Standard solution and Titration م.م زینب یحیی کاظم

Standard solution and Titration

Titration



Volumetric Analysis - Principles Standard Solutions

- "**Titrimetric**" determination of <u>analyte</u> by reaction with measured amount of standard reagent
- "Standard Solution" (<u>titrant</u>) reagent of known concentration
- **"Titration**" slow addition of titrant to analyte solution from a volumetric vessel (buret)
- "Equivalence Point" reached when amount of added titrant is chemically equivalent to amount of analyte present in the sample.
- "End Point" the occurrence of an observable physical change indicating that the equivalence point is reached. Might differ from Eq.Pt.!

Standard solution

In analytical chemistry, a standard solution is a solution containing a quite known concentration of an element or a substance, a known weight of solute is dissolved to make a specific volume. It is prepared using a standard substance such as a primary standard.

Standard solution

Standard solutions are used to determined the concentrations of other substance such as solutions in titration. The concentrations of standard solutions an normally expressed in units of moles per liter (mol/L, often abbreviated to M for molarity), moles per cubic decimeter (mol/dm3),

Properties

The properties of a standard solution for titrations are:

1. Its concentration must remain constant all the time. This is so that there is no need for restandardization.

2. Its reaction with the analyte must be rapid in order to minimize the waiting period after addition of each reagent.

3. Its reaction must be reasonably complete.

4. It should be possible to describe the reaction by a balanced chemical reaction.

5. A method must exist for detecting the equilibrium point.

How to mix a Standard Solution



Process of Making a Standard Solution from Liquids



Volumetric Analysis - Principles Standard Solutions

- Primary Standard "-
 - highly purified compound used as a reference material in titrimetry
- Properties:
- High purity
- Stable in air
- Independent of relative humidity
- Readily available
- Reasonable solubility
- Large formula weight

Volumetric Analysis - Principles Standard Solutions

- "Secondary Standard"
 - do not meet requirements for a primary standard but are available with sufficient purity and properties to be generally acceptable
- Desirable properties of a Standard Solution:
- Prepared from primary standard
- Stable
- Reacts rapidly and completely with analyte
- Reacts selectively with analyte

Volumetric Analysis - Principles Examples of Standard Materials

• Primary

- Potassium Acid Phthalate
- KHC₈H₄O₄ (FW 204.23)
- Benzoic Acid
- C₆H₅COOH (FW 122.12)
- Na_2CO_3 , $KH(IO_3)_2$
- Arsenio us Oxide (As₂O₃)
- Sodium Oxalate $(Na_2C_2O_4)$
- KI, $K_2Cr_2O_7$, Fe(pure)

• <u>Secondary</u>

- NaOH, KOH, $Ba(OH)_2$
- HCl, HNO_3 , $HClO_4$
- Sulfamic Acid (HSO₃NH₂)
- $KMnO_4$, $Na_2S_2O_3$
- $Ce(HSO_4)_4$ (FW 632.6)

A standard solution has known molarity.

A **primary standard** is made by **weighing** a **pure solid** and diluting in a volumetric flask.

A **secondary standard** requires a titration to calibrate its concentration. It was made using an acid or base with **suspect purity**.

Not suitable	Example	Reason	
Arrhenius bases	NaOH	Hydroscopic	
Strong acids	HCl	volatile liquids or gases	

Suitable solid bronsted bases solid weak acids

 Na_2CO_3 $H_2C_2O_4$ pure solid pure solid

Primary Standard

 $H_2C_2O_{4(s)}$ $Na_2CO_{3(s)}$ $C_6H_5COOH_{(s)}$ $KC_6H_5COO_{(s)}$

Secondary Standard H₂SO_{4(l)} NH_{3(g)} NaOH_(s) HCl_(g)

Titrations

Strong Acid - Strong Base $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(1)$

pH changes slowly initially, changes rapidly through pH = 7 (equivalence point) and then changes slowly again

If the analyte is a strong acid, pH increases as base is added



Titrations

If the analyte is a strong base, pH decreases as acid is added



Strong Acid-Weak Base and Weak Acid - Strong Base



Titrations

Changes in pH during a titration of a weak acid/base with a strong base/acid:

Halfway to the stoichiometric point, the $pH = pK_a$ of the acid

The pH is greater than 7 at the equivalence point of the titration of a weak acid and strong baseThe pH is less that 7 at the equivalence point of the titration of a weak base and strong acid

Beyond the equivalence point, the excess strong acid or base will determine the pH of the solution What was the molar concentration of 51.4 mL of a solution of HNO₃ that required 29.20 mL of a 0.0160 M standard solution of KOH for complete neutralization?

