

CXL.—*Studies of Valency. Part XV. Absorption Spectra of Polyhalide Ions.*

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IN a preceding paper (Part VI, J., 1926, 622) the similarity between the absorption bands of iodoform and of potassium tri-iodide was discussed, but no structural formulæ were put forward to account for this resemblance, as it appeared to be beyond the scope of our present theories of valency. In order to throw more light on this obscure problem, it was decided to investigate the absorption spectra of other polyhalides, and to compare them with those recorded previously. An investigation on these lines is accompanied by quite exceptional risks of error in the interpretation of the experimental data, since there are at least four different causes which may make the spectra recorded differ from those of the compounds which they are supposed to represent: (i) The polyhalides may be hydrolysed by water, $\text{H}_2\text{O} + \text{RI}_3 \rightleftharpoons \text{ROH} + \text{HI}_3$; (ii) they may be reduced by alcohol, $\text{C}_2\text{H}_6\text{O} + \text{RI}_3 \longrightarrow \text{RI} + 2\text{HI} + \text{C}_2\text{H}_4\text{O}$; (iii) the polyhalide ions may dissociate into simple halide ions and free halogen, $\text{I}_3' \rightleftharpoons \text{I}' + \text{I}_2$ or $\text{ICl}_2' \rightleftharpoons \text{I}' + \text{Cl}_2$; and

(iv) the mixed polyhalide ions may undergo double decomposition, $3I_2Br' \rightleftharpoons 2I_3' + Br_3'$ or $3IBr_2' \rightleftharpoons I_3' + 2Br_3'$.

That these possibilities of decomposition cannot be ignored is proved by the experiments of Batley (*Trans. Faraday Soc.*, 1928, **24**, 438), who was able to show that a solution of iodine in alcohol has only one absorption band, in the visible region at 4470 Å.U., with a general absorption at the extreme limit of the range of observation in the ultra-violet. The ultra-violet bands, of which either one or two had been recorded by all previous observers, were shown to be due to hydrogen tri-iodide, HI_3 , formed by a photochemical reduction of the iodine in the alcoholic solution, $C_2H_6O + 3I_2 = 2HI_3 + C_2H_4O$. This could be avoided by taking the altogether exceptional precaution of examining the spectrum of the solution *in presence of ozone*.

In the present instance we were working with ready-formed polyhalides, which could only undergo a change of converse type; but our anxiety to avoid all risk of errors of this kind led to a very long delay in the completion of the work for publication. Thus, after studying a series of synthetic solutions of potassium polyhalides (compare Tinkler, J., 1907, **91**, 996; 1908, **93**, 1611), we held back our measurements until we had confirmed them by preparing a complete series of eight crystalline caesium polyhalides, described by Wells and Penfield in 1892 (*Amer. J. Sci.*, **43**, 17); and after making a complete series of observations on a group of seven aromatic polyhalides, prepared by McCombie and Reade (J., 1923, **123**, 142; 1924, **125**, 148; 1926, 2528), in ordinary alcohol, we thought it worth while to repeat the whole of our measurements in absolute alcohol, which had been dried with special care, and to check these observations by similar measurements of the whole series of caesium polyhalides in the same dry solvent.

In view of these precautions we believe that our observations are themselves entirely trustworthy, and in the later part of the paper we are able to cite evidence to show that the spectra recorded cannot be due to any of the types of decomposition discussed above, although these might reduce the intensity of the observed absorptions. We therefore propose to discuss them on the assumption that, when no evidence of chemical change could be detected, the solutions actually contained the ions of the salts which had been used in preparing them and could in nearly every case be recovered from the solution by evaporation.

EXPERIMENTAL.

