic A/B rxn: $CO_3^{2-}_{(aq)} + 2H^+_{(aq)} \rightarrow H_2CO_{3(aq)}$

Carbonic acid is unstable: $H_2CO_{3(aq)} \rightarrow CO_{2(g)} + H_2O_{(\ell)}$

Overall net rxn: $CO_3^{2-}_{(aq)} + 2H^+_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(\ell)}$

Overall molecular equation: limestone "dissolves" in acid, via rxn:

$$CaCO_{3(aq)} + 2HNO_{3(aq)} \rightarrow Ca(NO_3)_{2(aq)} + CO_{2(g)} + H_2O_{(\ell)}$$

5.6 Types of solution rxns: what drives them to occur?

Reactions are "product-favoured" (go nearly to completion)
if the products are:
- Particularly stable (compared to reactants)   OR
- Able to 'escape' from the ⇨ solids ppt out…
                                        gases bubble out…

Reaction type	What happens…	Driving force
Precipitation	Ion exchange	Formation of an insoluble compound
Acid-base (neutralization)	Proton transfer	Formation of new, stronger covalent bond to H^+ ⇨ usually forming water
Gas-forming	Various…	Evolution of a gas
Oxidation-reduction	Electron transfer	Products more stable than reactants… *(discuss these rxns next)*

Predicting which type of rxn will occur in soln…

- Precipitation ("pptn") rxns involve ion exchange <u>only</u>
- Acid-base rxns involve forming a new covalent bond to H^+
  - H^+ moves from acid to base…so both reactants must be there…

Q1: What types of species are present in the reactant solutions ?	Q2: What happens… ?
	- Strong electrolytes: use ion-exchange trick 　• if products soluble & ionic ⇨ "NO RXN" - If acid & base react: 　• products likely soluble (*new* strong A or B)

$HNO_3(aq)$ + $CsI(aq) \rightarrow$ No base ⇨ Ion exchange only. Ppt forms?

$NH_3(aq)$ + $HCl(aq) \rightarrow$ Acid-base rxn.   Product soluble?

$NaOH(aq)$ + $CaBr_2(aq) \rightarrow$ No acid ⇨ Ion exchange only. Ppt forms?

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5.7   Oxidation-reduction (redox) reactions

WHAT do these reactions involve?

⇒ electrons transferred from one species to another!

SOME TERMS:
Loss of e^- :   "oxidation"
Gain of e^- :   "reduction"

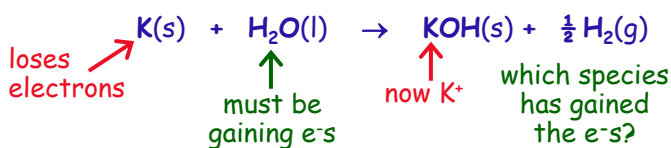**LEO the lion says GER…**

electrons LOST by one species
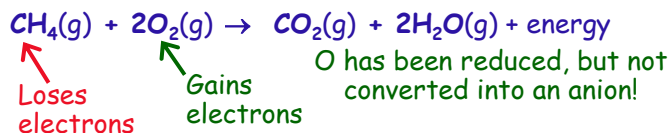<u>must be</u> GAINED by another

Oxidation & reduction occur as a PAIR
hence: "REDOX" reaction

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Characteristic chemical feature of redox rxns
= electrons transferred from one species to another

$$K(s) \ + \ H_2O(l) \ \rightarrow \ KOH(s) \ + \ \tfrac{1}{2}\,H_2(g)$$

loses electrons

must be gaining e⁻s

now K⁺

which species has gained the e⁻s?

EXAMPLES: when ions are formed from elements (& vice versa…)
but can also involve only covalent compounds

$$CH_4(g) \ + \ 2O_2(g) \rightarrow \ CO_2(g) \ + \ 2H_2O(g) + energy$$

Loses electrons

Gains electrons

O has been reduced, but not converted into an anion!

How do we know:
· **if a process involves electron transfer?**
· **which substance loses *vs.* gains electrons?**

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Keeping track of e⁻s is important…

OXIDATION STATE (or OXIDATION #)
▪ every atom is assigned an imaginary charge
▪ denoted using roman numerals

For monatomic ions: oxidation state matches charge
   anion: extra e-s ⇨ -ve ox.#
   cation: missing e⁻ ⇨ +ve ox.#

So, in Fe_2O_3 ?

