

## ELECTRON AFFINITY OF HALOGEN ATOMS

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**ABSTRACT.** Electron affinities of Fluorine, Chlorine, Bromine and Iodine have been evaluated in the case of twenty monomers of alkali metal halides, using the relation

$$E = D_e + I - \frac{e^2}{r_e} \left[ 1 - \left\{ \frac{k_e r_e^3}{e^2} + 3 \right\}^{-1} \right]$$

where  $D_e$  is the dissociation energy of polar diatomic molecules  $AX$ ,  $I$  is the ionization potential of atom  $A$ ,  $e$  is the electronic charge,  $k_e$  is the force constant for infinitesimal amplitude and  $r_e$  is the equilibrium internuclear distance.

These  $E$  values have been compared with those obtained by other experimental and theoretical methods.

## INTRODUCTION

In a recent communication (Tandon *et al.*, 1966) it has been shown that the relation between electron affinity and other molecular constants deduced from potential function having gaussian form repulsion term, leads to results much better than ones obtained by other theoretical methods of evaluating electron affinities. This is due to the fact that such a potential function adequately includes the polarizability, Van der waal and short range repulsion effects (Bleick and Mayer, 1934; Kunimuni, 1950; Rice and Klemperer, 1957; Varshni and Shukla, 1961), which are important in the case of polar diatomic molecules. In the present communication this relation has been used to calculate the electron affinities of halogen atoms in the case of monomers of alkali metal halides. The results have been discussed in the light of those obtained by other theoretical and experimental methods.

## CALCULATION OF ELECTRON AFFINITIES

The following relation between electron affinity and the molecular constants deduced earlier by authors (1966), has been used to evaluate  $E$ , the electron affinity of halogen atoms ( $X$ ).

$$E = D_e + I - \frac{e^2}{r_e} \left[ 1 - \left\{ \frac{k_e r_e^3}{e^2} + 3 \right\}^{-1} \right] \quad \dots (1)$$

where  $D_e$  is the dissociation energy of polar diatomic molecule  $AX$ ,  $I$  is the ionization potential of atom  $A$ .

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zation potential of atom  $A$ ,  $e$  is the electronic charge,  $k_e$  is the force constant for infinitesimal amplitude and  $r_e$  is the equilibrium internuclear distance.

#### DATA AND PROCEDURE

The observed values of dissociation energy  $D_e$ , referred to 0°K, are expressed in electron volts and collected in Table I, values followed by "(H)" are taken from Herzberg's molecular data (1950). Similarly "(G)" refers to data taken from Gaydon's book (1953) and that referred by Herzberg (1950) as Gaydon's data.

The ionization potential ( $I$ ) values for alkali metals, expressed in e.v. (Table I) are those given by Hodgman (1963).

The values of equilibrium internuclear distance ( $r_e$ ) are expressed in Å (Table I) and are taken from the "Tables of Interatomic distances and configuration of molecules and ions" (The Chemical Society, London, England, 1958) except where indicated. The  $r_e$  values in paranthesis are roughly estimated ones.

The values of force constant for infinitesimal amplitude  $k_e$  expressed in md/Å have been calculated from molecular data given by Herzberg (1950) unless stated otherwise.

Using these values of the molecular constants the electron affinities of halogen atoms have been calculated from equation (1). These values have been collected in Tables II-V along with values obtained by other theoretical and experimental methods for comparison.

#### DISCUSSION

Study of equation (1) reveals that  $r_e$  values must be very accurately known, since higher powers of  $r_e$  appear. While accurate  $k_e$  values, except in few cases, are available for a large number of molecules, accurate  $r_e$  values are available for few. In such cases divergence from observed values is expected.

The experimental methods which have so far been used for estimating the electron affinities of atoms use electron attachment phenomena, electron impact measurements, equilibrium measurements and kinetics of electrodes processes and the theoretical ones involve calculation of lattice energies, heats of solvation of ions, and extrapolation of ionization potentials. For details of these methods reference may be made to the review by Pritchard (1953). It is of interest to note that these methods often yield very conflicting values. The values of  $E$  obtained by these methods have been collected for Fluorine, Chlorine, Bromine and Iodine in Tables II, III, IV and V, respectively. In nearly all cases the extrapolation methods yield  $E$  values much different from observed ones. The  $E$  values calculated for different halogen atoms using equation (1) agree with those obtained by other methods (Table II to V). However, the difference may

be due to the approximations involved in different methods and the use of inaccurate  $r_e$  values.

