

CCCL.—*The Influence of Intensive Drying on Inner Equilibria. Part III.*

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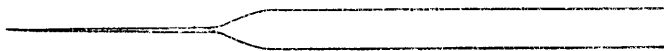
IN 1923 we began extensive investigations on intensive drying. Its influence on the boiling point of benzene was studied first: in agreement with the experiments of Baker, it was found that the boiling point of the intensively dried liquid was raised, and in agreement with experiments carried out by Smits in co-operation with Baker, it was observed that dried benzene behaved as a mixture (J., 1924, **125**, 1068).

These experiments did not settle whether this drying process was a fixation of the inner equilibrium, or whether it was a displacement of the inner equilibrium followed by fixation. As is shown in the "Theory of Allotropy," p. 320, the best way to answer this question is to study the influence of intensive drying on the vapour pressure, and since 1923 several pieces of apparatus for measuring vapour pressures have, therefore, been constructed in which different substances have been submitted to the process of intensive drying.

Since it was desirable to bring about intensive drying as rapidly as possible, the glass was first prepared. It is well known that any glass tubing contains extremely fine capillaries which may become filled with water during the cleaning process, and it requires a long treatment at high temperatures to remove the last traces of water.

To secure the removal of these capillaries each tube of high-melting Jena glass was first drawn out at one end (see Fig. 1), the capillaries at the sealed end being thus removed by fusion. The capillaries running along the wall of the tube are still open at the right-hand side, but all capillaries can be removed by slowly heating

FIG. 1.



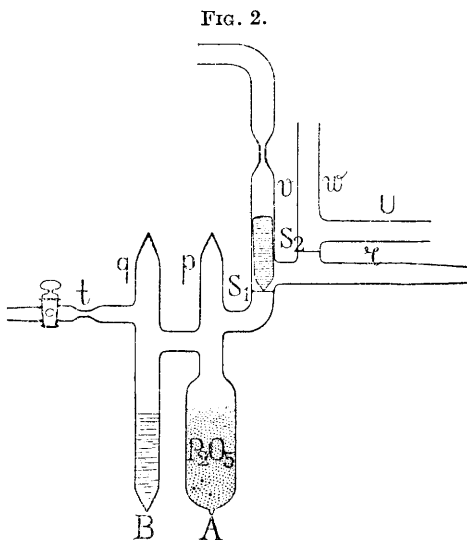
the tube from left to right to such a temperature that fusion takes place. The tubes obtained in this way have a different appearance and are more brilliant than those which have not been so treated; they look more like quartz glass, which is also free from capillaries—quartz has also been used in some cases.

In our recent work all apparatus was constructed from high-melting Jena glass, freed from capillaries as described. The apparatus was then cleaned with a solution of potassium chromate and nitric acid, steamed, heated in a current of dry air, and finally evacuated, to test whether it was completely air-tight.

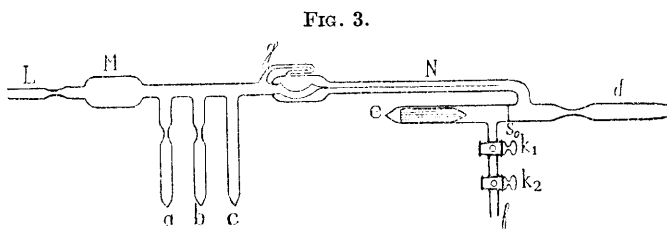
The removal of capillaries appeared to be extremely effective, since an apparatus with a volume of 2 litres could be evacuated within $\frac{1}{2}$ hour with the new Gaede steel mercury-vapour diffusion pump to such an extent that no discharge could be observed in the dark with a 3 cm. spark, even when the apparatus was heated to the melting point—a result which could never be obtained with glass not freed from capillaries.

