Precipitation: A Part of Gravimetric Analysis - A Review

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Abstract:

Precipitation is an important part of gravimetric analysis. It is used in quantitative analysis of various elements and substances. Various techniques are now available to deeply study the process of precipitation. A number of processes and phenomena are related to the process of precipitation. In this paper we will discuss precipitation, theory of precipitation, various types of contamination that may occur in precipitates, and the treatment of precipitates including digestion and washing of precipitates.

Key Words: Precipitation, co-precipitation, solubility, post precipitation, filterability, simultaneous precipitation.

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Introduction:

Precipitation is a process in which (on adding some chemical called precipitating reagent) any ion which is present in solution comes out of solution in a solid form as precipitate. The process or the concept of precipitation is helpful in quantitative analysis of any element through gravimetric analysis.

Theory of precipitation: Precipitation occurs when ionic product of any substance exceeds its solubility product, i.e. for precipitation:

ionic product > solubility product

This condition is achieved by adding a reagent (precipitating reagent) which has an ion that will be utilized in exceeding the ionic product than solubility product. On continuously adding the precipitating reagent, a stage comes when concentration and hence ionic product become higher than solubility product. For example if we add $BaCl_2$ in a solution having Ba^{2+} and SO_4^{2-} ions then the ionic product of $BaSO_4$ becomes higher than their solubility product so $BaSO_4$ precipitate will be formed.

Parameters affecting formation of precipitates:

1) Temperature effect: Temperature plays a very important role in the formation of precipitates, or we can say that solubility of precipitates in mother liquid is largely affected by temperature. Generally precipitates are more soluble in hot solutions than in cold solutions. But along with precipitates, impurities are also more soluble in hotter conditions. The gradient of effect of temperature varies for precipitates of different substances. For example, if we increase temperature from 10 degree centigrade to 100 degree centigrade of a solution containing silver chloride, the solubility of silver chloride increases significantly from 1.7 mg/litre to approx 21.3 mg/litre. But, on the other hand, the solubility of $BaSO_4$ increases just negligibly from 2.2 mg/litre to 3.8 mg/litre. Filtration of hot solutions are preferred for those precipitates in which the effect of temperature is lower for precipitates than effect of temperature on impurity. So that impurities could get dissolved and separated from precipitate through filtration. In this process of filtration of hot solutions, the pure precipitate will be obtained on filter paper while the impurities (being more soluble in hot solutions) will come down along with mother liquid.

2) Effect of common ion: The presence of any ion, which is common to the desired precipitates, will decrease the solubility of

precipitates, meaning hereby that, more and more precipitate will be formed as we increase the concentration of common ion. For example, any substance having molecular formula AB, will dissolve as A^+ and B^-, but if we add any common ion (suppose A^+), then concentration of A^+ in solution will increase, as a result of which more and more precipitate of AB will form in order to minimize the effect of addition of extra A^+ ion from outside. This effect of the common ion is in accordance with the well-known Le chatelier's principle.

Properties of precipitates that we want: There are some desired properties of precipitates as discussed below:

1. Purity it is the most desired property for any precipitates precipitate should be free from any impurity and should be in prostate so that we can utilize or separate them in pure state directly
2. Solubility: Solubility of precipitates should be negligible, meaning hereby that precipitate should be insoluble in mother liquid so that at the time of filtration any loss of precipitates because of high solubility could be avoided and we get maximum content of precipitates in solid form.
3. Filterability: The precipitate formed should be of larger size i.e. having bigger particle size so that the precipitate could be filtered easily and may not pass through the filter paper. This could only be achieved if the diameter of precipitates is more than the pore size of the filter paper, otherwise the precipitate will go through the pores of filter paper and v we will not be able Tu to separate them from Mother liquid
4. Non Hygroscopic: The precipitates should be non-hygroscopic in nature. Hygroscopic precipitates are those which absorb moisture from the atmosphere. So if our desired precipitates are of hygroscopic nature we will not be able to weigh the precipitates exactly because the moisture content will alter the weight and we will get incorrect readings. The weight of moisture will add up in the weight of precipitates and we get higher weight than the actual weight because of that moisture. So the nature of precipitates should be such that it does not absorb the moisture or we can say that precipitates should be non-hygroscopic.
5. Non Reactive: The precipitates should be non reactive. They should not react with mother liquid or any ion present in the mother liquid, other our precipitates will react with that and may probably form some other compound.

Contamination of Precipitates: The precipitates sometimes may have some impurities. The presence of impurities in the precipitates is called contamination. The impure precipitates are known as contaminated precipitates. Generally, the contamination of precipitates occurs in three ways. These ways differ from one another in the manner in which contamination gets induced in the desired precipitates. The three possible ways are discussed below:

1. Simultaneous Precipitation: As we know, for precipitation to take place we have to add some precipitation reagent in the mother liquid. During this process if the ionic product of some undesired product also gets exceeded than the solubility product of that salt, then in this scenario, this undesired product will also get precipitated out along with our desired product. For example if we add Silver Nitrate in a solution containing Sodium Chloride and Sodium Bromide, then the ionic product of Silver Bromide also gets exceeded together with Silver Chloride. So Silver Bromide will be formed as contamination to Silver Chloride. As the contamination occurs simultaneously to the desired product, this process is known as Simultaneous Precipitation.
2. Co-precipitation: It is a type of precipitation in which the impurities are otherwise soluble in mother liquid but on the addition of precipitating reagent, when the desired or required precipitates starts growing, then the impurities are adsorbed/absorbed on the precipitates and so the precipitates gets contaminated by these impurities. For example, if we add sulphuric acid (H_2SO_4) to a solution which have $BaCl_2$ & $FeCl_3$, we expect only $BaSO_4$ to be precipitated out because $Fe_2(SO_4)_3$ is soluble in water, but what happens actually is $Fe_2(SO_4)_3$ also gets precipitated with $BaSO_4$. So we can say that $Fe_2(SO_4)_3$ salt is co-precipitated with $BaSO_4$.

