# CCCLXI.—*The Influence of Intensive Drying on Inner Equilibria. Part V.*

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## *Experiments with* n-*Hexane.*

IN a former publication on this subject (J., 1926, 2667) we stated that when our vapour-pressure apparatus containing intensively dried *n*-hexane was placed in a thermostat at 42·8°, a considerable decrease of the vapour pressure was observed after one-third of the liquid had been distilled off, but this pressure gradually rose again as shown, and nearly reached its normal value after 2 hours :

(Distillation experiment I ; dried hexane.)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Mins. after distillation ... | 0 | 15 | 35 | 65 | 95 | 125 | 155 | 185 |
| Vapour press. (cm. Hg) ... | 22·0 | 26·2 | 28·2 | 29·9 | 30·7 | 30·8 | 30·9 | 30·9 |

It was thought possible that, although the apparatus was in a thermostat, the temperature of the phosphoric oxide and of that part of the hexane which was with it in the bulb, had decreased. Hence the following experiment was performed. The apparatus was taken out of the thermostat and placed on the table, during which period the greater part of the hexane condensed in a side tube which will hereafter be called the condensation tube. After 4 hours the vapour pressure, determined at room temperature (24°), was about 15 cm. Then the apparatus was replaced in the thermostat at 42·8° and the vapour pressure was found to rise with time, as follows :

("Dipping" experiment I; dried hexane.)

| Minutes | 0 | 2·5 | 5·5 | 9 | 12 | 19 | 28 | 51 | 64 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|
| Vapour press. (cm. Hg) | 22·0 | 25·2 | 26·3 | 26·9 | 28·4 | 29·2 | 30·1 | 30·6 | 30·85 | 30·85 |

This table shows that the vapour pressure rose slowly, but not so slowly as after the distillation experiment. Our conclusion, therefore, was that the intensively dried hexane, during the rapid distillation, behaved as a mixture, and that the slow rise of the vapour pressure after distillation was due to the slow establishment of the inner equilibrium that had not been fixed during 6 months' drying. Later, however, not feeling completely satisfied with this explanation, we thought it desirable to carry out the two characteristic experiments mentioned above with an apparatus of exactly the same shape and size and filled with the same quantities of phosphoric oxide and hexane, the latter being moist. Since it was our intention to prevent the hexane from being dried by the phosphoric oxide, the experiment was carried out in the following way. Immediately after filling, the moist hexane was kept in the condensation tube by cooling the latter. Then the cooling bath was removed, and when the liquid had risen to room temperature (vapour pressure about 15 cm.), the apparatus was placed in the bath at 42° and the increase of vapour pressure with time was measured. It must be mentioned that, since the phosphoric oxide does not attain the temperature of the bath as rapidly as the hexane in the condensation tube, a part of the hexane condenses in the bulb containing this oxide. This might, of course, have been prevented if, before the experiment, we had heated the bulb with the pentoxide to slightly above the bath temperature, but we omitted this precaution because our earlier experiments had been carried out without it. We did not fear any influence of drying, however, since part of the moist hexane was left in the condensation tube. The result of this experiment was a very rapid rise in pressure, thus :

("Dipping" experiment II; moist hexane.)

| Time after placing in bath (mins.) | 0 | 1 | 2 | 5 | 7 | 10 |
|---|---|---|---|---|---|---|
| Vapour press. (cm. Hg) | 22·0 | 23·0 | 24·7 | 27·2 | 28·1 | 29·2 |
| Time after placing in bath (mins.) | 13 | 19 | 23 | 39 | 60 | |
| Vapour press. (cm. Hg) | 29·6 | 30·2 | 30·3 | 30·4 | 30·4 | |

Immediately after this experiment, the apparatus being still in the bath and only a small part of the hexane being left in the condensation tube, one-third of the hexane was distilled off, and the change of vapour pressure with time measured. This distillation, which can be compared with our first experiment with dried hexane, gave the following results, which show that the vapour pressure increased just as rapidly as in the preceding experiment.

(Distillation experiment II; moist hexane.)

| Mins. after distillation | 0 | 0·75 | 2·75 | 5·5 | 9 | 12·5 | 17 | 23 | 45 |
|---|---|---|---|---|---|---|---|---|---|
| Vapour press. (cm. Hg) | 22·0 | 23·7 | 25·9 | 27·4 | 29·0 | 29·7 | 30·2 | 30·4 | 30·4 |

Further, we see that here the vapour pressure rises much more rapidly than in the first "dipping" experiment with dried hexane, where, at the beginning of the experiment, there had certainly been more liquid in the condensation tube.

