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Solid Solutions in Bromine-Iodine Mixtures. II

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At −23·5 °C. the unit-cell volumes fall on a discontinuous plot which is not inconsistent with the existence of 3 ranges of solid solutions containing a predominance of Br–Br, Br–I and I–I molecules respectively.

Introduction

In the earlier part of the present work (Heavens & Cheesman, 1950) it was found possible to follow compositions only as far as 38 atomic% of bromine. A 9 cm. camera has now been developed in which it is possible to maintain temperatures down to −100 °C. or lower, and it has been found that with this the whole range of Br_2–I_2 mixtures can be readily photographed at −23·5 °C. In the region where the measurements overlap those previously obtained at room temperature, the new values lie on a line parallel with the earlier ones, the coefficients of expansion being in good agreement with those given by Straumanis (1943) for iodine. The observed values for *a*, *b* and *c* for the various compositions are shown in Table 1.

Fig. 1 shows the product of *a*, *b*, *c*, viz. the effective unit-cell volume as a function of composition; three straight lines have been drawn through groups of points, in accordance with the hypothesis that three types of lattice arrangement succeed one another as the composition changes. Plots of the individual lattice constants exhibit similar breaks at the same

Table 1. *Observed values for a, b and c*

Composition (atomic % I)	*a*	*b*	*c*
0	4·548 Å	6·737 Å	8·761 Å
4·99	4·567	6·758	8·801
15·02	4·582	6·804	8·879
20·19	4·594	6·816	8·920
24·97	4·612	6·839	8·944
29·88	4·620	6·830	9·000
34·98	4·619	6·876	9·016
40·11	4·626	6·889	9·036
45·05	4·607	6·900	9·083
49·99	4·637	6·900	9·165
55·14	4·650	6·960	9·231
59·68	4·664	6·986	9·287
67·03	4·685	7·030	9·359
75·03	4·697	7·073	9·457
79·99	4·709	7·093	9·550
89·86	4·735	7·144	9·665
100·00	4·753	7·219	9·789

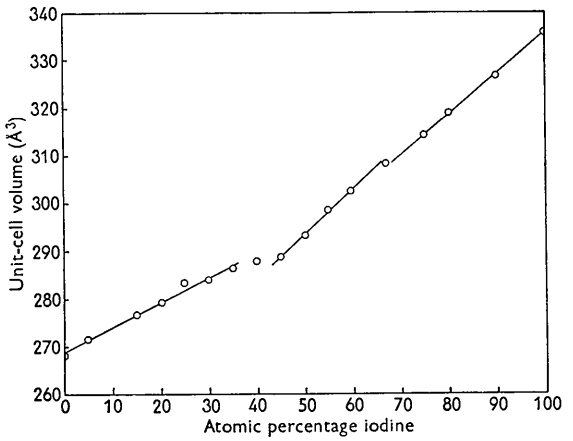

Fig. 1. The effective unit-cell volume as a function of composition.

compositions. As the diffraction pattern is found to remain recognisably similar over the whole range of composition, it seems that the structure itself must remain essentially constant, and that the presence in the centre of the range of unsymmetrical Br–I molecules must be accommodated either by randomising the orientations of these unsymmetrical molecules within the *Ccma* space group, or by changing over to the similar *Ccm* space group which allows for it. Apart from the evidence presented by Heavens and Cheesman (1950), the second alternative accords with the presence of two discontinuities in the graph of cell-volume; but it is not possible on the present series of photographs to discriminate satisfactorily between the *Ccma* and *Ccm* arrangements as suggested in Part I since the number of lines consistently observed was not sufficiently large to enable the rather small difference in intensity distribution to be detected with certainty.

It is to be expected that solid solutions differing only in the symmetry of the arrangement of IBr molecules would show very little physical difference, and early phase-rule studies (Terwogt, 1905; Kruyt & Helderman, 1918) were interpreted as indicating continuous solid solution between the two halogens. However, by careful examination of vapour pressures and similar measurements it has been possible to detect the presence of two slight discontinuities in the solid solutions which correspond approximately with the breaks shown in plot of the unit-cell volume, and this correspondence is the ground for advancing the present hypothesis. The phase-rule and related data will be presented elsewhere in due course.

Experimental

Specimens were prepared as in the earlier part of this work, the only significant modification being the deliberately rapid freezing of the mixtures in the capillaries. This was accomplished by emptying the liquid halogen mixtures and capillaries on to a porcelain plate which had been cooled to −80 °C. The capillaries were then sealed and used immediately. Recrystallisation was found to present a serious problem for specimens containing less than 70 atomic % I if the specimen was allowed to remain at room temperature for more than a few minutes, and specimens containing less than 50 atomic % I were further treated by a re-melting of the halogen mixture after mounting and centering the capillary in the specimen holder, followed by a rapid quench in liquid nitrogen.

The camera design and construction were such that the specimen holder was easily removable from the loaded camera and could be quickly returned into place without affecting the centering of the specimen. Exposures were by Cu $K\alpha$ radiation in conjunction with the previously mentioned 9 cm. camera of Bradley–Jay type with a slit collimator. The entire camera was maintained at the temperature of −23·5 °C. during exposure by being surrounded by a CCl_4 bath held at freezing temperature by the addition from time to time of lumps of solid CO_2: by using this cooling system, temperature fluctuations during exposure were negligible, the maximum observed deviation being 0·5 °C. during the course of an eight hour exposure.

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