

respond to the average temperature. In this case one can calculate the expected change in temperature, taking  $E$  as its root mean square value.

Since  $\Delta T = CE^2$ , where  $C$  is a combination of the molecular constants, and using standard values<sup>2</sup> one finds that  $C$  in m.k.s. units equals 5.3, 5.5 and  $5.7 \times 10^{-17}$  for methanol, ethanol, and isopropanol respectively. Hence, for example, methanol at 5 kV./cm. will show a rise of boiling point of  $1.3 \times 10^{-5}$  deg. C. At 5 kV./cm. Katti and Chaudhri observed boiling point depressions of 2.0, 0.7, and 0.4 deg. C. for methanol, ethanol, and isopropanol, respectively, in complete disagreement with theory.

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<sup>1</sup> Katti, P. K., and Chaudhri, M. M., *Nature*, **190**, 80 (1961).

<sup>2</sup> Lange, N. A., *Handbook of Chemistry* (Handbook Publishers, Inc., Sandusky, 1949); *International Critical Tables* (McGraw-Hill, New York, 1926).

SINCE the publication of our communication in *Nature*, several attempts have been made to explain this phenomenon and to calculate the magnitude of the lowering of the boiling points. These attempts naturally deal with the application of thermodynamics to the mechanical effects arising out of the application of strong electrical fields to dielectrics. These models, however, predict very small lowering of the boiling points (of the order of  $10^{-5}$  deg. C. for fields of the order of 5 kV./cm.).

In fact we ourselves were led to this investigation nearly two years ago because of a suggestion by Prof. D. S. Kothari based on the Clapeyron equation with change of pressure replaced by  $KE^2/8\pi$ . We did not refer to this in our communication because a reference to it was made in an earlier book on physical chemistry and secondly because the sign and the magnitude of the observed changes in the boiling points are not in agreement with this model.

The main purpose of our communication was to point out the unusually large depression of the boiling points of the liquids under the experimental conditions used. More experimental work is clearly necessary, and we hope to report on further results in due course.

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### The Optical F Absorption Band

In a recent communication<sup>1</sup> a new model for the optical  $F$  absorption band was proposed for the alkali metal azides. From a study of irradiation-produced bands in the visible and infra-red region of the absorption spectrum of the azides, it was shown that the anion ( $N_3^-$ ) was intimately related to the  $F$  absorption band and it was suggested that the  $F$  band was caused by a 'charge-transfer' complex of the type discussed extensively in the chemical literature, especially by Mulliken<sup>2</sup>. The 'charge-transfer' complex consists of a dative bond being established

Table 1. ENERGY DIFFERENCE BETWEEN FIRST ULTRA-VIOLET PEAK AND THE  $F$  BAND\*

|      | $h\nu_1 - h\nu_{FP} = C$ | $h\nu_1 - h\nu_{FP} = C$ |                   |
|------|--------------------------|--------------------------|-------------------|
| LiF  | 12.4 - 5.0 = 7.4         | LiBr                     | 7.2 - 2.7 = 4.5   |
| NaF  | 10.6 - 3.6 = 7.0         | NaBr                     | 6.78 - 2.3 = 4.48 |
| KF   | 9.95 - 2.7 = 7.25        | KBr                      | 6.77 - 2.0 = 4.77 |
| LiCl | 8.3 - 3.1 = 5.2          | RbBr                     | 6.6 - 1.8 = 4.8   |
| NaCl | 7.95 - 2.7 = 5.25        | KI                       | 5.8 - 1.8 = 4.0   |
| KCl  | 7.76 - 2.2 = 5.56        | RbI                      | 5.7 - 1.6 = 4.1   |
| RbCl | 7.5 - 2.0 = 5.5          |                          |                   |

\*  $h\nu_1$ , energy of first ultra-violet band from Eby, J. E., Teegarden, K. J., and Dutton, D. B., *Phys. Rev.*, **116**, 1099 (1959);  $h\nu_{FP}$ , energy of the  $F$  band from Dekker, A. J., *Solid State Physics* (Prentice Hall, 1959);  $h\nu_1$ , for LiF estimated from H. C. Kremers, *Indust. and Eng. Chem.*, **32**, 1478 (1940).

between one electron donor and an electron acceptor with a concomitant electronic absorption belonging to the complex as a whole.

For the azides, the following mechanism was proposed for the formation of the 'charge-transfer' complex and the resulting absorption band. Under ultra-violet irradiation an interstitial metal atom is ionized, this metal ion now moves to a position of lower potential energy, that is, to a cation vacancy and as a consequence the equilibrium crystal field is so perturbed (in an unspecified manner) as to set up a 'charge-transfer' complex between that cation and a neighbouring anion. Thus in the proposed model the  $F$  absorption band depends on the existence of cation vacancies rather than anion vacancies.

I feel that the phenomena in the halides cannot be essentially different from those in the azides. If one accepts the importance of cation vacancies then several phenomena in the halides can be understood in a straightforward manner. For example, the following experimental facts strongly suggest the importance of the cation vacancy. The electrical conductivity of crystals is decreased by darkening<sup>3</sup>. Plastic strain which enhances conductivity enhances darkening by X-ray irradiation<sup>3</sup>. Divalent cation impurities which increase ionic conductivity enhance colorability by irradiation<sup>3</sup>.

The role of the anion in the  $F$  band in the halides is not easily demonstrated as in the azides, since there is no infra-red vibration associated with it except for the lattice vibration. However, I suggest that the correlation between the  $F$  band and the first ultra-violet absorption band in the halides, first pointed out by Glasner and Tompkins<sup>4</sup>, be interpreted in a manner similar to that in the azides. Table 1 lists the difference in energy between the first ultra-violet absorption band in uncoloured crystals and the  $F$  band produced in the crystals. It can be seen that the energy difference is a constant for any particular anion. It is generally accepted<sup>5</sup> that the first ultra-violet absorption peak in the halides is caused by the removal of an electron from a halogen ion to a neighbouring metal ion. Our suggested model for the  $F$  band is the partial removal of an electron to a neighbouring metal ion so that it is not surprising that there exists a relationship between the ultra-violet band and the  $F$  band. Further, a colourless electronegative ion with an absorption band in the ultra-violet, under a perturbing influence (the formation of a bond with increasingly greater covalent character), would expect to have an absorption band increase in wave-length proportional to the degree of perturbation<sup>6</sup>. One might expect that any such perturbation would have the greatest effect on the most ionic system. If we use Pauling's function<sup>6</sup>,  $1 - \exp(-\frac{1}{2}(X_a - X_b)^2)$  (where  $X_a$  and  $X_b$  are the electro-negativities of the atoms in the bond), as a measure of the ionic character for the halides, then the fluorides appear to be most ionic and the iodides least so and the difference in energy between