The storage apparatus of capillary-free Jena glass, in which the substance to be studied was dried, is shown in Fig. 2. Before the vessel *B* was charged with this substance, phosphorus pentoxide had to be distilled into vessel *A*. Tube *p* was therefore sealed to the distilling tube, so that pure phosphorus pentoxide could be

distilled in a current of dried oxygen, whilst tube *q* was sealed off and *t* was connected to a U-tube containing phosphorus pentoxide and a wash-bottle of sulphuric acid. Previous to this, the apparatus was dried in the way previously described (J., 1924, 125, 2554). Pure phosphorus pentoxide was first distilled into vessel *A*, tube *q* opened, and vessel *B* filled with the substance to be studied, whilst a current of oxygen escaped by *q*, tube *t* being closed temporarily. After cooling *B* in a mixture of alcohol and solid carbon dioxide or in liquid air, *q* and *p* were sealed off successively and *t* was connected with the high-vacuum pump. When a high vacuum was reached, the capillary of tube *t* was sealed off. The substance in *B* was now distilled on to the phosphorus pentoxide in vessel *A*, and the storage apparatus was ready.



Two types of vapour-pressure apparatus were used, the first containing a glass-spring indicator and the second a mercury indicator. One of the first type is shown in Fig. 3. The newer patterns are made of capillary-free Jena glass with a glass-spring

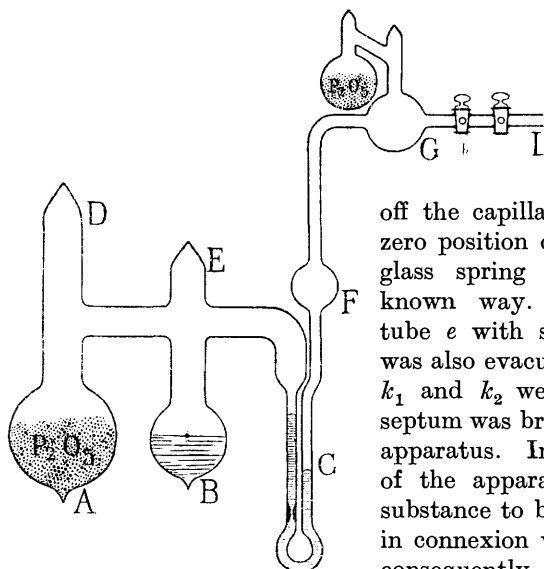


indicator substantially as described already (J., 1924, 125, 2554). The apparatus was filled in the following way: Vessel *M* was sealed to the phosphorus pentoxide distilling tube, and tube *d* to tube *r* of the storage apparatus, which had been allowed to stand for some months. After heating the tubes, vessels, and breaker in a current of dried oxygen, the capillary ends of the tubes *a*, *b*, and *c* were

sealed off successively, and finally the oxygen left the apparatus by way of the breaker-tube *v*, connected to a U-tube with phosphorus pentoxide and a wash-bottle containing sulphuric acid.

Pure phosphorus pentoxide was now distilled into vessel *M*, *L* was sealed off, and tube *v* connected to the mercury-diffusion pump. When a high vacuum had been reached, *v* was sealed off. The septum *S*₁ was now broken by shaking the apparatus, and a small quantity of the previously-dried substance was distilled into tube *c* by cooling the latter. After sealing off tube *d*, the vapour-tension

FIG. 4.



apparatus was set up rigidly, *M* cooled in liquid air, the connexion between the mantle of the glass spring and the vessel *M* broken by sealing

off the capillary tube *g*, and the zero position of the needle of the glass spring fixed in the well-known way. Subsequently the tube *e* with septum *S*₀ (Fig. 3) was also evacuated, the two cocks *k*₁ and *k*₂ were closed, and the septum was broken by shaking the apparatus. In this way, that part of the apparatus containing the substance to be studied was never in connexion with the cocks, and consequently it was completely

free from the vapour of the tap grease. After determinations of the vapour pressure at 20°, 30°, 40°, 50°, and 60°, the substance to be intensively dried was distilled on to the phosphorus pentoxide and the apparatus put aside.

