CCXIX.—*Manipulation in Intensive Drying.*

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SEVERAL papers have been published during the past year recording failures to obtain results which might be expected in this line of investigation. It is possible that it may be useful to publish in some detail certain points in manipulation, the neglect of which will inevitably lead to failure.

Glass. I have found Jena glass superior to all others and use it whenever possible. When, for instance, ammonium chloride is volatilised in a dry, soft-glass tube in a vacuum, the tube after heating is found to be full of ammonia gas, the hydrogen chloride having been absorbed by the heated glass. An interesting observation (Kistiakowsky, *J. Amer. Chem. Soc.*, 1929, **51**, 1395) is that Pyrex glass is reduced by hydrogen at its softening point, producing water. Post-war glass is without doubt inferior. Owing to insufficient heating of the melt or insufficient stirring, or both, modern glass contains a large number of bubbles, which, when drawn out into tubing, lead to the formation of capillaries inside or outside the tubes. These fill with water, and if the tube is worked at both ends in the blowpipe a long bulb containing water from the cleansing will be left in the finished apparatus, and since their walls are very thin, the water may accidentally be liberated in the dried apparatus.

In selecting tubing, therefore, the end is dipped into chromic acid, the tube washed with water and examined. Sometimes, red streaks, a millimetre broad, are visible; in others, a magnifying lens is necessary to enable one to see them. A tube showing any streaks should be rejected : no treatment by heating will be safe. What has been said of glass applies to silica in a more marked degree.

Cleaning. The cleaning of the tubing is most important. If a piece of glass tubing is brought into the blowpipe flame without previous cleaning, a white deposit is formed on each side of the heated portion, which no subsequent treatment, except with hydrofluoric acid, will remove. Fused silica behaves in the same way. A tube should be cleaned by first washing with water, plugs of clean cotton wool being pushed backwards and forwards over the wet surface until the last one shows no stain. It is then filled with concentrated nitric acid to which has been added enough chromium trioxide to produce a dark red colour. After an hour's standing, the tube is washed by a stream of distilled water and dried. A tube cleaned in this way gives no indication of white deposit when heated in the blowpipe flame. If it is necessary to block the end of a tube while working, white woolly asbestos is the best material to use. Plasticine, which is used in some laboratories, is quite inadmissible. The finished apparatus is filled with chromic acid mixture, which is, if possible, boiled in it. If the form of the apparatus makes this impossible, the mixture should be allowed to stand in the apparatus for 24 hours. It is washed in a stream of distilled water and then steamed from ammonia-free water. If the preliminary rubbing with cotton wool has been omitted and is tried at this stage, a grey deposit will be rubbed off which has resisted the action of the oxidising mixture. If the cleaning with chromic acid cannot be performed in the finished apparatus, *e.g.*, a Plücker tube with aluminium electrodes, a tube containing solid potassium hydroxide between asbestos plugs should be inserted in the tube used for blowing air into the heated apparatus while it is being made. For the drying of such an apparatus another method of procedure is adopted. The apparatus is connected with a three-way tap, heated, and then exhausted. Air dried by phosphoric oxide is then admitted, and the heating, exhaustion, and re-admission of dried air are repeated a dozen times.