Materials.—Of all the precautions indicated above, we regarded it of prime importance to assure ourselves that all the polyhalide

ions which we proposed to examine in solution actually existed in the solid state. Evidence that mixed polyhalide ions exist in aqueous solutions of iodine in potassium chloride, bromide, and iodide and of bromine in potassium chloride and bromide has been advanced by Tinkler (*loc. cit.*), whose observations we confirmed by quantitative measurements of the molecular extinction coefficients of solutions prepared in a similar way. At a later stage, however, we were fortunate in being able to secure from Professor Dennis of Cornell University an authentic specimen of the caesium dichloroiodide with which Wyckoff (*J. Amer. Chem. Soc.*, 1920, **42**, 1100) had made his X-ray analysis of the crystals of this salt; and subsequently we prepared in crystalline form the whole of the series of eight caesium polyhalides described by Wells and Penfield (*loc. cit.*). These were made by adding the appropriate halogen or halogens in correct stoicheimetical proportions to an aqueous solution of the requisite caesium halide. The bromodi-iodide, CsI_2Br , is decomposed by water and was therefore recrystallised from alcohol; the other seven salts were recrystallised twice from water. They separate in long needles, which show a striking gradation of colour with change of molecular weight. The eight compounds were easily identified by their colours and melting points. These properties, which agree exactly with those recorded by Wells and Penfield, are set out in the following table :

| Salt. | Colour.* | M. p. |
|--------------------------------|---------------------------------|-----------------------|
| CsI_3 | Blue-black (coppery brown) | 210° |
| CsBrI_2 | Dark red-brown (reddish-brown) | 208 |
| CsBr_2I | Cherry red (orange) | 246 |
| CsIBrCl | Light red (sandy yellow) | 238 |
| CsBr_3 | Deep orange (orange-red) | 180, in a closed tube |
| CsClIBr_2 | Light orange | 191, in a closed tube |
| CsCl_2I | Apricot (bright yellow) | 238 |
| CsCl_2Br | Bright yellow (greenish-yellow) | 205, in a closed tube |

* The colours shown in parentheses are those of the aromatic (Qm) polyhalides described below.

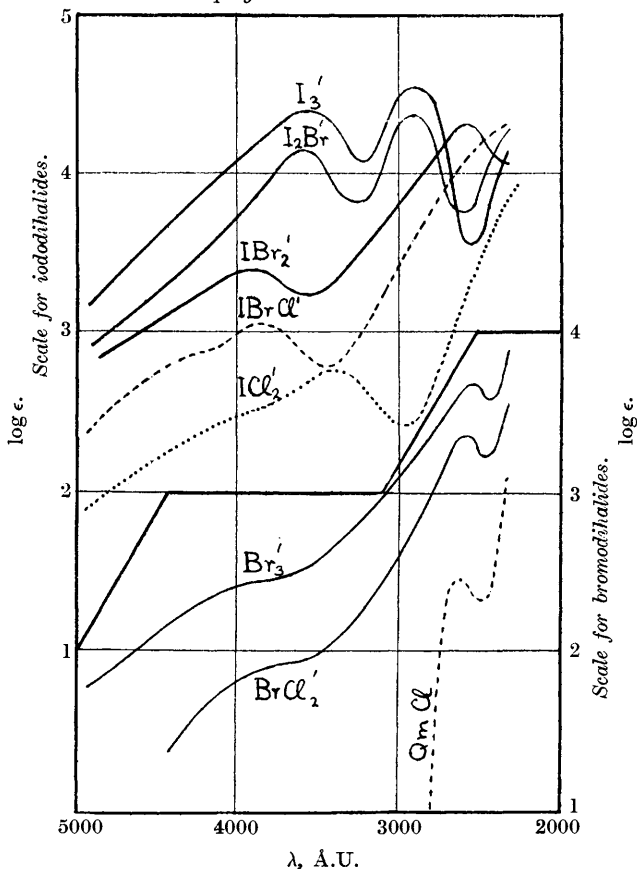
All these salts, except the tri-iodide, are more soluble in water than in alcohol.

