232. *A Hydrate of Potassium Dichloroiodide.*

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Potassium dichloroiodide exists as a monohydrate as well as the anhydrous compound.

The compounds $KIBr_2$ and $KICl_2$ were reported by Wells, Wheeler, and Penfield[1] but the analyses given show deficiencies of about 6%. Cremer and Duncan[2] and Cheeseman and Martin,[3] working separately but in association, showed that for the dibromoiodide the analytical deficiency was attributable to the formation of a hydrate $KIBr_2,H_2O$ when the substance was crystallised from or produced in the presence of water. This hydrate gave a dissociation pressure in agreement with values reported by Ephraim,[4] but the anhydrous material gave pressures considerably lower.

Cremer and Duncan[2] maintained that a similar explanation could not be applicable in the case of $KICl_2$, since material dried for several months over phosphoric oxide gave dissociation pressures similar to those reported by Ephraim for material crystallised from water. On the other hand, Cremer and Duncan reported that in the equilibrium $KICl_2$(solid)–KCl(solid)–ICl (in carbon tetrachloride) a concentration of ICl amounting to 0·029N was set up at 25°. This, combined with Blair and Yost's data,[5] corresponds with a dissociation pressure of about 0·6 mm. The pressures reported by Cremer and Duncan (actually measured by Duncan and Cheesman) were 7 mm. at 21·9° and 17 mm. at 31·9°; extrapolation of Ephraim's curve leads to a similar estimate, and these values are more than 10 times larger than those calculated from the experiments in carbon tetrachloride. As it therefore seems possible that the dissociation pressures reported by Cremer and Duncan may be erroneous, and that their conclusion regarding the non-existence of a hydrate of $KICl_2$ was invalid, the question has been re-examined.

Potassium dichloroiodide was prepared by both wet and dry methods and the deficiency in the analysis of the former confirmed and shown to correspond with the formula $KICl_2,H_2O$. Its dissociation pressure accorded well with Ephraim's values and those reported by Cremer and Duncan on reputedly dry material. On the other hand, material prepared by the dry method and enclosed in an apparatus provided with a phosphoric oxide bulb gave much lower dissociation pressures which accord more closely with those estimated from the equilibrium in carbon tetrachloride. Finally, the two materials gave quite distinct *X*-ray diffraction patterns. both of which differ from that of potassium chloride, which might be present in each as an impurity.

The formation of a hydrate also explains the anomalous effect, reported by Cremer and Duncan, of dehydration at the " melting point " of the dichloroiodide.

It thus appears that the dichloroiodide, like $KIBr_2$ and KI_3, forms a monohydrate. Of the three, KI_3 alone is unknown in the anhydrous state.

Experimental

The wet method of Wells *et al.*[1] was found most suitable. Sufficient water was added to powdered potassium chloride to produce a thin slurry when boiling (2—3 ml. for 5 g.), and the theoretical amount of finely ground iodine mixed in (8·5 g.). Chlorine was then added, the mixture being kept well stirred and at 80—90°, until all the iodine had dissolved, slightly less than the theoretical amount of chlorine being taken up. Orange crystals up to 15 mm. long formed on cooling (m. p. 50—60° in a sealed tube).

The anhydrous material was prepared by Cremer and Duncan's method. Dry chlorine was

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[1] Wells, Wheeler, and Penfield, *Z. anorg. Chem.*, 1892, **1**, 442.

[2] Cremer and Duncan, *J.*, 1931, 2243.

[3] Cheesman and Martin, *J.*, 1932, 2640.

[4] Ephraim, *Ber.*, 1917, **50**, 1069.

[5] Blair and Yost, *J. Amer. Chem. Soc.*, 1933, **55**, 4489.

passed over finely ground potassium dibromoiodide (prepared in the dry way from potassium iodide and bromine) spread on a watch glass in an 8 oz. bottle containing a layer of calcium chloride. The liberated bromine was sucked off and the material reground and spread at intervals until nearly uniform in colour, then stored in the stoppered bottle for ½ hr., after which it was uniformly bright yellow. It was stored in a weighing bottle over phosphoric oxide. It did not melt in a sealed tube but whitened above 200°.