If precipitation is carried out in concentrated solutions, then co-precipitation is very high. The co-precipitation contamination may occur in two ways, each of these are discussed below:

a) This first type of contamination happens when impurities are adsorbed by precipitates. If the desired precipitates have more surface area then the impurities may grow up by getting adsorbed on the desired precipitates. This type of contamination occurs more when the impurity and required precipitates both have one common ion present in them. For example, if we try to precipitate out CaC_2O_4 when Magnesium is also present in the solution then MgC_2O_4 also gets precipitated along with our desired precipitates of CaC_2O_4. This contamination obeys Paneth Fazan Hahn's rule of adsorption. This rule says that, that salt will be adsorbed preferentially which has lower solubility than any other salt having more solubility in that liquid. This rule could be easily understood by the following example: While precipitating $BaSO_4$ in presence of Calcium ions and Magnesium ions, calcium sulphate is adsorbed on $BaSO_4$ preferentially over magnesium sulphate because $CaSO_4$ precipitates are less soluble than the precipitates of $MgSO_4$ so this is in accordance with above said rule. Similarly, While the process of precipitation of silver iodide in the presence of NO_3^- and CH_3COO^- takes place, then CH_3COOAg gets adsorbed more than $AgNO_3$, because the former is less soluble than later one.

b) This second type of co-precipitation occurs when the impurities and the precipitates are of similar composition and size. The impurities or contamination gets fit into the structure of crystal during the growth of the precipitates.

3. Post Precipitation: if a solution which is under consideration has two ions which can be precipitated by the same precipitating agent could get precipitated along with desired precipitate depending upon the rate of precipitation and solubility product. As we know the rate of reaction and even of precipitation is different for different substances so this post precipitation occurs after the precipitation of desired precipitate or main precipitate. This contamination of post precipitation type occurs after the formation of main precipitate so this type of contamination is called post precipitation. Post precipitation will be more if more and more time we give to contaminate particle to grow after the formation of main precipitate, so in order to reduce this post precipitation we should filter the main precipitates as soon as possible after their formation so that the contaminate particles did not get much time to grow after the formation of desired precipitate or main precipitate. By filtering the main precipitate immediately after their formation we can reduce the chance of post precipitation contamination because the main precipitates are formed first and the impurities in the form of Post precipitation will form after some time so we can utilize this time to minimize the post precipitation contamination.

Post precipitation and co precipitation both could be avoided by taking the following precautions

1. The precipitating agent should be added in moderately dilute form
2. The precipitating reagent should be poured in a slow stream.
3. If solubility of precipitate permits then precipitation should be done in hot solutions.
4. After the formation of precipitates, the process of digestion of precipitate should be carried out thoroughly.

All these above precautions will minimize the contamination that may be caused either by post precipitation or by co-precipitation.

Treatment of precipitates: Precipitates are treated in the following sequence of processes so that we can get quality precipitates.

1. Digestion of precipitate is the process in which we allow the precipitates to stand in contact with mother liquor for some time (in most of the cases about 1-2 hours). The main objective of digestion is to ensure complete precipitation or maximum precipitation of the precipitates so that the precipitates could be filtered easily. Sometimes digestion of precipitate is also carried out by warming the solution at a temperature which is not very

high. Digestion of precipitate should be avoided where the possibility of post precipitation is high because if we allow the precipitates for digestion to stand 1 to 2 hours then the contamination through post precipitation will get enough time to occur. While the process of digestion occurs the smaller size particles dissolve in solution and redeposit on the larger particles so the size of precipitates grows and the filtration will become easy. As the small precipitates dissolves so the coprecipitation decreases because the impurity will go into the solution along with the smaller precipitates and when the precipitates reposit on medium size particles then the precipitates will grow in regular shape and geometry. The impurities which are previously entrapped in the crystal or adsorbed on the smaller particles having large surface area will now dissolve into solution and we get a more pure form of precipitates. In a simple way, we can say that the process of digestion makes the precipitate more pure and give them regular shape and also improve the filterability of precipitates.

2. Filtration followed by washing of the precipitates: Filtration is a process in which the precipitates are separated from mother liquid by passing the content from a filter crucible or through simple filter paper. While doing so the precipitates are collected on the filtering material (filter paper or filter crucible) and the mother liquor passes through it and collected in a beaker below the filtering apparatus. The precipitates so collected are then washed with a suitable liquid known as washing solvent. There are some properties of washing solvent which a solvent must have to act as a good washing solvent. Some of these properties of good washing solvent are discussed below

a. The precipitates should be completely insoluble in the washing solvent, but the impurities should dissolve in washing solvent readily.

b. The washing solvent should not react with the precipitates.

c. The washing solvent should be volatile so that after the washing of precipitate the process of drying of precipitate may occur easily.

There are some precautions also which we must keep in our mind while we carry out the process of washing of precipitate with washing solvent. This precautions are explain below:

- Washing should be carried out with the least amount of solvent because all the precipitates have a tendency to get dissolved in all the liquids so the washing solvent should be used in a very small amount (as less as possible).
- Washing should be done a number of times with a small amount of washing solvent.
- Second slot of washing solvent should be introduced after the first slot has completely drained off.

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