The caesium polyhalides which contain iodine are the most stable and may be exposed to a damp atmosphere for several days without changing. The others decompose in about 2 hours, but can be kept indefinitely in sealed glass tubes, after being drained by means of a filter pump and then pressed with a filter-paper on the surface of a porous plate. Wells and Penfield state that the dibromiodide is more stable than the bromodi-iodide, and that the dichlorobromide is more stable than the chlorodibromide, so the stability of the polyhalide does not depend entirely on its molecular weight, but may be influenced also by its symmetry (see below).

The seven *p*-bromophenyltrimethylammonium polyhalides, provided by Mr. Reade, were crystalline compounds, for which complete analytical data had already been given (*loc. cit.*). Their colours show the same striking gradation as those of the cæsium salts with change of molecular weight. They are formulated below as

FIG. 1.

Molecular extinction coefficients of *p*-bromophenyltrimethylammonium polyhalides in alcohol.



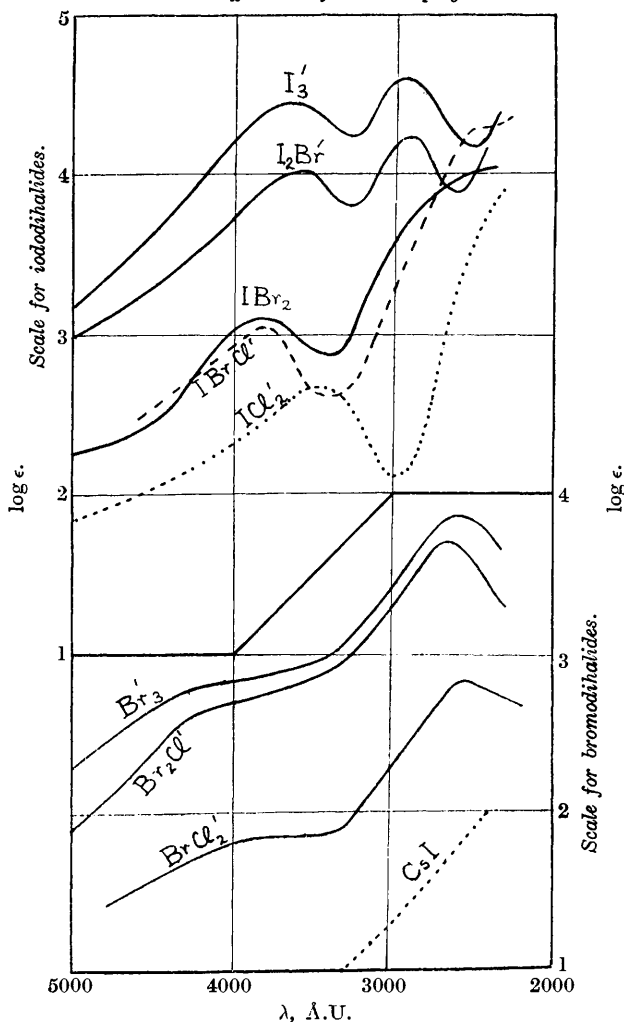
QmI_3 to QmBrCl_2 , where Qm represents the aromatic cation, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}(\text{CH}_3)_3^+$.

Solvents.—The first measurements were made with potassium salts in water and Qm salts in undried alcohol. Since these solutions were not comparable, the cæsium salts (which are soluble both in alcohol and in water) were measured in both solvents, except the

bromodi-iodide, which decomposes in water and was therefore examined in alcoholic solutions only. It was then found that the absorptive powers of the salts were much lower in water than in

FIG. 2.

Molecular extinction coefficients of caesium polyhalides in alcohol.



alcohol, a result which indicated that their absorptive power was given more correctly by the use of alcoholic rather than of aqueous solutions. For this reason a fresh series of observations was made

TABLE I.

Molecular Extinction Coefficients of Polyhalides in Alcohol.(a) *p*-Bromophenyltrimethylammonium salts.

