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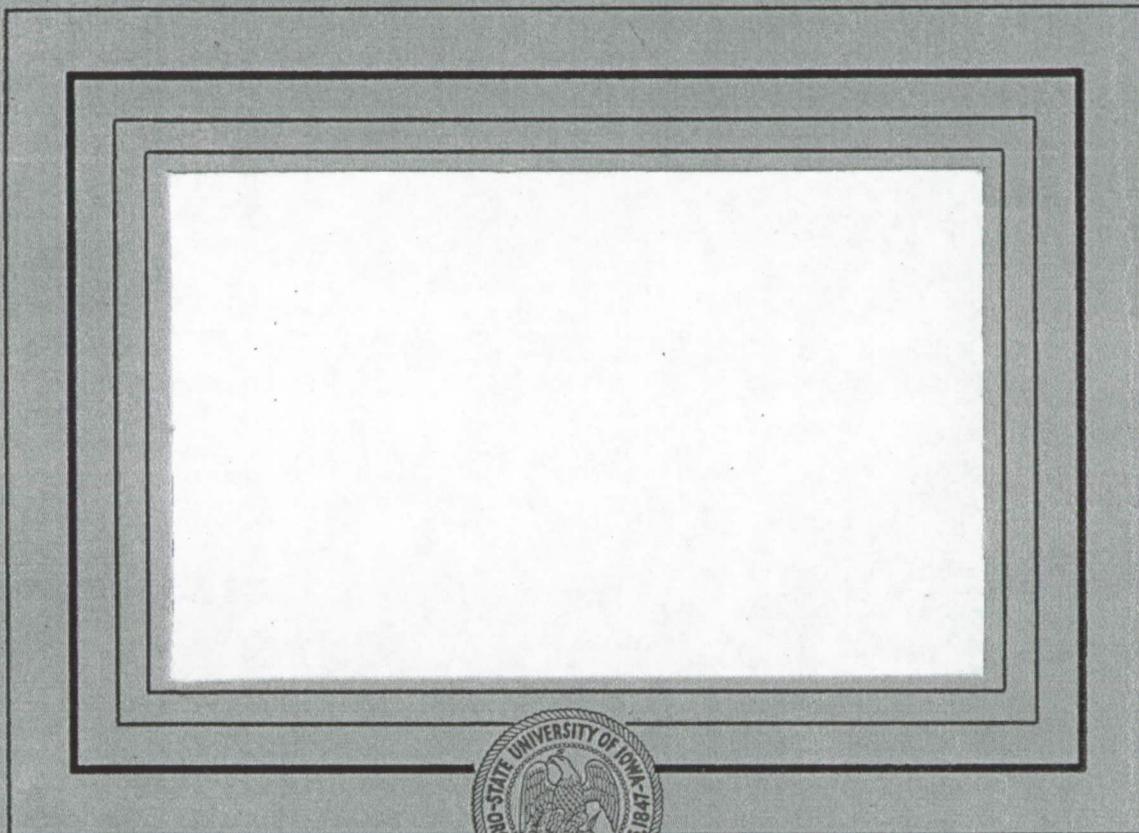
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SEMIEMPIRICAL THEORIES OF THE AFFINITIES OF NEGATIVE ATOMIC IONS*

by

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ABSTRACT

The determination of the electron affinities
of negative atomic ions by means of direct experi-
mental investigation is limited. To supplement the
meager experimental results, several semiempirical
theories have been advanced. One commonly used tech-
nique involves extrapolating the electron affinities
along the isoelectronic sequences. The most recent
of these extrapolations is studied by extending the
method to include one more member of the isoelectronic
sequence. When the results show that this extension
does not increase the accuracy of the calculations,
several possible explanations for this situation are
explored.

A different approach to the problem is suggested
by the regularities appearing in the electron affinities.
Noting that the regular linear pattern that exists for
the ionization potentials of the p electrons as a
function of Z, repeats itself for different degrees
of ionization q, the slopes and intercepts of these
curves are extrapolated to the case of the negative

ion. The method is placed on a theoretical basis by calculating the Slater parameters as functions of q and n, the number of equivalent p-electrons. These functions are no more than quadratic in q and n.

The electron affinities are calculated by extending the linear relations that exist for the neutral atoms and positive ions to the negative ions. The extrapolated slopes are apparently correct, but the intercepts must be slightly altered to agree with experiment. For this purpose one or two experimental affinities (depending on the extrapolation method) are used in each of the two short periods.

The two extrapolation methods used are: (A) an isoelectronic sequence extrapolation of the linear pattern as such; (B) the same extrapolation of a linearization of this pattern (configuration centers) combined with an extrapolation of the other terms of the ground configurations. The latter method is preferable, since it requires only one experimental point for each period. The results agree within experimental error with all data, except with the most recent value of C^-, which lies 10% lower.

I. INTRODUCTION

Important problems in several fields have drawn
increasing attention to negative ions in recent years.
A few of the more prominent examples for which a know-
ledge of negative ions is required are as follows:

1. The <u>continuous emission spectrum</u> of the sun
and stars is influenced by the presence of negative ions
in their outer atmospheres. It is known that the absorp-
tion of negative hydrogen ions present in the solar
photosphere determines the spectral distribution in the
observable region. The H$^-$ ion proves to be the major
source of the sun's atmospheric opacity in the red and
infrared -- a factor which determines the depth to which
the photosphere may be observed. The realization of the
importance of absorption by H$^-$ helps to resolve certain
difficulties connected with the spectral distribution of
the radiation emitted by other stars. For instance, when
the color temperature* of a star is greater than the

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* color temperature - The temperature obtained from
  the intensity gradient in the visible region.

effective temperature*, it suggests that the stellar atmospheric absorption coefficient is an increasing function of λ in this wavelength range. This effect is known to be produced by the presence of H⁻ in sufficient quantity. Negative ions other than H⁻, such as O⁻ and C⁻, are thought to be important in <u>atmospheric absorption</u>, too. Since the star's radiation is the sole means of gaining information about the star, it is very important that the properties of negative ions be fully understood.

2. The <u>ionized layers</u> in the upper atmosphere (Kennelly-Heaviside layers) are known to possess negative ions as important constituents. These layers, for the most part, are subject to solar control and possess special properties. For instance, the ozone layer, at an average height of about 20 km, strongly absorbs solar radiation with wavelengths below 3000 A. At greater heights, the E and F regions (120-300 km) have a consider-

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* effective temperature- The temperature such that the total intensity emitted by the star is the same as that which would be emitted if it were a black body at that temperature.

able concentration of ions and electrons -- the F layer
possessing the added feature of dividing into two regions
during the day. The D layer lies below the E region
(70-120 km). The ionization of the D layer is normally
weak, but may be enhanced considerably during periods
of increased solar activity -- producing radio fade-outs,
etc. Additional properties and features of these ionized
layers may be found in the literature[1]. It appears as
though negative ions do not exert a major influence at
the level of the E layer or above. However, at lower
levels they become progressively more important due to
the increase in the rate of attachment with gas density.
In this respect, the negative ion concentration is signi-
ficant in determining the free electron density. There-
fore, the identity of the negative ions formed, the ion's
properties, and the rates of ion formation and destruction
must be determined to understand the individual atomic
processes concerned.

3. The binding energy of the excess electron on
the negative ion must be known before important data,
such as dissociation energies or heats of vaporization,
may be determined.

4. The negative ion spectra of complex molecules are sometimes simpler and more revealing than the molecule's positive ion spectra in mass spectroscopy.

5. In nuclear physics, the effective energy of electrostatic generators could possibly be increased using high current negative ion sources.

All these examples, and many more, demand a more exact understanding of the properties of negative ions.

Considerable information has been accumulated regarding these properties. A review of experimental and theoretical work to 1957 will be found in the literature.[2,3] However, this report will be restricted to review and elaboration of recent work concerning the negative ion's electron affinity.

The electron affinity of an atom is defined as the energy difference between the ground state of the negative ion and the ground state of the atom with a free electron at rest at infinity. This energy is equal to the ionization potential, i.e., the energy necessary to detach an electron from the ion. If the electron affinity is positive, the negative ion is stable. The qualitative nature of the problem is to determine which negative ions exist in a stable state. The quantitative problem is the determination of the

ionization potential of the ground state (affinity) and
of the excited states (if any).

The electron affinity for most negative ions is
a very small quantity -- perhaps on the order of an
electron volt or less. Consequently, it is quite
difficult to measure the affinities of the ions exper-
imentally. There are a few exceptions, such as the
halogens, which have affinities sufficiently large
that consistent experimental values have been obtained.

To supplement the experimental work, several
theoretical techniques have been advanced to determine
these unknown electron affinities. The accuracy of
these methods is usually checked by comparing the
results with the known experimental values. Most of
the theories meet with considerable difficulty, however,
because of the relatively great fragility of negative
ions. Since the binding energy is relatively small, the
error associated with the theoretical evaluation will
be comparable in magnitude to the calculated affinity.
Thus, for neutral atoms or positive ions, an error of
$\pm$ 0.5 electron volts will be but a small percentage of
their ionization potential; but this same error will be
enormous in the case of negative ions, being of the same

order as their ionization potentials.

One promising semiempirical technique was employed by Johnson and Rohrlich.[4] They computed the electron affinities for several negative atomic ions by extrapolation from the ionization potentials of the corresponding isoelectronic sequences. The method involved the evaluation of five parameters -- which in turn required an accurate knowledge of the ionization potential of the neutral through the triply ionized member of the sequence. The method will be discussed more extensively in a succeeding chapter. It will be sufficient to mention that the results agree with four of the five measured affinities. Relatively large errors for many of the ionization potentials given in the literature[5] were thought to be the primary reason for the one discrepancy found.

Recently, Edlén[6] modified this technique. He used a somewhat simpler procedure which required a knowledge of the ionization potentials through the doubly ionized member only. Also, he assigned a constant value to one of the adjustable parameters following theory in zeroth order, which is confirmed in the semi-empirical approach of Johnson and Rohrlich.

These alterations, together with improved experimental data for the ionization potentials, allowed Edlén to compute the electron affinities for several negative atomic ions which were, for the most part, more precise than the previous calculations, resulting in agreement with all experimental data.

Several questions are raised at this point. First, does the new experimental data for the ionization potentials account for the improvement in Edlén's electron affinities for the negative atomic ions? Second, if this data were used with the method of Johnson and Rohrlich, would better or worse agreement result? Third, if a compromise between the two methods were used with the new data, would there be any increase in the accuracy of the computed values? It is the purpose of the following chapter to investigate these questions.

Since the results of this investigation are negative, we study a different procedure for the computation of electron affinities in chapter III. This new procedure will enable us to predict the affinities to rather high accuracy if one affinity is known in each period of the periodic table.

II. STUDY OF ISOELECTRONIC EXTRAPOLATION PROCEDURES

A. History

Direct calculations of electron affinities are very difficult for all but the lightest elements. Because of this difficulty, an empirical method of predicting electron affinities from spectroscopic data on neutral atoms and positive ions is often employed.

Glockler[7] was the first to apply this technique. From the known experimental values, he determined the best parabola showing the relation between the ionization potential and the atomic number as

$$I = (1/n^2)(aZ^2 - bZ + c) \tag{1}$$

The ionization potentials were thus computed by a quadratic extrapolation of ionization potentials. While this formula is known to be accurate for neutral atoms, it is too crude to find the very weak binding energies of negative ions. The difficulty stems from the fact that large numbers are subtracted to give the small result.

Geltman[8] attempted to improve upon this method by extending the above relation to include cubic,

quartic, etc., extrapolations of the ionization potentials. He assumed that the best value of the electron affinity is that extrapolated value corresponding to the lowest energy. With this assumption, the extended extrapolation procedure gives lower limits to the electron affinities which are reasonably consistent with experimental values. However, this technique appears to have no physical basis.