We have communicated these experiments expressly to show that one may easily obtain results giving the impression that a drying effect is present. Let us therefore consider how a legitimate drying effect would manifest itself in the experiments mentioned. If the establishment of the inner equilibrium is appreciably retarded by drying, and the heating takes place so rapidly that the inner transformations cannot immediately follow the rise of temperature, the vapour pressures at the different temperatures of the liquid will not correspond to the ordinary vapour pressures, obtained after inner equilibrium has been established. (In a future communication, it will be shown that, according to the nature of the liquid, the vapour pressure may be either too low or too high.) If the velocity of heating is diminished continuously, this difference will decrease and finally disappear completely. In the experiments now described, the apparatus having room temperature was dipped in a bath at about 42°. If now the rate of rise of temperature of the hexane had always been the same, so that, *e.g.*, 20 minutes after the dipping, the hexane had in every case attained the bath temperature, then those experiments in which the vapour pressure after 20 minutes had not yet reached the final value would indicate a drying effect, which would be the stronger the longer the time necessary to reach this final value.

It was thus of interest to follow the rise of temperature, and accordingly we repeated some experiments with an apparatus of exactly the same construction, but containing a thermometer with its bulb immersed in the centre of the phosphoric oxide (of which more was used than ever before), since it was necessary to know the lowest temperature in the apparatus. It is obvious that, for the rapid establishment of temperature equilibrium, the presence of liquid hexane in contact with the glass wall is a very favourable circumstance. The liquid, having a greater conductivity for heat than the finely divided phosphoric oxide, takes up the heat rapidly and is distilled to the colder pentoxide, where its heat of condensation effects a more rapid heating of the latter. The retarding influence of phosphoric oxide is illustrated by an experiment with the same apparatus filled with the same quantity of hexane, the bulb for the pentoxide, however, being left empty: when this apparatus was placed in the bath, a vapour pressure corresponding with the bath temperature was reached within 5 minutes. From this point of view, it is evident that it may make a great difference whether the hexane is poured into the bulb with phosphoric oxide without shaking, the liquid being in contact with the wall, or whether the liquid and pentoxide are shaken together, so that a paste is obtained more or less surrounded by the badly conducting pentoxide. Table I shows the results; the rise of temperature in the phosphoric oxide bulb and the rise of vapour pressure with time are recorded, together with the vapour pressures corresponding with the temperature of the pentoxide, all vapour pressures being in cm. of mercury. Table II gives the result of another experiment after all the hexane had been poured into the phosphoric oxide bulb and strongly shaken.

TABLE I.

"Dipping" experiment III; moist hexane. (All hexane poured into the bulb with phosphoric oxide, without shaking.)

Bath temperature 41·7°.

| Mins. after placing in bath. | Temp. of $P_2O_5$. | V.P., calc., in cm. Hg. | V.P., obs., in cm. Hg. | Diff., in cm. Hg. |
|---|---|---|---|---|
| 0 | 28·0° | 17·29 | 17·60 | +0·31 |
| 2 | 34·75 | 22·95 | 23·16 | +0·21 |
| 4 | 37·9 | 26·02 | 26·17 | +0·15 |
| 6 | 40·3 | 28·50 | 28·10 | −0·40 |
| 8 | 40·85 | 29·10 | 29·29 | +0·19 |
| 10 | 41·3 | 29·66 | 29·91 | +0·25 |
| 13 | 41·6 | 30·00 | 30·13 | +0·13 |
| 16 | 41·7 | 30·10 | 30·12 | +0·02 |

TABLE II.

"Dipping" experiment IV; moist hexane. (All hexane in the bulb with $P_2O_5$ and shaken.)

