

## Chapter 5

### Introduction to Reactions in Aqueous Solutions

1

#### Aqueous Solutions

- **Solvent**  
liquid water
- **Solute**  
substance being dissolved
- **Electrolyte**  
substance that, when dissolved in a polar solvent like water, produces a solution that can conduct electricity (because it produces ions, which are charged)

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2

#### Electrolytes

##### Strong electrolyte:

When dissolved in water, dissociates almost completely into ions

- Highly water-soluble ionic compounds (e.g. NaCl,  $K_2SO_4$ )
- Strong acids (e.g. HCl,  $H_2SO_4$ )
- Strong bases (e.g. KOH)

In this course, **we will assume that all ionic compounds dissolve as separated cations and anions**

##### Weak electrolyte:

When dissolved in water, only some of it produces ions

- Weak acids (e.g.  $HC_2H_3O_2$ )
- Weak bases (e.g.  $NH_3$ )

##### Non-electrolyte:

Does not dissociate into ions at all (e.g. sugars, alcohols, oils)

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#### Electrolyte solutions conduct electricity

ions can carry the electric charge through the solution

KCl	Acetic Acid	Sugar
High conductivity	Low conductivity	No conductivity
<b>Strong Electrolytes</b> conduct current efficiently (bulb shines brightly at high concentration)	<b>Weak Electrolytes</b> conduct only a small current (bulb glows dimly even at high concentration)	<b>Nonelectrolytes</b> conduct no current (bulb remains unlit).

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4

#### Be aware:

The terms “strong electrolyte” or “weak electrolyte” refers to the **substance** dissolved (i.e. solute)

- A **concentrated** solution of a strong electrolyte is a good conductor and can make the bulb glow bright.

#### But ...

- A **dilute** solution of a strong electrolyte won't conduct much electricity, and the bulb will not glow bright.
  - Even if the dissolved “strong electrolyte” fully dissociated, if there isn't much of it, it will still have low conductivity

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On the other hand,

Even a concentrated solution of a weak electrolyte is not a good conductor and will not make the bulb glow bright.

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A molecular substance like hydrogen chloride (HCl), which is not ionic, but fully dissociates into ions when dissolved in water, is also a strong electrolyte.

- Because it's a strong acid, fully dissociating into  $H^+(aq)$  and  $Cl^-(aq)$  ions

*Note: Acids produce  $H^+$  ions in water, along with an anion*

Strong acids are strong electrolytes

-- fully ionize in water

Weak acids are weak electrolytes

-- only partially ionize in water

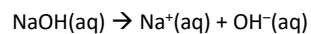
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7

Almost all the bases we see in this course are **metal hydroxides** like NaOH or KOH, and are strong electrolytes (because they are ionic compounds).

- Remember: we will assume that all ionic compounds fully dissociate into their ions when dissolved

*Note: Bases produce  $OH^-$  ions in water, along with a cation*



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8

One **weak base** we encounter is ammonia:  $NH_3$

- A **molecular compound** (as opposed to the usual metal hydroxide like NaOH)
  - no guarantee it will fully ionize
  - indeed it doesn't
- A small portion reacts with water to form  $NH_4^+$  and  $OH^-$  ← Produced by reacting with water
- Not fully converted to ions
  - so it is a **weak electrolyte**

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9

### Types of Chemical Reactions we will look at:

- Precipitation
  - Acid–Base
- } *Double-displacement reactions*  
*Also called:*  
*Double-replacement*  
*Exchange*  
*Methathesis*
- Oxidation–Reduction  
*A wide variety of reactions*

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10

### Precipitation Reactions

A **double displacement** reaction in which a solid forms and separates from the solution.

Precipitate (*verb*): to drop out of solution

Precipitate (*noun*): the solid that forms

We will consider precipitation of ionic compounds

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11

### Precipitation Reactions

Remember: When ionic compounds dissolve in water, the resulting solution contains the **separated ions**.

If ions from **two soluble ionic compounds**

**cation** from one, **anion** from the other

correspond to an **insoluble** compound

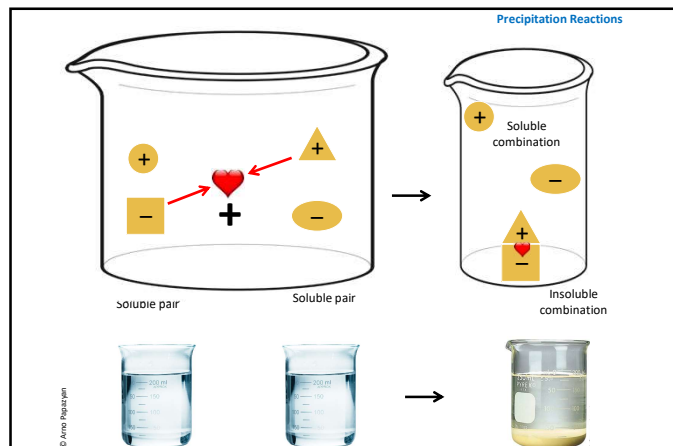
**they combine and precipitate**

if they are in the same solution

- it doesn't matter if there are soluble combinations
- **insoluble combination wins**
  - Because these ions are "happier" together in solid form
  - That's why that combination is insoluble

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12



13

Precipitation Reactions

### Terms related to precipitation

- **Soluble:** solid dissolves in solution; (aq) is used in the reaction equation.
- **Insoluble:** solid does not dissolve in solution; (s) is used in reaction equation.
- **Insoluble** and **slightly soluble** are often used interchangeably. We will do that too.
  - What's called "soluble" or "insoluble" may differ slightly, depending on the industry, discipline, or preferences of an instructor
- **Marginally soluble:** considered "soluble", but barely -- cannot have concentrated solutions

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14

Precipitation Reactions

### Solubility Rules for cation-anion pairs

Before you get scared by a bunch of rules to memorize, observe that the solubility rules are ordered in decreasing solubility:

Always soluble

↓

Less soluble as we go down the list of rules

↓

"Always" insoluble

Always **soluble** cations (with any anion!)  
➤ They never precipitate!

