

Chapter 4: Reactions in Aqueous Solutions

Water

- 60 % of our bodies
- heat modulator
- solvent for reactions
- covers 70% of Earth

Chapter 4 3 types of reactions that occur in H₂O

1. precipitation
2. acid-base
3. redox

4.1 General Properties of Aqueous (H₂O) Solutions (soln)

- **solution** - homogeneous (uniform) mixture of two or more substances, consisting of:

solvent - the bulk medium, e.g., H₂O (usually the larger amount)

solute(s) - the dissolved substance(s), e.g., NaCl (usually present in lesser quantities)

aqueous soln - H₂O is the solvent

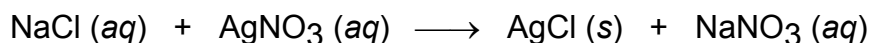
- **concentration** - measure of relative solute/solvent ratio
- **standard solution** - accurately known concentration
- **saturated solution** - contains maximum amount of solute
- **solubility** - concentration of a saturated solution, e.g.,

solubility of NaCl is about 36 g NaCl / 100 g H₂O ("soluble")

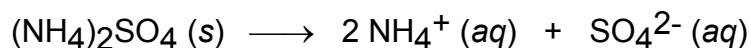
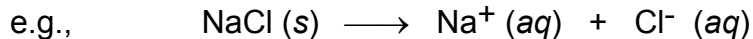
solubility of CuS is about 10⁻⁵ g CuS / 100 g H₂O ("insoluble")

- **precipitate** - an "insoluble" reaction product

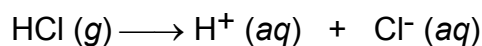
e.g., a *precipitation reaction* where the precipitate is AgCl:



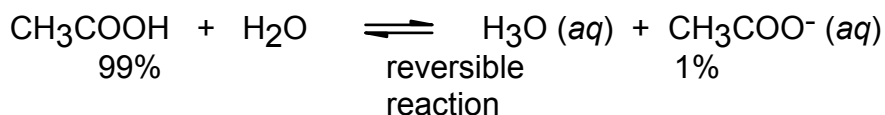
- **Electrolytes** - solutes that produce ions in solution via **dissociation** (these solutions can conduct electricity)



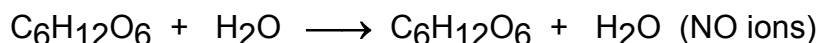
- ions dissolve in H_2O because it is polar (see Fig 4.2)
 - **hydration** -- process of surrounding ions by H_2O
1. **"strong" electrolytes** -- **100% ionized**
salts and acids can be electrolytes



2. **"weak" electrolytes** -- substances that are **partially ionized (< 100%)**
weak acid (acetic acid)



3. **non-electrolytes** -- substances that are **not ionized** and do not conduct electricity



Memorize the Strong, Weak, Non-Electrolytes
Table 4.1, page 117 or chart below ↓

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl, HBr, HI HNO ₃ HClO ₄ H ₂ SO ₄ soluble bases with OH ⁻ , i.e., NaOH, Ba(OH) ₂	CH ₃ COOH HF HNO ₂ NH ₃ H ₂ O	C ₆ H ₁₂ O ₆ (glucose) C ₁₂ H ₂₂ O ₆ (sucrose) CH ₃ OH (methanol) C ₂ H ₅ OH (ethanol) (NH ₂) ₂ CO (urea)

4.2 Precipitation Reactions

These are reactions that occur when aqueous solns are mixed and the reaction produces insoluble product (precipitate)

A. Solubility

- maximum amount of solute that will dissolve in a given quantity of solvent
- formation of insoluble product makes a reaction occur because it prevents the products from reforming the original reactants

Memorize the Solubility Rules
Table 4.2, page 119
 or chart below ↓

Solubility Rules for Common Ionic Compounds in Water

<u>Soluble</u>	<u>Insoluble</u>
Group I and NH_4^+	
nitrates bicarbonates chlorates	carbonates } phosphates } chromates } sulfides }
halides (except Ag^+ , Hg_2^{2+} , Pb^{2+})	hydroxides
sulfates (except Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Hg^{2+})	except Group I and NH_4^+ except Group I and Ba^{2+}