Wu[9] employed the theory of Bacher and Goudsmit[10] to calculate the electron affinity of B^-, C^-, N^-, and O^-. This theory utilizes the experimental ionization potentials of the atom and its ions to estimate the electron affinity of the atom. It possesses the added feature that the accuracy of the approximation is increased with the amount of experimental data available. Unfortunately, this data is limited, making the probable error in the approximation of the same order of magnitude as the extrapolated electron affinity.

B. Extrapolation Method of Johnson-Rohrlich

The semiempirical extrapolation formula proposed by Johnson and Rohrlich[4] possesses an advantage in that it can be justified on physical grounds. Since their

formula is fundamental to this paper, the derivation will be presented in the following paragraphs.

In the derivation of their formula, Johnson and Rohrlich assume the spin orbit interaction to be negligible. Then, the Hamiltonian for an atom, or ion, of nuclear charge Z and possessing N electrons is written

$$H = -\left(\frac{1}{2m}\right) \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \left(\frac{Z e^2}{r_i}\right) + \sum_{i>j}^{N} \left(\frac{e^2}{r_{ij}}\right). \qquad (2)$$

By defining the average free Hamiltonian per unit nuclear charge as

$$\overline{H}_o = \frac{1}{Z}\left[-\left(\frac{1}{2m}\right) \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \left(\frac{Z e^2}{r_i}\right)\right], \qquad (3)$$

they write

$$\overline{H} = \left(\frac{1}{Z}\right) H = \overline{H}_o + \left(\frac{1}{Z}\right)H_1 \qquad (4)$$

when

$$H_1 = \sum_{i>j}^{N} \frac{e^2}{r_{ij}} \qquad (5)$$

Using perturbation theory, the solution of

$$\overline{H}\psi = \overline{E}\psi \qquad (6)$$

is found to be

$$E(Z) = Z\overline{E}(Z) = E_o + \left(\frac{1}{Z}\right)E_1 + \left(\frac{1}{Z^2}\right)E_2 + --- \qquad (7)$$

when H_1 is treated as the perturbation. The E_i are known to possess a factor Z^2 and the ionization potential, or ground state energy, is $E = -I$.

To obtain a faster converging series, a spherically symmetric part is separated from H_1 and combined with H_o. Then, instead of (3), they write

$$\bar{H} = \bar{H}'_o + \left[\frac{1}{(Z-\sigma)}\right]H'_1 \qquad (8)$$

Using the above expansion, with E_i proportional to $(Z - \sigma)^2$, the ionization potential is written as

$$I(Z) = \alpha(Z-\sigma)^2 + \beta(Z-\sigma) + \gamma + \sum_{k=1}^{\infty}\left[\frac{a_k}{(Z-\sigma)^k}\right] \qquad (9)$$

where σ depends on the rearranged spherically symmetric part. They define σ uniquely by choosing it such that the β term disappears. Then,

$$I(Z) = \alpha(Z-\sigma)^2 + \gamma' + \sum_{k=1}^{\infty}\left[\frac{a_k}{(Z-\sigma)^k}\right] \qquad (10)$$

is the general form for the ionization potential. Because of the limited supply of accurate data available, Johnson and Rohrlich computed but five parameters (α, γ', a_1, a_2, and σ) -- the formula becoming

$$I \approx I_2(Z) = \alpha(Z-\sigma)^2 + \gamma' + \left[\frac{a_1}{Z-\sigma}\right] + \left[\frac{a_2}{(Z-\sigma)^2}\right] \qquad (11)$$

Physical significance can be placed on two of these parameters. The constant α is simply $1/n^2$, where n is the principal quantum number of the valence electron, while σ is the screening constant for the atom or ion.

The parameters were computed by comparing (11) with the observed ionization potentials of the members of an isoelectronic sequence -- which were obtained from a National Bureau of Standards circular.[5] The data that is relevant to this report has been listed in Table I at the end of this report. With the exception of S^-, Johnson and Rohrlich's computed electron affinities agreed with experimental values. These results, as well as those results from a quadratic extrapolation, are listed in Table II.

C. Extrapolation Method of Edlén

The recent work of Edlén[6] used essentially the same extrapolation formula. It differs mainly in the fact that three parameters and three ionization potentials are required, while five parameters and four ionization potentials were used in the preceding method. He accomplishes this simplification by assuming the parameter $\alpha = 1/n^2$ and by dropping the inverse square

term $\left[a_2/(Z - \sigma)^2\right]$. When $\zeta = Z - (N-1)$ and $Z - \sigma = \zeta - a$, (11) can be written as

$$T_\zeta = \left(\frac{R}{n^2}\right)\left[(\zeta+a)^2 - b' + \frac{c}{(\zeta+a)}\right] \qquad (12)$$

for the binding energy T of an electron with principal quantum number n. This may be written

$$T_\zeta / \left(\frac{R}{n^2}\right) = \zeta^2 + 2a\zeta - b + \frac{c}{\zeta+a} \qquad (13)$$

when

$$b = b' - a^2 \qquad (14)$$

To facilitate the calculations, (13) is transformed into an expression that relates the electron affinity of the negative ion (T_0 for $\zeta = 0$) into terms corresponding to the first three members of the isoelectronic sequence (T_1, T_2, T_3 for $\zeta = 1, 2, 3$, respectively). For instance, using

$$T_0' = T_0 / \left(\frac{R}{n^2}\right) = -b + \frac{c}{a} , \qquad (15)$$

$$T_1' = T_1 / \left(\frac{R}{n^2}\right) = 1 + 2a - b + \frac{c}{1+a} , \qquad (16)$$

$$T_2' = T_2 / (\tfrac{R}{n^2}) = 4 + 4a - b + \frac{c}{2+a}, \quad (17)$$

$$T_3' = T_3 / (\tfrac{R}{n^2}) = 9 + 6a - b + \frac{c}{3+a}, \quad (18)$$

the parameters a, b, and c can be eliminated to obtain T_0' in terms of T_1', T_2', and T_3'. It is however, more convenient to write T_0' in the form

$$T_0' = 3T_1' - 3T_2' + T_3' + Q. \quad (19)$$

Q is then found to be

$$Q = \frac{3(T_1' - 2T_2' + T_3' - 2)(-T_1' + 2T_2' - T_3' + 6)}{T_1' - 4T_2' + 3T_3' - 12}. \quad (20)$$

Edlén calculated the electron affinities of He⁻ through Cl⁻ using these equations. The results of his calculations are given in Table II. It is apparent that they, for the most part, agree with experimental values. However, much of the spectroscopic data that he used differs significantly from that given in the literature. The new, presumably better, data is given in Table I. The number of decimals retained is taken as an indication of the estimated accuracy.

D. Extension of Edlén's Method

The success of these extrapolation formulas suggests an extension to four parameters and the use of four experimental ionization potentials, since the accuracy of this technique should increase with the number of terms retained. The general equation (13) would then become

$$T_\zeta / \left(\frac{R}{n^2}\right) = \zeta^2 + 2a\zeta - b + \frac{c}{\zeta + a} + \frac{d}{(\zeta + a)^2}. \quad (21)$$

The additional term requires the ionization energies of the triply ionized ion of the isoelectronic sequence. Unfortunately, many of these energies are known with little precision -- the most recent values* being listed in Table I. Despite these difficulties, an investigation of this extension appears desirable.

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* I am indebted to Mrs. Sitterly, National Bureau of Standards, Washington, D.C. for transmitting these data to me.

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Carrying through the same procedure for the four parameters, as was done for the three parameters, is a somewhat tedious task. The five equations obtained from equation (22), i.e., T_0, T_1, T_2, T_3, and T_4 for $\zeta = 0, 1, 2, 3,$ and 4 respectively, can be inserted into the interpolation formula for four terms to yield

$$Q \equiv T_0' - 4T_1' + 6T_2' - 4T_3' + T_4' \; {}^* \qquad (22)$$

$$Q = \frac{24c}{a(1+a)(2+a)(3+a)(4+a)} \qquad (23)$$

$$+ \; \frac{24d(24+100a+105a^2+40a^3+5a^4)}{a^2(1+a)^2(2+a)^2(3+a)^2(4+a)^2}$$

From these formulas one obtains the following quadratic equation in a,

$$(T_4' - 3T_3' + 3T_2' - T_1')a^2 + (8T_4' - 18T_3' + 12T_2'$$

$$-2T_1' - 24)a + (16T_4' - 27T_3' + 12T_2' - T_1' - 60) = 0 \qquad (24)$$

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* The primes on T have the same meaning as in equations (15) - (18).

The substitution, a = x - 2, is recommended in an effort to take advantage of the symmetry of the problem. Using this substitution, (23) can be given as

$$Q = \frac{12(T_3' - 2T_2' + T_1' - 2)}{x^2 - 4} + \frac{48d}{(x^2 - 4)^2(x^2 - 1)}. \quad (25)$$

Equation (25) is best derived by computing the expression $T_3' - T_2' + T_1'$, solving for c, and substituting it into (23).

A similar procedure may be used to eliminate the parameter d. To facilitate the computations, the substitution x = y - 1 (or a = y - 3) is made. The determination of the quantity $T_4' - T_3' + T_2'$ permits us to write another expression for Q in terms of d and y.

$$Q = \frac{12(T_4' - 2T_3' + T_2' - 2)}{(y - 3)(y - 2)} \quad (26)$$

$$+ \frac{24d(2y - 5)}{y(y^2 - 1)(y - 2)^2(y - 3)^2}.$$

The parameter d is eliminated by the simultaneous solution of (25) and (26). Then, upon resubstitution of

$y = a + 3$ and $x = a + 2$, the expression for Q becomes

$$Q = \frac{4}{a^2}\left[\, 2a\left(-T_4' + 3T_3' - 3T_2' + T_1'\right) \right.$$
$$\left. + \left(-4T_4' + 9T_3' - 6T_2' + T_1' + 6\right)\right]. \tag{27}$$

With these expressions, a possible method of solution is evident. When equation (24) is solved for a, one of the roots is negative and may be ignored. Once a is known, it may be inserted into the expression for Q (27). Then, the binding energy for the negative ion (T_0) will be given by (22),

$$T_0' = 4T_1' - 6T_2' + 4T_3' - T_4' + Q. \tag{28}$$

The electron affinity of O^- was computed using this technique. O^- was chosen because its experimental electron affinity is known with considerable accuracy. Therefore, it serves as a good check point for theoretical investigations. Edlén's data for T_1, T_2 and T_3 was used for these calculations. The accuracy of his computations indicates that this data is the best available. The remaining term, T_4, was

obtained from Mrs. Sitterly*. The electron affinity was calculated to be 1.80 electron volts -- which is to be compared with the experimental value of 1.47 electron volts.

Because of the similarity between this extrapolation formula, Johnson and Rohrlich's method, and Edlén's formula, the parameters of equations (21) and (13) were computed. The results of these calculations are shown in Table III.

The computed electron affinity of O^- by this extended extrapolation formula is worse than either Johnson and Rohrlich's or Edlén's result (see Table II). The question arises whether this discrepancy can be attributed to poor spectroscopic data. Because of the accuracy with which it is used in the three term extrapolation formula, one must exclude the data for T_1, T_2, and T_3. However, this is not true for T_4-- which is not well known in many cases. It is therefore essential

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* See footnote page 15.

to calculate just what effect the ionization potential of T_4 (Mg^{+++}) has on the computed electron affinity. Will the experimental error in the ionization potential for Mg^{+++} account for the difference between 1.80 and 1.47 ev?