Always **soluble** anions (with any cation!)  
➤ They never precipitate!

Generally **soluble** anions -- with exceptions

Generally **insoluble** anions -- with exceptions

"Others": **insoluble** anions -- except with "always soluble" cations

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15

Precipitation Reactions

### Solubility Rules for cation-anion pairs

1. Alkali metal (**Group 1**) cations and  $\text{NH}_4^+$  are always soluble
2. **Nitrate** (& perchlorate, chlorate, acetate) salts are always soluble.
3. Most  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  salts are soluble (except with  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$  halides).
4. Most **sulfates** are soluble (except with  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$ ; and  $\text{Ag}_2\text{SO}_4$  is only "marginally soluble").
5. Most **hydroxides** are insoluble or only slightly soluble.  
Exceptions: see Rule 1, and  $\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  are somewhat soluble
6. Salts of "**other**" anions ( $\text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$  etc. we see in General Chemistry\*\*) are insoluble (exceptions: see Rule 1)

\* anions *not mentioned explicitly in the rules*  
\*\* *not literally all other anions known to humankind!*

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16

Precipitation Reactions

### Additional observations about alkaline earth ionic compound solubilities

For Group 2 metals, hydroxide & sulfate solubility trends are opposite of each other

$\text{Mg}(\text{OH})_2$  not soluble

↑

decreasing solubility of hydroxides

$\text{Ba}(\text{OH})_2$  soluble

19.0122
12
Mg
Magnesium
24.305
20
Ca
Calcium
40.078
38
Sr
Strontium
87.62
56
Ba
Barium
137.33
88

$\text{MgSO}_4$  soluble

↑

increasing solubility of sulfates

$\text{BaSO}_4$  not soluble

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17

Precipitation Reactions

### On sulfides:

- Sulfide ion,  $\text{S}^{2-}$ , is generally **insoluble** (except, as always, with alkali metals and ammonium)
- Sulfides of Group 2 metals (alkaline earth) **are** soluble.

But:

- Sulfide ion in water is unstable in the long term.
- It slowly reacts with water to produce  $\text{H}_2\text{S}$  gas.

Because its solutions are unstable, I don't include sulfide in the "normal" rules of solubility.

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18

**A silly way to remember the Solubility Rules**

- mnemonics are about the exceptions
- exceptions are insoluble in rules 3 & 4, and soluble in later rules

19

**Some silly mnemonics for the Solubility Rules**

- Group I and ammonia **"I am"** always soluble
- perchlorate, chlorate, acetate, nitrate **"pecan"** always soluble
- Halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) generally **soluble**
  - except with  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$
  - "He lost his halo at the Silver Hog Pub"**
- Sulfate ( $\text{SO}_4^{2-}$ ) generally **soluble**
  - except with  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$
  - "So 4 his fun, Sr. (Señor) Baca goes to the Silver Hog Pub"**
- Hydroxide ( $\text{OH}^-$ ) generally **insoluble**
  - except with  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$
  - "Oh, except for Sr. Baca!"**
- Compounds of other anions are **insoluble** (exception: Rule 1)
  - Others are powders, except where I am**

20

Which of the following ions forms a compound with  $\text{Pb}^{2+}$  that is **soluble** in water?

- $\text{S}^{2-}$
- $\text{Cl}^-$
- $\text{NO}_3^-$
- $\text{SO}_4^{2-}$
- $\text{Na}^+$

21

Precipitation reactions can be represented in three different forms:

- **Molecular** equation
- **Complete ionic** equation
- **Net ionic** equation

22

**"Molecular" Equation**

A better term would have been "Formula Equation", or maybe "Chemical Equation" since there are no molecules around.

- All ions or ionic compounds
- Reactants and products shown as compounds
  - instead of the dissociated ions
- Use solubility rules to determine which compounds are aqueous and which compounds are solids.



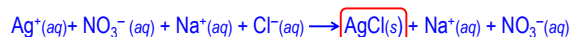
$\text{Ag}^+$  and  $\text{Cl}^-$  are not soluble together

23

**Complete Ionic Equation**

All **soluble** substances that are ionized in aqueous solution are represented as ions.

**Only the precipitate is written as a compound**



Precipitate is not written as separate ions!

Spectator ion

Spectator ion

Spectator ions don't participate in the reaction.

They appear on both sides of the reaction in the same state.

24

**Net Ionic Equation**

- Includes only the ions that do something.  
i.e. the ions that precipitated



- No spectator ions  
 $\text{Na}^+$  and  $\text{NO}_3^-$  are spectator ions. They remain in solution. So they don't show up in the net ionic equation

25

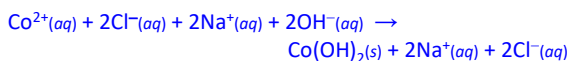
**Concept Practice**

Write the correct "molecular" equation, complete ionic equation, and net ionic equation for the reaction between cobalt(II) chloride and sodium hydroxide.

