2. A form of apparatus is described which has proved altogether satisfactory as a means of securing mixtures of air and carbon dioxide in fixed proportions. It could be used with equal success in other cases in which the composition of a gas phase must be maintained within narrow limits; for instance, to furnish constant mixtures of hydrogen with carbon dioxide, so as to enable one to apply the hydrogen electrode to carbonate solutions.

3. A modification of the Pettenkofer method of analysis is described, which yields more accurate results, particularly when the proportion of carbon dioxide is very small.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE INFLUENCE OF WATER ON CERTAIN CHEMICAL REACTIONS. I. THE EFFECT OF VARIOUS CONCENTRATIONS OF WATER VAPOR ON THE REACTION BETWEEN CHLORINE AND POTASSIUM IODIDE AND CHLORINE AND POTASSIUM BROMIDE[1]

BY L. B. PARSONS

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Although both solid potassium iodide and solid potassium bromide react immediately with moist chlorine to liberate the corresponding halogens, there is no appreciable reaction if the various substances are dry. The effect of different concentrations of water vapor upon these reactions constitutes the subject of this investigation. The method of attack consisted in passing chlorine containing a known concentration of water vapor over the potassium halides and subsequently determining the quantity of the halide converted to the chloride.

Method.—The extent of the reaction between the chlorine and the salts was measured by obtaining the loss in weight of the well-dried halide after the halogen set free by the chlorine had been removed by evacuating and heating to 200–250° in a current of dry air. Suitable precautions were taken to insure that at the initial and final weighings the walls of the reaction chamber were in the same state and that the material was dry. Since in most cases the loss in weight amounted to 0.003–0.1 g. this method gave sufficiently accurate results.

The partial pressure of the water vapor in the chlorine for amounts up to 15 mm. was controlled by bubbling the gas through saturators containing various concentrations of sulfuric acid at suitable temperatures; for partial pressures of water vapor greater than that indicated above, the gas was passed through water. The vapor pressures of the sulfuric acid solutions were interpolated from Sorel's data.[2] The saturators, leads

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[1] The work included in this paper is from the thesis presented by L. B. Parsons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

[2] Sorel, *Z. angew. Chem.*, 3, 272 (1889).

and reaction tubes were kept at suitable constant temperatures by means of three thermostats.

In all of the experiments the halides were recrystallized twice, dried at 120° and powdered while hot to 40–60 mesh. They were kept in a desiccator over phosphorus pentoxide until needed. From 1 to 2 g. of the halide was used in each experiment and it was shaken from time to time during the passage of the chlorine to prevent caking and to expose new surface. Ordinary tank chlorine, dried by two towers of sulfuric acid and four tubes of phosphorus pentoxide, was used.

Results. Potassium Iodide and Chlorine.—A number of experiments showed that dried chlorine had no appreciable effect on the weight of potassium iodide at room temperature (20–24°) even after the chlorine had been passed over it for longer than an hour. The only evidence of even a slight reaction was the fact that the iodide turned to a very pale straw color.

The following results show the effect of various concentrations of water vapor in the chlorine. In each case the chlorine was passed for one hour at the rate of 100 bubbles per minute at a temperature of 20–24°. Each result is an average of several experiments, the individual results differing by a few per cent. of their value.

TABLE I

EFFECT OF VARIOUS CONCENTRATIONS OF WATER VAPOR ON THE REACTION BETWEEN POTASSIUM IODIDE AND CHLORINE

Partial pressure of water vapor	0.0	4.2	7.3	10.0	14.2	23.5
Conversion of iodide, %	.04	0.4	1.7	3.6	5.6	10.7

The Effect of Temperature and Concentration of Water Vapor on the Reaction between Potassium Bromide and Chlorine

It was found in the preceding experiments that the potassium iodide became coated with a film of iodine which was very tenaciously adsorbed at the surface of the solid material. Moreover, the particles tended to stick together even at very low concentrations of water vapor. This necessitated constant shaking of the reaction chamber in order to have comparable conditions in the different experiments.

Experiments proved that potassium bromide was more suited to this investigation because the free bromine was very volatile and was swept out as fast as it was liberated. In addition, the particles did not have as great a tendency to stick together as in the case of potassium iodide. Further experiments were carried out with this material.

In the investigation with potassium iodide no attempt was made to control the temperature of the reaction chamber. It was thought advisable to make runs with potassium bromide at two different temperatures with various concentrations of water vapor in the system.

