THESIS IN CHEMISTRY - 1.

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Double Cesium and Rubidium Salts of Lead Tetrabromide.

Salts in which lead is quadrivalent are comparatively unstable and usually they readily pass over into the coresponding compounds in which the lead is divalent. Salts of Hexa-chloroplumbic acid $2HCl.\ Pb\ Cl_4$ are known and may be prepared from a solution of lead chloride in concentrated hydrochloric acid in which there is an excess of chlorin. If Cesium Chloride is added to this solution the double salt $2CsCl\ Pb\ Cl_4$ crystalizes out. This double salt may also be formed similarly from a solution of lead dioxide at a temperature below zero. Under these conditions lead tebra chloride is formed.

$PbO_2 + 4\ H\ Cl = P\ b\ Cl_4 + 2\ H_2O$. At ordinary temperature lead chloride is formed and chlorine is given off.

$PO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O$.

I prepared a 45 percent solution of hydrobromic acid by passing hydrogen sulphide through a solution of bromine in water.

$2Br_2 + 2H_2S = 4HBr + S_2$.

I purefied the acid from the sulphur by filtering through glass wood and asbestos.

I dissolved in this acid lead dioxide at 15° below zero. A large amount of a white compound which I took to be principly lead bromide was deposited in the bottom of the test tube. To some of the solution powred off from this, Ammonium bromide, Cesium bromide and Rubidium bromide was added. Cesium bromide seemed the most likely of the three formed a yellow compound, which was analysized for bromine lead and Cesium. It was soluble in HBr and was decomposed by water and could not therefore be washed free from an excess of Cesium bromide.

Analysis A.

Weight of sample = .0984.
" of Precipitate $PbSO_4$ = .0335

$\frac{Pb}{PbSO_4} = \frac{206.9}{302.96} = \frac{X}{.0335}$

$\frac{.0335 \times 206.9}{302.96 \times .0984} = 23.25\%$ lead.

Wwight of precipitate $Cs_2 PtCl_6$ = .07804

$\frac{Cs2}{Cs_2PtCl_6} = \frac{265.8}{673.3} = \frac{X}{.07804}$.

$\frac{.07804 \times 265.8}{673.3 \times .0984}$ = 31. 31 % Cesium .

Analysis B--

Weight of sample .0888

" of precipitate AgBr. .07805

$\frac{Br}{AgBr} = \frac{79.97}{187.96} = \frac{X}{.07805}$

$\frac{.07805 \times 79.96}{187.96 \times .0888} = 37.40\%$ Bromine.

By analysis.

23.25 % Lead

31.31 % Cesium

37.40 % Bromine

91.96 %

Before analysis the excess of hydrobromic acid had acted upon filter paper.

$\frac{23.25}{31.31} \div 91.96 = 25.14$ % lead.

$\div 91.96 = 33.82$ % Cesium.

$37.40 \div 91.96 = 41.04$ % Bromine

$25.14 \div 206.9 = 1.21$

$33.82 \div 132.9 = 2.54$

$41.04 \div 79.96 = 5.205$

Therefore the compound is $2CsBr\ PbBr_2$ with aslight excess of Cesium bromide.

Prepared lead bromide by the action of lead nitrate on patassiun bromide-

$2KBr + Pb(NO_3)2 = 2KNO_3 + PbB_2$

Dissolved some of the lead bromide in hydrobromic acid and to this was added a solution of Cesium to the one previously prepared- And owing to the fact that there was an excess of lead bromide over what was required to form the double salt white lead bromide also arystalized out. And in order to get the double salt uncomtaninated by the lead bromide a small amount of cesium bromide solution was added to the lead bromide solution.

This compound was analysied similar to the one previous for Bromine lead and Cesium -

Analysis A.

Weight of sample = .1022 grams

Weight of precipitate $PbSO_4$ = .0396 grams.

$$\frac{Pb}{PbSO_4} = \frac{206.9}{302.96} = \frac{X}{.0396}$$

$$\frac{.0396 \times 206.9}{303.96 \times .1022} = 26.46\ \%\ \text{lead.}$$

Analysis B-

Weight of sample = .1018 g.
" of precipitate $PbSO_4$ = .098g.

$$\frac{Pb}{PbSO_4} = \frac{206.9}{302.96} = \frac{X}{.0398.}$$

$$\frac{.0398 \times 206.9}{302.96 \times .1018} = 26.7\ \%\ \text{lead-}$$

Analysis 1 C.

Weight of sample .1060g.

" of precipitate AgBr = 1000g.

$$\frac{Br}{AgBr} = \frac{X}{.1000} = \frac{79.96}{187.89}$$

$$\frac{.1000 \times 79.96}{187.89 \times .1060} = 40.14\ \%\ \text{Br.}$$

Weight of precipitate Cs_2PtCl_6 = .0876

$$\frac{Cs_2}{Cs_2PtCl_6} = \frac{265.8}{673.3} = \frac{X}{.0876}.$$

$$\frac{.0876 \times 265.8}{673.3 \times .1060} = 32.63\ \%\ \text{Cesium}.$$

Analysis D-

Weight of sample = .1250

" of precipitate AgBr = .1185

$$\frac{Br}{AgBr} = \frac{79.96}{187.89} = \frac{X}{.1185}$$

$$\frac{.1185 \times 79.96}{187.89 \times .1250} = 40.33\ \%\ \text{Bromine}.$$

By analysis-

26.60 percent lead

40.20 " Bromine

32.63 " Cesium

26.60 ÷ 206.9 = 1.27

40.20 ÷ 79.96 = 5.026

32.63 ÷ 132.9 = 2.46.

Therefore the formula of this compound was shown to be $2CsBr\ PbBr_2$

I also attempted to oxidize a lead bromide solution in the presance of Cesium bromide but ~~if any~~ there was no oxidation in the solution.

While this work hasbeen handicaped a great deal by insufficient time it indicates that very interisting work may be done on the double cesium valts of lead tebrabromide.

Respectfully submitted

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