

*The Absorption Spectra of Halogens and Inter-halogen Compounds
in Solution in Carbon Tetrachloride.*

By A. E. GILLAM and R. A. MORTON.

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When two solutions are mixed the absorption spectrum of the new solution will be the mean of those of the separate solutions provided that no chemical interaction occurs. The mere fact of a departure from additivity does not, however, necessarily denote the formation of true chemical compounds. The solute or solutes may undergo solvation, loosely bound aggregates may occur, and even when marked deviations from the simple law of mixtures are observed it is rarely possible to prove the quantitative formation of a given chemical compound from spectroscopic data alone.

The above considerations apply with some force to the problem of the absorption spectra of halogens and inter-halogen compounds in an inert solvent. The three elements show perfectly characteristic absorption bands, they are known to interact with the formation of some quite stable compounds, some relatively stable compounds, and some apparently very unstable compounds.

There is, for instance, no doubt whatever that iodine monochloride, iodine trichloride, and iodine monobromide are definite compounds, whereas until very recently there was no convincing physicochemical evidence for the existence of bromine chloride BrCl . The present investigation was planned as follows :—

- (a) The absorption curves for solutions of the halogens, chlorine, bromine and iodine, in an inert solvent were to be determined.
- (b) Summation curves were to be constructed on the assumption that solutions containing different halogens in stoichiometric proportions would obey the simple mixture law.
- (c) Experimental absorption curves were to be obtained with solutions of definite inter-halogen compounds.
- (d) Experimental curves for mixtures in proportions corresponding with known compounds, and with compounds the existence of which remained doubtful, were to be measured.

It will be seen at once that if the absorption spectrum of iodine chloride in relation to iodine and chlorine is comparable with the absorption spectrum of iodine bromide in relation to iodine and bromine, then bromine chloride, if it exists, should exhibit precisely the same relationship to bromine and chlorine.

Experimental.

Solvent.—The solvent chosen for the work needs to be transparent to visible and ultra-violet light and must not interact with the solutes. Carbon tetrachloride, if free from carbon bisulphide, the commonest impurity, transmits freely as far as $265 \mu\mu$, and is completely inert towards the halogens.*

Technique of Absorption Spectra Measurements.—Two Hilger E3 quartz spectrographs were used in conjunction with sector photometers. In one case the light source was an iron-nickel arc (line spectrum), whilst in the other, a high-tension under-water spark between tungsten electrodes was used (continuous spectrum). Fiduciary lines in the work with a continuous light source, were obtained by photographing the aluminium spark in air at the top and bottom of each plate. Match points were usually determined visually as it

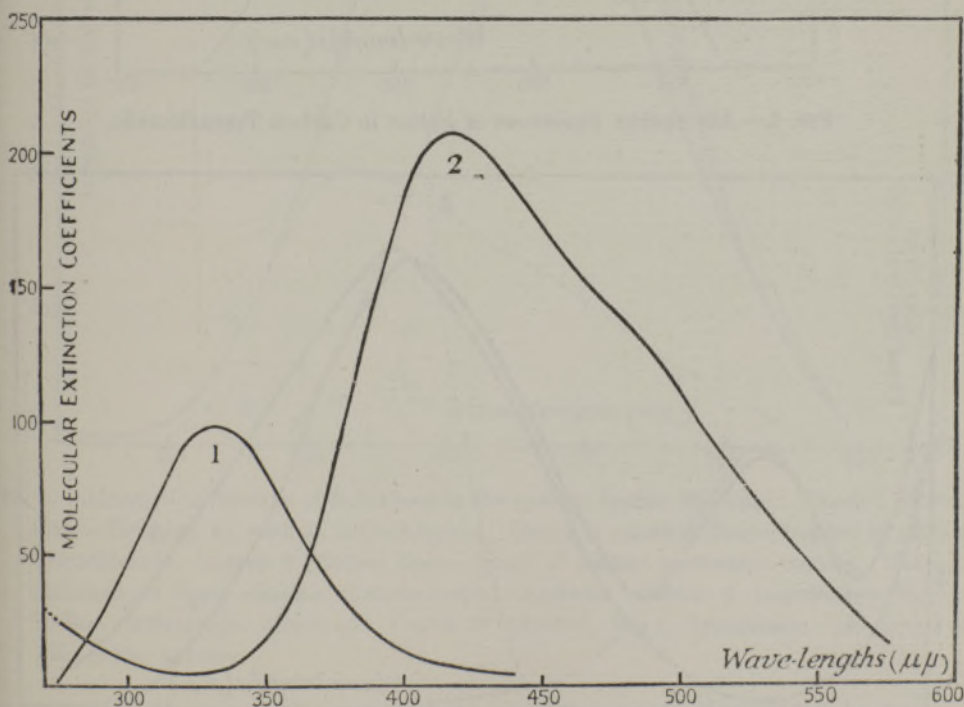


FIG. 1.—Absorption Spectra of Chlorine and Bromine in Carbon Tetrachloride.
Curve 1—Chlorine solution. Curve 2—Bromine solution.