The other type of vapour-pressure apparatus comprised a mercury indicator, such as has been used in this laboratory for many years. The construction of the apparatus, which is made of capillary-free Jena glass, is at once clear from Fig. 4, and it was filled as follows : Bulb *A* was filled with fine, distilled phosphorus pentoxide from a storage vessel and tube *D* sealed off while a strong current of dried nitrogen was passing through in the opposite direction. Bulb *B* was then filled in the same way with the substance to be studied and, after cooling this bulb, tube *E* was sealed off as short as possible. Subsequently bulb *G* was filled with about 10 c.c. of

pure dried mercury and sealed. Tube *L* was connected to the high-vacuum pump, whilst *B* was cooled in a bath of alcohol and solid carbon dioxide, or in liquid air, and bulb *A* was heated in a water-bath at 80°. In the meantime, the mercury was heated to drive out dissolved air. After closing cock *k*, the substance in bulb *B* was heated, to fusion if possible, and then cooled again. Cock *k* was then opened and the apparatus evacuated again. This process was repeated three times. Finally, cock *k* was closed again and the connexion to the high-vacuum pump broken. The tubes *C* were filled with mercury by inclining the apparatus, which was now ready. The mercury manometer is used here just as the glass spring is used in the first type and therefore we speak of a mercury indicator.

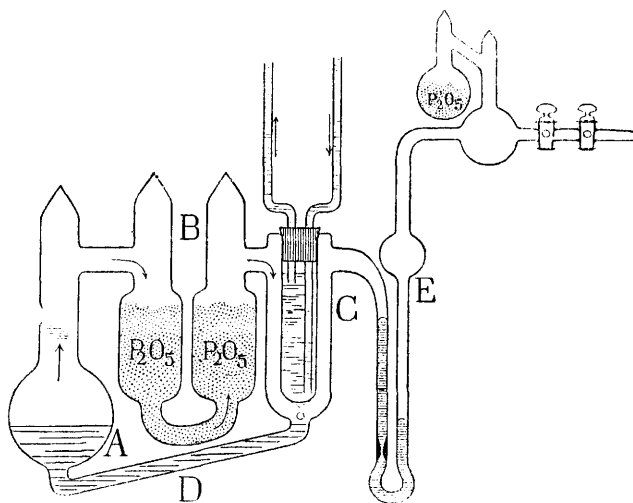
Wide tubes were considered very favourable for achieving rapid intensive drying, hence this last type of apparatus was made of tubes of 25 mm. internal diameter, and the quantity of phosphorus pentoxide was very large in proportion to the quantity of the substance to be dried. In our first investigations (1923), the quantity of phosphorus pentoxide was not so large and that is probably the reason why the experiments then made at 60° with a rather complicated apparatus containing a mercury indicator gave only negative results. At the time we thought this was due to the use of mercury and we continued our investigations with glass-spring indicators. Later, however, we found that the use of very pure dry mercury ought not to have an unfavourable influence, hence mercury was again used.

Since we wished to study the influence of distillation on the vapour pressure of intensively dried substances, it was necessary when using an apparatus of the first type (Fig. 3) that it should be provided with several tubes with capillaries. After a portion of the substance has been condensed in such a tube, the capillary can be sealed off and the vapour pressure determined again. The only difficulty here is that the process of intensive drying in an apparatus containing capillaries will require a much longer time than in an apparatus with very wide tubes.

With an apparatus of the second type (Fig. 4), capillaries are not necessary, for should it be desired to distil off a portion, it may be done quite easily in the following way. The pressure-difference between the left- and the right-hand side of the mercury indicator is raised to such a degree that the mercury is pressed up slowly into bulb *F* and vapour bubbles through it. When a sufficient quantity of the substance has been distilled off in this way, the mercury is passed back again into the U-tube *C* and the vapour pressure determined.

With the object of accelerating the drying process, we have modified the second type of apparatus in the way shown in Fig. 5. In this apparatus a circulation method is used especially for liquids. This circulation is caused by cooling the inner tube of the double-walled vessel *C* by means of a current of tap-water. Since the whole apparatus is placed in a bath at 45°, the vapour of the liquid is condensed on the outer wall of the inner tube of *C* and the condensed liquid drops into tube *D*, through which the liquid runs to the wide vessel *A*. Here the liquid is evaporated again, and after passing through the wide U-tubes, filled with very fine, pure phosphorus pentoxide, the vapour is again condensed in *C*, and so on.