Position of maxima, etc.

| Substance. | log ϵ . | | λ . | log ϵ . | | λ . |
|----------------------------|--------------------|----------|-------------|------------------|----------|-------------|
| | Maximum | Step-out | | Maximum | Step-out | |
| QmI ₂ | 4.38 | — | 3580 | 4.55 | — | 2900 |
| QmI ₂ Br | 4.16 | — | 3600 | 4.38 | — | 2900 |
| QmIBr ₂ | 3.4 | — | 3900 | 4.32 | — | 2580 |
| QmIBrCl | 3.04 | — | 3840 | — | — | — |
| QmICl ₂ | 2.75 | — | 3400 | — | — | — |
| QmBr ₃ | 2.45 | — | 4000 | 3.7 | — | 2580 |
| | to 2.5 | — | 3600 f | — | — | — |
| QmBrCl ₂ | 1.9 | — | 3900 | 3.36 | — | 2580 |
| | to 1.95 | — | 3550 f | — | — | — |
| QmCl | — | — | — | 2.48 | — | 2600 |
| (b) <i>Cæsium</i> salts. | | | | | | |
| CsI ₂ | 4.46 | — | 3600 | 4.60 | — | 2900 |
| CsI ₂ Br | 4.02 | — | 3580 | 4.22 | — | 2900 |
| CsIBr ₂ | 3.08 | — | 3800 | — | — | — |
| CsIBrCl | 3.0 | — | 3840 | 4.25 | — | 2500 |
| | — | — | — | to 4.3 | — | 2300 f |
| CsICl ₂ | 2.58 | — | 3460 | — | — | — |
| CsBr ₃ | 2.76 | — | 4200 | 3.86 | — | 2560 |
| | to 2.85 | — | 3800 f | — | — | — |
| CsBr ₂ Cl | 2.5 | — | 4400 | 3.7 | — | 2660 |
| | to 2.72 | — | 3600 f | — | — | — |
| CsBrCl ₂ | 1.73 | — | 4200 | 2.8 | — | 2540 |
| | to 1.88 | — | 3400 f | — | — | — |
| CsI | General absorption | | 2.0 | — | — | 2400 |
| | | | 1.0 | — | — | 3300 |

TABLE II.

Molecular Extinction Coefficients of Polyhalides in Water.(a) *Cæsium* salts.

Position of maxima, etc.

| Substance. | log ϵ . | | λ . | log ϵ . | | λ . |
|-----------------------------|------------------|----------|-------------|------------------|----------|-------------|
| | Maximum | Step-out | | Maximum | Step-out | |
| CsI ₂ | 3.3 | — | 3520 | 3.44 | — | 2900 |
| CsIBr ₂ | 2.45 | — | 4000 | 3.06 | — | 2550 |
| CsIBrCl | 2.62 | — | 4200 | 3.27 | — | 2500 |
| CsICl ₂ | 2.49 | — | 4600 | — | — | — |
| CsBr ₂ Cl | 2.0 | — | 3950 | 2.4 | — | 2650 |
| CsCl ₂ Br | 1.65 | — | 3850 | — | — | — |
| CsBr ₃ (1) | 2.13 | — | 3900 | 2.58 | — | 2640 |
| (2) | 1.60 | — | 4000 | 2.26 | — | 2660 |
| | to 1.66 | — | 3600 f | — | — | — |
| (3) | — | — | — | 1.8 | — | 2640 |

(b) *Potassium* salts.

