

only the delivery tube projecting into the same. This generator in daily and almost constant use has been found to work without refilling or other attention for three months at a time, and would perhaps be best appreciated in college laboratories and others requiring an abundant and reliable supply of hydrogen sulphide. It can also be advantageously employed for generating carbon dioxide, hydrogen, and other gases.

### A STUDY OF THE MIXED HALIDES AND HALO-THIO-CYANATES OF LEAD.

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IT has recently been shown<sup>1</sup> by one of us (Herty) that the so-called compound  $\text{Pb} \begin{matrix} \text{I} \\ \text{Cl} \end{matrix}$  is not a true chemical compound, but a mixture of lead chloride and lead iodide. More recently Herty and Smith<sup>2</sup> have confirmed McMurtry's<sup>3</sup> observation that the substance  $\text{Hg} \begin{matrix} \text{Cl} \\ \text{CNS} \end{matrix}$  is a true chemical compound, and not a mixture of mercuric chloride and mercuric thiocyanate. This suggested the question, Is the formation of mixed crystals in the one case and a true chemical compound in the other due to the character of the metal present or to the difference in the character of the negative radicals present in each case? To determine this a systematic investigation of the products formed by dissolving lead chloride and lead thiocyanate was undertaken. It has been found that  $\text{Pb} \begin{matrix} \text{Cl} \\ \text{CNS} \end{matrix}$  is a true chemical compound, just as in the case of  $\text{Hg} \begin{matrix} \text{Cl} \\ \text{CNS} \end{matrix}$ . Plainly, the character of the metal present is not the determining factor. If then, the difference be due to the character of the negative radicals present, the so-called salt  $\text{Hg} \begin{matrix} \text{I} \\ \text{Cl} \end{matrix}$  should be a mixture and not a true chemical compound.

However, before beginning work on this point, it has been deemed advisable to make a thorough study of the compounds of lead with the halogens and with thiocyanogen, including all

<sup>1</sup> *Am. Chem. J.*, 18, 293.

<sup>2</sup> *This Journal*, 18, 906.

<sup>3</sup> *J. Chem. Soc.*, 1889, 50.

possible combinations of these. In this way the following have been studied:

Lead chloride	with	lead	bromide.
“	“	“	“ iodide.
“	bromide	“	“ “
“	chloride	“	“ thiocyanate.
“	bromide	“	“ “
“	iodide	“	“ “

In each case seven solutions in water have been prepared, all containing the same weight of lead, but varying proportions of the acid radicals. The middle solution in each series contained the salts in centi-molecular proportions. In the other members of each series arbitrarily taken quantities of one substance were replaced by equivalent quantities of the other substance.

The hot solutions were allowed to crystallize and the crystals thus obtained were dried by pressing between folds of drying paper. The mother-liquors from the first crops were evaporated to two-thirds original volume, and a second crop of crystals obtained. Finally the mother-liquors from the second crops were allowed to evaporate to dryness spontaneously, giving thus a third crop of crystals. Each crop was carefully examined with the microscope to determine its homogeneity. The work is as yet incomplete, but sufficient results have been obtained to justify a description of the work to date.

#### I. LEAD CHLORIDE AND LEAD BROMIDE.

These two compounds are isomorphous, and we would naturally expect mixtures containing varying proportions of the ingredients. Such have been found. The effect of light upon these crystal masses is worthy of note. Wells<sup>1</sup> and Norris<sup>2</sup> have already called attention to the fact that lead bromide is darkened on exposure to light. So in these mixed crystals, this property of lead bromide is retained, the amount of darkening depending on the proportion of lead bromide in the mixed crystal.

#### II. LEAD BROMIDE AND LEAD IODIDE.

Only four solutions were here prepared, beginning with the

<sup>1</sup> *Am. J. Sci.*, 45, 134.

<sup>2</sup> *Am. Chem. J.*, 17, 189.

centi-molecular proportion and replacing portions of lead iodide by equivalent quantities of lead bromide.

In each case crystals of lead iodide alone separated as the first crop, even where the proportion of lead bromide to lead iodide was three and one-half grams to two-tenths gram.

The second crops of crystals, however, were prismatic, resembling, somewhat, lead bromide. These crystals show the presence of both bromine and iodine. The color of the respective crops varies from a greenish-yellow to a light sulphur-yellow. All are darkened by exposure to light. The crops are homogeneous. While no analyses have yet been made it is evident that these crystals are mixtures of lead bromide and lead iodide, in which the lead bromide is largely in excess.