FIG. 5.



This circulation is excellent; in an apparatus filled with 15 c.c. of benzene, 40 drops were formed per minute, so that the whole quantity in the vapour state passed through the U-tube containing phosphorus pentoxide about every 13 minutes—the rate may be regulated quite easily.

We have also constructed an apparatus which enables us to determine, not only the vapour tension of the residue, but also that of the distilled fraction. This apparatus, together with results obtained with carbon tetrachloride and benzene, will, however, be described in another paper. The present paper contains results obtained so far with nitrogen tetroxide and *n*-hexane with apparatus of the two types described. The vapour tensions of these dry, but not intensively dried, substances were determined in an apparatus of either type but without the bulb containing the phosphorus

pentoxide. The determinations were carried out at 20°, 30°, 40°, 50°, and 60°, so that the vapour-pressure curves of our preparations in the not-intensively dried state were known exactly.

In some experiments, the apparatus was placed in a bath at about 45°, and in others it was kept at room temperature, the intensive drying taking place at these temperatures. As is explained in the "Theory of Allotropy," it was very important to examine whether the vapour tension was changing *at these temperatures*, for, if this should be the case, a shifting of the inner equilibrium is proved. It is interesting also to determine the vapour pressures at intervals at higher temperatures, for, supposing the vapour pressure is not changed at the drying temperature, there is still the possibility that the inner equilibrium is fixed and that consequently the substance behaves as a mixture. If the temperature increases, a portion of the liquid evaporates and this brings about a change in the composition of the co-existing gaseous and liquid phases, which would correspond with a decrease in the vapour tension. That is the reason why the vapour pressure, although unchanged at the drying temperature, may show a decrease at higher temperatures.

At the same time, it follows that if the vapour pressure already decreases at the drying temperature, the decrease will become greater at higher temperatures. If, however, the vapour pressure increases at the drying temperature, this increase will become greater at slightly higher temperatures, but at still higher temperatures it will become smaller and may even change into a decrease.

Nitrogen Tetroxide.

We will first give the results obtained on drying nitrogen tetroxide, using three pieces of apparatus of the first type containing glass-spring indicators. The intensive drying here took place at room temperature. The nitrogen tetroxide had been prepared by Scheffer and Treub (*Z. physikal. Chem.*, 1912, **80**, 300) and the vapour-pressure curve as determined by these investigators was confirmed completely by our determinations. The phosphorus pentoxide was *completely* free from lower oxides.

Apparatus I (not capillary-free glass).

Duration of drying at room temp.	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
0	17.70°	64.9	64.8	+0.1
20 months	20.00	72.9	72.0	+0.9*
24 ,,	20.38	75.1	73.35	+1.7

* After 20 months there was liquid in the capillary tubes. These tubes were now turned upward and the liquid was run into the bulb with phosphorus pentoxide.

Apparatus II (not capillary-free glass).

Duration of drying at room temp.	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
$\frac{1}{2}$ month	22.00°	78.6	78.9	-0.3
3½ months	17.20	63.55	63.0	+0.5
20 "	19.80	72.4	71.2	+1.2
23 "	20.65	76.00	74.1	+1.9

On the day the last measurements were made we determined, with the same apparatus, vapour pressures at temperatures above the drying temperature, with the following results :

23 months	25.00°	92.95	90.6	+2.3
" "	30.05	114.95	113.0	+1.9

As was expected, as the temperature rose the pressure increase passed through a maximum.

A quarter of the liquid was now distilled off into one of the tubes, and after sealing this off the vapour pressure was determined again at the drying temperature, with the following result :

23 months	20.65°	74.65	74.2	+0.4
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Hence by distilling off a portion, the increase in the vapour pressure was diminished at 20.65° from +1.9 cm. to +0.4 cm. Eleven days later, the vapour pressure was again observed :

23¼ months	22.20°	81.07	79.60	+1.47
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Thus the vapour pressure after 11 days had nearly re-attained its value before distillation.