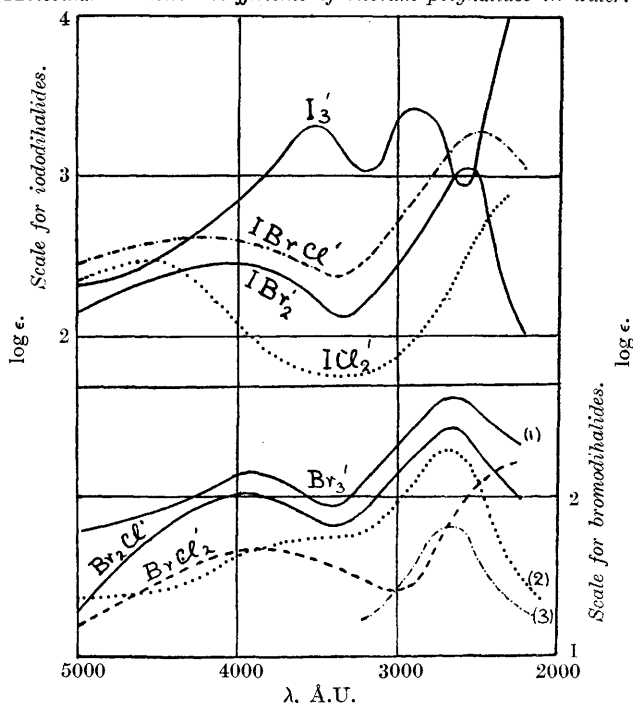
Position of maxima, etc.

| Solution. | Ion. | log ϵ . | λ . | log ϵ . | λ . |
|-------------------------------------|---------------------|------------------|-------------|------------------|-------------|
| I ₂ in KI | I ₃ ' | 3.8 | 3600 | 3.9 | 2900 |
| I ₂ in KBr | I ₂ Br' | 3.4 | 3700 | 3.6 | 2750 |
| I ₂ in KCl | I ₂ Cl' | 1.7 | 3900 | 3.2 | 2500 |
| I ₂ in H ₂ O | | 1.79 | 4650 | 1.79 | 2850 |
| Br ₂ in KI | IBr ₂ ' | 2.6 | 3750 | 3.6 | 2700 |
| Br ₂ in KBr | Br ₂ ' | 1.8 | 3900 | 3.2 | 2650 |
| Br ₂ in KCl | Br ₂ Cl' | 1.8 | 4000 | 2.8 | 2600 |
| Br ₂ in H ₂ O | | 1.9 | 3950 | 2.1 | 2600 |

of the Qm salts in the same anhydrous alcohol,* whereby the results were brought into close agreement with those recorded for the corresponding caesium salts.

In addition to caesium bromodi-iodide, which is decomposed at once by water, aqueous solutions of the tri-iodide and dichloriodide also deposit iodine slowly. An aqueous solution of caesium tri-bromide also loses much of its absorptive power after two days. These decompositions are much less marked in alcoholic solutions,

FIG. 3.
Molecular extinction coefficients of caesium polyhalides in water.



but even in alcohol the unstable chlorodibromide loses its yellow colour after about 2 days. For this reason great care was taken, not only to use dry alcohol, but also to make the measurements as quickly as possible after preparing the solutions. In practice the last plate was generally exposed within 2 or 3 hours, whereas notable

* The alcohol was dried by distilling it three times from freshly-burnt lime, twice from anhydrous copper sulphate, and then repeatedly from aluminium amalgam until no further action could be observed. Its density agreed within one unit in the fifth decimal place with that recorded by Hartley.

changes of colour were usually observed only after one or two days had elapsed.

Results.—The absorption spectra of the aromatic polyhalides in alcohol are shown in Fig. 1, and those of the cæsium salts in alcohol and in water in Figs. 2 and 3. The principal constants of the absorption curves are collected in Tables I and II.

Discussion.

(a) The spectra of the cæsium and Qm salts *in alcohol* agree so closely that the general characteristics of the polyhalide ions are perfectly clear, in spite of the instability to which attention has already been directed. The principal point of contrast between the two series arises from the presence in the spectrum of the simple aromatic chloride, QmCl, of a shallow absorption band, with maximum $\log \epsilon = 2.48$ at 2600 Å.U., which has no parallel in the absorption spectrum of cæsium iodide, where only a weak general absorption is recorded. This band may be attributed to the aromatic radical, $\text{Br}\cdot\text{C}_6\text{H}_4\cdot\overset{+}{\text{N}}\llcorner$; but it is too weak to affect the curves for the highly absorptive polyhalides derived from it. Thus, when superposed on the absorption of a polyhalide ion with a molecular extinction coefficient $\log \epsilon = 4.0$, the band in question would increase this number only by 0.013; and its "persistence" of 0.2 is so small that the ripple produced by the band would extend over a range of only 0.007 on the scale of $\log \epsilon$.

