A handbook of chemical manipulation

Williams, Charles Greville

London, 1857

Section X. Solution

urn:nbn:at:at-ubi:2-3808

SECTION X.

SOLUTION.

140. It is well known that one of the greatest obstacles to the free exertion of chemical affinity is the attraction of aggregation, the force, namely, by means of which the particles of bodies are held together; pulverization to a great extent obviates this source of sluggish action; but solution, by separating the particles to considerable distances, and by conferring mobility upon them, enables bodies which have a tendency to react upon each other, to do so, and that under the most favourable circumstances, for allowing a free exercise of their mutual action.

Moreover, by solution we are frequently enabled to separate substances of unequal solubility from each other; sometimes the separation is perfect, while at others the operation has to be repeated many times to ensure a complete division.

141. Water is by far the most widely employed and generally convenient solvent, but there is scarcely any liquid procurable with moderate ease, that may not be used with advantage under certain circumstances. It becomes therefore an extremely important matter that the chemist should so familiarize himself with the deportment of substances towards solvents generally, that he may in most instances be able with certainty to pronounce upon the best menstruum to be employed in any case which may come under his observation.

Among the fluids in ordinary use in research, the following may be mentioned; they are placed nearly in the order of their frequency of application:—Water, acids, alcohol, ether, alkaline solutions, wood-spirit or methylic alcohol, benzole, chloroform, and turpentine.

142. A few instances of the circumstances in which each of these liquids are applied will be of serviee to the beginner, and are properly prefaced by a glance at the general properties of solvents.

No fluid should be applied at random in endeavouring to bring a solid body into solution, but in every case it should be carefully considered what the object is that has to be attained; whether, for instance, it is desired merely to dissolve, or to have a chemical action exerted, and if the latter, of what kind. If the substance be a salt, water will generally effect our purpose; a little may be introduced in the state of powder or small fragments into any of the vessels mentioned below, and, water being added, the vessel must be agitated; if the substance disappears, the question is answered; if otherwise, the mixture is to be boiled, and, if still ineffectual, one or more of the solvents to be mentioned must be tried, carefully considering the chemical action which it is capable of exerting.

143. The acids most generally in use are the hydrochloric, nitric, sulphuric, acetic, and hydrofluoric; the first of these is the most resorted to in inorganic chemistry, as its compounds with metals are pretty generally soluble; and, moreover, its chemical effects are more limited than those of the nitric or the sulphuric. It is particularly valuable in analysis, from the fact of its forming an insoluble chloride with silver; if, therefore, we precipitate the chlorine of a metallic chloride by nitrate of silver, we at once, by ascertaining the amount of the latter, get a clue to the formula of the salt under examination. Chlorine, moreover, forms an insoluble protosalt with mercury, and a difficultly soluble one with lead; most other chlorides dissolve with comparative ease in water, and many are extremely deliquescent. On the other hand, we are acquainted with many examples in organic chemistry, of salts which are regarded in the light of bi-hydrochlorates and are yet almost insoluble. We may adduce in this manner, the bi-hydrochlorates of the chloro-compounds of some alkaloids and the bi-hydrochlorate of platino-pyridine.

144. In organic chemistry hydrochloric acid has many uses, as, for example, in extracting alkalies from plants, and condensing ammonia and other volatile bases in processes undertaken with a view to their purification or estimation: the chlorides of all the volatile bases, except ammonia, are exceedingly soluble

in alcohol; we thus have a valuable method of separation; and it is singular that the presence of the chloride of a volatile base diminishes the solubility of sal-ammoniac in alcohol, and thus greatly increases the accuracy of the result.

145. Nitric acid has many, and in fact, almost an equal number of uses, but of a different kind; before using it, we must remember its peculiar tendency to part with oxygen to the metals or other substances dissolved in it; in many instances this property may be turned to valuable account, but in others the reverse happens. Tin and antimony are converted into insoluble peroxides by its action, and are sometimes by this means separated from other metals which form soluble salts with it. Iron, or its proto-compounds, are quickly converted, especially on boiling, into salts of peroxide; copper, silver, and a few other metals, are more readily dissolved in nitric than any other acid.

