

Laboratory in Chemistry

2nd semester / Spring 2021

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Lecture 2

- ❖ Synthesis of Organic and Inorganic Compounds
 - Acetylsalicylic acid
 - Melting Point (M.P.)
 - Potassium Trioxalate Ferrate (III) Trihydrate
- ❖ Volumetric Analysis and Titration
 - Titration of a strong *monoprotic acid* (HCl)

Synthesis of Acetylsalicylic Acid: Introduction

3.1 Synthesis of Acetylsalicylic Acid (Experiment 4)

Main theme: *“In this experiment, acetylsalicylic acid will be synthesized and its physical properties (in particular, the melting point) will be determined.”.*

Acetylsalicylic acid is the active component of aspirin, a widely used pain reliever and antipyretic.

Learning Objective: At the end of this experiment, you should be able to

1. precipitate an organic compound from a reaction mixture by addition of water
2. isolate a solid by filtration
3. recrystallize a compound from water
4. determine melting points
5. calculate the yield of a product

You will learn basic procedures in organic and inorganic synthesis and determining physical properties

Read the Chemicals and Instruments sections and adhere to the safety principles described!!!

Be careful in handling acetic anhydride and concentrated (98%) sulfuric acid!!!

They are located under the hood. When sampling acetic anhydride and concentrated sulfuric acid,

ONLY USE SPECIFICALLY DESIGNATED PIPETTES !!

Never return the sampled acids from your own vessel back to the original bottle.

Synthesis of Acetylsalicylic Acid: Steps of the Synthesis

Synthesis Steps:

Reaction of **ACTIVE CARBOXYLIC ACID DERIVATIVES** with

+

ALCOHOLS, PHENOLS, PRIMARY AMINES or **SECONDARY AMINES**

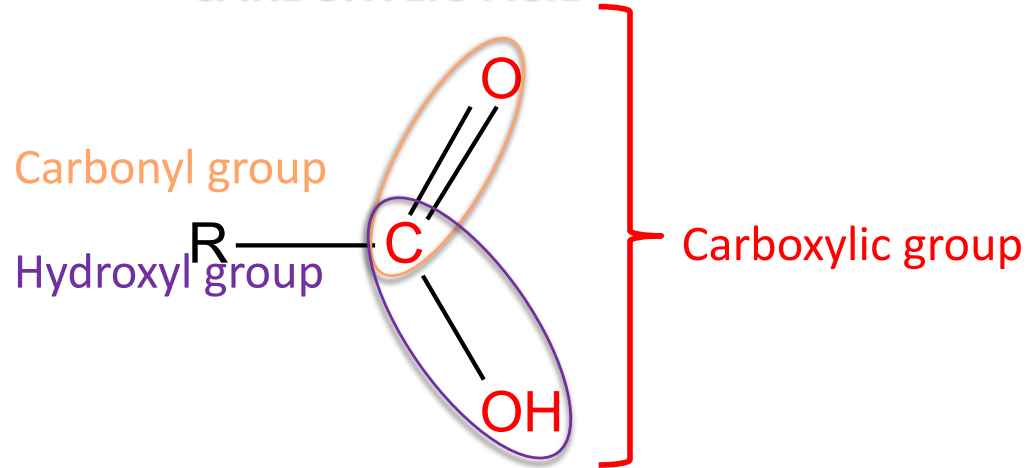
INTRODUCES THE ACYL GROUP (-COR) into the **HYDROXYL OR AMINO GROUP**, thus forming the corresponding

CARBOXYLATE ESTERS or **CARBOXYLIC AMIDES**, respectively.

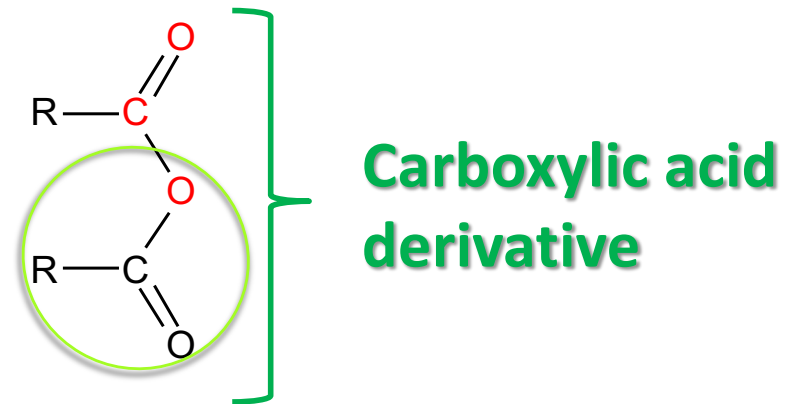
This reaction is known as the **ACYLATION REACTION**. The **ACYL GROUP** derived from **ACETIC ACID** is called the **ACETYL GROUP (-COCH₃)**.

Synthesis of Acetylsalicylic Acid: Steps of the Synthesis

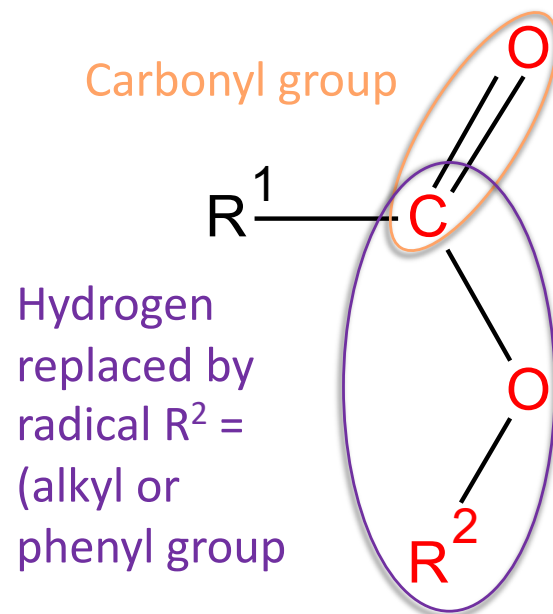
CARBOXYLIC ACID



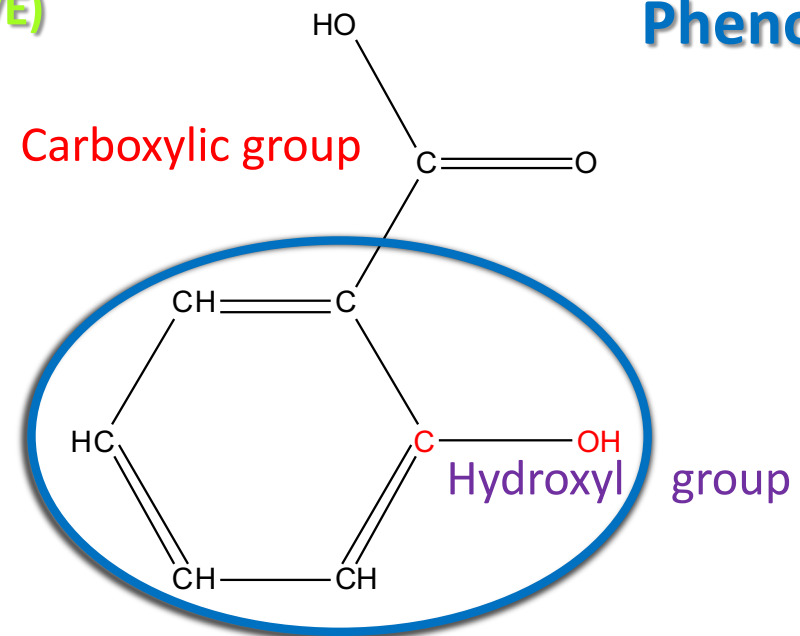
acetic anhydride



CARBOXYLATE ESTERS (ALSO A DERIVATIVE)

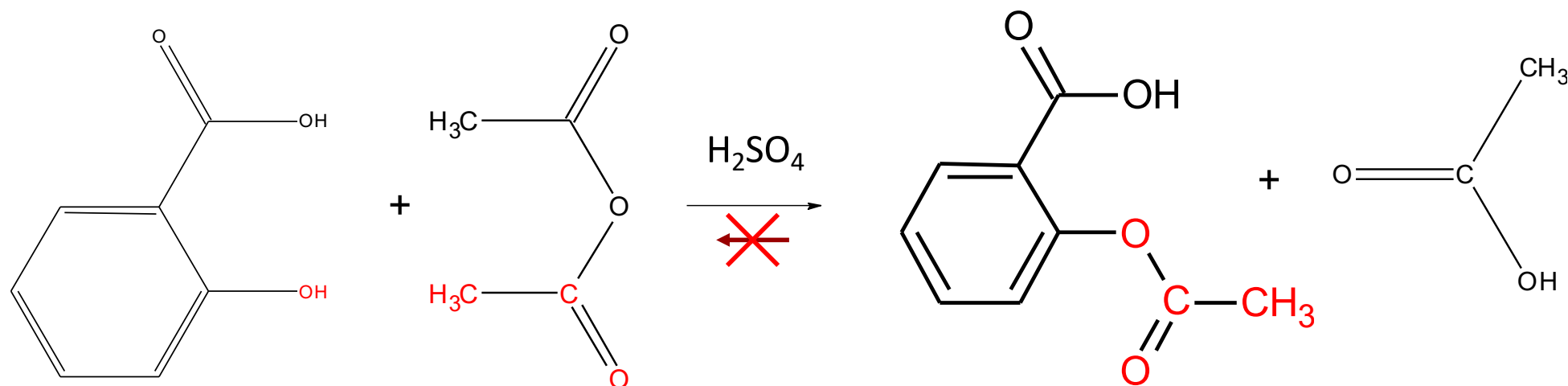


Phenols



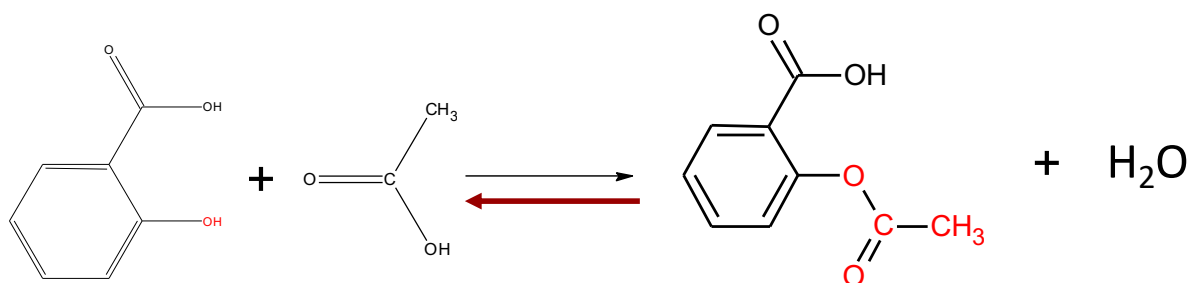
Synthesis of Acetylsalicylic Acid: Steps of the Synthesis