Analysis.—The oxidising equivalent of the material was found by adding excess of aqueous potassium iodide and titrating with thiosulphate. Absence of iodate was checked by adding sulphuric acid at the end of the titration. The proportion of volatile constituents was estimated by the conversion into monohalide on gentle ignition.

The following analytical figures were obtained: data for the dibromoiodide are included as it was the starting material for the dichloroiodide:

	Titre (ml. of N-$Na_2S_2O_3$/g.)		Loss on ignition (%)	
	Found	Calc.	Found	Calc.
$KIBr_2$	6·13	6·14	63·66	63·48
$KICl_2$	8·05, 8·10	8·44	68·32	68·53
$KICl_2,H_2O$	7·70, 7·76	7·83	71·73, 71·68	70·74

The discrepancies may be due to slight contamination of the dichloroiodide with potassium chloride due to loss of halogen, and the difficulty of drying $KICl_2,H_2O$ completely without risk of excessive decomposition.

Dissociation Pressures.—These were measured in a glass-spring manometer similar to that used by Cremer and Duncan. The apparatus was evacuated with a mercury diffusion pump and the sample cooled with liquid oxygen whilst being sealed. With the anhydrous material phosphoric oxide was sublimed into the centre section from an additional side arm, which was then removed before being sealed off from the pumps. This apparatus was set aside for 24 hr. to allow the phosphoric oxide to absorb any small traces of water.

The following pressures were recorded for anhydrous $KICl_2$:

Temp. (°c)	32·5	53·2	71·5	81·5	92·0	100	111	124	132	138
Pressure (mm.)	3·4	5·6	19·2	32·8	48·7	67·6	79·1	123·9	189·0	250·3

The agreement of the present observations on the hydrate with those of Ephraim and of Cremer and Duncan, and their relationship with the measurements on the anhydrous material, were demonstrated graphically.

The hydrated material recombined immediately on cooling, whereas the anhydrous was slow, recombination not being complete some 6 days later.

X-*Ray Diffraction Patterns.*—These were obtained with a rotated sealed glass capillary in a 19 cm. camera with unfiltered copper radiation. The hydrous material was packed at low temperature in a deep-freeze unit to minimise decomposition.

The following lines were observed: $KICl_2$: θ = 11·16(w), 12·43(vs), 13·34(w), 13·58(w), 14·46(w), 14·78(vs), 15·96(vw), 16·40(vw), 17·15(w), 19·01(vs), 19·39(w), 21·93(w), 22·84(w), 24·42(s), 25·26(w), 25·98(w), 28·07(w), 28·67(s), 30·03(w), 33·14(s), 38·98(w). $KICl_2,H_2O$: θ = 9·21(w), 9·39(s), 9·87(w), 10·56(w), 10·86(w), 11·01(s), 11·31(s), 12·39(vs), 13·26(w), 13·52(vw) 14·04(s), 14·54(vw), 14·72(vs), 16·34(s), 17·00(vs), 17·60(w), 18·95(vs), 19·33(w), 19·54(s), 19·75(vw), 19·87(vw), 21·18(s), 21·63(w), 21·93(w), 22·12(s), 22·75(w), 23·22(s), 23·74(w), 24·39(s), 24·78(s), 25·23(w), 25·74(w), 25·97(w), 27·17(s), 28·82(s), 29·50(w), 29·92(w), 30·16(w), 31·30(s), 33·34(s), 33·75(w), 34·80(w), 35·40(w), 35·99(w), 36·74(vw), 38·98(vw), 39·89(vw), 40·50(vw), 40·94(vw), 44·22(vw), 46·77(vw), 66·40(vw), 66·68(vw).

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