Examples:

Ag_2SO_4	insoluble	CuS	insoluble
CaCO_3	insoluble	$\text{Cu}(\text{OH})_2$	insoluble
Na_3PO_4	soluble	$\text{Zn}(\text{NO}_3)_2$	soluble

B. Molecular and Ionic Equations

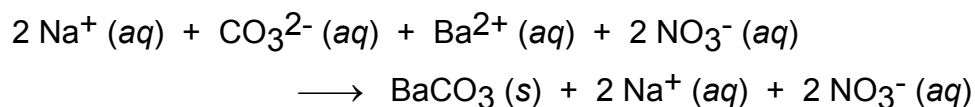
Metathesis Reaction (also called "double displacement")

Ions from two different reactants simply trade partners,



This was written as a **molecular equation** in which all reactants and products are shown as complete, neutral chemical formulas.

It could also have been written as a complete **ionic equation** in which all **soluble** ionic compounds are split up into their ions,

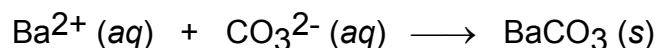


Here, the Na^+ and NO_3^- ions are called "**spectator ions**" because they appear unchanged on both sides of the equation.

The **spectator ions** do not participate in the chemically important part of the reaction -- the precipitation of BaCO_3

The essential chemical process can be written without the spectator ions in the

net ionic equation,



The **net ionic equation** shows that, in general, a precipitate of BaCO_3 will form whenever the ions Ba^{2+} and CO_3^{2-} are combined in aqueous solution, regardless of their sources.

Summary of the three types of balanced chemical equations

Molecular Equation

- shows all compounds with complete, neutral molecular formulas
- useful in planning experiments and stoichiometry calculations

Ionic Equation (complete)

- all strong electrolytes are shown in their dissociated, ionic forms
- insoluble substances and weak electrolytes are shown in their molecular form
- "spectator ions" are included
- useful for showing all details of what is happening in the reaction

Net Ionic Equation

- "spectator ions" are omitted
- only the essential chemical process is shown, i.e., formation of a:
 - solid precipitate,
 - gaseous product, or
 - weak electrolyte (e.g., water)
- useful for generalizing the reaction -- same important product can often be formed from different sets of reactants

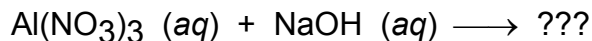
When will a precipitate form?

**KNOW the *ELECTROLYTES and SOLUBILITY RULES*
Tables 4.1 and 4.2 !!!**

Example:

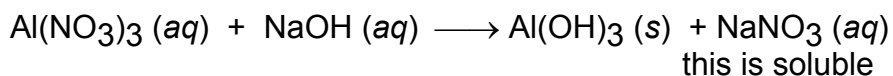
Write the net ionic equation for the reaction of $\text{Al}(\text{NO}_3)_3$ with NaOH in water.

Step 1: Write the **molecular reaction**

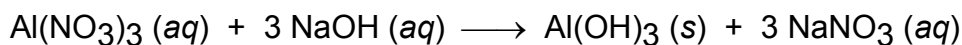


switch ions and check for solubility
Is $\text{Al}(\text{OH})_3$ soluble?

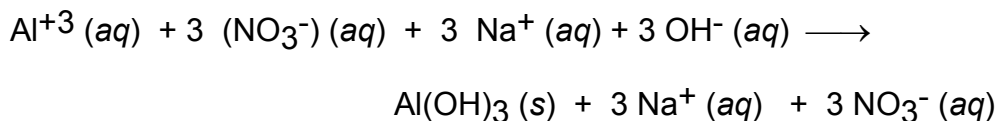
No



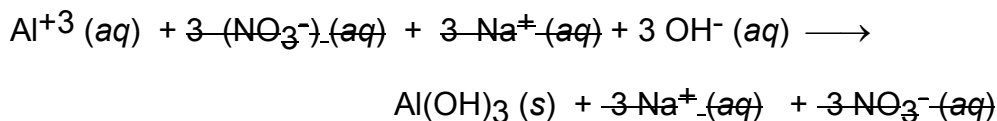
Step 2: Balance the molecular equation



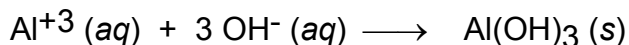
Step 3: Show dissociated ions – **ionic equation**