The **PHENOLIC HYDROXYL GROUP** in **SALICYLIC ACID** is **ACETYLATED** with **ACETIC ANHYDRIDE** to yield **ACETYLSALICYLIC ACID** as shown below



Why is acetic anhydride used and not acetic acid?

↪ In case of acetic acid:

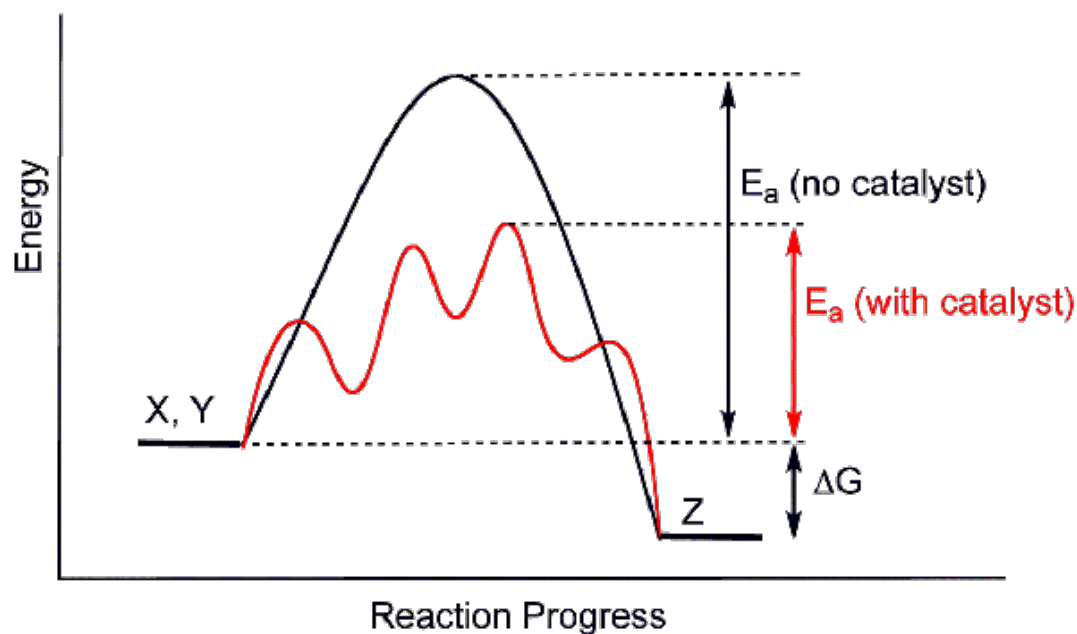


Phenols cannot be acetylated *satisfactorily* in aqueous solution:

Acetylation of phenol proceeds readily with acetic anhydride in the presence of a little concentrated sulfuric acid as **catalyst**.

Synthesis of Acetylsalicylic Acid: What is a Catalyst?

- A substance that **INCREASES THE RATE OF A CHEMICAL REACTION** without itself undergoing any *permanent* chemical change.
- A catalyst is a substance that speeds up a given chemical reaction by **LOWERING ITS ACTIVATION ENERGY WITHOUT ITSELF BEING USED UP**.
- Catalysts may affect the reaction environment favorably, or **BIND TO THE REAGENTS TO POLARIZE BONDS**, e.g., *acid catalysts* for reactions of *carbonyl compounds*, or form specific intermediates that are not produced naturally.



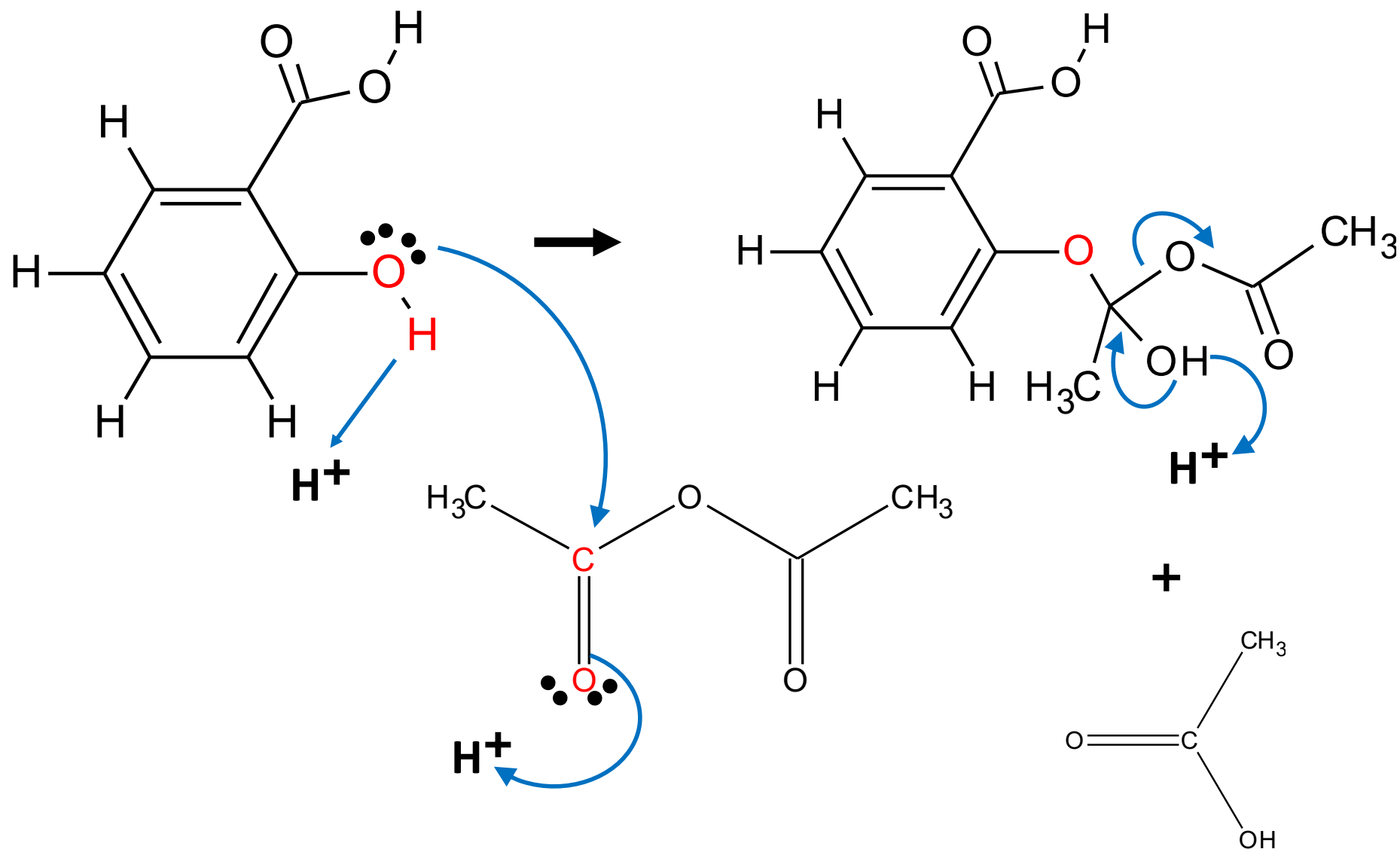
https://en.wikipedia.org/wiki/Potassium_ferrioxalate

Generic potential energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical reaction X + Y to give Z. The presence of the catalyst opens a different reaction pathway (shown in red) with a lower activation energy. The product and the overall thermodynamics are the same[§]

[§] In case of *isomers* (more than one product), the catalyst need to be selected so that the favored product will be formed with the highest yield.