Formula (Molecular) Equation:



Complete Ionic Equation:



Net Ionic Equation:



26

**Acids, Bases, and Their Reactions**

Acid-base "neutralization" reactions are also "double-displacement"

We touched on acids and bases earlier

- When we discussed inorganic nomenclature
- And earlier in this chapter when we considered electrolytes

We will now look at them at more depth

27

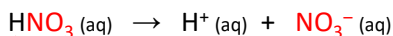
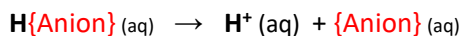
**Acids & bases as defined by Arrhenius**

- Oldest acid-base concept
- Applies in aqueous solutions
- **Acids provide  $\text{H}^+$  in aqueous solution**
- **Bases provide  $\text{OH}^-$  in aqueous solution**
- When an acid and a base "neutralize" each other
  - $\text{H}^+$  and  $\text{OH}^-$  combine to form  $\text{H}_2\text{O}$
  - Remaining parts of the acid and the base form a "salt"

28

**Acids as defined by Arrhenius ("Arrhenius Acids")**

**Acid: provides  $\text{H}^+$**



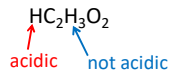
"Acidic" hydrogens are attached to an anion

$\text{H}^+(\text{aq})$  produced actually attaches to a water molecule, forming  $\text{H}_3\text{O}^+$

$\text{H}_3\text{O}^+(\text{aq})$  is called "hydronium"

29

- In the formula of an Arrhenius acid, the acidic hydrogen is written first.
- Any other hydrogens later in the formula are not acidic.



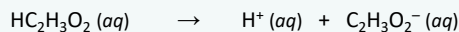
- An acid with one acidic hydrogen is "monoprotic"  
 $\text{HNO}_3$
- An acid with two acidic hydrogens is "diprotic"  
 $\text{H}_2\text{SO}_4$
- An acid with three acidic hydrogens is "triprotic"  
 $\text{H}_3\text{PO}_4$

30

Acids &amp; Bases as defined by Arrhenius

**Weak acids:**

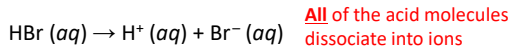
Only some of the weak acid molecules dissociate into ions



Most acetic acid molecules remain undissociated

Only some of the molecules dissociate into ions

The format of a reaction equation gives the impression that all reactions are always complete. That's not true

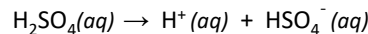
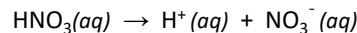
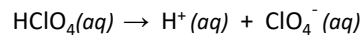
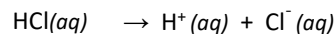
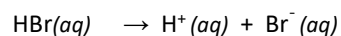
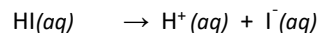
**Strong acids:**Practically all of the strong acid molecules dissociate into  $\text{H}^+$  and the anion of the acid.

All of the acid molecules dissociate into ions

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31

Acids &amp; Bases as defined by Arrhenius

**List of "Strong Acids" we need to know:**Binary hydrogen compounds of halogens, except  $\text{HF}(aq)$ Even for a strong acid like  $\text{H}_2\text{SO}_4$ , if there is more than one acidic H, only the 1<sup>st</sup> dissociation is complete. The 2<sup>nd</sup> H doesn't dissociate easily.

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32

Acids &amp; Bases as defined by Arrhenius

**"Weak Acids" we need to know:**

- Any acid not listed among the "strong"
  - Some may be fairly strong, but just don't dissociate fully
- Organic acids such as acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ )
- $\text{HF}(aq)$
- $\text{H}_3\text{PO}_4$
- The anion produced after diprotic or triprotic acids, even if they are strong in releasing their first acidic H
 
$$\text{HSO}_4^-(aq) \rightarrow \text{H}^+(aq) + \text{SO}_4^{2-}(aq)$$
 Incomplete dissociation

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33

Extracurricular knowledge, if you enjoy obscure info 🤔

**The strange case of Hydrogen Fluoride (HF)**

- HF is normally regarded as a weak acid.
- In dilute aqueous solution, after HF dissociates fully,  $\text{F}^-$  forms a tight ion pair with the  $\text{H}_3\text{O}^+$  just created
  - makes  $\text{H}_3\text{O}^+$  unavailable to function as free  $\text{H}^+(aq)$
- Actually when there isn't much water around, HF is a stronger acid than our usual "strong" acids like  $\text{H}_2\text{SO}_4$ , HCl, etc.

**Nevertheless:**In the world of General Chemistry where aqueous (and not very concentrated) solutions rule, **we will regard HF as a "weak acid"**

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34

Acids &amp; Bases as defined by Arrhenius

**Bases as defined by Arrhenius ("Arrhenius bases")****Base: provides  $\text{OH}^-$** 

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35

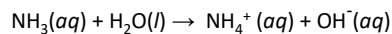
Acids &amp; Bases as defined by Arrhenius

- Bases in the Arrhenius definition act by producing  $\text{OH}^-$  ions
- Most inorganic bases are metal hydroxides, such as NaOH, KOH,  $\text{Ca}(\text{OH})_2$ .
- In General Chemistry it's common to assume all metal hydroxides to be strong bases.
- Ammonia ( $\text{NH}_3$ ) is the only weak base we will need to know in this course.

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36

$\text{NH}_3$ , a molecular compound and a weak base, creates the hydroxide ion by reacting with water:



Since it is a weak base, the reaction is not complete, and most of the ammonia molecules dissolved in water remain as  $\text{NH}_3$  molecules.

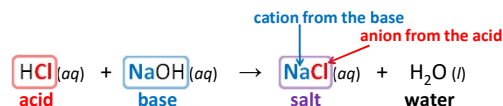
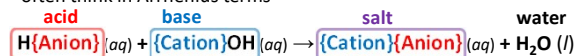
When you see a reagent bottle labeled “ $\text{NH}_4\text{OH}$ ” or “ammonium hydroxide”, it is mostly dissolved ammonia rather than the “compound”  $\text{NH}_4\text{OH}$ .

