

crystallization, the salts differing in their degree of solubility in the menstruum employed, the crystals first formed will contain relatively a greater amount of the more insoluble salt, while the crystals formed at the end will be correspondingly rich in the more soluble salt.

Judged by these rules, Dr. Endemann's supposition seems to be contradicted by the facts brought out in the investigation.

In regard to the rule first laid down, I would call the attention of the Society to the dibromated compound, $K_2PtBr_2Cl_4$, described at the November meeting; this was formed when 0.5 grm $PtCl_4$ was added to 4.0 grms KBr in solution, the solution being kept cold. It will be perceived that the amount of KBr is here 12 times the quantity required to form the compound in question, yet in 3 experiments, the amount of Pt yielded on decomposing the salt, was 34.32 against a theoretical 34.35 per cent.

Not only this, but the experiment was performed under varying circumstances since, preserving the same amount of platinic chloride and potassium bromide in all, to the solution from which the first crystals were obtained, were added 2 c.c. of concentrated HCl , to the second solution 1 c.c., and the third solution none at all.

It would be supposed, that under these circumstances, the compound formed in the solution strongly acid, with HCl , if really a mixture of isomorphous salts, would contain more of the double chloride; but an analysis of the three salts produced showed no such result.

It is, however, chiefly on the second rule, that of fractional crystallization, that I would depend, as proving the chemical as opposed to the mechanical nature of these compounds.

The rule involved in fractional crystallization presupposes a difference in the solubility of the salts to be separated. If these salts are not isomorphous, they can be separated completely; on the other hand, if they have the same crystalline form, the crystals will contain both salts, one in part substituting the other.

Now, if the solution of these isomorphous salts of different solubility, is fractioned, the crystals produced will contain different proportions of the two salts, if they are mechanical compounds, while if a definite compound salt has been formed, the crystals produced at different concentrations will have a constant composition.

As to the constancy of these salts under fractional crystallization, let me select, as an example, the monobromated compound. In order to form it, 4.888 grms of K_2PtCl_6 , and 1.512 grm of K_2PtBr_6 , were employed. Three crops of the crystals yielded respectively, 36.97,

37.04 and 36.99 per cent. of platinum ; the theoretical percentage being 37.05.

It now remains to consider the difference in solubility of the double bromide, and double chloride of platinum and potassium.

As these salts were crystallized from boiling solutions, a comparison of solubility in water at 100° C. will answer the question.

The solubility of the double chloride in boiling water, as given by Elliot and Storer, is 1 part of the salt in 19 parts of water.

The solubility of the double bromide has never, so far as I can find, been published in anything but general terms; Elliot and Storer stating, "sparingly soluble in water, insoluble in alcohol."

I found it necessary, therefore, to determine the solubility of this salt in boiling water.

10 grms of the double bromide were kept at the boiling point, with 50 c.c. H_2O , for four hours, the flask being frequently shaken. The flask was heated by being placed inside of a beaker of water, kept boiling ; by this means, the contents of the flask were kept at 100° and, at the same time, so quiet, that a measured quantity of the clear solution could be easily removed by a pipette.

5 cubic centimeters were taken for the first trial, and yielded, by evaporation, and drying at 100° , 0.495 grm of K_2PtBr_6 ; after boiling one hour more, another 5 c.c. were taken, and 0.498 of the dried double bromide recovered ; as 5 c.c. of water at the boiling point, weigh not quite 5 grms, the solubility of the double bromide in boiling water is, as near as possible, 1 part in 10.

In concluding, I would remark that in the case of the monobromated compound, it seems impossible, on the supposition of isomorphous mixture, to have the double bromide crystallize out each time in the right proportion, when but one-third as much of it was employed as of the double chloride, and when its solubility is twice as great.

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