Synthesis of Acetylsalicylic Acid: Reaction Mechanism

One possible Reaction mechanism for the **EXAMPLE OF 2-ACETOXYBENZOIC ACID (SALICYLIC ACID)**



Synthesis of Acetylsalicylic Acid: Measuring of the Melting Point

3.1.2 Measurement of the Melting Point

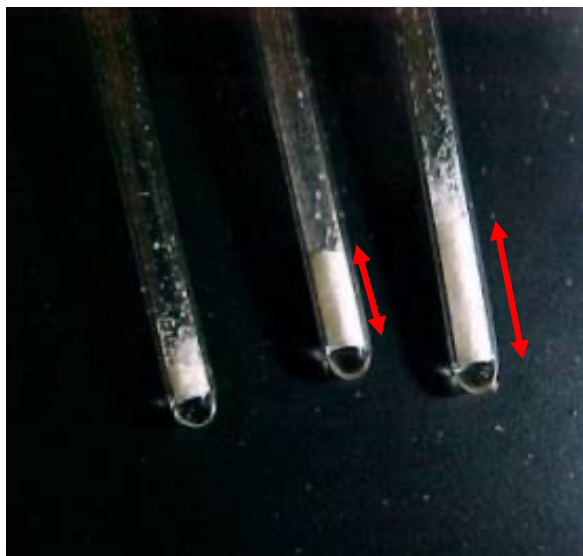
- **THE MELTING POINT IS A CONSTANT**, which is characteristic for the substance.
- **MIXING TWO DIFFERENT SUBSTANCES** results in a **DECREASE IN THE MELTING POINT** of the mixture, even if both samples have the identical melting points.
 - ↳ **Any impurity has a similar effect!**
- Accordingly, when an *unknown sample* is mixed with the known substance, the *melting point of the mixture* can be used to *identify the unknown sample* (**MIXED MELTING-POINT DETERMINATION**).

Some tips about measuring the melting point

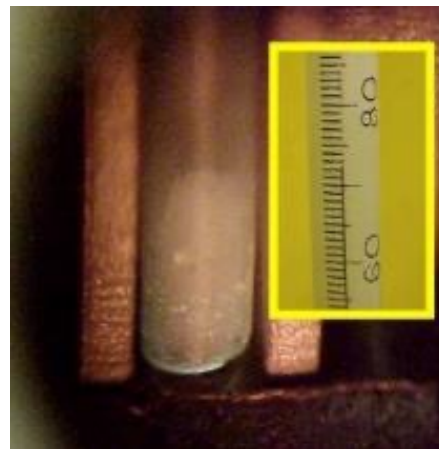
- Experimental melting points should be always reported as a range, for example, 42-44°
- A pure organic compound usually melts over a range of two degrees or less
- A **higher melting point** than stated in the literature **cannot be measured in the lab!**
- A **given sample is only used once** to determine the melting point!

Synthesis of Acetylsalicylic Acid: Measuring of the Melting Point

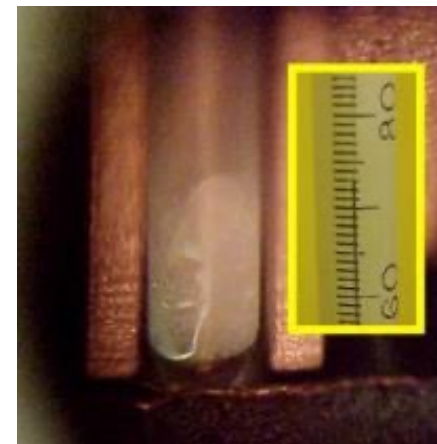
Left: Probably right
Middle: Good (tightly packed)
Right: Too much sample



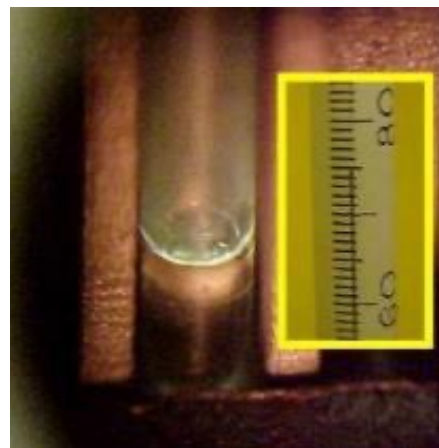
Melting sequence (Ibuprofen sample)



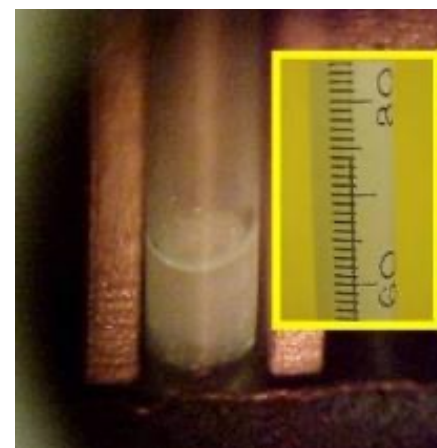
Formation of tiny drops (72°)



Liquid becomes visible (73°)



Clear liquid (75°)



Mixture of liquid and crystals (74°)

The melting point (MP) of this sample is reported as:

72 - 75°



Synthesis of Potassium Trioxalate Ferrate (III) Trihydrate

3.2 Synthesis of Potassium Trioxalate Ferrate (III) Trihydrate (Experiment 5)

Main theme:

“Potassium trioxalate ferrate (III) will be synthesized herein as an example of an inorganic compound synthesis.

The complex decomposes upon irradiation with light, and you will study this process of photochemical decomposition.”.

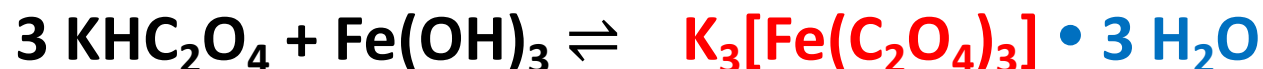
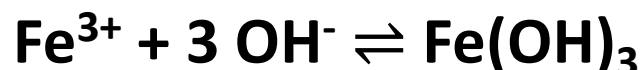
Read the Chemicals and Instruments sections and adhere to the safety principles described!!!

Chemicals once transferred to other vessel should never be returned to the original bottle.

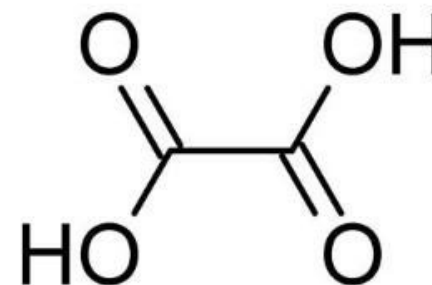
Synthesis of Potassium Trioxalate Ferrate (III) Trihydrate

- **Synthesis of Potassium Trioxalate Ferrate (III) Trihydrate^{/*}**

The Potassium trioxalate ferrate (III) trihydrate complex can be synthesized by heating ferric hydroxide ($\text{Fe}(\text{OH})_3$) with an excess aqueous solution of potassium hydrogen oxalate. Potassium trioxalate ferrate (III) trihydrate is then purified by recrystallization.



- Compounds with two potential coordination sites in a mostly organic molecule are called “**bidentate**” ligands (e.g., $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, ethylenediamine).
- Oxalate is also a “**bidentate**” ligand!

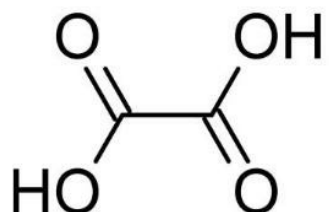
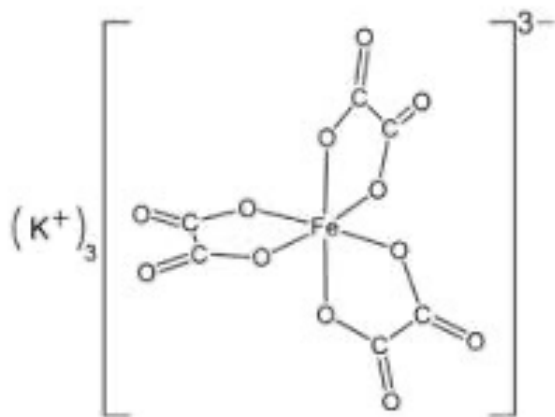


Oxalic acid

^{/*} Trihydrate: The **Trihydrate** or “**• 3 H₂O**” symbolizes “**water of crystallization**”, which is water incorporated into the crystal during the recrystallization procedure.

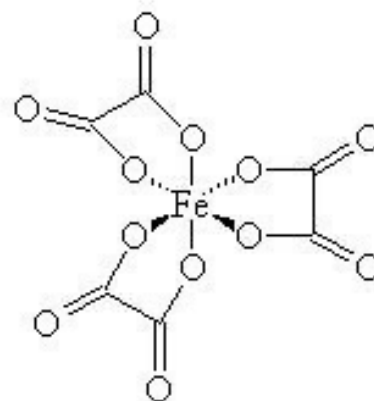
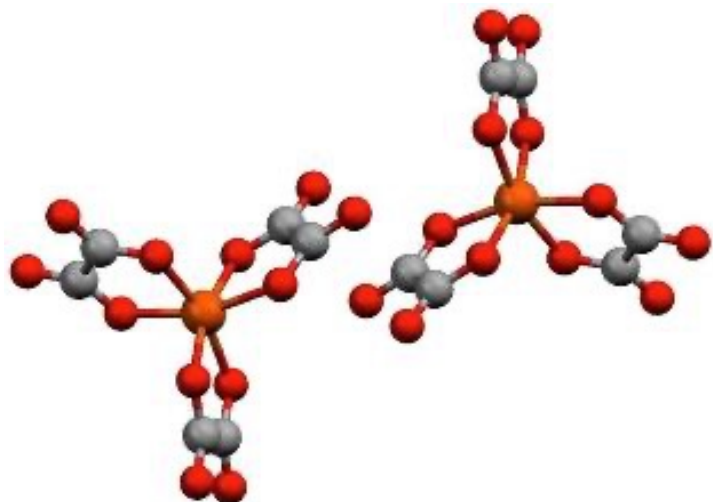
Structure of Potassium Trioxalate Ferrate (III) Trihydrate

- Structure of Potassium Trioxalate Ferrate (III) Trihydrate

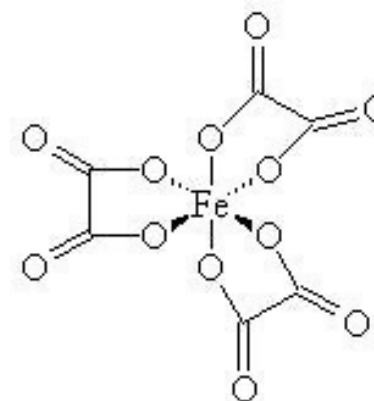


Oxalic acid

The ferrioxalate metal ion complex exhibits **optical activity** since there are **two** non-superimposable **stereoisomers of the complex**. In accordance with the IUPAC convention, the isomer with the left-handed screw axis is assigned the Greek symbol Λ (lambda). Its mirror image with the right-handed screw axis is given the Greek symbol Δ (delta).