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37

### Arrhenius acid-base reactions (Neutralization)

When we think about acid-base neutralization reactions, we often think in Arrhenius terms



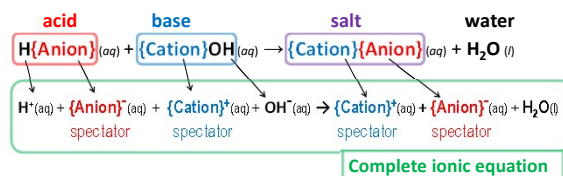
- Ions are shown only as part of compounds above.
- So it is the “molecular equation” representation of an acid-base reaction.

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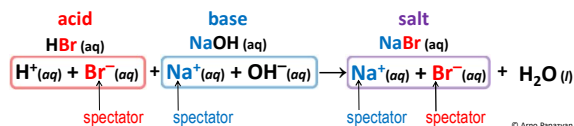
38

### Complete ionic equation for Arrhenius acid-base reactions

Acid, base, and the produced salt written as ions



Example:

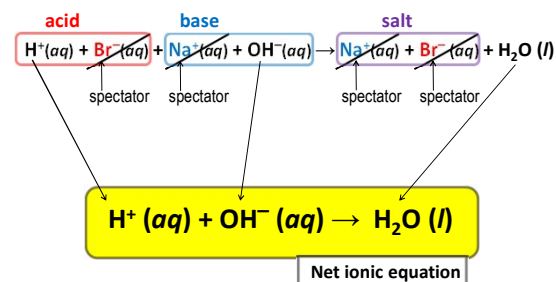


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39

### Net ionic equation for an Arrhenius acid-base reaction

Obtained when we eliminate spectator ions from the complete ionic equation



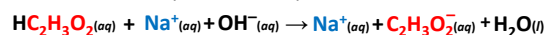
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40

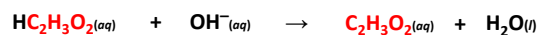
It is part of general chemistry folklore to write ionic equations of acid-base reactions of weak acids with an undissociated **weak acid** molecule because their ionization is incomplete when alone.

For a weak acid like acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ):

“Traditional” Complete Ionic Equation



“Traditional” Net Ionic Equation

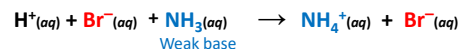


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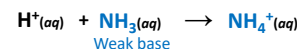
41

Similarly, for a **weak base**, the “traditional” way to write the ionic equations is:

“Traditional” Complete Ionic equation



“Traditional” Net Ionic equation



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42

That reasoning is probably not right, because:

- $H^+$  cation diffuses drastically faster than the undissociated acid molecule, and will generally reach the  $OH^-$  first
- $H^+$  reacts much more readily than the undissociated acid molecule because  $H^+$  is the strongest possible acid in aqueous solution (the weaker the acid, the more drastic this difference becomes)

Undissociated acid concentration being higher than the  $H^+$  concentration is unlikely to justify the traditional way the ionic equations are written.

A similar argument can be made for most weak bases as well.

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43

**However:**

In future courses, you might be expected to “know” to write the ionic equations for weak acid and bases in the “traditional” way.

- I will not ask you to write weak acid/base ionic equations
- But it would be wise to be aware of this tradition

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44

## Redox Reactions

### Oxidation-Reduction reactions

- One or more electrons are transferred.
- Electrons are not created or destroyed in chemical reactions:

number of **electrons gained** = number of **electrons lost**

**Reduction**

(yes, it's confusing, but there is a reason for the name)

**Oxidation**

Remember by:

Oxidation Is Loss of  $e^-$

Reduction Is Gain of  $e^-$

**OIL RIG**

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45

Originally “oxidation” referred literally to combining with oxygen

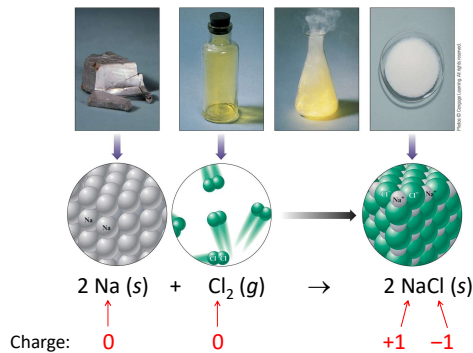
- The more oxygens combined with an atom, the more “oxidized” it was
- Oxygen was thought of as “oxide” in its compounds (with its  $-2$  charge)
- So, the more oxygens bonded to an atom, the more positive it was
  - To have a neutral compound
- Oxidation was then generalized to mean an increase in “charge” (and not necessarily bonding to oxygen)
- And charge itself was generalized to the more abstract “oxidation state” (which is often not an actual charge)

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46

## A simple redox reaction:

### Reaction of Sodium and Chlorine



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47

## We keep track of electron gain and loss using Oxidation numbers (Oxidation states)

- They are like charges, but not exactly
- Oxidation numbers are the charges that would exist if the atoms always formed ionic bonds, with the electron ending up on the atom that likes them more.
  - e.g. oxygen likes electrons more than hydrogen
- Oxidation numbers are often not actual charges
  - when the bonds the atom makes is not ionic
  - But charges on ions are real
- Even when they are not actual charges, the net change in oxidation states does determine the net number of electrons transferred

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48



Redox Reactions

### Hierarchy of Rules for Assigning Oxidation States

- The oxidation state of an atom in a free element is 0.
- The oxidation state of a monoatomic ion is equal to its charge.
- The sum of the oxidation states of all atoms in
  - a neutral molecule or formula unit is 0
  - a polyatomic ion is equal to the charge of the ion

**Sum of oxidation states in an entity = net charge**

- In their compounds,
  - Group I metals have an oxidation state of +1
  - Group II metals have an oxidation state of +2
- In their compounds, nonmetals are assigned oxidation states according to a hierarchical table. **Elements higher in the table have priority over lower entries.**

Fluorine	-1
Hydrogen	+1
Oxygen	-2
Group 7A	-1
Group 6A	-2
Group 5A	-3

"Oxygen is -2" can be overridden by a "higher" rule like "Fluorine is -1"

