LIV.—On *Evaporation in Vacuo*.

By HERBERT McLEOD.

THE ordinary method of evaporation *in vacuo* by placing the liquid in a dish over sulphuric acid in an air-pump receiver is very slow, and for three reasons: firstly, the aqueous vapour reaches the surface of the acid by diffusion only, for by an ordinary air-pump it is possible only to obtain a considerable rarefaction, and not to remove all the air from the receiver; secondly, the surface of the sulphuric acid is limited, and as the dilute sulphuric acid has a lower density than the oil of vitriol it forms a layer on the surface of the latter, and much retards the absorption; and, lastly, heat is supplied only very slowly to the evaporating liquid, principally by radiation, for not much heat will be carried by convection in a highly attenuated atmosphere. In an experiment tried in order to determine the rate of evaporation under these conditions, 50 c.c. of distilled water placed in the vacuum of a good air-pump over 250 c.c. of sulphuric acid required $2\frac{1}{4}$ days for complete evaporation.

I was led to try some experiments on the evaporation of water at low temperatures by some remarks in Professor J. W. Mallet's paper "On the Determination of Organic Matter in Potable Water" (*Chem. News*, **46**, 62, 73, 90, 101, 108), and the method was suggested by Mr. A. W. Wright's "Apparatus for the Distillation of Mercury *in Vacuo*" (*ibid.*, **44**, 311). When the experiments were nearly concluded, another paper by Professor Mallet appeared in the *Chemical News* (**47**, 218, 252), in which an apparatus is described which bears a very close resemblance to one which I had constructed in the early part of the investigation, and although this seems to have answered all the purposes for which it was designed, it may not be without interest to describe some of the most successful forms at which I have arrived.

In distilling mercury in Wright's apparatus, it is at once obvious that the operation proceeds very much more rapidly and at a much lower temperature, and also without ebullition, when the last traces of air are removed; hence it seemed necessary in the evaporation of water to arrange the apparatus so that the condensed water should itself pump out the gas that is liberated during the evaporation.

One form of the apparatus consists of a horizontal flat brass ring, *a*, 118 mm. in its outside diameter and 92 inside; to the upper side of the ring a dome of copper, *b*, is soldered. The dish containing the water to be evaporated is attached to the lower surface of the brass ring in a manner that will be afterwards described. The dome is pro-

Scale, $\frac{1}{4}$ full size.

vided with a horizontal copper tube, *c*, 18 mm. wide, by which it is connected with a copper condenser, *d*, consisting of a truncated cone within a cylinder, the space between the two being enclosed at the top and bottom by means of copper rings soldered on. This forms a condenser of small capacity and with a large cooling surface; it is fixed in a tin can, through which a stream of water can be made to flow. It is necessary that the connecting tube between the dome and the condenser should be wide, so as to permit of the rapid passage of the rarefied aqueous vapour. The bottom of the condenser is provided with a narrow brass tube, to which is attached a glass tube with a bend, *e*, near its upper end, in which the drops of water are formed which produce the exhaustion. In a laboratory where a fall of about 35 feet is obtainable this might constitute the whole apparatus, but not having at my disposal a greater height than that of the laboratory bench, the lower end of the fall-tube is fitted into the neck of a Woulfe's bottle, which latter is connected with a Körting's jet pump to remove the air at the commencement of the operation. The Woulfe's bottle is also provided with a siphon for the removal of the condensed water.

The dish, *f*, in which the evaporation is performed is an ordinary hemispherical glass evaporating dish about 100 mm. in diameter, and with its edge ground smooth. A wetted red india-rubber ring, *g*, is placed on the lower surface of the brass ring attached to the dome, the edge of the dish being pressed upwards against it, and the jet pump set in action. The atmospheric pressure soon holds the dish firmly in position. The red india-rubber ring is preferable to ordinary sheet india-rubber, as it does not adhere firmly to the glass when the dish has to be removed; it also may be used a large number of times. When the vacuum is as good as the pump will make, a small quantity of distilled water is allowed to flow into the dish from a supply tube provided with a stopcock and attached to a small tubulure on one side of the dome. This supply tube terminates in a small funnel which touches the inside of the dish so that the admitted water flows down the side of the dish in a thin film. The dish is then surrounded by a water-bath heated to 50°. The last traces of air are thus expelled from the dish and condenser, and a current of water is then turned on to the condenser. It is necessary also that the Woulfe's bottle and the fall-tube should be kept cool, and this is best effected by allowing the overflow from the condenser to run down the outside of the fall-tube into a vessel surrounding the bottle. When the vacuum is complete, the water around the condenser is removed, and the water to be evaporated is allowed to flow slowly into the dish. 50 c.c. at a time may be admitted, the water-bath being maintained at 40° or 50°, preferably with the aid of a thermostat. Much of the