* Medicinal carbon tetrachloride made by Messrs. Albright and Wilson is quite suitable.

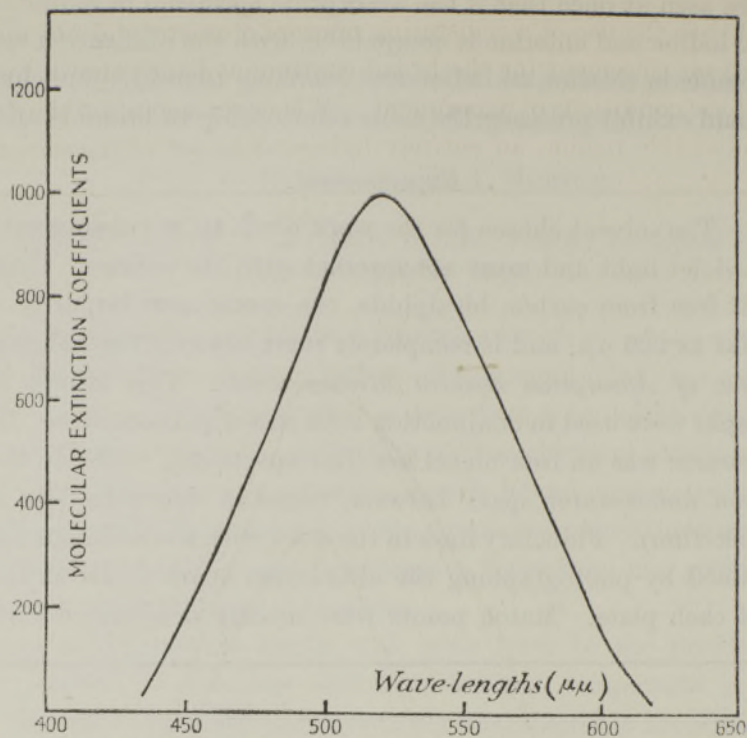


FIG. 2.—Absorption Spectrum of Iodine in Carbon Tetrachloride.

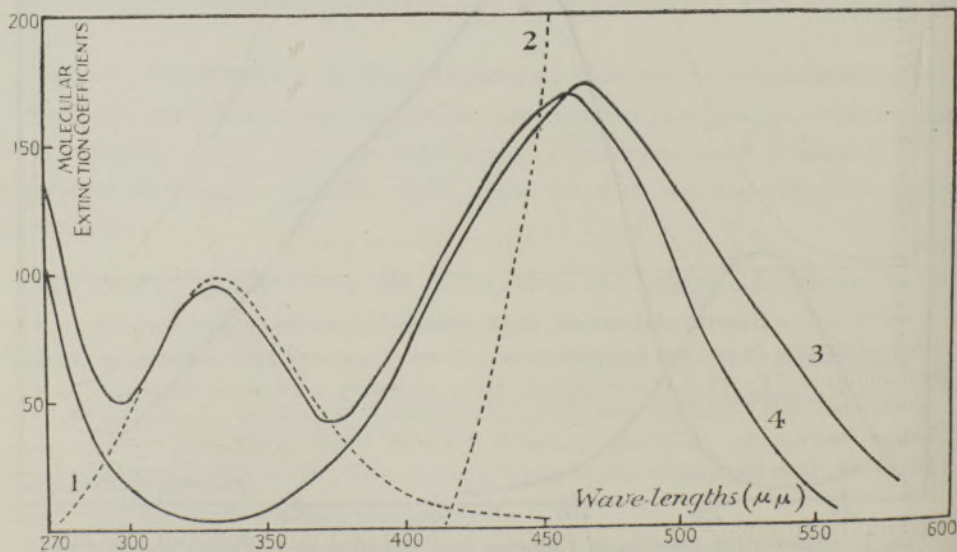


FIG. 3.—Absorption Spectra of Solutions in the system Iodine-Chlorine. Curve 1 (dotted)—Chlorine. Curve 2 (dotted)—Iodine. Curve 3 (continuous)—Iodine monochloride observed. Curve 4 (continuous)—Iodine trichloride observed.

