## CHEMISTRY 203

## ACID-BASE TITRATION

## Purpose:

1. To study and practice the important analytical technique of Acid-Base titration.
2. To prepare a primary standard solution of potassium hydrogen phthalate (KHP).
3. To standardize a sodium hydroxide solution using the primary standard.
4. To determine the concentration of an unknown monoprotic acid using the standardized NaOH solution.

$\begin{aligned} & \text { Strong Electrolyte }-100 \% \text { dissociation } \\ & \mathrm{NaCl}(s) \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{Na}^{+}(a q)+\mathrm{Cl}(a q)\end{aligned}$
Weak Electrolyte - not completely dissociated
$\mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(a q)+\mathrm{H}^{+}(a q)$

Strong Acids are strong electrolytes
$\mathrm{HCl}(a q)+\mathrm{H}_{2} \mathrm{O}() \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{Cl}^{-}(a q)$
Weak Acids are weak electrolytes
$\mathrm{HF}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(1) \Longleftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{F}^{-}(\mathrm{aq})$
Strong Bases are strong electrolytes
$\mathrm{NaOH}(\mathrm{s}) \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{Na}^{+}(a q)+\mathrm{OH}^{-}(a q)$
Weak Bases are weak electrolytes
$\mathrm{F}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}\left(\eta \rightleftarrows \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{HF}(\mathrm{aq})\right.$

## Acid-Base Properties of Water

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{n}) \rightleftarrows \mathrm{H}^{+}(a q)+\mathrm{OH}^{-}(a q)
$$

## autoionization of water




## The Ion Product of Water

$\mathrm{H}_{2} \mathrm{O}\left(\Omega \rightleftarrows \mathrm{H}^{+}(\right.$aq $)+\mathrm{OH}^{-}($aq $) \quad K_{c}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{O}\right]} \quad\left[\mathrm{H}_{2} \mathrm{O}\right]=$ constant

$$
K_{c}\left[\mathrm{H}_{2} \mathrm{O}\right]=K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

The ion-product constant ( $\boldsymbol{K}_{\boldsymbol{w}}$ ) is the product of the molar concentrations of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ions at a particular temperature.

|  | $\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]$ <br> $\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right]$ | Solution Is |
| :---: | :---: | :---: |
|  |  | neutral |
| $\text { At } 25^{\circ} \mathrm{C}$ |  | acidic |
| $K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$ | $\left[\mathrm{H}^{+}\right]<\left[\mathrm{OH}^{-}\right]$ | basic |

## pH - A Measure of Acidity

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]
$$

Solution Is
neutral

$$
\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]
$$

At $25^{\circ} \mathrm{C}$

$$
\left[\mathrm{H}^{+}\right]=1.0 \times 10^{-7} \quad \mathrm{pH}=7.00
$$

$$
\text { acidic } \quad\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right] \quad\left[\mathrm{H}^{+}\right]>1.0 \times 10^{-7} \quad \mathrm{pH}<7.00
$$

$$
\text { basic } \quad\left[\mathrm{H}^{+}\right]<[\mathrm{OH}] \quad\left[\mathrm{H}^{+}\right]<1.0 \times 10^{-7} \quad \mathrm{pH}>7.00
$$

$$
\mathrm{pH} \mid
$$

$$
\left[\mathrm{H}^{+}\right]
$$

$$
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]
$$

$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$

$$
\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=K_{w}=1.0 \times 10^{-14}
$$

$$
-\log \left[\mathrm{H}^{+}\right]-\log \left[\mathrm{OH}^{-}\right]=14.00
$$

$-\log \left[\mathrm{H}^{+}\right]-\log \left[\mathrm{OH}^{-}\right]=14.00$

$$
\mathrm{pH}+\mathrm{pOH}=14.00
$$

## Volumetric analysis

Volumetric analysis: is a technique for determining the amount or concentration of a certain substance by doing a titration.
In titration a solution of accurately known concentration, called a primary standard, is added gradually (using a buret) to another solution of unknown concentration, until the chemical reaction between the two solutions is complete.

(a)


## Equipment:

- Mettler Balance: Used to weigh KHP, the primary standard.
- Volumetric Flask: Used for making up solutions to a given volume; calibrated to contain (TC) the volume specified at the specified temperature.
- Pipet: Used to transfer accurately measured small volumes of solution; calibrated to deliver (TD) at the specified temperature.
- Buret: Used for dispensing any volume, calibrated to deliver.

A volumetric flask, pipet, or buret is read by looking horizontally at the bottom of the meniscus of the liquid.

## Standard Solution

Standard solution: A solution of accurately known concentration.
Primary standard: An exact amount of a sample is dissolved in an exact volume.
e.g. Potassium Hydrogen Phthalate KHP


Molar mass $=204.23 \mathrm{~g} / \mathrm{mol}$



Standard solution: (continued)
Secondary standard: Is titrated with a primary standard to determine its concentration.
e.g. Sodium Hydroxide NaOH

- Sodium hydroxide is not a good primary standard solution. Solid NaOH absorbs water from air (hygroscopic), and its solution reacts with carbon dioxide. It has to be standardized against a primary standard solution.