It must not be forgotten, that nitric, and indeed most acids, act in very different ways, as they are more or less diluted; for instance, nitric acid has much less oxidizing action when very weak and at low temperatures, than when stronger and at higher temperatures; very weak nitric acid acts on excess of metallic iron with formation of protonitrate; but if the solution be even moderately heated, yellow fumes are evolved, and a pernitrate is the result. Again, if to a mixture of the oxides of cerium and lantanium which has been ignited, an acid solution containing 99 parts water and 1 part nitric acid be added, the oxide of lantanium is dissolved, to the almost complete exclusion of the cerium.

146. Sulphuric acid, in its concentrated form, has comparatively few uses as a mere solvent, but in a diluted state it acts upon some oxides and metals with ease; it is characterized by the insolubility of its compounds with lead, baryta, strontia, and lime; the three first being almost entirely insoluble in water, and the latter equally so in spirits of wine.

147. Hydrofluoric acid is extremely limited in its application, being seldom used except for the purpose of separating silica from compounds, from which it is with difficulty removed by other

means; hydrofluosilic acid being volatile, it may be expelled at a moderate heat.

148. Alcohol is much employed in organic chemistry as a solvent for alkaloids and numerous other bodies; one of its uses has already been alluded to under hydrochloric acid; it is also a solvent for some resins, and in fact, its uses in the organic are almost as manifold as that of water in the inorganic branches of the science. It is frequently necessary to subject organic bodies, generally mixtures from which it is wished to extract certain soluble constituents, to the action of alcohol or ether for a very long time, in order to thoroughly exhaust them.

149. Ether is chiefly used for dissolving resins and resinous matters, also as a solvent for fatty acids and many other substances.

150. Alkaline solutions are seldom used as solvents in inorganic chemistry; alumina, glucina, and uranium are, perhaps, the most commonly occurring instances; but in the organic branch many crystalline substances are separated from resinous impurities by means of them.

151. Wood-spirit is sometimes employed for the same purposes as ether, but its uses are more limited; it forms a good menstruum for shell-lac when required in the fluid state for cement. Its properties as a solvent are perhaps less known than those of alcohol and ether, and it is probable that they may be very much extended; methylated spirit, however, may be used with as good results as pure alcohol for almost every purpose requiring a spirituous menstruum.

152. Benzole, or the lighter portion of coal naphtha, boiling at 176° Fahr., is becoming much used as a solvent for alkaloids, especially for quinine, as in the processes of Herring and others; it may also be used for the preparation of cantharidine, strychnine, and many other organic bodies.

153. Chloroform is sometimes, but rarely employed; a solution of gutta percha in it is used as a species of collodion, and amber dissolved in it forms a beautiful varnish for photographic purposes. It also dissolves camphor and other resinous matters.

154. Turpentine holding camphor in solution is used as an assistant in glass-cutting with files, and other operations which will be mentioned in their proper places; it moreover dissolves caoutchouc, resin, and many other substances.

155. *Apparatus for Solution.*—The apparatus for containing substances while exposed to the action of solvents, is generally of the simplest character, consisting of test-tubes, retorts, flasks, basins, and porcelain and platinum capsules. They will be noticed in the order in which they have been named.

156. Test-tubes are of almost universal application in chemistry; they are thin cylinders of glass with rounded bottoms; the most convenient forms are those in figs. 87, 88, and 89, where they are depicted half the real size.

157. Where substances are to be dissolved in acids, and much vapour is evolved in the operation, it is essential, if exactitude is required in the experiment, to prevent the loss of particles mechanically removed with the escaping steam. This may be effected by placing the flask in a sloping direction; or, if the matter is carried over partly chemically and partly mechanically, as is the case with osmium during the solution of the ore of platinum in aqua regia, it is better to use a retort and receiver, as in fig. 90.

