mitted by state and Federal authorities in foods, and of the amounts normally present in plants and animals.

FARGO, NORTH DAKOTA

THE INFLUENCE OF WATER ON THE COMBINATION OF THE HALOGENS WITH HYDROGEN

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Recently Lewis and Rideal[1] have reported a research from which they conclude that intensive drying makes impossible not only the combination of hydrogen and chlorine, but also that of hydrogen and bromine and of hydrogen and iodine. They assume further, as a consequence, that all three reactions do not take place between the molecules but that in all these reactions the atoms of the halogens are the actual reacting substances.

We shall discuss not the authors' conclusions, but only their experiments, and shall correct an error which they have made in regard to the old equilibrium measurements on hydriodic acid.

Concerning this last point, they cite a table of 1894 which states that the equilibrium is not independent of the pressure, as required by theory. In doing so, they overlook the fact that this disagreement was the occasion of a thorough investigation[2] in which the basis of the discrepancy was fully cleared up; it lay in an error in the method of analysis used in the first research. In this paper we can add the following table, which was worked out some 15 years ago by Sachtleben for Bodenstein. His object was to show by exact measurements for lecture purposes the independence of the equilibrium from pressure.

Pressure of HI at filling (at 20°)	1 Atm.	$^2/_3$ Atm.	$^1/_3$ Atm.
Decomposed at 500°, %	23.94	24.01	24.12
Decomposed at 440°, %	21.88	22.06	21.96
Decomposed at 400°, %	20.49	20.67	20.36

These figures are certainly very useful for application in lectures, but their communication in a paper is certainly no longer necessary, for the proof that the decomposition of hydriodic acid obeys the law of mass action was given adequately in the paper[2] of 1897.

As to the probability that a reaction expressed by the equation $H_2 + I_2 = 2HI$, corresponding to an entirely correct bimolecular reaction, goes by means of atoms, we shall say nothing here. However, we shall show that the experiments of Lewis and Rideal are no evidence for this view, that in the intensively dried state the reaction goes differently than in the presence of water vapor.

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[1] Lewis and Rideal, THIS JOURNAL, **48**, 2553 (1926).

[2] Bodenstein, *Z. physik. Chem.*, **22**, 1 (1897).

In order to be sure of absolute drying, the authors placed phosphorus pentoxide in the tube which was to contain the hydriodic acid, and then heated this with the hydriodic acid. Here they obtained almost complete decomposition, while under ordinary conditions the decomposition in equilibrium amounts to only 21%. They ascribe the difference to the water content of the gases usually employed, and they do not observe that in doing so they have found a *perpetuum mobile*—introduce a trace of water vapor into dry, completely decomposed hydriodic acid and we obtain 21% decomposition by a reaction performing work, then remove the trace of water and we have 99% decomposition, again with the performance of work.

The basis of their observations is naturally that the strong reducing agent, hydriodic acid, reacts with the phosphorus pentoxide, forming water and iodine. Since they use the last substance as a measure of the change, it is not surprising that they find up to 99% decomposition.

It is scarcely necessary to confirm these ideas by particular experiments. Nevertheless, we have made a few such experiments, as is easily done. Some phosphorus pentoxide was sublimed into tubes of borosilicate glass of about 25 cc. capacity, the adsorbed oxygen was then thoroughly pumped off, and finally hydriodic acid was passed in up to 1 atm. pressure at 20°. The capillary stems of the tubes were sealed off and the tubes then heated in sulfur vapor. After this heating, one end of each tube was opened under a solution of potassium iodide. The solution entered the tube, leaving a volume of hydrogen which was determined by weighing the tube in this condition and when it was completely filled with solution. The iodine was determined by titration. The results were as follows.

Time of heating	Cc. of HI at filling	Cc. of I_2 after heating	Cc. of H_2 after heating	I_2 free, %	I_2/H_2
60 min.	21.88	6.74	0.45	61.6	15
75 min.	22.81	6.80	.57	59.6	12

The mass of the substances is given in cubic centimeters at 0° and 760 mm. This little table needs no addition. At most one can calculate the "equilibrium constants" from it; $K = [H_2].[I_2]/4[HI]^2$. They are 0.0095 and 0.0115. The correct constant for the temperature of sulfur vapor is 0.0198; the difference is not great and from the concurrence of both the reactions for the decomposition of hydriodic acid is quite intelligible.

Lewis and Rideal made similar measurements with hydrobromic acid with the difference that they investigated here the formation of the compound from the elements in the presence of phosphorus pentoxide. They found that experiments with the pentoxide were slower than those made without it. It was also possible here that hydrobromic acid reduced the pentoxide, forming free bromine and thus retarding the reaction. It is not easy to say whether or not this is correct; bromine is freed from hydrobromic acid with much greater difficulty than iodine from hydriodic acid. Consequently, we made some experiments in which tubes filled with phosphorus pentoxide and hydrobromic acid were heated.

The tubes showed, on removal from the sulfur vapor, a brown coloration of the intensity of about 75 mm. of bromine vapor at room temperature, which undoubtedly showed the presence of bromine. The color disappeared on cooling, however, and yellow crystals separated on the walls of the tube amongst the more or less melted pentoxide; these also gradually decomposed and disappeared.

The interpretation of these observations is doubtless as follows: on heating, the formation of phosphorus pentabromide takes place—$P_2O_5 + 10HBr = 2PBr_5 + 5H_2O$. The water is removed from the gas phase by the excess of pentoxide, so that it is not able to hydrolyze the pentabromide. Part of the pentabromide is of course broken up into phosphorus tribromide and bromine. This decomposition becomes less on cooling and the phosphorus pentabromide condenses, but then hydrolysis sets in. It is surprising that the solid is decomposed and not the vapor. However, phosgene in the gas phase also strongly resists the action of water vapor, while it is extraordinarily rapidly hydrolyzed by liquid.

It is impossible to prove these considerations by analysis of the contents of the tubes; the phosphorus pentabromide first formed would, after hydrolysis, appear only as hydrobromic acid. Therefore, one cannot say with the same finality as one can with hydriodic acid that the introduction of phosphorus pentoxide into the heated gas is an error, but its use clearly introduces uncertainty into the results.

Naturally we cannot conclude from the foregoing that intensive drying does not retard the action of hydrogen with bromine or iodine or that it makes it impossible; we must say that this retardation is absolutely unproved by the experiments of Lewis and Rideal.

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