CCCLIX.—*The Effect of Intensive Drying on the Rate of Distillation and on the Vapour Pressure of Ethyl Bromide.*

By John William Smith.

It has been observed by several investigators that dry liquids boil only with difficulty. Apart from the historical experiments of Prof. and Mrs. Baker (J., 1922, **121**, 568; 1923, **123**, 1223), Roberts and Bury, for instance, found (J., 1923, **123**, 2037) that on several occasions when nitrobenzene was kept with phosphoric oxide for over a week, its behaviour on distillation recalled Baker's observations. The author (J., 1927, 869) noticed that the rate of distillation of nitrogen tetroxide, between baths at approximately constant temperatures, decreased considerably as the substance was dried. These results suggested the possibility that the abnormal behaviour observed with liquids after intensive drying might be due, at least partially, to the slowing down of the rates of evaporation and condensation of liquids after such treatment. This explanation seemed all the more probable because there was some evidence that intensively dried solids show the same phenomenon even more markedly. Besides the " slow " behaviour of very pure dry sulphur trioxide and phosphoric oxide (Smits and others, J., 1924, **125**, 2554, 2573; 1926, 1108, 1603; *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 514, 619; *Z. physikal. Chem.*, 1930, **149**, 337), two other series of experiments indicate this effect, *viz.*, the apparent zero vapour pressure of very dry calomel (Smith and Menzies, *Z. physikal. Chem.*, 1911, **76**, 713) and the retardation of the evaporation and condensation of ammonium chloride (Rodebush and Michalek, *Proc. Nat. Acad. Sci.*, 1928, **14**, 131; *J. Amer. Chem. Soc.*, 1929, **51**, 748).

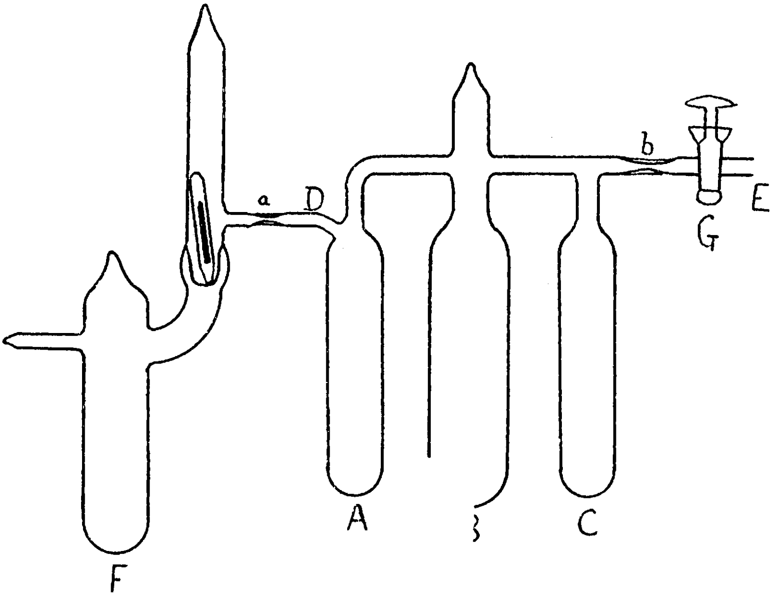
The author's earlier observations upon nitrogen tetroxide were not altogether convincing, owing to there being a column of phosphoric oxide between the two bulbs. Hence the experiment was repeated under conditions to which such a criticism would not apply. Stable liquids with relatively high vapour pressures are not numerous, so the choice fell on ethyl bromide, which, in the absence of oxygen, showed no sign of decomposition on standing, even in the light.

EXPERIMENTAL.

Preparation of Materials.—The ethyl bromide was purified by shaking it several times with sulphuric acid, then several times with sodium carbonate solution; it was then washed, dried over calcium chloride, and fractionally distilled three times. It was introduced into storage bulbs, together with resublimed phosphoric oxide, and the bulbs were evacuated and sealed. These bulbs were closed by a sealed-in glass septum, so that the liquid could be distilled directly into a drying apparatus without contact with moisture.

