

GRAVIMETRIC TITRATIONS

Q. what is Von Weimann's theory of supersaturation?

Ans. A supersaturated solution is the solution that contains greater concentrations of solute than corresponds to equilibrium solubility at temperature under consideration. Supersaturated solution is unstable state that becomes stable by addition of crystal of the solute (seeding).

Initial rate of precipitation is directly proportional to relative supersaturation.

$$\text{Relative supersaturation (R)} = \frac{Q-S}{S},$$

Where Q-S, is the degree of supersaturation, when precipitation begins.

Q, is Actual concentration of solute/ Total concentration of substances momentarily produced in solution by mixing reagents.

S, is equilibrium solute concentration / equilibrium solubility of precipitates/ Force resisting precipitation or causing precipitates to re-dissolve.

Larger the Q-S, greater is the nuclei formation and many smaller particles/crystals of precipitates are formed.

So, our main aim is to keep the Q-S small, so that less number of nuclei is produced and larger particles of precipitates are formed.

Therefore the value of Q should be less and S should be more.

Q can be lowered by using dilute solutions, By addition of dilute precipitating reagents slowly and with stirring & large volumes of solution .

S can be increased by using hot solutions of the reagents, maintain the pH as low as possible to precipitate.

Q. Write a note on colloidal state. Differentiate between Lyophobic and Lyophilic colloids.

Ans. Colloidal state is a state, where the particles are of the size 0.1 μm & 1 nm. They also behave like true solutions (particle size 0.1 nm - 10^{-8}cm). They show property like Tyndall effect. Tyndall effect was demonstrated by John Tyndall. It is phenomenon of scattering the light by colloidal suspension.

| SN | Lyophobic | Lyophilic |
|----|---|--|
| 1 | These are Dispersions/ Sols. | They set to jelly like masses known as gels. |
| 2 | Slightly viscous | Very Viscous |
| 3 | Eg. Sols of Metals, AgX, M ⁺ S etc. | Eg. Sols of silicic acid, Tin (IV) oxide, gelatin. |
| 4 | Minute concentration of an electrolyte results in flocculation. | Large concentration of electrolyte results in precipitation/ salting out. |
| 5 | Change in irreversible. If water is added, it has no effect on flocculated solid. | Change in reversal. If water (solvent) is added reversal effects are seen. |
| 6 | They have definite electrical charge. The charge can be changed only by specific methods. | They can change their charge readily. In acidic medium, they get positive charge & in basic medium they get negative charge. |

| | | |
|---|--|--|
| 7 | Under ultra microscope they appear as bright particles in vigorous motion. (Brownian movement) | They exhibit a diffuse cone of light under ultra microscope. |
|---|--|--|

Q. . Write a note on peptization.

Ans. Process of dispersing an insoluble material into a liquid as a colloid is called peptization. It is opposite of coagulation.

Coagulation of colloidal suspension is brought about by ions other than those that precipitate it off.

When coagulation of colloid takes place, coagulating ions may be dragged down with the precipitates. If these ions are dissolved when a precipitate is washed, solid particles will go back into the colloidal dispersion and pass through the filter paper.

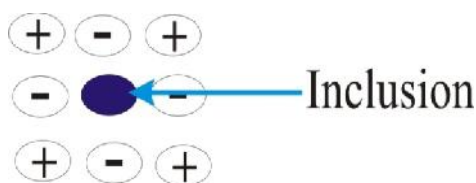
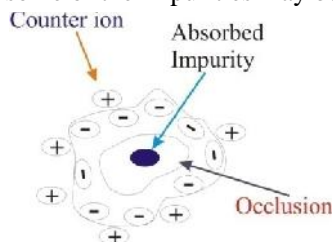
As per rule, same sign repels each other. Colloidal particles are assumed to be composed of electrical double layer. By adding electrolyte that reduces the repulsion of particles, i.e particles will remain as flocs, which are easy to filter. By adding salt of multivalent ions solution remains as flocculated.

Q.. Write a note on Co-precipitation.

Ans. When a precipitate is formed it separates from the solution and is not always perfectly pure. i.e. it contains varying amounts of impurities depending upon the conditions of precipitation. Contamination by substances which are generally soluble in mother liquor is termed as co-precipitation.

Co-precipitation is of two types :

- Adsorption at the surface of the particles exposed to solution: Surface adsorption is greatest for gelatinous precipitates and least for microcrystalline character.
The theory can be explained by Panath-Fajan's –Hahn adsorption Rule, which states that; ion that is most strongly adsorbed by an ionic substance (crystal lattice) is that ion which forms the least soluble salt.
Eg: On sparingly soluble Sulphate, Calcium ions are more readily adsorbed when compared to Magnesium sulphate ($MgSO_4$), because Ca^{++} are less soluble than Mg^{++} . Deformability of adsorbed ions and electrolytic dissociation of adsorbed compounds plays important role. Lesser the dissociation of compound greater is the adsorption. Eg. H_2S is a weak electrolyte and therefore strongly adsorbed by metallic sulphides.
- Occlusion of foreign substances takes place during growth of crystal from primary particles. Primary particles are subjected to some amount of surface adsorption during the coalescence. Impurities get partially eliminated if large single crystals are formed, process takes place very slowly, or if coalescence is fast, large crystals composed of loosely bound small crystals may be produced and some of the impurities may be eliminated within the walls of large crystals.



Q.. What is post precipitation?

Ans. This is a type of precipitation which occurs on the surface of 1st precipitate after it is formed. It occurs with sparingly soluble substances which form supersaturated solutions. Usually; they have an ion in common with that of the primary precipitate. Eg. In precipitation of calcium as oxalate in presence of magnesium (Mg), Mg-oxalate separates gradually upon calcium oxalate. Longer the precipitate is allowed to stand in contact with solution, greater is the error due post-precipitation.

Q.. Differentiate between post-precipitation and co-precipitation.

Ans.

| NO. | Post-precipitation | Co-precipitation |
|-----|---|------------------------------------|
| 1. | Contamination increases with time that the precipitate is left in contact with mother liquor. | Contamination decreases with time. |
| 2. | Contamination increases, the faster the solution is agitated by either mechanical or thermal means. | Contamination decreases |
| 3. | Magnitude of Contamination is high | Less |