VOLUMETRIC ANALYSIS (TITRATION)

Many different kinds of titration, can be loosely classified by the kind of reaction used:

1. Acid-base titration
2. Precipitation titration
3. Complexometric titration
4. Redox (oxidation-reduction) titration

REACTIONS FOR TITRATION

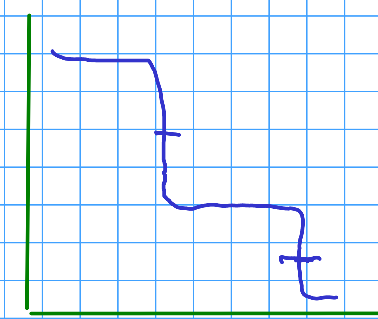
- these characteristics apply to all types of titration

1. STOICHIOMETRIC - react in a well-defined way with analyte

2. NO SIDE REACTIONS - All interferants must be removed prior to titration

3. CLEAR ENDPOINT - must give a well-defined change in some property of the solution at the end of the titration

4. RAPID REACTION



5. EQUIVALENCE POINT SHOULD COINCIDE WITH ENDPOINT

6. QUANTITATIVE reaction - equilibrium point lies far towards PRODUCTS

high K_c !

PRIMARY STANDARDS

- highly pure materials used to accurately determine ("standardize") the concentration of a less-pure material.

Examples:

KHP (potassium acid phthalate) - a primary-standard ACID

$HOOC-C_6H_4-COO^-K^+$

sodium carbonate - a primary standard BASE

Na_2CO_3

$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$

weak acid

PRIMARY STANDARD QUALITIES

- Pirmary standards should have these characteristics:

1. Available at 100.00% purity

2. Stable over time and at various temperatures (ex: high-temperature drying)

3. Readily available

4. High formula weight { solid at room temp, non-volatile

TITRATION CALCULATIONS

- To perform titration calculations, we need to know:

1. A BALANCED EQUATION for the titration

2. An accurate CONCENTRATION OF TITRANT

3. VOLUME OF TITRANT (usually in mL)

4. AMOUNT OP SAMPLE (may be volume or mass)

TITRATION CALCULATIONS

- Once we have the required information, we then:

1. Find the mmol (millimoles) of titrant used $mL \times \underline{M} = mmol$

2. Relate the mmol titrant to mmol analyte using the balanced equation
$$H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$$
$$2\ mmol\ NaOH = 1\ mmol\ H_2SO_4$$

3. Find mmol analyte

4. Convert mmol analyte to desired measurement (mass or moles)

5. Report mass, mass percentage, or concentration of analyte, depending on SOP requirements

STANDARDIZATION

- It's often not possible to directly use a primary standard for your analysis. If this is the case, you'll need to STANDARDIZE the titrant you actually DO use!

What;'s that mean? Use the titrant to titrate a known quantity of a STANDARD, then calculate the concentration of the titrant!

To STANDARDIZE a solution, you'll need to find:

$$\text{mmol} = \frac{\text{mg}}{\text{FW}}$$

1. mmol of STANDARD used (usually from a mass and a formula weight)

2. mmol TITRANT - use the balanced equation to relate the STANDARD with the TITRANT

3. $$\frac{\text{mmol TITRANT}}{\text{mL TITRANT}} = \text{M titrant (molarity)}$$

A COMMON TITRATION PROBLEM

- Ideally, we'd like to use only titration reactions that proceed RAPIDLY.

- However, not all potentially usable reactions proceed rapidly.

- A process called BACK-TITRATION is useful for dealing with slow reactions.

BACK-TITRATION

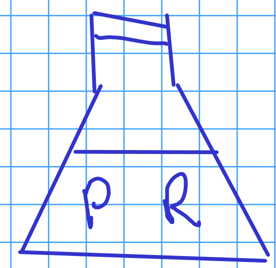
add lots of "R"!

- How is this done?

$$A + R \rightarrow P \quad \text{slow}$$

1. Add a measured amount of a REAGENT to the sample. The added amount is IN EXCESS of the amount needed to completely react the analyte

2. Allow this reaction to go to completion.



3. TITRATE the EXCESS REAGENT using a FAST reaction with a distinct ENDPOINT

$$R + T \rightarrow Q \quad \text{Fast!}$$

BACK-TITRATION CALCULATIONS

A + R → P

- To determine the amount of analyte in a back-titration procedure, do this: R + T → Q

1. Find the TOTAL mmol of ADDED REAGENT — total R

2. Find the mmol TITRANT — T

3. Relate mmol TITRANT to mmol EXCESS REAGENT using the balanced equation between TITRANT and REAGENT — R + T → Q

4. Find mmol EXCESS REAGENT — leftover R

5. mmol REACTED REAGENT = mmol TOTAL REAGENT - mmol EXCESS REAGENT

6. Relate mmol REACTED REAGENT with mmol ANALYTE using the balanced equation between ANALYTE and REAGENT — A + R → P

7. Convert the mmol ANALYTE to desired form, depending on SOP

NORMALITY AND TITRATION

- Normality is similar to molarity, but gives the concentration of a solution in terms of MOLES OF REACTING UNITS than actual moles of a substance

- Normality is an attempt to cut STOICHIOMETRY out of routine calculations.

$$N = \frac{eq}{L} = \frac{meq}{mL}$$

, where "eq" means "number of equivalents" — moles of reacting units

$$\text{equivalent weight} = \frac{\text{Formula weight of substance}}{\text{number of equivalents per mole of substance}}$$

equivalent weight is similar to formula weight!

$$eq = \frac{mass}{\text{equivalent weight}}$$

similar to calculation of moles from mass using formula weight

Where's the stoichiometry? Buried in the calculation of the equivalent weight and the number of equivalents!

NORMALITY AND TITRATIONS

- Once concentrations are expressed in N, chemical calculations proceed as if all reagents react in a 1:1 ratio!

... but how do you actually determine what a "reacting unit is?"

REACTING UNITS FOR TITRATIONS

- two of the more common titration types are ACID-BASE titrations and REDOX titrations!

(1) ACID-BASE

- the REACTING UNIT is the PROTON (in other words, the H^+ ion)

- if the reagent is an ACID, how many reactive protons does it have?

H_2SO_4: two reactive protons

$HC_2H_3O_2$: one reactive proton

H_3PO_4: three reactive protons

- if the reagent is a BASE, how many protons is it able to react with?

$NaOH$: reacts with one proton

$Ca(OH)_2$: reacts with two protons

NH_3: reacts with one proton

REACTING UNITS FOR TITRATIONS

(2) REDOX

- the REACTING UNIT is the ELECTRON (e^-)

- For a REDUCING AGENT, how many electrons does the reagent give up?

$Na \rightarrow Na^+ + 1e^-$: one electron

- For an OXIDIZING AGENT, how many electrons does the reagent accept?

$Br_2 + 2e^- \rightarrow 2Br^-$: two electrons

TITRATION CALCULATIONS WITH NORMALITY

- Normailty is supposed to make routine calculations simpler!

1. Find the concentration of TITRANT in normality units (N). This involves determining REACTING UNITS if it has not already been done.

2. Find the EQUIVALENT WEIGHT of the analyte

3. Since titrant "T:" and analyte "A" react in a 1:1 ratio by equivalents, then find the composition in percent A (%A) by simple dimensional analysis

$$\%A = \frac{N_T \times \text{eq wt } A \times mL_T}{\text{mg sample}}$$

$[N_T \times \text{eq wt } A \times mL_T] = mg_A$

This relationship is true for ALL titrations when you use normality units!

$$ppm_A = \frac{mg_A}{\text{L sample}}$$