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49

Redox Reactions

### Examples on monatomic species

Cu(s)      Oxidation state = 0  
 H<sub>2</sub>(g)     Oxidation state = 0  
 H<sub>2</sub>(l)      Oxidation state = 0  
 H (g)      Oxidation state = 0  
 H<sup>+</sup>(aq)    Oxidation state = +1  
 S<sub>8</sub>(s)     Oxidation state = 0  
 S<sup>2-</sup>(s)    Oxidation state = -2  
 Fe<sup>3+</sup>(aq)   Oxidation state = +3

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50

Redox Reactions

### Finding the oxidation states of elements in a compound or polyatomic ion

- If you recognize a polyatomic ion, treat it separately first
- Find the lowest priority element in compound or ion
  - Deal with it last
  - Its oxidation state will be determined by higher-priority rules
- Assign other elements their preferred oxidations states
- Determine the oxidation state of the last (lowest priority) element using the oxidation states of other elements and Rule 3
  - It might not agree with its "default" oxidation state (e.g. oxygen might end up with -1 or +2 instead of the "default" -2). That's completely ok.

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51

Redox Reactions

Find the oxidation states for each of the elements in:

Lowest priority (doesn't even have a preferred oxidation state)

Oxygen is -2 (from Rule 5); and not overridden by a higher rule

+4   -2  
CO<sub>3</sub><sup>2-</sup>

No specific rule; determined from oxygen's, using the rule "sum of oxidation numbers equals the charge of the ion"

(1)x + 3(-2) = -2    ⇒    x = +4

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52

Redox Reactions

Find the oxidation states for each of the elements in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

Suppose we didn't recognize the Cr<sub>2</sub>O<sub>7</sub> part as the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion and we looked at the entire formula

The oxidation state of a monatomic ion is equal to its charge (Rule 2); Group 1A metals are always +1 in compounds

Lowest priority (doesn't even have a preferred oxidation state)

Oxygen is -2 (from Rule 5); and not overridden by a higher rule

+1   +6   -2  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

No specific rule; determined from others, using the rule "sum of oxidation numbers in a compound equals zero"

(2)(+1) + (2)x + 7(-2) = 0    ⇒    x = +6

We got lucky because K has a high-priority oxidation state

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53

Redox Reactions

Find the oxidation states for each of the elements in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

Suppose we recognized the Cr<sub>2</sub>O<sub>7</sub> part as the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion

Lowest priority (doesn't even have a preferred oxidation state)

determined from oxygen and "sum of oxidation numbers in an ion equals ion charge"

Oxygen is -2 (from Rule 5); and not overridden by a higher rule

+6   -2  
Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>

(2)x + 7(-2) = -2    ⇒    x = +6

Then we would have determined the oxidation state of the metal as we always did. Its charge needs to neutralize the anion(s) in the formula. But we already know K is always +1.

+1   +6   -2  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

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54

Redox Reactions

Find the **oxidation states** for each of the elements in  $\text{CuSO}_4$

Here we must recognize  $\text{SO}_4$  as  $\text{SO}_4^{2-}$ . Otherwise we either can't determine both Cu and S, or worse, we assign -2 to S as "higher priority" than Cu (since there is a rule for S, but there isn't one for Cu), and end up assigning +10 to Cu!

"sum of oxidation numbers in an ion equals ion charge"  
 $x + 4(-2) = -2 \Rightarrow x = +6$

Oxygen = -2 as highest priority element here

Because it needs to neutralize the 2- charge of the sulfate. We could do this before learning about oxidation numbers!

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55

Redox Reactions

Find the **oxidation states** for each of the elements in:

Fluorine is -1 (from Rule 5); and not overridden by a higher rule

+2 -1  
 $\text{OF}_2$

Rule 5 value of -2 overruled by higher priority Fluorine; oxidation state of O is then determined from "sum of oxidation numbers in a compound equals zero"

$(1)x + 2(-1) = 0 \Rightarrow x = +2$

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56

Redox Reactions

Find the **oxidation states** for each of the elements in:

Group 1 metals: +1 in their compounds (Part of Rule 4)

+1 -1  
 $\text{LiH}$

Lower priority; its preference is part of Rule 5

Rule 5 value of +1 overruled by higher priority Rule 4 and Rule 2: "sum of oxidation numbers in a compound equals zero"

$(1)(+1) + (1)x = 0 \Rightarrow x = -1$

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57

Redox Reactions

**Re-stating "oxidation" and "reduction" in terms of oxidation state (instead of electrons)**

**Oxidation:** increase in oxidation state (loss of electrons)

**Reduction:** decrease in oxidation state (gain of electrons)

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58

Redox Reactions

**Oxidation and reduction are coupled**

- Electrons lost by one atom must be gained by another.
- Electrons are not lost; they are transferred

Number of electrons lost = Number of electrons gained

- If there is an atom getting oxidized, there must be at least one other atom getting reduced
- If there is an atom getting reduced, there must be at least one other atom getting oxidized

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59

Redox Reactions

**Oxidation and reduction are coupled**

**Oxidized substance: reducing agent**

- If something is **oxidized**, it must be **reducing** something else

**Reduced substance: oxidizing agent**

- If something is **reduced**, it must be **oxidizing** something else

**And remember:**

- "oxidizing agent" and "reducing agent" are always **on the reactant side!**
- They **cannot be products!**

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**An oxidizing agent (oxidant)**

- causes another substance to be oxidized
- contains an element whose oxidation state *decreases* in a redox reaction
- *gains* electrons (electrons are found on the left side of its half-equation)
- is reduced

61

**A reducing agent (reductant)**

- causes another substance to be reduced
- contains an element whose oxidation state *increases* in a redox reaction
- *loses* electrons (electrons are found on the right side of its half-equation)
- is oxidized

62

Redox Reactions

In a redox reaction:

- What we said about electrons applies equally to oxidation states.
- An increase in the oxidation state of an atom is coupled with a decrease in the oxidation state of another atom

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63

Redox Reactions

**It's a redox reaction if ...****The oxidation state of any element changes in the reaction**

Remember: If there is an element that changed its oxidation state, there must be another that also changed in the opposite direction

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64

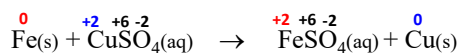
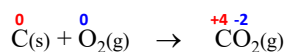
Redox Reactions

**It's probably a redox reaction if there is an elemental substance such as O<sub>2</sub>(g), Cu(s), etc., anywhere in the reaction**

Oxidation state is zero for an elemental substance

In a compound atoms normally have nonzero oxidation states.