was found that the use of a registering microphotometer did not increase the accuracy of measurement for the broad continuous bands shown by the halogens under the conditions of experiment. Whenever a solution showed absorption in the visible region, an entirely independent set of measurements was

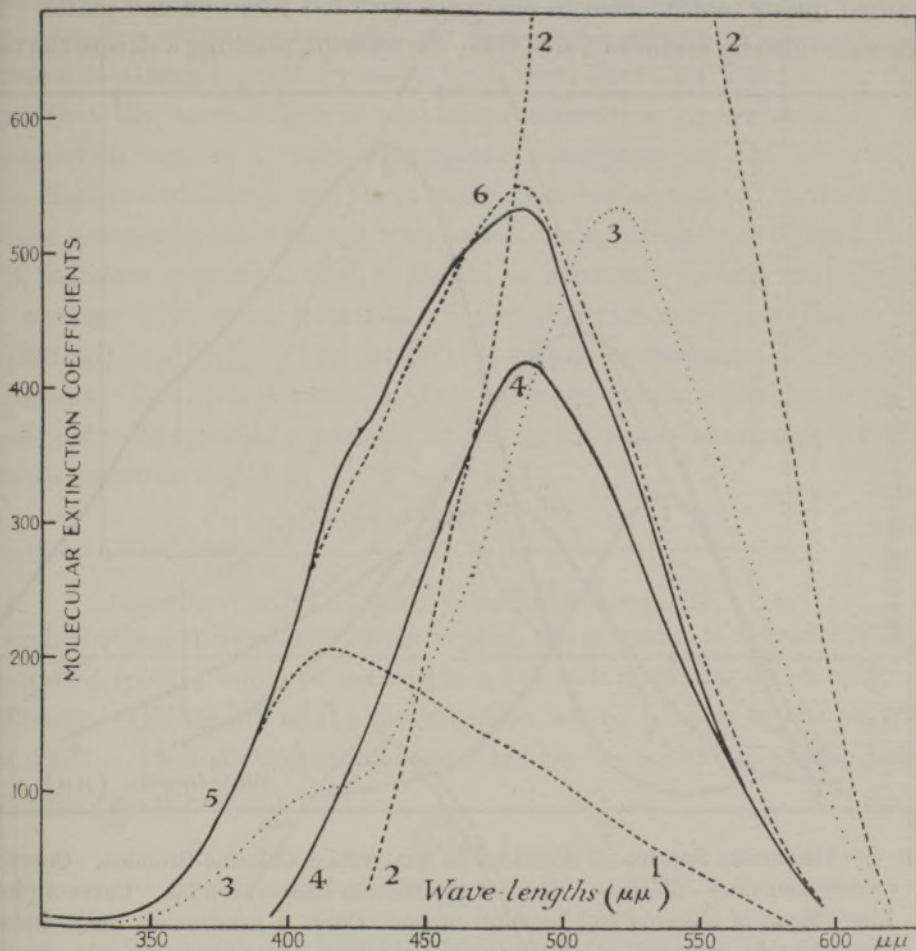


FIG. 4.—Absorption Spectra of Solutions in the system Iodine-Bromine. Curve 1 (dotted line)—Bromine in carbon tetrachloride. Curve 2 (dotted line)—Iodine in carbon tetrachloride. Curve 3 (dotted line)—Mean of iodine + bromine curves. Curve 4 (continuous line)—Iodine monobromide observed. Curve 5 (continuous line)—Iodine tribromide observed. Curve 6 (dotted line)—Summation of observed $\text{IBr} + \text{Br}_2$ curves.

carried out in duplicate by two observers working on a new model of the Hilger-Nutting visual spectrophotometer. The majority of the curves shown in figs. 1 to 5 are the result of concordant photographic and visual determinations.