Step 4: Cancel spectator ions



Step 5: Write the **net ionic equation**



4.3 Acid-Base Reactions

Arrhenius definition:

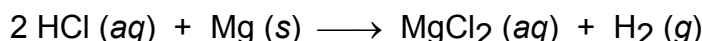
Acids give H^+ when dissolved in water and **bases** give OH^- .

Common acids: vinegar, lemon juice, aspirin

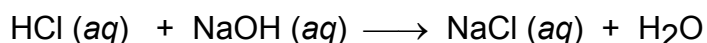
Common bases: milk of magnesia, lye

A. Properties of acids

- taste sour
- cause color changes in dyes (litmus: blue to red)
- react with metals (Zn, Mg, Fe) to form H_2 gas

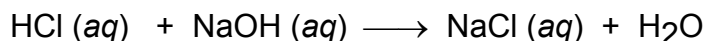


- react with carbonates and bicarbonates to form CO_2 gas
- aqueous solutions conduct electricity (because there are ions present)
- react with bases to form salts and water



B. Properties of Bases

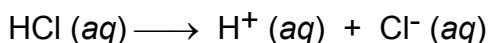
- taste bitter
- feel slippery (e.g., soaps)
- cause color changes in dyes (litmus: red to blue)
- aqueous solutions conduct electricity (because there are ions present)
- react with acids to form salts and water



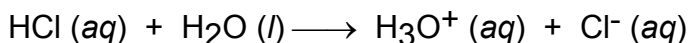
C. Bronsted definition (broader)

Acid - proton (H^+) donor **Base** - proton acceptor

Bronsted Acid

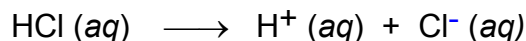


more correctly

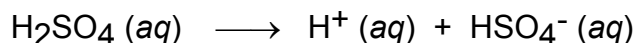


H_3O^+ is a hydrated proton called the **hydronium ion**

- **monoprotic** acids - donate one hydrogen ion upon ionization



- **diprotic** acids - donate two hydrogen ions upon ionization



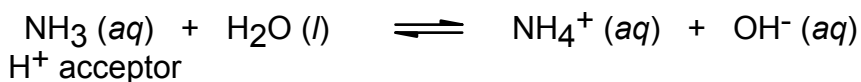
2 steps with the second being incomplete

- **triprotic** acids - donate three hydrogen atom (H_3PO_4)

Bronsted base



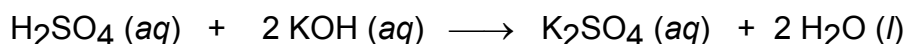
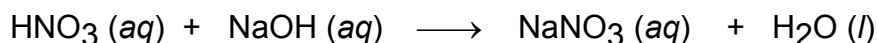
proton acceptor



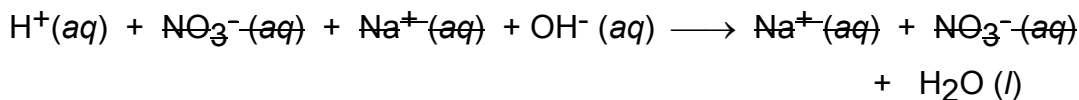
H^+ acceptor

weak electrolyte since it only partially dissociates

D. Acid-Base Neutralization



ionic equation:



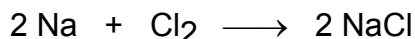
net ionic equation:



4.4 Oxidation-Reduction Reactions

- reduction-oxidation - **redox**
- electron transfer reactions

Examples: burning fossil fuels, bleach, rusting
some occur in water, others don't