The ionization potentials for the first three members of the isoelectronic sequence (T_1, T_2, and T_3) containing O^- as its zeroth member will therefore be assumed correct in the following discussion. If $\overline{T}'_o$ and $\overline{T}'_4$ are the correct ionization potentials for O^- and Mg^{+++}, respectively, we can write

$$\overline{T}'_o = f\left(\overline{T}'_4\right). \tag{29}$$

The computed value, T'_o, can be written

$$T'_o = f\left(\overline{T}'_4 + \epsilon\right) \tag{30}$$

when ϵ is the error in the experimental ionization potential. Expanding, (30) becomes

$$T'_o = f\left(\overline{T}'_4\right) + \frac{\partial f}{\partial T_4} \cdot \epsilon + \cdots \tag{31}$$

$$= \overline{T}'_o + \frac{\partial f}{\partial T_4} \cdot \epsilon.$$

The expansion has been limited to the first derivative since ϵ is assumed to be small. By computing $\frac{\partial f}{\partial T_4'}$, the affect of T_4' on T_0' can be determined. Using (28)

$$\frac{\partial f}{\partial T_4'} = \frac{\partial}{\partial T_4'}\left(4T_1' - 6T_2' + 4T_3' - T_4' + Q\right)$$

$$= -1 + \frac{\partial Q}{\partial T_4'} . \tag{32}$$

But,

$$Q = Q\left[T_4', a(T_4')\right]. \tag{33}$$

Employing the chain rule,

$$\frac{dQ}{dT_4'} = \frac{\partial Q}{\partial T_4'} + \frac{\partial Q}{\partial a}\frac{\partial a}{\partial T_4'} . \tag{34}$$

All these partial derivatives can be calculated for 0^- by using equations (27) and (24). They are computed to be

$$\frac{\partial Q}{\partial T_4'} = -1.929 \tag{35}$$

$$\frac{\partial Q}{\partial a} = -0.634 \tag{36}$$

$$\frac{\partial a}{\partial T_4}' = 3.016 \tag{37}$$

The insertion of these numbers into (35) and (33) gives

$$\frac{dQ}{dT_4}' = -3.841 \tag{38}$$

and

$$\frac{\partial f}{\partial T_4}' = -4.841. \tag{39}$$

Assume $\overline{T}_0 = 1.47$ electron volts (11.83 kilokaysers) and $T_0 = 1.80$ electron volts (14.70 kilokaysers). Then, the estimated error is

$$\epsilon = \frac{T_0 - \overline{T}_0}{\frac{\partial f}{\partial T_4}} \tag{40}$$

$$= -0.60 \text{ kilokaysers} = 0.074 \text{ ev}$$

If the ionization potential were decreased by 0.60 kilokaysers, the extrapolation formula for four parameters would agree exactly with experiment. However, the experimental error in the measurement of this ionization potential presumably is of the order or less than 0.1 kK, as is apparent from Edlén's unpublished result giving 881.1 kK. Therefore the spectroscopic data above apparently do not account for this discrepancy.

We must now examine other possible explanations for the poor agreement. One is led to the nature of the equations used for the computations. The extrapolation formula is known to form an oscillating power series for many sequences[4], that is, in (10), a_k is positive when k is even and is negative when k is odd. That this relationship might hold true for the O^- sequence is indicated by the parameters listed in Table III for the four parameter calculations.

It can be argued that a better approximation of the ionization potential for the negative ion is made if the last term of (10) involves an even, rather than an odd, power of $Z - \sigma$. This argument assumes the extrapolation formula approaches the correct ionization potential asymptotically with increasing k. Therefore, if a_k is positive (k even) for the last term of the series, the computed ionization potential will match the correct value more closely than if it were negative. This, of course, presupposes the fact that successive terms for increasing k in (10) will become smaller in magnitude. Or, in other words, that the series converges.

However, this is not apparent for the example of O^-. The parameters and terms show considerable variation -- depending upon the method employed. The three-

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parameter form gives a positive a_1 and a fairly large γ'. In agreement with the above discussion, the four-parameter form gives negative values for a_1 and positive values for a_2, the magnitude of a_1 being considerably smaller than that of a_2. The same qualitative relations hold for the parameters found by Johnson and Rohrlich[4].

To demonstrate the importance of each term, equation (21) is written as

$$T_0' = -b + \frac{c}{a} + \frac{d}{a^2}$$
$$= -0.352 + \frac{-0.230}{2.049} + \frac{4.196}{(2.049)^2}$$
$$= 0.536$$

(41)

when $\gamma = 0$ for the ionization potential of the negative ion. Similarly, (15) becomes

$$T_0' = -b + \frac{c}{a}$$
$$= -1.050 + 1.487$$
$$= 0.437$$

(42)

for the three-parameter form.

The terms of (41) indicate the d-term is more important than the c-term. While successive terms

obviously do not converge for this form, there is the
possibility that the positive and negative terms would
exhibit convergence separately if a sufficient number
of terms were available. Unfortunately, the extension
of this procedure to $a_n > a_2$ is not experimentally
feasible.

The fact remains, however, that Edlén's three-
parameter form (42) agrees well with experiment. Since
some series are known to converge for a certain num-
ber of terms, then diverge for all succeeding terms
(semi-convergent series) a possible explanation is
suggested. Edlén's three-parameter form may be the
best choice. Then, for any additional terms, the
series is not convergent.

Finally, there is some arbitrariness in form-
ulas of type (10), i.e., in the use of the parameter
a in the denominators of the terms in (21). It can
be argued that another constant, different from a,
could be added to $\mathcal{S}$ when it occurs in the denominator.
The arguments presented in reference 4 assume conver-
gence of the perturbation series.

Summarizing, we conclude that either (1) Edlén's
selection of three terms is the best choice and the

series is not convergent; or (2) the series converges,
but we need more terms to establish this fact. In
that case an additional term $\frac{e}{(\zeta+a)^3}$ would very near-
ly cancel the contribution from $\frac{d}{(\zeta+a)^2}$, recovering
Edlén's good agreement with experiment.

III. .ELECTRON AFFINITIES FROM HORIZONTAL

ANALYSIS OF IONIZATION POTENTIALS

A. Introduction

Despite the discrepancies that appear in the

extension of his method to four parameters, Edlén's

extrapolated electron affinities using the first three

members of the isoelectronic sequence agree well with

experimental values. A graph displaying Edlén's elec-

tron affinities and the experimental values is given in

Fig. 1.

Several interesting features are noted from this

graph. For example, consider only the 2p electrons --

beginning with Be⁻ and ending with F⁻. A definite

pattern seems obvious for these six electron affinities.

Be⁻, B⁻, and C⁻, representing the first three electrons

in the 2p shell, lie approximately on a straight line.

Similarly, N⁻, O⁻, and F⁻, representing the $2p^4$, $2p^5$,

and $2p^6$ electrons, possess a linear relation. Fig. 2

shows the experimental ionization potentials for atoms

or ions of a given designation for different degrees of

ionization*, q. The same linear properties mentioned above are present in these curves. This pattern is even more obvious with the 3p electrons. The study of such patterns for fixed q and as a function of Z is called horizontal analysis.

B. Extrapolation of Horizontal Analysis

The above regularities suggest an alternative method of extrapolating the negative ion's electron affinity for the p electrons. Assuming a linear relationship for n = 1, 2, 3, an equation for the ionization potentials may be written as

$$\text{I.P.}(q,p^n) = \alpha'(q)n + \beta'(q), \quad n = 1,2,3 \quad (43)$$

when q is the degree of ionization, $\alpha'(q)$ is the slope

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* The degree of ionization, q, is the net charge of the ion or atom. For example, q = 0 for the neutral atom, q = 1 for the singly ionized positive ion, etc.

of the curve and $\beta'(q)$ is the intercept for $n = 0$.
Similarly, the ionization potentials for $n = 4, 5, 6$
may be written as

$$\text{I.P.}(q, p^n) = \alpha''(q) n + \beta''(q), \qquad n = 4, 5, 6 \qquad (44)$$

with the double primes referring to the fact that the
slopes and intercepts are for $n = 4, 5, 6$ only. The
experimental slopes and intercepts for the 2p and 3p
shells are listed in Table IV. $\alpha'(q)$, $\alpha''(q)$, $\beta'(q)$,
and $\beta''(q)$ may be determined experimentally as a function
of q from this data. Once these expressions are known,
it is a simple matter to extrapolate to the case of the
negative ion -- i.e., for $q = -1$.

This extrapolation may be placed on a theoretical
basis by utilizing energy relations involving the Slater
parameters. These parameters are functions of the con-
figuration and the net charge, or degree of ioniza-
tion of the atom. The energy relations for the con-
figurations of interest are written below.[11] The
electron interactions the parameters represent are
shown in parentheses. For instance, $E(q; p, s^2; s^2 p^n)$
represents the energy due to the interaction of one p
electron with the s^2 shell for a given degree of

ionization, q, and configuration, s^2p^n; $F_o(q; s, p;$ $s^2p^n)$ is one of the Slater parameters representing this interaction; etc. Then,

$$E(q; s^2; s^2p^n) \equiv E_o(q; s^2; s^2p^n) =$$
$$F_o(q; s^2; s^2p^n) \tag{45}$$

$$E(q; p^n, s^2; s^2p^n) = n \big[2F_o(q; s, p; s^2p^n)$$
$$- G(q; s, p; s^2p^n) \big] \tag{46}$$

$$E(q; p^n; s^2p^n) = f_o^{(n)} F_o(q; p,p; s^2p^n)$$
$$+ f_2^{(n)} F_2(q; p, p; s^2p^n) \tag{47}$$

where $f_o^{(n)}$ and $f_2^{(n)}$ are given by the following:

n	1	2	3	4	5	6
$f_o^{(n)}$	0	1	3	6	10	15
$f_2^{(n)}$	0	-5	-15	-7	-4	-6

The energy of the s^2p^n configuration may be written as the energy of the s electrons plus the energy of the p electrons plus the interaction energy between the s and p electrons.

$$E(q, s^2 p^n) = E(q; s^2; s^2 p^n) + E(q; p^n; s^2 p^n)$$
$$+ E(q; s^2, p^n; s^2 p^n) \qquad (48)$$
$$= F_o(q; s^2; s^2 p^n) + f_o^{(n)} F_o(q; p,p; s^2 p^n)$$
$$+ f_2^{(n)} F_2(q; p,p; s^2 p^n)$$
$$+ n\left[2 F_o(q; s,p; s^2 p^n) - G_1(q; s,p; s^2 p^n)\right].$$

With this expression for the energy of a given configuration and degree of ionization, an equation for the ionization potential may be written. The ionization potential of an atom is the energy necessary to remove an electron from the ground state of the atom and place it at rest at infinity. Therefore, for a p electron,

$$I.P.(q, s^2 p^n) = E(q+1, s^2 p^{n-1}) - E(q, s^2 p^n). \qquad (49)$$

To facilitate the computations, three substitutions are made. They are

$$H(q; s,p; s^2 p^n) = 2 F_o(q; s,p; s^2 p^n) \qquad (50)$$
$$- G_1(q; s,p; s^2 p^n),$$

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$$A(q; p^n; s^2 p^n) = F_0(q; p, p; s^2 p^n)$$
$$- 5 F_2(q; p, p; s^2 p^n) \quad \text{(51)}$$

$$B(q; p^n; s^2 p^n) = 23 F_2(q; p, p; s^2 p^n). \quad \text{(52)}$$

Then, in abbreviated notation, the energy express-
ions become

$$E(q; s^2) = E_0(q) = F_0(q) \quad \text{(53)}$$

$$E(q; s^2, p^n) = n H(q; s^2 p^n) \qquad n \geq 1 \quad \text{(54)}$$

$$E(q; p^n) = \frac{n(n-1)}{2} A(q, p^n) + (n-3) B(q, p^n) \quad \text{(55)}$$

where B (q, p^n) = 0 for n = 1, 2, 3.