The phosphoric oxide was resublimed in a current of very dry oxygen. That used in the storage bulbs was once so treated, whilst that employed in the drying apparatus proper was twice distilled, being sublimed into the apparatus itself on the second occasion. The method employed was similar to that described previously (J., 1927, 869). The resublimed phosphoric oxide was tested for lower oxides or free phosphorus by the permanganate method (this vol., p. 528).

FIG. 1.



" Durosil " glass was used, and t ıs freed from capillaries by the method described by Smits ar ıers (J., 1926, 2657). For the construction of most of the apparatus, wide tubing was used. It was first re-fused until no sign of capillaries remained, and then drawn down to suitable diameter for use.

Apparatus, Type A.—To test in the simplest possible manner whether the rate of distillation of ethyl bromide was changed after careful drying, the simple apparatus illustrated in Fig. 1 was employed. This consisted of two bulbs, *A* and *C*, which could be immersed in baths at known temperatures to known depths, and a wide tube *B* to contain phosphoric oxide. The apparatus could be connected through the tube *D* with a storage tube *F*, whilst tube *E* was connected to a high-vacuum pump system.

After careful cleaning and washing, the apparatus was dried by heating it almost to softening point whilst a current of dry air was drawn through it. It was then connected to the pumps and to the storage bulb, and was highly evacuated for several days, the whole being heated periodically almost to the softening point of the glass. At intervals, the evacuation was interrupted, the apparatus flooded with dry air, and then evacuated again. After this treatment, dry air was admitted to the system under slight pressure, the top of the tube from *B* was cut off, and a current of dry air maintained through the apparatus during the short period whilst the phosphoric oxide sublimation tube was placed in position. Phosphoric oxide was distilled into the vessel *B*, the top of this tube being finally drawn off with the oxygen current still passing. The evacuation and heating processes were then repeated with the exception that tube *B* was kept cool throughout. With the apparatus still evacuated, the whole was shut off from the pump system at tap *G*, and the septum of the storage bulb was broken by the small electromagnetically operated breaker.

The liquid was then distilled from the storage bulb to *A*, and the capillary *a* sealed off. Bulb *A* was cooled in a mixture of carbon dioxide snow and alcohol, whilst the apparatus was evacuated so as to remove as much dissolved air as possible. The liquid was then cooled in liquid air, and the apparatus exhausted to a high vacuum. After the tap *G* had been closed, the liquid was allowed to melt again, after which it was frozen and the apparatus re-evacuated. To remove the occluded air as completely as possible, the process was repeated twice again, after which there was no appreciable residual pressure in the apparatus when the liquid had been allowed to warm to the ordinary temperature and been frozen again in liquid air. Finally, with the apparatus at a high vacuum, and with the liquid frozen at liquid-air temperature, capillary *b* was sealed off.

Extensive series of distillations, performed during the first few days after sealing each apparatus, showed that the times recorded for the distillation of a fixed quantity of liquid between baths at constant temperatures were reproducible to about 2%. To dry the ethyl bromide, it was distilled on to the phosphoric oxide in *B*. The quantity of drying agent was very large compared with that of the liquid.

Four pieces of apparatus of this type survived a sufficient period of drying to enable extensive series of measurements to be made, and each showed interesting results bearing on the problem under investigation.

Apparatus A. 1.—This was a failure. During the night after sealing a crack developed in the tube connecting bulb *A* to the phosphoric oxide tube *B*, and, therefore, moist air was drawn into the apparatus. The following morning the apparatus was re-fused to the vacuum pumps, the crack repaired, and the sealing-off process repeated as before. In spite of the precautions which were taken, however, sufficient moist air must have come into contact with the phosphoric oxide and with the ethyl bromide to cause considerable deactivation of the drying agent. Hence a retardation of the drying effect or a completely negative result was not unanticipated : there was no retardation in the rate of distillation over a period of 15 months.