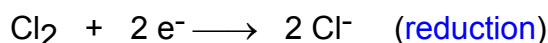
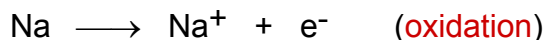


Overall process involves **two Half Reactions**:

oxidation -- loss of electron(s)

reduction -- gain of electron(s)

half reactions:



related terms:

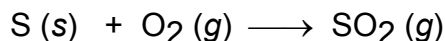
oxidizing agent = the substance that is **reduced** (Cl_2)

reducing agent = the substance that is **oxidized** (Na)

Oxidation and reduction always occur together so that there is no *net* loss or gain of electrons overall.

A. Oxidation Numbers (oxidation states)

sometimes electron transfer is not as clear cut, but because partial transfer of electrons occurs it is still a redox reaction



Oxidation Number: a "charge" that is *assigned* to an atom to aid in balancing redox reactions

Generally, oxidation number is the charge that would result if all of the bonding electrons around an atom were assigned to the more electronegative element(s).

Learn Rules for assigning oxidation numbers

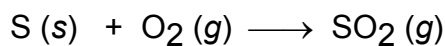
see page 129 or below ↓

Practice with many examples !!!

1. Free elements - oxidation number = 0

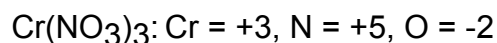
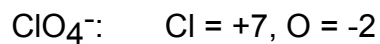
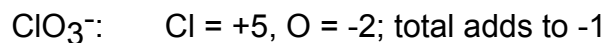
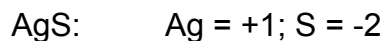
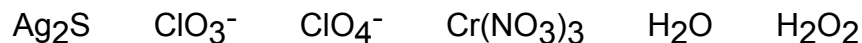
2. Ions of one atom: oxidation number = charge
3. Oxygen - usually -2; in peroxides (H_2O_2), O = -1
4. Hydrogen is usually +1, except when bonded to metals, e.g., LiH, NaH in which H = -1
5. F = -1; Cl, Br, I (ions) = -1, but as molecular compounds, the charge varies and is positive
6. Sum of oxidation numbers = 0 in neutral compounds and equals the charge in polyatomic ions
7. Oxidation numbers are not always integers, e.g., O_2^- (superoxides) = -1/2

Thus for



- S (s) = 0
- O_2 (g) = 0
- SO_2 (g): S = +4 and O = -2

e.g., assign all oxidation numbers in:



B. Types of Redox Reactions

- combination
- decomposition
- displacement
- disproportionation

C. Balancing Redox Reactions

Chapter 19, pages 798 to 800

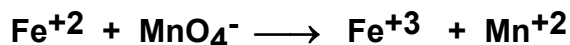
ION-ELECTRON METHOD for Balancing Redox Equations

1. Write unbalanced *ionic* equations for the two half-reactions. (Look at oxidation numbers in the “skeleton equation”)
2. Balance atoms other than H and O.
3. Balance O with H₂O.
4. Balance H with H⁺.
5. Balance charge with appropriate number of electrons.
6. If in acidic solution, then skip to step 7. If in basic solution, then add equal number of OH⁻ to both sides to cancel all of the H⁺.
7. Rewrite the balanced half reactions.
8. Multiply balanced half-reactions by appropriate coefficients so that the number of electrons are equal.
9. Add the half-reactions together.
10. Cancel species that appear on both sides to get the balanced Net Ionic Equation.
11. If necessary, add spectator ions to get the balanced molecular equation.

Check the Final Balance (atoms and charges) !

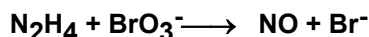
Example:

Balance the following reaction that occurs in acidic medium using the ion-electron method.



Example: (do this one on your own)

Balance the following reaction that occurs in *basic* solution. Write *complete, balanced equations* for the oxidation and reduction *half-reactions* and the *net ionic equation*.



- (1) Check oxidation numbers to determine what is oxidized and what is reduced.

