

CCCVI.—*A Study of the Polyhalides. Part II.*
Physical Properties.

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Dissociation Pressures.—All polyhalides dissociate spontaneously, giving off the vapour of a halogen, halogen halide, or mixture of halogens, and leaving a residue of a monohalide. The present investigation has definitely confirmed that the monohalide produced, in the absence of a solvent, is always the compound of the metal or other kation with the most electronegative halogen present in the original polyhalide. Thus, potassium dichloroiodide, KICl_2 , gives off a vapour of the composition ICl and leaves a residue of potassium

chloride. The dissociation pressure of a trihalide is constant at constant temperature, provided that both solid trihalide and the resultant solid monohalide be present, the system containing three phases and two components. This tendency of the polyhalides to dissociate is of great importance in the investigation of their physical properties and chemical reactions. There is a close correlation between the dissociation pressures and other physical properties, and dissociation is frequently the first stage in their reactions with other substances. One instance of the way in which variation in dissociation pressure can influence the course of a reaction has already been given (J., 1930, 2751). From a comparison of the dissociation pressures of a large number of polyhalides, the factors influencing their stability have been determined; *e.g.*, it is found that the polyhalides containing one iodine atom are very much more stable than those containing none, whereas the introduction of further iodine atoms has the reverse effect. Such observations are of importance in the elucidation of the structure of these compounds (p. 2250).

The four chief methods available for the determination of the dissociation pressure of a polyhalide are: (i) direct measurement by means of a manometer; (ii) static method, in which the concentration of halogen in the vapour phase after equilibrium has been reached is determined by ordinary analytical methods (compare Wildermann, *Z. physikal. Chem.*, 1893, **11**, 407); (iii) gas-streaming method (Naumann, *Inaug. Diss.*, Berlin, 1907); (iv) organic-solvent method. The authors have employed methods (i) and (iv), and have also determined the vapour pressure of bromine at 25° by method (ii), obtaining the value 213 mm., in good agreement with Ramsay and Young (J., 1886, **49**, 453).

The dissociation pressures of most of the trihalides of potassium, rubidium, caesium, and ammonium have been determined over a range of temperature by Ephraim (*Ber.*, 1917, **50**, 1096), using a mercury manometer with traps of sulphuric acid and phosphorus to prevent the halogen vapours from attacking the mercury. McCombie and Reade (J., 1924, **125**, 148) attempted to measure the dissociation pressures of some phenyltrimethylammonium polyhalides, but they omitted to use any trap, and, possibly for this reason, their measurements appear to be untrustworthy. The consistency of measurements on the same substance at different temperatures may be tested by means of the equation (Jackson, J., 1911, **99**, 1066)

$$\log_e p_2/p_1 = q/R \cdot (1/T_1 - 1/T_2)$$

On plotting $\log p$ against $1/T$, a straight line should be obtained. Ephraim's data give, in most cases, smooth curves which approxi-

mate closely to straight lines, whereas the values obtained by McCombie and Reade give no such result.

Since, in Ephraim's apparatus, halogen is being continually absorbed, it might be suspected that he would not have succeeded in reaching a true equilibrium. Since the error due to this cause would be approximately proportional to the dissociation pressure, it would not be apparent on testing the results by the above method. In order to examine this point, the authors have determined the dissociation pressures of potassium dichloriodide and dibromiodide, employing a spring manometer made entirely of glass, as described by Jackson (*loc. cit.*, p. 1067, bulb of form 2). In addition, the dissociation pressure of potassium chlorobromiodide has been measured for the first time. The sensitivity was such that a 1 mm. deflexion of the pointer corresponded to a pressure difference of about 1 mm. The potassium dichloriodide was prepared as described in Part I (this vol., p. 1863, last method) and gave a satisfactory analysis (Found: K, 16.50; thiosulphate titration, 8.45 c.c. Calc.: K, 16.50%; titre, 8.44 c.c.). It had been dried for six months over phosphoric oxide; the exposure to the air during transference to the apparatus was sufficient to eliminate any effects due to intensive drying (see p. 2252). Air was thoroughly removed by a vacuum pump before sealing, the material being cooled in liquid air during this process. A series of pressure readings was first obtained with the temperature rising, and afterwards another series with the temperature falling. The pressure fell again to zero on cooling in liquid air. Melting begins rather below 60°, but it is far from sharp, there being some solid phase (probably potassium chloride) present even at 100° (see p. 2251). Table I gives our results, Ephraim's data over the same temperature range being added for comparison (pressures are in mm. of Hg in every case):

TABLE I.

