Estimated Electron Affinities of the Light Elements

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The electron affinities of the light elements have been estimated by an empirical method of extrapolation. The ionization potentials (I) of isoelectronic systems are considered to be parabolic functions of the atomic number (Z). The Moseley curves $I^{\frac{1}{2}} : Z$ of the first ionization potential of the electronic systems containing from one to eighteen electrons have been completed. They are nearly straight lines except in their lower extremities where they show a bending towards the axis of atomic number Z. Wherever a check was possible it is found that the estimated electron affinities agree with experiment or with other calculation as obtained from wave mechanics or from thermochemical considerations by means of a Born-Haber cycle. The estimated electron affinities (in electron-volts) are: H (+0.7), He (−0.5), Li (+0.3), Be (−0.6), B (+0.1), C (+1.37), N (+0.04), O (+3.8), F (+3.9), Ne (−1.20), Na (+0.1), Mg (−0.9), Al (−0.2), Si (+0.6), P (+0.2), S (+2.1), Cl (+3.7), A (−1.0), Ni (+0.3), Cu (+1.2), Ag (+1.0), Hg (+1.8).

I. Introduction

The total energy W of any atomic system can be expressed by equations of the form

$$W=\Sigma[(Z-s)/n]^2 \qquad (1)$$

where Z = charge on the nucleus, s = screening constant and n = effective quantum number.[1, 2] This relation can be used to calculate the ionization potential I of the outermost electron for any isoelectronic sequence. It is seen that the relation between ionization potential I and atomic number Z will be of the form of a parabola. These parabolas have been calculated from experimental data and they are used below to obtain the electron affinities of the atoms of the first two periods of the periodic table. These parabolas are considered a more satisfactory representation of the relations mentioned than the usual Moseley-curves ($I^{\frac{1}{2}} : Z$).

II. Wave Mechanics

Of the eighteen atoms mentioned, only the two and three electron systems have been treated on the principles of wave mechanics by Hylleraas, Eckart, Wilson and others.[3–5] The results of these calculations check satisfactorily but they involve enormous labor of calculation. It may therefore be permissible to suggest a very simple, empirical method of extrapolation, which will permit the calculation of electron affinities.

III. Empirical Method of Extrapolation

It is suggested to establish the complete Moseley-curves for isoelectronic systems indicating in each case the removal of the first or outer electron. From the fact that the two and three electron systems show Moseley curves which have a bend near smaller atomic numbers it is evident that straight line extrapolation as indicated by Bartlett[6] and Braunbek[7] will not yield the most accurate values.

From the known experimental values[8] the best parabola is obtained (Fig. 1) showing the relation between ionization potential and atomic number:

$$I=(1/n^2)(aZ^2-bZ+c), \qquad (2)$$

$$dI/dZ=(1/n^2)(2aZ-b), \qquad (3)$$

$$d^2I/dZ^2=2a/n^2. \qquad (4)$$

The slope Eq. (3) were found to be straight lines which are parallel for the K, L and M shells as seen in Fig. 3. The values of the constant a (Eq. (2)) expected are $a=27.08$ (K); $a=\frac{1}{4}\times 13.54=3.39$ (L); $a=\frac{1}{9}\times 13.54=1.504$ (M) while the experimental quantities are nearly constant and

$$a=27.08\ (K);\quad a\doteq 3.6\ (L);\quad a\doteq 1.8\ (M).$$

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[1] C. Zener, Phys. Rev. **36**, 51 (1930).
[2] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[3] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[4] C. Eckart, Phys. Rev. **36**, 878 (1930).
[5] E. R. Wilson, J. Chem. Phys. **1**, 210 (1930).
[6] J. H. Bartlett, Nature **125**, 459 (1930).
[7] W. Braunbek, Zeits. f. Physik **63**, 20 (1930).
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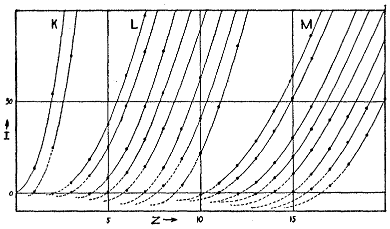

FIG. 1. Ionization potential of the outer electron for isoelectronic systems as parabolic function of the central charge.

The constants a, b and c of the empirical parabolas are given in Table I. Differences between theoretical and experimental values can be expressed as a quantum defect.

For some of the systems considered very little data are available and the slopes of the curves (Fig. 3) representing the 7, 9, 12, 14, 15, 16 and 17 electron system were obtained by interpolation. It is believed that the consistency of the whole scheme justifies this procedure.