(b) Inspection of the curves shows at once that the twin maxima of the "iodoform band," which have already been recorded in aqueous solutions of potassium tri-iodide, are reproduced in the spectra of cæsium tri-iodide in water and in alcohol, and of the quaternary ammonium tri-iodide in alcohol, with the following coefficients :

| | |
|---------------------------|---|
| CHI_3 in alcohol | $\log \epsilon = 3.45$ at 3450 and 3.5 at 2940 Å.U. |
| KI_3 in water | $\log \epsilon = 3.8$ at 3600 and 3.9 at 2900 |
| CsI_3 in water | $\log \epsilon = 3.3$ at 3520 and 3.44 at 2900 |
| CsI_3 in alcohol | $\log \epsilon = 4.46$ at 3600 and 4.60 at 2900 |
| QmI_3 in alcohol | $\log \epsilon = 4.38$ at 3580 and 4.55 at 2900 |

The difference between the values for potassium and cæsium tri-iodides in water may be attributed to the fact that the halogen in the latter was present in the stoichiometric proportion of the elements in the crystalline salt, whilst the values for the former were deduced from a standard solution of iodine in an excess of potassium iodide. The values recorded for solutions in absolute alcohol are much higher, probably as a result of the repression in alcoholic

solutions of a tendency, which the tri-iodide ion certainly possesses in aqueous solutions, to dissociate into iodide ion and free iodine.

(c) Curves showing the same twin maxima were also given by CsI_2Br and QmI_2Br , but the maxima are only about half as intense as in the tri-iodides, thus :

CsI_2Br in alcohol, $\log \epsilon = 4.02$ at 3580 and 4.22 at 2900.

QmI_2Br in alcohol, $\log \epsilon = 4.16$ at 3600 and 4.38 at 2900.

These ultra-violet bands are of much shorter wave-length than the true iodine band, which has a maximum in the blue region of the spectrum at 4470 (Batley, *loc. cit.*); they are therefore genuine characteristics of the polyhalide ions, the dissociation of which would weaken them, but without producing any other important influence on the ultra-violet spectrum.

(d) An abrupt change of type occurs on passing from $\text{I}_2\text{Br}'$ to IBr_2' . The separation between the two maxima increases abruptly from $3600 - 2900 = 700$ Å.U. to $3900 - 2600 = 1300$ Å.U.; and instead of being nearly equal in intensity, the band of longer wave-length becomes about 8 times weaker than that of shorter wave-length. This change brings the spectra into close agreement with that already recorded for thallium tri-iodide in methyl alcohol (Berry and Lowry, J., 1928, 1752), thus :