Using these expressions, equation (48) becomes

$$E(q; s^2 p^n) = E_0(q) + n H(q; s^2 p^n) + \frac{n(n-1)}{2} A(q; p^n) + (n-3) B(q; p^n). \quad \text{(56)}$$

The parameters are known in good approximation
to be linear functions of n from previous investiga-
tions.[12] However, to allow the equation for the ion-
ization potential to be as general as possible, the

coefficient of n and its intercept are both desig-
nated as functions of q. Then, the following sub-
stitutions can be made.

$$E_o(q) = F_o(q) = \varphi_o(q) \tag{57}$$

$$A(q, n) = V_A(q) \, n + \varphi_A(q) \tag{58}$$

$$B(q, n) = V_B(q) \, n + \varphi_B(q) \tag{59}$$

$$H(q, n) = V_H(q) \, n + \varphi_H(q) \tag{60}$$

When equations (56) through (60) are inserted into
the expression for the ionization potential (49), the
resulting equation is of the following form:

$$I.P.(q, s^2 p^n) = a_3 \, n^3 + a_2 \, n^2 + a_1 \, n + a_o \tag{61}$$

where

$$a_3 = \tfrac{1}{2} \, \Delta V_A(q)^* = O \tag{62}$$

$$a_2 = \Delta V_H(q) - \tfrac{1}{2} \Delta V_A(q) - \tfrac{3}{2} V_A(q)$$
$$+ \tfrac{1}{2} \Delta \varphi_A(q) + \Delta V_B(q) = O \tag{63}$$

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* $\Delta V_A(q) \equiv V_A(q+1) - V_A(q),\ \Delta V_H(q) \equiv V_H(q+1) - V_H(q),\ etc.$

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$$a_1 = -2 \, \nu_H(q+1) + \Delta \, \varphi_H(q)^* + \tfrac{5}{2} \, \nu_A(q+1) - \tfrac{1}{2} \Delta \, \varphi_A(q)$$
$$- \varphi_A(q+1) - 3 \Delta \, \nu_B(q) - 2 \, \nu_B(q+1) + \Delta \, \varphi_B(q) \quad (64)$$

$$a_0 = \Delta \, \varphi_0(q) + \nu_H(q+1) - \varphi_H(q+1) - \nu_A(q+1) + \varphi_A(q+1)$$
$$+ 4 \, \nu_B(q+1) - 3 \Delta \, \varphi_B(q) - \varphi_B(q+1). \quad (65)$$

It has been previously assumed, and the experiments confirm this to good approximation, that the ionization potential is linear in n. We shall not attempt to exceed this approximation. Therefore, a_3 and a_2 must be zero. a_1 becomes $a'(q)$ for n = 1, 2, 3 and equals $a''(q)$ for n = 4, 5, 6. Similarly, a_0 equals $\beta'(q)$ and $\beta''(q)$ for n = 1, 2, 3 and n = 4, 5, 6, respectively.

The object of the following analysis is to compute all possible parameters from the experimental relations involving the slopes and intercepts of the ionization potentials. Immediately, it is obvious from equation (62) that ν_A is independent of q. Since the B terms in (64) and (65) occur only for n = 4, 5,

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* $\Delta \, \varphi_H(q) = \varphi_H(q+1) - \varphi_H(q)$ and analogous meaning of $\Delta \, \varphi_B(q)$, $\Delta \, \varphi_A(q)$, etc.

6, the difference of the slopes and the intercepts should involve only these terms. The following relations result for the 2p shell when ν_8 is assumed to be a linear function of q $[\nu_8(q) = \nu_8' q + \xi_8]$ and ν_H is assumed constant. (These are the simplest consistent assumptions concerning these parameters.)

$$\alpha''(q) - \alpha'(q) = -2[(q+1)\nu_8' + \xi_8] - 3\nu_8' + \Delta \nu_8(q). \quad (66)$$

But this difference is found experimentally to be linear in q (confer Table IV). Therefore,

$$\alpha''(q) - \alpha'(q) = \alpha_1 q + \alpha_0 \quad (67)$$
$$= -0.5 q + 6.9. \,^*$$

Equation (66) becomes

$$\Delta \nu_8(q) = (\alpha_1 + 2\nu_8')q + \alpha_0 + 5\nu_8' + 2\xi_8 \quad (68)$$

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* Unless otherwise specified, the units employed will be kilokaysers (kK).

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or

$$\varphi_B(q) = \frac{\alpha_1 + 2\nu_B'}{2} q^2 + \left(\alpha_o - \frac{1}{2}\alpha_1 + 4\nu_B' + 2\xi_B\right)q + \chi_B' \quad (69)$$

when χ_B' is a constant.

The difference of the β terms becomes

$$\beta''(q) - \beta'(q) = 4(q+1)\nu_B' + 4\xi_B - \varphi_B(q+1) - 3\Delta\varphi_B(q) \quad (70)$$

$$= -\frac{\alpha_1 + 2\nu_B'}{2}q^2 - \left(\alpha_o + \frac{7}{2}\alpha_1 + 8\nu_B' + 2\xi_B\right)q$$

$$-\left(4\alpha_o + 16\nu_B' + 4\xi_B + \chi_B'\right).$$

But, experimentally (see Table IV),

$$\beta''(q) - \beta'(q) = \beta_2 q^2 + \beta_1 q + \beta_o$$
$$= 0.6q^2 - 10.7q - 60.2 \quad (71)$$

Equating the coefficients of the q terms permits the complete determination of B (q, n).

$$B(q,n) = (-0.35q + 4.17)n - 0.6q^2 + 13.6q + 21.5 \quad (72)$$

Then, equation (63) becomes

$$\varphi_A(q) = (3\nu_A + 0.7)q + \chi_A' \quad (73)$$

and

$$A(q,n) = \nu_A n + (3\nu_A + 0.7)q + \chi_A' \quad (74)$$

when χ_A' is a constant.

$\Delta\varphi_o(q)$ represents the energy difference of the s electrons for a given configuration and is to a good

approximation a linear function in q.[13] From the experimental data for $2s^2$, $\Delta \mathcal{Y}_0(q)$ becomes

$$\Delta \mathcal{Y}_0(q) = 55.79q + 127.62 \tag{75}$$

The addition of $\alpha''(q)$ and $\beta''(q)$ is the last independent operation to be utilized. The theoretical and experimental expressions become

$$\begin{aligned}
\alpha''(q) + \beta''(q) &= \Delta \mathcal{Y}_0(q) - \mathcal{V}_H - \mathcal{Y}_H(q) \\
&\quad + 0.6q^2 - 10.7q - 52.1 \\
&= 28.8q^2 + 90.3q + 13.3.
\end{aligned} \tag{76}$$

Then,

$$H(q, n) = \mathcal{V}_H(n-1) - 28.2q^2 - 45.2q + 62.2. \tag{77}$$

Therefore, all but three parameters, $\mathcal{V}_A$, χ_A', and $\mathcal{V}_H$, can be derived from the experimental slopes and intercepts. The final results are given by equations (72), (74), (75), and (77).

The same analysis was carried out with the 3p shell. The results, both experimental and theoretical, are summarized below.

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$$\alpha''(q) - \alpha'(q) = -0.3q + 3.6 \tag{78}$$

$$\beta''(q) - \beta'(q) = -0.2q^2 - 3.2q - 33.7 \tag{79}$$

$$B(q,n) = (0.35q - 1.05)n + 0.2q^2 + 3.1q + 17.9 \tag{80}$$

$$A(q,n) = \nu_A n + (3\nu_A - 0.7)q + \chi_A' \tag{81}$$

$$\Delta\varphi(q) = 28.09q + 90.19 \tag{82}$$

$$\alpha''(q) + \beta''(q) = 13.9q^2 + 65.8q + 18.0 \tag{83}$$

$$H(q,n) = \nu_H(n-1) - 14.1q^2 - 41.3q + 45.4 \tag{84}$$

With the successful evaluation of the Slater parameters, a theoretical basis for the extrapolation of the ionization potentials using the slopes and intercepts is provided. As will be seen the numerical values of the constants ν_A, χ_A', and ν_H which are not provided by the above analysis, will not be relevant for the extrapolation. The numerical values of the electron affinities can be obtained without knowing these quantities.

C. Results of Extrapolation of Horizontal Analysis.

The formulae for the ionization potentials that best fit the experimental data for q = 0, 1, 2 are the following:

$$I.P.(q, 2p^n) = (18.1q + 25.2)n + 28.2 q^2 + 83.4q + 41.4 \qquad n = 1, 2, 3 \tag{85}$$

$$I.P.(q, 2p^n) = (17.6q + 32.1)n + 28.8 q^2 + 72.7q - 18.8 \qquad n = 4, 5, 6 \tag{86}$$

for the 2p shell and

$$I.P.(q, 3p^n) = (9.6q + 21.8)n + 14.1 q^2 + 49.4q + 29.9 \qquad n = 1, 2, 3 \tag{87}$$

$$I.P.(q, 3p^n) = (9.9q + 18.2)n + 13.9 q^2 + 56.2q - 3.8 \qquad n = 4, 5, 6 \tag{88}$$

for the 3p shell. The resulting extrapolation of the negative atomic ion's ionization potential is shown as the dashed line in Fig. 3.

These values lie below the experimental points. However, the slopes compare well for the p^5 and p^6 configurations, so that the discrepancy is presumably almost entirely due to the intercepts. Since β is a

quadratic function of q , a correction of a few kilo-
kaysers represents a small variation in the curve (as
can be seen in Figs. 6 and 7). This suggests raising
the curve to fit the experimental points -- bringing
the β terms into agreement with experiment in the pro-
cess. The best corrections are for the 2p shell

$$\delta\beta' = 2.3 \tag{84}$$

$$\delta\beta'' = 3.1 \tag{90}$$

and for the 3p shell

$$\delta\beta' = 2.4 \tag{91}$$

$$\delta\beta'' = 2.4 \tag{92}$$

The solid curve in Fig. 3 shows these new linear
extrapolations. Now the extrapolated points follow the
same pattern that was noted for the cases of the neutral
atom and positive ions. The ionization potential of
atoms as the configurations p, p^3, p^4, and p^6 lie
slightly above the curves (a few tenths of a kilokayser),
while the ones as the configurations p^2 and p^5 lie
slightly below. In other words, the p, p^2, and p^3 (and

p^4, p^5, and p^6) ionization potentials do not lie exact-
ly on the straight lines. However, the amount by which
they differ from the straight line is a constant quanti-
ty for different degrees of ionization. These differ-
ences are listed below for the negative ions.

Configuration	p	p^2	p^3	p^4	p^5	p^6
Correction (2p)	0.4	-0.8	0.4	0.4	-1.1	0.5
Correction (3p)	0.2	-0.5	0.2	0.2	-0.5	0.2

Therefore, the linear extrapolation can be made to agree
more exactly with experiment by correcting for this dis-
placement.

The ionization potentials for the negative ions are
then evaluated in the following manner. First, the dir-
ect extrapolation to the case of the negative ion ($q = -1$)
is performed. This will give a linear relation for the
three points. Second, the correction for the non-linear-
ity of the ionization potentials is added. Third, the
points are then shifted by the amount necessary for exact
agreement with the best experimental value. Fourth, the
remaining ionization potentials are then directly deter-
mined. These values, regarded as the best results by
this method, are listed in Table IV.

The experimental values selected for n = 4, 5, 6 were O⁻ (11.81 kK) for the 2p shell and Cl⁻ (29.75 kK) for the 3p shell. For n = 1, 2, 3, the experimental value picked for the 2p shell was C⁻ (10.08 kK). Unfortunately, no experimental data is available for the 3p shell when n = 1, 2, 3. A somewhat arbitrary shift was assumed -- that of displacing these points the same distance as those for n = 4, 5, 6. The more regular behavior of the ionization potentials of the 3p shell and the smaller β displacement for n = 4, 5, 6 were used as the basis for this assumption.

D. Extrapolation of Center of Configuration Horizontal Analysis.

A means of checking these extrapolated ionization potentials is available by utilizing the energy difference between the centers of configuration $(\overline{I.P.})$, rather than the energy difference between the ground states (I.P.) of the atoms and ions. The relationship between the two ionization potentials is

$$I.P.(q, p^n) = \overline{I.P.}(q, p^n) - [\Delta E(q+1, p^{n-1}) \quad (93)$$
$$- \Delta E(q, p^n)]$$

when $\Delta E\ (q + 1,\ p^{n-1})$ is the energy difference between the ground state and the center of configuration for the atom or ion with n - 1 electrons and one electron at rest at infinity, and $\Delta E\ (q,\ p^n)$ is the same difference for the atom or ion with n electrons.