Bromine goes from +5 in BrO_3^- to -1 in Br^- . Thus, BrO_3^- is being reduced.

Nitrogen goes from -2 in N_2H_4 to +2 in NO . Thus, N_2H_4 is being oxidized.

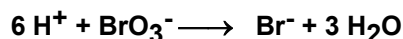
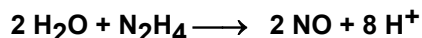
So, the two unbalanced half reactions are:



- (2) Balance atoms other than H and O: $\text{N}_2\text{H}_4 \longrightarrow 2 \text{NO}$

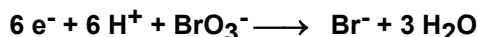
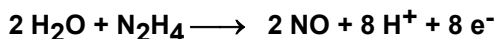
- (3) Balance O with H_2O , and then

- (4) Balance H with H^+

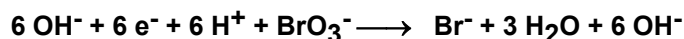
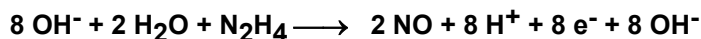


(Note: the atoms are balanced at this point but the charges are not!)

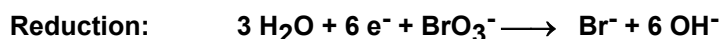
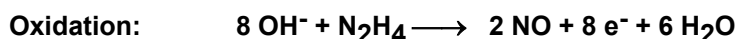
- (5) Balance charge with electrons



- (6) Since the reaction is occurring in *basic solution*, the hydrogen ions (H^+) must be neutralized by adding equal numbers of OH^- ions to both sides of the equations.

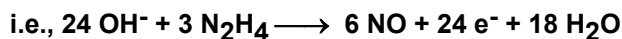
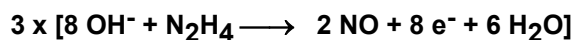


Now simplify by combining H^+ with OH^- and subtracting H_2O where possible

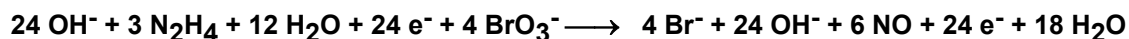


- (7) You should now have the complete, balanced half-reactions! Rewrite them and *check the balance of all atoms and charges*.

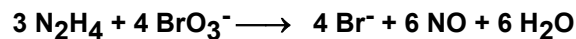
- (8) Multiply the balanced half-reactions by appropriate coefficients to make the number of electrons cancel. In this case, multiply the reduction by 3 and the oxidation by 4 for a total of 24 electrons on each side.



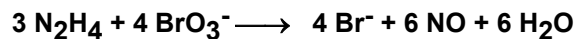
- (9) Add the half-reactions together, being careful not to omit anything.



- (10) Cancel species like H_2O , OH^- , or H^+ that may appear on both sides. In this case, subtract 24e^- , 24OH^- and $12 \text{H}_2\text{O}$ from each side.



- (11) If necessary add spectator ions to get the balanced molecular equation. That is not possible in this case because we started with an unbalanced *ionic* equation. Then, *check the final balance* -- all atoms and *total charges* must be equal on both sides of the equations.



Summary

acid-base reactions - transfer of H^+

redox reactions - transfer of electrons or change in oxidation #

4.5 Concentration of Solutions

- to do reactions in solution, need to control amounts
- concentration - amount of solute in a given quantity of solvent

A. Molar Concentration (Molarity)

Molarity (M) = moles solute / liter of solution

- units: moles/L or moles/1000 mL
- another conversion factor

Thus, 0.10 M NaCl solution contains 0.10 mole or 5.84 g NaCl per liter of solution

Example:

What mass of MgCl₂ is required to prepare 60.0 mL of 0.100 M solution?

