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A handbook of chemical manipulation

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Section XI. Precipitation

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SECTION XI.

PRECIPITATION.

167. Precipitation is one of the most valuable processes for separating substances from each other, and is perhaps the most frequently used operation in research. It depends upon the conversion of substances from a soluble to an insoluble state, with reference to the menstruum employed. When a substance in solution has a reagent added to it which contains a body capable of forming with it a comparatively insoluble compound, the latter falls to the bottom of the liquid with different degrees of readiness, depending upon its state of density, aggregation, or insolubility, and is then said to be precipitated. It sometimes happens, although the matter previously in solution becomes insoluble and separates, that, from its want of density, it floats or remains suspended; nevertheless, by a convenient expression, it is generally said to be precipitated.

The instance last alluded to, where a substance is added capable of forming an insoluble compound with the matter which it is wished to separate, is by far the most common kind of precipitation, but there are numerous other cases arising from very different circumstances. A change of temperature of the solvent will frequently induce precipitation, but then the matter separating in the solid state frequently assumes a regular form, and is said to crystallize, the term precipitation being more frequently used to designate an amorphous condition. As an instance of the effect of temperature upon precipitation, may be cited the case of an admixture of a soluble salt of lime with a very dilute solution of a soluble sulphate; no precipitation takes place in the cold, but, on boiling, the sulphate of lime assumes the crystalline form and precipitates. Titanic acid is sometimes separated in the insoluble state by the mere boiling for a considerable period of the solution containing it.

168. Precipitation is also frequently effected by converting

substances from one state to another, by passing a gas, generally carbonic acid, sulphuretted hydrogen or chlorine, into a solution containing them. Alteration of the nature or proportions of the solvent present will also effect precipitation: if excess of nitric acid be added to a moderately strong solution of nitrate of baryta, the salt is precipitated, being comparatively insoluble in nitric acid; it is highly desirable to be quite familiar with cases of this kind, persons often concluding that nitric acid contains sulphuric acid from the fact, that, on adding strong solution of nitrate of baryta to the undiluted acid, they have found a white powder fall. The precipitation of alcoholic solutions of the resins and of camphor by the addition of water is also a somewhat similar case.

169. It will be seen, from what has been said, that precipitation is one of the best and most generally applicable means of separation of bodies, and that it is essential for the student to acquire a good general knowledge of the nature of precipitates, and of the methods of separating substances by this means as a step towards their estimation. A careful operator will always consider, before adding a precipitant, the order of sequence, and the substance best adapted for the purpose. If, for example, it be desired to ascertain the presence of sulphuric and hydrochloric acids in the same portion of a solution, some judgment is required; for, if chloride of barium be added to demonstrate the presence of the sulphuric acid, it becomes impossible to test the same portion of liquid for hydrochloric acid, as chlorine has been introduced in combination with the baryta; but if nitrate of baryta be added, and the precipitated sulphate be filtered off, it is possible to detect the chlorine in the filtrate by nitrate of silver.

It will be seen to be imperative that a pure salt be used in testing, for if the nitrate of baryta used is contaminated by the presence of chlorine, of course a source of error is at once introduced. Fortunately, however, nitrate of baryta is more easily freed from chlorine than most other salts.

170. Sometimes it is desirable to remove one substance from a solution without introducing any other matter into the resulting

product, as in precipitating the sulphuric acid from the sulphates of potash or soda in the process for preparing the pure caustic alkalies; this may be done by adding caustic baryta somewhat in excess to the solution until the whole of the sulphuric acid is rendered insoluble as sulphate of baryta, the small excess of baryta being easily removed, for as the liquid is boiled down, it attracts carbonic acid from the air and becomes insoluble.

171. Where exact precipitation is required, as so frequently happens in analytical operations, the precipitant must be added by degrees, it being generally advisable to agitate the liquid the whole time, in order to facilitate subsidence; this may be done by stirring with a glass rod. When the solution to which the precipitant has been added is dilute, it is generally easy to ascertain the completion of the process, because the precipitate falling leaves a portion of the liquid clear, so that the action is easily controlled; but where strong solutions are used, the fluid frequently becomes nearly solid (this is well seen by adding ammonia to acid solutions of cinchonine, quinine, or peroxide of iron); here it is advisable to dilute the whole of the solution with water, but if this is inadmissible, a little of the mass may be stirred up in a small glass with a little water, and, after filtration, be tested. It is requisite in cases of this kind to thoroughly stir the thick mass before any is removed to be tested, as otherwise it is impossible to make sure that the precipitant has been perfectly incorporated with the solution to be precipitated.

