

Letters to the Editor.

On the Dissociation of Some Molecules with Free Valencies.

IN continuation of an earlier paper¹ the correlation between the electronic terms of molecules of the type BeO, BeF and NO and those of the constituent atoms has been examined with the following conclusions:—

(i) Among the oxides and halides of the metals of the second group a good agreement between the energy of excitation of the products of dissociation and the terms of the metal atom obtains always, if the ground level of the molecule is correlated to the excited term sp^3P of the metal. Besides the molecules BeF, MgF, CaF, SrF, already examined before, the following have been considered: BeO, MgO, CdF, BeCl, MgCl, CaCl.

(ii) In some of the molecules of these types also a correlation of the ground level to the repulsive term s^2^1S would appear to be possible, but others strictly contradict such a correlation. This is particularly evident in a case like CdF. Here the term difference $5s\ 5p^3P - 5s^2^1S$ is enlarged, the metal belonging to the sub-group of the periodic table, while the energies of excitation and dissociation of the molecule are not very different from others of this type. Consequently one would have to assume that the linear extrapolation of the vibrational levels is incorrect by about 85 per cent. in order to obtain a correlation of the lowest state of the molecule to the 1S term of Cd. The correlation to the excited term always agrees to about 1 to 2 per cent. with the experimental data.

This not only establishes the repulsive character of the s^2 group, but also, since no perturbation is observed in the bands, the absence of that type of hybridisation, which involves more than one term of the metal atom (q -linkage). This is also borne

out by the crystal structure of the oxides which cannot be explained unless the single molecule exhibits still free valencies.²

(iii) In all the above molecules, terms whose energy of excitation is larger than that of the ground level are automatically correlated to an *anomalous* term of the metal atom.

(iv) In the molecules NO, PO and AsO the term with an increased energy of dissociation involves a configuration of the corresponding atom of the fifth group in which one electron is already excited to the next shell. A reasonable correlation can be obtained in SbO on the assumption that it behaves similarly. Of the different electronic terms whose relation is not yet known experimentally, the final state of the D system is to be regarded as the ground level of the molecule and the common final state of the B and C systems as the term with increased energy of dissociation.

This shows again that the increase of stability on excitation in these molecules is always due to the excitation of that electron which does not take part in the linkage but represents a free valency.

A detailed report will be given elsewhere.

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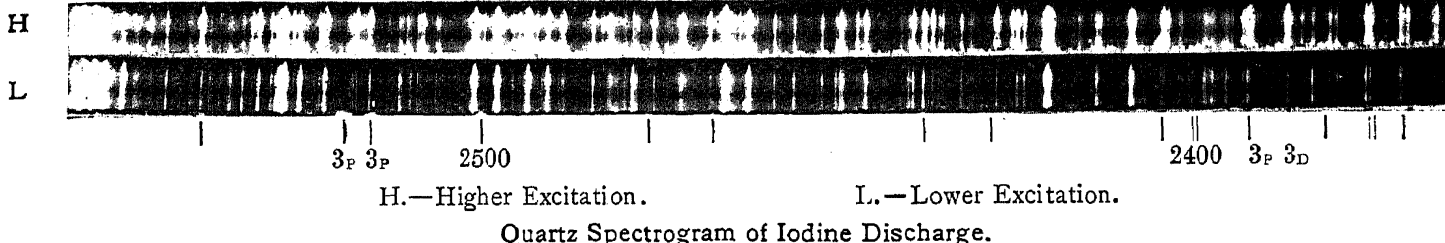
Muslim University,
Aligarh,
May 15, 1935.

¹ H. Lessheim and R. Samuel, *Zs. f. Phys.*, 1933, 84, 637; 88, 276.

² F. Hund, *Zs. f. Phys.*, 1932, 74, 1.

Regularities in the Spectrum of Iodine IV.