The experiment was now repeated and a portion distilled off again :

23¼ months	22.20°	79.60	79.60	0.00
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Again a decrease of the vapour pressure was observed, and it had become identical with the vapour pressure of the moist liquid at the same temperature. The following day, however, an increase of 0.5 cm. was again observed. It is proposed to study the change of the vapour pressure with the time after distillation with another apparatus filled with a larger quantity of nitrogen tetroxide. It should then be possible to change the increase into a decrease.

The results mentioned above show that the dried liquid behaves as a mixture, as though the inner equilibrium were not yet fixed. There is still a slow transformation in the direction of a new inner equilibrium, the position of which seems to be determined by the degree of dryness. The drying effect has not yet reached its maximum value in either of the two pieces of apparatus considered here; this can be proved by the results obtained with the third apparatus made of *capillary-free* Jena glass, which gave a larger

and still increasing effect in half the time, as is shown in the following table. Undoubtedly this rapid drying is to be ascribed to the use of capillary-free glass.

Apparatus III (capillary-free glass).

Duration of drying at room temp.	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
0	19.80°	72.1	72.2	-0.1
10 months	18.20	67.8	66.0	+1.8
10½ "	19.75	73.1	70.8	+2.3
11 "	19.55	73.0	70.3	+2.7
16 "	22.90	85.4	82.1	+3.3

This series of experiments shows a much more pronounced rise of vapour tension, which will probably reach a much higher value after a longer interval has elapsed. Therefore the distillation experiments were not repeated here; the vapour-pressure measurements at higher temperatures had been made after 13½ months:

13½ months	20.75°	77.59	74.4	+3.2
" "	25.23	95.33	90.9	+4.4
" "	29.55	113.20	110.8	+2.4

Again, it is seen that on raising the temperature above the temperature of intensive drying the increase of the vapour pressure passed through a maximum.

Colour of the Intensively Dried Liquid.

Finally, we have studied the influence of intensive drying on the colour of the liquid. Two pieces of apparatus, each containing an observation tube of exactly 5 mm. diameter, were filled with nitrogen tetroxide, but one contained purest distilled phosphorus pentoxide also. After 22 months equal quantities of tetroxide were condensed in the observation tubes of each piece of apparatus and the colour of the liquid columns was compared at the drying temperature. The dried liquid had become darker brownish-red than the moist liquid. It is clear that the changes of both the vapour pressure and the colour at the drying temperature prove that the drying process brings about a shift of the inner equilibrium in the direction $N_2O_4 \rightarrow 2NO_2$, *i.e.*, in the direction of an endothermic reaction.

It is of interest to notice that, whilst we find that the vapour pressure of nitrogen tetroxide is increased by the process of intensive drying, H. B. Baker and Mrs. Baker (J., 1912, **101**, 2239) found that the boiling point of the intensively dried liquid had risen more than 47°. This seems to be contradictory, but it is not really so. When the boiling point is determined in the way given by H. B.

Baker and Mrs. Baker, a certain amount of liquid evaporates before the boiling point is reached. Now it is evident that, although the inner equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ is shifted to the right-hand side, *i.e.*, the side of the more volatile pseudo-component, by intensive drying, which causes an increase in the vapour tension, a rise of the boiling point may nevertheless be observed, for, before the boiling point is reached, the liquid is partly evaporated, and while the inner transformations have become exceedingly slow, or have stopped completely, this evaporation will cause a change in the composition of the liquid, so that the vapour pressure, which showed an increase at first, now shows a decrease, corresponding with a rise of boiling point.

As Baker himself mentioned, it was not the true boiling point of the tetroxide which was observed: the liquid evaporated before the boiling point was reached and the thermometer recorded a temperature 47° above the boiling point. If the boiling point had been observed with the intensively dried liquid boiling under a reflux condenser while the volume of the vapour was kept very small, a *fall* in the boiling point should have been found, assuming the absence of superheating.

So we see that, as pointed out in "The Theory of Allotropy," p. 320, the determination of the vapour pressure is to be preferred for studying the process of intensive drying.

n-Hexane.