172. It is frequently extremely advantageous to add a considerable excess of the precipitant if rapid subsidence is desired; an excess of acid also is sometimes used for this purpose with great success; and further, it often happens that a precipitate which otherwise requires a long time to settle, does so rapidly on the application of heat. In some instances, as that of the precipitation of sulphuric acid by nitrate of baryta or chloride of barium, it is proper to add the precipitant in excess to a hot solution, and then boil for a short time; by this means rapid subsidence is effected, and error arising from the tendency of the precipitate to pass through the filter is obviated. As in all laboratories a vessel is

kept to receive the silver solutions which are constantly accumulating, it is of no importance, in an economical point of view, that an excess of nitrate of silver be employed in precipitating hydrobromic or hydrochloric acids. It is desirable always to have an excess of hydrochloric acid in the silver-washing recipient, so that it is merely necessary to pour off the liquid and throw it away when the vessel becomes filled, as the whole of the metal will be found at the bottom as chloride.

173. It is by no means indifferent whether, as a general rule, precipitants are added to hot or to cold solutions, for the condition of the resulting product is often materially influenced by this cause alone; if, for instance, hot liquids be used in precipitating iodide of lead or biniodide of mercury, the whole of the salt is not deposited immediately, but on cooling a considerable quantity of crystals fall, and from their extreme beauty, this process is often adopted purposely.

In organic chemistry it is frequently inadmissible to heat solutions previous to precipitation, as this method of procedure would often decompose substances of no great stability. Solutions of the platinum salts of organic bases undergo remarkable alterations by even short exposure to temperatures at or even below 212° Fahr.

In analytical investigations it is very common to wish to ascertain by precipitation whether a substance suspected to be present be really so or not, and cases of this kind are so numerous, that it is difficult to propose a general rule which shall be applicable at all times; there are, nevertheless, a few points worthy of being remembered. If the precipitate looked for be coloured, the cylinder containing the solution to which the precipitant has been added may be placed upon a sheet of white paper, when, if any perceptible quantity be present, it will become evident, after a short time, on looking down the vessel, so as to observe through a considerable thickness of fluid. If precipitation is not immediate, stirring will not unfrequently determine its formation; if this be unsuccessful, heat may be applied; if this does not effect the purpose, it is seldom that any other operation will enable us to obtain the indi-

cation sought, unless, as sometimes happens, the solutions were too dilute; by evaporation of a considerable portion of liquid to a small bulk this difficulty may of course be overcome, and this is the method adopted in the analysis of mineral waters, where, from the extreme dilution of the solutions, almost the only matters capable of ready precipitation are the sulphuric and hydrochloric acids.

174. It sometimes occurs that the addition of alcohol will cause a precipitation, and this method is often used for the separation of sulphate of lime, as such, from solutions.

Potash, soda, and ammonia are constantly in request for precipitating metallic oxides, but there are also numerous *salts* which are separated from solutions containing them by those reagents, and it is of much importance to be aware of this in order to avoid serious error. If either of the alkalies alluded to be added to solutions of alumina or peroxide of iron containing phosphoric acid, the whole of the latter is also removed as phosphate of iron or alumina. Phosphate of lime is also precipitated by them. A series of reactions, arising from the singular manner in which phosphoric acid tends to follow metallic oxides while being precipitated, led one of the most illustrious of modern chemists into the error of raising the subphosphate of yttria to the dignity of a new metallic oxide.

175. Metallic oxides, when precipitated by alkalies, frequently carry down with them a considerable portion of the precipitant, which it is often very difficult, and sometimes impossible, to remove perfectly by washing; this makes ammonia extremely valuable as a precipitant of such substances, from the facility with which it is removed by ignition.

176. It has been said that agitation frequently assists in determining the subsidence of a precipitate; this must not be lost sight of in performing the assay of silver by the volumetric method; in this process the solution of silver is contained in a stoppered flask, and if, after each addition of the standard solution of chloride of sodium, the flask be violently agitated, the chloride of silver settles with remarkable rapidity. Sometimes the precipitate adheres to the vessel only in the places where the glass rod

has touched ; this peculiarity has not, it is believed, as yet met with a really satisfactory explanation.

177. Where metallic oxides are to be precipitated by sulphuretted hydrogen, it not unfrequently happens that if present in very minute quantity, the only effect of the gas is to create a slight change of colour, best seen by looking down the test-glass.