Λ -[Fe(C₂O₄)₃]³⁻

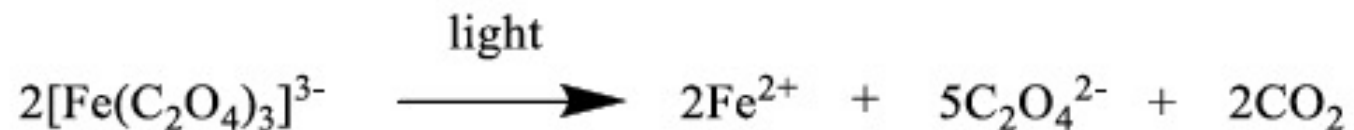


Δ -[Fe(C₂O₄)₃]³⁻

Photochemical Reaction of Potassium Trioxalate Ferrate (III) Trihydrate

The Photochemical Reaction of Potassium Trioxalate Ferrate (III) Trihydrate

- The trioxalate ferrate (III) complex ion undergoes the photochemical redox reaction below. This reaction is used as the **chemical actinometer**, since the **amount of the absorbed light** can be determined by **quantifying the ferrous (II) ion generated**.
- In this experiment, you will determine the change in color. (Not a quantitative analysis just a qualitative analysis – description – of the observed changes)
- **Since this photochemical reaction occurs under visible light, the solution used as the che**



From Wikipedia: Actinometers are instruments used to measure the heating power of radiation. They are used in meteorology to measure solar radiation as pyrheliometers.

An actinometer is a chemical system or physical device which determines the number of photons in a beam **integrally or per unit time**. This name is commonly applied to devices used in the ultraviolet and visible wavelength ranges. For example, solutions of iron(III) oxalate can be used as a chemical actinometer, while bolometers, thermopiles, and photodiodes are physical devices giving a reading that can be correlated to the number of photons detected.

Chemical actinometry involves measuring radiant flux via the yield from a chemical reaction. It requires a chemical with a known quantum yield and easily analyzed reaction products.

4. Volumetric Analysis and Titration

3.1 Acid-base titration and the titration curve (Experiment 6)

Main theme: *“In these experiments, you will use strong and weak acids as sample solutions, to which a strong base is added as the titrant.*

In order to obtain a pH titration curve, you will plot the measured pH values against the quantity of the titrating reagent added.”

Learning Objective:

*By analyzing the pH titration curves, you will learn how **concentration** is **related to dissociation** in the sample and at what range of pH the given indicators change color*

Read the Chemicals and Instruments sections and adhere to the safety principles described!!!

As there are large quantities of strong alkali solution on your shelf, be careful while conducting your experiment.

Use only your own reagents for your experiment because the reagents on other benches may have slightly different concentrations. If, for some reason, you cannot avoid changing benches, confirm that the concentration of KOH standard solution at the new bench is the same as the one on the old bench

Volumetric Analysis and Titration: Acid/Base Definitions

Definitions of acids and bases

- *Arrhenius*

acid: generates $[H^+]$ in solution

base: generates $[OH^-]$ in solution

normal **Arrhenius equation**: acid + base \rightleftharpoons salt + water

example: $HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$

- *Brønsted-Lowery*

acid: anything that donates a $[H^+]$ (proton donor)

base: anything that accepts a $[H^+]$ (proton acceptor)

normal **Brønsted-Lowery equation**: acid + base \rightleftharpoons acid + base

example: $HNO_2(aq) + H_2O(aq) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$

Each acid has a **conjugate base**, and each base has a **conjugate acid**. These conjugate pairs only differ by a proton. In this example: NO_2^- is the conjugate base of the acid HNO_2 and H_3O^+ is the conjugate acid of the base H_2O .

- *Lewis*

acid: accepts an electron pair

base: donates an electron pair

The advantage of this theory is that many more reactions can be considered acid-base reactions because they do not have to occur in solution.

Volumetric Analysis and Titration: Acid/Base Definitions

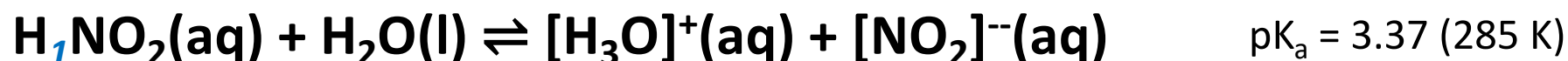
Examples of *monobasic* and *dibasic* acids

Monobasic acids



Nitric acid

Nitrate ion



Nitrous acid

Nitrite ion



Hypochlorous acid

Hypochlorite ion

Dibasic acid



Sulfuric acid

Hydrogensulfate ion



Hydrogensulfate ion

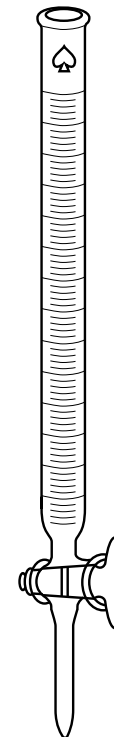
Sulfate ion

Volumetric Analysis and Titration: Principle

- An **ACID-BASE TITRATION** is the determination of the **CONCENTRATION OF AN ACID OR BASE** by **exactly neutralizing** the acid/base with an acid or base of known concentration.
- This allows for **QUANTITATIVE ANALYSIS OF THE CONCENTRATION OF AN UNKNOWN ACID OR BASE** solution.
- It makes use of the neutralization reaction that occurs between acids and bases and the knowledge of how acids and bases will react if their formulas are known.