In the preliminary work absorption cells of the ordinary type were used,

but it was found that the solute, particularly if it were chlorine, was liable to escape from the solution during the period necessary for the completion of the measurements. All the preliminary data were therefore rejected and fresh determinations carried out using a different type of cell. The new cells were of fused quartz, constructed in one piece with flat fused-on end plates. The cells were filled by means of a side tube, the solution reaching well into the tube,

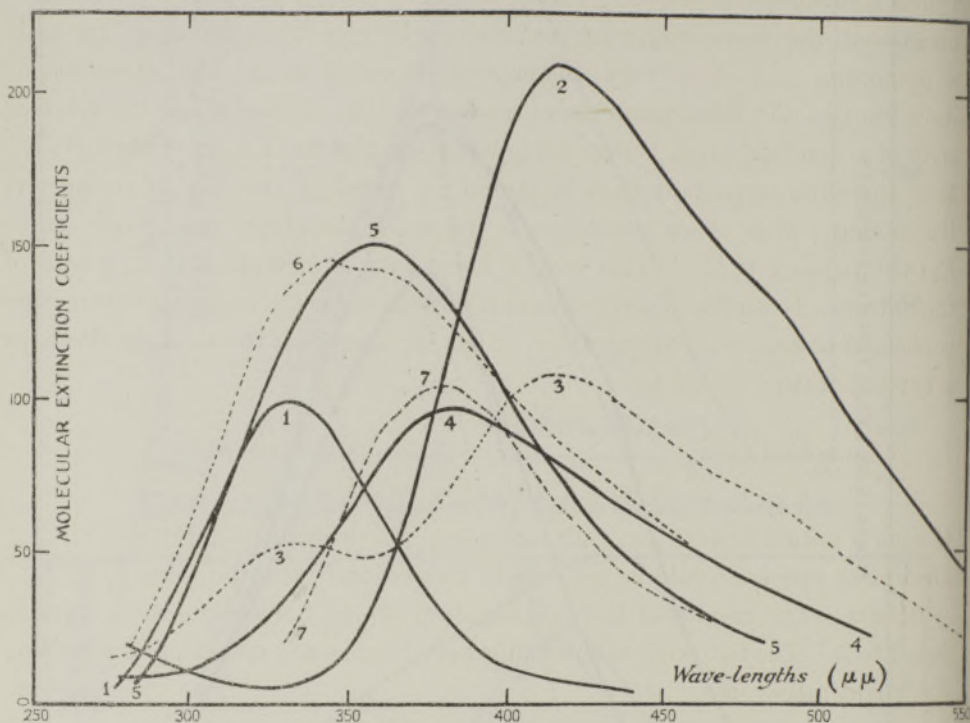


FIG. 5.—Absorption Spectra of Solutions in the system Chlorine-Bromine. Curve 1—(continuous line)—Chlorine. Curve 2 (continuous line)—Bromine. Curve 3 (dotted line)—Mean of chlorine and bromine curves. Curve 4 (continuous line)—Bromine monochloride, observed. Curve 5 (continuous line)—Bromine trichloride, observed. Curve 6 (dotted line)—Summation of observed $\text{BrCl} + \text{Cl}_2$ curves. Curve 7 (dotted line)—Observed BrCl_3 curve minus Cl_2 curve.

which could then be closed so as to eliminate the escape of gas. Comparison cells were used throughout to correct for the absorption and reflexion losses, due to the solvent and the cell materials.

Statement of Results.—The molecular extinction coefficient e has been plotted against wave-length, e being defined by the well-known equation $\log I_0/I = ecd$, c being the molar concentration and d the thickness in centimetres. It is usual to describe an absorption band as showing e maximum, at a certain wave-

length, the maximum being fixed by the two parameters, wave-length and extinction coefficient. Now that the study of absorption spectra of solutions is becoming more and more quantitative, a more precise notation seems to be called for.

In order to reproduce a given measurement it is necessary to know the cell thickness, the concentration, and the photometer setting at the maximum. Unless a substance is perfectly stable, and obeys Beer's law strictly, the statement that the wave-length of maximum absorption occurs at $x \mu\mu$ with e maximum = y , is a very incomplete description of the observation. As v. Halban and Eisenbrand* have made clear, the accuracy, *i.e.*, the relative error of e , depends, other things being equal, on the magnitude of $\log I_0/I$ (E). It is therefore important that E should be specified, directly or indirectly. By analogy with other notations in physical chemistry one might write $e_d^c(350 \mu\mu) = 1 \cdot 0_{1 \text{ cm.}}^{0 \cdot 1 \text{ M}}$. This would constitute a complete description of the datum. It would, however, make it necessary for the molecular extinction coefficient to be specified separately, or left for the reader to calculate. Perhaps a better notation would be

$$e_d^c(350 \mu\mu) = 10,$$

i.e., in an actual case

$$e \text{ max. } (350 \mu\mu) = 10_{1 \text{ cm.}}^{0 \cdot 1 \text{ M}}.$$

If such a notation were generally accepted, the problem of reproducibility in absorption spectra would be reduced to a question of manipulation only.