One of the uses of precipitation arises from the facility with which it enables us to obtain organic acids in a state of purity from their compounds with lead, silver, baryta, or lime ; the acid having been precipitated in combination with either of these oxides, or obtained in that state by some other means, it is possible in each case to remove the base by selection of the proper precipitant, and a careful performance of the operation. When acids are obtained in combination with lead, the latter is generally removed by sulphuretted hydrogen gas ; silver may be separated by the cautious addition of hydrochloric acid ; baryta by a dilute solution of sulphuric acid, and lime by oxalic or sulphuric acids : in the latter case, it is generally necessary to add excess of alcohol to determine the complete separation of the sulphate of lime.

178. Certain salts of acids are sometimes met with in nature : the dark brown semi-crystalline deposit from the concentrated decoction of cinchona bark consists chiefly of kinate of lime, which was contained in the bark ; and after purification of the salt, the earth may be removed in the manner above indicated, and the kinic acid obtained pure and white by crystallization and treatment with animal charcoal.

In quantitative estimations, it must not be forgotten that the stirring-rods almost invariably remove some of the precipitate ; this portion should be recovered by the use of the washing-bottle.

179. The student cannot be sufficiently careful to render himself familiar with the habitudes of substances, in order that he may be enabled successfully to modify his processes according to the peculiarities of the materials which may come under his notice. It is generally necessary to neutralize acid, and sometimes even alkaline solutions, before adding precipitants ; this must not be lost sight of in practice.

It very commonly occurs that the electro-chemical relations of metals may be made available for their separation and examination; in fact, one of the prettiest applications of science to the arts is the electrotype, by which it is possible to obtain facsimiles in copper, gold or silver, of almost any object capable of being copied in wax or plaster. If a plate of copper be immersed in an acid solution of silver, the whole of the latter metal is deposited in a state of purity in the form of a powder; and the method affords an easy, and frequently extremely convenient, method of obtaining the metal in a state fit for conversion into nitrate or other salts of silver. If a solution of cadmium be placed in a platinum crucible with a piece of zinc immersed in the fluid, the whole of the former metal is deposited on the platinum, and after washing, which may be performed without fear of removing the coating, the pure cadmium may be dissolved in nitric acid.

180. When chloride or bromide of silver is fused in porcelain capsules in the process for estimating hydrochloric or hydrobromic acids, it becomes so strongly attached that it is generally unsafe to attempt its removal by mechanical means; but if a piece of zinc be placed in the capsule touching the fused mass, and a little hydrochloric acid added, it may, after a few minutes, be removed with facility.

There are some few cases where, although a precipitant has been added in excess, the action, nevertheless, is incomplete, a certain portion of the metal, &c. remaining in solution; it is then sometimes admissible to finish the precipitation with another reagent; this procedure is frequently applied to zinc in analysis, and sometimes even in manufacturing operations; if, for example, the solution procured by digesting excess of zinc with iodine and water, in the process for making iodide of ammonium (a salt once much used in photography), has excess of carbonate and some caustic ammonia added, the greater portion of the metal present will be removed as a bulky white precipitate of carbonate of zinc; but a somewhat considerable amount still remains in solution, and must be precipitated by sulphide of ammonium, the latter also removing any

iron which may have been present in the zinc and not precipitated by the mixture of carbonate and caustic ammonia.

181. Substances may often exist in solution, yet not in the condition in which they afford characteristic reactions; when this occurs, it becomes necessary so to modify their state that they may with proper reagents afford the reactions required; for instance, if iron is present in the state of protoxide, it is generally essential to peroxidize it before adding the usual precipitants to it, unless, of course, it is intended to throw it down as protoxide or proto-sulphuret. When calomel is to be examined in the humid way, and it is desired to form the very characteristic scarlet iodide of mercury, it may be boiled with nitric acid and evaporated gently to dryness, after which treatment it can be precipitated as periodide by the careful addition of iodide of potassium.

It is necessary to be on our guard against the many circumstances which modify and sometimes prevent the action of precipitants; organic matters especially have a retarding influence upon precipitation: it has been said before that a very small quantity of sugar or other organic matter prevents the complete precipitation of oxide of copper by potash, even after protracted boiling. Moderately acid solutions of antimony are precipitated by water, but if tartaric acid be added, it enables us to dilute the solution to any extent that may be required; this peculiarity may be made valuable use of in the analysis of minerals and alloys containing that metal, the more especially since organic matters have no power to prevent the precipitation of antimony by sulphuretted hydrogen.

