Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

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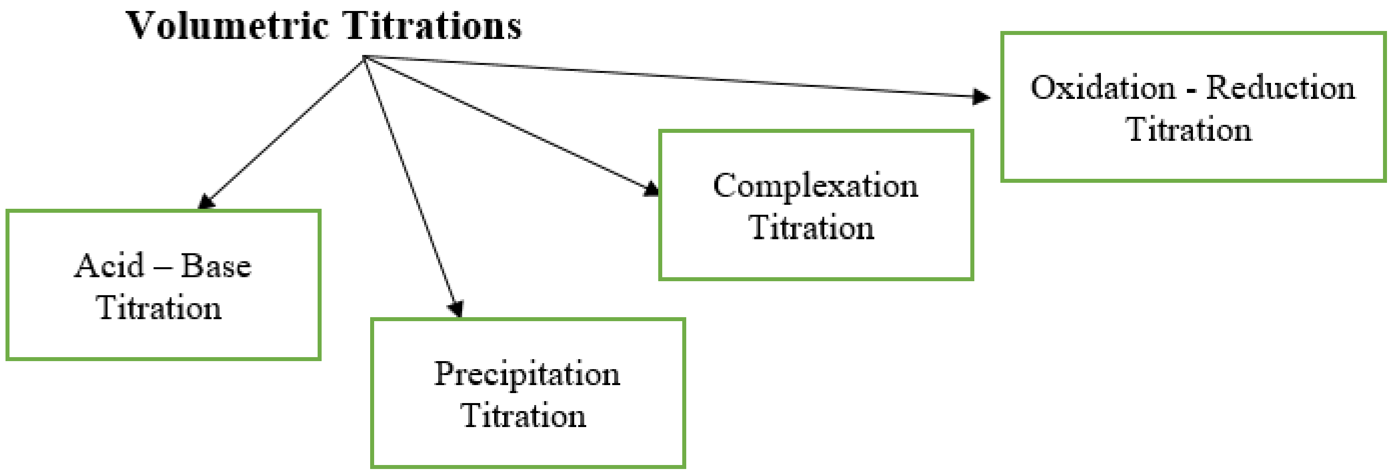
Precipitation titrations:

- **Precipitation titrations are volumetric methods based on the formation of a slightly soluble precipitate.**
- **In precipitation titration we are using molar concentration and we are not using normal concentration.**



Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Precipitation titrations:

Limitations of volumetric precipitation titrations:

- Volumetric precipitation reactions have several limitations combining those of the titrimetric methods in general, and some of those of the **gravimetric methods.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Precipitation titrations:

The precipitate:

- **needs not be separated**
- **needs not be pure**
- **the impurity does not consume titrant.**

The equivalence point:

- **The equivalence point is reached (نصل)when an equivalent amount of the titrant has been added.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Argentimetric Processes:

- **Because of the precipitating titration based upon utilizing silver nitrate**
- **($AgNO_3$) as a precipitating agent, then it called "*argentimetric processes* ".**
- **Precipitation titration is a very important, because it is a perfect method for determine halogens and some metal ions.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Argentimetric Processes:

Table 1: Substances determined by precipitation titrations with Ag^+.

AsO_4^{3-}, Br^-, CNO^-, CO_3^{2-}, CrO_4^{2-}, CN^-, Cl^-, $C_2O_4^{2-}$, I^-, PO_4^{3-}, SCN^-, S^{2-}, fatty acids

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Argentimetric Processes:

Table 2: Miscellaneous precipitation titrations

Analyte	Reagent	Precipitate
Cl^-, Br^-	$Hg_2(NO_3)_2$	Hg_2Cl_2, Hg_2Br_2
SO_4^{2-}, MoO_4^{2-}	$Pb(NO_3)_2$	$PbSO_4$, $PbMoO_4$
Zn^{2+}	$K_4Fe(CN)_6$	$K_2Zn_3[Fe(CN)_6]_2$
PO_3^{4-}, $C_2O_4^{2-}$	$Pb(OAc)_2$	$Pb_3(PO_4)_2$, PbC_2O_4

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Argentimetric Processes:

Limitations of argentometric titrations:

(1) Reducing agents (العوامل المختزلة)→ must be removed (فصله) by previous oxidation.

- **Example**: such as, **sulfur dioxide (SO_2) interfere by reducing the silver ions, and must be removed by previous oxidation.**

(2) Silver halides are sensitive to photodecomposition (هاليدات الفضة حساسة للتفكك الضوئي)

- **the titration should be carried out in diffused daylight, or artificial light.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Argentimetric Processes:

Limitations of argentometric titrations:

(3) Most cations except (ما عدا) the alkali and alkaline earths interfere (تتداخل) in several ways. Example:

(a). Fe^{3+} form **insoluble coloured hydroxide** in **neutral or slightly acid medium**;

(b) Al^{3+}, hydrolyses to insoluble basic salts in neutral or slightly acid solution, showing a tendency to coprecipitate chloride;

(c) Hg^{2+} form soluble complexes with halides of the type $[HgI_4]^{2-}$.