Drying. In the drying of an apparatus, I consider a waving Bunsen burner to be better than an electric furnace. It is easy, by cautious use of a flame, to heat every part of an apparatus, even glass taps, really hot. A current of air, dried first by sulphuric acid and then by phosphoric oxide, is drawn or blown through the apparatus during both the heating and the subsequent cooling. It is doubtless less trouble to heat the apparatus in a furnace while it is being exhausted, for several hours, but obviously the drying of the glass must be less effective. It must never be forgotten how absorbent glass is for water vapour. All the drying described must be regarded as preliminary only. An exposure to moist air for a very brief period, such as is necessary during the introduction of a substance into a dried apparatus, is sufficient to nullify, as far as these experiments are concerned, the preliminary drying of the apparatus. It is necessary to have a bulb containing phosphoric oxide sealed to the apparatus. It is useless to expect results when, as in some experiments recently published, a liquid is dried by phosphoric oxide, while the glass above is left undried—a chain is no stronger than its weakest link. Glass resembles charcoal in that the water adsorption is not confined to the surface, but penetrates the mass of the glass. An experiment was shown at a recent meeting of this Society which illustrated this point. A glass bottle was heated to about 150° while a current of air dried by sulphuric acid was drawn through it. When it was cool it was filled with clean sodium amalgam. After 2 days, bubbles of hydrogen began to appear between the glass and the amalgam, and after 3 days the whole of the glass was covered with bubbles. Since these did not appear in the first 12 hours, their formation could not be ascribed to surface water. It is this deep-seated water which, I think, causes the difficulty of working glass in the blowpipe flame after a long spell of damp weather: the glass often flies when the tube is brought even into the luminous flame. Failure to recognise the slowness of the escape of this deep-seated water is responsible for the want of success of many attempts to repeat experiments on intensive drying. When two gases, previously dried, are to be mixed, I deprecate the use of a glass wall to be shattered by a glass rod. I have only once seen the want of union of ammonia and hydrogen chloride, and never that of nitric oxide and oxygen, when the broken glass wall was used. This may be due to the liberation of deep-seated water from the broken glass, or it may be due to another cause. When glass is broken in a closed space the gas surrounding it is ionised, and some of my earlier experiments indicate a close connexion between ionisation and chemical action.

Lubricants. The use of taps is limited by the difficulty of finding a lubricant which will exert no chemical influence. The lubricant devised by Sir William Ramsay, of burnt rubber and vaselin, has a distinct smell, which means that a foreign body will be introduced into the pure gases. For nitric oxide and oxygen, I used a lubricant of metaphosphoric acid in the middle of the barrel of the tap, while a band of purified vaselin was smeared at the top and bottom of the barrel to prevent the deliquescence of the metaphosphoric acid caused by external moisture. For ammonia and hydrogen chloride, no lubricant whatever could be used. For these experiments, I used taps which I had myself polished by hand with rouge and water until the opposing surfaces were quite bright. I lost only two by sticking. In all cases where taps are used it is necessary to introduce phosphoric oxide into the hole in the barrel.*

Materials. Purity of the materials far beyond the standard required for atomic-weight purposes is absolutely essential for the

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* The lubricant I usually use for ordinary experiments may be mentioned, as it is superior to any which I have tried so far. White vaselin is stirred well with dilute sodium hydroxide, and washed with constant stirring until all trace of alkalinity is lost. It is then heated for several hours until it shows a tendency to darken. About 5% of solid paraffin is then added and the hot mixture well stirred. In an apparatus which I am now using, there are four unprotected glass taps lubricated with this mixture. The apparatus was exhausted to *X*-ray vacuum at the end of the Christmas term, and the *X*-ray fluorescence was just as bright at the end of the four weeks' vacation.

experiments in question. In some experiments recently published in America on the vapour pressure of dried ammonium chloride, the authors admit that the salt turned yellow on heating. It is quite certain that when obvious impurities are shown to be present no success can be anticipated. For five years I experimented on the union of hydrogen and oxygen, trying to get methods of purification which would render these gases inert when dried. Even when Mr. Wilson and I discovered the method of electrolysis of barium hydroxide solution, it was necessary to recrystallise the barium hydroxide 15 times, with all imaginable precautions, before the gases were obtained in a state of sufficient purity. A short time after the discovery of this method, Prof. Bone, who had, of course, served a long apprenticeship in this delicate branch of investigation, was able to repeat the experiments perfectly.

Purification by recrystallisation is always a difficult matter owing to the intrusion of dust. Even in country air, dust is always present and the most stringent precautions are necessary to guard against it. It is probable that the drying of an apparatus by heating in a current of air instead of in a vacuum owes its efficiency to the burning up of invisible particles of dust. It took several years for the importance of using pure phosphoric oxide to be recognised, and it is hoped that these other details, equally important, may serve to make work in this field more general and more fruitful.

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