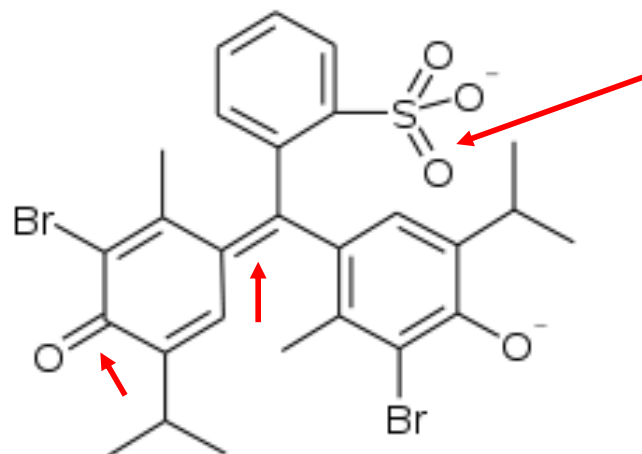
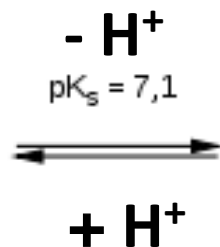
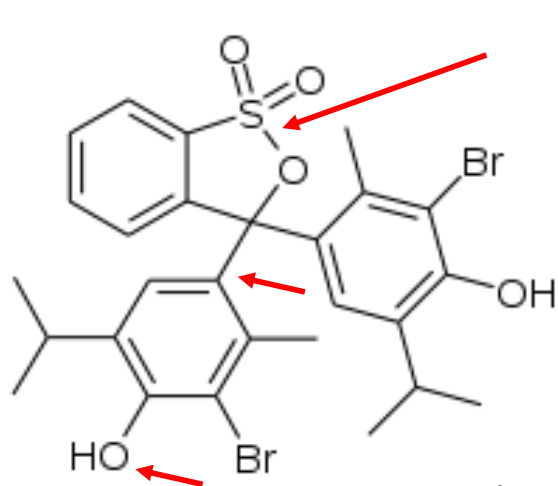
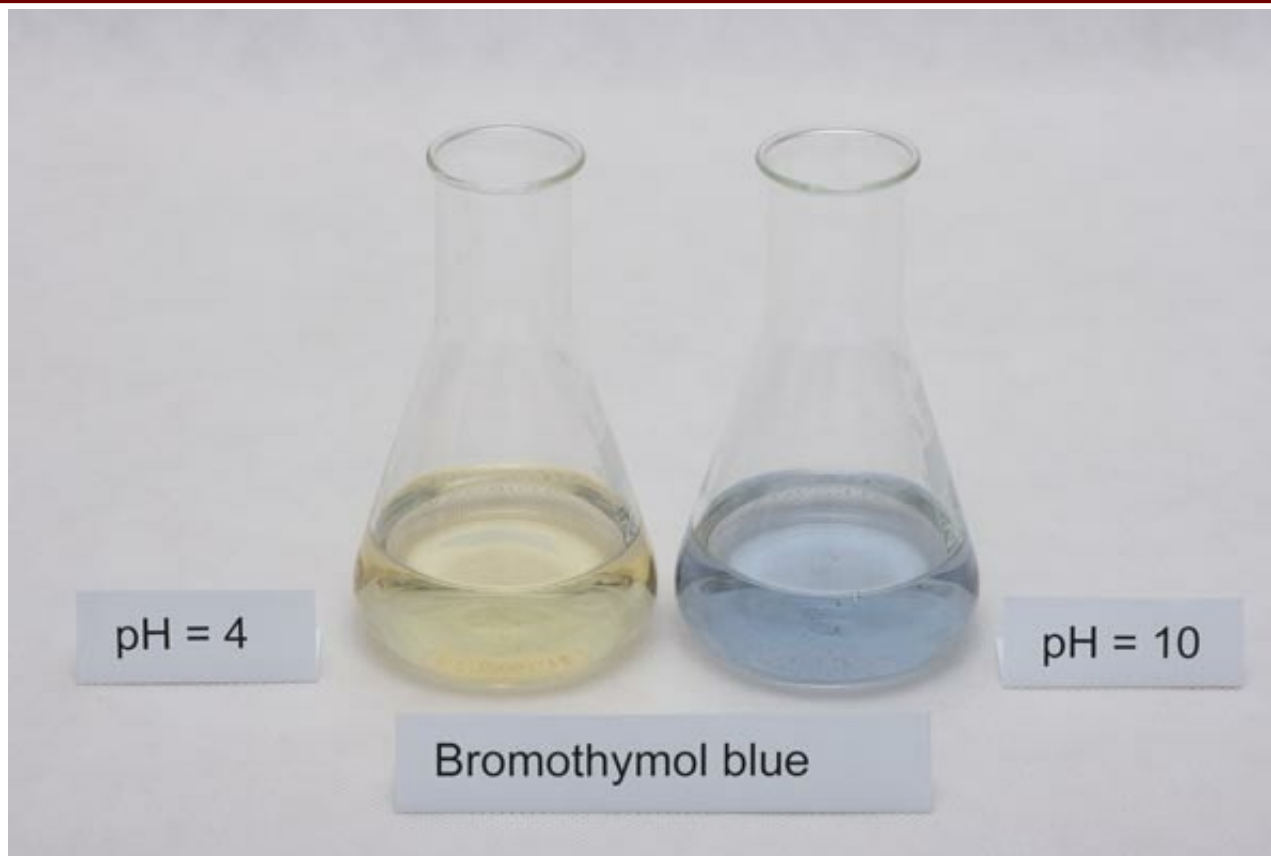
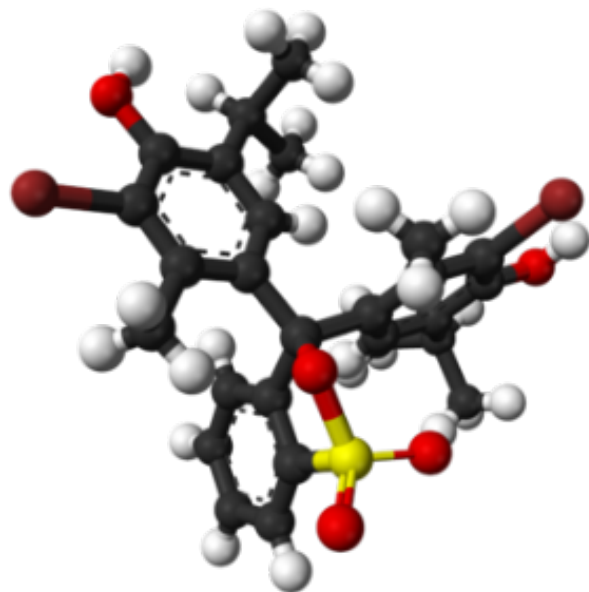
Before starting the titration, a **suitable pH indicator** must be chosen.

The point at which the indicator changes color is called the **END POINT**. A suitable indicator should be chosen, preferably one that will experience a change in color (an **end point**) **close to the EQUIVALENCE POINT** of the reaction.



Volumetric Analysis and Titration: pH Indicator

Indicator example: Bromothymol blue



Highly
conjugated
structured

↳ deep
blue color

https://en.wikipedia.org/wiki/Bromothymol_blue

Volumetric Analysis and Titration: Equivalence Point

- The **EQUIVALENCE POINT** of the reaction, the **point** at which **equivalent amounts of the reactants have reacted**, will have a **pH dependent on the relative strengths of the acid and base used**.
- The pH of the equivalence point can be estimated using the following rules:
 - A strong acid will react with a strong base to form a neutral (pH=7) solution.
 - A strong acid will react with a weak base to form an acidic (pH<7) solution.
 - A weak acid will react with a strong base to form a basic (pH>7) solution.

When a weak acid reacts with a weak base, the equivalence point solution will be basic if the base is stronger and acidic if the acid is stronger. If both are of equal strength, then the equivalence pH will be neutral.

However, weak acids are not often titrated against weak bases because the color change shown with the indicator is often quick, and therefore very difficult for the observer to see the change of color.

Volumetric Analysis and Titration



A **titration curve** is a plot of **pH** vs. the **amount of titrant added**. Typically, the **titrant** is a strong (completely) dissociated acid or base. Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.

Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

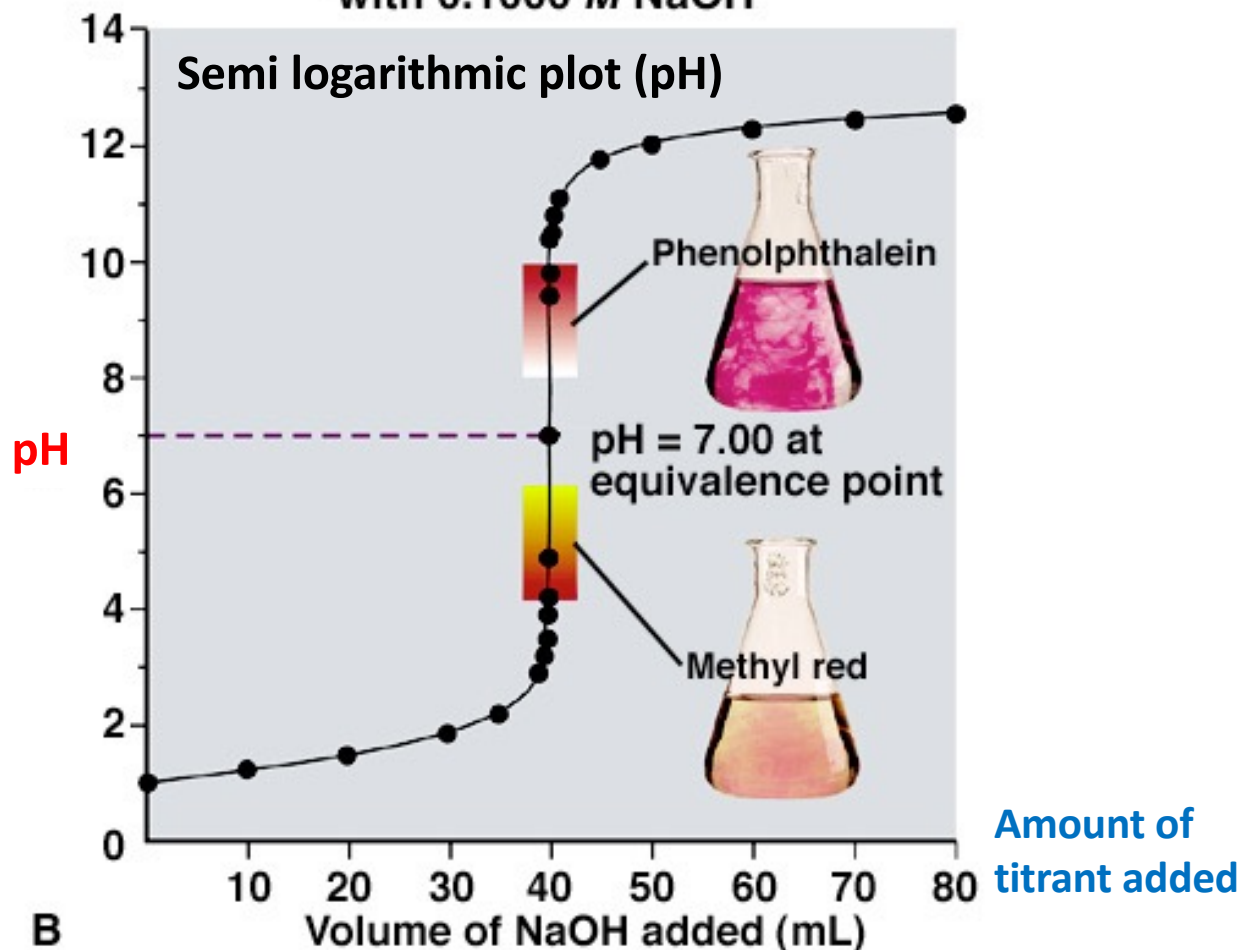
Strong Acid-Base Titration Curve

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52



A

Titration of 40.00 mL of 0.1000 M HCl with 0.1000 M NaOH



Volumetric Analysis and Titration: pH Change by Adding the Titrant

1. The pH starts out low, reflecting the high $[\text{H}_3\text{O}^+]$ of the strong acid and increases gradually as acid is neutralized by the added base.
2. Suddenly the pH rises steeply. This occurs in the immediate vicinity of the equivalence point. For this type of titration, the pH is 7.0 at the equivalence point.
3. Beyond this steep portion, the pH increases slowly as more base is added.