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

- A **saturated solution** is one in which the maximum amount of solute has been dissolved. The opposite is a dilute solution; this solution can accept more solute.
- Pressure and temperature affect solubility. This topic discusses the solubility of compounds in water at room temperature and standard pressure.
- A compound that is soluble in water forms an aqueous solution.

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Ions	Except
Salts of ammonium (NH_4^+) and Group IA are always **soluble.**	
All chlorides (Cl^-), bromides (Br^-) and iodides (I^-) are **soluble**	1. AgCl, Hg_2Cl_2, and $PbCl_2$ which are **insolube** 2. AgBr, Hg_2Br_2, $HgBr_2$, and $PbBr_2$ which are **insoluble.** 3. AgI, Hg_2I_2, HgI_2, and PbI_2 which are **insoluble**.
Chlorates (ClO_3^-), nitrates (NO_3^-), perchlorate (ClO_4^-) and acetates (CH_3COO^-) are **soluble.**	

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Ions	Except
Chlorates (ClO_3^-), nitrates (NO_3^-), perchlorate (ClO_4^-) and acetates (CH_3COO^-) are soluble.	
Sulfates (SO_4^{2-}) are soluble	except $CaSO_4$, $SrSO_4$, $BaSO_4$, Hg_2SO_4, $HgSO_4$, $PbSO_4$, and Ag_2SO_4 which are **insoluble**.
Nitrates (NO_3^-), acetates ($C_2H_3O_2^-$), chlorates (ClO_3^-), and perchlorate, and ClO_4^- are soluble	
Carbonates (CO_3^{2-}), oxalates ($C_2O_4^{2-}$), chromates ($C_2O_4^{2-}$), and phosphates (PO_4^{3-}) are insoluble	except NH_4^+ and Group IA compounds are **soluble**.

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Ions	Except
Sulfides (S^{2-}) are insoluble	Calcium, barium, strontium, magnesium, sodium, potassium, and ammonium Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Na^{+}, K^{+}, and NH_4^{+}
Hydroxides (OH^{-}) are insoluble	Alkali metals (Group I), and Group IIA from calcium down, transition metals, aluminum (Al^{3+}), and ammonium (NH_4^{+}).
All metallic oxides (O^{2-}) are insoluble	except NH_4^{+} and Group IA compounds.

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Net Ionic Equation:

- Net ionic equations are useful in that they show only those chemical species directly participating in a chemical reaction.
- They are thus simpler than the overall equation, and help us to focus on the “heart” of the chemical change in a particular reaction.
- **The keys to being able to write net ionic equations are the ability to recognize monatomic and polyatomic ions, the solubility rules, and the rules for electrolyte behavior.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Precipitation Reactions:

- $Pb(NO_3)_{2(}aq) + NaI(aq) \rightarrow$
- **Step 1:** Write the **balanced** general reaction including the reactants and the products
- $\mathbf{Pb(NO_3)_2(aq) + 2\ NaI(aq) \rightarrow PbI_2 + 2\ NaNO_3}$
- **Step 2:** Look up the products on your solubility chart and insert the subscripts (for solid, and **(aq)** for aqueous) If something is insoluble you use the solid subscript, if it is soluble you use the **(aq)** subscript)
- $\mathbf{Pb(NO_3)_2(aq) + 2\ NaI(aq) \rightarrow PbI_2\,(s) + 2\ NaNO_3\,(aq)}$

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Precipitation Reactions:

- **Step 3:** Break all reactants and products into ions, (can not break up pure liquids, solids, or gases). This is the **COMPLETE IONIC EQUATION**. If you have polyatomic ions such as nitrate (NO_3^-) that is an ion, do not break it up further
- **$Pb^{2+}(aq) + 2\ NO_3^-(aq) + 2\ Na^+(aq) + 2\ I^-(aq) \rightarrow PbI_2(s) + 2\ Na^+(aq) + 2\ NO_3^-(aq)$**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Precipitation Reactions:

- **Step 4:** Cancel out any **spectator ions. Spectator ions are ions that appear in the reactant side and the product side.** (they have to be exactly the same, you could cancel out NO_3^- & NO_3^- but not Fe^+ & Fe^{3+}, the oxidation # of iron has changed therefore it is not the exact same on the reactant side as the product side

$$Pb^{2+}(aq) + 2\,NO_3^-(aq) + 2\,Na^+(aq) + 2\,I^-(aq) \rightarrow PbI_2(s) + 2\,Na^+(aq) + 2\,NO_3^-(aq)$$

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Rules (قواعد الاذابة):

Precipitation Reactions:

- **Step 5:** Re-write the chemical reaction without the spectator ions. This is the **NET IONIC EQUATION**

$$Pb^{2+}(aq) + 2\ I^{-}(aq) \rightarrow 2\ PbI_2(s)$$

- **Step 6:** Check yourself. The only chemicals on the reactants side should be what makes up the solid product. In this case **(PbI_2)** is the product so only **(Pb^{2+})** and **(I^-)** should be on the reactant side.