If the elemental substance like O<sub>2</sub>(g), H<sub>2</sub>(g), S<sub>8</sub>(s), Fe(s) appears on either side of a reaction, it must occur in a compound on the other side of the reaction.



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65

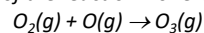
Redox Reactions

There are exceptions to:

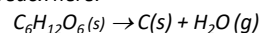
*"It's probably a redox reaction if there is an elemental substance such as O<sub>2</sub>(g), Cu(s), etc., anywhere in the reaction"*

**Exception:**

*When the element is in an "elemental state" on both sides of the reaction. For example, there is no redox here:*

**Exception:**

*When the element happens to have an average of zero oxidation state in a compound. For example, there is no redox here:*



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66



### Balancing Redox Equations

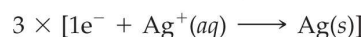
- In this case, the half-reactions are already balanced with respect to mass—the number of each type of atom on both sides of each half-reaction is the same.
- However, the equations are not balanced with respect to charge.
- We balance the charge of each half-reaction individually by adding the appropriate number of electrons to make the charges on both sides equal.



73

### Balancing Redox Equations

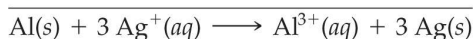
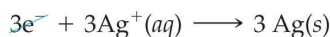
- Since these half-reactions must occur together, the number of electrons lost in the oxidation half-reaction must equal the number gained in the reduction half-reaction.
- We equalize these by multiplying one or both half-reactions by appropriate whole numbers to equalize the electrons lost and gained.



74

### Balancing Redox Equations

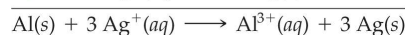
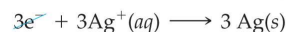
- Add the half-reactions together, canceling electrons and other species as necessary.



75

### Balancing Redox Equations

- Verify that the equation is balanced, with respect to both mass and charge.



Reactants	Products
1 Al	1 Al
3 Ag	3 Ag
+3 charge	+3 charge

- Notice that the charge need not be zero on both sides of the equation—it just has to be *equal* on both sides. The equation is balanced.

76

### Balancing Redox Reactions in Aqueous Solutions

Balancing redox reactions in aqueous solution might look like alchemy where the initial equation might be missing an element or two (or more) on one side of the equation or the other!

You might feel like you are doing things we are not supposed to do in balancing, such as adding new reactants or products to the equation. That's because aqueous-solution redox reactions are often given in "bare-bones" form.

- We are expected to "fill in the blanks" and create a complete equation while balancing it.
- Actually, it's easier to start balancing without the species that are not involved in redox and then add them later. We just need to get used to it.

77

### Balancing Redox Reactions in Aqueous Solutions -- "ionic" or "net ionic" equations

The "bare-bones" (i.e. skeletal) reactions are usually given in "net ionic" form

- Some authors seem to use the term "ionic equation" to mean "net ionic equation"; so beware!

"ionic equation" and "net ionic equation" are analogous to those for double-displacement (metathesis) reactions:

- Ionic equation: include the "counter-ions" that would allow you to combine ions into neutral chemical formulas
- Net-ionic equation: do not include spectator ions (those "counter-ions" of ions that are actually involved in redox)

78

### Balancing Redox Reactions in **Acidic** Conditions

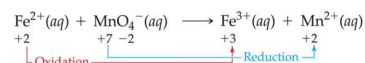
- Write both half reactions (oxidation & reduction)
- Balance all atoms other than O and H
- Balance O by adding H<sub>2</sub>O
- Balance H by adding H<sup>+</sup>
- Balance charge by adding e<sup>-</sup>
- Multiply both half reactions by a factor to equate no of e<sup>-</sup>
- Add the two half-reactions and cancel out the e<sup>-</sup>'s and any substances appearing on both side
- Double check: ✓All elements balanced  
✓Charges balanced

79

### EXAMPLE / PRACTICE

Balance the redox reaction  $\text{Fe}^{2+}(aq) + \text{MnO}_4^{-}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq)$  in **acidic** solution, using the half-reaction method

1. Assign oxidation states to all atoms and identify the substances being oxidized and reduced.



2. Separate the overall reaction into two half-reactions, one for oxidation and one for reduction.

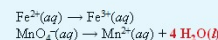


3. Balance each half-reaction with respect to mass in the following order:

- Balance all elements other than H and O.

All elements other than hydrogen and oxygen are balanced, so you can proceed to the next step.

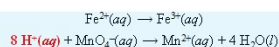
- Balance O by adding H<sub>2</sub>O.



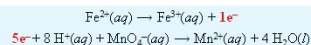
80

Balance the redox reaction  $\text{Fe}^{2+}(aq) + \text{MnO}_4^{-}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq)$  in acidic solution, using the half-reaction method (*continued*)

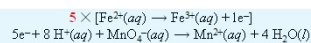
- Balance H by adding H<sup>+</sup>.



