INVESTIGATION OF THE HALIDE COMPLEXES OF INTERHALOGENE COMPOUNDS

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The halide complexes of interhalogene compounds were subjected to investigations.

1. The examination of a solution of bromine choride in hydrochloric acid proved the existence of a complex form of bromine chloride in an aqueous solution containing chloride ions. The presence of this chloride complex of bromine chloride was verified by establisling the ultraviolet absorption curves of bromine chloride in water, sulphuric acid, hydrochloric acid and chloride solutions. The aqueous solution of bromine chloride containing chloride ions showed a characteristic «sharp» absorption maximum at wave-length 343 mμ which peak did not appear in the absorption curves of solutions of bromine chloride containing no excess of chloride ions.

2. Also the correlation of the redox potentials of aqueous solutions of interhalogene containing halide ions with the concentration of these halide ions was investigated. In the knowledge of the correlation, the authors succeeded in evolving a formula suitable for the calculation of the stability constants and coordination numbers of the halide complexes of interhalogene compouds:

$$E - k = \frac{0,058}{2} \log \frac{[XY_{weighed}]}{[Y^-] + K[Y^-]^n}$$

where E is the actually measured value of redox potential; k the redox potential of a solution of interhalogene containing no excess halide ions, for the case when the interhalogene compound is dissociated in 5o % (value obtained by extrapolation;) $XY_{weighed}$ the concentration of interhalogene compound weighed, X denoting the positiv component, Y the negative one; $[Y]$ the activity of halide ions in the solution; K the stability constant and n the coordination number.

By substituting the stability constants and coordination numbers obtained by calculation, into the evolved formula, the values of redox potentials belonging to given concentrations of halides were calculated. Values derived by measurement and by calculation were in fair accordance within the limits of experimental error. (Tabl. I.)

According to the investigations of the authors, the central bromine atom in the chloride complex of bromine chloride possesses the coordination number 6,

Effect of concentration of hydrochloric acid on the redox potential of a solution of bromine chloride in hydrochloric acid.

BrCl mole	HCl mole	Redox potentials measured mv.	calculated mv.
	0,2	1323	1317
	0,5	1290	1300
	1,0	1268	1263
	1,5	1237	1239
0,005	2,0	1230	1219
	2,5	1209	1206
	3,0	1195	1191
	4,0	1170	1175
	5,0	1156	1154
	0,6	1356	1361
	1,0	1336	1332
0,05	1,5	1309	1308
	2,0	1283	1288
	2,5	1267	1276
	3,0	1253	1260

the stability constant of the complex ranging $(2,6 \pm 1,0).10^2$. Thus, the complex has the formula $BrCl_6^{5-}$ (or $CrCl_5$ HCl).[X]

The central iodine atom in the chloride complex of iodine chloride has coordination number 6, the stability constant of the complex ranging $(4,3 \pm 2,2).\ 10^2$. The formula of the complex is ICl_6^{5-} (or ICl.5 HCl).

The central iodine atom in the bromide complex of iodine bromide proved to have coordination number 4, whilst the stability constant of the complex was $(5,0 \pm 1,0).10^2$. The complex has the formula IBr_4^{3-} (or IBr.5 HBr).

The results of the investigations of the triiodide complex verified the existence of the presumed complexes.

[X] According to our most recent investigations the formula of chloride complex of bromine chloride is $Br(HCl)_6^{+}$. The details will be published elswhere.