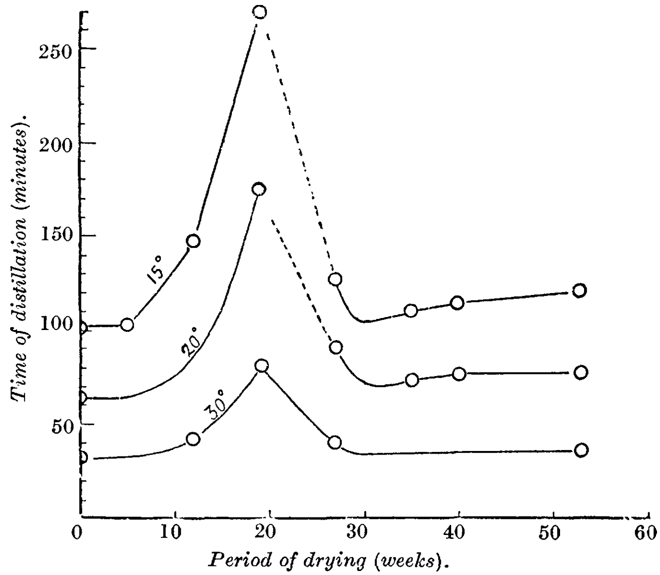
This apparatus, however, served a useful rôle as a " blank " experiment in which phosphoric oxide was present. First, it showed that the effects observed with the other pieces of apparatus were not due to the decomposition of the ethyl bromide during the period of the measurements, and secondly, it established the reproducibility of the method, which had also been checked by blank experiments with apparatus containing no phosphoric oxide.

Apparatus A. 2.—The second apparatus, on the other hand, showed a very pronounced change after quite a short period of drying. It was intended to observe two distinct series of rates of distillation, with the ethyl bromide evaporating first without, then with ebullition. The first series gave a perfectly reproducible rate, but with the ebullitional distillation the results were much less concordant, since the time of distillation seemed to depend considerably on the vigour with which the ebullition was initiated. As drying proceeded, the ebullition occurred with diminishing vigour, so that even violent shaking of the apparatus caused ebullition only when the heating bath was at quite a high temperature.

The time of the non-ebullitional distillation rose steadily during the first 4½ months, till it reached about 2½ times its original value. That this was not due to the admission of permanent gas or to the products of a reaction inside the vessel, was shown by the fact that after a further period of 8 weeks the time required for distillation had fallen again, but not quite to its original value. The most probable explanation seems to be that, in spite of the careful preparation of the glass, a small capillary had remained in the walls of the apparatus, and that between the 19th and 27th weeks of the drying process this capillary had burst and ejected moisture and nuclei into the apparatus. The time of distillation continued to fall for a short time, but never reached its initial value. It showed a slight rise again after 40 weeks, and this rise continued slowly. The results obtained for distillation in one direction through the apparatus for three different temperatures of the warm bath are plotted in Fig. 2. The cold bath was at 0° in each case. Readings were also taken for distillation in the opposite direction, and showed exactly the same type of change with the time of drying.

The reluctance of the ethyl bromide inside the closed apparatus to enter into a state of ebullition remained, however, even after the disappearance of the distillation effect. Measurements were made of the lowest bath temperature at which the liquid in one bulb would maintain a permanent state of ebullition after vigorous shaking, whilst the other bulb was immersed in ice. The results were slightly irregular, but the following average values could be obtained to ± 1° :

Fig. 2.



Period of drying (weeks)	0	12	19	27	53
Bath temp. required for ebullition ...	35°	40°	45°	48°	60°

Apparatus A. 3.—This apparatus again showed a pronounced effect, but not so great as in the experiment last described; the rates of distillation measured are summarised in Table I. Supposing that the effect were due to a polymerisation of the molecules in the dry state, accompanied by a slowness in the attainment of the internal equilibrium, it seemed probable that if the whole apparatus were heated for some time to a temperature higher than that at which it had been standing, it might be possible to dissociate these polymerised molecules and obtain a liquid which should be even less associated than the normal liquid. Therefore, after 5 months' drying, the apparatus was placed in an air thermostat at 50° for 2 days.