For covalent cmpds: "pretend" ionic ! (sum "charges" = 0)
▪ Covalent bonds: 2e⁻ shared between 2 atoms

▪ **Nonpolar bonds: e⁻s shared equally**
      both atoms look "normal" ⇨ ox.# = 0

I_2, H_2, O_2, N_2 *etc…*
FOR EACH ATOM,
ox'n state = 0

▪ **Polar bonds: e⁻s shared unequally**
   · pretend atom with stronger pull on e⁻ has both e⁻s
      ⇨ ox.# = -ve (like anion)
   · pretend other atom has neither e⁻
      ⇨ ox.# = +ve (like cation)

WATER: H_2O
H ox'n state = +I
O ox'n state = -II

(12)

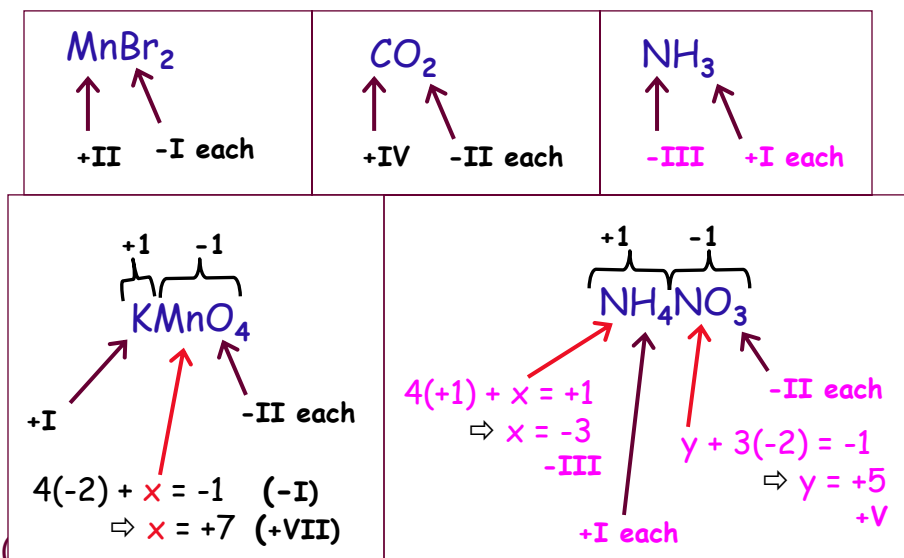## TABLE 4.2   Rules for Assigning Oxidation States   (Zumdahl)

The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	$Na(s), O_2(g), O_3(g)$
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+, Cl^-
• Fluorine is −1 in its compounds	Fluorine: −1	HF, PF_3
• Oxygen is usually −2 in its compounds	Oxygen: −2	H_2O, CO_2
Exception: peroxides (containing O_2^{2-}) in which oxygen is −1		
• Hydrogen is +1 in its covalent compounds	Hydrogen: +1	H_2O, HCl, NH_3

Ox.# = Same as CHARGE on most common ION !!!

Kotz? p.200

Assigning oxidation states

- **If ionic:**   divide into ions 1st, then assign ox.#s
- **In all cases:** sum of ox.#s = net charge on species

$MnBr_2$
+II   −I each

CO_2
+IV   −II each

NH_3
−III   +I each

+1   −1
$KMnO_4$
+I   −II each

$4(-2) + x = -1$ (−I)
$\Rightarrow x = +7$ (+VII)

+1   −1
NH_4NO_3

$4(+1) + x = +1$
$\Rightarrow x = -3$
−III

+I each

−II each

$y + 3(-2) = -1$
$\Rightarrow y = +5$
+V

A CLASSIC REDOX REACTION: Combustion

Burning substances in presence of oxygen…
…especially organic compounds --- *e.g.,* natural gas