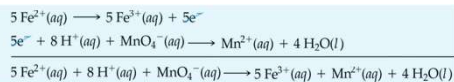
4. Balance each half-reaction with respect to charge by adding electrons to the right side of the oxidation half-reaction and the left side of the reduction half-reaction. (The sum of the charges on both sides of each equation should be equal.)



5. Make the number of electrons in both half-reactions equal by multiplying one or both half-reactions by a small whole number.



6. Add the two half-reactions together, canceling electrons and other species as necessary.



81

Balance the redox reaction  $\text{Fe}^{2+}(aq) + \text{MnO}_4^{-}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq)$  in acidic solution, using the half-reaction method (*continued*)

7. Verify that the reaction is balanced with respect to both mass\* and charge.

Reactants	Products
5 Fe	5 Fe
8 H	8 H
1 Mn	1 Mn
4 O	4 O
+17 charge	+17 charge

\* Not literally "mass". It just means the number of atoms for each element

82

### Balancing Redox Reactions in **Basic** Conditions

- Write both half reactions
- Balance all atoms other than O and H
- Balance O by adding H<sub>2</sub>O
- Balance H by adding H<sup>+</sup>
- Balance charge by adding e<sup>-</sup>
- Multiply both half reactions by a factor to equate no of e<sup>-</sup>
- Add the two half-reactions and cancel out the electrons

Start like acidic

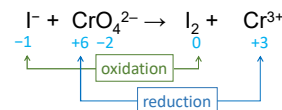
- "Neutralize" H<sup>+</sup> by adding same no. of OH<sup>-</sup> to both sides
- Combine H<sup>+</sup> and OH<sup>-</sup> on the same side to make H<sub>2</sub>O
- Cancel appropriate no. of H<sub>2</sub>O (and any other species) appearing on both sides, so that the remainder appears on only one side
- Double check: ✓All elements balanced  
✓Charges balanced

83

### Practice – Balancing redox reactions, Basic Conditions

Balance the reaction equation  $\text{I}^{-} + \text{CrO}_4^{2-} \rightarrow \text{I}_2 + \text{Cr}^{3+}$

assign oxidation states and determine element oxidized and element reduced



separate into oxidation & reduction half-reactions



84

Balance the reaction equation in basic solution  $I^- + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$   
(continued)

⋮

- balance atoms other than O and H
  - oxidation:  $I^- \rightarrow I_2$
  - $2I^- \rightarrow I_2$
  - reduction:  $CrO_4^{2-} \rightarrow Cr^{3+}$
- balance O by adding  $H_2O$  to side that lacks O
  - $CrO_4^{2-} \rightarrow Cr^{3+} + 4H_2O$
- balance H by adding  $H^+$  to side that lacks H
  - $CrO_4^{2-} + 8H^+ \rightarrow Cr^{3+} + 4H_2O$
- balance each half-reaction with respect to charge by
  - adding electrons on product side for oxidation
    - $2I^- \rightarrow I_2 + 2e^-$
  - adding electrons on reactant side for reduction
    - $CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$

85

Balance the reaction equation in basic solution  $I^- + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$   
(continued)

⋮

Multiply, if needed, each half-reaction by an appropriate factor so that both involve the same number of electrons (and they are the smallest possible integers)

$$\begin{array}{l} (2I^- \rightarrow I_2 + 2e^-) \times 3 \\ (CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O) \times 2 \end{array}$$

↓

$$\begin{array}{l} 6I^- \rightarrow 3I_2 + 6e^- \\ 2CrO_4^{2-} + 16H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O \end{array}$$

Add the half reactions and cancel electrons

$$2CrO_4^{2-} + 16H^+ + 6I^- + \cancel{6e^-} \rightarrow 2Cr^{3+} + 8H_2O + 3I_2 + \cancel{6e^-}$$

$$2CrO_4^{2-} + 16H^+ + 6I^- \rightarrow 2Cr^{3+} + 8H_2O + 3I_2$$

86

Balance the reaction equation in basic solution  $I^- + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$   
(continued)

⋮

So far it has been the same as for balancing in acidic solution

Now add enough  $OH^-$  to neutralize  $H^+$  to produce  $H_2O$ , and the same number of  $OH^-$  to the other side

$$2CrO_4^{2-} + \underbrace{16H^+ + 16OH^-}_{16H_2O} + 6I^- \rightarrow 2Cr^{3+} + 8H_2O + 3I_2 + 16OH^-$$

$$2CrO_4^{2-} + 16H_2O + 6I^- \rightarrow 2Cr^{3+} + 8H_2O + 3I_2 + 16OH^-$$

Cancel  $H_2O$  (and any other species appearing on both sides at this point)

$$2CrO_4^{2-} + \cancel{8H_2O} + 6I^- \rightarrow 2Cr^{3+} + \cancel{8H_2O} + 3I_2 + 16OH^-$$

**Balanced in basic solution**  $2CrO_4^{2-} + 8H_2O + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 16OH^-$

87

Balance the reaction equation in basic solution  $I^- + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$   
(continued)

⋮

Finally, make sure that all the elements as well as charges are balanced:

$$2CrO_4^{2-} + 8H_2O + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 16OH^-$$

reactant side	Element	product side
2	Cr	2
6	I	6
16	O	16
16	H	16
-10	charge	-10

88

**Solving Stoichiometry Problems for Reactions in Solution**

- Identify the species present in the combined solution, and determine what reaction occurs.
- Write the balanced equation (net ionic or "molecular", depending on which seems more convenient) for the reaction.
- Calculate the moles of reactants.
- Determine which reactant is limiting.
- Calculate the moles of product(s), as required.
- Convert to grams or other units, as required.