A plot of the center of configuration energy differences for q = 0, 1, 2 is shown on Fig. 4. Instead of two linear portions of the curve, there is now but one. The p and p^6 energies are essentially the same as the ionization potentials with the p^2, p^3, p^4, and p^5 energies lying on the straight line joining these points. Then the equation for the energy differences becomes

$$\overline{I.P.}(q, p^n) = \alpha(q)\, n + \beta(q) \qquad n = 1, 2, 3, 4, 5, 6 \tag{94}$$

for the p shells.

Analysis of the slopes and intercepts results in the following experimental formulae:

$$\overline{I.P.}(q, 2p^n) = (0.2q^2 + 15.3q + 21.4)\,n \tag{95}$$
$$+ 27.9q^2 + 86.5q + 43.5$$

for the 2p shell and

$$\overline{I.P.}(q, 3p^n) = (0.05q^2 + 8.85q + 15.80)\,n \tag{96}$$
$$+ 13.86q^2 + 60.78q + 31.13$$

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for the 3p shell.

ΔE ($q = -1$, p^n) may be calculated from the term values given by Bates and Moiseiwitsch[14] for B^-, C^-, N^-, Al^-, Si^-, and P^-. The term values were obtained using the quadratic extrapolation formula,

$$E_{SL}(q=-1, p^n) = 3 E_{SL}(q=0, p^{n-1})$$
$$- 3 E_{SL}(q=1, p^{n-2}) + E_{SL}(q=2, p^{n-3}) \quad (97)$$

where the subscripts S and L refer to the term involved. Equation (97) is used to calculate the term values for the O^- and S^- ions.*

Once all the terms of the ground state are known, the centers of configuration can be calculated. However, a correction must be made for the values given by Bates and Moiseiwitsch. They select the ground level, rather than the ground term, as the zero energy reference point. Therefore, we computed the ground term as well, using the above extrapolation formula (97).** Thereupon, the

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* O^- and S^- are the only other energy differences of importance in these calculations. The p and p^6 energies agree well with their ionization potentials. Therefore, the difference between these expressions (see equation (93)) would be negligible.

** The completed list of levels is given in Table VI.

center of configuration, $E_{C.G.}$, can be computed. The quantity ΔE for the negative ion, which is defined as the difference between $E_{C.G.}$ and the ground level, is then just equal to $E_{C.G.}$. Since this energy is measured relative to the ground level,

$$\Delta E(q, p^n) = E_{C.G.}(q, p^n). \quad \text{when measured relative to the ground level}$$

Knowing ΔE (q = -1, p^n), the quantity $\delta(\Delta E) = \Delta E$ (q = 0, p^{n-1}) - ΔE (q = -1, p^n) of equation (93) is determined to be that given by the following table:

Ion (2p Shell)	Be⁻	B⁻	C⁻	N⁻	O⁻	F⁻
$\delta(\Delta E)$	-0.02	-2.30	-5.80	13.13	7.50	0.14
Ion (3p Shell)	Mg⁻	Al⁻	Si⁻	P⁻	S⁻	Cl⁻
$\delta(\Delta E)$	-0.02	-1.69	-4.15	7.91	4.50	0.29

These quantities must be subtracted from the energy difference between the centers of configuration $(\overline{I.P.})$, in order to obtain the ionization potentials according to equation (93).

The results of the extrapolation are shown on Fig. 5. Again, the extrapolated ionization potentials lie below the experimental values -- in fact, the amounts by which the curve must be raised to fit the best

experimental value in each shell are of the same order
of magnitude as in the previous calculations.

The experimental value for O^- was used for the 2p
shell, while that for Cl^- was used for the 3p shell.
The extrapolated values were all displaced by an amount
which would bring the $2p^5$ value in exact agreement
with that for O^-. Similarly, the $3p^6$ term and all other
values in the 3p shell was shifted by an amount such that
the extrapolated value for $3p^6$ agreed with the experi-
mental value for Cl^-. The applied shifts are

$$\delta\beta = 3.4 \qquad\qquad\qquad (99)$$

for the 2p shell and

$$\delta\beta = 2.4 \qquad\qquad\qquad (100)$$

for the 3p shell. The ionization potentials were thus
calculated by applying the same shift to all terms in
each shell. The results are shown in Table V, column B1.

There is an alternative method of extrapolating
the center of configuration energy differences. As
noted earlier, the experimental points do not follow
an exactly linear curve, but will lie along a slight
arc. This suggests forming a quadratic equation in n
to account for this curvature. Then, instead of (94),

$$\overline{I.P.}(q,n) = \overline{\alpha}(q)n^2 + \overline{\beta}(q)n + \overline{\gamma}(q) \qquad (101)$$

Using (101), the experimental values for q = 0, 1, 2 lie within 0.1 kK, rather than within the 1-2 kK difference of the straight line approximation.

The expressions $\overline{a}(q)$, $\overline{\beta}(q)$, and $\overline{\gamma}(q)$ are determined from the data for the neutral atoms and positive ions. The results may be summarized as follows:

$$\overline{I.P.}(q,n) = (0.02q^2 - 0.07q + 0.59)n^2$$
$$+ (0.02q^2 + 15.85q + 17.37)n$$
$$+ (28.12q^2 + 85.80q + 48.95)$$

for the 2p shell and

$$\overline{I.P.}(q,n) = (-0.004q^2 - 0.029q + 0.351)n^2$$
$$+ (0.040q^2 + 9.106q + 13.422)n$$
$$+ (13.924q^2 + 60.401q + 34.410).$$

The extrapolation of this formula to q = -1 no longer needs to be corrected for deviations from the formula (101). Only the common shift $\delta\beta$ need be

applied. The results* are given in Table V column E2.
It is interesting to note that the results for this
extrapolation compare well with those obtained by the
preceding method (confer Table V, column A2). How-
ever, the present method is preferable, since it
requires only one experimental electron affinity in
each shell.

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* Instead of fitting (101) to $E_{c,c}$, we could have
applied a correction to the results of Table V
column B1, taking account of the deviations of the
points from the linear behavior assumed in (93).
Such a correction can be applied to each point
individually. The result agrees with column B2
to within 0.1 kK.

TABLE I

THE IONIZATION POTENTIALS OF ISOELECTRONIC

SEQUENCE MEMBERS FOR NEGATIVE IONS

OF THE TWO SHORT PERIODS

The data is obtained from the National Bureau of
Standards circular[5] and from the recent paper of Edlén[6].
However, the T_4 data (doubly-ionized ions) listed in
the column for Edlén was obtained from Mrs. Sitterly
of the National Bureau of Standards, Washington, D. C.
If the T_4 term is not listed in this column, there is
no improved data.

TABLE I

Negative Ion	Atom or Ion	Ionization Potential (NBS) (kilokaysers)	Ionization Potential (Edlén) (kilokaysers)
He⁻	Li	43.487	43.487
	Be⁺	146.882	146.882
	B⁺⁺	305.931	305.93
	C⁺⁺⁺	520.178	520.177
Li⁻	Be	75.192	75.192
	B⁺	202.895	202.81
	C⁺⁺	386.214	386.22
	N⁺⁺⁺	624.851	624.89
Be⁻	B	66.93	66.93
	C⁺	196.659	196.66
	N⁺⁺	382.626	382.75
	O⁺⁺⁺	624.397	624.397
B⁻	C	90.814	90.814
	N⁺	238.751	238.751
	O⁺⁺	443.026	443.00
	F⁺⁺⁺	703.020	702.83

Negative Ion	Atom or Ion	Ionization Potential (NBS) (kilokaysers)	Ionization Potential (Edlén) (kilokaysers)
C^-	N	117.214	117.22
	O^+	283.244	283.44
	F^{++}	505.41	505.5
	Ne^{+++}	783.173	783.3
N^-	O	109.837	109.837
	F^+	282.190	281.94
	Ne^{++}	511.778	511.8
	Na^{+++}	797.741	797.8
O^-	F	140.524	140.524
	Ne^+	331.35	330.4
	Na^{++}	578.637	577.8
	Mg^{+++}	881.759	881.1
F^-	Ne	173.932	173.932
	Na^+	381.528	381.2
	Mg^{++}	646.364	646.32
	Al^{+++}	967.714	967.714

Negative Ion	Atom or Ion	Ionization Potential (NBS) (kilokaysers)	Ionization Potential (Edlén) (kilokaysers)
Ne^-	Na	41.449	41.449
	Mg^+	121.267	121.268
	Al^{++}	229.454	229.44
	Si^{+++}	364.098	364.09305
Na^-	Mg	61.669	61.669
	Al^+	151.860	151.860
	Si^{++}	269.941	270.14
	P^{+++}	414.312	
Mg^-	Al	48.279	48.279
	Si^+	131.818	131.836
	P^{++}	243.290	243.40
	S^{+++}	381.541	
Al^-	Si	65.743	65.743
	P^+	159.1	159.3
	S^{++}	281.660	280.9
	Cl^{+++}	430.568	

Negative Ion	Atom or Ion	Ionization Potential (NBS) (kilokaysers)	Ionization Potential (Edlén) (kilokaysers)
Si⁻	P	84.58	84.58
	S⁺	188.825	188.2
	Cl⁺⁺	321.936	319.5
	Ar+++	482.4	
P⁻	S	83.559	83.559
	Cl⁺	192	192.07
	Ar⁺⁺	328.320	328.6
	K⁺⁺⁺	491.519	
S⁻	Cl	104.996	104.60
	Ar⁺	222.82	222.848
	K⁺⁺	369	369.2
	Ca⁺⁺⁺	542	
Cl⁻	Ar	127.110	127.110
	K⁺	256.637	254.9
	Ca⁺⁺	413.127	410.7
	Sc⁺⁺⁺	596.3	

TABLE II

COMPILATION OF ATOMIC ELECTRON AFFINITIES

(all units in ev).

Experimental electron affinities are from the following sources:

(a) L. M. Branscomb, Advances in Electronics and Electron Physics, (Academic Press) Vol. IX, (1957).

(b) L. M. Branscomb and M. Seman, 2nd International Conference on the Physics of Electronic and Atomic Collisions, Abstract of Papers, University of Colorado, 1961.

(c) C. R. Lagergren, Thesis, University of Minnesota (1955) (unpublished).

(d) L. M. Branscomb, D. S. Burch, S. J. Smith and S. Geltman, Phys. Rev. 111, 504, (1958).

(e) D. Cubicciotti, J. Chem. Phys. 31, 1646 (1959).

(f) I. N. Bakulina, Autorreferat C. Diss., Leningrad (1957).

Also, the electron affinities for Li⁻ and Na⁻ were calculated to be 0.54 ev and 0.48 ev, respectively, when calculated by the Hartree-Fock method. These calculations

are from the following sources:

(g) T. D. Strotskite and A. P. Iutsis, Akademiia
     Nauk Litovskoi SSR, Trudy, Ser. B, No. 1:11-
     19 (1958) (Li).

(h) T. D. Strotskite and A. P. Iutsis, Akademiia
     Nauk Litovskoi SSR, Trudy, Ser. B, No. 2:17-
     24 (1958) (Na$^-$).

TABLE II

Ion	Quadratic Extrapolation	Johnson-Rohrlich	Edlén	Experimental	
He⁻			0.19		
Li⁻			0.82	(0.54) (Hartree)	
Be⁻			-0.19		
B⁻	0.42	0.82	0.33	>0	(a)
C⁻	1.34	1.21	1.24	1.25 ± 0.03	(b)
				1.12 ± 0.05	(c)
N⁻	-0.1 ± 0.1	0.54	0.05	<0	(a)
O⁻	1.20	1.47	1.47	1.465 ± 0.005	(d)
F⁻	3.44	3.62	3.50	3.48 ± 0.05	(e)
				3.62 ± 0.09	(a)
Ne⁻			-0.57		
Na⁻			0.47	(0.48) (Hartree)	
Mg⁻			-0.32		
Al⁻	1.01	1.19	0.52	>0	(a)
Si⁻	1.86		1.46		(e)
P⁻	1.08	1.33	0.77	>0	(a)

Ion	Quadratic Extrapolation	Johnson-Rohrlich	Edlén	Experimental	
S^-	2.58	2.79	2.15	2.07 ± 0.07	(a)
				2.33 ± 0.10	(f)
Cl^-	3.56	3.84	3.70	3.69 ± 0.05	(e)
				3.82 ± 0.06	(a)

TABLE III

PARAMETERS FOR O⁻

The parameters have been converted to σ, γ', a_1, and a_2, or a, b, c, and d, using $a = c/n^2$, $a_2 = d/n^2$, $\sigma = N - 1 - a$, $\gamma' = (-a^2 - b)/n^2$. The parameters involved are given by equations (11) and (21).