$$CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(g)}$$

-4 (-IV)   +1 each (+I)   0 each   +4 (+IV)   -2 each (-II)   +1 each (+I)   -2 (-II)
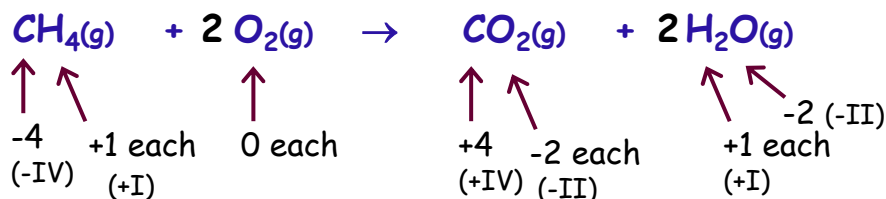
O becomes REDUCED	C becomes OXIDIZED
(formally gain 2 e⁻ per O atom)	(formally loses 8 e⁻ per C atom)
O's ox'n # goes ↓	In rxn, C's ox'n # goes ↑
O_2 = *oxidizing agent*	CH_4 = *reducing agent*
CAUSES oxidation of C.	CAUSES reduction of O.

(15)   Remember: oxidation numbers are not real charges
they just help us keep track of e⁻s…

Recognizing redox agents (Table 5.4)

Ox'n (e⁻ loss): ox. # ↑
Red'n (e⁻ gain): ox. # ↓

Oxidizing agent = oxidant
- contains "high" ox. state atom(s)
  relative to that element's preference…
- causes others to be oxidized (steals e⁻)
- itself becomes REDUCED

Reducing agent
- contains "low" ox. state atom(s)
  relative to that element's preference…
- causes others to be reduced (gives away e⁻)
- itself becomes OXIDIZED

Oxidizing Agent	Reaction Product	Reducing Agent	Reaction Product
O_2, oxygen	O^{2-}, oxide ion or O combined in H_2O	H_2, hydrogen	$H^+(aq)$, hydrogen ion or H combined in H_2O or other molecule
Halogen, F_2, Cl_2, Br_2, or I_2	Halide ion, F^-, Cl^-, Br^-, or I^-	M, metals such as Na, K, Fe, and Al	M^{n+}, metal ions such as Na^+, K^+, Fe^{2+} or Fe^{3+}, and Al^{3+}
HNO_3, nitric acid	Nitrogen oxides* such as NO and NO_2	C, carbon (used to reduce metal oxides)	CO and CO_2
$Cr_2O_7^{2-}$, dichromate ion	Cr^{3+}, chromium(III) ion (in acid solution)		
MnO_4^-, permanganate ion	Mn^{2+}, manganese(II) ion (in acid solution)		

Recognizing redox reactions: change in ox.#s

- "Obvious" clue:
  - Substance in elemental form on one side of reaction equation…but not on the other…

  $$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2Pb(SO_4)_2(s) + 2H_2O(l)$$

- Not-so-obvious cases:
  - Assign oxidation #s for all elements – do any change?

  $$K_2CO_3(aq) + 2HIO_4(aq) \rightarrow 2KIO_4(aq) + CO_2(g) + H_2O(l)$$
  (This one's not redox…)
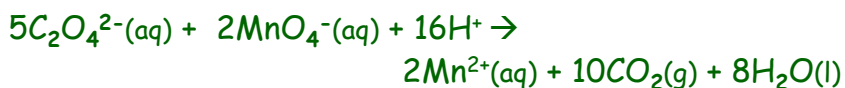
  $$5C_2O_4{}^{2-}(aq) + 2MnO_4{}^-(aq) + 16H^+ \rightarrow$$
  $$2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$
  (This one is redox…)

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Summary: common types of solution reactions

1. **Precipitation reaction = Ion-exchange reaction**
   ⇒ **if new salt(s) less soluble, solid precipitates out**
   $$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$$

2. **Acid-base reaction = H⁺ transfer reaction**
   ⇒ **base takes H⁺ from acid; both become "neutralized"**
   $$KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$$
   $$NH_3(aq) + HBr(aq) \rightarrow NH_4Br(aq)$$

3. **Oxidation-reduction reaction = e⁻ transfer rxn**
   ⇒ **oxidizing agent takes e⁻ from reducing agent**
   $$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$
   $$Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

Gas-forming rxn = any rxn yielding net production of gas
chemistry involved usually redox or acid-base

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Practical twists to stoichiometry problems:

CAN I REMOVE THE TOXIC Pb^{2+} FROM A WASTE SOLUTION?
- Via a precipitation reaction: choose reactants?
- Given a certain mixture, which reactant is limiting?
- Assuming 100% yield, how much solid product forms?
- What are the concentrations of all species left
  in the solution after the precipitation is complete?
     (spectator ions? excess reactants?)