TABLE I.

Time of drying (weeks).	Time of distillation (mins.) with the warm bath at 10°.	15°.	20°.
0	87	58	38
4	88	60	38
7	104	69	45
12	130	86	52
17	150	96	56
21	160	101	62
*21	160	101	—
26	163	103	64

* After heating at 50° for 2 days.

It was then allowed to cool to room temperature and the distillation experiment was repeated. Exactly the same time of distillation was found as that observed immediately before this operation.

After the ethyl bromide in this apparatus had been drying for 6 months there was no tendency for the time required for distillation to fall in the manner observed with the second apparatus, but it was still rising, although after this period the rate of increase was very slow. As no septum had been connected to this apparatus, it could not be attached to a vapour-pressure gauge. However, another apparatus of similar design was constructed and filled to a fixed mark with some of the ethyl bromide which had been purified at the same time as the sample used in this apparatus. The apparatus was evacuated and sealed with the usual precautions, and the time of distillation of this " moist " ethyl bromide in the apparatus determined. The apparatus was emptied again, and connected to a glass-spring manometer, a mercury gauge, and a vacuum-pump system. It was dried and charged with phosphoric oxide in the same way as the previous pieces of apparatus, and ethyl bromide from the drying apparatus A. 3 was introduced to the same mark as was used for the undried specimen. The apparatus was then evacuated and sealed in such a manner that the inside of the glass-spring indicator was in contact with the vapour, whilst air could be admitted to balance the pressure on the outside of the gauge. This pressure was read on the mercury gauge. Vapour-pressure measurements were then made at 0°, 5°, 10°, and 15°. The values obtained, however, were, within experimental error, identical with those obtained previously with pure, but not very intensively dried, ethyl bromide. Nevertheless, the time of distillation of this sample of ethyl bromide was also found to be almost identical with that of the undried ethyl bromide (the average time for one distillation at 15° was one minute longer than for the undried sample). This last fact renders the vapour pressure results valueless, since sufficient moisture must have been absorbed during the rapid transfer to destroy the slow distillation effect. It was intended to leave the ethyl bromide to dry over phosphoric oxide whilst still connected to the pressure gauge, but, owing to a breakdown in the thermostatic arrangements, the gauge was broken.

Apparatus A. 4.—This contained a glass capillary tube in bulb *C* to enable surface-tension measurements to be made. The lower end of this capillary tube was expanded to a bell shape, holes being made in the sides of the bell to allow of the free passage of liquid in and out of the tube. After the usual cleaning precautions, this capillary tube was dried by heating it for a long time almost to its melting point, whilst a current of dried and filtered air was drawn through, and it was placed in position in the apparatus whilst still at as high a temperature as was consistent with safety.

This apparatus, however, showed no change in either surface tension or rate of distillation during 3½ months, after which a crack developed. The diffusion of moisture from the walls of the capillary tube to the phosphoric oxide must have been very slow, so it seems probable that the ethyl bromide never reached such a dry state as in the other pieces of apparatus. This non-appearance of a surface-tension change, therefore, has no significance.

Apparatus B. 1.—To make a more thorough investigation of the effect of intensive drying on the rate of distillation of liquids, it was desirable to accelerate the drying process as much as possible, and also to be able to connect the apparatus, after drying, to a pressure gauge, in order to test whether or not the vapour pressure of the liquid changes at the same time as the rate of distillation. It would have been preferable to have had a pressure gauge connected to the apparatus throughout the investigation, but it was considered that there was too great a danger of fracture during the period of drying. Hence the apparatus was closed by a sealed-in glass septum, arranged so that it could be connected later to a pressure gauge. The apparatus shown on the left-hand side of Fig. 3 was adopted, the circulation principle described by Smits, de Liefde, Swart, and Claassen (J., 1926, 2659) being employed. As the tubes for the distillation experiments were quite distinct from the circulating and drying portion of the apparatus, no uncertainty was introduced owing to possible compression of the phosphoric oxide. Redoubled precautions were taken to eliminate moisture from the surface of the glass, and the apparatus was charged in the usual way.