TABLE I. *Ionization potentials of isoelectronic systems as parabolic functions of nuclear charge.*

Shell	No. of electrons	$I_1=aZ^2-bZ+c$			
		a	b	c	a/n^2
K	1	13.54	—	—	13.54
	2	13.54	16.87	4.06	
L	3	3.43	11.25	8.25	3.39
	4	3.43	15.10	14.77	
	5	3.57	23.28	35.43	
	6	3.58	28.23	51.87	
	7	3.67	34.6	76.85	
	8	3.77	43.04	116.6	
	9	3.75	48.95	155.4	
	10	4.0	58.47	206.1	
M	11	1.75	30.41	127.9	1.504
	12	1.8	33.87	154.9	
	13	1.7	35.59	181.3	
	14	1.7	37.62	201.6	
	15	1.7	39.70	223.2	
	16	1.85	47.20	291.9	
	17	2.0	55.14	372.3	
	18	2.0	58.00	411.5	

The eighteen parabolas enumerated in Table I fit the experimental ionization potentials very well wherever sufficient experimental data were found to make a test. The first three shells of electrons (K, L and M) were found to yield very satisfactory results by this method of treatment. However the atoms beginning with potassium do not add the next electron into the last M subshell. The situation is here more complicated but it appears that the electron affinity of argon is negative, i.e., A^- is unstable whether the electron would tend to enter the $3d(M)$ or the $4s(N)$ shell.

IV. ELECTRON AFFINITY

In the study of atomic structure as well as in the consideration of chemical processes the affinity of neutral atoms or molecules for electrons is a quantity of very great interest. A few direct determinations[9–11] have been made, optical methods have been attempted[12] and in the case of the hydrogen atom the only satisfactory knowledge which exists is the calculation of the electron affinity of hydrogen by Hylleraas.[13] Since both the experimental determination and the calculation of the electron affinity appear to present great difficulties, either of experimental manipulation or of intricate calculation it should be of some interest to use the above empirical extrapolation method for their evaluation. It is believed that it gives entirely satisfactory values of the electron affinity of the atoms which fit well into the whole scheme of our present knowledge of these quantities.

The method consists in the extrapolation of the known ionization potential of the stripped atoms of the same number of electrons as the negative ion. For example the two electron systems

$$H^- \rightarrow H + E^-$$
$$He \rightarrow He^+ + E^-$$
$$Li^+ \rightarrow Li^{++} + E^-$$
$$A^{+(Z-2)} \rightarrow A^{+(Z-1)} + E^-$$

are all isoelectronic structures and one parabola represents their first ionization potential or one Moseley curve (second curve of Fig. 2) pertains to them. From the eighteen parabola shown in Table I the electron affinities of the atoms have been estimated. The values are shown in Table II and in Fig. 4.

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[9] J. E. Mayer, Zeits. f. Physik **61**, 798 (1930).

[10] L. Rolla and G. Piccardi, Atti acad. Lincei [6] **3**, 410 (1926).

[11] G. Piccardi, Atti. acad. Lincei [6] **3**, 413 (1926); **3**, 566 (1926).

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[13] E. A. Hylleraas, Zeits. f. Physik **60**, 624 (1930).

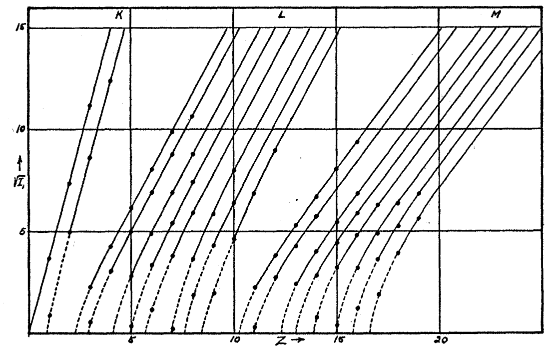

FIG. 2. Moseley curves of the ionization potentials of the outer electron of isoelectronic systems.

TABLE II. *Electron affinities of the light atoms.*

Atom	E. Aff.	Atom	E. Aff.
H	+0.76	Ne	−1.20
He	−0.53	Na	+0.08
Li	+0.34	Mg	−0.87
Be	−0.57	Al	−0.16
B	+0.12	Si	+0.60
C	+1.37	P	+0.15
N	+0.04	S	+2.06
O	+3.80	Cl	+3.70
F	+3.94	A	−(1.0)
Ni	+0.25	Ag	+0.95
Cu	+1.17	Hg	+1.79

V. General Considerations

It is seen that the electron affinities of the rare gases He, Ne and A are negative, i.e., the negative ions He⁻, Ne⁻ and A⁻ are unstable. This is to be expected when it is recalled that the mobility of the negative carrier in these gases reaches very high values,[14] which can only mean that free electrons abound in these gases when very pure and they do not attach themselves to form negative ions. The negative rare gas ions do not occur in the mass-spectrograph. In only one case has He⁻ been reported.[15] The present considerations would throw doubt on the correctness of the interpretation of these mass-spectroscopic findings. The negative He⁻ ions may not be due to the neutral atom but may be due to excited helium which may well possess an affinity for electrons.