- 40 ml HCl, $[\text{HCl}] = 0.1 \text{ M}$ $\Rightarrow [\text{H}^+] = 0.1 \text{ M}$, $\text{pH} = -\log(10^{-1}) = 1.00$
- 40 ml HCl + 10 ml NaOH $[\text{NaOH}] = 0.1 \text{ M}$ $\Rightarrow [\text{H}^+] = (30\text{ml} \times 0.1 \text{ M HCl})/50 \text{ ml} = 0.0600 \text{ M}$
 $\Rightarrow \text{pH} = -\log(6.00 \times 10^{-2}) = 1.22$ \Rightarrow **¼ of acidity neutralized but only small change in pH!**
- 40 ml HCl + 30 ml NaOH $\Rightarrow [\text{H}^+] = (10\text{ml} \times 0.1 \text{ M HCl})/70 \text{ ml} = 0.0143 \text{ M}$
 $\Rightarrow \text{pH} = -\log(1.43 \times 10^{-2}) = 1.85$ \Rightarrow **¾ of acidity neutralized but only small change in pH!**

Volumetric Analysis and Titration: Required Titrant Volume for a Given pH

First step is as usual calculation of concentrations of all substances entered into the solution. What we do next depends on the titrated substance.

If the titrated substance is strong (**fully dissociated**) we assume the **neutralization** reaction to proceed **quantitatively** - and **pH depends only on the amount of excess of titrated substance (before the equivalence point) or excess of titrant (after the equivalence point)**. **Equivalence point pH is 7.00** (unless ionic strength and activities are considered). **Very close to the equivalence point WATER DISSOCIATION must be accounted for.**

If - still in the case of strong acid HA (HCl) and strong base BOH (KOH) - we want to calculate the volume of titrant for a **given** pH, we will make the same assumption that neutralization went to completion. We will also assume both acid and base to be completely dissociated. That means that the **solution is described by just two equations**. One is **charge balance**:

$$1: [\text{H}^+] + [\text{K}^+] = [\text{Cl}^-] + [\text{OH}^-] \quad \text{or} \quad [\text{H}^+] + [\text{B}^+] = [\text{A}^-] + [\text{OH}^-] \quad \{2 (+) = 2 (-)\}$$

the other one the **water ion product**: (self dissociation constant of water, K_w)

$$2: [\text{H}^+] \times [\text{OH}^-] = K_w = 1.00 \times 10^{-14}$$

Volumetric Analysis and Titration: Definition of the pH

Reminder: **pH**

$$[\text{H}^+] \times [\text{OH}^-] = K_w = 1.00 \times 10^{-14}$$

What is of interest in this reading, however, is the acid-base nature of a substance like water. **Water behaves both like an acid and a base.** (*Brønsted-Lowery*) The acidity or basicity of a substance is defined most typically by the pH value, defined as below:

$$\text{pH} = -\log[\text{H}^+]$$

At equilibrium, the concentration of H^+ is 1.00×10^{-7} , so we can calculate the pH of water at equilibrium as:

$$\text{pH} = -\log[\text{H}^+] = -\log[1.00 \times 10^{-7}] = 7.00$$

Solutions with a pH of seven (7) are said to be neutral, while those with **pH values below seven (7) are defined as acidic** and those **above pH of seven (7) as being basic.**

Volumetric Analysis and Titration: The Logarithmic pH Scale

$[\text{H}_3\text{O}^+]/\text{mol L}^{-1}$

1

1×10^{-7}

1×10^{-14}

$[\text{OH}^-]/\text{mol L}^{-1}$

1×10^{-14}

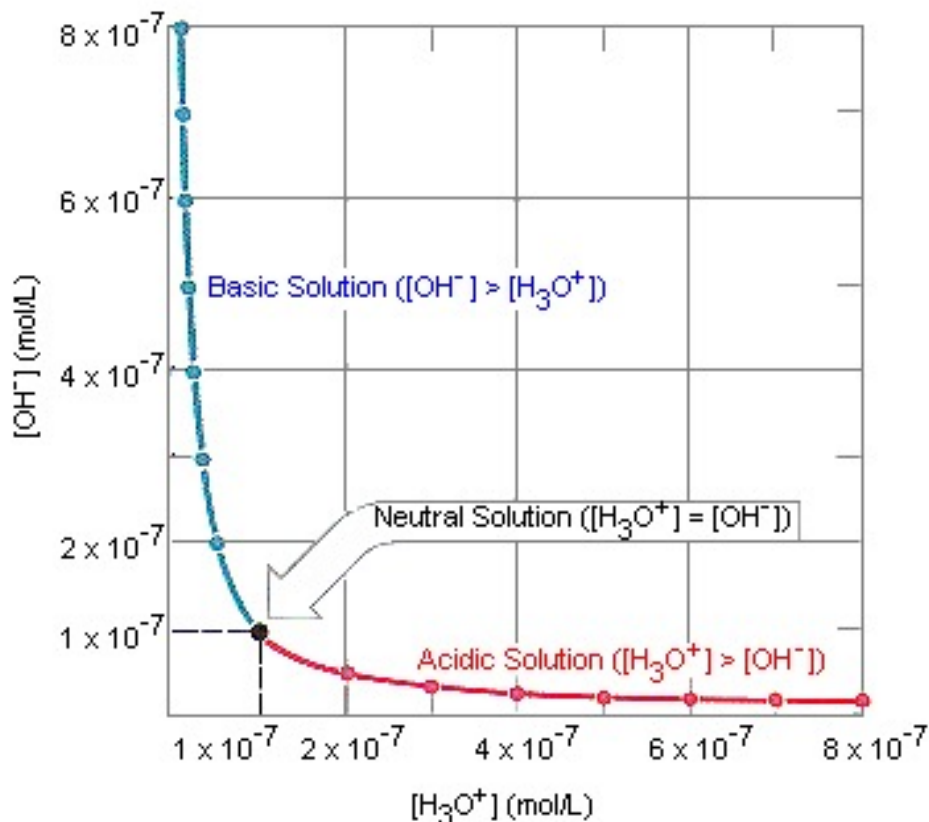
1×10^{-7}

1

Not possible to print into one graph!

↪ Logarithmic mathematics to condense the range of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ (1909, S. P. L. Sørensen)

<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch17/ph.php>



Søren Peter Lauritz Sørensen (født 9. januar 1868 i Havrebjerg ved Slagelse, død 12. februar 1939 i Charlottenlund) var en dansk kemiker, kendt for fastlæggelsen af pH-skalaen for syrer og baser.

Volumetric Analysis and Titration: Volume of the Added Titrant

Relations between $[H^+]$, $[A^-]$, $[B^+]$, V_A and V_B

$$\left(M(X)_{total} = \frac{V_X \times M_X}{V_{total}} \right)$$

- Let V_A be the initial volume of the acid, C_A its initial concentration, V_B the volume of the titrant added and C_B its concentration. If so, the concentrations of A^- and B^+ are

$$[A^-] = \frac{C_A V_A}{V_A + V_B} \quad [B^+] = \frac{C_B V_B}{V_A + V_B} \quad [H^+] + [B^+] = [A^-] + [OH^-] \quad [H^+] \times [OH^-] = K_w$$

- All above equations can be **combined**:

$$[H^+] + \frac{C_B V_B}{V_A + V_B} = \frac{C_A V_A}{V_A + V_B} + \frac{K_w}{[H^+]}$$

- If we want to find the volume of the added titrant and its the only unknown variable, the equation can be easily solved for:

$$V_B = \frac{-[H^+]^2 + [H^+]C_A + K_w}{[H^+]^2 + [H^+]C_B - K_w} V_A$$

Volumetric Analysis and Titration: Calculation of the Titrant pH

Practical Example: What is the pH of 0.1023 M HCl solution titrated 75% with a 0.08976 M solution of NaOH?

After the solution has been titrated 75% there is 25% of original strong acid left. However, this **acid is diluted by the titrant addition**. Let's assume we have started with V_{HCl} mL of acid, and its concentration was C_{HCl} . Let's name the volume of the added base V_{NaOH} and the base concentration C_{NaOH} .