Measurements of the rates of distillation were made between bulbs *D* and *E*, whilst during the periods when the apparatus was left for the material to dry, it was placed in an air-bath at about 30°, and cold water passed through the inner tube of the double-walled vessel *A*, thus causing circulation of the ethyl bromide vapour.

After the " no drying " standardisation, distillation tests could not be made for 7 weeks, the time required having then risen considerably. Hence it is impossible to say whether the time of drying–time of distillation curve showed an initial period during which little or no change occurred, followed by a sharp rise, as in the other two cases. It continued to rise steadily, but did not show such a large change as in either of the previous pieces of apparatus. This was not unexpected : the apparatus being of a more complex form, there was not only a greater surface of the glass vessel to dry, but also the diffusion of the water vapour from these walls to the phosphoric oxide must have been retarded considerably. The results are given in Table II.

FIG. 3.

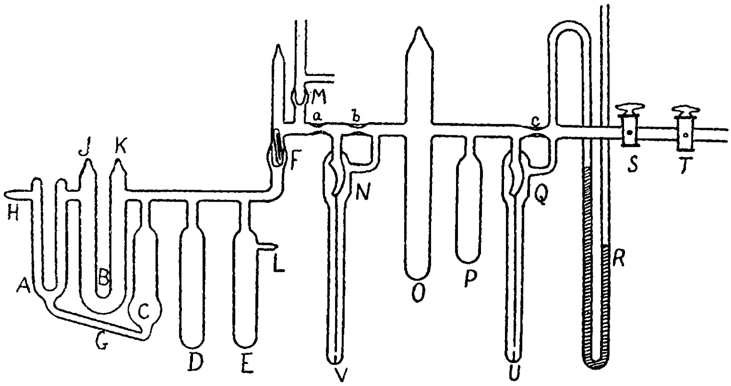


TABLE II.

Period of drying (weeks).	Time of distillation (mins.) with the warm bath at 10°.	15°.	20°.
0	96 ± 1	63 ± 1	41 ± 1
7	156	96	63
10	165	100	68
18	177	107	72
23	180	110	74
29	184	112	76

Similar effects were observed with the rate of ebullitional distillation, but the results were less closely reproducible.

After 6 months' drying, the apparatus was connected to a system of pressure gauges as shown on the right-hand side of Fig. 3. The side tube above the septum *F* was connected to a further septum *M*, a glass-spring gauge *N*, and thence through a constriction *b* to a wide tube *O* to contain phosphoric oxide, a wide side tube *P*, and a second glass gauge *Q*. The last was connected through the constriction *c* with the mercury manometer *R*, and through taps *S* and *T* to the vacuum pumps. After this part of the apparatus had been tested for leakage, it was connected to the drying apparatus and baked out whilst evacuated. Resublimed phosphoric oxide was then introduced into *D*, the apparatus baked again, and finally sealed off under high vacuum at the constriction *c*, thus isolating the portion up to the inside of the spring of *Q* from the mercury manometer and the pumps. It was then allowed to stand for 6 weeks, to enable the glass tubes to dry as completely as possible. During this period the whole of the new portion of the apparatus except *O* was warmed periodically to drive the moisture to the phosphoric oxide.

After this interval, the null position of the gauge *Q* was fixed, comparison being made with the reference pointer *U*. The ethyl bromide was condensed in *E*, and frozen with liquid air. The septum *F* was then broken, bringing the vapour from the drying apparatus into contact with the vapour-pressure gauges up to the inside of *Q*. No detectable rise in pressure could be observed on this gauge, showing that no permanent gas had been produced during the prolonged standing of the apparatus. The temperature of the liquid was then allowed to rise, the vapour pressure being balanced by admitting air to the outer sheath of gauge *Q*. The bulb *E* was then immersed in a constant-temperature bath at 0°, and the vapour pressure determined. Similar measurements were made also at 5°, 10°, and 15°, both after raising and after lowering the temperature, but the values observed (Table III) were almost identical with those which had been obtained previously with ordinary ethyl bromide.

