Bond Energies of Some Alkali Fluorides

THE attenuation of microwaves by flames containing traces of alkali metals may be used to determine the electron concentration, arising from the ionization of the alkali, in these flames^{1,2}. If a halogen is added to such a flame, the electron concentration is reduced directly by the formation of negative ions, and indirectly by the formation of the alkali halide^{3,4}. Flame photometric studies show that the halogens also reduce the excess hydrogen atom concentration in the flame⁵; but it has been observed that fluorine has the least effect⁶. This reduction makes it difficult to estimate the bond energies of the alkali halides from microwave studies⁷, because of the indirect nature of the arguments used in the estimations⁸. In the case of fluorine, however, the argument is simplified by the unimportance of the negative ion effect, since the electron affinity of fluorine is low relative to the bond energies of the alkali fluorides, and by the much smaller disturbance produced in the hydrogen atom concentration. In addition, the observations are made at high temperatures where the hydrogen atom concentration approaches equilibrium⁵ and it is possible to obtain reliable and consistent results, which it is of interest to place on record.

Sodium fluoride has been examined over the temperature-range 2,300–2,600° K., using perfluoromethylcyclohexane as source of fluorine, and the dissociation constant determined, assuming the dissociation energy of hydrogen fluoride⁹ to be 134 kcal. A graphical determination of the dissociation energy (Fig. 1) gives a value of 124 kcal., equivalent to 119 kcal. at 0° K., in agreement with a statistical 'Third law' value of 120 kcal., calculated from the measurement at 2,400° K. It is also possible to estimate the difference between the bond energies of hydrogen fluoride and sodium fluoride directly from the experimental results. This difference is 14 kcal., which indicates that the bond energy of sodium fluoride is 120 kcal. This concordance shows that the disturbing effects described above are, indeed, negligible. Potassium fluoride could not

conveniently be examined over this temperature-range; but a statistical calculation at 2,400° K. gave the bond energy as 117 kcal. Lithium fluoride could only be examined at the highest temperature (2,600° K.) and a statistical calculation put the bond energy at 141 kcal. These values are in good agreement with the thermodynamic predictions of Smith and Sugden¹⁰ but differ somewhat from other authorities^{11,12}. They are, however, in good agreement with some values determined by flame photometry in these laboratories recently¹³.

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¹ Belcher and Sugden, *Proc. Roy. Soc., A*, **201**, 480; **202**, 17 (1950).

² Smith and Sugden, *Proc. Roy. Soc., A*, **211**, 31, 52 (1952).

³ Page, *Disc. Farad. Soc.*, **19**, 87 (1955).

⁴ Sugden, *Disc. Farad. Soc.*, **19**, 68 (1955).

⁵ Bulewicz, James and Sugden, *Proc. Roy. Soc., A*, **227**, 312 (1958).

⁶ Bulewicz and Page (unpublished work).

⁷ Page, thesis (Cambridge, 1955).

⁸ Page and Sugden (to be published).

⁹ Cottrell, "The Strengths of Chemical Bonds" (Butterworths, London, 1954).

¹⁰ Smith and Sugden, *Proc. Roy. Soc., A*, **219**, 204 (1953).

¹¹ Gaydon, "Dissociation Energies—Spectra of Diatomic Molecules" (London, 1957).

¹² Barrow and Caunt, *Proc. Roy. Soc., A*, **219**, 120 (1953).

¹³ Bulewicz and Sugden (to be published).

Tetrahedral Co-ordination in Ni(II)

LINGAFELTER¹ has suggested that the occurrence of blue-coloured $\text{Ni en}_2(\text{NCS})_2$ and $\text{Ni en}(\text{H}_2\text{O})_4(\text{NO}_3)_2$ for which X-ray evidence gives 6 co-ordination for the nickel atom contradicts the criteria for identifying tetrahedrally co-ordinated Ni(II) suggested in my earlier communication of the same title², with the implication that these criteria are invalid.

The basic criterion laid down² was the disappearance of the characteristic peak in the region of 400 m μ of octahedrally co-ordinated Ni(II), which usually has a green colour. With the disappearance of this peak, a deep blue colour would be expected to result, other things being equal. A property which would suggest the possibility of a tetrahedral 4 co-ordinate condition would therefore be possession of a blue colour. However, since a shift of the 400-m μ peak to slightly lower wave-lengths could give the same effect so far as the eye alone is concerned, verification by spectral analysis would be an obvious requirement.

Ballhausen³ has used the absorption spectra of the various stages of complexing of Ni(II) with ethylene diamine to show the spectra of $[\text{Ni en}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Ni en}_2(\text{H}_2\text{O})_2]^{2+}$, and in fact the 400 m μ peak (as well as the others) has been shifted towards lower wave-lengths, but increased, not diminished, in intensity. Dr. R. G. Wilkins, of the University of Sheffield, has kindly shown me a solid preparation of the salt, $[\text{Ni en}(\text{H}_2\text{O})_4](\text{NO}_3)_2$, which is light blue, and the absorption spectra he has obtained for ice-cold aqueous solutions of the salt correspond closely to that given by Ballhausen³. This blue-coloured complex cation therefore meets the criteria for 6 co-ordination of Ni(II), and it is no surprise that X-ray investigation of the related salts verifies this.

Fig. 1