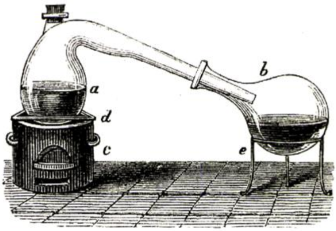
Fig. 87.

Fig. 88.

Fig. 89.

The forms of flasks which may be used for solutions are very various, and depend, to a great extent, upon the fancy of the operator. It is advisable to have them, when required exclusively for solution or precipitation, of the shape shown at fig. 94, which, it will be seen, has no shoulder or projecting parts where any solid matter can lodge, so as to be with difficulty removed. They may be held during the operation upon any of the supports mentioned in the section upon that subject. It is better to have them with flat bottoms. The flasks, figs. 91 and 92, are extremely useful for various analytical purposes during solution, filtration, digestion, or precipitation; but other forms are required in various other processes, and will be described in their proper places.

Fig. 90.



The porcelain vessel, fig. 93, is very convenient, from the ease with which it can be cleaned out, and the porcelain capsules (figs.

Fig. 91.

Fig. 92.

Fig. 93.

Fig. 94.

Fig. 95.

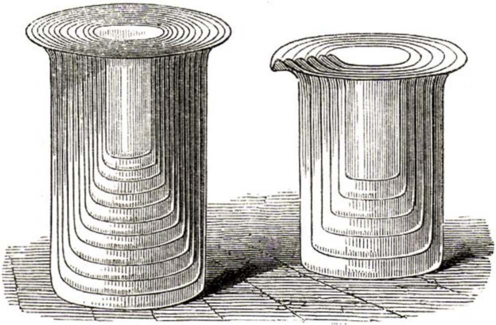
Fig. 96.

95 and 96), from the facility with which they are handled when hot. Beakers (figs. 97 and 98) are vessels of perhaps more extended use than any others in the laboratory; there is scarcely an operation in which they are not more or less required. From their thinness, they admirably withstand sudden changes of temperature; and their form particularly adapts them for precipitations, from the extreme ease with which every particle may be removed. They are generally sold in nests, and the laboratory should be well stocked with them.

158. Several glass rods, formed from what is known in the glass-houses as "cane" by cutting off lengths with a file, as

described under glass-cutting, and rounded by fusion at the ends,

Fig. 97. Fig. 98.



must be provided as an adjunct to the other apparatus for solution.

159. It should be remembered that great advantage is derived from a minute state of division, when it is desired to bring refractory substances into solution; as an instance of this, may be cited the fact, that if a little flint-glass be very finely powdered, and, after moistening, be laid on reddened litmus paper, the latter will be restored to its original blue by the alkali dissolved out of the glass by the water*.

160. It is of great importance, when a flask containing a solid matter and a fluid is to be heated, that the temperature is not raised too rapidly, as it is liable to endanger its safety; and the moisture which almost invariably condenses on the bottom should be removed with a cloth. Flasks, and other glass or porcelain vessels, when hot, must not be placed to cool on rapidly conducting surfaces, as such a proceeding is almost sure to cause its fracture. A very convenient stand for this purpose may be easily constructed, by winding list round tin or copper rings. A cold liquid should not be added to another when boiling; if unavoidable, it must be poured in by small portions, and over different parts of the surface of the hot fluid.

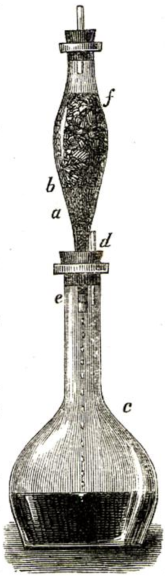
* See also Pelouze on the action of water on glass, Chem. Gaz., Sept. 15, 1856, and Comptes Rendus, July 21, 1856, p. 117.