Among the substances which we have intensively dried at about 40° , none gave distinct effects as rapidly as hexane, although other substances behaved qualitatively in the same way, and the results with this compound are therefore given now:

Apparatus II (of capillary-free glass).

Duration of drying at <i>ca.</i> 40° .	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
0	42.20°	30.80	31.00	-0.20*
4 weeks	42.10	30.45	30.90	-0.45
7 "	42.20	30.48	31.00	-0.52
10 "	40.15	28.05	28.70	-0.65
14 "	46.13	34.90	35.80	-0.90

* The liquid used was previously kept in a bottle with phosphorus pentoxide. We found that already this preliminary drying had caused a decrease of the vapour pressure of about 0.2 cm.

In contrast with what is observed with nitrogen tetroxide, the process of intensive drying brings about a decrease of the vapour pressure. Consequently, in this case the inner equilibrium is shifted in the direction of the less volatile pseudo-component.

As mentioned above, it was to be expected in these circumstances that, for temperatures above the drying temperature, the lowering of the vapour pressure relative to that of not-intensively dried hexane would increase. We carried out these experiments at the moment the decrease of the vapour pressure at about 42° was -0.52 cm. The following table shows the results :

Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
42.20°	30.48	31.00	-0.52
50.76	41.75	42.30	-0.55
61.20	59.42	60.20	-0.78

After distilling off a portion, the vapour pressure was as follows :

42.8°	20.60	31.60	-11.00
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i.e., a very large decrease of the vapour pressure was found. This low vapour pressure, however, was not constant but rose slowly, so that after 2.5 hours the decrease was again about 1 cm.

Though the apparatus was in a thermostat, it was possible that, the liquid being partly distilled off, the temperature decreased. The following experiment was therefore carried out. The apparatus was taken out of the thermostat and placed on the table; after 2 hours, it had cooled to room temperature (the vapour pressure being 15 cm.) and was again placed in the thermostat, the rise of the vapour pressure with time being noted. The vapour pressure rose *very rapidly*, and the curve obtained in this way showed a very great difference from that obtained after distillation. It was thus proved that the slow rise of the vapour pressure after distillation was due to a slow inner transformation. From this we conclude that the inner equilibrium was not yet fixed, but the inner transformations were already very slow.

The original form of the explanation given by Smits (*Z. physikal. Chem.*, 1922, **100**, 477) of the observations made by H. B. Baker and Mrs. Baker (*J.*, 1912, **101**, 2339) was that by intensive drying the inner transformations in a unary phase are stopped, the inner equilibrium is fixed, and a mixture is obtained which on distillation will, in general, give a distillate with a lower boiling point (higher vapour pressure) and a residue with a higher boiling point (lower vapour pressure) than the original liquid. It was concluded that the boiling points observed by Baker were abnormally high because the liquid mixture before reaching the boiling point had already partly evaporated.

Subsequent to the Bakers' later investigations (*J.*, 1922, **121**, 568; 1924, **125**, 1068) Smits supplemented the original form of his explanation by the assumption that in the drying process the inner equilibrium can be displaced and *then* fixed. The experiments now

described with nitrogen tetroxide and hexane have proved that in these two cases the drying process effects a displacement of the inner equilibrium, and these two examples are contrasts, since in the case of nitrogen tetroxide the inner equilibrium is shifted in the direction of the more volatile, and in the case of hexane in the direction of the less volatile pseudo-component. Smits has indicated these two possibilities (see preceding paper).

From the fact that the effect obtained by partial distillation is followed by a return to the value before the distillation, it follows that the shifted inner equilibrium is not yet fixed.

