A handbook of chemical manipulation

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Section XIX. Sublimation

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SECTION XIX.

SUBLIMATION.

385. Sublimation differs essentially from distillation in the fact, that the product of the operation is obtained in the solid instead of the fluid state; the apparatus used is generally extremely simple, and presents far less variety than that employed in distillation.

386. Very frequently, in manipulating with the small quantities used in research, the arrangement recommended by Berzelius (which for simplicity leaves nothing to be desired) will answer equally well with far more complicated appliances; it merely consists of two platinum crucibles, one rather larger than the other, the larger being inserted so as to penetrate a short distance inside the smaller. The upper one is filled with cold water during the process, which, if required, may be removed with a pipette as it becomes heated, and be replaced with fresh. Two porcelain crucibles may sometimes be substituted with advantage for the platinum; but in this case it is generally unsafe to fill the upper one with water, as such a proceeding would, in all probability, be the cause of fracture. Two porcelain or earthen basins, placed mouth to mouth, and having a strip of paper pasted round the line where they join, for the twofold purpose of confining the vapour and keeping the vessels together, is frequently a good arrangement. In all cases of sublimation it is essential to have a small aperture in some part of the apparatus to allow of the expansion of the air, as, if confined, it would, on heat being applied, break the connexions. It is seldom, however, that it is necessary to make this aperture purposely, as the apparatus for sublimation is seldom quite air-tight.

387. In subliming iodine on the small scale, with a view to its purification, it may be placed in rather large and shallow evaporating-basins, covered with others, which are to be inverted and placed with their mouths downwards against the under ones.

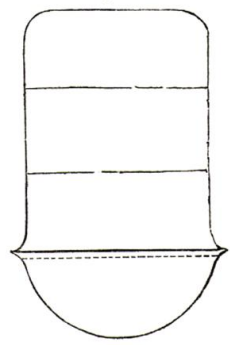
little bulb, any traces which may be found to adhere to any part of the tube are to be carefully removed from the narrow portion by means of a wire with a small piece of linen or thread tied to it, and from the large tube by a piece of wood having something similar but on a larger scale attached. In many operations of qualitative analysis an open tube is used, in order that air may have free access, for the double purpose of oxidizing the metals sought for, and, by establishing a current of air, carrying the vapours forward: in this operation a piece of ordinary tube, from $\frac{1}{8}$th to $\frac{1}{4}$th of an inch in diameter, about 5 inches long, and open at both ends, is employed; it is held almost horizontally at first, the specimen under examination occupying a position about 1 inch from the end exposed to the flame. A spirit-lamp should be used in order to prevent smoke. The heat employed, gentle at first, should be gradually increased, in order to observe all the phenomena that may present themselves. It is to be noticed that the current of air through the tube is greater, the more the position in which it is held approaches the vertical; much command is therefore obtained over the process of oxidation by this means. Every point is to be noticed: the ease with which the sublimate rises, its colour, odour, its appearance when chased by the flame from one part of the tube to the other, whether it melts, or globules are formed, &c. If water is evolved, care must in all cases be taken to prevent its running back upon the hot glass, and thereby causing its fracture. Sometimes, but this is comparatively seldom, the flame of a spirit-lamp is insufficient to volatilize the substance; when this occurs, the blowpipe must be used to urge the flame; this is generally necessary with tellurium, which requires a powerful heat for volatilization.

394. Sublimation is sometimes conveniently effected in common, or preferably, Hessian crucibles; two are taken, one a little smaller than the other; the one is inverted inside the other, and, if necessary, luted to prevent escape of the sublimate.

The place of juncture is to be made tight (with the exception of a very small air-hole) by means of the almond and linseed luting frequently alluded to in the section on Distillation. The apparatus, after being put together, is placed upon a moderately hot part of the sand-bath for some hours, and is then to be removed to a cooler portion, and allowed to become cold very slowly. When perfectly cold, the basins are to be taken apart and the iodine removed with a strip of glass, or even with a strong feather; it is, however, better to avoid the contact of organic matter. The largest crystals are generally found upon the bottom dish, in the form of magnificent sword-blades, sometimes several inches long, when the quantity sublimed is large. If a considerable quantity of pure iodine is required, as in many researches, the ordinary porcelain dishes in use in the laboratory are too small to be really serviceable, and it is better to use the large earthenware dishes known as milk-pans: the arrangement is precisely the same as with the evaporating-basins.

