

than one covalent bond. Hence the average ionic character of each bond will be 5/6, i.e., 83% which is in good agreement with the values (83—86%) calculated from the partial ionic character of bond energies. Similarly in the case of caesium chloride each caesium being surrounded by eight chlorines and forming one covalent bond the partial ionic character should be  $7/8=0.875$  which compares favourably with the values .91, .93 and .90 for caesium chloride, bromide and iodide respectively.

A further support to the partial ionic character of alkali halides comes from the data on magneto-optical anomaly (Faraday effect) of these salts found by Darwin and Watson (1927), ( $r = 0.8$ ) and recently by Ramaseshan (1948), ( $r = 0.85$ ) and from the dielectric constants and dipole moments as shown by us in a previous note.

Indian Inst. of Sci., S. K. KULKARNI JATKAR.  
Bangalore 3, (MISS) S. B. KULKARNI.  
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1. Darwin and Watson, *Proc. Roy. Soc., London*, 1927, 114A, 474. 2. Jatkar and Kulkarni, *Curr. Sci.*, Under publication. 3. Ramaseshan, *Proc. Ind. Acad. Sci.*, 1948, 28A, 360.

### IONIC CHARACTER OF HYDROGEN AND ALKALI HALIDES

THE object of the present note is to point a remarkably simple relationship between the internuclear charges and ionic character.

The dipole moment of hydrogen halides in gaseous state as measured by Smyth and Zahn are in agreement with the measurements of dielectric constants of pure solids, liquids and solutions by using a new equation as shown elsewhere. The experimental values of the ionic character are 0.43, 0.17, 0.11 and 0.05 for HF, HCl, HBr and HI respectively.

Table I shows that relationship between ionic character of hydrogen and alkali halides as given by  $\frac{Z_A}{Z_A+Z_B} \times n$  where

$Z_A, Z_B$  are the nuclear charges and  $n$  is a screening constant which is 8/8 for CsF and increases to 8/3. The calculated ionic character of HF (0.267) while in agreement with the bond energy data is lower than the observed value 0.43.

The dipole moments of alkali halides in vapour state have been determined by the molecular beam method. Scheffer's values are  $\sqrt{3}$  times lower than those obtained by Rhodebush. No data is available for NaCl and NaBr in vapour state. The calculated values of ionic character  $(Z_A/Z_A+Z_B) \times n$  seem to be in good agreement with ionic characters obtained from Rhodebush's data. In view of the fact that Cs is the most electro-positive and F is the most electro-negative of all the elements, the high value 0.86 for CsF is quite reasonable and is in agreement with the value 0.91 assigned by Smyth.

TABLE I  
Ionic Nature of Hydrogen and Alkali Halides (Gases)

Bond	Distance	$\frac{Z_A}{Z_A+Z_B}$	$n$	Ionic nature	
				cal. $\frac{Z_A}{Z_A+Z_B} \times n$	obs. $\frac{\mu}{e \cdot d}$
HF ..	0.92	0.100	8/3	0.267	0.43
HCl ..	1.28	0.0557	..	0.149	0.17
HBr ..	1.43	0.0278	..	0.074	0.11
HI ..	1.62	0.0183	..	0.049	0.052
NaCl ..	2.51	0.393	8/6	0.64	..
NaBr ..	2.64	0.239	8/3	0.64	..
NaI ..	2.90	0.174	..	0.45	0.35 <sup>S</sup>
KCl ..	2.79	0.528	8/6	0.71	0.70 <sup>R</sup> 0.47 <sup>S</sup>
KBr ..	2.94	0.350	8/4	0.70	0.77 <sup>R</sup>
KI ..	3.23	0.264	8/4	0.71	0.71 <sup>R</sup> 0.44 <sup>S</sup>
CsF ..	2.60	0.859	8/8	0.86	0.58 <sup>Hu</sup> 0.91 Smyth
CsI ..	3.41	0.509	8/6	0.68	0.74 <sup>R</sup>

P—Pauling, L., *The Nature of the Chemical Bond*.

S.—Sheffers, *Phys. Zeit.*, 1934, 35, 425.

R—Rhodebush, *J. Chem. Phys.*, 1936, 4, 372.

Hu—Hughes, H. K., *Phys. Rev.*, 1946, 70, 570.

Ind. Inst. of Sci., S. K. KULKARNI JATKAR.  
Bangalore 3, (MISS) S. B. KULKARNI.  
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### BOND ENERGY AND IONIC CHARACTER OF HYDROGEN AND ALKALI HALIDES

A STRONG support to the values of the ionic character of bonds should naturally come from bond energy data. Considerable amount of work has been done on this

subject using the empirical electro-negativity data of Pauling.