- Initially there were $n_{\text{HCl}} = V_{\text{HCl}} C_{\text{HCl}}$ and $n_{\text{NaOH}} = V_{\text{NaOH}} C_{\text{NaOH}}$ moles of acid and base
- After 75% has been titrated

$$n_{\text{NaOH}} = 0.75 V_{\text{HCl}} C_{\text{HCl}}$$

- The required volume is $V_{\text{NaOH}} = 0.75 \frac{V_{\text{HCl}} C_{\text{HCl}}}{C_{\text{NaOH}}}$

- Total volume of the solution is

$$V = V_{\text{HCl}} + 0.75 V_{\text{HCl}} \frac{C_{\text{HCl}}}{C_{\text{NaOH}}}$$

and actual concentration of acid left is

$$C'_{\text{HCl}} = \frac{0.25 V_{\text{HCl}} C_{\text{HCl}}}{V_{\text{HCl}} + 0.75 V_{\text{HCl}} \frac{C_{\text{HCl}}}{C_{\text{NaOH}}}}$$

25% of initial $n_{\text{HCl}} = V_{\text{HCl}} C_{\text{HCl}}$

Volumetric Analysis and Titration: Calculation of the Titrant pH

$$C'_{HCl} = \frac{0.25 V_{HCl} C_{HCl}}{V_{HCl} + 0.75 V_{HCl} \frac{C_{HCl}}{C_{NaOH}}} = \frac{V_{HCl} \times 0.25 \times C_{HCl}}{V_{HCl} \times \left(1 + 0.75 \times \frac{C_{HCl}}{C_{NaOH}}\right)}$$

- Note, that V_{HCl} **cancels out** and we are left with

$$C'_{HCl} = \frac{0.25 C_{HCl}}{1 + 0.75 \frac{C_{HCl}}{C_{NaOH}}}$$

- Put in the known numbers...

$$C'_{HCl} = \frac{0.25 \cdot 0.1023}{1 + 0.75 \frac{0.1023}{0.08976}} = 0.01195$$

- And the resulting pH is

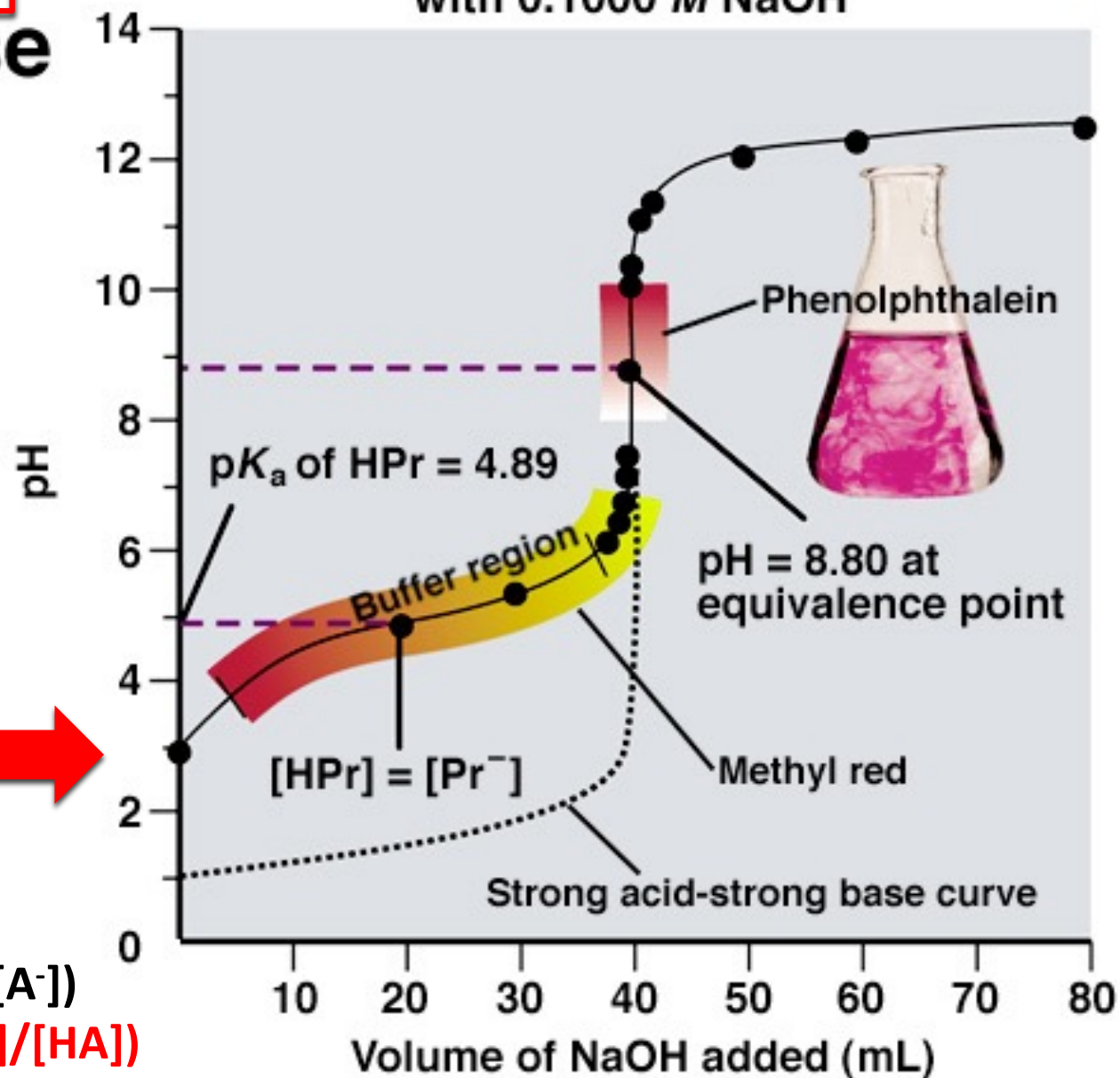
$$pH = -\log(0.01195) = 1.92$$

Volumetric Analysis and Titration: Weak Acid Strong Base Titration

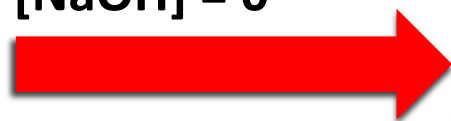
Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

Weak Acid- Strong Base Titration Curve

Titration of 40.00 mL of 0.1000 M HPr
with 0.1000 M NaOH



[NaOH] = 0



But $pH \neq -\log [Pr^-]$
 $= -\log(K_A [HA]/[A^-])$
 $= -pK_A + \log([A^-]/[HA])$

The four Major Differences Between a Strong Acid-Strong Base Titration Curve and a Weak Acid-Strong Base Titration Curve

1. The initial pH is higher
2. A gradually rising portion of the curve, called the buffer region, appears before the steep rise to the equivalence point
3. The pH at the equivalence point is greater than 7.00
4. The steep part of the curve spans a narrower pH range

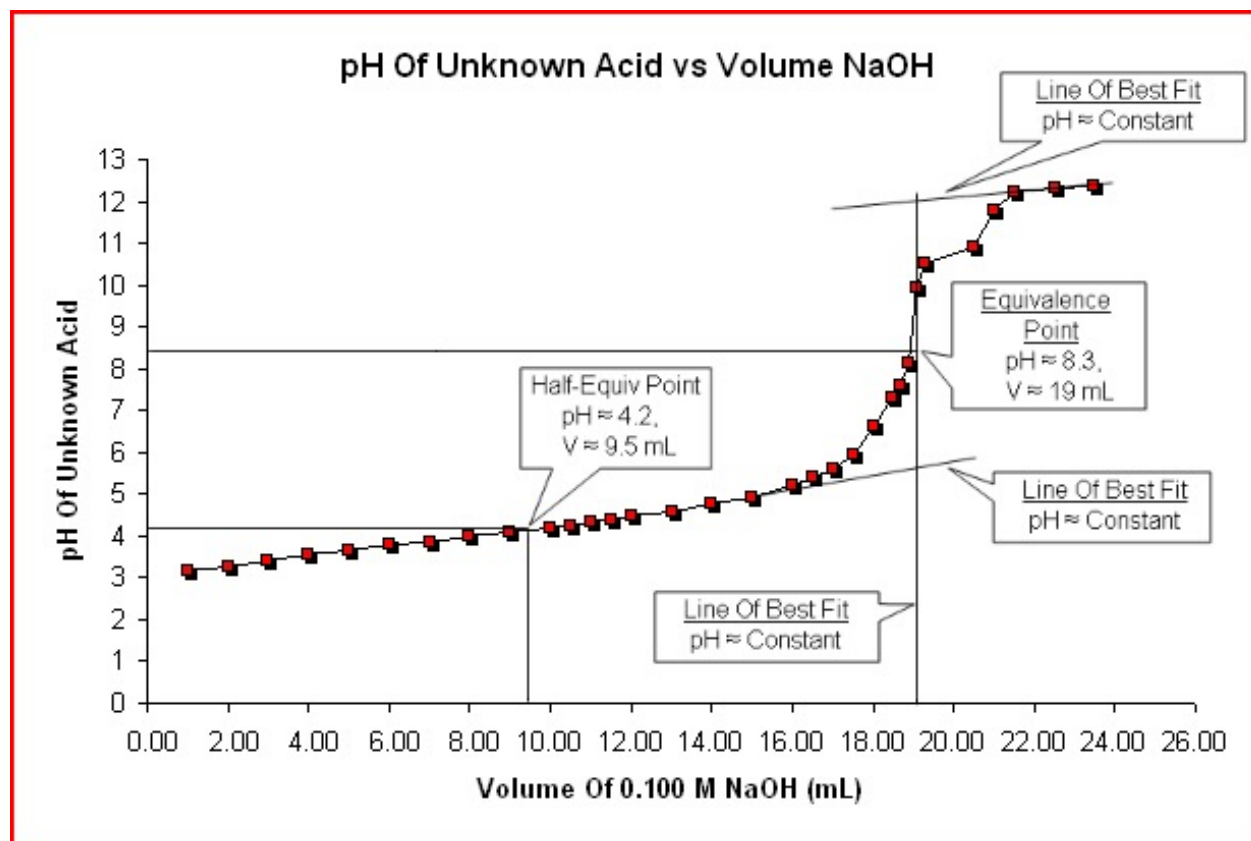
Volumetric Analysis and Titration: Titration of Weak Acid with Strong Base

The following sample data models the titration of a weak acid with a strong base.

The titration curve on the right, pH vs Titrant Volume, represents the sample titration data.