Results.—The results of the investigation are to be seen in the curves in figs. 1 to 5. The following tabular summary has the advantage of emphasising the quantitative side.

Table I.

	Chlorine.	Bromine.	Iodine.
λ maximum $\mu\mu$	332	417	520
e max. $\frac{c}{d}$	$[99]_2^{0 \cdot 00655}$	$[208]_4^{0 \cdot 00157}$	$[985]_2^{0 \cdot 000713}$
Atomic weight	35.5	80	127

It will be noticed that the extinction coefficients and the positions of the maxima show the periodicity usually associated with the properties of the halogens.

* 'Roy. Soc. Proc.,' A, vol. 116, p. 153 (1927).

Table II.

	Bromine chloride (BrCl).	Iodine chloride (ICl).	Iodine bromide (IBr).
λ maximum $\mu\mu$	380	464	487
e max. $\frac{e}{d}$	$[97]_2^{.006}$	$[173]_2^{.00426}$	$[420]_2^{.00174}$

Discussion.—As regards the halogens it is only necessary to state that our materials were carefully purified by standard methods and the concentration determined by means of potassium iodide-thiosulphate titrations immediately before the absorption was studied. The results are in good agreement with earlier work as will be seen from the following summary.

Living and Dewar* described an absorption in chlorine vapour at 302–356 $\mu\mu$, whilst v. Halban and Siedentopf† recorded a maximum in the vapour at 334 $\mu\mu$, as against our determination of 332 $\mu\mu$ in carbon tetrachloride. The very recent data of Barratt and Stein‡ are in agreement.

Plotnikow§ has measured the absorption of bromine in various solvents for four mercury lines. He found that Beer's law was obeyed, and also concluded that the visible absorption consists of two super-imposed absorption bands. Ribaud|| recorded a maximum in bromine vapour at 419–422 $\mu\mu$, whilst Dobbie and Fox¶ gave the maximum as 417 $\mu\mu$. Bovis** finds that liquid bromine in very thin films shows a band at λ maximum 417–421 $\mu\mu$, λ minimum 348 $\mu\mu$. In carbon tetrachloride he found two maxima at 258 and 415 $\mu\mu$ respectively.

The colour of iodine solutions has been much studied. Some solvents yield brown solutions, others violet; the differences being generally ascribed to differences in solvation. The violet solutions such as are formed in carbon tetrachloride are regarded as normal and the solutes are not, it would appear, appreciably solvated. The absorption of the violet solutions indicates a maximum very near to that shown by the vapour, namely, at 520 $\mu\mu$ or

* 'Proc. R. Inst.,' vol. 10, p. 245 (1883).

† 'Z. Phys. Chem.,' vol. 103, p. 71 (1922); 'Z. Elektrochem.,' vol. 28, p. 496 (1922).

‡ 'Roy. Soc. Proc.,' A, vol. 122, p. 582 (1929).

§ 'Z. Phys. Chem.,' vol. 79, p. 357 (1912).

|| 'Ann. Physik,' vol. 12, p. 107 (1919).

¶ 'Roy. Soc. Proc.,' A, vol. 99, p. 456 (1921).

** 'C. R.,' vol. 178, p. 1964 (1924), *ibid.*, vol. 185, p. 57 (1927); 'Ann. Physique,' vol. 10, p. 232 (1928).

thereabouts, whereas the brown solutions show a maximum at 447 $\mu\mu$, cf. Batley.*

For solutions in chloroform, carbon tetrachloride and carbon bisulphide, Rigollot† gives the maximum as 520 $\mu\mu$; Carelli‡ records a maximum at 515 $\mu\mu$ in the latter solvent, whilst Brode§ finds the head of the band in carbon tetrachloride to be at 518 $\mu\mu$. Getman,|| on the other hand, in a very recent paper, records measurements with a Nutting photometer showing the maximum to be at 540 $\mu\mu$ in all three solvents. In our data the band occurs at 520 $\mu\mu$.