182. Gases, particularly hydrosulphuric acid, are greatly used as precipitants in both organic and inorganic research; it becomes important therefore that the student should acquire familiarity with the methods of using them: the details of the processes will be found in the chapter on Gas Manipulation, but as there are several points which more particularly belong to this section, they will be pointed out.

Gases should never be passed directly from the generating vessel into the solution to be acted on, as it is invariably found

that they carry over mechanically a portion of the acid, &c. into the fluid under examination, thereby involving a source of error. The methods of preventing this are numerous, and will be pointed out in their proper place.

Gases are not only used with the intention of causing precipitation, but sometimes also to modify the state in which a substance exists in solution, so that it may afterwards be separated from others, which, although existing in the same fluid, are either not at all, or much less acted on by the same reagent; for example, in Rose's excellent method of separating cobalt and nickel, chlorine is passed into the hydrochloric solution until the cobalt is peroxidized, while the nickel remains unaltered, after which carbonate of baryta is added until the cobalt is precipitated, the nickel remaining in solution.

The action of sulphuretted hydrogen upon metallic solutions has been so well studied, that it has become one of the most valuable methods of qualitative, and in some cases quantitative separation. Its action is different according as the solutions exposed to it are acid or alkaline; the nature of the compounds formed, and the subdivision of the metals, &c. into groups by the action of hydrosulphuric acid, sulphide of ammonium, &c., belong to manuals of analysis, and will not therefore be dwelt upon here; but it may, notwithstanding, be mentioned, that some clue to the nature of the precipitate is frequently to be obtained by observing the colours of the precipitates. When, after the passage of hydrosulphuric acid gas through a metallic solution, a white precipitate is obtained, which proves to be quite volatile, it consists entirely of sulphur, and is generally due to the presence of peroxide of iron, which is reduced to the state of protoxide by the hydrogen of the gas, the sulphur being at the same time precipitated. We shall allude to this again in another part of the work.

If the precipitate is yellow, we may look for cadmium, persalts of tin, arsenic, or antimony; a black one, on the other hand, may be occasioned by the presence of copper, lead, protosalts of tin, gold, bismuth, platinum, palladium, and several others of the same group. Zinc is precipitated from neutral solutions as a white or

pinkish sulphide; it is also thrown down from its solution in acetic, but not hydrochloric acid.

When a nitric solution of vanadate of lead is precipitated by sulphuretted hydrogen a peculiar blue tint is produced, the vanadic acid being at the same time reduced to a lower state of oxidation.

183. It is very often necessary to pass a stream of carbonic acid through solutions containing free lime, in order to remove the latter as carbonate; in this case it is imperative to heat the solution after the passage of the gas and before filtering, in order to expel excess of the gas, which might have redissolved any of the lime as bicarbonate; as an example may be mentioned the solution formed by neutralizing with lime the acid liquor produced by distillation of sugar or starch with peroxide of manganese and sulphuric acid in the preparation of formic acid; the filtered liquid is found to contain excess of lime; on passing carbonic acid through, the free lime is thrown down, and, if continued long enough, is partly redissolved; on heating the solution to boiling for a short time, however, the carbonate of lime is all removed on filtration, and the solution contains no lime save what is in combination.

Lime is much used as a precipitant of iron, more especially on the large scale and in technical operations, but it is essential that for this purpose the metal should be in the state of peroxide; and there are several other precautions which are necessary to success, all of which, perhaps, are required in producing the commercial white fused chloride of zinc, much used in medicine. In giving the details of the operation, it is to be understood that the same process, or a modification of it, will be necessary in almost every case where a substance containing protoxide of iron is to be freed from it by lime, and it is of course for this purpose that the method is introduced. Commercial metallic zinc is to be dissolved in hydrochloric acid, a considerable excess of zinc being present; the whole is digested for a day or two, by which means the lead, copper and some other metallic impurities are thrown down and removed. The liquid is filtered and concentrated by heat,

while boiling nitric acid is added in small quantity until the iron is converted into peroxide; the whole is then boiled to dryness and fused; the cake is, when cast out to cool, of a red colour, and is to be dissolved in cold water; the liquid becomes heated during the process of solution, and must therefore be allowed to repose until quite cold: if, now, the moderately diluted fluid has a little cream of lime, or, preferably, an ounce to the gallon of prepared chalk added, and the whole be well mixed, and after about ten hours filtered, the liquid which comes through will be perfectly colourless and not contain a trace of iron. When fused, the salt, if the previous directions have been carried out, will be of the purest white. The same procedure with regard to the nitric acid and subsequent operations may be employed in preparing white fused chloride of calcium, and in many other operations.