Ans. It is first necessary to determine the stoichiometry of the reaction

HNO₃(aq) + KOH(aq) \longrightarrow H₂O(I) + K⁺(aq) + NO₃⁻(aq) The net ionic equation is

 $H^+(aq) + OH^-(aq) \implies H_2O(I)$

The stoichiometry is $1 \text{ HNO}_3/_1 \text{ KOH}$, and therefore

 $M_{acid} \ge V_{acid} = M_{base} \ge V_{base}$ $M_{acid} \ge 51.4ml = 29.20ml \ge 0.0160_M$ $M_{acid} = 0.0091_M$

Titration Calculation 6.50 mL of 0.100 M $H_2C_2O_4$ is required to neutralize 10.0 mL of NaOH solution in a titration. Calculate the base concentration.

	0.0100 L		
[NaOH] =		1 L	1 mole H ₂ C ₂ O
	0.00650 L H ₂ C ₂ O ₄	x <u>0.100 mole</u>	x 2 mole NaOH
0.100 M	? M		
0.00650 L	0.0100 L		
$1H_2C_2O_4$	+ 2NaOH	\rightarrow Na ₂ C ₂	$O_4 + 2H_2O$

= 0.130 M

What was the molar concentration of 32.80 mL of an H_2SO_4 solution which required 31.72 mL of a 0.0240 *M* standard solution of KOH for complete neutralization?

Ans. First determine the stoichiometry of the reaction

 $H_2SO_4(aq) + 2KOH(aq) \implies 2H_2O(I) + 2K^+(aq) + SO_4^{2-}(aq)$

The net ionic equation is

 $2H^+(aq) + 2OH^-(aq) \implies 2H_2O(I)$

The stoichiometry is $1 \text{ H}_2\text{SO}_4/2$ KOH. We must therefore take this into account in our calculations. Our formula basically tells us that in a neutralization reaction

Moles acid = moles base

$$\frac{\text{mol(acid)}}{\text{L(acid)}} \left[\text{L(acid)} \right] = \left(\frac{\text{mol(base)}}{\text{L(base)}} \right) \left[\text{L(base)} \right] \left(\frac{1 \text{mol(acid)}}{2 \text{ mol(base)}} \right)$$

 $(mM_{(acid)}/ml) \ge 32.80ml_{(acid)} = (0.0240 \ mM_{(base)}/ml) \ge 31.72ml_{(base)} \ge (1/2)$ $(mM_{(acid)}/ml) = M_{(acid)} = 0.0116M$ What was the molar concentration of 28.92 mL of an H₃PO₄ solution which required 91.21 mL of a 0.0390 M standard solution of KOH for complete neutralization?

Am. Here again, the reaction stoichiometry is central:

 $H_3PO_4(aq) + 3KOH(aq) \implies 3H_2O(I) + 3K^+(aq) + PO_4^-(aq)$ The net ionic equation is

 $3H^+(aq) + 3OH^-(aq) \implies 3H_2O(I)$

Taking the stoichiometry, 1 mol acid/3 mol base, into account:

 $(mM_{(acid)}/ml) \ge 28.92ml_{(acid)} = (0.0390 \ mM_{(base)}/ml) \ge 91.21ml_{(base)} \ge (1/3)$ $(mM_{(acid)}/ml) = M_{(acid)} = 0.0410M$

Titration Error

- 1. Difference between endpoint and equivalence point
- 2. Corrected by a blank titration
- 3. repeat procedure without analyte
- 4. Determine amount of titrant needed to observe change
- subtract blank volume from titration



Buffers

Buffer solutions : resists change in pH even with addition of small amounts of acid or base.

Buffer solutions are mixed solutions: mixture of a weak acid and its conjugate base or a weak base and its conjugate acid.

Human blood has a pH maintained at pH = 7.4 due to a combination of carbonate, phosphate and protein buffers.

The ocean is buffered to a pH of ~ 8.4 by buffering that depends the presence of hydrogen carbonates and silicates.

BUFFER SOLUTIONS

A buffer is a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH of a solution.

Buffers are used in all types of chemistry whenever it is desirable to maintain the pH of a solution at a constant and predetermined level

What Are the Unique Properties of Buffer Solutions? Buffers do not maintain pH at an absolutely constant value, but changes in pH are relatively small when small amounts of acid or base are added.

