

ACTION OF HYDROCHLORIC ACID GAS UPON SULPHATES, SELENATES, TELLURATES, AND PHOSPHATES.

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EXPERIMENTS have been made at various times in this laboratory upon the action of the gaseous haloid acids on metallic oxides and sulphides. Frequently new methods of separation have resulted. These have proved very satisfactory in every respect, from the standpoint of the analyst.

In the following paragraphs we give additional data collected from the same field, and trust that they may not be devoid of interest to the reader.

Knowing that selenic and telluric acids could be expelled from their salts by hydrochloric acid gas we endeavored to ascertain whether, if a sulphate were mixed with one or both of the preceding salts, it would be possible to drive out the selenic or telluric acid and leave the sulphate intact. Accordingly a perfectly dry mixture of a sulphate and a selenate was exposed to the action of well-dried hydrochloric acid gas. The selenic acid was not only expelled but also varying amounts of sulphuric acid were driven out. Thus, two trials were made with definite amounts of the salts. The results were these:

Potassium sulphate taken. Gram.	Potassium selenate taken. Gram.	Sulphur remaining in the salt acted upon. Per cent.
0.4323	0.4567	33.59
0.3338	0.1583	33.51

In brief, about sixty-five per cent. of the sulphur originally contained in the potassium sulphate was expelled in the presence of the selenate. When a tellurate was mixed with the sulphate and the two subjected to the action of hydrochloric acid gas, not only was the tellurium driven out from its combination but the sulphur also in amounts, which varied with the working conditions. The original idea, therefore, of effecting a separation was abandoned.

We next exposed pure, dry potassium sulphate to the influence

of the haloid acid. A weighed amount of the salt was introduced into a porcelain boat, placed in a combustion tube of hard glass, through which the gas was conducted in the cold. It was very soon observed that the salt had increased very considerably in weight (as much as twelve per cent). After a time the boat was removed and the residue in it analyzed. Thus, 1.0896 grams of potassium sulphate after exposure for three and one-half hours to the gas, in the cold, weighed 1.1162 grams—an increase of 0.0266 gram. The salt was dissolved in water and the hydrochloric acid in it determined. It equaled 0.0268 gram, or a difference of 0.0002 gram from the observed increase in weight. This product (an addition product evidently) maintained its composition when exposed to 130° in a drying oven. It did not lose in weight on standing over soda-lime, in a vacuum desiccator, for fifteen hours.

When dry potassium sulphate was heated in hydrochloric acid gas from 200° to a dull red heat, an examination of the water in the receiving vessel showed the presence of sulphuric acid, while the substance remaining in the boat after this treatment weighed more than the original substance. It gave an acid reaction to litmus and decolorized a red phenolphthalein solution. As much as nineteen per cent. of the sulphuric acid in the salt was expelled in this way. The quantity of acid driven out was greater in the presence of a selenate or tellurate, equaling in several instances seventy-five per cent.

This deportment of sulphuric acid confirms an early observation of Heusgen,¹ who found that "Kalium sulfat wird weder in der Kälte noch bei gewöhnlicher Temperatur von Salzsäure angegriffen bei 360° liess sich in dem vorgelegten Wasser schon eine wägbare Menge Schwefelsäure nachweisen, bei dunkler Rothgluth erfolgt jedoch die Zersetzung *fast* quantitativ in Chlormetall und freie Schwefelsäure." The gas evidently attacks the salt in the cold. This is proved by the formation of the addition product. We never observed a complete elimination of the sulphuric acid. It was not, indeed '*fast quantitative*.' And, Prescott,² trying the action of aqueous hydrochloric acid upon metallic salts, observed that upon evaporating a gram of sodium sulphate with 4.035 grams of

¹ *Ber. d. chem. Ges.*, (1876), 1671.

² *Chem. News*, 36, 178.

aqueous hydrochloric acid, containing 1.251 grams of hydrochloric acid, he obtained only 0.070 gram of sodium chloride, and 0.807 gram of undecomposed sulphate remained.

The question as to how the sulphuric acid is expelled from its salt is worth consideration. The thought first suggested was that the addition compound, $K_2SO_4 + HCl$, is produced when the gas acts upon the salt, and this upon the application of heat decomposes, forming potassium chloride and acid potassium sulphate, the latter being changed by the same heat into $2KHSO_4 = K_2SO_4 + H_2O + SO_3$. If this were true then the addition compound, which in theory was formed at first, when heated alone in dry air should give up its sulphuric acid in part at least and it should be found in the water of the receiver. Several trials were made. Sulphuric acid was not found in the receiver, but instead about eighty-six per cent. of the hydrochloric acid originally present with the potassium sulphate was discovered to be there. After numerous experiments of various sorts we concluded that this remarkable expulsion of sulphuric acid from one of its stable salts is to be attributed to mass action. This is emphasized by its more complete expulsion when a selenate or a tellurate is present.

It is a well-established fact that phosphoric acid is not expelled by the gaseous haloid acids from its salts.

A mixture of dry sodium tellurate and dry sodium pyrophosphate was exposed to the action of hydrochloric acid gas. Care was taken that the temperature did not become so intense as to melt the mass in the boat. When this occurs the telluric acid is apparently reduced very rapidly. In the analysis, which will be introduced, the tellurium was merely expelled. No attempt was made to estimate its amount. The residual phosphate, after solution in water, was invariably examined for tellurium but it was not detected. The phosphoric acid was determined in the usual manner.

ANALYSES.

	Phosphorus present in the $Na_2P_2O_7$. Gram.	Amount of sodium tellurate taken. Gram.	Phosphorus found as $Mg_2P_2O_7$. Gram.
1	0.1030	0.1247	0.1026
2	0.1197	0.1632	0.1199
3	0.1096	0.0832	0.1094

Sodium selenate was next mixed with sodium pyrophosphate. Much less time was required for the volatilization of the selenic acid than for that of the telluric acid. The temperature was gradually raised to 450°C. It was not allowed, nor was it necessary, to go beyond this point.

ANALYSES.

	Phosphorus present in the $\text{Na}_2\text{P}_2\text{O}_7$ used. Gram.	Sodium selenate. Gram.	Phosphorus found as $\text{Mg}_2\text{P}_2\text{O}_7$. Gram.
1	0.0728	0.1763	0.0729
2	0.1057	0.2017	0.1054
3	0.1198	0.1416	0.1199

The preceding results with phosphates and tellurates and those with selenates and phosphates leave no doubt as to the complete separation of their respective acids, in the manner indicated. The method is free from all disturbing factors and may be executed without difficulty.

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THE PRECIPITATION OF COPPER BY ZINC.

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AT various times during the past year attempts have been made in this laboratory to make a direct comparison between silver and cadmium, with the hope that in this way the atomic mass of the latter metal might be definitely established. The most carefully purified metallic cadmium in weighed amounts was allowed to act upon various soluble salts of silver. The precipitation of the latter metal was rapid and complete. The results while very fair in a quantitative respect could not be used for the purpose designed. The precipitated silver contained cadmium. It was not undissolved portions of the latter but metal originating from the salt which was acted upon, which salt became in some way encased in the silver so that the most painstaking efforts failed to eliminate it. Nor did it seem to make any difference as to which silver salt was acted upon. Cadmium, in small amounts it is true, but nevertheless, cadmium was invariably discovered in the beautiful deposits of silver.