184. Precipitation, when the result of a somewhat sluggish chemical decomposition, may be facilitated by exposure of the reacting materials to a very gentle heat. To illustrate this, the precipitation of gold by protosulphate of iron or oxalic acid, may be mentioned; moreover, nitrobenzole, when being acted on by alcoholic solution of sulphide of ammonium, should be placed in a moderately warm situation. This is an instructive example, because the amount of sulphur is an index to the quantity of aniline produced, and the reaction may be viewed as the type of many others, where, the substance sought being in a fluid state, the amount formed during the operation may be estimated by the quantity of precipitate. This process is, however, not the best means of obtaining aniline from nitrobenzole, protacetate of iron being far more effectual.

185. In organic chemistry, perhaps more care is required in the choice of precipitants, and in the method of adding them, than in the inorganic department of the science; and this is caused partly by the easy decomposability of organic substances generally, and partly by the fact, that when the precipitate is obtained, the liquid frequently has to be examined for other complex substances, which would be more difficult of separation after the addition of an unnecessarily large quantity of the precipitating reagent.

Sometimes much advantage may be gained, where two precipitants at the first glance appear equally eligible, by a careful selection; narcotine is equally well precipitated by ammonia and potash, but if the latter be used, the resins present are retained in solution, and the narcotine is obtained pure and white with much greater ease than it would otherwise have been. In the preparation of picric acid, the same precaution may be taken, but greater care is required to prevent solution of the salt, which takes place where too great an excess is used.

186. In laboratories where a valuable substance, not absolutely insoluble, is frequently being precipitated, it is sometimes advisable to preserve the mother-liquids, and at a convenient time to concentrate them, and recover by proper methods the portion dissolved.

It is sometimes found that where two substances exist in solution, each capable of forming an insoluble salt with some reagent, that nevertheless by a careful addition of the latter, the whole of one of the two ingredients in the solution may be thrown down in the first portions of the precipitate, that subsequently obtained containing the other material; this method of research, which is termed fractional precipitation, is probably capable of being much extended. A mixture of fatty acids may be separated by adding solution of nitrate of silver in small portions to a solution of the soda or ammonia salts, and filtering after each addition. The first precipitates, of course, contain those acids forming the most insoluble salts with silver.

187. The apparatus used for precipitation is almost the same as for solution: Phillips's jar, fig. 102, is employed for the collection of precipitates, and, from the conical form, allows them to subside rapidly, but the beakers, figs. 97 and 98, are equally or better adapted for the purpose; and in fact the beaker is in most cases preferable, not only from the extreme convenience of its shape, but also from the facility which it affords for heating the liquid before or after precipitation.

The test-glass, fig. 104, is the most convenient shape I have seen; it may be made about one and a half times the size of the

engraving, unless required longer for demonstration. The tall glass, fig. 103, is well adapted for lecture experiments, if made of

Fig. 102.

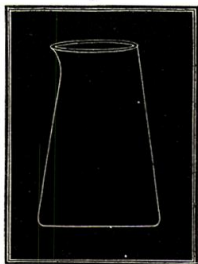
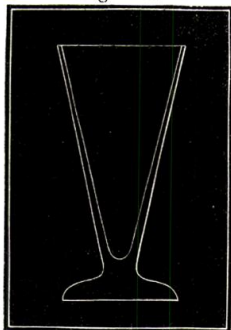


Fig. 103.



Fig. 104.



a considerable size. They are sometimes made of the same shape as that represented in fig. 103, but blown at the lamp and exceedingly thin, and thus resemble a test-tube on a foot; they are very convenient in many experiments of a delicate character.

Flasks of the form and size of the porcelain digester, fig. 94, page 117, are admirably adapted for the precipitations in quantitative analysis, where only small quantities are worked upon; their shape renders them extremely easy to cleanse, as it is possible to insert the finger against any part.

188. In precipitations on the more minute scale, as in micro-chemical experiments, test-tubes may sometimes be employed; but they are far from convenient in quantitative experiments, unless made short and wide.

Porcelain vessels from their opacity are objectionable in precipitations, and are therefore seldom employed.

The washing of precipitates is an operation which is so much more conveniently discussed under the head of Filtration, that it has been placed in the next section.