CAN I REMOVE THE HARD-WATER SCUM FROM MY BATHTUB?
- Find a rxn that converts solid to a soluble salt...
   - If scum = metal hydroxide salt...reacts with acid!
- Will all the starting material end up "dissolving"?
- If not, how much remains unreacted?
- How much reactant would we need to add to react away
  all the insoluble material?

See tests on website for examples of many types of questions!

House-cleaning stoichiometry... (modified from MT F2004)

Oxalic acid ($H_2C_2O_4$) is commonly used to remove rust (*e.g.,* Fe_2O_3)
   from household surfaces like toilet bowls and bathtubs:

$$Fe_2O_3(s) + 6H_2C_2O_4(aq) \rightarrow 2Fe(C_2O_4)_3{}^{3-}(aq) + 6H^+(aq) + 3H_2O(\ell)$$

(a) What type of reaction is this?
     Precipitation?   Acid-base?   Redox?   Gas-forming?

(b) Imagine your toilet bowl has accumulated 0.685 g of $Fe_2O_3(s)$.
    If you treat it with 500 mL of a 0.100 M oxalic acid solution,
    will all of the rust be removed from the toilet bowl or will some
    remain? *Show calculations to justify your choice...*

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ASSIGNED READINGS

▪ BEFORE NEXT CLASS:

   Read rest of Ch. 5 & 20.1
         & work on Ch.5 & 20.1 exercises

▪ Practice identifying reaction types
▪ Practice balancing redox reaction equations
▪ Practice solution stoichiometry problems

MIDTERM EXAM:	Tues. March 4th during class
	Ch.1-5 (all) but not 20.1
	see sample MTs on website

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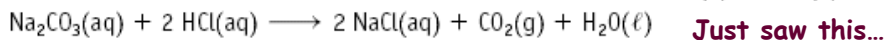## More examples of gas-forming rxns…

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Table 5.3

- *Products of some acid-base rxns can decompose:*

Metal carbonate or bicarbonate + acid ⟶ metal salt + $CO_2(g)$ + $H_2O(\ell)$

$Na_2CO_3(aq)$ + 2 $HCl(aq)$ ⟶ 2 $NaCl(aq)$ + $CO_2(g)$ + $H_2O(\ell)$ **Just saw this…**

Metal sulfite + acid ⟶ metal salt + $SO_2(g)$ + $H_2O(\ell)$

$Na_2SO_3(aq)$ + 2 $HCl(aq)$ ⟶ 2 $NaCl(aq)$ + $SO_2(g)$ + $H_2O(\ell)$

SO_3^{2-} picks up H^+: SO_3^{2-} + H^+ → HSO_3^-   Similar to
then another: HSO_3^- + H^+ → H_2SO_3   carbonate
& this decomposes: H_2SO_3 → H_2O + SO_2   salts
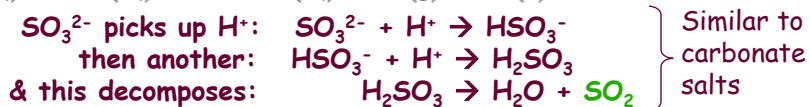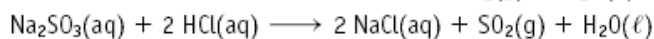
- *sometimes the A/B rxn product itself is simply a gas:*

Metal sulfide + acid ⟶ metal salt + $H_2S(g)$ **1ˢᵗ: S^{2-} + H^+ → SH^-**

$Na_2S(aq)$ + 2 $HCl(aq)$ ⟶ 2 $NaCl(aq)$ + $H_2S(g)$ **then: SH^- + H^+ → H_2S**
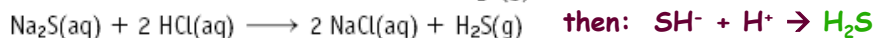
Ammonium salt + strong base ⟶ metal salt + $NH_3(g)$ + $H_2O(\ell)$

$NH_4Cl(aq)$ + $NaOH(aq)$ ⟶ $NaCl(aq)$ + $NH_3(g)$ + $H_2O(\ell)$

(23)   **H^+ removed from NH_4^+: NH_4^+ + OH^- → NH_3 + H_2O**