Bath temperature 41·7°.

| Mins. after placing in bath. | Temp. of $P_2O_5$. | V.P., calc., in cm. Hg. | V.P., obs., in cm. Hg. | Diff., in cm. Hg. |
|---|---|---|---|---|
| 0 | 27·65° | 16·99 | 16·73 | −0·26 |
| 1 | 30·0 | 18·80 | 19·15 | +0·35 |
| 3 | 31·8 | 20·30 | 20·71 | +0·41 |
| 5 | 33·7 | 21·96 | 22·22 | +0·26 |
| 7 | 35·45 | 23·60 | 23·78 | +0·18 |
| 10 | 36·85 | 24·97 | 25·08 | +0·11 |
| 12 | 37·9 | 26·02 | 26·20 | +0·18 |
| 14 | 38·85 | 26·95 | 27·14 | +0·19 |
| 17 | 39·7 | 27·90 | 28·07 | +0·17 |
| 20 | 40·35 | 28·54 | 28·79 | +0·25 |
| 23 | 40·8 | 29·10 | 29·32 | +0·22 |
| 26 | 41·35 | 29·70 | 29·72 | +0·02 |
| 30 | 41·55 | 29·90 | 29·92 | +0·02 |
| 34 | 41·7 | 30·10 | 30·12 | +0·02 |

These tables show that the measured vapour pressure was slightly higher than that which would be expected from the temperature of the phosphoric oxide. It is interesting to notice that, although distillation was taking place in the apparatus, this did not prevent the principle of Watt from holding. These results also demonstrate that the time required for the pentoxide to reach the bath temperature depended on whether the liquid had been mixed with the pentoxide by shaking or not. In the first case the time required was 34 minutes, and in the second only 16. The fact that the measured pressure always corresponds with that required by the temperature of the centre of the mass of the pentoxide proves that this difference is not due to drying which has taken place during the experiment. Other experiments have been carried out in apparatus containing an extremely large amount of pentoxide, and in all cases this reached the bath temperature within 35 minutes. These experiments seem to us to be extremely important when considering results attributed to intensive drying. Unfortunately, the apparatus with which the experiments on dried hexane were carried out did not contain a thermometer, but it did contain considerably less phosphoric oxide and most of the liquid was kept in the side tube. In spite of these conditions, which are favourable for rapid heating, we have seen that the vapour pressure only became constant after 64 minutes.

If it were justifiable to assume that in this case also the inner part of the phosphoric oxide had reached the bath-temperature in 35 minutes, we might have concluded that the establishment of the inner equilibrium was distinctly retarded, but now we are not sure. Another point is this : we have seen that the observed vapour pressure, even during the distillation of hexane to the colder inner part of the pentoxide, corresponds practically with this lowest temperature, and from this it seems most probable that the temperature at the first reading in the distillation experiment I was the same as in the second " dipping " experiment. Now the remarkable thing is that, whilst in the first experiment a constant pressure was only reached after 2 hours, in the second it did not increase after 64 minutes. This difference may be explained by the fact that in the second experiment the greater part of the liquid was in the condensation tube. However this may be, it seems necessary, if convincing results are to be obtained, to repeat these drying experiments with a thermometer in the bulb with phosphoric oxide : the results of such experiments will be communicated later.

### *Experiments with Nitrogen Tetroxide.*

We have some additional results to report on the intensive drying of nitrogen tetroxide. It has been observed that, a few days after being filled, our vapour-pressure apparatus containing highly purified, freshly distilled phosphoric oxide and the purest nitrogen tetroxide, which had previously been dried over phosphoric oxide, showed a pressure increase of some cm. of mercury. Since a trace of water in the gas would not cause a permanent increase of pressure, we attributed it to the presence of a trace of nitric acid, which reacted thus: $4HNO_3 + 2P_2O_5 = 4HPO_3 + 2N_2O_5$; $2N_2O_5 = 2N_2O_4 + O_2$. Further, it appeared that there was a residual pressure in the apparatus after the side tube had been cooled in liquid air; this is in agreement with the above assumption, and also indicates that further evacuation should remove the disturbing factor. An apparatus was constructed with two septa so that, after being dried for a time, it could be re-evacuated and sealed off again from the pump. The results of this experiment are given in Table III.