Present data.				Temp. falling.		Ephraim's data. (?) Temp. rising.	
Temp. rising.		Temp. falling.		Temp. falling.		Temp. rising.	
Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
21.9°	7	70.2°	103	21.4°	17	41°	28
31.9	17	73.6	117	40.4	38	58	58
38.4	26	77.2	132	57.4	71	71.5	114
47.3	45	82.6	161	64.8	82	79.5	153
52.6	55	88.6	195	75.6	133	90	210
57.8	69	96.6	247			102	292
65.6	86	100.2	276				

On plotting $\log p$ against $1/T$, it will be found that the points obtained as the temperature was raised, and also those obtained by Ephraim, lie on two straight lines which intersect at the m. p., thus confirming Ephraim's data, with the exception of his value at 58°,

which may be a misprint. The points obtained with temperature falling lie on the same straight line as the others above the m. p., but below it they lie on the continuation of this line, there being no break in this case. This is due to a supercooling effect which will be discussed later (p. 2252).

The following values were obtained for the dissociation pressure of potassium dibromiodide :

Temp.	25°	30°	40°	50°	60°
Press., mm.	2.5	3	4	5.5	8

These values are considerably below those of Ephraim, who, however, obtained his material by crystallisation from water. The authors have found that potassium dibromiodide crystallises from water as a *monohydrate*, m. p. 58° (Found : H₂O, 5.40. KIBr₂.H₂O requires H₂O, 5.24%), so that Ephraim's figures probably relate to this compound. The water content was determined after the crystals had been dried to constant weight over the anhydrous salt (compare Grace, this vol., p. 608). This result was confirmed by leaving the anhydrous substance over a saturated solution of the same material, whereby it became converted into monohydrate, which also separated from the solution. It was shown that potassium dichloriodide and tetrachloriodide do not form any hydrate at room temperature. As pointed out by Grace, Ephraim's data for potassium tri-iodide are really those of a hydrate.

Potassium chlorbromiodide, KClBrI, being a new compound, no measurements of its dissociation pressure are on record :

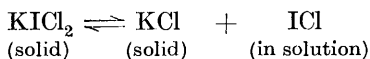
Temp.	20.2°	23.5°	29.7°	39.7°	43.6°	52.0°	65.1°	78.9°
Press., mm.	11	12	18	30	36	53	87	166

From the form of the curve, the m. p. would appear to be about 36°. These determinations were carried out in collaboration with G. H. Cheesman, to whom the authors wish to express their thanks for valuable assistance in this and other matters connected with the research.

The method most employed for determining dissociation pressures was that due to Abegg and Hamburger (*Z. anorg. Chem.*, 1906, **50**, 403), who determined by its means the dissociation pressures of the alkali polyiodides at 25°. The polyhalides are left in contact with a suitable organic solvent in a closed vessel in a thermostat until equilibrium is reached. The concentration of halogen in the solvent is then determined. For any one solvent this equilibrium concentration is always the same for a given trihalide at a given temperature, provided the monohalide formed by its dissociation be present. It is easy to determine this value for a number of trihalides at the same temperature with the same solvent. In this

way one can obtain a table of constants for different trihalides, such as those given in Table II. These values provide an excellent measure of the relative stabilities of the different compounds, and they may generally be determined more accurately than the actual dissociation pressures, which are in most cases very small at room temperature. If required, the dissociation pressures may be calculated from these values, Henry's law being assumed to apply to solutions of the halogens in the solvent in use, as was done by Abegg and Hamburger. Alternatively, instead of assuming Henry's law, the relationship between the partial pressure of halogen in the vapour phase and the concentration of halogen in the liquid may be determined experimentally by means of Wildermann's apparatus (*loc. cit.*). The authors have worked mainly, however, with solutions of iodine monobromide to which the last two methods could not well be applied, owing to the unequal distribution of iodine and bromine between the liquid and the vapour phase.