Volume Of Base (mL)	pH	Volume Of Base (mL)	pH
1.00	3.15	15.00	4.90
2.00	3.24	16.00	5.20
3.00	3.39	16.50	5.40
4.00	3.54	17.00	5.60
5.00	3.63	17.50	5.95
6.00	3.78	18.00	6.60
7.00	3.85	18.50	7.30
8.00	3.98	18.70	7.60
9.00	4.11	18.90	8.15
10.00	4.20	19.10	9.95
10.50	4.26	19.30	10.50
11.00	4.31	20.50	10.90
11.50	4.39	21.00	11.80
12.00	4.47	21.50	12.20
13.00	4.60	22.50	12.30
14.00	4.75	23.50	12.35



This method estimates the equivalence point from the **inflection point** of the titration curve. To determine the equivalence point, draw two best-fit lines along the portions of the curve where the pH values are fairly constant. A third best-fit vertical line is drawn for the portion of the curve where the pH changes rapidly. **The midpoint of this vertical line represents the equivalence point.**

Inflection point: Point of a curve at which the sign of the curvature changes

Volumetric Analysis and Titration: Titration of Weak Acid with Strong Base

Once the **volume at the equivalence point** is determined, then one-half that volume represents the volume of strong base needed to neutralize one-half the weak acid. The equilibrium constant expression for the weak acid is given by:

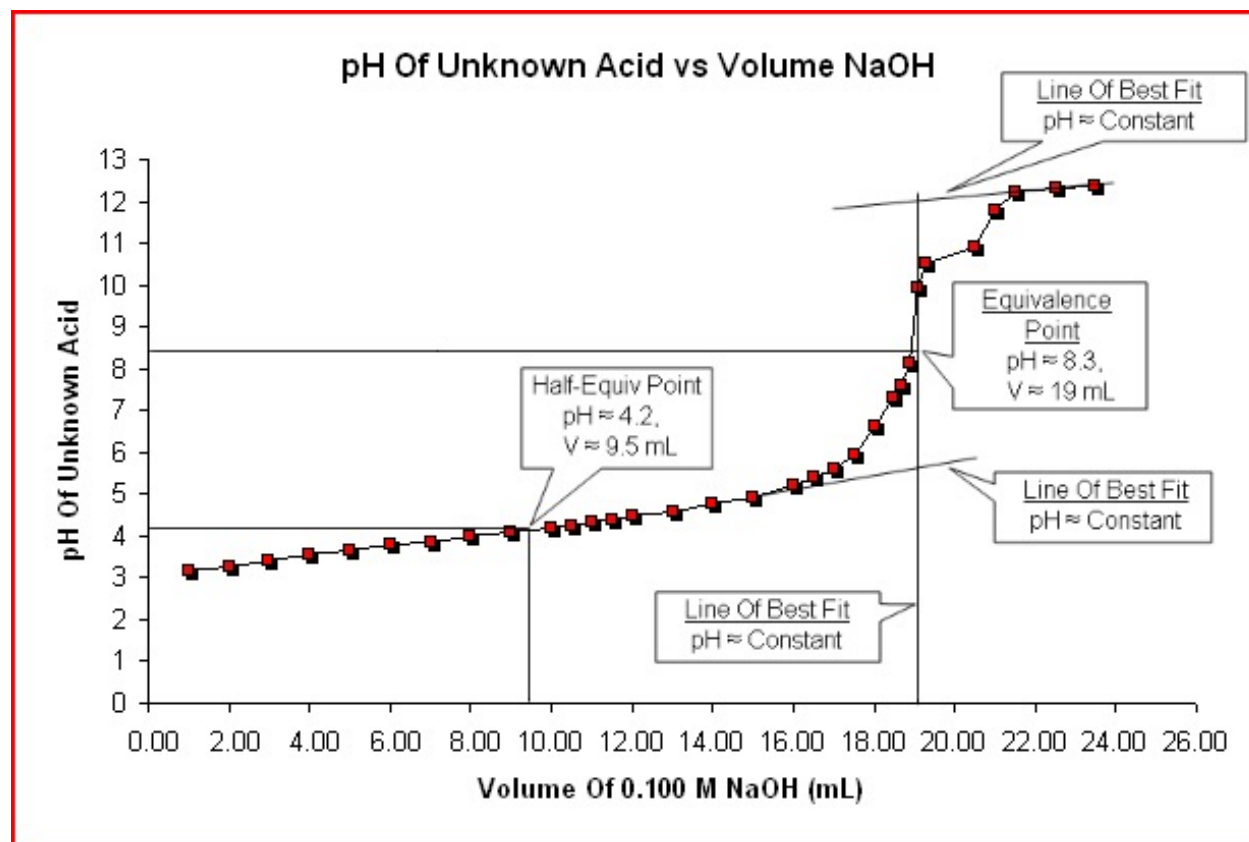
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

When the **acid is half neutralized**, **$[HA] = [A^-]$** , and the **concentration terms cancel leaving**

$$K_a = [H^+]$$

Taking the $-\log$ of both sides and rearranging results in

$$-\log[H^+] = -\log K_a \text{ or } \text{pH} = \text{p}K_a.$$



http://www.geocities.ws/junebug_sophia/AcBaTi.htm 2022.4.6



Volumetric Analysis and Titration: The Buffer Effect

If the titrated substance is weak, calculation of the pH before the end point is done using the *Henderson-Hasselbalch equation* describing pH of **buffer solutions**.

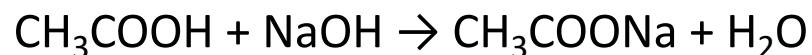
To do so we assume that neutralization went to completion, and we calculate concentration of the weak acid (base) and its conjugate base (acid) treating the titrant as a limiting reagent.

pH at equivalence point is calculated as effect of hydrolysis of the salt, and pH after the equivalence point depends solely on the titrant excess.

Practical example: Calculate pH of a 0.1012 M acetic acid solution after 5.14 mL of 0.1231 M NaOH have been added to 25 mL sample. $pK_a = 4.75$.

First of all we will convert the given information to titration fraction.

We started with 25 mL of 0.1012 M acetic acid solution, that is **$0.025 \times 0.1012 = 0.00253$ moles of acid** (2.53 mmoles). To that we have added 5.14 mL of 0.1231 M NaOH solution, that is **$0.00514 \times 0.1231 = 6.33 \times 10^{-4}$ moles of base**. As acetic acid reacts with sodium hydroxide 1:1



we can easily calculate that **$6.33 \times 10^{-4} / 0.00253 = 0.25$ (25%)** of acid was neutralized.

As we have explained earlier, for a weak acid titration it is best to use the Henderson-Hasselbalch equation:

Volumetric Analysis and Titration: The Henderson-Hasselbalch Equation

Henderson-Hasselbalch equation

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

We know 25% of the acid was neutralized, that means 75% is still intact. Note, that **we don't have to calculate exact concentrations of acid and conjugate base, as we are interested only in their ratio**. Even if we will express exact concentrations by initial concentration, titration percentage and solution volume, **everything but titration percentage will cancel out (try to check it by yourself)**. Thus, we can just plug known numbers into the equation:

$$pH = 4.75 + \log\left(\frac{25}{75}\right) = 4.27$$

And **pH of 4.27 is the final answer**

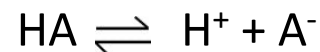
In chemistry, the Henderson–Hasselbalch equation describes the derivation of pH as a measure of acidity (using pK_a , the negative log of the acid dissociation constant) in biological and chemical systems. The equation is also useful for estimating the pH of a buffer solution and finding the equilibrium pH in acid-base reactions (it is widely used to calculate the isoelectric point of proteins).

Volumetric Analysis and Titration: What is a Buffer?

A buffer is an **AQUEOUS SOLUTION** consisting of a **MIXTURE OF A WEAK ACID AND ITS CONJUGATE BASE** or a weak base and its conjugate acid.

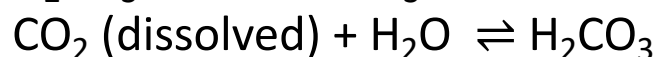
- Its pH changes very little when a small amount of strong acid or base is added to it and thus it is used to prevent any change in the pH of a solution
- Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications
- Many life forms thrive only in a relatively small pH range, so they utilize a buffer solution to maintain a constant pH. One example of a *buffered solution* found in nature is *blood* (*Do you know the buffer?*)[§]

Buffer solutions achieve their resistance to pH change because of the presence of an equilibrium between the acid HA and its conjugate base A⁻



When some strong acid is added to an equilibrium mixture of the weak acid and its conjugate base, the equilibrium is shifted to the left, in accordance with **LE CHATELIER'S PRINCIPLE**. Because of this, the hydrogen ion concentration increases by less than the amount expected for the quantity of strong acid added (Buffer effect!!)

[§] *physiologic buffer system: bicarbonate* (pH 7.35 ~ 7.45)



Lecture 2: Summary & Remarks

Week 7 to 9 experiments will introduce you to two very important topics of laboratory in chemistry:

- **Synthesis**
- **Quantitative Analysis**

Learning those fundamental skills is required for almost all kind of laboratory work. The correct handling of glass, chemicals and laboratory instruments is essential for successful results in either synthesis or analysis.

- Always take detailed notes of every step you are doing in the lab. Note date, time, any observation you have made.
- Having a detailed lab report does not only help you if you need to repeat something but also others to understand your work.
- Every scientific journal requires a detailed description of your experimental work so that your results and conclusions become clear and understandable.
- If something does not work out, think about where a mistake might have happened and then try to avoid repeating the same mistake.

“Pure logical thinking cannot yield us any knowledge of the empirical world; all knowledge of reality starts from experience and ends in it.”

Einstein, Albert. *Ideas And Opinions* (p. 271). Three Rivers Press, NY (Kindle Edition)