TABLE III.

| Time after filling. | Temp. of observation. | Pressure of drying liquid, in cm. Hg. | Pressure of moist liquid, in cm. Hg. | Diff., in cm. Hg. |
|---|---|---|---|---|
| 1 Day | 21·08° | 78·40 | 75·52 | +2·88 |
| 6 Days | 21·72 | 83·20 | 77·90 | 5·30 |
| 2½ Months | 19·34 | 75·43 | 69·43 | 6·00 |
| The apparatus was then evacuated again and sealed off, and measurements were repeated on the same day and on three other occasions. | | | | |
| 2½ Months | 20·22 | 72·45 | 72·44 | +0·01 |
| ,, ,, + 1 day | 20·05 | 72·36 | 71·90 | 0·46 |
| ,, ,, + 7 days | 21·80 | 78·64 | 78·20 | 0·44 |
| ,, ,, + 1 month | 23·36 | 84·56 | 83·68 | 0·88 |
| The apparatus was once more evacuated and sealed off. | | | | |
| 3½ Months | 21·85 | 78·45 | 78·40 | +0·05 |
| ,, ,, + 1 day | 22·73 | 82·06 | 81·48 | 0·58 |
| 6 ,, | 20·06 | 72·64 | 71·80 | 0·64 |
| 9 ,, | 20·14 | 72·90 | 72·10 | 0·80 |
| 14 ,, | 18·22 | 66·53 | 65·90 | 0·63 |
| 19 ,, | 18·26 | 66·74 | 66·00 | 0·74 |

The same experiments were repeated with a second apparatus which gave the results shown in Table IV. This second apparatus was unfortunately broken on the day of the last observation. From all these experiments we see that there is a relatively large increase of the vapour pressure after some days' drying. Each time the apparatus was evacuated the nitrogen tetroxide was cooled in liquid air, the apparatus connected to the pumps, the septum broken, and the remaining gas removed. After the nitrogen tetroxide was melted and resolidified, the apparatus was re-evacuated and this process repeated three times. It is evident that it is not certain that all the gas could be removed in this way, since a small part of it might have been dissolved in the solid nitrogen tetroxide at −190°.

TABLE IV.

| Time after filling. | Temp. of observation. | Pressure of drying liquid, in cm. Hg. | Pressure of moist liquid, in cm. Hg. | Diff., in cm. Hg. |
|---|---|---|---|---|
| Same day ............... | 16·87° | 61·80 | 61·80 | 0 |
| 1 Day .................. | 15·89 | 61·30 | 58·90 | +2·40 |
| 1 Month and 10 days | 20·63 | 79·27 | 73·90 | 5·37 |
| After 1 month and 13 days the apparatus was again evacuated and sealed off. | | | | |
| 1 Month and 17 days | 15·95 | 59·57 | 59·05 | 0·52 |
| 2 Months ,, 21 ,, | 17·60 | 64·60 | 63·97 | 0·63 |
| After 3 months and 7 days it was again evacuated and sealed off. | | | | |
| 3 Months and 7 days | 19·58 | 70·26 | 70·20 | 0·06 |
| 3 ,, ,, 8 ,, | 18·53 | 67·44 | 66·85 | 0·59 |

Measurements immediately after evacuation and sealing off showed, however, that the vapour pressure was then practically normal. From the above it seems probable that the observed increases in the vapour pressure of nitrogen tetroxide on prolonged drying do not indicate that the inner equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ has been shifted to the right, but must be attributed to the action described. Therefore the change in colour (J., 1926, 2667) remains as the only valid indication that there is any displacement in inner equilibrium and this phenomenon must be studied again as accurately as possible.

### *Experiments with Ammonia.*

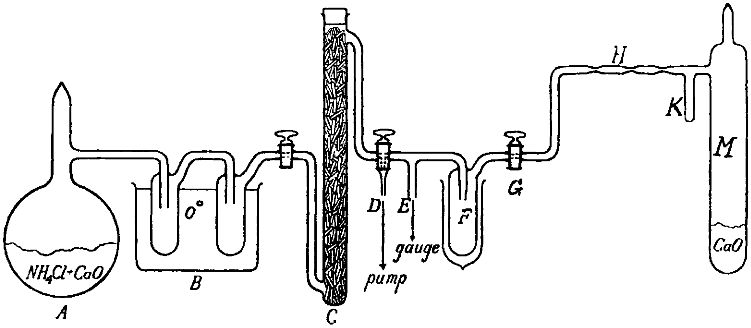
It is known that Baker has dried ammonia intensively over phosphoric oxide after pre-drying over calcium oxide. Several investigators have tried to repeat this experiment, but none has succeeded. Tramm (*Z. physikal. Chem.*, 1923, **105**, 398) writes : " Wenn wir den nach der Bakerschen Vorschrift getrockneten Ammoniak zu dem trocknen Phosphorpentoxyd treten liessen, erfolgte momentane Vereinigung unter starker Wärme Entwickelung. Dann versuchten wir den Ammoniak über Bariumoxyd zu trocknen. Wir vermieden jegliche Hähne. Die Gefässe waren durch Erhitzen im Hochvakuum sorgfältig von Wasserdampf befreit. Wir kondensierten den Ammoniak zur Trocknung über metallischen Natrium, das sich in ihm zu einer blauen Flüssigkeit löst und sehr scharf trocknend wirkt. Alle diese Massnahmen waren vergeblich. Der Ammoniak reagierte stets sofort mit dem sorgfältig sublimierten Phosphorpentoxyd."