**Not really different from general stoichiometry questions!**

**We just use volumes and concentrations to find moles (or vice versa)**

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89

Any reaction that can occur in solution can be the subject of solution stoichiometry, such as:

- Acid-base neutralization reactions
- Redox reactions
- Precipitation reactions

90

To do anything useful, we must know:

- The nature of the reaction.
- The amounts of chemicals present in the solutions.
  - And to know the amount of a chemical present in solution, we need to know the volume of the solution and its concentration

91

### Performing Calculations for Acid–Base Reactions

- No different from other reactions, really.
- Often we do “titrations”
- In a titration there is no limiting reactant, by definition
- Balancing is easy because  $\text{H}^+$  and  $\text{OH}^-$  must come in equal moles
  - we can even do the stoichiometry without writing the reaction
  - but don't feel you must be able to

92

### Acid–Base Titrations

**Titration:** delivery of a measured volume of a solution of known concentration (the titrant) into a solution containing the substance being analyzed (the analyte).

**Equivalence point:** exactly enough titrant added to react completely with the analyte.

- The ideal we try to achieve at the end of titration

**Endpoint:** the indicator changes color so you can tell the equivalence point has been reached. It's an experimental approximation of the equivalence point.

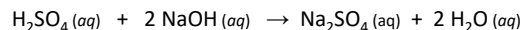
- What we can achieve in practice, with our indicator

**There is no limiting or excess reactant in titrations -- by design**

93

### Practice

For the titration of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) with sodium hydroxide ( $\text{NaOH}$ ), how many mL of 0.1054 M sodium hydroxide would be required to react with 1.00 L of 0.500 M sulfuric acid to reach the endpoint?



$$n_{\text{H}_2\text{SO}_4} = c_{\text{H}_2\text{SO}_4} V_{\text{H}_2\text{SO}_4} = (0.500)(1.00) = 0.500 \text{ mol H}_2\text{SO}_4$$

$$n_{\text{NaOH}} = 0.500 \text{ mol H}_2\text{SO}_4 \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4} = 1.00 \text{ mol NaOH}$$

$$n_{\text{NaOH}} = c_{\text{NaOH}} V_{\text{NaOH}}$$

$$1.00 \text{ mol} = (0.1054 \text{ mol/L}) V_{\text{NaOH}}$$

$$\Rightarrow V_{\text{NaOH}} = 9.49 \text{ L} = 9.49 \times 10^3 \text{ mL}$$

94

When the acid and base are used in stoichiometric amounts, such as during titrations, you can use the following formula:

$$\alpha c_{\text{acid}} V_{\text{acid}} = \beta c_{\text{base}} V_{\text{base}}$$

Moles of  $\text{H}^+$  from acid
Moles of  $\text{OH}^-$  from base

Where  $\alpha$  = number of acidic H's in the acid formula  
 $\beta$  = number of OH's in the base formula

$\alpha = 1$ for HCl	$\beta = 1$ for KOH
$\alpha = 2$ for $\text{H}_2\text{SO}_4$	$\beta = 2$ for $\text{Ca}(\text{OH})_2$
$\alpha = 3$ for $\text{H}_3\text{PO}_4$	$\beta = 3$ for $\text{Al}(\text{OH})_3$

**Don't confuse it with the dilution formula!**

95

Then the previous example:

For the titration of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) with sodium hydroxide ( $\text{NaOH}$ ), how many mL of 0.1054 M sodium hydroxide would be required to react with 1.00 L of 0.500 M sulfuric acid to reach the endpoint?

could be solved this way:

$$\alpha c_{\text{acid}} V_{\text{acid}} = \beta c_{\text{base}} V_{\text{base}}$$

$$(2) (0.500) (1.00) = (1) (0.1054) V_{\text{NaOH}}$$

$$V_{\text{NaOH}} = 9.49 \text{ L} = 9.49 \times 10^3 \text{ mL}$$

96



Acid-base neutralization and redox reactions are often used in titrations where, by design, there is no limiting or excess reactant.

Titration with a redox reaction (or any reaction) is in principle similar to that with acid-base reaction.

With precipitation reactions, we often have a limiting reactant – therefore also excess reactant(s).

We don't often see precipitation reactions in the context of titration.

97

### Practice

10.0 mL of a 0.30 M sodium phosphate solution reacts with 20.0 mL of a 0.20 M lead(II) nitrate solution (assume volumes add up perfectly). Will there be a reaction? If so, what is the product?

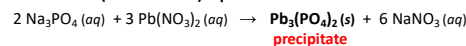
With two solutions of ionic compounds, typically we think of a double-displacement reaction of the "precipitation" kind.

Will there be a precipitate? If not, the ions would still be floating around just as before the two solutions were mixed, and there would be no reaction.

sodium phosphate:  $\text{Na}_3\text{PO}_4(\text{aq})$  exists as  $3 \text{Na}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$

lead (II) nitrate:  $\text{Pb}(\text{NO}_3)_2(\text{aq})$  exists as  $\text{Pb}^{2+}(\text{aq}) + 2 \text{NO}_3^-(\text{aq})$

"Molecular" (or "formula") equation:



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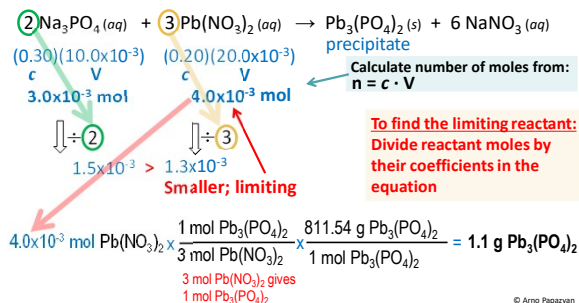
98

Calculations with Reactions in Solutions – Precipitation reactions

### Practice

10.0 mL of a 0.30 M sodium phosphate solution reacts with 20.0 mL of a 0.20 M lead(II) nitrate solution (assume volumes add up perfectly).

What mass of precipitate will form?



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99