

Chemistry. — “*The Influence of Intensive Drying on Internal Conversion*”. I. By Prof. A. SMITS. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of March 24, 1923).

In December 1921 a communication was published in the 100th volume of the *Z. f. physik. Chemie* under the same title as is given above. In manuscript this communication was at first more extensive, for it also contained a possible explanation of the great influence found by BAKER of intensive drying on the chemical reactivity of gases, and besides a discussion of the sa-ammoniac problem¹⁾. The reason why for the present I withheld this part was as follows.

I was at the time still in doubt whether in intensive drying it should be assumed that a fixation or a shifting of the inner equilibrium takes place. The results of BAKER's researches²⁾ published then spoke greatly in favour of a shifting, but at first this assumption seemed open to objections, because it is then necessary to assume that the slightest trace of moisture can give rise to a great displacement of the inner equilibrium.

Afterwards, when BAKER had published³⁾ a new series of experiments, it seemed nevertheless the most probable conclusion that here a shifting of the inner equilibrium takes place, which from a thermodynamic standpoint means that very much work is required to withdraw the last traces of water from a system.

Accordingly I showed in the English and in the French edition of the *Theory of Allotropy*, in which I devoted a chapter to BAKER's experiments, that in my opinion intensive drying gives rise to a displacement of the internal equilibrium. Since then my own investigation, which I carried out with some of my pupils, has confirmed this supposition.

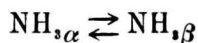
The explanation of the influence of intensive drying on reactivity, which I left unpublished so far, is exceedingly simple, for we

¹⁾ Also the influence of intensive drying on the properties of Sal ammoniac, becomes explicable, when this substance is assumed to contain two kinds of molecules, one of which is dissociable, and the other is not.

²⁾ *Trans. Chem. Soc.* **51**, 2339 (1903).

³⁾ *Trans. Chem. Soc.* **121**, 568 (1922).

have only to apply the theory of allotropy, i.e. we have to assume that every phase of these substances contains at least two different kinds of molecules, which are of course in inner equilibrium in the case of unary behaviour, to which we add the supposition that at least one of these kinds of molecules is chemically inactive. This is very well possible, since the mechanism of the transformation into another type of molecule will be an entirely different one from that of chemical action with other substances. To represent the case as simply as possible we can then assume that there are only two different kinds of molecules, one of which is active, the other inactive. When for ammonia we denote them by $\text{NH}_3\alpha$ and $\text{NH}_3\beta$, we have in each phase in the case of unary behaviour, the following inner equilibrium:



My supposition was this that on intensive drying this inner equilibrium is shifted towards the inactive side, and in this case, *completely*, so that in the ammonia remains that only contains the inactive kind of molecules.

I will just mention here that I emphatically pointed out before that the expression "different kinds of molecules" should be taken in its widest sense. It should comprise not only the isomer and polymer molecules, but also the electrically charged dissociation products, ions + electrons, and it stands to reason that in many cases the difference between the different kinds of molecules lies in a difference in the atomic structure.

It is particularly the more recent views of atomic structure that have brought to light that between the different atoms very subtle differences are possible, which are e.g. in connection with a change of the quanta values of the valency-electron-paths, and this leads to kinds of molecules with more subtle differences than those which are assumed to exist between the ordinary isomers. The fact, however, remains that also these different kinds of molecules may be ranged under this category when the sense in which the idea "isomery" is taken, is very wide.

During my investigation there appeared a publication by BALY and DUNCAN¹⁾, in which they communicate among other things that the rapidity at which gaseous ammonia, withdrawn from an iron cylinder with liquid ammonia, is decomposed by a platinum spiral heated at a definite temperature, is dependent on the velocity of evaporation of the liquid ammonia. On rapid evaporation ammonia gas

¹⁾ J. Chem. Soc. 121 en 122, 1008 (1922).

was obtained of much smaller velocity of decomposition than on slow evaporation. BALY and DUNCAN expressed the opinion that this difference is probably caused by this, that on rapid evaporation there is formed a gas phase rich in the kind of molecules that preponderate in the liquid phase, whereas on slow evaporation there has been a possibility for the conversion of this kind of molecules into another, of which the gas phase chiefly consists in ordinary circumstances.

One kind of molecules, which chiefly occurs in liquid ammonia, would then be the inactive kind, and the other kind of molecules, of which the ordinary ammonia gas chiefly consists, the active one. They further pointed out that the existence of inactive and active kinds of molecules probably accounts for the chemical inactivity of the gas dried by BAKER.

So we see that in this paper BALY and DUNCAN already express the supposition at which I had also arrived, though I did not publish it because my investigation was not yet sufficiently advanced. BALY-DUNCAN's results, however, are not very convincing, as BRISCOE¹⁾ observed, because they can also be explained in another way. He says: "It is known, that ordinary commercial ammonia, dried over lime, contains about 1 per cent of water²⁾, and that rapid, irreversible distillation, such as may occur by free discharge of gas from a cylinder of liquid, is a very effective means of separating the constituents even of a constant boiling mixture³⁾, so that the gas thus obtained may well be considerably drier than that in real equilibrium with the cylinder liquid. BALY has found that the addition of water vapour to ordinary ammonia increases its reactivity, drying certainly decreases its reactivity, and so the greater dryness of the "inactive" form would appear to be capable of explaining the whole of the observations, including the "recovery" of the gas in cylinders on standing (by acquisition of the equilibrium content of water vapour) identity of slowly released cylinder gas with laboratory preparations dried by lime, recovery of inactive gas in the experimental tube, when the wire is heated at 200° (release of absorbed water from the wire or walls) and the increase in reactivity of "inactive" ammonia with increase of temperature of the wire".

These remarks of BRISCOE's, which are very true in my opinion, deprive BALY's published experiments for the present of all their

¹⁾ Annual Reports of the Progress of Chemistry vol. 19 1922, p. 37.

²⁾ Briscoe refers here to WHITE T. 121, 1688 (1922), but this must be a mistake for WHITE has not found this.

³⁾ MULLIKEN J. Amer. Chem. Soc. 44, 2389 (1922).

cogeneity as a proof of the existence of an active and an inactive kind of molecules in ammonia.

I wanted to test my supposition in another way and took, accordingly, an entirely different course.

After having convinced myself that the pure P_2O_5 , which I prepared by BAKER's method, had really the same properties as that of BAKER¹⁾, I began with some of my pupils an investigation of the influence of intensive drying on the point of transition, the melting-point, the vapour tension of the solid and liquid state, and the electrical resistance of the liquid phase of a great number of substances, and among them those substances, of which BAKER found that the chemical activity disappeared by intensive drying, occupy a very particular place on account of the great importance of this phenomenon. Of this latter group first of all NH_3 , HCl , CO , and O_2 were taken in hand.

In a following communication our results and the particulars of the experiments will be discussed.

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Amsterdam, March 20th 1923.

¹⁾ I became acquainted with this method through a private communication by Prof BAKER before it was published, which saved me a great deal of trouble and time. I will avail myself of this opportunity to express my cordial thanks to Prof. BAKER for his kindness.