To standardize: To determine the exact concentration.

## Properties of a good Properties of a good primary standard: titration:

- High molar mass
- Stable
- Not hygroscopic
- Highly pure
- Cheap and available
- must be fast
- must go to completion
- should be between reactants that react stoichiometrically


## Neutralization:

Acid-base titration involves a neutralization reaction which is the complete reaction between an acid and a base.

$$
\text { Acid }+ \text { base } \rightarrow \text { Salt }+ \text { water }
$$

$$
\mathrm{HCl}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

$$
\mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

$\mathrm{KHC}_{8} \mathrm{H}_{4} \mathrm{O}_{4}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{KNaC}_{8} \mathrm{H}_{4} \mathrm{O}_{4}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
or

$$
\mathrm{KHP}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{KNaP}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

or

$$
\mathrm{HP}^{-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{P}^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

net ionic equation

## When do we stop the titration?

## - Equivalence point:

Is the point at which all the acid has completely reacted or has been neutralized with the base, it is a theoretical concept.

## - End-point:

Is the point in a titration when a physical change (change in color) occurs that is associated with the condition of chemical equivalence.


## Indicators:

- Indicators are used to detect the end point.
- They are substances that have distinctly different colors in acidic and basic media, they are weak organic acids or bases that change their color at the equivalence point:

$$
\underset{\text { (acidic) }}{\mathrm{HIn}}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+} \underset{\text { (Basic) }}{+\mathrm{In}^{-}}
$$

$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]} \mathrm{K}_{\mathrm{a}}=$ Acid dissociation constant

## Indicators: (continued)

- Rearranging the above equation $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{Ka} \frac{[\mathrm{HIn}]}{\left[\mathrm{In}^{-}\right]}$
- Taking the -log of both sides

$$
\begin{gathered}
-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log \mathrm{Ka}-\log \frac{[H I n]}{\left[I n^{-}\right]} \\
\mathrm{pH}=\mathrm{pKa}+\log \frac{[I n-]}{H I n}
\end{gathered}
$$

If $\frac{[\mathrm{HIn}]}{\left[I n^{-}\right]} \geq 10 \quad$ the color of the acid (HIn) predominates
If $\frac{[\mathrm{HIn}]}{\left[I n^{-}\right]} \leq 0.1 \quad$ the color of the base $\left(\mathrm{In}^{-}\right)$ predominates

- The end point of a titration does not occur at a specific pH ; rather , there is a range within which the end point will occur, we choose the indicator whose end point lies on the steep part of the titration curve.
- In general, $\mathrm{pH}=\mathrm{pKa} \pm 1$

Some common acid base indicators:

| Indicator | Color in acid | Color in base | pHrange |
| :--- | :--- | :--- | :--- |
| Bromophenol blue | Yellow | Bluish pupple | 3.04 .6 |
| Mthyl red | Red | yellow | $4.2-6.3$ |
| Phenolphthalein | colorless | pink | $8.3-10.0$ |

## Units and Calculations:

Molarity: is the number of moles of solute per liter of solution

$$
\mathrm{M}=\mathrm{n} \text { of moles of solute } .
$$ Volume of solution in liters

$$
\mathrm{n}=\frac{\text { Mass }}{\text { MolarMass }}
$$

At the equivalence point:
Complete neutralization $n$ of moles $\mathrm{H}^{+}=\mathrm{n}$ of moles $\mathrm{OH}^{-}$

## Procedure:

1. Preparation of a Primary Standard Potassium Hydrogen Phthalate (KHP) Solution:

- Weigh a bottle containing KHP on the Mettler balance. $\left(\mathrm{KHC}_{8} \mathrm{H}_{4} \mathrm{O}_{4}\right.$, Molar mass $\left.=204.23 \mathrm{~g} / \mathrm{mol}\right)$ - Transfer the solid KHP quantitatively to a 250.0 mL volumetric flask.
- Add distilled water to $2 / 3$ the capacity of the volumetric flask.
- Dissolve the solid completely in the distilled water.
- Then dilute the solution to the mark.
- Weigh the empty bottle.

Calculate the Molarity of KHP

## 2. Standardization of the NaOH Solution:

- Rinse your clean buret with distilled water and then with few ml of the NaOH solution.
- Fill the rinsed buret with NaOH , make sure there are no air bubbles.
- Record the upper buret reading.
- Pipet 25.00 mL of KHP into a 250 mL Erlenmeyer flask.
- Add 25 mL of distilled water.
- Add 2 drops of phenolphthalein indicator
- Titrate against KHP to the end point ( light pink color).
- Record the lower buret reading.
- Repeat at least three times.

Calculate the Molarity of NaOH
3. Analysis of the unknown:
-Proceed as in part 3 using the unknown instead of KHP
Calculate the Molarity of the unknown

## 4. Blank Titration:

Run a blank titration to determine the blank correction for possible acids other than KHP. Proceed as in part 2, with distilled water instead of the KHP. A very small volume of the base will be needed to reach the end point. Theoretically, this volume should be subtracted from each of the proper titrations. However, since it can be as small as only one drop, you can neglect it in your calculations.