388. Many organic substances, such a naphthaline, pyrogallic acid, &c., may be very conveniently sublimed in the apparatus shown in fig. 209. It consists of an evaporating-basin having a beaker inverted over it, the join being made with paper pasted round. Rings are then made of annealed iron-wire, of the exact size of the inside of the glass: these are covered with muslin, which is sewn on. The object of these discs (which are placed in the beaker in the positions indicated by the lines) is to retain the sublimate and prevent it falling into the dish again.

Fig. 209.



389. As a general rule, it is proper to employ a gentle and steady heat, only just sufficient, in fact, to vaporize the substance, many volatile bodies of unstable composition being partially, or even entirely decomposed by an undue elevation of temperature. This is particularly the case with pyrogallic acid, previously alluded to. No matter

how carefully the operation may be performed, a certain quantity of this, at present, useless metagallic acid is formed, but by careful management the amount may be considerably reduced.

390. With fusible sublimates much is absorbed by the diaphragm; this must never be lost sight of, as in some instances it may be recovered by solution in alcohol or ether, and subsequent crystallization. In the case of the curious substance obtained from sulphopianic acid, as much, or more, is obtained in this manner as in the state of sublimate.

391. Indigo may be sublimed between two porcelain dishes, or by mixing it into a paste with plaster of Paris, forming the mixture into a cake, and placing it in a warm place to become dry; when this has been effected the temperature is raised, and crystals will form on the surface of the plaster, and may be removed with a feather. Biniodide of mercury may be obtained in magnificent scarlet crystals by careful sublimation between porcelain capsules.

There is a well-known peculiarity of the last-named substance which has been only imperfectly accounted for, namely, that when first sublimed it is of a beautiful pale-yellow, which, by contact with a glass rod, becomes scarlet, a peculiar motion taking place at the same time among the crystals, indicating some structural change. This difference in colour between substances before and after sublimation is by no means uncommon: bisulphuret of mercury, if formed by precipitating corrosive sublimate with sulphuretted hydrogen, is quite black before, but brilliant red after sublimation, and is then known as vermilion. Changes of this kind are, however, not peculiar to the process of sublimation: many colours prepared by the wet method acquire different tints by digestion at certain temperatures; the arsenite of copper prepared in the manner adopted for the beautiful emerald-green, acquires its beauty by the maceration of the ingredients for some time. The wet method of preparing vermilion is also an example of the same kind of change.

392. A current of air or certain gases appears to greatly facilitate the crystallization of some substances: if naphthaline is heated to the subliming-point, and air is drawn through the

apparatus, the product is denser, and apparently whiter and purer, than when sublimed in an apparatus with diaphragms, such as is represented in fig. 209. If the crude mixture of chrysène and pyrène be heated in a test-tube, it melts and creeps up the sides, but does not volatilize even at a very considerable temperature; but if air is drawn through the apparatus, a dense yellow vapour rises, and may be condensed at some distance; it is possible, however, that some decomposition takes place in this case. In the process for forming the sesquichloride of chromium, much trouble is sometimes found in obtaining the crystals at a sufficient distance from the mixture of oxide and charcoal; if, however, a very powerful current of chlorine is employed, and the heat is sufficiently raised, this difficulty does not appear.

393. Sublimations on the small scale are often conveniently observed in glass tubes, as for instance, in the operation of testing for arsenic. Great care should be taken in selecting tubes for this purpose, as if the ordinary flint-glass containing lead is used, and it has to be exposed to a reducing flame, or even if heated in contact with carbon in any way, the lead becomes reduced, and much uncertainty may arise from this point alone. In the sublimation of mixtures containing arsenic in minute quantities, according to the directions found in elementary works, very small tubes are employed of the size and shape seen in fig. 210; and a little care is required in so inserting the charge at *a*, as not to leave any upon the tube. Perhaps the best way of doing this is to place the mixture upon a little paper gutter, and, the tube being held horizontally, the gutter is to be placed in it; the tube is now to be raised, when the whole of the charge will fall about *b*, a small portion, however, dropping in its place at *a*; the rest is to be got down the narrow tube by the use of a small wire and a gentle tapping. If the substance is sufficiently dry and in fine powder, no difficulty will be found in effecting this. After the charge is inserted in the

Fig. 210.