Only if the ammonia had finally been passed through a liquid mixture of sodium and potassium could Tramm have obtained ammonia that would not react with phosphoric oxide. He did not determine whether there was an " absorption " by measuring the pressure. Had he done so, he would certainly have found that after some days the ammonia had almost completely disappeared. This conclusion follows from the fact that, after moist air had entered the apparatus in which dried hydrogen chloride and also dried ammonia were present, as he assumed, not a thick cloud, but only "*ein weisser Beschlag* von chlorammonium auftrat."

We observed this several years ago, but, in this case, we did not consider the experiment a successful one.

However, we are glad to be able to report that after some unsuccessful attempts we have carried out Baker's directions satisfactorily, and have been able to keep ammonia over phosphoric oxide for a number of years. For the preparation of the ammonia we used ammonium chloride, purified according to Baker's method (J., 1898, **73**, 422), and calcium oxide prepared from purest marble. The apparatus (Fig. 1) consisted of a 1-litre fractionation vessel *A*, two condensation vessels *B*, blown in one piece, a vertical tube *C* (5 cm. internal diameter and 120 cm. high) filled with sticks of potassium hydroxide, and a three-way cock *D*, the vertical tube of which led to the air pump, and the third to a **T**-piece. The vertical tube of the latter was connected at *E* to an open mercury manometer, and the other tube was sealed to a condensation vessel *F*, of 4 cm. internal diameter and 20 cm. high, with an inner tube 6 cm. long. The outlet tube of *F* was sealed to a tap, which was not lubricated but polished with stannic oxide and dipped in a vessel with mercury.* At the other side this tap was connected to a large cylinder *M*, in which the ammonia was stored over calcium oxide; this had an inner diameter of 8 cm. and a length of 150 cm., and was provided with a condensation tube *K*, and a tube *H* with two or more capillaries. Before *M* was filled with calcium oxide, this cylinder, the condensation tube *K*, and the tube *H* had been baked out in a current of dried air.

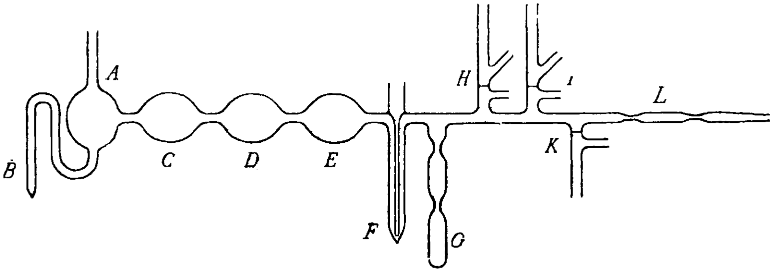
FIG. 1.



* The figure is drawn schematically.

After *A* had been filled with a mixture of ammonium chloride and 100% excess of freshly prepared calcium oxide, the filling tube was sealed off and the whole apparatus evacuated. Then the condensation vessels *B* were placed in a bath at 0° to condense moisture and the vessel *A* was carefully heated on a sand-bath, whilst the condensation vessel *F* was placed in a Dewar vessel filled with alcohol and solid carbon dioxide, the cock *G* being closed. When the evolution of ammonia had stopped, the Dewar vessel was replaced by one containing liquid air, and then the three-way tap *D* was turned in order that the right-hand part of the apparatus could be evacuated once more. Now the second Dewar vessel was removed and replaced by one containing cooled alcohol; the solid ammonia melted, and whilst there was still connexion with the pump, one-third of the liquid was evaporated. Then tap *D* was turned so that connexion with the pump was broken, cock *G* was opened, the middle fraction of the liquid ammonia was distilled carefully into the tube *K*, and the extreme left-hand capillary of *H* was sealed off. The liquid ammonia in *K* was now evaporated, and the cylinder was brought to a horizontal position, shaken in order to spread out the calcium oxide as much as possible, and stored in this position.