TABLE III

Parameter	Johnson-Rohrlich	Edlén	This Calculation
a	2.017	2.084	2.049
b	0.178	1.050	0.352
c	-0.199	3.098	-0.230
d	2.647	--	4.196
σ	5.983	5.916	5.951
γ'	-1.062	-1.348	-1.138
a_1	-0.050	0.776	-0.057
a_2	0.662	--	1.049

TABLE IV

EXPERIMENTAL SLOPES AND INTERCEPTS FOR THE
2p AND 3p SHELLS

The α and β refer to the slope and the intercept, respectively, of the various straight lines. The single primes indicate n = 1, 2, 3 and, for the double primes, n = 4, 5, 6.

TABLE IV

Shell	Degree of Ionization q	$\alpha'(q)$	$\alpha''(q)$	$\beta'(q)$	$\beta''(q)$
2p	2	61.38	67.3	320.99	241.8
2p	1	43.29	49.7	152.97	82.7
2p	0	25.15	32.05	41.35	-18.81
3p	2	38.05	41.05	205.1	164.2
3p	1	28.2	31.4	103.4	66.3
3p	0	15.15	21.78	29.90	-3.81

TABLE V

EXTRAPOLATED IONIZATION POTENTIALS

(all units are in kK)

Method A refers to the direct extrapolation of the ionization potentials. Column 1 shows the extrapolated values after the intercept has been adjusted to fit the best experimental point for each curve. Those ions designated by an asterisk refer to the fact that this extrapolation is somewhat arbitrary. No experimental point is available for this slope. Column 2 shows the extrapolated values after the values of Column 1 have been adjusted for the non-linearity of the curves. Method B is the extrapolation of the center of configuration energy differences. The extrapolated values, plus the shift necessary to agree with the best experimental value, are given in Column 1 for the linear extrapolation. Column 2 shows the final extrapolation for the case of the extrapolation with a n^2 term. References for the experimental ionization potentials are given in the caption for Table II.

TABLE V

Ion	Method of Extrapolation				Experimental Ionization Potential
	Method A		Method B		
	A1	A2	B1	B2	
Be⁻	-4.4	-4.0	-5.9	-3.1	
B⁻	2.6	1.8	2.6	2.7	
C⁻	9.7	10.1	12.3	11.1	10.08 ± 0.25
N⁻	-1.6	-1.2	-0.1	-1.2	
O⁻	12.9	11.8	11.8	11.8	11.81 ± 0.04
F⁻	27.8	27.9	25.4	28.0	28.05 ± 0.4
Mg⁻*	-4.7	-4.5	-4.9	-4.9	
Al⁻*	3.6	3.1	4.0	2.3	
Si⁻*	11.9	12.1	13.3	11.0	
P⁻	5.1	5.3	8.1	5.8	
S⁻	17.3	16.8	18.5	16.8	16.68 ± 0.56
Cl⁻	29.5	29.7	29.7	29.7	29.75 ± 0.4

TABLE VI

THE ENERGY LEVELS OF NEGATIVE IONS

This table lists the excited levels of the ground
state for the first five negative ions of the two
short periods. The term value (and also the center
of configuration) for the sixth ion of the period
is zero. The energies of the terms were obtained from
Bates and Moiseiwitsch[14] with the exception of the
levels of ground terms. These were calculated using
equation (97). The value of $^2P^0$ in Si⁻ of reference
14 was found to be in error and has been corrected.

TABLE VI

Ion	Level	kK	Term	Center
Be^-	$^2P_{1/2}$	0	0.020	0.020
	$^2P_{3/2}$	0.030		
B^-	$^3P_0$	0	0.029	2.323
	$^3P_1$	0.015		
	$^3P_2$	0.042		
	$^1D_2$	4.905	4.905	
	$^1S_0$	10.067	10.067	
C^-	$^4S^0$	0	0	10.665
	$^2D^0$	11.325	11.325	
	$^2P^0$	16.674	16.674	
N^-	$^3P_2$	0	0.048	5.126
	$^3P_1$	0.100		
	$^3P_0$	0.135		
	$^1D_2$	10.817	10.817	
	$^1S_0$	22.366	22.366	
O^-	$^2P_{3/2}$	0	0.077	0.077
	$^2P_{1/2}$	0.230		

Ion	Level	kK	Term	Center
Mg⁻	$^2P_{1/2}$	0	0.023	0.023
	$^2P_{3/2}$	0.030		
Al⁻	$^3P_0$	0	0.061	1.764
	$^3P_1$	0.029		
	$^3P_2$	0.092		
	$^1D_2$	3.569	3.569	
	$^1S_0$	8.616	8.616	
Si⁻	$^4S^0$	0	0	7.372
	$^2D^0$	7.588	7.588	
	$^2P^0$	11.925	11.925	
P⁻	$^3P_2$	0	0.104	3.393
	$^3P_1$	0.212		
	$^3P_0$	0.304		
	$^1D_2$	6.771	6.771	
	$^1S_0$	16.109	16.109	
S⁻	$^2P_{3/2}$	0	0.169	0.169
	$^2P_{1/2}$	0.509		

FIGURE 1

IONIZATION POTENTIALS OF NEGATIVE ATOMIC IONS

The experimental ionization potentials (see Table II) and the computed ionization potentials of Johnson and Rohrlich[4] and of Edlén[6] are given for the negative atomic ions.
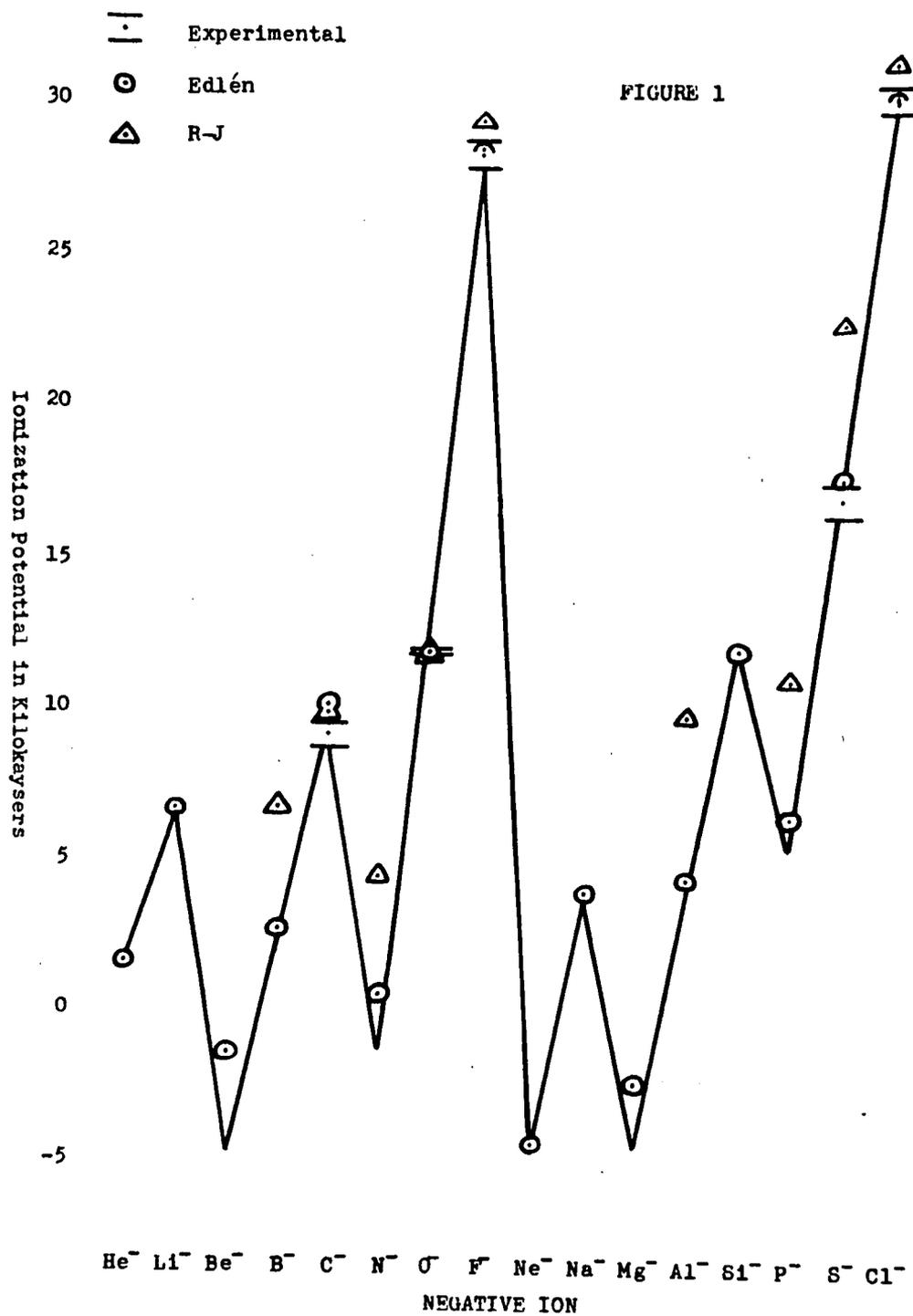
FIGURE 1

Ionization Potential in Kilokaysers

Experimental
Edlén
R-J

He⁻ Li⁻ Be⁻ B⁻ C⁻ N⁻ O⁻ F⁻ Ne⁻ Na⁻ Mg⁻ Al⁻ Si⁻ P⁻ S⁻ Cl⁻
NEGATIVE ION

FIGURE 2

IONIZATION POTENTIALS OF NEUTRAL ATOMS AND SINGLY-
AND DOUBLY-IONIZED POSITIVE IONS

The ionization potentials of the members of an
isoelectronic sequence are plotted on the same ordi-
nate for different degrees of ionization, q. The
dashed curve for q = -1 represents the extension of
these curves to the case of the negative ion. The
crosses show the location of the experimental ioniza-
tion potentials.