Benzene, the solvent employed by Abegg and Hamburger for polyiodides, is unsuitable for work of a more general nature, where halogens and halogen halides which attack benzene are liberated. It is desirable that ionisation and solvation of the halogen should not occur, and essential that no solid solvates be formed, a condition not fulfilled by benzene (Grace, *loc. cit.*). The solvent must not be one in which either the monohalides or the polyhalides themselves dissolve: only the halogens must pass into solution, equilibria such as



being established. Carbon tetrachloride admirably fulfils all these requirements and was employed throughout the present research. The pure solvent was dried for at least a week by means of phosphoric oxide, and filtered before use. It did not affect the p_{H} of water with which it was shaken, and did not give any colour with potassium iodide-starch solution. It distilled completely within 0.1° of the correct b. p. and had the correct density at 25° .

Starting with a mixture of the polyhalide, the monohalide formed by its dissociation, and carbon tetrachloride, and shaking the mixture mechanically in a thermostat at $25^\circ \pm 0.05^\circ$, equilibrium could be reached in one day, but at least a week was normally allowed. Starting with the monohalide and a concentrated solution of the halogen or halogen halide in carbon tetrachloride, several months were often required to reach even approximate equilibrium.

The concentration of halogen was determined by running a measured volume of the carbon tetrachloride solution from a pipette into an aqueous solution of potassium iodide in a stoppered bottle,

and titrating with sodium thiosulphate with frequent shaking, starch solution being used as indicator. The thiosulphate solutions varied from 0.9 to 0.005*N*, the latter being freshly standardised against solutions of iodine bromide in carbon tetrachloride of known concentration.

Apparently the only data hitherto obtained by this method have been for the polyiodides of the alkali metals and ammonium (Abegg and Hamburger, *loc. cit.*). The authors have obtained similar data (see Table II) for other series of polyhalides formed by the alkali

TABLE II.

Equilibrium concentrations of halogen or halogen halide in carbon tetrachloride over various trihalides of the alkali metals and ammonium at 25°.

Kation.	Anion.			
	I ₃ . Conc. of I ₂ .	IBr ₂ . Conc. of IBr.	IBrCl. Conc. of IBr.	ICl ₂ . Conc. of ICl.
K	No compound *	0.0473	0.61	0.029
Rb	0.0059	0.0010	0.0108	0.00035
Cs	0.00075	0.00014	0.00035	0.00006
NH ₄	0.0120	0.00842	0.122	0.0057

* See Grace, *loc. cit.*

metals and ammonium, and have measured the equilibrium concentrations for a series of polyhalides having the same anion but a wide variety of kations. For the latter purpose the dibromiodides were chosen. The concentrations are expressed in g.-atoms of halogen per litre. The figures for the tri-iodides are calculated from those obtained by Abegg and Hamburger, using benzene as solvent, it being assumed that Henry's law applies to solutions of iodine in both solvents. In order to test this point, the equilibrium value for ammonium tri-iodide and carbon tetrachloride was determined directly and found to be 0.0130, a satisfactory agreement in view of the assumptions made and the uncertainty in the published values for the solubility of iodine in these solvents. The authors have redetermined the solubility of iodine in carbon tetrachloride at 25° and obtained the value 2.88 g. per 100 c.c. of solution (*d* 1.594 g./c.c.) or 1.81 g. per 100 g. of solution, making the saturated solution 0.227*N* and the "mol-fraction" of iodine 0.0110, agreeing exactly with Hildebrand (*J. Amer. Chem. Soc.*, 1920, **42**, 2185), who, however, does not give any density or volume data. Earlier published values differ considerably among themselves.

