

## NOTE ON THE ABSORPTION SPECTRUM OF CaI.

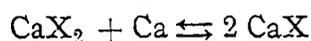
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WOEHLER and RODEWALD<sup>1</sup> prepared subhalides of calcium, directly chilling suddenly a mixture of dihalide and metal after heating it for some hours to high temperatures, where the equilibrium of the reaction



is shifted to the right. It seemed therefore to be of interest to investigate the absorption spectrum of the calcium sub-iodide prepared in this manner. Equal molecular amounts of  $\text{CaI}_2$  and Ca metal were heated in a steel bomb for 10 to 12 hours at a temperature of 800 till 900° C. and chilled in water of 0° C. The yield contained besides  $\text{CaI}_2$  and Ca, a large amount of yellow-brownish crystals. Similar results were obtained by heating two equivalents of Ca with one equivalent of iodine. The crystals are extremely reactive and are attacked at once by oxygen. They react with all organic substances but can be preserved for a short time under carbon disulphide. The whole yield was therefore at once covered with  $\text{CS}_2$  and the brown crystals collected under a microscope. The crystals thus collected in  $\text{CS}_2$  were then introduced in an absorption tube of fused silica, the carbon disulphide was pumped off and the substance heated in vacuum at various temperatures between 800 and 1100° C. As source of light the continuous spectrum of hydrogen was used for the ultra-violet, a point light lamp for the visible region and various spectrographs used as resolving instruments. Two absorption tubes of 10 and 20 cms. length were used. The plates obtained were measured by the recording microphotometer.

The results were by no means always identical. Sometimes the bands of iodine vapour appeared in the visible, sometimes they were replaced by a weak pseudo-continuous spectrum with a maximum at 5600 A.U. An end-absorption in the ultra-violet was always observed on all plates of the quartz spectrograph, whether or not the iodine spectrum appeared in the visible. The composition of the vapour varies apparently not only with temperature but also with the speed of heating. The optimum temperature

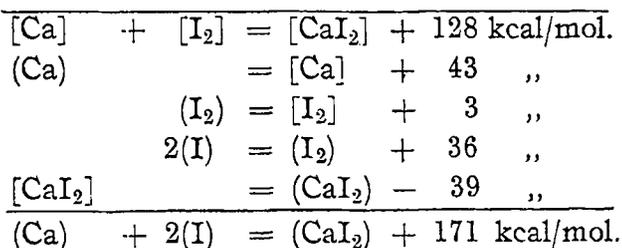
for the existence of the subiodide CaI seems to be about  $850^{\circ}\text{C}$ ., higher temperatures and slow heating favour its subsequent decomposition.

The visible spectrum belongs certainly to free  $\text{I}_2$  molecules. This is obvious for those plates, on which the band structure can be distinguished. The continuous absorption with a maximum of intensity at 5600 A.U. is obviously the envelope of this band spectrum, more vibrational levels of the ground-state of  $\text{I}_2$  being excited on account of high temperature and pressure, the more so since the same envelope as selective absorption of the violet iodine solution has its maximum at about 520 till 540  $m\mu$ . Thus even in the non-decomposed vapour of CaI traces of free  $\text{I}_2$  are often present. The brown colour of the crystals is almost certainly due to them since Hilsch and Pohl<sup>2</sup> have shown that the selective absorption maximum of thin layers of solid iodine is shifted towards shorter wavelength (at about 450  $m\mu$  according to their graph) which accounts very well for the brown colour. This is also the region in which the selective maximum of the brown solutions of iodine lies.