FIGURE 2

q = 2

q = 1

q = 0

q = -1

Ionization Potential in Kilokaysers

2s 2s² 2p 2p² 2p³ 2p⁴ 2p⁵ 2p⁶ 3s 3s² 3p 3p² 3p³ 3p⁴ 3p⁵ 3p⁶

Designation

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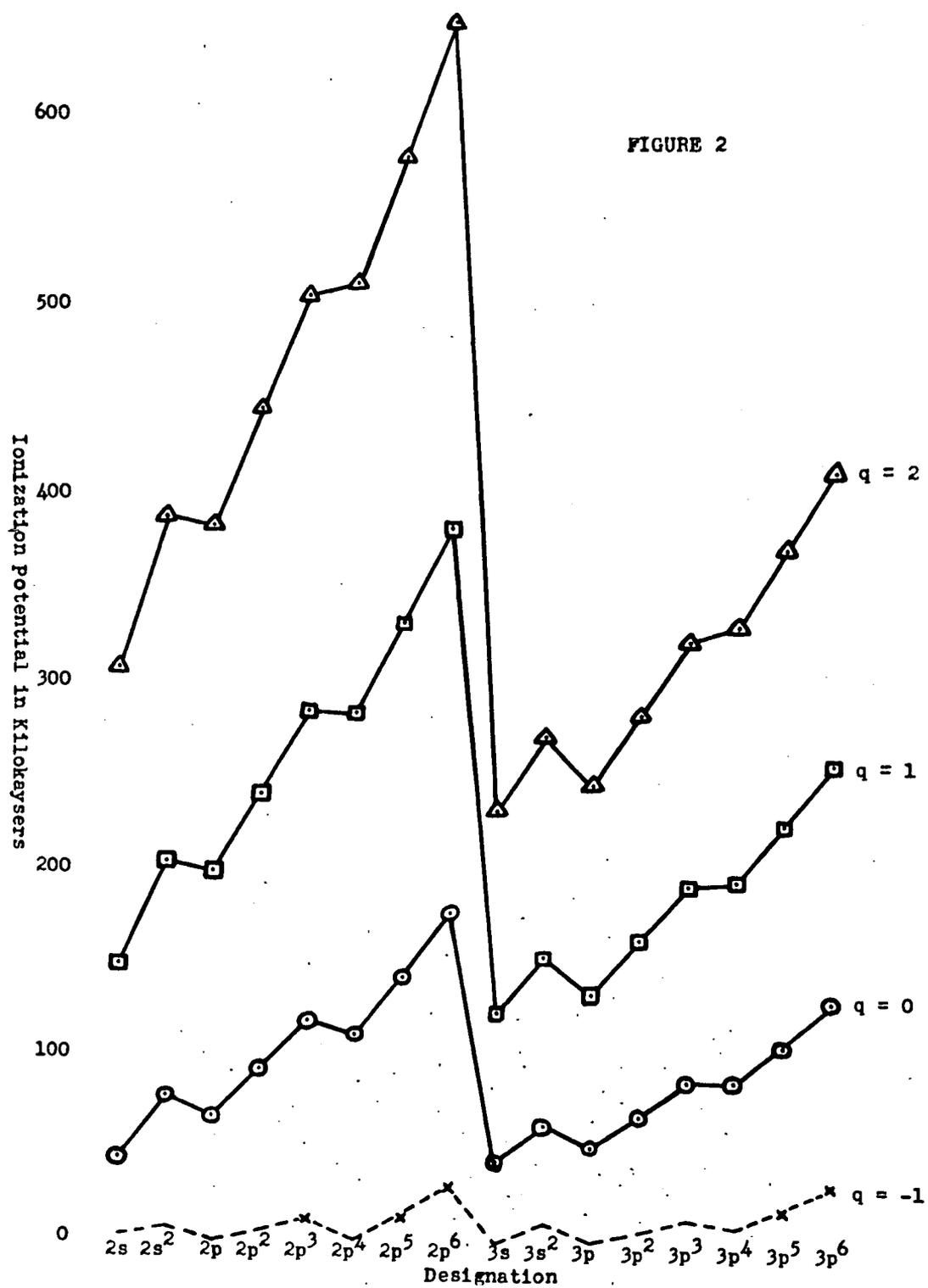
FIGURE 3

EXTRAPOLATED IONIZATION POTENTIALS

The ionization potentials for the negative ions
result from an extrapolation of the ionization poten-
tials of the isoelectronic sequence. The dashed curve
represents the direct extrapolation, while the solid
curve shows the effect of shifting these curves to
match the best experimental value for each curve.
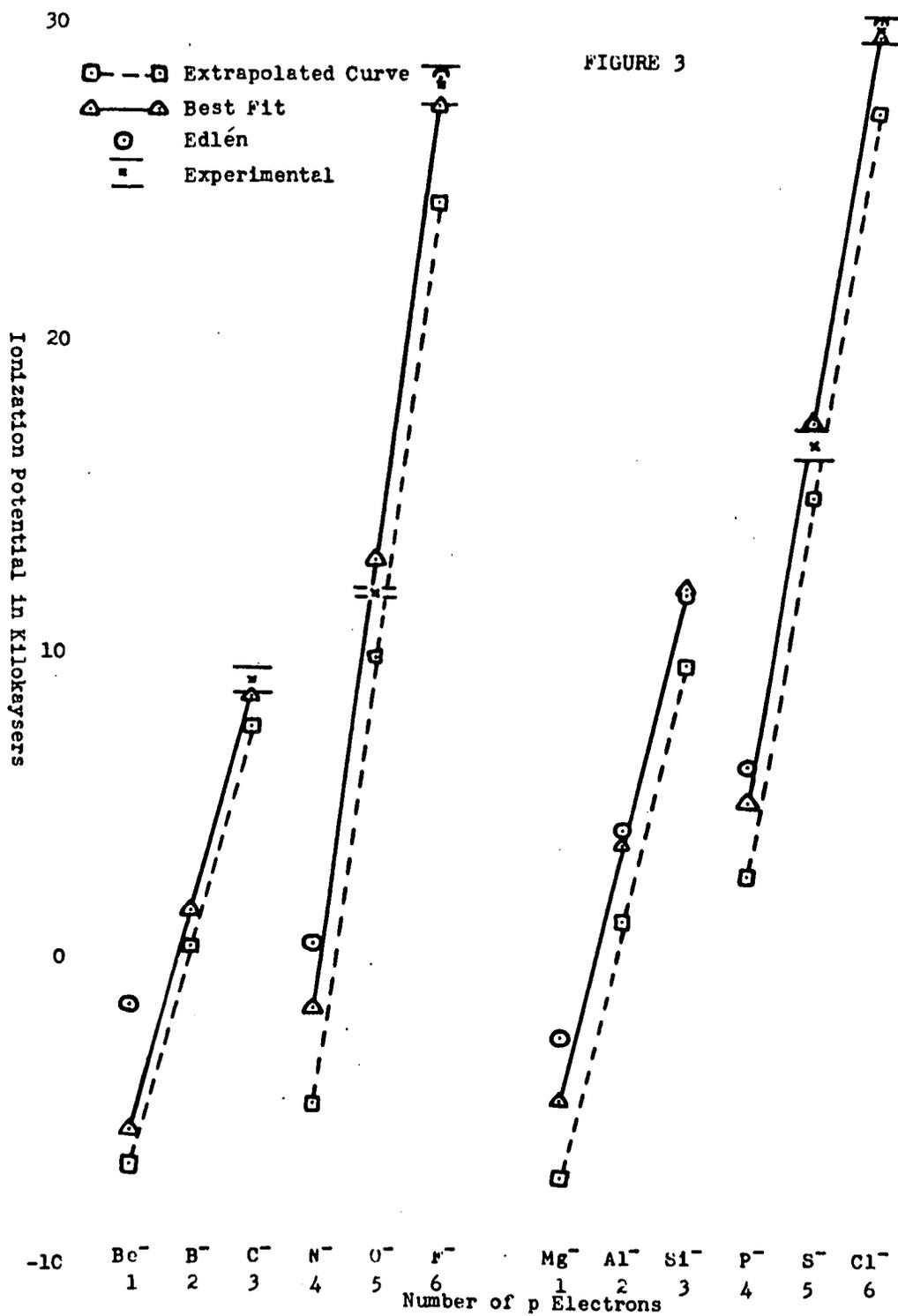
FIGURE 3

FIGURE 4

CENTER OF CONFIGURATION ENERGY DIFFERENCES OF NEUTRAL

ATOMS AND SINGLY- AND DOUBLY-IONIZED POSITIVE IONS

The energy differences between the centers of
configuration are plotted for a given configuration
and degree of ionization, q. The extension of this
curve to the case of the negative ion is shown by the
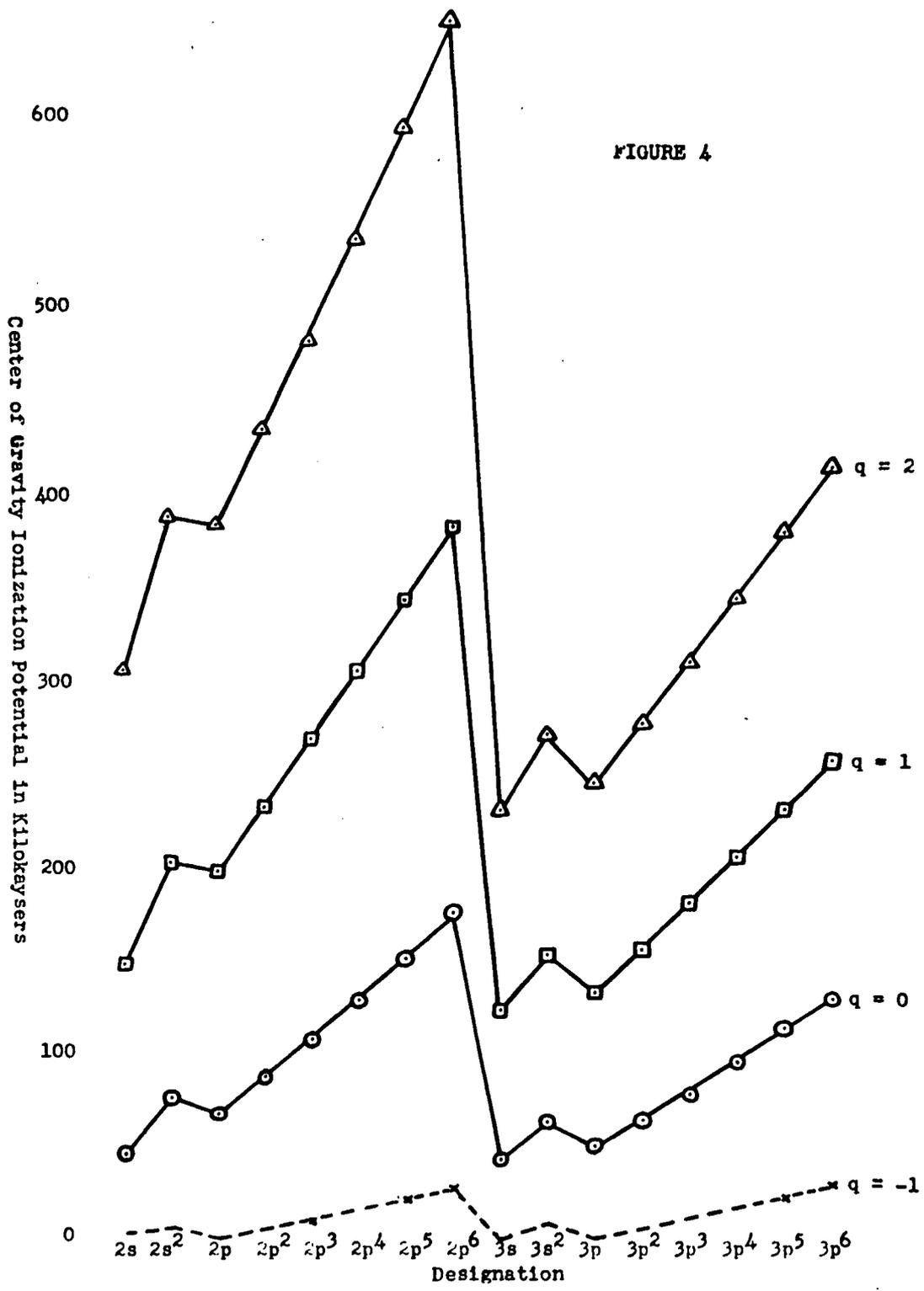dashed curve. The crosses show the positions of the
experimental values.