Further, a crystal of lead iodide placed in a cold saturated solution of lead bromide is very gradually changed as the solution evaporates spontaneously and finally disappears, the mass being composed, at dryness, of prismatic, faint yellow crystals. This shows the ability of lead iodide to mix in very small quantities with lead bromide.

### III. LEAD CHLORIDE AND LEAD IODIDE.

Results already published show that these two substances form mixed crystals, but with lead chloride always present in excess. Engelhardt<sup>1</sup> has also shown that lead iodide and lead chloride can form mixed crystals.

A crystal of lead iodide placed in a cold saturated solution of lead chloride begins to change almost immediately. Examined under a microscope the bright yellow hexagonal plate is seen to grow dark, and soon the crystal is seen to break into prismatic crystals of very slight color.

This can be shown on a larger scale by dissolving three and one-half grams lead chloride and 2.4869 grams lead iodide in 350 cc. hot water. On cooling, crystals of lead iodide separate in large quantities. On standing over night in contact with the mother-liquor all of these crystals are changed to yellowish-green prismatic crystals.

All of the evidence thus far obtained tends to show that lead

<sup>1</sup> *Chem. Centrbl.*, 1855, 817.

iodide and lead chloride will crystallize together, the lead chloride being present in excess.

If we consider such substances as instances of solid solution, the results show that lead iodide dissolves in lead chloride to a greater extent than in lead bromide.

#### IV. LEAD CHLORIDE AND LEAD THIOCYANATE.

A microscopic examination of the twenty-one crops of crystals obtained in this series showed three substances present, either singly or crystallizing singly side by side, lead thiocyanate, lead chloride, and a new salt, the lead chloro-thiocyanate, formed from the solution containing the ingredients present in centimolecular proportions. There is no evidence of the formation of any mixed crystals.

#### V. LEAD BROMIDE AND LEAD THIOCYANATE.

The results in this series are exactly analogous to those obtained in IV. Chemical union takes place between the lead bromide and lead thiocyanate.

#### VI. LEAD IODIDE AND LEAD THIOCYANATE.

In this series no evidence was obtained of the formation either of a chemical compound or of mixed crystals. In every case it was observed that the two original salts crystallized side by side, each retaining all of its properties.

#### SUMMARY.

Lead chloride with lead bromide forms isomorphous mixtures in all proportions.

Lead chloride with lead iodide forms mixed crystals, always excess of lead chloride.

Lead chloride with lead thiocyanate forms a true chemical compound.

Lead bromide with lead chloride forms isomorphous mixtures in all proportions.

Lead bromide with lead iodide forms mixed crystals, always large excess of lead bromide.

Lead bromide with lead thiocyanate forms a true chemical compound.

Lead iodide with lead chloride forms mixed crystals, chloride in excess.

Lead iodide with lead bromide forms mixed crystals, bromide in large excess.

Lead iodide with lead thiocyanate forms neither mixed crystal nor true chemical compound.

Lead thiocyanate with lead chloride forms a true chemical compound.

Lead thiocyanate with lead bromide forms a true chemical compound.

Lead thiocyanate with lead iodide forms neither a compound nor mixed crystals.

These results can be summarized more suggestively thus :

$\text{PbCl}_2$ and $\text{PbBr}_2$ .	$\text{PbBr}_2$ and $\text{PbI}_2$ .	$\text{PbCl}_2$ and $\text{PbI}_2$ .
Form isomorphous mixtures in all proportions.	Form mixed crystals. The bromide always in excess.	Form mixed crystals. The chloride always in excess.
$\text{PbCl}_2$ and $\text{Pb}(\text{CNS})_2$ .	$\text{PbBr}_2$ and $\text{Pb}(\text{CNS})_2$ .	$\text{PbI}_2$ and $\text{Pb}(\text{CNS})_2$ .
Form a true chemical compound.	Form a true chemical compound.	Form neither mixed crystals nor a chemical compound.

What is the explanation of these phenomena? Several lines of thought suggest themselves :

1. The relative solubilities of the individual substances.
2. The crystal form of the constituents.
3. The electro-potential character of the negative radicals.
4. The amount of dissociation in solution.

It is probable that the explanation is to be found, not alone in any one of the above suggestions, but in several. At the present it is not safe to draw any conclusions or make any generalizations, for there are still a considerable number of facts to be supplied. The work is being carried on as rapidly as possible, and it is hoped soon to have sufficient definite information to throw some light on the question of "chemical compound or mixed crystals."

A series of investigations on mercuric salts is now being carried on in this laboratory analogous to the work on the lead salts. The evidence from this may throw still more light on the question.