TlI_3 in MeOH $\log \epsilon = 3.9$ at 4000 and 4.35 at 2600

CsIBr_2 in water $\log \epsilon = 2.45$ at 4000 and 3.06 at 2550

CsIBr_2 in alcohol $\log \epsilon = 3.08$ at 3800 — —

QmIBr_2 in alcohol $\log \epsilon = 3.4$ at 3900 and 4.32 at 2580

Just as in the case of thallium tri-iodide, the change in the wave-lengths of the maxima affords conclusive evidence that the absorption spectrum is an authentic property of the salt and is not due to tri-iodide ions, which might be formed in this case by a reversible decomposition, $3\text{IBr}_2' \rightleftharpoons \text{I}_3' + 2\text{Br}_3'$. Moreover, since the maximum for the tri-iodide ion in alcohol ($\log \epsilon = 4.6$ at 2900 Å.U.) is 6 times stronger than the maximum ($\log \epsilon = 3.8$ at 2560) for the tribromide ion, the whole decomposition suggested above would inevitably result in the development of a peak on the absorption curves, whereas, in fact, there is no indication even of a broadening of the band on the side of longer wave-lengths. Again, if the spectra attributed to the $\text{I}_2\text{Br}'$ and IBr_2' ions were not due to these ions, but to I_3' and Br_3' ions formed from them by double decomposition, the intensity of the maximum at 3600 Å.U. should fall by 0.176 and 0.477 only on the scale of $\log \epsilon$, on passing from I_3' to $\text{I}_2\text{Br}'$ and IBr_2' . Actually, this logarithm was diminished by 0.4 and 1.2 in the case of the potassium salts, by 0.44 and 1.38 in the caesium salts,

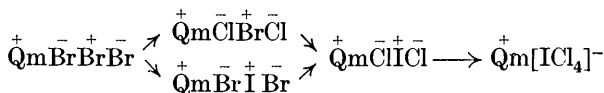
and by 0.36 and 0.98 in the Qm salts, the larger change of intensity being accompanied in each case also by a change of about 300 Å.U. in wave-length.

(e) On passing from IBr_2' to IBrCl' and ICl_2' , the band at 2600 disappears into the remote ultra-violet, giving rise to a strong general absorption, whilst the band on the edge of the visible spectrum persists, but is displaced from 3850 in the dibromiodides to 3400 in the dichloriodides. Conversely, when we go over from the series in which iodine is the heaviest atom to compounds containing the ions Br_3' , $\text{Br}_2\text{Cl}'$, and BrCl_2' , the band at 2600 persists but the band of long wave-length is reduced to a mere step-out.

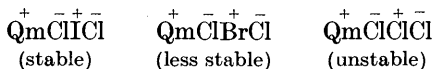
(f) The wave-lengths of the two bands cited above are remarkably like those which we have found for bromine in water, *viz.*, $\log \epsilon = 1.9$ at 3950 and 2.1 at 2600, but this can only be regarded as a coincidence, since the two bands in QmIBr_2 are respectively 30 times and 160 times stronger than the bands of similar wave-length in bromine. In the same way, the band at 2580 in QmBrCl_2 , instead of being 50% weaker than in bromine, as it would be if the solution contained a mere mixture of QmCl , chlorine, and bromine, is 18 times stronger. Attention may be directed, however, to a hump in the visible region of the spectrum in the curves for QmIBrCl and QmICl_2 , in alcohol, and in a still more striking form in the curves for aqueous solutions of CsIBrCl and CsICl_2 , since this can perhaps be attributed to free iodine, which produces a stronger absorption than either iodoform or potassium tri-iodide at wave-lengths longer than 4500 Å.U. Similar evidence of the slow liberation of bromine from caesium tribromide in aqueous solutions is afforded by a comparison of the curves (1), (2) and (3) in Fig. 3, representing the absorptions respectively of (1) a freshly prepared solution, (2) a solution which was stored in the dark and in a glass-stoppered flask for 2 days before dilution, and (3) a solution which was stored for 30 hours after dilution. The weakening of the band at 2600 and the disappearance of the band at 3900 show that the intense absorptions now recorded are due to the polyhalide ions themselves and not to free halogen liberated from them.

Structure of the Polyhalides.—Reade was able to show experimentally that QmBr_3 can be converted by successive iodination and chlorination into QmIBr_2 and QmICl_2 , or by successive chlorination and iodination into QmBrCl_2 and the same QmICl_2 , which can be converted finally into a tetrachloriodide by the action of an excess of chlorine. These results were interpreted by attributing a positive charge to one halogen and a negative charge to the other two. The electropositive atom is always the heaviest halogen which the complex contains, and is replaceable only by a heavier halogen,

while the two electronegative atoms are replaceable only by a lighter halogen. Positive bromine can therefore be replaced by more positive iodine and negative bromine by more strongly negative chlorine :



For the same reason, the dichlorobromide is less stable than the dichloriodide, and the trichlorides are so unstable that only one compound of this type has so far been isolated :



The discrimination thus made between one central and two outer atoms of halogen has been vindicated by the X-ray analysis of caesium dichloriodide by Wyckoff, who assigns a linear structure to the complex anion, with the iodine centrally placed at the mass-centre of the two chlorines (compare also Clark, *Proc. Nat. Acad. Sci.*, 1922, 8, 90; 1923, 9, 117, 126).