It should be noted that Mali (*Z. anorg. Chem.*, 1925, **149**, 155) has studied the alteration of vapour pressure caused by drying carbon tetrachloride, benzene, and carbon disulphide for 5 months at 28° and also for 5 months at 44°. Since Mali did not record the vapour pressures of his moist preparations at different temperatures, it is safest to regard the vapour pressures of the preparations dried at 28° as corresponding with those of the moist substances; these preparations are hereafter, for the purpose of discussion only, referred to as the moist substances. The vapour pressures after 5 months' drying at 44° gave the following results on comparison with those of the moist substances, both kinds being at 44° :

Substances dried 5 months at 44°.	Drying effect at 44° (cm. Hg).
Carbon tetrachloride	—3·3
Benzene	—0·9
Carbon disulphide	—1·6

Hence Mali found very distinct decreases in the vapour pressures at the drying temperature after 5 months' drying at 44°. He did not emphasise the fact that only the results obtained at the drying temperature can throw light upon what happens in the drying process, but his conclusions are correct nevertheless.

Mali's experiments prove that the process of intensive drying produces a displacement of the inner equilibrium—in the direction of the less volatile pseudo-component in this instance. He did not distil the dried liquid but determined the vapour pressures at different temperatures. If we plot these vapour pressures against the temperature we see that the "moist" and "dry" curves at first diverge but subsequently converge at higher temperatures. The first effect is caused, as mentioned already, by the evaporation of the liquid, and the second is due, as we have found, to the fact that the mercury in the manometer is drying very slowly, so that, during the first period, the heating of the mercury causes a decrease in the degree of dryness. We found, on repeating the experiment after some weeks of intensive drying, that this effect of the mercury had diminished or vanished.

Mali's experiments show very distinctly, in agreement with ours, that intensive drying takes place more rapidly at 44° than at 28°.

Our next paper will deal with results obtained with other substances.

Summary.

In order to bring about intensive drying as rapidly as possible the glass was prepared by freeing it from its capillaries, and in the later experiments the apparatus was of high-melting Jena glass treated in this way.

Two types of vapour-pressure apparatus have been used: one with a glass-spring indicator and condensing tubes, and the other with a mercury indicator; in both cases the liquid from the storage vessel was distilled in the apparatus to effect intensive drying by purest distilled phosphorus pentoxide.

The second type of apparatus was made of wide tubes (25 mm. internal diameter) and the quantity of phosphorus pentoxide was relatively large, both these factors facilitating rapid intensive drying. An apparatus in which drying is expedited by a circulatory system is also described.

Some substances were dried at the ordinary temperature and some at about 45°. It was important to ascertain whether the vapour pressure was changing at the drying temperature, for, if so, a displacement of the inner equilibrium is proved (see "Theory of Allotropy").

The results are given of intensively drying nitrogen tetroxide at the ordinary temperature in an apparatus of the first type but with glass which had not been freed from capillaries: After 23 months' drying, the vapour pressure had risen 1.9 cm. Hg; a part of the liquid was distilled off and the increase in vapour pressure then fell to 0.4 cm., but after a further 11 days this had risen to 1.47 cm., *i.e.*, it had nearly regained its value before distillation.

In another apparatus, probably owing to the capillary-free glass, a greater drying effect was achieved in about half the time—after 16 months the vapour pressure had increased by 3.3 cm. On raising the temperature above that of the intensive drying, the increase of vapour pressure passed through a maximum, as had been anticipated on theoretical grounds.

The colour of the intensively dried liquid was a deeper brownish red than that of the "moist" liquid.

The changes of both the vapour pressure and the colour prove that the drying process had effected a displacement of the internal equilibrium in the direction $N_2O_4 \rightarrow 2NO_2$.

The observation of H. B. Baker and Mrs. Baker that the boiling

point of the intensively dried liquid had risen more than 30° can be explained by the fact that a certain amount of the liquid had evaporated before the boiling point was reached.

The second substance dealt with is hexane. In contrast with the case of nitrogen tetroxide, the intensive drying here effects a decrease of vapour pressure. Other substances give similar but less pronounced effects. After only 14 weeks the decrease of vapour pressure had reached 0.9 cm., showing that the internal equilibrium is here displaced in the direction of the less volatile pseudo-component. The decrease of vapour pressure was augmented by raising the temperature above that of the drying, and a strong effect was obtained by distilling off a portion of the liquid at the drying temperature, as was expected.

After distillation the vapour pressure tends to revert to that before distillation, and this fact indicates that the displaced inner equilibrium is not yet fixed.

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