1st - find moles of MgCl₂ required:

$$60.0 \text{ mL} \times \frac{0.100 \text{ moles MgCl}_2}{1000 \text{ mL}} = 0.0060 \text{ moles MgCl}_2$$

2nd - convert to grams of MgCl₂:

$$0.0060 \text{ moles MgCl}_2 \times \frac{95.21 \text{ g MgCl}_2}{1 \text{ mole MgCl}_2} = 0.572 \text{ g MgCl}_2$$

- Prepare this solution by weighing 0.572 g MgCl₂, dissolving in some H₂O (about 30 mL), and then diluting to the 60.0 mL mark. (see Fig.4.18)
- In this solution
 - $\text{MgCl}_2 \longrightarrow \text{Mg}^{2+} + 2 \text{Cl}^-$
 - Concentration [Mg²⁺] = 0.100 M
 - Concentration [Cl⁻] = 0.200 M
 - every mole of MgCl₂ gives 3 moles of ions: 2 moles of Cl⁻ and 1 mole of Mg²⁺

B. Dilution of Concentrated Solutions

concentrated solution + H₂O → dilute solution

$$(\text{moles solute})_{\text{conc}} = (\text{moles solute})_{\text{dil}}$$

(moles solute)_{before dilution} = (moles solute)_{moles after dilution}

$$V_i M_i = V_f M_f \quad (\text{where } i = \text{initial and } f = \text{final})$$

USE THIS ONLY FOR DILUTION !!!!

not for acid-base titration!!!!

Example:

A 5.00 M NaCl "stock" solution is available. How would prepare 300 mL of a 0.100 M NaCl "standard" solution?

$$V_i \times (5.00 \text{ M}) = (300 \text{ mL}) \times (0.100 \text{ M})$$

$$V_i = (300 \text{ mL}) \times (0.100 \text{ M}) / (5.00 \text{ M}) = 6.00 \text{ mL}$$

Measure out 6.00 mL of the 5.00 M "stock" solution, then add H₂O to a total volume of 300 mL.

4.6 Gravimetric Analysis

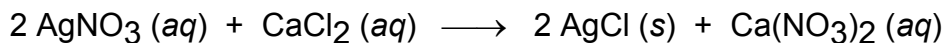
(Stoichiometry of Reactions in Solution)

analytical technique based on measuring mass of precipitate

Use the Mole Method !!!

Example:

For the following reaction,



- (a) What volume of 0.250 M AgNO_3 is required to react completely with 250 mL of 0.400 M CaCl_2 ?
- (b) What mass of AgCl should be produced?

stoichiometry: 2 mole $\text{AgNO}_3 \Leftrightarrow$ 1 mole $\text{CaCl}_2 \Leftrightarrow$ 2 mole AgCl

Part (a): volume of AgNO_3 ?

1st, find moles of CaCl_2

$$(250 \text{ mL}) \times \frac{0.400 \text{ mole}}{1,000 \text{ mL}} = 0.100 \text{ mole } \text{CaCl}_2$$

2nd, find moles of AgNO_3

$$(0.100 \text{ mole } \text{CaCl}_2) \times \frac{2 \text{ mole } \text{AgNO}_3}{1 \text{ mole } \text{CaCl}_2} = 0.200 \text{ mole } \text{AgNO}_3$$

3rd, find volume of AgNO_3 solution

$$(0.200 \text{ mole } \text{AgNO}_3) \times \frac{1,000 \text{ mL } \text{AgNO}_3}{0.250 \text{ mole } \text{AgNO}_3} = 800 \text{ mL } \text{AgNO}_3$$

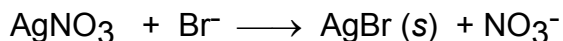
Part (b): mass of AgCl ?

$$(0.100 \text{ mole } \text{CaCl}_2) \times \frac{2 \text{ mole } \text{AgCl}}{1 \text{ mole } \text{CaCl}_2} = 0.200 \text{ mole } \text{AgCl}$$

$$(0.200 \text{ mole } \text{AgCl}) \times \frac{143 \text{ g } \text{AgCl}}{1 \text{ mole } \text{AgCl}} = 28.6 \text{ g}$$

Example:

A sample of 0.3220 g of an ionic compound containing Br⁻ is dissolved in H₂O and treated with excess AgNO₃. If the mass of AgBr precipitate that forms is 0.6964 g, what is the percent by mass of Br⁻ in the original compound?