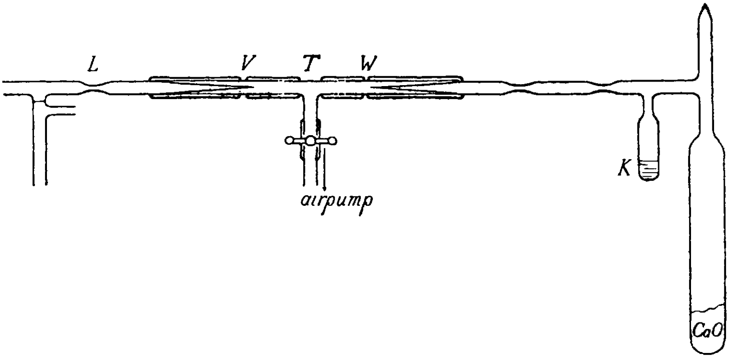
FIG. 2.



In the meantime, an apparatus, which we refer to as a four-bulb apparatus, was constructed for the intensive drying of the ammonia by pure phosphoric oxide. It was made of streak-free, high-melting Jena glass (see Fig. 2) and contained, besides the four bulbs of 500 c.c. each, a vessel *F* with an inner tube for the determination of the melting point, a tube *G* which enabled us to study the influence of a partial distillation, and a number of **T**-pieces, *H*, *I*, *K*, with septa.

After the apparatus had been cleaned with sodium dichromate and nitric acid, steamed, and dried by heating in a current of dried oxygen, the tube *A* was sealed to the bent part of the tube for the distillation of phosphoric oxide (see J., 1924, **125**, 1068). When the distilling tube had been filled with pentoxide, a stream of pure dry oxygen was passed, and every part of the four-bulb apparatus was baked out in turn. During the sublimation of the pentoxide the tube *L* was connected by a rubber tube to a U-tube containing pentoxide and a sulphuric acid wash-bottle through which the oxygen escaped to the air. All rubber tubes were cleaned by a warm solution of sodium hydroxide, washed with distilled water, and finally dried in a current of dried oxygen. If necessary, the rubber tube was closed by a pinch-cock. As we have already stated (*loc. cit.*), the sublimed coarse crystalline pentoxide is deposited in the bent part of the distilling tube and can be introduced into the first of the four bulbs by tapping with a thick rubber tube; when a sufficient quantity has thus been introduced, tube *A* is sealed off, a pinch-cock on the rubber tube on *L* is closed, its free end is connected to the mercury diffusion pump as quickly as possible, and the apparatus is evacuated. After the capillary on the extreme right of tube *L* is sealed, the pentoxide is divided between the four bulbs and the apparatus is ready to be filled with ammonia that has already stood drying over calcium oxide for at least two months.

FIG. 3.



For this purpose the four-bulb apparatus was connected (see Fig. 3) to the cylinder containing this ammonia by means of a T-piece *T*, which was joined to two steel tubes *V* and *W* by rubber tubes. Pieces of rubber tubing were attached to the free ends of the steel tubes, and then the T-piece and the rubber tubes were dried by a current of dried nitrogen. These rubber tubes were now pushed over the drawn-out and sealed tubes of the four-bulb apparatus and cylinder in such a way that the drawn-out parts were inside the steel tubes. The vertical tube of the T-piece was connected to the air pump, and the connecting rubber tube was provided with a pinch-cock. All rubber tubes were prepared and dried as before and were finally painted with picene. Then the ammonia was condensed in *K* and cooled by liquid air, the T-piece was evacuated, the drawn-out ends, which had previously been scratched by a glass-knife, were broken by moving the steel tubes, and the combined apparatus was once more evacuated as highly as possible. The connexion with the pump was broken by screwing up the pinch-cock, and by cooling one of the vertical tubes of the four-bulb apparatus ammonia was distilled into that apparatus. When a sufficient quantity had been distilled, the ammonia in both apparatus was cooled by liquid air and both were sealed off. The tube of the four-bulb apparatus in which the ammonia had been condensed was placed in an empty Dewar vessel to obtain a very slow evaporation.