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FIGURE 4

FIGURE 5

CENTER OF CONFIGURATION EXTRAPOLATED

IONIZATION POTENTIALS

The ionization potentials resulting from an

extrapolation of the center of configuration energy

differences is shown. For comparison, the ionization

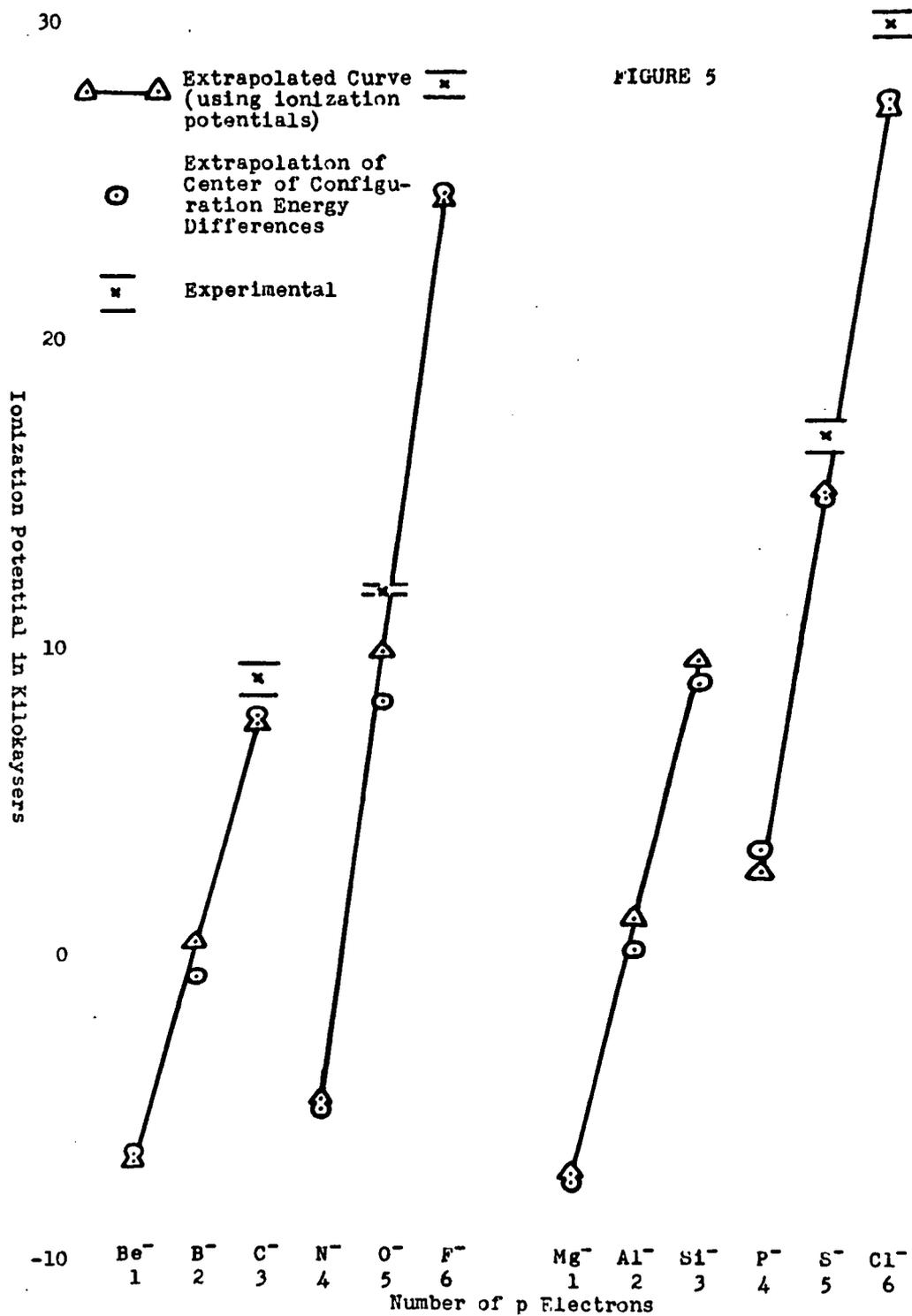potential extrapolated curve and the experimental

values are shown, also.

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FIGURE 5

FIGURE 6

INTERCEPT EXTRAPOLATION FOR THE 2p SHELL

The intercepts $\beta'(q)$ and $\beta''(q)$, for $n = 1, 2, 3$ and $n = 4, 5, 6$, respectively, are drawn for the 2p shell for $q = -1, 0, 1, 2$. These terms are given in equations (85) and (86). To demonstrate the sensitivity of these expressions for the case of $q = -1$, the effect of shifting the curve by a distance necessary to exactly satisfy the best experimental ionization potential is shown by the dashed line.
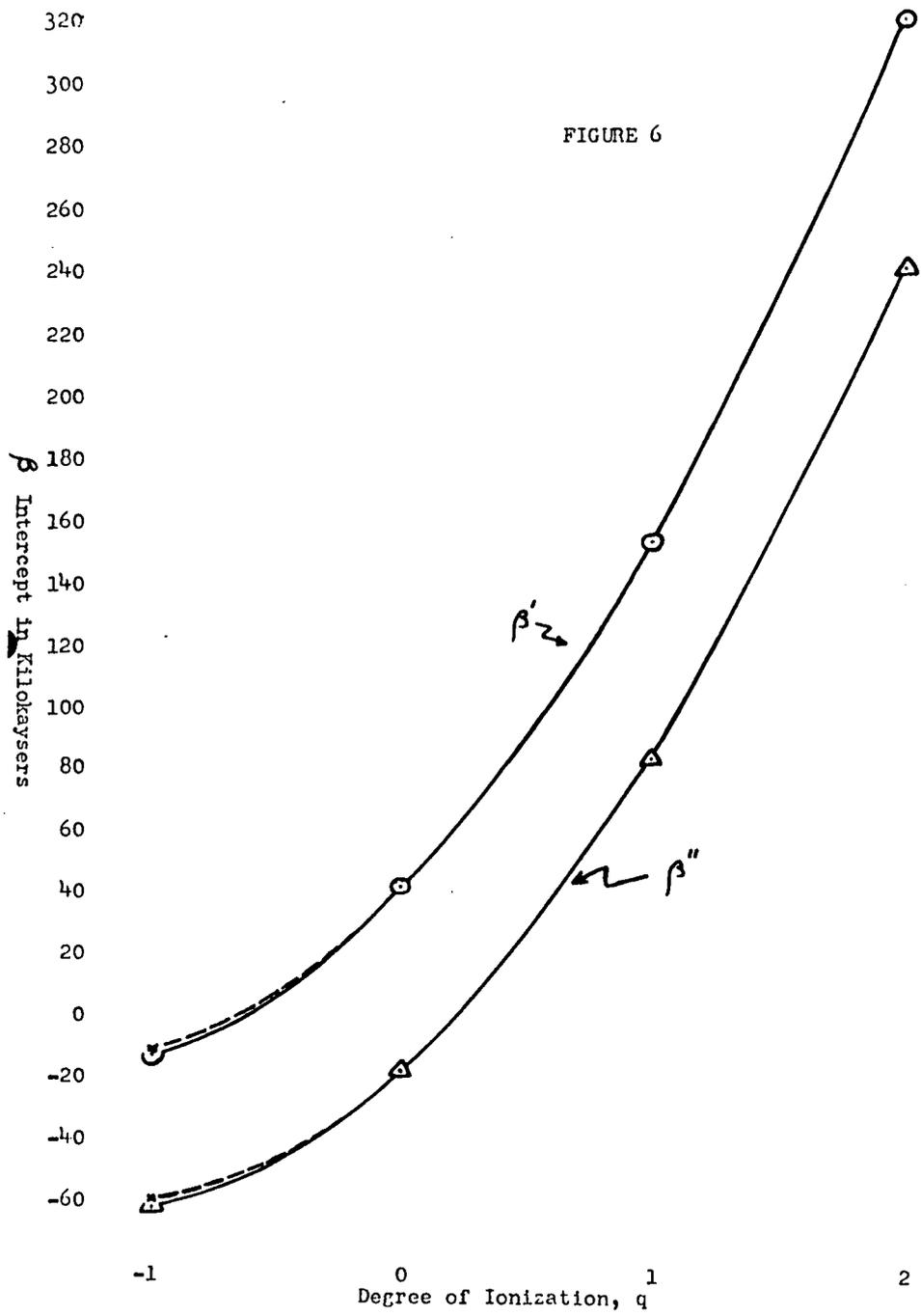
FIGURE 6

FIGURE 7

INTERCEPT EXTRAPOLATION FOR THE 3p SHELL

From equations (87) and (88), the intercepts,
$\beta'(q)$ for n = 1, 2, 3 and $\beta''(q)$ for n = 4, 5, 6,
are drawn for q = -1, 0, 1, 2. When the correction
necessary to exactly satisfy the best experimental
ionization potential for each intercept is made,
the dashed curve results. The sensitivity of the
term for the case of q = -1 is used to justify the
shift of the extrapolated values.

FIGURE 7

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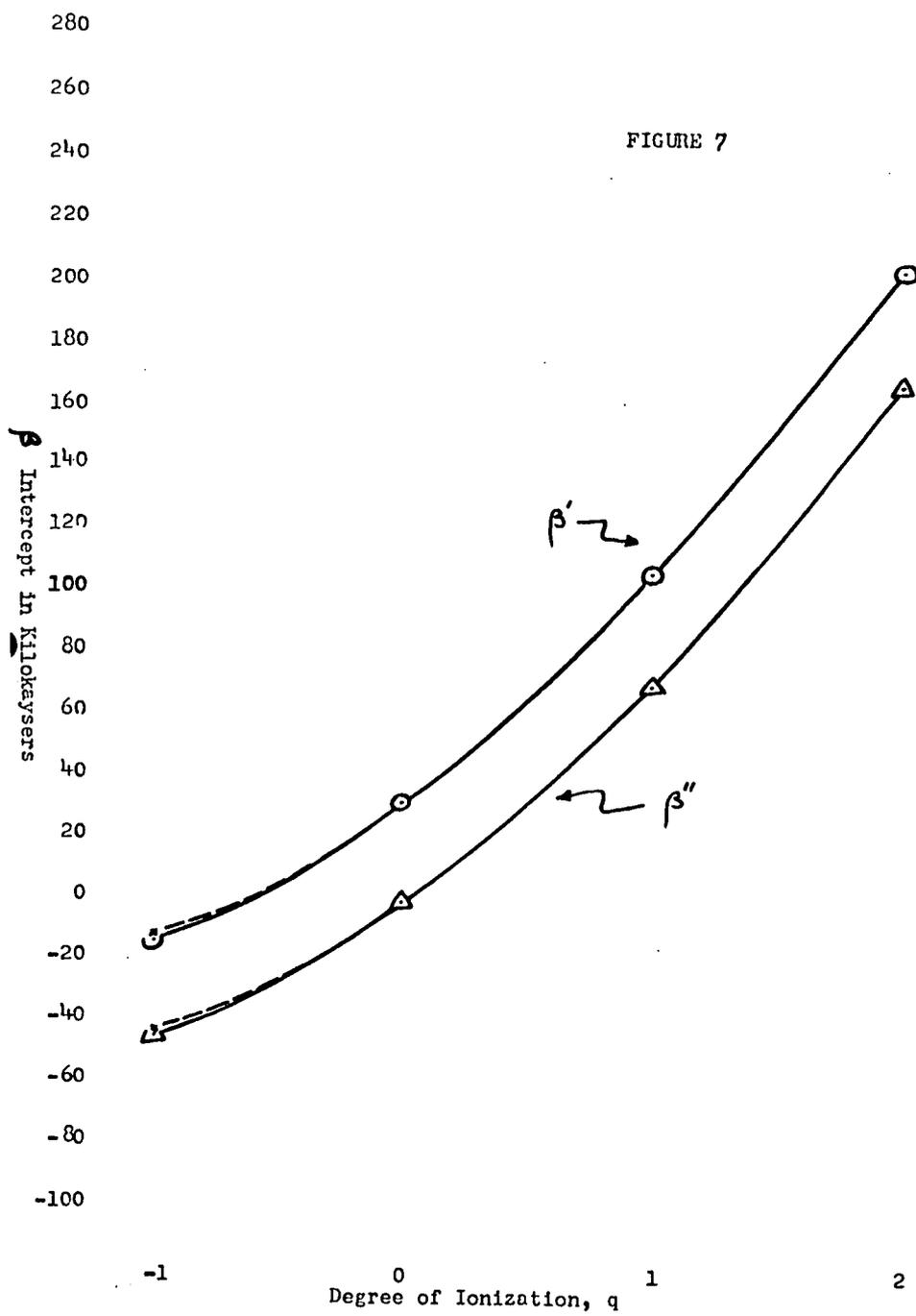
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