According to Abegg and Hamburger, there is no unsolvated polyiodide of sodium stable at 25°; evidence has already been given (this vol., p. 1857) showing that mixed polyhalides of sodium may exist, but it is impossible to quote any definite values for the equi-

brium concentrations, which are probably greater than N . No data are available for lithium compounds.

For caesium tribromide, the equilibrium concentration was found to be $0.0438N$, and for the compound CsI_2Br it was $0.0155N$. On the other hand, when potassium bromide was shaken with a saturated solution of iodine in carbon tetrachloride, no fall in concentration occurred, indicating the non-existence of any compound of potassium bromide and iodine at 25° . Similar evidence was obtained that no compound of potassium nitrate and iodine bromide exists. These negative results show that no fall in concentration occurs owing to adsorption.

Caesium fluoride was found to absorb iodine bromide vapour, forming a yellow compound which would appear to be *caesium fluorobromiodide*, CsIBrF . This gave an equilibrium concentration of $0.01N$.

It will be seen from Table II that the stability of a polyhalide in the solid state depends on both the metal and the polyhalide group. It will be shown later that in solution the stability is independent of the metal, being the same for all polyhalides of the same series. Hence, it would appear that in solution the metal does not form part of the complex ion, although, of course, it does form part of the solid crystal structure, and so affects the stability in the solid state.

For the different kations the order of increasing stability is $\text{Na} < \text{K} < \text{NH}_4 < \text{Rb} < \text{Cs}$. The fact that the order is the same for each of the polyhalide anions indicates that, in order to determine the tendency which different kations have to form stable polyhalides, it is sufficient to measure the equilibrium concentrations for one series of polyhalides, all having the same anion (see Table III).

TABLE III.

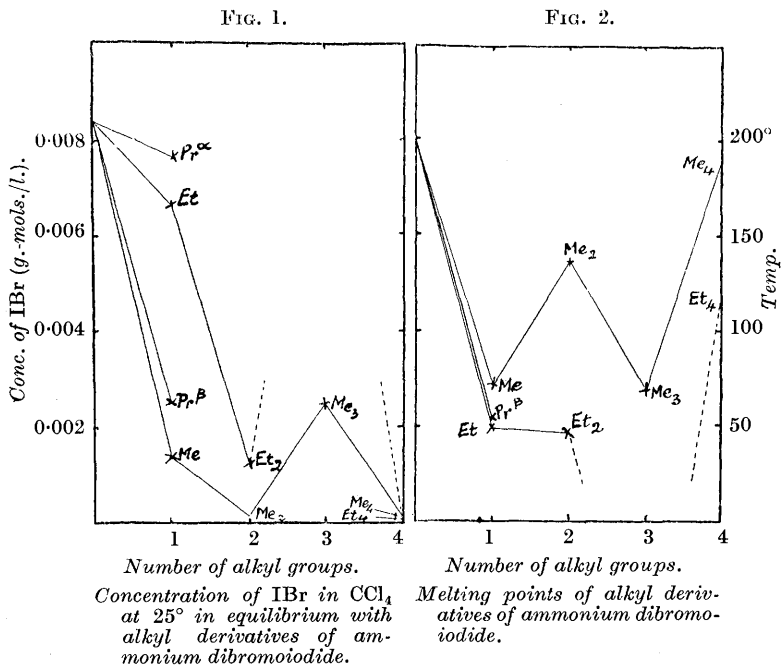
Equilibrium concentrations of iodine bromide in carbon tetrachloride at 25° over dibromiodides of the type $[\text{NR}_1\text{R}_2\text{R}_3\text{R}_4][\text{IBr}_2]'$.

