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Abnormal Vapor Densities

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Early in the present century, the Italian chemist, Avogadro, while studying the physical properties of gases was led to believe that "Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules." This is known as "Avogadro's Hypothesis," which is to-day one of the most important assumptions of chemical theory. For fifty years this hypothesis was tested in many ways, but was always found to be infallible. Among the facts which were finally brought forward as evidence against it were the abnormal vapor densities of some compounds, particularly of the ammonium salts. Many investigators now became interested in solving this problem.

In 1857 St. Claire Deville published his work on an investigation concerning the dissociation of chemical compounds by heat. Moved by this, Cannizaro, Kopp and Kekulae showed almost simultaneously that the abnormal vapor densities are the same as those which could be calculated for the compounds in question, on the assumption that they broke down under the influence of heat into components, which again combined on cooling. Kopp occupied himself with the vapor densities of ammonium chlorid, ammonium cyanide, phosphonium bromid, am-

monium sulphid, ammonium hydro-sulphid, phosphorus pentachlorid and amido-formic acid, all of which agreed with the vapor densities calculated under the acceptance of a decomposition. Now a violent dispute arose, as to whether components having a marked affinity for each other could exist uncombined, side by side, in a vapor.

Pabal made an experiment, in which he showed that out of the vapor of ammonium chlorid could be isolated, by diffusion, hydrochloric acid and ammonia. He placed the ammonium chlorid in the upper part of a tube above an asbestos stopper. Above this in the pointed end of the tube was a small opening, through which a small amount of hydrogen could be conducted. Over this he placed a second tube, which served also as a conductor of hydrogen. In order to ascertain the presence of ammonia and hydrochloric acid, the free hydrogen would be conducted by A and B over the wet litmus paper. When the apparatus was raised to the temperature at which ammonium chlorid would be quickly vaporized, the paper at B was turned blue by the diffusion of ammonia, because the lighter ammonia diffuses more quickly through the stopper

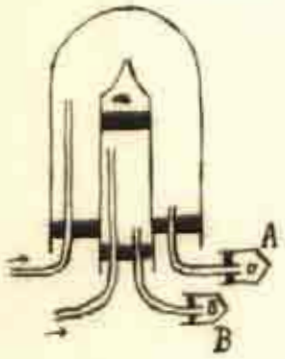

Fig. 1.

than the heavier hydrochloric acid. The residue in the upper part of the tube, contained therefore an excess of hydrochloric acid, which was displaced by the further evolution of ammonium chlorid vapor, and with the help of the current of hydrogen was led to A. The reaction was always sharp and indisputable. One of the chief objections made by many to Pebal's conclusion was a possible influence of the asbestos stoppers. Than performed this experiment in a simple manner, using ammonium chlorid itself for a diaphragm. His result was exactly the same as that of Pebal.

Wanklyn and Robinson sought to overcome this difficulty by letting the diffusion take place wholly without the diaphragm through the neck of a flask, as shown in Fig. 2. The wide opening of a second flask was pushed over the neck of a flask A, in which the vapor in question was present. Air was led into a tube which had been melted into the second flask, and escaped through the opening between the necks of the flasks.

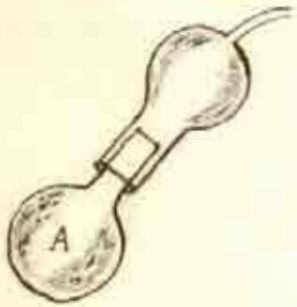

Fig 2.

These men tried sulfuric acid and phosphorus pentachlorid, finding that both gave undoubted decomposition. In the beginning of the experiment the sulfuric acid contained

five per cent. of water; after continuing an hour, there was forty per cent. of sulfur tri-oxid and sixty per cent. of sulfuric acid. In the experiment with phosphorus penta-chlorid they found free chlorine in the air, and the residue in the flask when dissolved in water with mercuric chlorid gave a precipitate of mercurous chlorid showing the formation of phosphorus tri-chlorid.

As a result of this work, which was carried on with the greatest circumspection, it follows that the vapor of ammonium chlorid consists chiefly of hydrochloric acid, ammonia and a little ammonium chlorid. The vapor density gave a higher result twenty-nine and two-tenths, which answered to a mixture of the above mentioned components. The result should have been twenty-six and seven-tenths if the vapor had consisted wholly of hydrochloric acid and ammonia.