$$\frac{\text{mass of Br}^-}{\text{total mass}} \times 100\% = \text{percent Br}^-$$

1st calculate mass of Br⁻

$$\text{g Br}^- = 0.6964 \text{ g AgBr} \times \frac{1 \text{ mole AgBr}}{187.8 \text{ g}} \times \frac{1 \text{ mole Br}^-}{1 \text{ mole AgBr}} \times \frac{79.90 \text{ g}}{1 \text{ mole Br}^-}$$

$$\text{mass Br}^- = 0.2963 \text{ g}$$

2nd calculate the percent of Br⁻ relative to the whole sample

$$\frac{0.2963 \text{ g}}{0.3220 \text{ g}} \times 100\% = 92.01 \%$$

4.7 Acid-Base Titrations

another way to determine the quantity or amount of something in an unknown sample

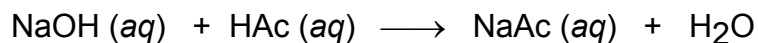
Titration: An unknown amount of one reactant is combined exactly with a precisely measured volume of a **standard solution** of the other.

End-point: When exact stoichiometric amounts of two reactants have been combined. (also called equivalence-point or in acid-base reactions, the point of neutralization)

Indicator: Substance added to aid in detection of the endpoint (usually via a color change). For acid base titrations this is often phenolphthalein (colorless in acid and pink in solution)

Example:

Vinegar is an aqueous solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, which is often written as HAc for simplicity. A 12.5 mL sample of vinegar was titrated with a 0.504 M solution of NaOH. The titration required 15.40 mL of the base solution in order to reach the endpoint. What is the molar concentration of HAc in vinegar?



moles NaOH = moles HAc

$$(15.4 \text{ mL NaOH}) \times \frac{0.504 \text{ mole NaOH}}{1,000 \text{ mL}} \times \frac{1 \text{ mole HAc}}{1 \text{ mole NaOH}}$$

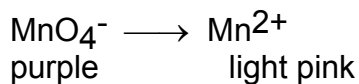
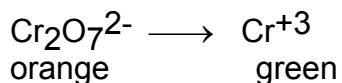
$$= 0.007762 \text{ mole HAc}$$

$$\text{Molarity HAc} = \frac{0.007762 \text{ mole HAc}}{12.5 \text{ mL}} \times \frac{1000 \text{ mL}}{1.00 \text{ L}}$$

$$\text{M HAc} = 0.621 \text{ M}$$

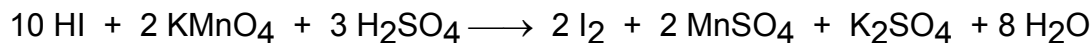
4.8 Redox Titrations

indicators - often one of the species involved in the reaction that changes color



Example:

How many mL of 0.206 M HI solution are needed to reduce 22.5 mL of a 0.374 M KMnO_4 solution?



step 1: moles KMnO_4

$$22.5 \text{ mL} \times \frac{0.374 \text{ moles KMnO}_4}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 8.415 \times 10^{-3} \text{ moles KMnO}_4$$

step 2: moles HI

$$8.415 \times 10^{-3} \text{ moles KMnO}_4 \times \frac{10 \text{ mole HI}}{2 \text{ moles KMnO}_4} = 4.208 \times 10^{-2} \text{ moles HI}$$

step 3: volume HI

$$4.208 \times 10^{-2} \text{ moles HI} \times \frac{1 \text{ L}}{0.206 \text{ moles HI}} = 0.204 \text{ L or } 204 \text{ mL}$$

The alcohol content in a 10.0 g sample of blood from a driver required 4.23 mL of 0.07654 $\text{K}_2\text{Cr}_2\text{O}_7$ for titration. Should police prosecute for intoxication if the legal limit is 0.1 % by mass?

Calculate the concentration of acid or base remaining when 10.7 mL of 0.211 M HNO_3 are added to 16.3 mL of 0.258 M NaOH .