The compounds iodine monochloride and iodine trichloride form a convenient starting point for the discussion of the absorption spectra of the interhalogen compounds. Discovered in 1814 by Gay-Lussac, their real existence as chemical compounds was definitely established by the work of Stortenbeker¶ in the freezing point curves of mixtures of iodine and chlorine. It was shown by Trapp** that iodine chloride exists in two forms differing in melting point and designated as the α and β forms. Little work appears to have been published on the absorption spectrum of iodine monochloride, except that Roscoe and Thorpe†† pointed out the resemblance between the spectrum of iodine chloride and bromine, and that Gernez‡‡ noticed that the spectrum of the vapour differs from that of either chlorine or iodine.

In the present work standardised solutions of iodine and chlorine were mixed so that the halogens were present in exactly equimolecular proportions, and allowed to stand for an hour until the violet colour of the free iodine had disappeared. The concentrations used varied between 0.004 and 0.01 molar with respect to iodine chloride. Measurements were made both by the visual and photographic methods. The absorption curve showed a maximum at 64 $\mu\mu$ and a minimum at 334 $\mu\mu$, and differed completely from the curves for chlorine and iodine. As a control, two different specimens of commercial iodine chloride labelled "pure" were dissolved in carbon tetrachloride and the absorption spectra determined. The curves obtained in this way agreed

* 'Trans. Faraday Soc.,' vol. 24, p. 438 (1928).

† 'C. R.,' vol. 112, p. 38 (1891).

‡ 'Rend. Accad. Sci. Fis. Mat. Napoli,' vol. 27, p. 274 (1921).

§ 'J. Amer. Chem. Soc.,' vol. 48, p. 1877 (1926).

|| 'J. Amer. Chem. Soc.,' vol. 50, p. 2883 (1928).

¶ 'Z. Phys. Chem.,' vol. 3, p. 11 (1889); 'Rec. Trav. Chim., Pays-Bas,' vol. 7, p. 152 (1889).

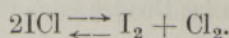
** 'J. Prakt. Chem.,' vol. 63, p. 108 (1854).

†† 'Phil. Trans.,' vol. 167, p. 207 (1876).

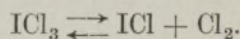
‡‡ 'C. R.,' vol. 74, p. 660 (1872).

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exceedingly well with those obtained with equimolecular mixtures. The results so far indicated that it was highly probable that the solutions contained a large amount of iodine chloride. It was, however, quite possible that some dissociation should occur in accordance with the expression



In order to test the possibility of dissociation, solutions 10 times as concentrated as those already used were examined in the ultra-violet and also in the visible to ascertain whether any trace of free chlorine or free iodine could be detected. The results were completely negative, so that it must be concluded that iodine chloride is quite stable under the conditions of the experiments. It must, however, be understood that this only applies to freshly prepared, cold, carbon tetrachloride solutions, as it is noticed that solutions of iodine monochloride in this solvent appear to decompose on standing in glass vessels exposed to daylight, when the characteristic violet colour of iodine solutions makes its appearance. The next step was to examine the absorption spectra of solutions containing three equivalents of chlorine to one of iodine, corresponding with ICl_3 . As will be seen from fig. 3 this mixture exhibits two maxima corresponding quite closely with those characterising chlorine and iodine monochloride. It would therefore seem as if iodine trichloride is not stable in dilute carbon tetrachloride solutions, but rather dissociates according to the equation

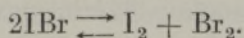


It will be noticed from fig. 3 that there is a slight discrepancy between the experimental iodine monochloride band and the similar "iodine trichloride" band. Any dissociation of iodine monochloride will be hindered by the presence of excess chlorine, and as iodine absorbs much more intensely than any other constituent of the solutions a very small proportion of free iodine would broaden the "ICl" band on the long wave side. The fact that the solutions containing three equivalents of chlorine to one of iodine are less absorbent on the long wave side of $464 \mu\mu$ than the equimolecular solutions, is consistent with a very small degree of dissociation of iodine chloride. A sample of commercial iodine trichloride was then examined under the same conditions. The absorption curve showed exactly the same maxima as before, but the $464 \mu\mu$ band was a little more intense and the chlorine band a little less intense. Probably, the material had lost some chlorine as a result of dissociation.