TABLE I  
Electron affinities of halogen atoms

Atom	Molecule	$k_e$	$r_e$	$I$	$D_e$	$E(\text{ev})$	$\bar{E}$ Mean (ev)
F	LiF	(2.36) <sup>a</sup>	(1.59) <sup>b</sup>	5.363	5.95 ± 0.2(G) ≤ 6.6(H)	3.431 ± 0.2 ≤ 4.081	3.843
	NaF	(1.465) <sup>a</sup>	(2.0) <sup>c</sup>	5.12	4.65 ± 0.2(G) ≤ 5.3(H)	3.462 ± 0.2 ≤ 4.112	
	KF	1.205 <sup>b</sup>	2.55 <sup>d</sup>	4.318	5.0 ± 0.25(G)	4.158 ± 0.25	
	RbF	1.39 <sup>b</sup>	(2.31) <sup>e</sup>	4.159	5.35 ± 0.2(G)	3.876 ± 0.2	
	CsF	1.451	2.345 <sup>e</sup>	3.89	5.5 ± 0.2(G)	3.782 ± 0.2	
Cl	LiCl	1.499 <sup>f</sup>	(1.97) <sup>c</sup>	5.363	5.0 ± 0.3(G)	3.973 ± 0.3	3.88
	NaCl	1.1 <sup>f</sup>	2.3606 <sup>e</sup>	5.12	4.24 ± 0.05(G)	3.918 ± 0.05	
	KCl	1.02 <sup>b</sup>	2.667 <sup>e</sup>	4.318	4.4 ± 0.05(G) 4.42(H)	3.793 ± 0.05 3.813	
	RbCl	1.076	2.787 <sup>g</sup>	4.159	4.5 ± 0.2(G)	3.891 ± 0.2	
	CsCl	0.95 <sup>b</sup>	2.906 <sup>e</sup>	3.87	4.6 ± 0.2(G)	3.894 ± 0.2	
Br	LiBr	1.248 <sup>f</sup>	2.17 <sup>e</sup>	5.363	4.35 ± 0.3(G)	3.856 ± 0.3	3.717
	NaBr	0.959 <sup>f</sup>	2.502 <sup>e</sup>	5.12	3.80 ± 0.1(G) 3.85(H)	3.77 ± 0.1 3.82	
	KBr	0.83 <sup>b</sup>	2.821 <sup>e</sup>	4.318	3.94 ± 0.05(G) 3.96(H)	3.619 ± 0.05 3.639	
	RbBr	0.788 <sup>b</sup>	2.945 <sup>e</sup>	4.159	4.0 ± 0.25 (G)	3.692 ± 0.25	
	CsBr	0.86 <sup>b</sup>	3.072 <sup>e</sup>	3.87	4.1 ± 0.25(G)	3.623 ± 0.25	
I	LiI	0.9727 <sup>h</sup>	2.392 <sup>e</sup>	5.363	3.5 ± 0.2(G)	3.531 ± 0.2	3.355
	NaI	0.7631 <sup>f</sup>	2.7115 <sup>e</sup>	5.12	3.07 ± 0.1(G) 3.16(H)	3.434 ± 0.1 3.524	
	KI	0.704 <sup>b</sup>	3.048 <sup>e</sup>	4.318	3.32 ± 0.05(G) 3.33(H)	3.321 ± 0.05 3.331	
	RbI	0.633 <sup>b</sup>	3.177 <sup>e</sup>	4.159	3.5 ± 0.1(G) 3.29(H)	3.362 ± 0.1 3.302	
	CsI	(0.665) <sup>a</sup>	3.315 <sup>e</sup>	3.87	3.4 ± 0.1(G) 3.31(H)	3.248 ± 0.1 3.148	

(a) Somayajulu (1960). (b) Barrow (1963). (c) Rittner (1951). (d) Grabner and Hughes (1950). (e) Hening *et al* (1954). (f) Rice and Klemperer (1957). (g) Tirschka Braunstein (1954). (h) Klemperer and Rice (1957).

TABLE II

Comparison of electron affinity of fluorine atom

E(e.v)	Methods	Authors
3.843	Equation(1)	Present
3.622	Surface ionization	Dukel's kil and Ionov.*
3.62	Dissociation of alkali fluorides	Stamper and Barrow (1958)
3.567	Magnetron	Bernstein and Metly (1951)
3.557	Spectrophotometric	Jortner <i>et al</i> (1959)
5.0	Linear extrapolation	Pritchard (1953)
4.133	Bornexles	Mayer and Helmholtz (1932)
3.94	Quadratic extrapolation	Glockler*
3.47	Lattice energy	Cubieciotti. (1959)

\*From Pritchard (1953)

TABLE III

Comparison of electron affinity of chlorine

E(e.v.)	Methods	Authors
3.88	Equation(1)	Present
4.021	Magnetron	Mitchell and Mayer (1940)
3.757	Surface ionization	Dukel' skil and Ionov.*
3.723	Magnetron	McCallum and Mayer (1943)
3.005	Electron impact	Hanson (1937)
4.8	Linear extrapolation	Pritchard (1953)
3.874	Lattice energy	Pritchard (1953)
3.68	-do-	Cubieciott. Jr. (1959)
3.70	Quadratic extrapolation	Glockler*
3.10	-do-	Bates*

\*Pritchard (1953)

**TABLE IV**  
Comparison of electron affinity of bromine atom

E(e.v.)	Methods	Authors
3.717	Equation (1)	Present
3.83	Dissociation of alkali halides	Mayer and Helmholtz (1932)
3.818	Space Charge	Glockler and Calvin (1936)
3.805	Electron impact	Blewett (1936)
3.773	Mass spectrograph	Blewett (1936)
3.761	Flame	Piccardi (1926)
3.64	Surface ionization	Ionov (1940)
3.47	-do-	Weisblatt (1938)
3.556	Absorption spectra	Lederie (1933)
3.49	Magnetron	Doty and Mayer (1944)
3.47	Dissociation of alkali Halides	Saha and Tandon (1937)
3.799	Bornecyles	Van Arkel, and De Boer (1927)
3.53	Lattice energy	Mayer and Helmholtz (1932)
3.526	Bornecyles	Huggins (1937)

**TABLE V**  
Comparison of electron affinity of iodine

E(e.v.)	Methods	Authors
3.355	Equation (1)	Present
3.557	Flame	Piccardi (1926)
3.31	Surface ionization	Ionov*
3.236	Space charge	Glockler and Calvin (1935)
3.141	Magnetron	Sutton and Mayer (1934, 1935)
3.002	Electron impact	Buchdahl (1941)
3.258	Lattice energy	Pritchard (1953)
3.14	-do-	Cubicciotti, Jr. (1959)

\*Pritchard (1953)

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