161. Many substances during solution emit corrosive and offensive fumes; such cases may be met by placing the vessel emitting them under a hood or chimney, or in the close closet; or if none of these appliances are at hand, a tube may generally be adapted to the apparatus which will convey the vapour out of the window.

The arrangements for forming solutions of gases in water belong to the section on Gas Manipulation, and will be described in that portion of the work.

There are several operations in organic chemistry in which the object is to extract the soluble parts of plants. Sometimes this may be done by mere *infusion*, which consists in pouring a hot liquid upon the substance whose valuable parts are to be extracted. *Decoction* consists in boiling the material to be exhausted, for a considerable time; it is chiefly resorted to in manufacturing processes.

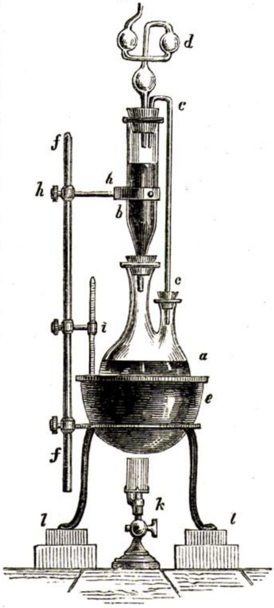
Fig. 99.



162. *Percolation* is frequently had recourse to in research, to extract the soluble constituents of vegetable substances. On the small scale, the apparatus, fig. 99, may be made use of; the lower end of the long tube at *e* is closed with a cork cut in notches, so as to allow the passage of the fluid; the vessel is then filled with broken glass to *a*, and moderately fine quartz sand to *b*; the substance to be exhausted is placed above this, and the solvent carefully poured on so as to avoid disturbing it; if properly done, the menstruum will slowly drop into the vessel, *c*; but even then the powder or other matter to be exhausted remains saturated with the liquid, and the latter has absorbed all the virtues of the material. We have now to displace this portion absorbed, by adding more of the liquid, equal in quantity to that remaining among the powder, in the same way that the first was introduced; the fresh liquid displaces the saturated portion,

which then drops into the lower vessel, and is ready for examination. If spirit is employed, the greater part may be recovered by distillation. The tube, *d*, is to allow the air to escape as the fluid drops into the lower vessel: it is advisable, where spirit is used in this process, to adapt a tube with a small aperture to the upper opening of the vessel, *e f*, so as to allow enough air to enter to permit the descent of the menstruum, without at the same time permitting the spirituous portion of the solvent to escape.

Fig. 100.



163. M. Payen has contrived an apparatus for extracting the soluble constituents of organic bodies by continuous distillation. It is represented in fig. 100, where *a* is a two-necked flask, the longer of the two orifices being fitted with a tube, *b*, intended to contain the organic matters to be exhausted; they are packed with equal care to those intended for the ordinary process. The flask, which contains alcohol or ether, is heated by the water-bath, *e*, the temperature of which is regulated by means of the thermometer, *i*, supported by a cork attached to a rod sliding on the vertical bar, *f f*, which in its turn is supported by passing through an aperture capable of being tightened with a screw. The vapour of the alcohol passes by the tube, *c c*, into *b*, where being condensed among the animal or vegetable matter, it falls back into the flask, to be again raised as before. The three-bulbed apparatus, *d*, acts as a safety-tube, and also serves to condense any of the spirituous vapour which might otherwise be lost. The digesting vessel, *b*, is supported by the clamp, *h h*, which slides on the rod, *f f*. The gas-burner, *k*, enables the temperature of the bath to be regu-

lated with more nicety than could be done with a spirit-lamp. The tripod is supported over the gas by the blocks of wood, *l l*.