Iodine monobromide was first prepared by Balard in 1826 as a solid melting

at 42°. Terwogt* studied the freezing points, boiling points, vapour pressures and specific gravities of iodine—bromine mixtures. The freezing point curves indicate the presence of a compound which is in all probability IBr, but the boiling point curves show that such a compound must dissociate very readily. There seems to be no evidence of the existence of iodine tribromide. The only reference we have been able to find to the absorption spectrum of iodine bromide is in a general paper by Ruff† dealing with the use of the spectroscope as a means of detecting compound formation in mixtures. It is stated that there is no evidence of compound formation in a highly diluted mixture of iodine and bromine in carbon tetrachloride.

Reference to fig. 4 will show that the absorption spectrum of an equimolecular solution of bromine and iodine shows very considerable deviation from the simple mixture law. Whether the observed curve differs greatly from the true curve for IBr will depend naturally on the degree of dissociation



When solutions containing three equivalents of bromine for one of iodine are examined, it is found that the observed curve is made up almost quantitatively of a summation of the observed "IBr" curve and the observed curve for bromine. It therefore seems reasonable to conclude that iodine tribromide, if it exists at all, must be almost completely dissociated into iodine bromide and bromine at the dilutions used. The difference between the summation curve for iodine and bromine and the observed curve for the equimolecular mixture is moreover so great that the IBr molecule must be regarded as the main constituent of the solute.

There seems to be considerable doubt concerning the existence of bromine chloride. Balard,‡ in 1826, followed by Loewig§ in 1829 and Schonbein|| in 1863, recorded the formation of a highly refracting yellow liquid when chlorine was passed into bromine cooled in a freezing mixture. There is, however, no proof that such a liquid is bromine monochloride. Loewig also claimed to have isolated a bromine chloride pentahydrate. In 1877, Borneman¶ described bromine chloride as a red brown liquid stable only at temperatures below 10°, but came to the conclusion that Loewig's pentahydrate was really a mixture of

* 'Z. Anorg. Chem.,' vol. 47, p. 203 (1905).

† 'Z. Phys. Chem.,' vol. 76, p. 21 (1911).

‡ 'Ann. Chim. Phys.,' vol. 32, p. 337 (1826).

§ 'Dissertation,' Heidelberg (1829).

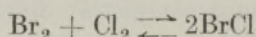
|| 'J. Prakt. Chem.,' vol. 88, p. 483 (1863).

¶ 'Liebig's Annalen,' vol. 189, p. 183 (1877).

the hydrates of bromine and chlorine. Berthelot* cast doubt on the early claims to have isolated bromine chloride because of the very small amount of heat which is developed when chlorine gas is led into liquid bromine. In more recent times Thomas and Dupois† have claimed that bromine chloride may be prepared by the action of bromine on liquid chlorine.

Lebeau,‡ in an important investigation, studied the freezing point curves for the system bromine-chlorine, only to find no evidence of compound formation in the liquid or solid states, although mixed crystals of varying composition were deposited. On the other hand, Andrews and Carlton§ discovered a marked contraction in volume when liquid chlorine and liquid bromine were mixed, a result not inconsistent with at least some compound formation. Karsten|| confirmed the work of Lebeau and concluded that the investigation of freezing points afforded no evidence for the existence of bromine chloride or bromine trichloride either in the solid or the liquid phase. Investigation of the boiling points for the system bromine-chlorine gave similar results.

The evidence for compound formation under these conditions would therefore appear to be extremely slender. When, however, the conditions are considerably different as in the work of Forbes and Fuoss¶ on the oxidation potentials of chlorine-bromine mixtures in dilute hydrochloric acid, evidence is forthcoming that the reaction



does in fact correspond with the experimental data.

There can be no doubt that the work of Simpson,** James, Walden, Delepine and Ville,†† and also of Hanson and James‡‡ in the field of organic chemistry is best interpreted on the assumption that bromine chloride can occur in solution. It was as a result of the recent work of Hanson and James (*loc. cit.*), that we decided to investigate this problem. These authors observed that an equimolecular mixture of chlorine and bromine, dissolved in carbon tetrachloride, reacted with cinnamic acid as bromine chloride were such a compound

* 'Ann. Chim. Phys.,' vol. 21, p. 375 (1880).

† 'C. R.,' vol. 143, p. 282 (1906).

‡ 'C. R.,' vol. 143, p. 589 (1906).

§ 'J. Amer. Chem. Soc.,' vol. 29, p. 688 (1907).

|| 'Z. Anorg. Chem.,' vol. 53, p. 365 (1907).