It is well known that the energy of a bond between unlike atoms is greater than the energy of a normal covalent bond between these atoms. According to Pauling the arithmetic mean or preferably the geometric mean of the bond energy values  $D(A-A)$  and  $D(B-B)$  is the energy of the ideal normal covalent bond between the atoms A and B. The additional bond energy  $\Delta AB = D(A-B) - \frac{1}{2}\{D(A-A) + D(B-B)\}$  was taken as the additional resonance energy due to the extra ionic character of the bond. In the present paper we have calculated the bond energy based upon the partial ionic character  $\Delta i = D(A-B) = (1-i)\sqrt{D(A-A) \cdot D(B-B)}$   
 $= i \frac{e^2}{r}$  where  $\frac{e^2}{r}$  is the Coulombic energy.

In Table I the values of  $\Delta i$  are calculated by using the theoretical ionic characters given by  $i = \left(\frac{Z_A}{Z_A + Z_B}\right) \times n$  which are close to the observed (cf. previous note).

TABLE I

## (A) Bond energies of homopolar bonds

Bond	Energy <sub>p</sub>	Bond	Energy <sub>p</sub>
H-H	103.4	I-I	35.4
F-F	70.0	Na-Na	18.4
Cl-Cl	56.9	K-K	12.6
Br-Br	45.2	Cs-Cs	10.1

## (B) Bond energy and partial ionic character

Bond	Distance r <sub>p</sub>	Energy D(A-B) <sub>p</sub>	i (cal.)	Ionic binding energy	
				cal. $i \frac{e^2}{r}$	obs. $\Delta i$
HF	0.92	147.5	0.267	96.0	91.0
HCl	1.27	102.7	0.149	38.0	37.0
HBr	1.41	87.3	0.074	19.0	24.0
HI	1.61	71.4	0.049	12.0	14.0
NaCl	2.51	97.7 <sup>Pi</sup>	0.64	85.0	87.0
NaBr	2.64	88.5 <sup>H</sup>	0.64	81.0	76.0
NaI	2.90	72.9 <sup>H</sup>	0.45	52.0	55.0
KCl	2.79	101.4 <sup>Pi</sup>	0.71	83.0	97.0
KBr	2.94	91.3 <sup>H</sup>	0.70	87.0	89.0
KI	3.23	78.9	0.707	71.0	73.0
CsF	2.60	131.9	0.86	110.0	128.0
			0.91 Smyth	116.2	129.5
CsI	3.41	75.0 <sup>Sp</sup>	0.68	72.0	70.0

P—Pauling, *The Nature of the Chemical Bond*.

Pi—Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2141.

H—Herzberg, *Molecular Spectra and Molecular Structure*.

Sp—Sponer., *Molekulspektren*.

The agreement between the results given in the last two columns is well within the uncertainties in the values of the bond energies.

Gen. Chem. Sec., S. K. KULKARNI JATKAR.

Ind. Inst. of Sci., (Miss) S. B. KULKARNI.

Bangalore 3,

March 5, 1949.

### ON RAPID VOLUMETRIC METHODS FOR THE ESTIMATION OF SILVER, BARIUM AND STRONTIUM IN AQUEOUS SOLUTIONS

*Determination of Silver.*—Though there are quite a number of methods for the quantitative determination of silver in aqueous solutions, a simple and rapid volumetric method has been described in this note. The method consists in the addition of a known excess of standard hydrochloric acid to a measured volume of silver solution, so as to ensure complete precipitation of silver chloride. Now, the excess of the acid remaining unused may be determined by titration against standard alkali solution using phenolphthalein as an indicator. The total amount of acid being known, the amount of hydrochloric acid reacted with silver ions may be found. The end point in this case is quite sharp and it has been found that the deviations in the results lie within permissible error. Since the solubility product of silver chloride is  $1.5 \times 10^{-10}$  at 25° C., and that of silver hydroxide at the same temperature is  $2.2 \times 10^{-8}$ , there are no chances of alkali being used up by silver chloride to form silver hydroxide.

*Determination of Barium and Strontium.*—

A similar method can be used for the estimation of barium and strontium in aqueous solutions by employing sulphuric acid for precipitating insoluble barium or strontium sulphate. The excess of sulphuric acid reacted with barium or strontium can be known. In this case too, the possibility of any reaction between the insoluble sulphate and alkali is absent, because the hydroxides of barium and strontium are far more soluble than the sulphates. It has been observed that the results