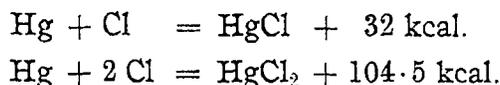
From this point of view it would appear as if the calcium subiodide prepared in this manner is only a mixed crystal or a solid solution. The existence of a true molecule CaI is, however, borne out by the extremely high reactivity of these crystals. They behave exactly like free radicals. That is just what we have to expect of a sub-halide in which the metal atom still possesses a free valency. Since the end absorption in the ultra-violet occurs also on such plates on which the absorption in the visible is nearly or completely absent, we infer that this is the real absorption of the CaI molecule. It could be said, that this continuum belongs to the ultra-violet band system of  $\text{I}_2$ , since also the band system in the visible part occurs sometimes as a pseudo-continuous spectrum. Indeed the ultra-violet system is known to extend at very high pressures and temperatures from shorter wavelengths even till 2700 A.U. The condition in our experiments are, however, nothing comparable to that. The absorption curve of violet iodine solution shows further, that the absorption coefficient for the ultra-violet ascent at about 230  $m\mu$  has about the same value as for the maximum at about 540  $m\mu$  and we obtained a number of plates on which the absorption was already complete at 2300 A.U. whereas that in the visible was either completely absent or very weak. We feel justified therefore in ascribing this end-absorption and only this to the molecule CaI. The red wavelength limit of this continuum lies at about 2350 A.U. or  $42540\text{ cm.}^{-1} = 5.3\text{ volts} = 121\text{ kcal/mol}$ . Bands are not observed.

To compare the above value with thermochemical data we have to calculate the heat of formation of  $\text{CaI}_2$  from the atoms. Neither the heat

of sublimation of  $\text{CaI}_2$  nor its boiling point are known and we compute the latter from the melting point and the melting and boiling points of the other calcium halides, to  $\sim 790^\circ \text{C}$ . By Grueneisen's formula<sup>3</sup> we obtain 28.5 kcal/mol. for the latent heat of evaporation and by Walden's formula<sup>4</sup> 13.7 kcal/mol. for the latent heat of melting. Thus we obtain  $\sim 42$  kcal/mol. for the heat of sublimation, while by the formula of Forcrand<sup>5</sup> we obtain 35 kcal/mol. Therefore we use the mean value which is 39 kcal/mol. Taking the other values from Landolt Boernstein's tables we calculated the atomic heat of formation of  $\text{CaI}_2$  as follows\*:-



It has been shown, however, by Spöner,<sup>6</sup> that the dissociation of the first halogen atom of a dihalide of the second group requires considerably more energy than that of the second one. For mercury dichloride the figures are as follows:-



A completely satisfactory explanation of this phenomenon has not yet been found but the fact remains and so we estimate the energy of the first Ca-I bond as about 2.5 volts in agreement with the known value of the energy of dissociation of other subhalides of this group. The continuous end-absorption with this belong to the transition from the ground-level of the molecule to a steep repulsive curve as in molecules like  $\text{CH}_3\text{I}$ .<sup>7</sup>

There remains of course another possible explanation, which cannot be excluded by the present experiments, *i.e.*, that the vapour consists of polymerised molecules  $(\text{CaI})_2$ . Comparing thermochemical data of molecules like  $\text{Hg}_2\text{X}_2$ , we may say that nothing indicates such a view. Since, however, the chemical composition of the crystals obtained according to Woehler and Rodewald is not beyond doubt, all our conclusions have to be taken with some reservation.

An interesting point is the absence of any bands. The absorption spectra of the oxides and sulphides of the second group have shown that the known emission bands do not appear in absorption and it has been

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\* Square brackets = solid, ( ) = gaseous state.

pointed out that this agrees with the existence of a repulsive term involving the  $^1S$  level of these metals.<sup>7</sup> Walters and Barratt<sup>8</sup> have, however, recorded also three sets of absorption bands of CaI, between 6600 and 6200 A.U., between 4330 and 4200 A.U., and from 3270 to 3120 A.U. We are not so sure whether the bands in the orange region are absent on our plates, since they may be overlapped by those of iodine. On those plates on which the iodine spectrum appears as a pseudo-continuous spectrum, we obtain sometimes weak subsidiary maxima in the region of 6300 A.U., but have not been able to identify bands due to CaI on other plates among the  $I_2$  bands. Bands in the blue and ultra-violet region are, however, certainly missing. It seems not impossible that the second and third set recorded by Walters and Barratt do not belong to the CaI molecule at all, since a great number of bands obtained in their experiments have been shown to belong to impurities.<sup>9</sup>

## REFERENCES.

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