¶ 'J. Amer. Chem. Soc.,' vol. 49, p. 142 (1927).

** Simpson, 'Roy. Soc. Proc.,' A, vol. 27, pp. 118, 424 (1879).

†† James, 'J. Chem. Soc.,' vol. 43, p. 37 (1883); Walden, 'Berlin Acad. Ber.,' vol. 30, p. 2883 (1897); Delepine and Ville, 'C. R.,' vol. 170, p. 1390 (1920).

‡‡ 'J. Chem. Soc.,' p. 1955 (1928).

existent, the products of addition being the two stereoisomeric β -chloro- α -bromo- β -phenyl-propionic acids. The whole of the experimental work recorded in the present communication had been completed when the work of Barrett and Stein (*loc. cit.*) appeared, on the bromine-chlorine system and anticipated our conclusions with regard to the existence of bromine chloride. These authors were the first to provide definite physicochemical evidence for the existence of this compound, and the present work provides ample confirmation of their conclusions especially since the data on iodine chloride and iodine bromide furnish a useful check on the validity of the reasoning.

Examination of the curves recorded in fig. 5 shows that for equimolecular solutions of chlorine and bromine, the observed curve is widely different from the summation curve obtained on the assumption of no interaction. The head of the band is now at $380 \mu\mu$ and the wave-length shift together with the absence of any marked inflexion near $330 \mu\mu$ shows definitely that a new absorbing entity must be present. When the curve for solutions containing three equivalents of chlorine to one of bromine is examined, it will be seen that it corresponds quite closely with the summation of chlorine and the "BrCl" curves. It is clear that bromine trichloride cannot exist at the dilutions we have used, and that its absorption is roughly that of chlorine plus that of the equimolecular mixture of chlorine and bromine. When, however, the chlorine curve is subtracted from the curve obtained with the Cl : Br = 3 : 1 mixture, it is found that the new curve, whilst agreeing as regards the wave-length of maximum absorption with the 1 : 1 curve, differs from it in that the "BrCl" portion of the curve shows a definitely narrower band in the 1 : 3 mixture than in the 1 : 1 solution. This can only mean that bromine chloride is dissociated appreciably into chlorine and bromine at the dilution used. Free chlorine would throw back the dissociation so that the BrCl portion of the 3 : 1 solution is nearer to the true absorption spectrum of bromine chloride, than the curve for the equimolecular solution.

Summary.

1. The absorption spectra of chlorine, bromine and iodine in carbon tetrachloride have been studied.

2. It is shown that iodine chloride, iodine bromide and bromine chloride possess absorption bands, the maxima of which are accurately measurable. At the dilutions necessary for the investigation of absorption spectra all three compounds are dissociated to some extent, with iodine chloride the dissociation is barely detectable, with iodine bromide it remains small, whilst

with bromine chloride it is much greater, but still remains probably less than 50 per cent.

3. Solutions containing halogens in the proportions necessary for the formation of iodine trichloride, iodine tribromide and bromine trichloride, were found to contain the monohalide and free halogen only.

*On the Emission of Soft X-Rays by Different Elements, with
Reference to the Effect of Adsorbed Gas.*

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College, London.

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[PLATE 6.]

1. *Introduction.*

The ejection of photoelectrons from a metal surface exposed to soft X-rays has been commonly used as the method for measuring the intensity of these rays. However, the relation between the intensity of soft X-rays and the photoelectric current as a function of the nature of the surface of the photoelectric detector seems to have received comparatively little attention. In the present work, the effect of adsorbed gas molecules on the photoelectric plate has been given special consideration. The investigation is an extension of the work of Richardson and Robertson* who measured the relative soft X-ray emissivities of 14 elements. The special conditions of the experiment like the polishing of the surface, the state of degassing of the photoelectric plate and the conditions of oxidation of the target faces, have been investigated more thoroughly. Having ascertained the conditions necessary for reliable values, the emission of soft X-rays has been compared for 11 elements, Si, Cr, Mn, Fe, Co, Ni, Cu, Pd, W, Pt, and Au.

2. *Apparatus and Connections.*

The apparatus used consisted of a quartz containing vessel, the details of which are shown in fig. 1. The part of the tube where soft X-rays are excited

* Richardson and Robertson, 'Roy. Soc. Proc.,' A, vol. 115, p. 280 (1927), *ibid.*, vol. 124, p. 188 (1929).