The structures thus indicated for the polyhalides enable us to summarise the absorption spectra of the ions as follows :

| Ion. | Weight. | Character of spectrum. | Wave-lengths of maxima. | |
|--|---------|------------------------|-------------------------|------|
| $\overset{-}{\text{I}}\overset{+}{\text{I}}\overset{-}{\text{I}}$ | 381 | Two bands | 3600 | 2900 |
| $\overset{-}{\text{I}}\overset{+}{\text{I}}\overset{-}{\text{Br}}$ | 324 | " | " | " |
| $\overset{-}{\text{Br}}\overset{+}{\text{I}}\overset{-}{\text{Br}}$ | 287 | " | 3900 | 2600 |
| $\overset{-}{\text{Br}}\overset{+}{\text{I}}\overset{-}{\text{Cl}}$ | 242 | Band and gen. abs. | 3900 | — |
| $\overset{-}{\text{Cl}}\overset{+}{\text{I}}\overset{-}{\text{Cl}}$ | 198 | " " | 3400 | — |
| $\overset{-}{\text{Br}}\overset{+}{\text{Br}}\overset{-}{\text{Br}}$ | 240 | Step-out and band | — | 2600 |
| $\overset{-}{\text{Br}}\overset{+}{\text{Br}}\overset{-}{\text{Cl}}$ | 195 | " " | — | 2600 |
| $\overset{-}{\text{Cl}}\overset{+}{\text{Br}}\overset{-}{\text{Cl}}$ | 151 | " " | — | 2600 |

It will be noticed that (i) the two bands at 3600 and 2900 are limited to the two compounds which contain *negative iodine* linked necessarily to *positive iodine*; (ii) the band at 3900 is limited to two compounds which contain *negative bromine* linked to *positive iodine*; (iii) the strong general absorption in the extreme ultra-violet occurs in the two compounds which contain *negative chlorine* linked to *positive iodine*; (iv) the step-out near the visible spectrum, replacing a band at 3900, 3600, or 3400 Å.U., is characteristic of the three compounds which contain *positive bromine*; and (v) this step-out

is associated with a band at 2600, which is not only independent of the nature of the negative halogens, but is also associated with a band at 3900 Å.U. in the dibromiodide.

These deductions may be regarded as a mere mnemonic, to assist in the classification of the absorption spectra. In any case, they are made without prejudice to the formulation of the ions as electronic systems, since this is a subject which we do not propose to discuss here. Attention may be directed, however, to a recent paper on "The Diamagnetism of Polyhalides" (Gray and Dakers, *Phil. Mag.*, 1931, **11**, 81), in which this problem has been discussed on the basis of measurements of the magnetic susceptibilities of Reade's compounds.

Summary.

(a) Molecular extinction coefficients are recorded for 7 aromatic polyhalides of the series $C_6H_4Br \cdot NMe_3^+$ in alcohol, for 8 caesium polyhalides in alcohol and in water, and for a series of aqueous potassium polyhalides prepared by adding free halogens to the potassium halides.

(b) The polyhalide ions from I_3' to $BrCl_2'$ give characteristic absorption spectra, which cannot be attributed to hydrolysis, dissociation, reduction, or double decomposition.

(c) Dissociation, which is specially marked in aqueous solutions, diminishes the intensity of the strong selective absorption of the ions but does not change the form of the absorption curves of which the principal features are tabulated (p. 1102).

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