FOLLOWING the analysis of Te III carried out in this laboratory, an investigation of the spectrum of Iodine IV of the same iso-electronic sequence was undertaken. The spectrum of a condensed discharge through Iodine vapour was photographed at various



stages of excitation, by using a Quartz Spectrograph of the Littrow type. The

data thus obtained has led to the discovery of the important interval $6s\ ^3P_1 - ^3P_2 =$

8252.3 cm^{-1} , along with all the terms of the 6p-configuration. Adopting for the level $6s^3P_1$, a value 200532 cm^{-1} extrapolated from the corresponding values in Sn I, Sb II and Te III, a number of odd levels of the values of 202767, 201270, 200339, 199981, 198423, etc., have been obtained. Some of the important lines in the spectrum are marked in the print above. The detailed scheme will be published shortly.

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Diamagnetism of Elements in the Powdered State.

It has been reported, that powders of bismuth,¹ antimony,² gold,³ silver,⁴ selenium,⁵ etc., have considerably different susceptibility values than the metals *en masse*. In 1930 Bhatnagar⁶ drew attention to the fact that the large changes reported in susceptibility could be due to a considerable extent to the presence of oxides and suboxides of the metals and to the adsorption of impurities by the fine powders. Mathur and Verma following this suggestion showed that after the removal of oxides both bismuth⁷ and antimony⁸ powders regain the original regulus value.

Rao⁹ from his work on bismuth and antimony maintains that he obtains a critical value corresponding to the size of the macrocrystal after which a rapid change in the susceptibility ensues.

From Rao's papers one does not feel convinced that a high order of purity of materials has been attained in his experimental work. In the case of antimony, for example, no effort has been made to free it from the oxides. In the case of bismuth also, while an attempt has been made to free it from the oxides by treatment with tartaric acid as suggested by Bhatnagar, no critical experimental evidence has been given to show that the oxide is really completely removed. Nor has the probability of contamination with carbonates or bicarbonates been excluded, since it is well known¹⁰ that these products are formed by keeping bismuth under water in the presence of air.

Selenium was examined by Dharmatti, who showed that on powdering, the diamagnetic susceptibility decreased and eventually changed in sign becoming paramagnetic. We have repeated Dharmatti's

work and have some interesting observations to record. The red and grey allotropic varieties of selenium were subjected to prolonged powdering under benzene or toluene to prevent oxidation as far as possible. Only in an extreme case the value decreased from -3.03×10^{-7} to -2.69×10^{-7} at a particle size of 0.4μ . In each case, however, the sample recovered the original value after washing with cold dilute hydrochloric acid. Also one of Dharmatti's paramagnetic samples made available to us through the courtesy of Prof. Mata Prasad regained the original value of Se on treatment with hydrochloric acid.

A very interesting observation made by us during the investigation was that the red variety gradually passed into the black one on protracted exposure to light. Transformation into the black variety has also been shown to take place under pressure by Von Schrott¹¹ and we suggest that the fall observed in certain cases may be due to the conversion on powdering into a metastable allotropic form having its susceptibility different from the original substance. This possibility seems particularly likely in the case of tin, which has been examined by Rao.¹² White tin *en masse* is weakly paramagnetic, but Rao finds that in the powdered form the susceptibility decreases with the particle size until for the smaller particles he finds that it becomes diamagnetic. As in previous cases, Rao has not taken care to discover the possibility of anything else responsible for the change. We are examining the case of tin and hope to communicate our results later.

In the end the authors wish to emphasise once again that in any work done with particles of colloidal sizes the exclusion of impurities which do accompany the powders on colloidalisation is of permanent importance for it is only this, that can be responsible for erroneous conclusions. The authors also take this opportunity of thanking Prof. S. S. Bhatnagar for his help and guidance at every stage.

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June 4, 1935.

¹ Vaidyanathan, *Indian Jour. Phys.*, 1930, 5, 559.

² Vaidyanathan, *loc. cit.*

³ Vaidyanathan and Singh, *Nature*, 1931, 128, 302.