TABLE III.

Temp.		0°	5°	10°	15°	15°	10°	5°	0°
Vapour pressure (mm.)	Undried	165·3	207·3	257·2	317·0	317·0	257·2	207·3	165·3
	Dried	165·6	207·4	256·9	316·6	316·8	257·1	207·4	165·7

These results do not agree with those of Smits, who found (*Z. physikal. Chem.*, 1927, **129**, 33) that intensive drying of ethyl bromide for 26 months at 22·90° increased the vapour pressure from 43·40 cm. to 44·85 cm. No great retardation was observed in the rate of attainment of a steady vapour pressure state.

Next, in order to determine whether the liquid could be separated into two fractions of different vapour pressure, bulb *P* was cooled in carbon dioxide snow and alcohol, and half the liquid allowed to distil from *E* to *P*; *E* was then also cooled, and the constriction *b* sealed off. Thus the vapour of the liquid in *E* was in contact with the inside of gauge *N*, whilst the vapour of that in *Q* was in contact with the outside of gauge *N* and with the inside of gauge *Q*. Any difference in vapour pressure between the two fractions should have been detectable through a deflexion in gauge *N*. Bulbs *E* and *P* were then immersed in the same constant-temperature bath at 0°, but no deflexion of the pointer of *N* could be detected. The vapour pressure of the head fraction, measured on gauge *Q*, was also the same as had been observed previously. This shows that if any fractionation had occurred, internal equilibrium must have been reattained almost completely during the short period before measurements could be made.

Discussion of Results.

These experiments indicate that the rate of distillation of ethyl bromide in a vacuum across a constant temperature gradient is retarded by intensive drying. During the initial stages of the drying, little or no change is observed, but afterwards there is a sudden rise in the time required, continuing for some time, but the rate of rise diminishing with time. The largest effects were observed in apparatus of simple design. The presence of excess moisture in the initial stages seems to prevent the effect completely, and a carefully dried capillary tube designed for surface-tension measurements had the same effect. The abnormality was destroyed immediately by transfer of the liquid from one apparatus to another, although contact with the atmosphere was minimised as far as possible. The vapour pressure of ethyl bromide showing this effect was completely unchanged, and if there was any retardation in the rate of attainment of a steady vapour pressure state this was not very marked. Also, during the drying some change occurred which caused considerable superheating to take place. When ebullition did occur, it was somewhat irregular, but there was none of the almost explosive violence usually associated with a superheated liquid. Such behaviour, however, did not run completely parallel to the change in the rate of distillation, since, after presumably a small amount of moisture had crept into Apparatus A. 2 and destroyed the distillation effect very considerably, the readiness of ebullition showed no corresponding change.

These facts suggest that intensive drying does not change the internal equilibrium between the various species of molecules, but that the effects observed are due to some other cause. The case may be parallel, perhaps, to that of a perfect crystal of a deliquescent or efflorescent substance, which remains quite stable so long as it is perfectly pure and subjected to no distortion. It seems probable that the prolonged contact with phosphoric oxide may cause the removal of nuclei of some type from the system, but whether this is a true drying effect or not is still uncertain.

Summary.

After intensive drying for a few months over phosphoric oxide, the rate of non-ebullitional distillation of ethyl bromide between bulbs at constant temperatures in a sealed apparatus was retarded considerably. The vapour pressure, however, remained unaltered and no difference could be detected between that of " head " and " tail " fractions after distillation. Ebullition occurred with considerably more difficulty in the dried liquid. The results are interpreted as indicating that the internal equilibrium in a liquid is not disturbed by intensive drying, but that the effects observed are due to some form of superheating, probably induced by the removal of nuclei of some type during the phosphoric oxide treatment.

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