R_1 .	R_2 .	R_3 .	R_4 .	Conc.	R_1 .	R_2 .	R_3 .	R_4 .	Conc.
H	H	H	H	0.00842	H	H	H	H	0.0084
Me	H	H	H	0.00134	Et	H	H	H	0.0066
Me	Me	H	H	0.00004	Et	Et	H	H	0.0012
Me	Me	Me	H	0.00249	Et	Et	Et	H	Not known
Me	Me	Me	Me	0.00004	Et	Et	Et	Et	0.00000
Et	Me	Me	Me	0.00002	Pr $^\alpha$	H	H	H	0.0076
					Pr $^\beta$	H	H	H	0.0025
Pyridine derivatives :—					$\overbrace{\text{C}_5\text{H}_5\text{NH}}$ $\text{C}_5\text{H}_5\text{NMe}$				0.00018
									0.00023

None of these substances has any detectable solubility in carbon tetrachloride, a fact that is in accordance with the supposition that they are strong electrolytes. Only iodine monobromide passes into

solution, the dibromiodide and monobromide (hydrobromide) of the base remaining undissolved. On the other hand, the compound of pyridine and iodine monobromide, C_5H_5NIBr , tends to dissociate into its constituents, both of which are soluble in carbon tetrachloride, so the substance does in effect dissolve (this vol., p. 1861).

Consideration of Table III or of Fig. 1 shows that there is an alternation in the dissociation tendencies of the ammonium dibromiodides, those with an even number of alkyl groups being more stable



than the related compounds having an odd number. The phenomenon is very pronounced with the methyl derivatives. The failure to isolate triethylammonium dibromiodide (this vol., p. 1860) is probably to be attributed to high dissociation pressure and more especially to low m. p. A similar well-marked alternation is seen in the m. p.'s (Fig. 2). There is no such alternation in the properties of the corresponding monohalides. It is the compounds containing the most symmetrical cations which are most stable. If we assume that the polyhalide anions have structures in which the most electropositive halogen (usually iodine) forms the positively charged central atom of the anion (compare Gilbert, Goldstein, and

Lowry; this vol., p. 1092), it will be seen that it is also the polyhalides containing the most symmetrical anions which are the most stable: the order of increasing stability is usually $\text{Br}^- - \text{I}^+ - \text{I}^-$, $\text{F}^- - \text{I}^+ - \text{Br}^-$, $\text{Cl}^- - \text{I}^+ - \text{Br}^-$, $\text{I}^- - \text{I}^+ - \text{I}^-$, $\text{Br}^- - \text{I}^+ - \text{Br}^-$, $\text{Cl}^- - \text{I}^+ - \text{Cl}^-$. In general, the factors favouring stability of a polyhalide are symmetry, a kation of large molecular volume, and the presence of one iodine atom (*i.e.*, of a large electropositive atom) at the centre of the anion; in order to produce the most stable polyhalide the other atoms should be light electronegative atoms, such as chlorine. The stability of organic polyiodides is to be attributed to the low volatility and chemical inactivity of iodine, which does not tend to destroy the organic kations.

Phenomena occurring on the Melting of Polyhalides.—In considering the general properties of the polyhalides, their tendency to dissociate into monohalide and halogen or halogen halide is of fundamental importance, and affords a satisfactory explanation of the phenomena occurring during melting. From a consideration of the phase rule, it follows that, when a polyhalide is heated in a closed space, a liquid phase will appear at a temperature which is constant for any given compound. This is the value commonly quoted as the m. p. in a sealed tube, and is practically identical with that in an open vessel. Above this temperature there can be only one solid phase, which is normally the monohalide. So long as this solid phase is present, the composition of the liquid and the dissociation pressure are fixed for any given temperature. Where partial dissociation of a halogen halide occurs, it is necessary to add the condition that the volume of the vapour phase be small. If the liquid phase consisted of the pure molten halogen (or halogen halide), the dissociation pressure would be equal to the vapour pressure of the halogen (or halogen halide), the polyhalide being completely dissociated. In such a case there would be a considerable quantity of solid monohalide present and the material would be pasty. It is found that the monohalide normally dissolves to some extent in the liquid phase (combining partially or completely), so the dissociation pressure is lower than the vapour pressure of the pure halogen. With a polyhalide of low dissociation pressure, the metallic monohalide dissolves completely or almost completely within a few degrees of the beginning of melting, so the substance melts almost as sharply as a non-dissociating compound; but in the case of a compound of high dissociation pressure, very little monohalide passes into the liquid phase, so the substance melts to a paste which may not become completely liquid even at a temperature considerably above the m. p. It follows that the sharpness of melting is a criterion of the stability of a polyhalide. The potassium salts, particularly the chlorobromiodide and di-

chloriodide, go through a pasty stage, whereas the cæsium salts melt sharply, the ammonium salts being intermediate.