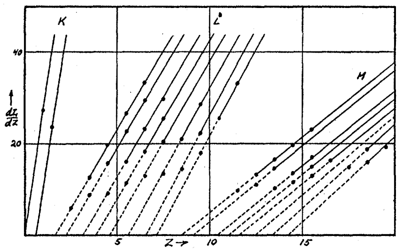

FIG. 3. First derivative of the ionization potential of the outer electron of isoelectronic systems as a function of the central charge.

The atoms beryllium and magnesium do not form Be⁻ and Mg⁻. It is of interest to recall that the neutral alkaline earth atoms are in a $^1S_0$ state as are the rare gases and it is easy to believe that a further electron added would not attach readily since it would have to enter an outer shell.

The alkali metal atoms have a positive electron affinity and Li⁻ and Na⁻ are stable. The potassium ion K⁻ has been reported.[16]

The halogens fluorine and chlorine have a large electron affinity as has been shown by many workers and especially by J. Mayer.[9] His determination is so well established that his values have been used by us to determine the

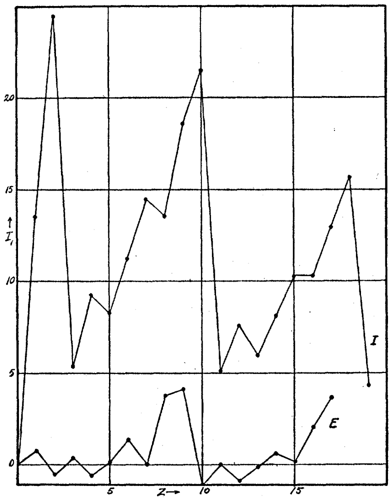

FIG. 4. Estimated electron affinities of light atoms *E* obtained from empirical extrapolation of the ionization potentials of analogous isoelectronic systems and experimental values of the ionization potentials *I* of the outer electron of the corresponding neutral atoms.

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[16] R. W. Ditchburn and F. L. Arnot, Proc. Roy. Soc. **A123**, 516 (1929).

slope of the derivative curves (Fig. 3) of the respective (10 and 18) electron systems. Our earlier calculated values were about 0.8 e.v. lower. Since the agreement was so close the present procedure seemed entirely justified.

The electron affinity of argon was estimated by assuming that the additional electron was added to the *3d* or *4s* shell. However the long extrapolation involved will only permit the statement that A^- is most likely unstable. Negative ions have been reported in argon[17] but they may be due to an impurity or to excited atoms.

The oxygen atom and the sulphur atom have large electron affinities as was to be expected. Of the other atoms dealt with, mercury has a large electron affinity of Hg^- ions have been reported in the mass-spectrograph by Nielsen.[18]

The general trend of these estimated electron affinities is entirely as expected.

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The Spectrum of Gallium Oxide

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The spectrum of gallium oxide has been photographed with a 21-foot grating. A band system lying in the region 3800–4200A has been identified as a $^2\Sigma \rightarrow {}^2\Sigma$ transition and a vibrational quantum analysis is given. The band-heads are approximately located by the equation

$$\nu = \left.\begin{matrix} 25{,}706.43 \\ 25{,}709.04 \end{matrix}\right\} + 763.63(v'+\tfrac{1}{2}) - 3.89(v'+\tfrac{1}{2})^2 - 767.69(v''+\tfrac{1}{2}) + 6.34(v''+\tfrac{1}{2})^2.$$

The spectrum of indium oxide is briefly discussed.

UNTIL recently there has been little study made of the band spectra of gallium and indium compounds. In 1916 Browning and Uhler,[1] while studying the atomic spectrum of gallium, discovered six new bands and eleven closely-spaced lines (believed also to be bands), and they suggested that these came from GaO or Ga_2. Within the past year work has been reported on the spectra of the halides of gallium and indium.[2, 3, 4] In a recent comprehensive study of these halide spectra Miescher and Wehrli[4] have discussed briefly the spectrum of GaO and have given vibrational quantum assignments to the bands observed. The analysis to be reported in this paper is based on spectrograms of this same system taken at higher dispersion. Measurements of the band-heads check those of Miescher and Wehrli and several additional bands have been noted. The more complete data now at hand indicate that the quantum assignments made by these workers are not entirely correct.

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[3] E. Miescher and M. Wehrli, Helv. Phys. Acta **6**, 256, 457 (1933).

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