Now it was found that if the previous drying had been very good, and the manipulations had been faultlessly carried out, the ammonia did not react at all with the phosphoric oxide. Sometimes the four-bulb apparatus contained also a glass-spring indicator which enabled us to determine the vapour pressure, and often the filling had been carried out so perfectly that even in a week no decrease of the pressure could be observed; for instance, in one case, when all the ammonia had evaporated, the pentoxide was completely loose and the pressure at 20° was 113 cm., whereas 9 days later it was 112·9 cm.: unfortunately, the glass spring was then broken.

If the previous drying of the ammonia had not been quite perfect, the appearance of the pentoxide did not change at all, and when the apparatus was shaken it became as loose as before, but some absorption of ammonia had taken place; this absorption soon decreased and the intensive drying took place without difficulty. If, however, the previous drying had been still less efficient, after some days all the ammonia was absorbed, although the pentoxide could be loosened by shaking and seemed completely unchanged. Further, if the previous drying had been quite inadequate, or if the filling had not been carried out perfectly, as was the case in our initial experiments, a reaction between ammonia and phosphoric oxide took place and a yellow or brown mass was formed with a large evolution of heat. Tramm's statement, " Der Ammoniak reagierte stets sofort mit dem sorgfältig sublimierten Phosphorpentoxyd," proves that his ammonia had not been sufficiently dried previously, or that the filling had not been carried out perfectly.

Although our definite experiments on the influence of intensive drying on the vapour pressure of solid and liquid ammonia are only in their early stages, we are able to report determinations of the melting point of intensively dried ammonia. For this purpose we used a four-bulb apparatus *A* in which ammonia had stood over phosphoric oxide since April 1923. In the same month, in order to have a standard for comparison, we filled a similar apparatus *B* with ammonia over calcium oxide. Some four years later (July 1927) a third apparatus *C* was filled with ammonia over phosphoric oxide.

For the actual determination of the melting point, we used a slight modification of the Poggendorff compensation method, the thermo-element being of copper (B and S 33) and constantan (B and S 30). The silk-covered wires had been soldered by silver, and the junctions had been treated with Bakelite varnish. One junction was dipped in the inner tube of the four-bulb apparatus, filled with a small quantity of mercury up to a height of 1 cm. (the surface of the mercury had to be a little lower than that of the condensed ammonia). As fixed points, we used the melting point of methyl alcohol (—98·5°), the sublimation point of carbon dioxide [$-78{\cdot}52° + 0{\cdot}16\ (b - 76)°$, $b$ being the barometric pressure], and the melting points of chloroform (— 63·7°) and mercury (— 38·89°).

When temperature–time curves for the melting of the ammonia were determined in March 1928, we found a horizontal part in the curve for each apparatus, corresponding with a temperature of $-77{\cdot}75° \pm 0{\cdot}02°$. Other determinations of the melting point of ammonia are: —77·70° (Postma, Thesis, Amsterdam, 1914), —77·71° (Henning, *Z. Physik*, 1921, **4**, 40, 226), —77·9° (Bergström, *J. Physical Chem.*, 1922, **26**, 358, 876), and —77·70° (Cragoe, Meijers, and Taylor, *J. Amer. Chem. Soc.*, 1920, **42**, 206).

From the fact that our ammonia dried over calcium oxide gave the same melting point as that dried over phosphoric oxide, even after 5 years' drying, we must conclude that most probably intensive drying for this period has no appreciable influence on the melting point of ammonia. Since it is necessary to obtain more certainty, we are repeating these experiments with a resistance thermometer. At the same time we shall study the influence of a partial distillation on the melting point and on the vapour pressure. We hope to be able to communicate results with hydrogen chloride later.

## *Summary.*

Velocity experiments on the vapour tension of *n*-hexane are described. Distillation and "dipping" experiments with both dried and moist hexane, in some of which a thermometer had been placed in the centre of the phosphoric oxide, have been carried out.

A difficulty encountered in the drying of nitrogen tetroxide has been overcome, and its bearing on previous work discussed.

From the melting-point determinations carried out up to the present, we must conclude that the melting point of ammonia has not been appreciably altered by 5 years' drying over phosphoric oxide.

THE UNIVERSITY, AMSTERDAM. [*Received, July* 17*th*, 1929.]