From the above treatment of the subject, it follows that the m. p. of a polyhalide is the temperature at which the dissociation-pressure curve of the solid polyhalide cuts the vapour-pressure curve of a saturated solution of the monohalide in the molten halogen (or halogen halide). Hence, one would expect the m. p. to be lower for a polyhalide of high dissociation pressure than for a more stable one. The change occurring at the m. p. is essentially partial dissociation, and in the case of an unstable polyhalide it involves almost complete decomposition into monohalide and free halogen. In practice a close correlation between m. p. and dissociation pressure is found, as may be seen, for example, from a comparison of Figs. 1 and 2, or from Table IV. Hence, the m. p., which is readily determined, forms a measure of the stability of a polyhalide. Inorganic polyhalides, however, melt higher than organic polyhalides of similar dissociation pressure, methyl compounds higher than ethyl, and so on.

Arrested Transformation.—The supercooling effect which occurs when molten potassium dichloriodide is cooled has already been mentioned (p. 2246). It would now appear that the effect is due to the fact that the recombination reaction $KCl + ICl = KICl_2$ is not instantaneous. The curve with temperature falling thus gives the vapour pressure of saturated solutions of potassium chloride in iodine monochloride, even below the m. p.

It is also found that the reverse change may be inhibited by thorough drying. Thus a specimen of potassium dichloriodide which had been dried for six months by means of phosphoric oxide did not melt even when heated in a sealed tube to 180° , at which temperature it appeared to be completely decomposed into solid potassium chloride and iodine monochloride vapour. After exposure to the air for a few minutes, the substance gave the normal m. p. (ca. 55°): it was not hydrated and contained only a trace of water (see analysis, p. 2245). The same effect has been observed in the case of potassium dibromiodide and tetrachloriodide. The m. p. of the dibromiodide was quoted by Wells and Wheeler (*Z. anorg. Chem.*, 1892, **1**, 442) as 60° , by Ephraim (*loc. cit.*) as rather below 60° and by the authors as 58° , although the figures given by the earlier authorities may really refer to the hydrate, which melts at approximately the same temperature. After drying for 24 months over phosphoric oxide, it did not melt or decompose until heated to 150° , but after a short exposure to the air it gave the normal value. The elevation of the m. p. of potassium dibromiodide has been confirmed by R. H. Purcell and G. H. Cheesman, by

whom the matter is being further investigated. Potassium tetrachloroiodide normally melts between 110° and 115°, but after drying over phosphoric oxide for a month it melted at about 150°, the original value being obtained again after exposure to the air.

Solubilities of Polyhalides.—The polyhalides are, in general, insoluble in liquids of low dielectric constant, with the exception of free halogens and halogen halides, but are partially decomposed as already described (p. 2247). They are, however, usually soluble in liquids of high dielectric constant, such as acetone, alcohols, and water, the organic polyhalides being more soluble in organic solvents and the inorganic compounds in water. As would be expected from theoretical considerations, the compounds of higher dissociation pressure are the more soluble. The solubility in water is complicated by hydrolysis: thus, when potassium tetrachloroiodide is shaken with water, compounds such as $2\text{KIO}_3, \text{HCl}$ appear in the solid phase, the system in effect containing 5 components, so that no true solubility can be quoted for such a substance. Nevertheless, for closely related compounds, the solubilities in water are roughly proportional to the dissociation pressures. Table IV shows

TABLE IV.