The fact that a rising temperature helps decomposition received strong confirmation from an experiment of Würtz. He found that the amyl-compounds. amyl-bromid, amyl-chlorid and amyl-iodid were formed through the direct addition of hydrochloric acid, hydrobromic acid and hydriodic acid to amylene. He also showed that amyl-bromid, when heated 60° above its boiling-point, gave the normal vapor density 152

(the theoretical 151): but when heated to 360° , gave only the half density 71, analogous to a decomposition of the compound amyl-bromid into amylene and hydrobromic acid. In fact as the temperature increased from 152° to 360° , the vapor density diminished. The amyl-chlorid was not decomposed at a high temperature. The amyl-iodid , however, was not volatile without decomposition. This compound when heated slightly above the boiling point gave the density less than the theoretical. Würtz also showed that at 130° , where the amyl-iodid is still but slightly decomposed, when amylene and hydriodic acid were brought together there was a marked evolution of heat; while at 220° the heat evolution became very slight.

The objection of Deville, that the phenomena of the amyl-bromid could be explained by the acceptance of a variable coefficient of expansion, can be easily accounted for; because the so-called variable coefficient of expansion of Deville itself requires an explanation, which is given by the acceptance of a decomposition.

The scholars of the Polytechnique school of Paris, Deville at the head, carried on another series of similar experimental discussions. The theoretical vapor density for

phosphorus penta-chlorid is 208.3, for phosphorus tri-chlorid plus chlorine is 104.15.

Wanklyn and Robinson found in conducting their diffusion experiments, that vaporized phosphorus penta-chlorid gives off chlorine; so that the explanation of the changed vapor density through the acceptance of a partial decomposition into phosphorus tri-chlorid and chlorine was very satisfactory. For the substantiating of the decomposition, Deville stated that the vapor of phosphorus penta-chlorid by rising temperature showed more the greenish-yellow of free chlorine. And Würtz affirmed for his side, that phosphorus penta-chlorid, which at a comparatively low temperature was vaporized, in an atmosphere of phosphorus tri-chlorid showed nearly the theoretical density.

Against the reliability of this determination the objection of Troost and Hautefeuille was advanced, which was in part well founded. They pointed out that the calculation of the specific weights of the constituents of the gas mixture from the observed value, could give the correct result only, if the gas in question followed Boyle's law. This did not happen in the case mentioned. They showed how silicon tetra-chlorid and phosphorus tri-chlorid deviated from Boyle's law

about 2 per cent., and that the coefficient of expansion could rise from .00367 to .00489.

All that these considerations indicate is, that in the vapor of the tri-chlorid, the phosphorus penta-chlorid does not volatize entirely unchanged. A finally valid determination of the essential question, whether the variable density of the vapor under investigation is caused by a partial decomposition into phosphorus tri-chlorid and free chlorine or not, would be made by a quantitative determination of the amount of decomposition for different temperatures, together with simultaneous determinations of the vapor density. As means to this end, seem the quantitative determinations of Deville's researches concerning the color of chlorid vapors; which with the use of the spectroscope promise to give important results.

A similar problem for further discussion is that of chloral hydrate. The vapor density of this body corresponds to that of chloral and water; accordingly we are led to believe that these compounds occur separately in the vapor.

Troost questioned this theory. A vapor which contains both chloral and water must show the properties of a moist gas; but one in which the water is bound chemically that of a dry

gas. He used potassium oxalate; after introducing this into the vapor of the chloral hydrate, he observed an increase of tension, and therefore concluded that the gas was dry. Würtz performed several analogous experiments along this line, and found that by using pure potassium oxalate the tension of chloral hydrate vapor did not increase. Therefore Troost's work was erroneous because he used an impure chemical.

Then other experiments were undertaken, which attempted to show the decomposition of chloral hydrate vapor. Wiedermann and Schultze found that through diffusion, there is a separation in the water vapor and the chloral. Naumann proved that by distillation of chloral hydrate, a distillate poorer in water, and a residue richer in water resulted. Moitessier and Engel noted that at the boiling temperature of chloral hydrate the vapor tension is greater than the pressure of the air.

Troost tried to meet these objections, but with little success. Corresponding discussions have occurred concerning a number of similar compounds; ammonium sulfid, mercurous chlorid, pyro-sulfury-chlorid, etc. In all these instances, the carefulness with which the experiments were conducted, goes to show that there was a decomposition, in which the de-

composition products could be isolated.

Nevertheless, there is no method at present by which the quantity of dissociation can be determined, without taking the density into consideration. Hence Avogadro's law is open to the objection , that the decomposition has been shown in a very limited number of cases, and that the observed abnormal density may be due to the undecomposed vapor in question.

But what is of greatest weight in favor of the hypothesis is that the found abnormal densities, in so far as they no longer vary with the temperature, remain equal to the average density of the decomposition products.