dissolved air escapes during the entrance, and, if time can be spared, it is advisable to allow the water to remain in the vacuum for an hour or so to avoid the violent ebullition which sometimes occurs. If it is necessary that the evaporation should be begun at once, it is better to raise the temperature of the water in the bath very slowly from 30° to 50° while the water is running round the condenser. No experiment has been made with water cooled with ice, that of the supply being always employed. Water soon begins to form in the condenser, and the drops flow down the fall-tube and pump out the air. When the air is removed the evaporation proceeds at a rapid rate, and in some cases in which the temperatures were observed, the water was at 26° whilst the temperature of the bath was 50° . Of course the temperature of the evaporating water will depend also on that of the water surrounding the condenser. It is hardly necessary to observe that although the temperature of the water is low, the solid residue is heated to the temperature of the water-bath.

Tumultuous ebullition sometimes takes place, and this is the principal objection to the process. If the water has been previously mixed with sulphurous acid and raised just to the boiling point before introduction into the apparatus, the evaporation proceeds much more quietly, the violent boiling being produced apparently by the escape of carbonic anhydride from the decomposition of acid carbonates. When the water is nearly all evaporated there is considerable effervescence.

The evaporation proceeds at about the rate of 50 c.c. in 2 hours. In an open dish over a water-bath the same quantity of water is evaporated in about $1-1\frac{1}{2}$ hours.

To avoid loss from spirting, the evaporation may be carried on in a wide test-tube (*h*), the condenser being provided with a glass plate (*i*), pierced with two holes, a large one through which the vapour enters the condenser, and a small one through which the supply tube passes into the evaporating tube; an india-rubber ring (*k*) makes an air-tight joint between the plate and the mouth of the tube. The test-tube is very slightly inclined to the horizontal, and is surrounded by a water-bath. The water to be evaporated is allowed to flow in slowly, and the evaporation carried out at the same time. Even if violent boiling takes place, the liquid is only thrown across the tube, and the residue is not lost. This form of apparatus may be useful when the residue is to be determined, and it is not necessary to remove the solid, and it has the further advantage that the tube may be closed during the weighing by a glass cap, which diminishes the rate at which the residue absorbs water from the air.

The evaporation in the tube is slower than in the dish for two reasons: firstly, the evaporating surface is smaller; and secondly, gas

continues to be evolved during the whole process, thus producing an increased pressure. A light spherical flask may be employed in place of the test-tube, and has the advantage of permitting 50 c.c. of the water to be introduced at a time, without danger of loss from ebullition.

When a combustion of the residue is to be made with cupric oxide, by Frankland and Armstrong's process, the evaporation might be performed in the combustion tube itself, and in contact with the oxide of copper. For this purpose one end of the combustion tube is connected to the condenser, and the other end which is drawn out and bent at right angles, is connected with the supply tube, and the tube heated in the water-bath. The increased surface thus obtained much hastens the evaporation. It remains for water analysts to ascertain if the method is practical.

Another modification of the method is to replace the condenser by a wide vertical tube (*l*), along the inner surface of which a thin layer of sulphuric acid is allowed to pass, the acid being admitted by a tubulure (*m*), and regulated by a stopcock. The water vapour is rapidly absorbed, and passes down the fall-tube as dilute sulphuric acid. In this way it is possible to conduct the evaporation at a temperature only a few degrees above the freezing point, the water-bath being maintained between 30° and 40°. By surrounding the wide tube with a flow of cold water, the evaporation is more rapid and the acid is much economised, one volume of water requiring about one of sulphuric acid for its evaporation; if the tube is not cooled about three volumes of acid are necessary.

Care is necessary in regulating the flow of acid, for if too rapid the water may be frozen and the evaporation much retarded; bubbles of gas also often form under the ice, resulting in violent boiling. As a thermometer plunged in the liquid would be inadmissible when the solid residue is required, the temperature may be estimated by means of a pressure gauge (*n*), the temperature corresponding to the pressure being given in the ordinary tables.

After use the sulphuric acid may be boiled in an open flask until it begins to fume. It can thus be used any number of times.

This modification of the apparatus is very efficient for drying solids. Salts very quickly lose their water of crystallisation, and this without fusion even at 100°, and the prevention of access of air may often prove advantageous. Magnesian sulphate thus loses 6 molecules of water at 100°, whereas it requires a temperature of 150° at the ordinary pressure. Sodid carbonate can also be well dried in this manner, although when a large quantity of the salt is placed in the dish, its bad conductivity prevents the access of heat to the interior of the mass. 170 grams of crystallised sodid carbonate lost all but 2 per cent.

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of the water in 12 hours; about 6 hours after the commencement of the operation the apparatus was opened, the salt powdered and dried for another 6 hours.

Although the use of this method of evaporation and drying cannot be said to be free from objections, yet possibly its description may prove of some value to those who may be experimenting in this direction.