CCCLXII.—*Necessary Procedures for the Exact Determination of Vapour Tensions.*

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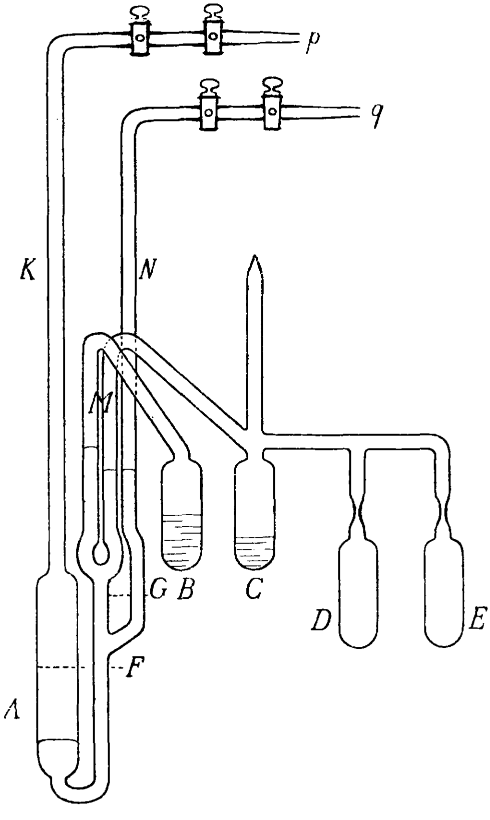
IN studying the influence of intensive drying on the vapour pressure of liquids, we have encountered a difficulty which may cause a serious inaccuracy in the results, namely, that of removing the last traces of air or other gases from a liquid. Our original method was alternately to solidify and liquefy the substance repeatedly during evacuation, but we have discovered that this procedure is quite ineffective, for the substance can retain sufficient air entirely to vitiate the accuracy of the determination. We have now found a method for the removal of these last traces of gas, and the following details may be of service to other investigators in this field.

The apparatus is a modification of that constructed by Smits for the preparation and testing of very pure cyanogen, and has been successfully used by Terwen (Thesis, Amsterdam, 1913; *Z. physikal. Chem.*, 1916, **91**, 469). It is not only a combination of a differential mercury manometer with a mercury vapour-pressure indicator, but also a distillation apparatus, for it contains two or more vessels with capillaries, which can be sealed off.

If we have filled tube *C* (see fig.) with a liquid, sealed off the filling tube, and cooled *C* in liquid air, the taps of tubes *p* and *q* being open, the mercury in tubes *A* and *F* will be level and if we then evacuate the apparatus *via* tubes *p* and *q*, the positions of the mercury surfaces will not change. During this evacuation the liquid is alternately frozen and melted. If the vacuum is now released by carefully opening the cocks of the tube *p*, the mercury can be pressed up to *G*, still leaving communication between *B* and *C*. Now, by removing the Dewar vessel containing the liquid air from *C* and cooling *B* in ice whilst *C* is warmed to room temperature, a part of the liquid is distilled from *C* into *B*. Whilst the distillation is going on, the mercury is allowed to rise into the differential manometer *M* and tubes *B* and *C* are immersed in a bath at, *e.g.*, 0°; the manometer *M* will then indicate the vapour-pressure difference between the residue in *C* and the distillate in *B*. In order to use the third tube *N* as a vapour-pressure indicator, we connect tube *q* with our arrangement for changing the pressure combined with a manometer, and bringing the mercury surface in *N* level with one of the two mercury surfaces in *M*, we find the absolute value of the vapour pressure.

This method affords a very delicate test for the purity of a substance: it is only when we have a really pure substance, *which* *shows a unary behaviour*, that fractional distillation produces no difference between the vapour pressure of the residue and that of the distillate.

When this experiment * was tried with hexane, we met with an unsuspected phenomenon; after we had distilled one-half from *C* to *B*, the gauge *M* showed that the vapour pressure of the distillate at 0° was about 5 mm. higher than that of the residue. We subsequently proved that this behaviour was not due to an impurity in the hexane, but to traces of gases that had not been removed by the alternate freezing and melting during evacuation. This difference disappeared when the mercury in *M* was lowered for one minute, but when the temperature of the bath was raised to 15° another difference arose which, in both sign and magnitude, depended on the relative volume of the *B* and *C* parts of the apparatus and on the quantities of liquid in them.



In one case, in which the volumes of the two parts were similar, immediately after one-third of the liquid had been distilled off at 0°, the distillate naturally had the higher vapour pressure (by 5 mm.), but after the short time of communication and subsequent warming of the bath to 15°, the sign of this difference, as shown by *M*, had changed, the vapour pressure of the distillate being now 7 mm. lower.

These phenomena indicate that the effect is caused by a trace of gas, a view which is supported by our method of obtaining the

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* In the first experiment the tubes *D* and *E* were not present, so there was no risk of dead ends having any influence.

liquid completely pure. For this purpose the apparatus was modified by the addition of the two tubes *D* and *E*. Most of the liquid was contained in *B*, only a few drops being left in *C* and *D*. The mercury in *M* was lowered to *G*, and *E* was cooled in ice while *B* was warmed with the hand. About two-thirds of the liquid was distilled, and, as the last drops were evaporating from *C* and *D*, the tubes *B* and *E* were dipped into freezing mixtures of solid carbon dioxide–alcohol and liquid air respectively. The temperature of the former mixture was above the melting point of the hexane but so low that its vapour pressure was practically zero.* During this operation it was, of course, necessary to change the pressure in *N* and *K* in order to keep the mercury at nearly the same level. Tube *E* was now sealed off, and by the procedure described above, the purity of the remainder of the liquid was tested; it usually proved to be completely pure, but if it should not be so, the manipulations would have to be repeated, for which purpose tube *D* is present.

Our experiments show that the common practice of testing for air in an apparatus with an electrical discharge after the liquid has been frozen in liquid air is quite untrustworthy. A substance cooled in a vacuum in liquid air may give the impression of being completely free from gas, but, when tested in an apparatus such as that described here, it is found still to contain an appreciable quantity, for if the gas is accumulated in a smaller amount of the substance, in the way described above, its presence can often be detected by electrical discharges.

Finally we may mention that, not only hexane and benzene, but also the other substances investigated by us show the same effect.

Summary.

It has been shown that the filling of an apparatus with a pure volatile substance, by cooling the latter and evacuating the apparatus, meanwhile melting and solidifying the substance several times, does not ensure that no appreciable amount of gas is left; generally, such an impurity cannot be detected by the ordinary electrical discharge method, but the procedure now described enables volatile substances to be completely freed from gases.

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* In dealing with a substance such as benzene, both tubes *B* and *E* are finally dipped in liquid air; and previously *B* had to be cooled in ice and *E* in carbon dioxide–alcohol.