164. In making solutions in analyses, it is constantly necessary to pour from one vessel to another, without spilling any of the liquid; and it is usual to have lips or spouts to vessels to facilitate the operation; but in most cases it is quite impossible, in spite of this arrangement, to prevent a small portion of the fluid from running down the outside of the spout, and consequently we are liable to a loss from this means sufficient to render an analysis worthless. In fact, when the vessels used have a flange (as in beakers, for instance), it becomes not only unnecessary, but a disadvantage, to have spouts; and with test-tubes and flasks, they are a great inconvenience. It is usual amongst chemists to prevent any source of error arising in this way, by first *slightly* greasing the lip of the vessel, and then pouring down a rod in the manner represented in the engraving, fig. 101; it is possible thus to avoid even the slightest loss, and the student should omit no opportunity of acquiring dexterity in operations of this kind.

Fig. 101.

It is advisable not only to apply a little grease to the lip of the vessel, but also to wet the rod with the liquid to be transferred, and, after placing it against the edge, to slowly raise the vessel until the fluid meets the glass rod; it will then run down it with perfect regularity, and may be directed even into the neck of a small flask as conveniently as by the use of a funnel.

165. Where basins are used for purposes requiring heat, the bottoms should be extremely thin, to enable them to bear rapid transitions of temperature; flasks also should have the bottoms thin; but as they are frequently used for gas manipulation and distillation, the necks should be somewhat stouter.

It is important to observe, that when a flask is to be placed upon a hot sand-bath, the bottom should be quite dry, as otherwise the water being converted rapidly into steam, scatters the sand about, and in all cases there is danger of fracture to the vessel if the precaution is neglected.

Much care is required in introducing weighed quantities of pulverulent substances into flasks where accuracy is desired; if, for instance, a piece of rough paper is used, or even if it be polished and yet not perfectly dry, the powder is liable to adhere, and thereby involve a loss; moreover, if the edge is not cut, irregularities will mechanically retain a portion of the material. Let it be supposed that a soluble substance is to be introduced from the platinum crucible, in which it was heated to redness and weighed, into a flask, as in the analysis of soda ash, by the methods of Fresenius and Will or Parnell; a flask must be selected the neck of which is not too narrow, and the contents of the crucible being dropped carefully into it, the washing-bottle (§ 200) may be used to rinse the crucible out. If, on the contrary, the substance is insoluble, and yet it is essential to transfer it into another vessel previous to its being dissolved, it may, as far as possible, be removed by dropping it from one vessel to the other, and the particles adhering to the first must be washed out by directing a stream of water upon it. The washing-bottle by which this is performed will be described in its place, at p. 142.

166. In operations connected with solution, it is necessary to be made acquainted with some circumstances which modify the solubility of substances in water; for instance, lime, which is only slightly soluble in pure water, dissolves abundantly in a moderately strong syrup, and the alkaline reaction of the lime is not in the slightest degree affected. This property may be made available in the solution of several analytical problems; a liquid of the kind is used by M. Peligot in his process for estimating nitrogen.

It is not uncommon in organic investigations to find crystals deposited, which on examination prove to be merely sulphate of lime, the solubility of which is, under certain circumstances, greatly increased by the presence of organic matter. The student will also find in his Manuals of analysis how greatly the action of reagents is modified by this cause; one instance among many is the difficulty of precipitating oxide of copper by potassa in a solution containing sugar or other vegetable or animal substances.

In organic chemistry it is a common process to separate one substance, or group of substances, from complex mixtures by taking advantage of the solubility of one of them in some menstruum to the exclusion of the others; thus, the acids of coal oil may be separated by agitation with a strong solution of caustic alkali, and the bases from the same source may equally well be removed by agitation with acids.

One group of hydrocarbons may sometimes be separated from others by treating the mixture carefully with fuming nitric acid: the benzole and $C^n H^n$ series dissolve, and fluids which I have ascertained to possess the composition and other properties of some of the organic radicals are left unacted on*.

* Proceedings of the Royal Society, May 22, 1856, and January 22, 1857.