Chapter (1) Volumetric Precipitation Titrations (Precipitimetry)

Solubility (الاذابة):

- **Solubility is the amount (grams) of substance which dissolves to form a saturated solution.**
- **Expressed in g/L**
- **Can change considerably as the concentrations of other solutes change**

Solubility process (عملية الاذابة):

- **The solubility of a substance is dependent on:**

(1) the forces holding the crystal together (the lattice energy)

(2) the solvent acting on these forces.

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Molar solubility (الاذابة المولارية):

- **Molar solubility is the number of moles of solute dissolving to form a liter of saturated solution.**
- **Expressed in mol/L or M or molar**

$$\mathbf{Molarity = \frac{no.\,moles}{Vol.\ (L)}}$$

Relationship between molarity and solubility:

Solubility (g/L) = Molarity x M.wt → $\mathbf{Molarity = \frac{Solubility}{M.wt}}$

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Product (حاصل الاذابة):

- **The solubility product is the molar concentration of ions raised to their stoichiometric powers.**
- Let us consider in the same way the saturated solution of the **sparingly soluble salt $X_m\ Y_n$** which dissociates into **m cation, X^{n+}** and **n anions, Y^{m-}**. The equilibrium for this saturated solution can be represented by the equation:

$$X_m\ Y_n\ (s) \rightleftharpoons m\ X^{n+}(aq) + n\ Y^{m-}(aq)$$

$$K_{SP} = [X^{n+}]^m . [Y^{m-}]^n$$ **At equilibrium**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Solubility Product (حاصل الاذابة):

- **For example:**

(1) $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^{-}(aq)$

$$K_{SP} = [Pb^{2+}].[I^{-}]^2$$

$$[I^{-}] = 2 \times [Pb^{2+}]$$

(2) $AgI(s) \rightleftharpoons Ag^{+}(aq) + I^{-}(aq)$

$$K_{SP} = [Ag^{+}].[I^{-}]$$

$$[Ag^{+}] = [I^{-}]$$

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

The Solubility- Product K_{SP}:

- The equilibrium constant expressing the **solubility of a precipitate** is the familiar **solubility product constant (K_{SP})**.
- **The solubility product constant (K_{SP}) is equal to the molar concentrations of ions raised to powers corresponding to the stoichiometric coefficients.**
- **K_{sp} – describes the dissolution of a solid which indicates how soluble the solid is in water.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

The Solubility- Product K_{SP}:

- **Calculating K_{sp} = product of ion concentrations involved in equilibrium.**
- **Smaller the K_{sp}, the lower the solubility**
- **Larger the K_{SP} , the greater the solubility.**

Relationship Between K_{sp} and Solubility at 25°C

No. of Ions	Formula	Cation/Anion	K_{sp}	Solubility (M)
2	$MgCO_3$	1/1	3.5×10^{-8}	1.9×10^{-4}
2	$PbSO_4$	1/1	1.6×10^{-8}	1.3×10^{-4}
2	$BaCrO_4$	1/1	2.1×10^{-10}	1.4×10^{-5}
3	$Ca(OH)_2$	1/2	6.5×10^{-6}	1.2×10^{-2}
3	BaF_2	1/2	1.5×10^{-6}	7.2×10^{-3}
3	CaF_2	1/2	3.2×10^{-11}	2.0×10^{-4}
3	Ag_2CrO_4	2/1	2.6×10^{-12}	8.7×10^{-5}

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Using K_{SP} In Calculations:

- Solubility product constants allow **us**
  1. **to estimate the solubility of a salt,**
  2. **to determine the relative solubility of salts,**
  3. **to identify solutions as saturated or unsaturated,**
  4. **to predict if a precipitate will form when two or more salt solutions are combined.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Ion Product (Q):

- **Ion product (Q) is the product of the molar concentrations of ions each raised to the power of their stoichiometric coefficients. For example:**

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

$$Q = [Ag^{+}]_o[Cl^{-}]_o$$

- **The subscript (o) reminds us that these are initial concentration and don't necessarily correspond to those at equilibrium.**

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Ion Product (Q):

- **For the dissolution of an ionic solid in aqueous solution, any one of the following conditions may exist:**
- **$Q < K_{sp}$ Unsaturated solution → no precipitate**
- **$Q = K_{sp}$ Saturated solution. → At equilibrium**
- **$Q > K_{sp}$ Supersaturated solution → precipitation**

occurs $Q = K_{sp}$

Chapter (1): Volumetric Precipitation Titrations (Precipitimetry)

Selective Precipitation of Ions:

- Separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or a few ions
- By using Table of Solubility Product Constants

Compound	Formula	K_{sp} (25 °C)	Compound	Formula	K_{sp} (25 °C)
Aluminium hydroxide	$Al(OH)_3$	3×10^{-34}	Magnesium fluoride	MgF_2	5.16×10^{-11}
Barium bromate	$Ba(BrO_3)_2$	2.43×10^{-4}	Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Barium carbonate	$BaCO_3$	2.58×10^{-9}	Magnesium hydroxide	$Mg(OH)_2$	5.61×10^{-12}