Table II shows the results of experiments at 20° and 30°.

The data in Table II show that there is a great and sudden increase in the percentage conversion of bromide to chloride at partial pressures of water vapor of 10–12 mm. and 19–22 mm. at temperatures of 20° and 30°, respectively. The great increase in conversion at these pressures and temperatures led to the idea that possibly the reaction was closely con-

TABLE II

THE EFFECT OF CONCENTRATION OF WATER VAPOR ON THE REACTION BETWEEN POTASSIUM BROMIDE AND CHLORINE

AT 20°

Partial pressure of water vapor	6.0	10.1	12.0	14.2	17.4
Conversion of bromide, %	0.5	1.6	12.5	14.5	20.3

AT 30°

Partial pressure of water vapor	14.2	19.6	22.1	25.0
Conversion of bromide, %	0.5	1.7	9.6	11.5

nected with the vapor pressure of a saturated solution of the several components in the system. Since this seemed to be the only possible explanation of the observations, measurements were made of the vapor pressures of the various solutions involved. The tensimeter method was used with concd. sulfuric acid in the zero bulb and a saturated solution of potassium chloride and potassium iodide in the presence of the crystals of these salts in the other bulb. Mercury was used as the balancing liquid, the vapor pressure being read off directly when equilibrium was attained. A value of 6 mm. at 21.5° was obtained.

Similar measurements were made on saturated potassium chloride and bromide solutions using duplicate tensimeters over a range of temperatures. These data are presented in Table III.

TABLE III

THE VAPOR PRESSURES OF A SATURATED SOLUTION OF POTASSIUM BROMIDE AND POTASSIUM CHLORIDE AT DIFFERENT TEMPERATURES

Temp., °C.	Vapor pressure, mm. of mercury		
	A	*B*	Av.
6.0	3.0	4.0	3.5
13.0	8.0	8.5	8.3
15.0	9.5	9.5	9.5
20.0	12.0	11.5	11.8
26.0	17.5	17.5	17.5
30.0	22.0	22.5	22.3

These values are not extremely accurate, but it is considered that the results are correct to ±1 mm., which is sufficient for the purpose.

Conclusions

From a consideration of the results presented in Table II it will be observed that at each temperature there is a minimum effective concentration of water vapor which must be present before any considerable reaction takes place. At a temperature of 20° the minimum effective concentration is at a partial water vapor pressure from 10–12 mm., while at 30° the corresponding value is from 19–22 mm.

The above results may be explained by the assumption that the reaction takes place in solution. If the partial water vapor pressure in the system is greater than the vapor pressure of a saturated solution of the various components, condensation would take place on the surface, and a solution would be formed. The amount of reaction would be dependent on several factors such as temperature, surface, rate of flow of chlorine, rates of diffusion, etc.

In Table III the observed vapor pressures of a solution saturated with potassium bromide and potassium chloride averaged 11.8 and 22.3 mm. at 20° and 30°, respectively. The close correspondence between the minimum effective concentrations and the vapor pressures of the saturated solutions cannot be entirely accidental.

In the case of potassium iodide and chlorine the point of minimum effective concentration is not so clearly marked. A study of Table I suggests that such a point does exist. The fact that there was no temperature control partly accounts for the obscuring of the result. The iodine replaced has, moreover, a much greater solubility than the bromine, and mention has been made of the adhesive nature of the reaction products. The vapor pressure of the saturated solution of potassium iodide and chloride was shown to be only 6 mm. at 21.5°. The vapor pressure of the saturated solution containing the reactants would no doubt be considerably below this value.

Summary

There is a minimum partial pressure of water vapor, for each temperature, which must be attained before any considerable reaction takes place between chlorine and potassium iodide or potassium bromide. This minimum effective partial pressure is approximately the vapor pressure of a saturated solution of the components present during the reaction.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE INFLUENCE OF WATER ON CERTAIN CHEMICAL REACTIONS. II. THE REACTION BETWEEN HYDROGEN SULFIDE AND IODINE IN ETHER SOLUTION[1,2]

BY L. B. PARSONS

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Although an enormous amount of research has been done on the influence of water on the rate of chemical reactions, most of the work has been qualitative in nature; very little attention has been given to the effect of changing the concentration of water. The object of this investigation

[1] The author wishes to acknowledge a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman, which made it possible to carry out this investigation.

[2] The work in this paper is from the thesis presented by L. B. Parsons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.