Formula.	Conc. in CCl_4 .	M. p.	Solubility in water.
KIBr_2	0.0473	58°	1 part H_2O dissolves 10—12 parts at 18°.
NH_4IBr_2	0.0084	198	Very high (sat. soln. syrupy).
$\text{Pr}^\alpha\text{NH}_2\text{IBr}_2$	0.0076	?	Similar.
$\text{Et}^\alpha\text{NH}_2\text{IBr}_2$	0.0066	49	Similar.
$\text{Pr}^\beta\text{NH}_2\text{IBr}_2$	0.0025	54	Readily soluble.
$\text{Me}_3\text{NHIBr}_2$	0.0025	67	Moderately soluble.
$\text{MeNH}_2\text{IBr}_2$	0.0013	71	Moderately soluble.
$\text{Et}_2\text{NH}_2\text{IBr}_2$	0.0012	46	Moderately soluble.
RbIBr_2	0.0010	225	Moderately soluble.
$\text{C}_5\text{H}_5\text{NMeIBr}_2$	0.00023	61	1.33% at 25°.
$\text{C}_5\text{H}_5\text{NHI}^\alpha\text{Br}_2$	0.00018	174	1.27% at 25°.
CsIBr_2	0.00014	247	4.45% at 20° (Wells).
$\text{Me}_2\text{NH}_2\text{IBr}_2$	0.00004	136	About 3% at 0°.
Me_4NIBr_2	0.00004	190	0.85% at 25°.
$\text{Me}_3\text{NEtIBr}_2$	0.00002	145	0.6% at 25°.
Et_4NIBr_2	0.00000	119	0.25% at 25°.

the degree of correlation between the dissociation pressure (as measured by the carbon tetrachloride equilibrium concentration), m. p., and solubility for a number of dibromoiodides, arranged in order of stability. With the exception of the value obtained by Wells, all the solubilities given have been obtained by the authors for the first time. The compounds with equilibrium concentrations greater than about 0.001*N* deliquesce in moist air and also absorb the vapours of bromine, iodine bromide, etc., forming semi-liquid

materials, but the more stable compounds do not do so. The properties of the members of the other series of polyhalides are similarly related to their dissociation pressures. Only the compounds of high dissociation pressure crystallise from water as hydrates (*e.g.*, $\text{KIBr}_2 \cdot \text{H}_2\text{O}$), whilst the most unstable compounds are known only in the solvated condition (*e.g.*, $\text{KI}_3 \cdot \text{H}_2\text{O}$).

Summary.

The relationship between the dissociation pressure and other properties of the polyhalides is discussed. The methods available for the determination of dissociation pressure are considered, and the work of earlier investigators criticised. The dissociation pressures of potassium dibromiodide, chlorobromiodide, and dichloriodide have been measured by means of a glass-spring manometer. The data for the dichloriodides agree with those of Ephraim, but those for the dibromiodide are considerably lower. It is suggested that Ephraim's material may have been hydrated, it being shown that a hydrate, $\text{KIBr}_2 \cdot \text{H}_2\text{O}$, exists.

The estimation of the dissociation pressure by shaking with carbon tetrachloride is discussed, and data are given for the tri-iodides, dibromiodides, chlorobromiodides, dichloriodides, and various other polyhalides of the alkali metals, and for a number of organic dibromiodides. It is confirmed that the order of stability of the different kations is $\text{Na} < \text{K} < \text{NH}_4 < \text{Rb} < \text{Cs}$, irrespective of the anion.

It is also shown that there is an alternation in the dissociation tendencies of the ammonium dibromiodides, those having an even number of alkyl groups being the most stable.

The general conditions favouring the stability of a polyhalide are deduced.

The phenomena occurring on the melting of polyhalides are discussed in the light of the phase rule, and the effect of prolonged drying is investigated.

Data are given for the solubilities of the dibromiodides in water, for that of iodine in carbon tetrachloride, and for the vapour pressure of bromine at 25° .

Evidence is given that the compound CsIBrF exists.