CCXVI.—*Cæsium Tetrabromide.*

By NORMAN RAE.

BRIGGS, GREENAWALD, and LEONARD (*J. Physical Chem.*, 1930, **34**, 1951) have recently demonstrated that the only solid cæsium polyiodides which exist at 25° are the tetra- and the tri-iodide. The former compound had previously been regarded as the penta-iodide, after the discoverers of these iodides (Wells and Penfield, *Amer. J. Sci.*, 1892, **43**, 17; Wells and Wheeler, *ibid.*, 1892, **44**, 43). It appeared to be of interest, therefore, to investigate the authenticity of the cæsium pentabromide described, together with a tribromide, by Wells and his co-workers.

Wells and Wheeler state "when a concentrated solution of cæsium bromide is shaken up with a large excess of bromine there is no separation of cæsium tribromide, as is the case when the theoretical amount of bromine is used. A large part of the cæsium bromide goes into solution in the liquid bromine, and on taking up a sufficient quantity of cæsium bromide this solution becomes lighter in colour than pure bromine." They further state that spontaneous evaporation below 0° of the above solution of cæsium bromide in bromine yielded a dark red solid which was prepared for analysis by pressing with papers at the same low temperature and then contained Cs, 29·93%. No doubt, in ascribing the formula $CsBr_5$ to this solid, Wells was influenced by the fact that at the time he was preparing the analogues of Filhol's salt $KICl_4$, in which the alkali metal is combined with five halogen atoms. His analysis, however, is in far better agreement with a tetrabromide (Calc. : Cs, 29·35%) than a pentabromide (Calc. : Cs, 24·95%).

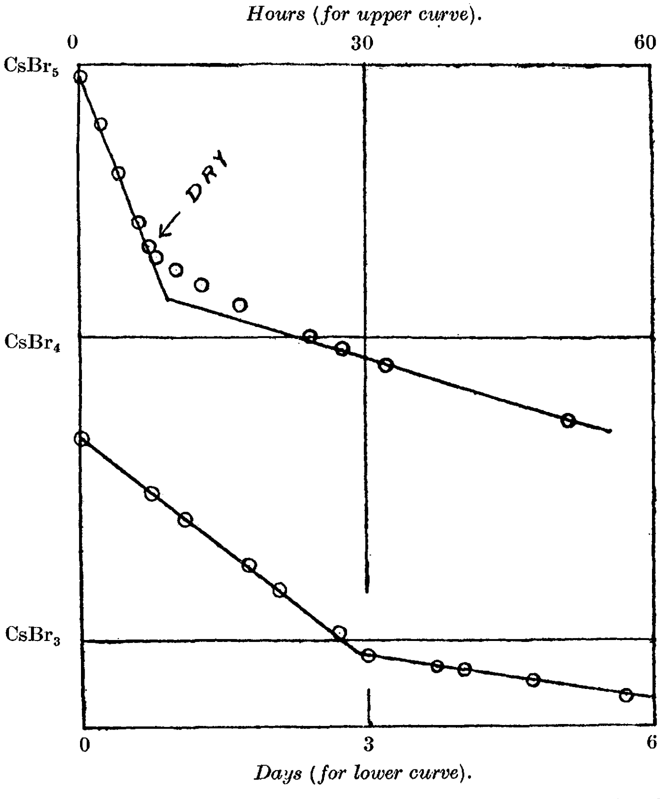
Wells stated that, after removal of adhering bromine by filter-paper, the solid "gave off bromine vapour very rapidly." The compound is unstable but not to the extent that Wells indicates, for at 28° it lost less than 1% of the polyhalide bromine in 3 hours over caustic soda. Experiments have now been made, using the method previously described (J., 1915, **107**, 1286), in order to see what polybromides are indicated by the rate of loss of bromine over caustic soda. This rate depends on the vapour pressure of the compound and, although not entirely satisfactory in theory, the method has been shown to give correct indications in practice.

4·27 G. of cæsium bromide were weighed into a squat-form weighing bottle containing a stirring rod. Bromine corresponding to the formula $CsBr_6$ was added, and the contents of the bottle were left for two days with the stopper on to allow equilibrium to be established. The open bottle was then placed in a large desiccator over caustic soda and was weighed at first every 2 hours and then at longer intervals; the contents were stirred with the rod before being replaced in the desiccator.

No change was observed in the rate of loss when the composition $CsBr_5$ was passed through, and liquid bromine was present at this stage. Continuation of the process revealed two breaks in the curve : these, together with the experimental points, are shown in Fig. 1. At the fourth point on the upper curve the solid was still moist in appearance, but seemed quite dry at the fifth point.

The slope of the first part of the curve is nine times that of the second, and leaves no doubt that cæsium tetrabromide has a much smaller vapour pressure than free bromine. The lower curve shows the change from the tetra- to the tri-bromide : the slope changes in the ratio 5 : 1 on account of the greater stability of the tribromide. After the tribromide has been formed, there is no further change in the slope of the curve until just before the composition of the monobromide is reached; *i.e.*, there is no indication of a compound such as a dibromide.

FIG. 1.



In view of the instability of the tetrabromide and the difficulty of drying it without loss of bromine, an indirect analysis was made. The amount of cæsium bromide available was small and it was desirable to recover it readily, so the usual method of analysis was somewhat modified. Into a small glass-stoppered bottle holding about 10 c.c., was introduced cæsium bromide which, after drying in the bottle, weighed 3·765 g.; and 2·857 g. of water were added, the weight being found by weighing the bottle and its contents. Bromine was then added; with a small quantity a red solid was formed with a light yellowish-red solution above and only a little bromine vapour. On the addition of a larger amount of bromine, the solid became dark red, as did also the solution (if more bromine was added two liquid layers were obtained as well as the solid); the amount of bromine added was 3·4945 g. The bottle was then shaken well and kept for 3 days, during which the crystals had become so compact that some of the liquid could easily be decanted for analysis without disturbing the solid. The liquid was poured into a 200-c.c. flask, and to this some ammonium iodide solution was at once added and the solution made up to the mark. The vapour pressure of the solution was not great enough to cause more than a little loss of bromine. Re-weighing of the bottle showed that 2·2365 g. of solution had been removed. One part of the solution was titrated with $N/10$-sulphurous acid standardised simultaneously against a standard iodine solution. Another part was evaporated in a platinum dish on the water-bath, then heated to a low temperature in the electric furnace to drive off the ammonium salt, and finally converted to chloride by repeated evaporation with hydrochloric acid. In this way the solution was found to have the composition: Br (polybromide), 0·3292 g.; CsBr, 0·5662 g.; H_2O, 1·3411 g. The 2·857 g. of water originally in the bottle therefore contained 0·7015 g. of free bromine and 1·2066 g. of cæsium bromide, whence the amounts in the solid were: polybromide bromine, 3·4945 − 0·7015 = 2·793 g.; cæsium bromide, 3·765 − 1·2066 = 2·558 g. The ratio, polybromide bromine : CsBr = 2·911 : 1, is in as good agreement as can be expected with the tetrabromide formula, $CsBr_4$.

With a mixture made up in the molecular proportions $CsBr : Br_2 : H_2O = 1 : 1·04 : 7$, the tribromide was obtained, and when these were altered to 1 : 1·48 : 10·7 the second liquid phase was observed.

Further work on this subject is projected.

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